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Δις ες τον αντον ποταμον ονκ άν εμβαίης.

(You can't step twice into the same river.)

Heraclitus, in Plato "Cratylus".

Water Quality in Estuarine Impoundments

Julian Paul Wright

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the regulations for the degree of Doctor of Philosophy
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Abstract

Water Quality in Estuarine Impoundments

Julian Paul Wright

The impounding of estuaries is currently a popular approach to urban regeneration in the UK, with barrages constructed (Tees, Wansbeck, Tawe, Cardiff Bay, Lagan and Clyde) or proposed (Usk, Loughor, Neath, Hayle, Avonmouth and Ipswich) nationwide. Impounding fundamentally alters the dynamics of estuaries with consequences in terms of sedimentation patterns and rates, ecology, flooding, groundwater, etc. This thesis presents the findings from research into the effects of impounding on estuarine water quality.

A series of surveys of a range of physical and chemical parameters were carried out within four estuaries representing the complete range of tidal modification by barrage construction. Internal versus external controls on water quality are distinguished. General water quality in estuarine impoundments is good, but significant problems occur where water bodies show entrenched density stratification, with anoxia and associated increases in ammonia and metal concentrations developing. Stratification related problems are worse in partial than total tidal exclusion impoundments (although a higher rate of tidal overtopping shortens the isolation periods of deep anoxic waters), and low water quality at depth is observed over the majority of the year. The potential for eutrophication is increased by barrage construction, although phosphorus (generally the limiting nutrient) is shown to be catchment sourced, with internal cycling from sediment insignificant. Sediment thickness is shown not to be a control on water quality, although sediment build-up over time eventually leads to a loss of amenity value. Sterol fingerprints are used to identify sewage inputs to the impoundments. Advice for barrage planners and designers is given, including the exclusion and removal of saline water, provision of destratification/aeration devices, control of nutrient inputs, and modelling of sediment loads and deposition. This study has shown that catchment management is fundamental in the sustainability of estuarine impoundments.

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I confirm that no part of the material presented in this thesis has previously been submitted by me or any other person for a degree in this or any other university. In all cases material from the work of others has been acknowledged.

Signed:

Date: 01/05/03

Contents

Chapter 1

Introduction

1.1 Outline of the problem

The impounding of estuaries is currently a popular approach to urban regeneration in the UK (Wright and Worrall, 2001). By creation of an aesthetically pleasing amenity impoundment, including the drowning of "unsightly" tidal mud flats, it is hoped that prestige development will be encouraged in the estuarine area (Burt and Cruickshank, 1996). Such barrage developments include the Tawe and Cardiff Bay in South Wales, the Lagan in Northern Ireland and the Tees in Northeast England. The concepts of impounding estuaries are also of international significance, with projects proposed or built worldwide (e.g. the Venice Lagoon Project (Cecconi, 1996)).

Negative impacts on water quality associated with impounding of estuaries have been reported (e.g. Worrall et al., 1998; Reynolds, 1996), including unacceptably low concentrations of dissolved oxygen and increased likelihood of algal blooms. Research has concentrated on either case studies of water quality in single impoundments (e.g. Evans and Rogers, 1996) or process-based water quality modelling (e.g. Maskell and Barraclough, 1996). Very little empirical modelling, and no comprehensive studies including comparison of a several estuarine impoundments, have been carried out. Broadly this research aims to address this shortfall in order to assess the impacts of impounding estuaries and allow suggestion of how negative water quality impacts may be mitigated.

1.2 Research objectives and structure of the thesis

The general aim of this research is to understand water quality in estuarine impoundments. The main objectives of the research may be summarised:

1. **Assess** the current state of water and sediment quality in estuarine impoundments.
2. **Measure** the importance of the factors of season, barrage design and impounding on estuarine water quality.
3. **Understand** the processes controlling water quality that are affected by impoundment (particularly in terms of sediment-water interactions).

The work carried out in order to achieve these research objectives and reported within this thesis includes:

1. **Water quality surveys** of a broad range of physical and chemical water quality parameters within a set of four estuaries showing differences in impoundment status (impounded or non-impounded; amount of tidal intrusion).
2. **Bed sediment surveys** of elemental concentrations and speciations from two estuaries of contrasting impoundment design (partial vs. total tidal exclusion).
3. **Pore water surveys** of elemental concentrations within the bed sediments close to the sediment-water column interfaces of two estuaries of contrasting impoundment design (partial vs. total tidal exclusion).
4. **Sewage input surveys** based on the extraction of sterol biomarkers from the sediments of two impoundments.

A series of water quality surveys were carried out on a range of periods between 1999 and 2001 for the Tees, Wansbeck, Blyth and Tawe estuaries. Chapter 2 presents the background to these water quality surveys including the survey designs, choice of water quality parameters included, sampling procedures and analytical methodologies, together with an overview of the data collected during the surveys. Chapter 3 presents statistical assessments of the seasonal differences in water quality within both the Tees and the Wansbeck impounded estuaries. Chapter 4 looks at the differences in water quality behaviour between designs of estuarine impoundment (the Tees, Wansbeck and Tawe impoundments). The effects of impoundment are discussed in chapter 5 through the comparison of an impounded with an equivalent un-impounded estuary (the Wansbeck and the Blyth respectively).

Cores of bed sediment were taken from the Tees and Wansbeck impounded estuaries in July 2001 and underwent sequential extraction and elemental analysis by ICP-OES. Chapter 6 presents the results from these experiments and discussion in terms of sediment quality, elemental speciation and environmental mobility within the sediments of estuarine impoundments.

The biogeochemistry of elements in the pore water phase of the sediments of estuarine impoundments was researched through the use of DET gel-probe technology pore water sampling within the Tees and the Wansbeck impoundments and is discussed in chapter

7. Within this chapter estimations of exchanges across the sediment-water column interface and the impacts on water quality are also presented.

Chapter 8 presents work carried out using sterol biomarker analysis from samples from the bed sediments of the Tees and Wansbeck to assess the inputs of sewage to these impoundments.

A summary of the major findings from chapters 2 to 8 together with a discussion of the implications of this research are presented in the final chapter of this thesis. Suggestions for further work in the subject of water quality in estuarine impoundments are also given.

1.3 Introduction to the study areas

1.3.1 Estuaries studied

Four UK estuaries were included in this study. The estuaries chosen represent the complete range of impacts of barrage construction on tidal intrusion to estuaries (figure 1.1). The location of the estuaries is shown in figure 1.2.

Non-impounded ("natural" estuary)			Total tidal exclusion (freshwater impoundment)
⟵			⟶
Blyth	Tawe	Wansbeck	Tees
(estuary)	(impoundment)	(impoundment)	(impoundment)
100 %	70 %	30 %	0 %

Figure 1.1. The estuaries included in this research showing the % of tides being able to enter the impoundments or estuary.

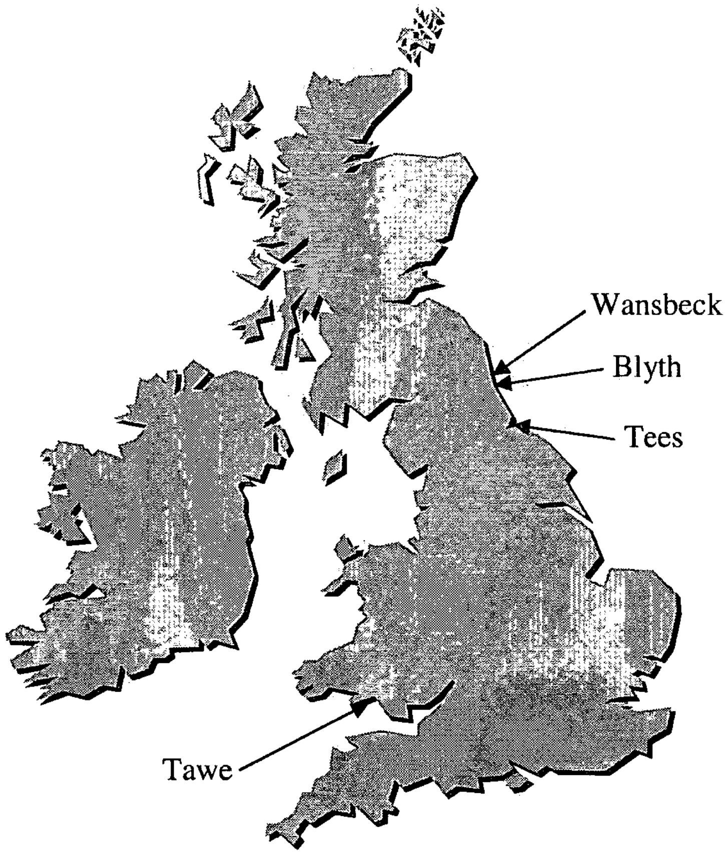

Figure 1.2. Approximate locations in the UK of the four estuaries included in this research (more detailed site maps are included in chapter 2).

1.3.2 The Tees Estuary

1.3.2.1 Tees River

The River Tees is located in NE England, and rises at Tees Head on the eastern slopes of Cross Fell in the Cumbrian Pennines at 893 m AOD. The river flows from west to east with an approximate length of 160 kilometres and a drainage area of 1930 km^2. Tributaries to the Tees include the Rivers Greta, Balder, Skerne, Leven, Lune and Billingham Beck. The upland Tees flows over open moorland to Cow Green Reservoir (built in 1970 to store 40 million m^3 of water for the then predicted heavy industrial growth on Teeside) which, together with the Selset and Grassholme Reservoirs on the Lune and Balderhead, Blakton and Hury Reservoirs on the Balder, acts to moderate flood flows and sustain a minimum flow during dry periods. Nevertheless, the Tees remains a 'flashy' river with water rising by as much as 1 m in 15 minutes during the summer (Archer, 1992). The Tees then flows ESE through Teesdale to Barnard Castle then turns E to Darlington, at which point the valley widens, the slope decreases and flow meanders over a wide flood plain. The lowland tributaries contribute little to the stormflow of the Tees, the majority of which is generated by rainfall on the Pennines. The upland Tees flows over solid geology of mainly limestones and sandstones of the Carboniferous Limestone Series (Dinantian) plus parts of the Whin Sill (doleritic igneous intrusion) and extensive areas of blanket peat. Within the lowland river and estuary the solid geology is overlain by drift deposits of clay, peat, alluvium, river gravels and blown sands.

The major industrial discharges to the Tees take place in the lower estuary (i.e. downstream of the barrage). The industrialisation of Teesside commenced with the opening of the Stockton – Darlington railway in 1825 and development of steel works. In 1926 Imperial Chemical Industries (ICI) was formed, this produced large-scale investment in chemical complex at Billingham. ICI produce fertilisers, heavy organic chemicals and chlorine. In 1934 British Titan Products (now BTP Tioxide) commenced production of titanium dioxide pigments at Billingham. More recently Monsanto, Rohm and Hahns (UK), Shell Oil and Phillips Petroleum came to Teesside. The Tees estuary has ~10% of total UK oil refining capacity. The river Tees before the industrialisation of Teesside had supported a flourishing fishing industry and was noted for its catches of salmon, sea trout, flounders and eels. By 1937 salmon had virtually been eliminated. In 1970 the river Tees was considered to be one of the most heavily polluted estuaries in the UK. The daily BOD load (>500 tonnes) from chemical, petrochemical, steel making industries and untreated domestic sewage left the estuary devoid of oxygen. Common Law control mechanisms had failed to prevent gross pollution of the river Tees. In 1972 Teesside Borough Council drew up a proposal to decrease pollution by domestic sewage. Large interceptor sewers were built to channel discharges from Stockton, Norton and Billingham in the north, and from Aklan, Linthorpe and Thornaby in the south, to a newly constructed treatment works at Portrack. A major pollution initiative in 1980 reduced the BOD discharge load to a quarter of the 1970s load. In 2001 estuarine water quality in the lower estuary was defined as generally fair according to EA General Quality Assessment methodologies, and good above the barrage. Improvements in levels of DO have meant that the Tees is now able to support runs of migratory fish, with 7000 salmon and 13000 sea trout estimated to have migrated through the Tees in 2000 (www.environment-agency.gov.uk).

1.3.2.2 Tees Barrage

The Teesside Development Corporation (TDC) was established in 1987 to encourage redevelopment of the Teesside area. Economic analysis suggested that construction of a barrage would have a positive impact on land and property values in the vicinity of the impoundment, and therefore the TDC submitted a Private Bill proposing such to Parliament in 1988. Royal Assent was given in 1990 and construction (by Tarmac Construction) started in November 1991. The Tees barrage came into operation in January 1995, with all construction work completed by April 1995.

The Tees Barrage (NZ 4616 1905) rests on a 5 m thick 70 m by 32 m reinforced concrete foundation, above which stand 5 concrete piers with 4 fish belly flap gates between them. Each gate is 13.5 m long and 8.1 m deep and hinged at the base with height controlled by hydraulic rams (figure 1.3), with crest height permanently maintained at between 2.4 and 2.8 m AOD. The piers incorporate low-level sluices designed to discharge any accumulated low level pollution or saline intrusion. There are pavilion buildings at each end of the barrage and a road linking to the A66 running along the top (figure 1.4). Ancillary works incorporated in the scheme include a white water course (for canoeing and white-water rafting), a 6 m wide navigation lock, fish pass and caravan and camping park and outdoor amphitheatre. The impoundment itself allows a range of water sports including rowing, sailing, jet-skiing and water-skiing.

Prior to construction of the barrage the tidal limit was at Low Moor (NZ 3655 1050) 44 km from the mouth of the Tees estuary, with saline intrusion penetrating approximately 28 km upstream from the mouth (Environment Agency, 1999). The strength of tidal currents was insufficient to produce complete mixing of fresh and saline water over the whole length of the estuary and the system was classified as partially stratified according to the classification scheme of Pritchard (1955). The Tees Barrage is a total tidal exclusion barrage, i.e. the crest height of the barrage is permanently kept higher than all high tides. The barrage therefore marks the upstream limit of saline intrusion with a completely freshwater impoundment maintained above this. The length of the Tees from the former tidal limit at Low Moor to the Tees Barrage is 26 km. The historic poor water quality of the lower Tees Estuary was a significant factor in the decision to construct the barrage as a total tidal exclusion system.

Figure 1.3. The hydraulically controlled flap-gates of the Tees Barrage.

Figure 1.4. The Tees Barrage viewed from the upstream (impounded) section.

1.3.3 The Wansbeck Estuary

1.3.3.1 Wansbeck River

The Wansbeck is a lowland river also in NE England. It flows from west to east for a distance of 39 km, with the highest point at 440 m AOD, draining a catchment of 339 km^2. Tributaries include the River Font, including the Font Reservoir, and Hart Burn. The geology of the Wansbeck catchment is of Carboniferous age, with the Fell Sandstone of the Carboniferous Limestone Series in the headwaters, Millstone Grit in the middle reaches, and Coal Measures in the lower reaches. Land-use on the catchment is predominantly agricultural, with an increase in intensity from the headwaters to the downstream stretches of the river as the river flows through the town of Morpeth. Flows in the Wansbeck average 2.85 m^3/s, with very low levels during dry summers (0.12 m^3/s reported in 1989 (Archer, 1992) having caused public water supply at Mitford to cease for 4 months (Archer, 1992)).

The Wansbeck is classified as eutrophic, and in June 2002 the River Wansbeck and the Amenity Lake (estuarine impoundment) were added to the list of Sensitive Areas under Urban Waste Water Treatment Regulations (DEFRA, 2002). These regulations, transposed from European Council Directive (91/271/EEC), require tertiary treatment (i.e. removal of phosphorus and/or nitrogen) within sewage treatment works (STWs) serving communities of greater than 10,000 discharging to the water course. The Wansbeck is subject to inputs from acid mine drainage from abandoned coal mines in the catchment.

1.3.3.2 Wansbeck Barrage

In 1972, the then Ashington Urban Council contracted Babtie, Shaw and Morton Consulting and Civil Engineers to carry out a feasibility study for construction of a barrage across the Wansbeck Estuary. The aim of barrage construction on the Wansbeck was the creation of an amenity area for the local population in the form of a riverside park, and thus to attract replacement industries to the area following the decline of the north-east coalfield. This contrasts with the major aims of urban redevelopment on the margins of the Tees and Tawe impoundments. Construction of a barrage commenced in January 1974 and the estuary was impounded in May 1975, thus making the Wansbeck Barrage the oldest amenity estuarine impoundment scheme in the UK.

The Wansbeck Barrage (NZ 2935 8536; figure 1.5) is a fixed crest concrete structure resting on a 0.5 m thick 9 m by 100 m concrete foundation. The crest height is 2.14 m AOD. A footbridge supported by piers at 8 m intervals runs over the barrage at a height of 2.7 m above the crest. Ancillary works include a navigation lock, fish pass, sluice gate to allow draining of the impoundment, and caravan park. The impoundment is used by Cambois Rowing Club, and to a minor degree by jet-skiers, although the shallow depth and trapping of tree branches carried by high flows can interfere with these uses. At present the lock is in a poor state of repair and cannot function to allow navigation, although it is used by Wansbeck District Council in attempts to drain the impounded area since the sluice gate lifting mechanisms are missing.

Figure 1.5. The Wansbeck Barrage viewed from the upstream (impounded) section.

The tidal limit of the Wansbeck estuary is 4 km upstream of the barrage at the weir at Sheepwash (NZ 2565 8587), with a maximum saline intrusion both pre and post-barrage construction through the majority of this distance. Prior to barrage construction, low freshwater discharges of the River Wansbeck caused exposure of large areas of tidal mud flats at low tides, and the covering of this 'black desolation' was a major motive for impoundment (Worrall and McIntyre, 1998). The crest height of 2.14 m allows high tides of 4.7 m and greater (30 % of high tides) to enter the impounded area. The decision on the height of the barrage crest was made on the basis of a desire to provide a sufficient water depth in the impoundment to allow navigation of boats of 1.6 m draft, and the false assumption that optimum water quality would be maintained by increasing turnaround of the impounded water under conditions of low freshwater flow by the intrusion of seawater. The volume of water stored in the Wansbeck impoundment is approximately 725000 m^3.

1.3.4 The Tawe Estuary

1.3.4.1 Tawe River

The River Tawe is located in South Wales. It rises in the Black Mountains at approximately 590 m AOD and flows in a south-westerly direction over a length of 48 km to meet the Bristol Channel at Swansea. The Tawe catchment is 272 km^2 and is heavily urbanised in its lower reaches with the towns of Ystradgynlais, Ystalyfera, Pontrdawe, Clydach and Swansea. The major tributary to the Tawe is the Afon Twrch. The River Tawe flows mainly over Carboniferous Coal Measures, with the Carboniferous Limestone Series and Millstone Grit series plus Old Red Sandstone (Devonian) exposed in upstream reaches. Flows in the Tawe averaged 12.7 m^3/s at the tidal limit between 1982 and 1992 (Russell et al., 1998).

The Lower Swansea Valley has a 240 year (1720-1960) history as a world centre for industrial metal smelting, which has left large areas of land contaminated with Cu, Zn, Pb, Cd and Ni. Metal pollution to the Tawe from these sources has declined since the 1960s as a result of cessation of smelting and remediation work carried out, but metal inputs are still significant during stormflow conditions (Bird, 1987). The Tawe is also subject to inputs of acid mine drainage from abandoned coal mines in the catchment.

1.3.4.2 Tawe Barrage

Following the decline of the heavy industrial use (metal smelting) of the lower Swansea Valley, Swansea City Council proposed construction of an amenity barrage as part of a redevelopment plan for the urban area. Feasibility studies, carried out by W S Atkins (Atkins, 1983), indicated that there were unlikely to be adverse effects from the proposed scheme, although the final structure differed significantly from the initial plans for which the impact assessment was carried out by being partial as opposed to total tidal exclusion. Permission for barrage construction was granted in the Swansea City Council (Tawe Barrage) Act in 1986, construction of the barrage began in 1990 and the estuary was impounded in July 1992.

Figure 1.6. The Tawe Barrage viewed from the downstream side.

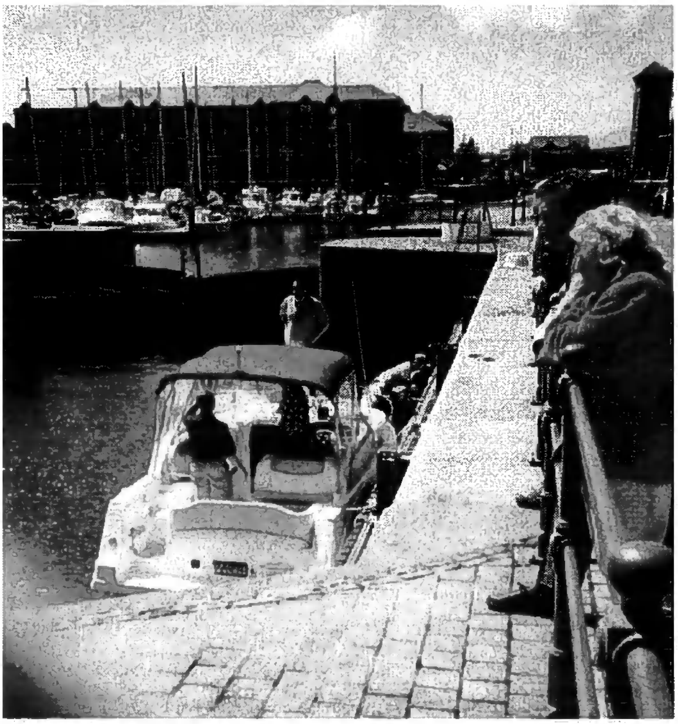

Figure 1.7. The navigation lock of the Tawe scheme showing the redevelopment of the marina area.

The Tawe Barrage (SS 6640 9260; figure 1.6) is a fixed crest concrete structure with a total length of 140 m, with a primary weir of 19 m length and a secondary weir of 45 m length. The crest height of the primary weir is 3.05 m AOD with the secondary weir at 3.35 m AOD. Low level sluices are included in the design to allow drawdown of the impoundment. Ancillary features of the Tawe Barrage include a navigation lock and a fish pass. The impounded area includes a popular marina development meaning that the navigation lock is in regular use (figure 1.7), and that the financial implications of drawdown of the impoundment are prohibitively large.

The tidal range at the Tawe estuary is large, and the crest height of the primary weir of 8.05 m AOD allows approximately 70 % of high tides to overtop the barrage, with influx of seawater occurring over 16 % of the time (Mee et al., 1996). Prior to impoundment there was little vertical variation in salinity, except for short periods around slack water (Shackley and Dyrynda, 1996), and the estuary was classified as partially mixed. The limit of saline intrusion was recorded to approximately 3.6 km upstream of the current barrage site, and the tidal limit is at Landore (SS 6660 9620) 5.6 km upstream from the barrage. Post-impoundment, saline stratification of the water body has been recorded up to 5 km upstream of the barrage (Russell et al., 1998).

1.3.5 The Blyth Estuary

1.3.5.1 Blyth River

The River Blyth was chosen as a suitable non-impounded estuary with which to test the effects of impoundment on the basis of its similarities with the River Wansbeck. The Blyth catchment is immediately south of that of the Wansbeck, and it also runs from west to east (meeting the North Sea approximately 4 km south of the mouth of the Wansbeck). The catchment of both rivers are of exactly the same size (339 km^2), and both rivers are predominantly lowland and run over the same geology (Carboniferous). The River Blyth is approximately 36 km long and the highest point within the catchment is 268 m AOD. Tributaries to the Blyth include How Burn, the River Pont and Sleek Burn. There are no dams in the catchment, although the course of the upper reaches is diverted to the Whittle Dene reservoirs in order to supply water for Newcastle. The only significant settlement on the river is the port and town of Blyth at the mouth.

1.3.5.2 Blyth Estuary

The Cramlington and Blyth STWs have a combined discharge to the estuary (NZ 2950 8249), with a maximum discharge of secondary treated sewage (with 70 % BOD removal according to the Urban Waste Water Treatment Directive) of 19880 m^3/day from Cramlington and 11664 m^3/day from Blyth. In terms of estuary classification, the tidal currents within the Blyth create an estuary with a partially mixed salinity structure.

	Tees	**Wansbeck**	**Tawe**	**Blyth**
River length	160 km	39 km	48 km	36 km
Catchment area	1930 km^2	339 km^2	272 km^2	339 km^2
Highest point	893 m	440 m	590 m	268 m
Geology	Carb. lsts. and ssts. Dolerite. Extensive drift (mainly peat and alluvial).	Carb. ssts., grits and coal measures.	Carb. ssts., lsts., grits and coal measures. ORS (Devonian)	Carb. ssts., grits and coal measures.

Table 1.1. Catchment characteristics for the rivers included in this research.

1.4 Water quality in estuarine impoundments: definitions and review of research

1.4.1 Types of barrage

An estuary is a semi-enclosed coastal body of water which has free connection to the open sea and within which sea water is measurably diluted with fresh water derived from land drainage (Cameron and Pritchard, 1963). An estuarine barrage is a structure which, for various reasons, is designed to modify or totally prevent the progression of the tide up an estuary or inlet (Burt and Rees, 2001). Major reasons for barrage construction include:

- Tidal power generation.
- Tidal surge flood protection.
- Water storage.
- Urban regeneration.
- Amenity use.

1.4.1.1 Tidal power barrages

Barrages for tidal power generation are periodically considered in regions with large (5-15 m) tidal ranges. Within the UK, schemes have been proposed for several estuaries of the west coast including the Severn, Dee, Ribble, Solway and Mersey estuaries. The economics of the costs of barrage construction vs. the revenues from the electricity produced have meant that few tidal power generation schemes have been built. Significant power is produced at the Rance Barrage in France and the Annapolis Royal Power Station in Canada. The Rance Barrage was completed in 1967, and with twenty four 10 MW turbines is the largest tidal energy scheme in the world (Burt and Cruickshank, 1996; Shaw, 1995). Operating and environmental problems encountered in the Rance include marine growth in the generators, sedimentation and accumulation of organic matter in the basin, reduction in littoral area, and loss of species diversity. The isolation of the estuary during the construction phase is given as particularly environmentally damaging, eradicating marine flora and fauna (Retiere, 1994). The Annapolis Barrage, successfully operating since 1984, is a 20 MW pilot project with the aim of assessing the potential for a large scale tidal power project in the Bay of Fundy. Increased primary production (due to both stratification of and reduced turbidity in the (non-nutrient limited) impounded water) is suggested as a consequence of such a scheme (Gordon, 1994; Tidmarsh, 1984). Parker (1993) suggests that the water quality implications of tidal power barrages are likely to be site specific, and strongly dependent on inputs to the impounded area.

1.4.1.2 Flood protection barrages

As opposed to power generation barrages, tidal surge protection barrages are relatively common. Surge protection is generally achieved by means of a movable barrier, which is only positioned to impede tidal ingress under periods of flood risk. Examples of such schemes include the Thames and Hull Barriers in the UK, and the Delta Works of SW Holland and the Venice Lagoon Project in Italy. The Thames Barrier is the largest navigable flood barrier in the world and was constructed to protect London from flooding during storm surge conditions in the North Sea. It consists of a series of rising sector gates set in sills at bed level such that the obstruction to normal tidal flows is minimal. The gates are raised only during tidal surges up the Thames (Wilkes, 1996). A similar scheme is proposed for the Venice Lagoon to avoid the increasingly frequent (average 45 times per year) acqua alta (floodings) of Venice (Bandarin, 1994; Cecconi, 1996). Flood protection estuarine barrages are generally designed to minimise the disruption of natural estuarine behaviour and thus have minimal impact on water quality, and are therefore not included this research. The Venice Lagoon may however undergo longer periods of tidal disruption and, as with tidal power barrages, pollution loads to the impounded area are suggested as critical in controlling water quality (Bernstein and Cecconi, 1996).

1.4.1.3 Water storage barrages

Estuarine impoundments may function as freshwater storage impoundments in regions with limited groundwater or space for inland reservoirs. Such embayments are built in Hong Kong (Don, 1973), but have been rejected as economically unviable in the UK (Water Resources Board, 1966).

1.4.1.4 Urban redevelopment and amenity barrages

The research described within this thesis concentrates on barrages constructed in relation to urban redevelopment and amenity use in the UK. The barrages on which sampling was carried out (the Tees, Wansbeck and Tawe) are described above. A large number of additional estuarine barrages have either been constructed or have been proposed throughout the UK. Barrages which have been constructed include the Lagan in Northern Ireland, the Clyde in Scotland and Cardiff Bay in South Wales. Barrages have been proposed for the Usk, Loughor and Neath in S Wales and at Hayle, Avonmouth and Ipswich in England (Burt and Rees, 2001). The Lagan Weir was completed in January 1994 as part of a regeneration programme for Belfast managed by the Laganside Corporation. The structure is a partial tidal exclusion design, and consists of five fish-belly flap gates creating a 5 km long impoundment (Mackey, 1994; Millington, 1997). A similar planning process by the Cardiff Bay Development Corporation led to the construction of the largest UK barrage scheme, with closure of the sluice gates in November 1999 creating a freshwater impoundment of 200 ha (Crompton, 2002). The proposed Usk Barrage project in Newport, S Wales, has not been constructed on the basis of economic and environmental grounds (Burt and Rees, 2001). The water quality and related issues relevant to the construction of urban redevelopment and amenity barrages are discussed below.

1.4.2 Water quality issues

The research carried out thus far on water quality in estuarine impoundments has tended to concentrate on sampling of post-impoundment water quality in specific systems (e.g. Worrall and McIntyre (1998) and Worrall et al. (1998) for the Wansbeck, Evans and Rogers (1996) and Taylor et al. (2002) for the Tawe, and Wright and Worrall (2001) for the Tees). Additional work has been carried out modelling the effects on water quality of proposed estuarine barrages (Broyd et al. (1984) for the Tawe, Bach and Jensen (1994) for the Usk, Watts and Smith (1994) for the Lagan, Nottage et al. (1991) for the Tees, and HR Wallingford (1987) for Cardiff Bay). These studies have highlighted a selection of water quality issues associated with impoundment of estuaries:

1.4.2.1 Stratification

Natural estuaries may be classified according to the extent of density stratification within them (Cameron and Pritchard, 1963). Estuaries with a high river flow relative to tidal flow (e.g. Mississippi) tend to be highly stratified, with little mixing between the overlying freshwater and saline water beneath. Fjords, which tend to be deep but with a shallower sill at their mouths, are also often highly stratified. Where tidal flows are large and river flows small estuaries are vertically homogenous (e.g. Deleware). Most natural UK estuaries are of intermediate partially mixed type, showing some mixing of fresh and saline water through turbulent eddies. The construction of a barrage fundamentally alters the tidal flow within an estuary and strong stratification of the water column has been reported for the Tawe, Wansbeck and Lagan estuarine impoundments (Shackley and Dyrynda, 1996; Worrall and McIntyre, 1998; Burt and Rees, 2001).

1.4.2.2 Dissolved oxygen

Reductions in dissolved oxygen (DO) to unacceptable levels have been associated with this saline stratification. The Environmental Protection Department of Northern Ireland originally set a water quality target of 30 % DO as a 95 percentile for the Lagan impoundment, but has since had to reduce this to a more realistic target according to the Estuarine and Coastal Waters Classification Scheme. The Environment Agency of England and Wales has set standards of 5 mg/l DO (at a percentile as yet undecided) for the Tawe and 5 mg/l (100 percentile) for Cardiff Bay (Taylor et al., 2002). Actual values of DO reported within partial tidal exclusion estuarine impoundments are >1 mg/l in the Tawe (Jones et al., 1996), 0 mg/l in the Wansbeck (Worrall and McIntyre, 1998) and 5 % saturation in the Lagan (Burt and Rees, 2001). Within the freshwater Cardiff Bay impoundment DO has also been encountered at reduced levels, and reoxygeneation of the water body has been required using bubbler boats (Phillips and Williams., 2000). Recycling of metals and nutrients from sediments and elevated ammonia concentrations have been suggested as additional effects of stratification and development of anoxia in impounded water bodies (Evans and Rogers, 1996; Worrall et al., 1998). These conditions have prompted the suggestion and use of a selection of remedial measures as described in section 1.4.2.5 below.

1.4.2.3 Sedimentation

The reductions in DO and recycling of metals and nutrients have been suggested to be closely linked to build-up of organic rich sediment (Dyrynda, 1994; Henry, 1992; Worrall and McIntyre, 1998), although prior to the work presented in this thesis no research had been carried out to quantify the sediment-water column exchanges occurring in impounded estuaries. Organic deposits in the Lagan were dredged prior to barrage construction. Sediment build-up is also significant in determining the lifespan of a barrage scheme, and a large amount of modelling work has been carried out to predict patterns and increases in rates of sediment deposition following impoundment. Burt and Littlewood (2002) and Burt (2002) report that modelling gave approximately 60 cm of sedimentation within the Cardiff Bay impoundment in 30 years and that dredging would be necessary every few years to avoid the risk of fluvial flooding as the bed level builds up. Modelling preceding construction of the Tees Barrage gave a maximum potential sedimentation rate of 300 mm/annum upstream of the barrage, with 75-80 % of siltation removed by the annual 100 m^3/s flood giving a net deposition of between 10 and 30 mm/annum, with this sedimentation rate having no negative impacts on the river (Fawcett et al., 1995). Sedimentation downstream of the barrage (where 90 % of the sediment deposited enters Tees Bay during easterly storms) was predicted to decrease due to a reduced tidal prism.

1.4.2.4 Eutrophication

Many UK rivers carry high nutrient loads but algal and cyanobacterial blooms are avoided through suspended material in the water column. If impounded, aggressiveness of flow is reduced, suspended material is deposited, light can penetrate further into the water column, and the residence time of the water is increased. These factors have the potential to increase the probability of nuisance and potentially toxic algal and cyanobacterial blooms (Reynolds, 1996). In addition the decrease in mixing between fresh and saline water give greater stability of salinity in the water body meaning that conditions are favourable for a greater range of species. Blooms have been observed in the Wansbeck impoundment (Worrall et al., 1998), and positive heterograde DO profiles are encountered in the Tawe and the Lagan impoundments due to concentrations of marine phytoplankton at the halocline (Burt and Rees, 2001). Prior to the construction of the Cardiff Bay Barrage predictive modelling of phytoplankton growth showed that average to above average flows would mean replacement of the water in the impoundment in < 8 days, allowing phytoplankton concentrations to increase to 3-4 times input values (no negative effects). Under low flow conditions the nutrient inputs of the rivers entering the impoundment would allow crops of > 200 mg chlorophyll/m^3 and a species dominance by cyanobacteria (Reynolds, 1989).

1.4.2.5 Remediation schemes

In several estuarine impoundments low water quality, particularly in terms of hypoxia as described above, has led to the introduction of apparatus and work to improve water quality. The most commonly used technique is aeration, with devices used in the Tawe, Lagan and Cardiff Bay impoundments (Taylor et al., 2002; Millington, 1997; Phillips and Williams, 2000). These consist of ceramic diffusers fitted to pumps inputting either air or oxygen to the water column and thus increasing levels of DO. Based on comparison of 1997 and 1999 data (pre and post diffuser instalment), the devices in the Tawe impoundment are reported to be generally effective in maintaining DO concentrations above the 5 mg/l level but a increase in the number of devices is recommended (Taylor et al., 2002). The Tawe impoundment also contains a mixing propeller immediately upstream of the barrage designed to expel saline water at depth. The success of these devices is further explored by Lamping (2003). Other remediation measures reported include relocation of outfalls, collection of algal material and selective draining of the impounded water bodies. Prior to the construction of the Tees Barrage, the Yarm and Clockwood Sewage Treatment Works (STW) were abandoned and their inputs diverted to Portrack STW downstream of the barrage, and sluice pipes are used to remove saline water at depth and avoid debris accumulation under the gates (Hall et al., 1995a). For the Cardiff Bay Project 16 major sewers were diverted to discharge points beyond the barrage prior to impoundment, and surface accumulating and filamentous algae will be collected and disposed to landfill or STW (Crompton, 2002). The Wansbeck is periodically drained by opening the navigation lock in an attempt to remove accumulated sediment (Wansbeck District Council, pers. com.).

1.4.3 Summary of related issues

In the planning and construction of estuarine barrages a broad range of inter-related environmental and socio-economic issues, in addition to those of water quality, must be considered. A brief summary of some of the most significant issues relating to estuarine impoundments follows:

1.4.3.1 Ecology

Estuaries are unique ecological environments and in their natural state support species poor but highly productive ecosystems. The construction of a barrage fundamentally changes the hydrodynamics and salinity structure of an estuary, and will thus alter the assemblage of species to which the estuary is favourable. These changes brought about by barrage construction may lead to the water quality problems described above and have negative impacts on biota. Inter-tidal mud flats commonly provide feeding grounds in winter for migratory wading birds and wildfowl. A major motive for barrage projects is that they will drown 'unsightly' mudflats. In addition, the physical presence of a barrage may form a barrier to migratory species of fish using passing through the estuary during various stages of their life cycles. The specific problems and solutions of fish migration are discussed below. Ecological concerns have recently become major causes of opposition to large civil engineering projects including estuarine barrages, and opposition to the Cardiff Bay Project was particularly strong (e.g. "Friends of the Earth is determined the Barrage will be stopped and we are consulting our lawyers with a view to block it in the courts." (Friends of the Earth, 1997)). Prior to impoundment Cardiff Bay contained the Taff-Ely Site of Special Scientific Interest (SSSI), so designated due to its importance to significant populations of wetland birds (Hill, 1996). In an average winter approximately 6000 birds, particularly dunlin and redshank used the mud-flats as feeding grounds. The Cardiff Bay Project included the compensatory measures of creation of wet reed beds, wet flooded grassland and shallow saline lagoons at alternative sites at a cost of £10.4 million (Crompton, 2002), and act described by FoE director Tony Juniper as "like knocking down the Tower of Pisa and building a cinema and calling it compensation.". The majority of studies of the ecological impacts of barrage construction have been predictive (e.g. Gough, 1996; Shaw, 1995), with little data gathered as yet for completed barrage projects, with the exception of the Tawe (Dyrynda, 1996).

1.4.3.2 Fisheries and fish passes

A universal ancillary feature in barrage designs is the inclusion of a fish pass for migratory species of fish. Migratory species such as shad, sea trout and Atlantic salmon need to pass through estuaries at least twice in order to complete their life cycles. In natural estuaries diadromous fish use tides to assist in their migrations (Dodson et al., 1972). Barrages affect tidal flows and form a physical barrier to these migrations, and fish passes are included as the principle attempt to minimise impact on migratory fish (Gough, 1996). Currently a large amount of research is taking place to monitor the success of fish passes in estuarine barrages, particularly in terms of the migration of salmonids (Atlantic salmon and sea trout), with provision made in the Tees and Cardiff Bay schemes for monitoring. For the Tawe it has been found that, although approximately half of the adult salmonids are attracted to the freshwater plume emanating from the fish pass, few fish ascend by the fish pass, most moving upstream on tidal overtopping of the barrage (Russell et al., 1998).

1.4.3.3 Groundwater

Rivers and estuaries are hydraulically connected to aquifers, and raising the water level by construction of a barrage may cause groundwater levels to rise in the vicinity of the impoundment. Rising groundwater levels have a number of potential impacts, including pollution of aquifers, impacts on property, and reduction in slope stability along the banks of the impoundment. Aquifers may be polluted by saline intrusion from the impoundment and, since many barrages are built on estuaries with a major industrial heritage, rising groundwater levels may mobilise pollutants within contaminated land. Effects on property include dampness and associated structural damage. Raising groundwater levels has the potential to increase pore water pressures and thus lead to slope instability (see e.g. Wright, 1996). Provision for monitoring of groundwater levels, preventative measures, and physical and legal protection may need to be included in barrage projects (Burt and Rees, 2001). In the planning stages of the Cardiff Bay Barrage computer modelling of groundwater predicted a maximum rise in water levels of 3 m in the gravel aquifer and 1.2 m in the made ground surrounding the impoundment. Up to 1600 properties were at risk in terms of dampness, but no structural damage was anticipated. Pre-impoundment surveying was carried out, with post-impoundment surveys 2 years after closure, and a legal responsibility of the Cardiff Bay Development Corporation or its successor to rectify damage that occurs. Dewatering wells and drains are installed in areas around the impoundment, and pumping will continue in perpetuity (Crompton, 2002). Within the Tees development, slope stability in the upper reaches of the impoundment was a major concern, and an extensive programme of site investigation and geomorphological mapping was carried out. Piezometers were installed in standpipes and parametric stability analyses were carried out. Widespread slope instability was discovered and monitoring is continuing to determine to what extent this is due to rising groundwater levels associated with impoundment (Hall et al., 1995b).

1.4.3.4 Flooding

Following a recent spate of floods and damage to property in the UK and Central and Eastern Europe, flooding is currently of high public interest. Around 5 million people, in 2 million properties, live in flood risk areas in England and Wales (www.environment-agency.gov.uk). Estuarine barrages may have both positive and negative impacts on the risk of flooding in catchments. As described above (section 1.4.1), barrages may be designed specifically to protect low lying areas from tidal surges. Other barrages with movable gates, such as the Tees, Lagan and Cardiff Bay, may also be raised to protect upstream areas from tidal surges assuming sufficient storage capacity in the channel for freshwater flows. Partial exclusion barrages with fixed crest heights will offer virtually no protection against tidal surges. In terms of fluvial floods, risk of flooding may be increased if the barrage structure impedes the flood flow or if sedimentation in the impounded area decreases the capacity of the river channel. Fluvial flooding downstream may potentially be reduced by drawdown of water in the impounded area during low tide to create storage for flood waters. Any such pre-emptive movements of barrage gates will rely on good flood warning. Prior to construction of the Cardiff Bay Barrage the major risk of flooding was from tidal surges. Samuels and Burt (2002) give that "The barrage has substantially eliminated the probability of tidal flooding, and the residual flood risk now depends on the ability of the inland bay to provide sufficient storage for river floodwater during periods of high tide." Probability analysis gives a frequency of exceedance of the 8.0 m development level in the Bay of 1 in 8000 years post-impoundment compared with 1 in 122 years pre-impoundment. Modelling of flood levels by Northumbrian Water Authority indicated only a very small increased risk of flooding in the Stockton and Yarm areas as a result of the Tees Barrage (Hall et al., 1995a). Management of the Tees Barrage during river flood conditions involves lowering the gates to maintain an upstream level of below 2.65 m AOD.

1.4.3.5 Amenity use

Barrages constructed to encourage urban redevelopment are often described as amenity barrages due to the incorporation of facilities for recreational use in their designs. Impoundments may provide facilities for a large range of water contact activities including rowing, white water rafting and canoeing, sailing, water skiing and jet-skiing. Surrounding areas may be landscaped to provide a pleasant environment for walking, caravanning and camping and outdoor concerts. Navigational rights may apply to estuaries to be impounded, thus necessitating the inclusion of navigation locks, and recreational boating in the area may be encouraged through provision of marina facilities. The ancillary features of the barrages included in this research are listed above. Use of the Wansbeck impoundment for water sports is restricted and less than that originally envisaged due to the shallow water depth and semi-submerged obstacles. Successful use of the impoundment by Cambois Rowing Club is limited during low river flows and following transport of debris into the impoundment by river floods. The poor state of repair precludes the use of the navigation lock by craft at present. An amenity survey carried out in 1996 showed that, in terms of activities carried out, the Wansbeck Riverside Park has a visitor profile similar to that of many urban parks (Worrall and McIntyre, 1998). In contrast, the use of the Tees Barrage impoundment for water contact activities is very successful, and the white water course is particularly popular. The Chief Executive of the Teesside Development Corporation quotes the editor of Canoeist magazine describing the inaugural slalom event as attracting "what may well have been the biggest crowd ever for a British canoeing event" (Hall, 1996). The use of estuarine impoundments for water contact activities is reliant on the maintenance of high water quality, particularly in terms of water-borne pathogens.

1.4.3.6 Costs and benefits

Recent barrage constructions in the UK have been a response to the decline in heavy industries along the margins of estuaries. By creation of a pleasant waterfront environment and associated infrastructure it is hoped that these areas may be redeveloped and economic growth of the region achieved. The primary decision to build an estuarine barrage is therefore currently economic, and the construction and environmental costs of construction must be outweighed by the predicted financial benefits. It must be determined whether a barrage is the best way to stimulate economic growth, or whether a similar amount of investment through other channels would give equal or better returns. Financial incentives offered to businesses locating in the area associated with development schemes may have the same effects independent of the presence or absence of a barrage. Anecdotal evidence suggests that regeneration on the Avon commenced as soon as the Bristol Development Corporation showed an interest in the area, prior to any proposal for barrage construction.

The Tees Barrage scheme is reported as an economic success (e.g. Hall, 1996). Economic evaluation of the Teesside Development Corporation's strategy suggested that it would create new employment opportunities (an estimated 8000 jobs) and financial investment (approximately £500 million), and provide new homes for the existing population and incoming employers (Price Waterhouse, 1988), and it is reported to be close to meeting these targets (Hall et al., 1995a). The Cardiff Bay Barrage is the centrepiece of a £24 billion regeneration scheme for Cardiff, and is also reported as having met its economic targets (Crompton, 2002). The Cardiff Bay Development Corporation's strategy was even more ambitious, and aimed to create 30000 new jobs and attract 2 million visitors/annum to Cardiff's waterfront. The cost of barrage construction per hectare of regenerated land equates to £180,000, with an average post development market value for this previously undesirable land of £500,000, and the Development Corporation has estimated that an estimated £170 million a year is returned to the public purse through taxation directly attributable to developments. Redevelopment of the Swansea Valley in association with the Tawe Barrage is acclaimed by the Council of Europe as an international example of Urban Renaissance (Phillips and Williams, 2000).

Chapter 2

Water Quality Surveys

2.1 Survey design

2.1.1 Experimental design

The water quality surveys undertaken were factorial in design (Miller and Miller, 1994; Wright and Worrall, 2001; Hillebrand, 2003; Jacquemyn et al., 2003). The general principle of the design of the surveys was that they should be able to produce datasets that allow statistical testing of the significance of a number of factors in controlling water quality in the impoundments. These factors include barrage design, position (longitudinal and depth) within impoundments, and external controls on water quality such as temperature, river flow, time of year and tidal state. Factorial design measures the response to combinations of factor levels, whereas in classical (one-at-a-time) experimental design each factor to be tested is run in an experiment in which all other factors are held constant. Obviously in a natural system such as an impoundment, factor levels will vary simultaneously and a classical approach would be impossible. However, factorial design also shows distinct advantages over classical design in that interactions between factors can be determined, and fewer sets of results are needed to gain the same precision as in a one-at-a-time design. Interactions are where the response to a combination of factors is greater or smaller than would be expected if the effects were solely additive.

2.1.2 Estuaries studied

Water quality surveys were carried out on a total of four estuaries, chosen to allow comparison between different ages and designs of impoundment (partial and total tidal exclusion and amount of tidal overtopping), and to include a non-impounded "control" estuary. These are the River Tawe in South Wales and the Rivers Tees, Wansbeck and Blyth in Northeast England (figure 1.2, chapter 1). UK estuaries were chosen for convenience and to minimise differences in climatic and land-use factors.

The River Tees, impounded in 1994, is a total tidal exclusion (freshwater) system. The River Wansbeck, impounded in 1975, is a partial tidal exclusion system which allows approximately 30% of tides to overtop the barrage. The River Tawe, impounded in 1992, is a partial tidal exclusion system which allows approximately 70% of tides to overtop the barrage. The River Blyth is of a similar size and runs roughly parallel to and to the south of the River Wansbeck, and is not impounded.

2.1.3 Sampling stations

The river sections studied for the three impoundments extend upstream from the barrages to the normal tidal limits representing the downstream limits of unidirectional flow (or pre-barrage normal tidal limit for the River Tees), taken from Ordnance Survey maps. These can be thought of as the sections of river which have undergone impoundment by the construction of the barrages. This project does not attempt to consider the effects of barrage construction on the sections of estuary downstream from the barrages. The section of the River Blyth studied extended downstream from the normal tidal limit to the dredged and pile-walled shipping channel of the Port of Blyth (i.e. a section representing the "natural" condition of the estuary was selected).

General practice was applied in choosing sampling sites (ISO, 1990; Bartram and Balance, 1996). A number of sampling stations (4 on Blyth, 7 on Tees, 5 on Wansbeck and 6 on Tawe) were established approximately equidistantly along the sections studied, and at the deepest point of the river cross-section at each of these distances. Stations were chosen at clearly identifiable points (i.e. at obvious landmarks such as bridges, buildings, weirs and river confluences) to ensure repeatability of sampling at the same points and, where data are gathered by the Environment Agency (EA), to correspond with EA sampling sites. For each river a site was chosen at the tidal limit with the objective of identifying the baseline conditions of water quality as it entered the systems under study. For the Tees, surveys sites were established immediately upstream of the confluence with, and within, the major tributary of Leven to allow its effect on water quality to be taken into account. Figures 2.1, 2.2 and 2.3 and table 2.1 show the locations of the sampling sites within each of the estuaries.

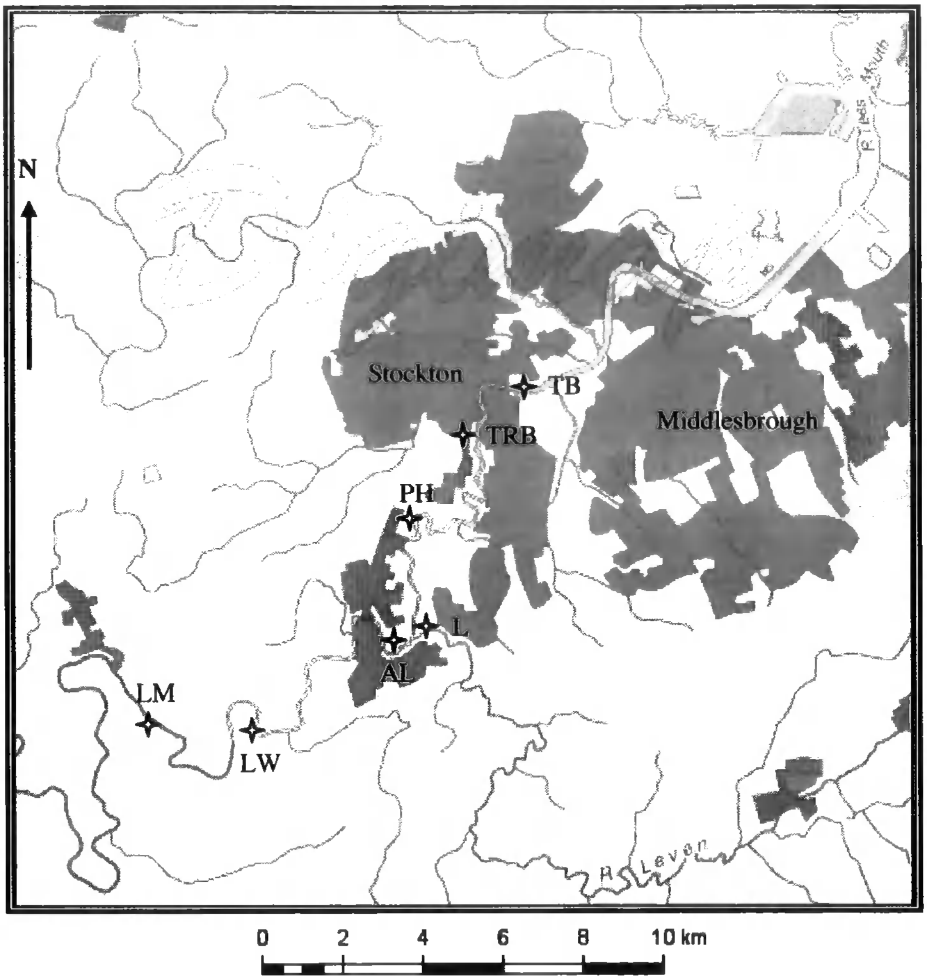

Figure 2.1. Locations of the sampling sites on the River Tees.

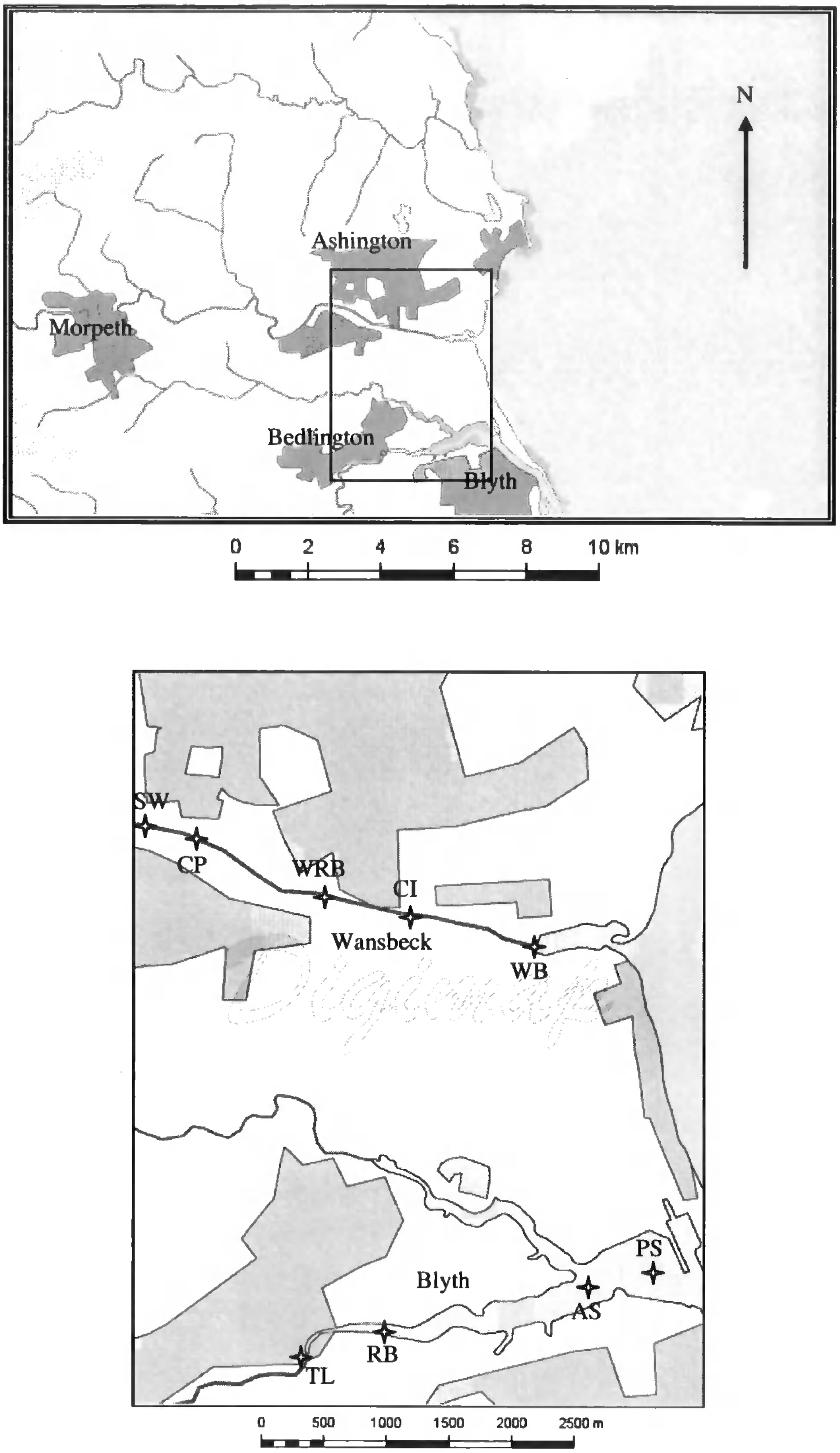

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Figure 2.2. Location of the sampling sites on the Blyth estuary and the Wansbeck estuarine impoundment.

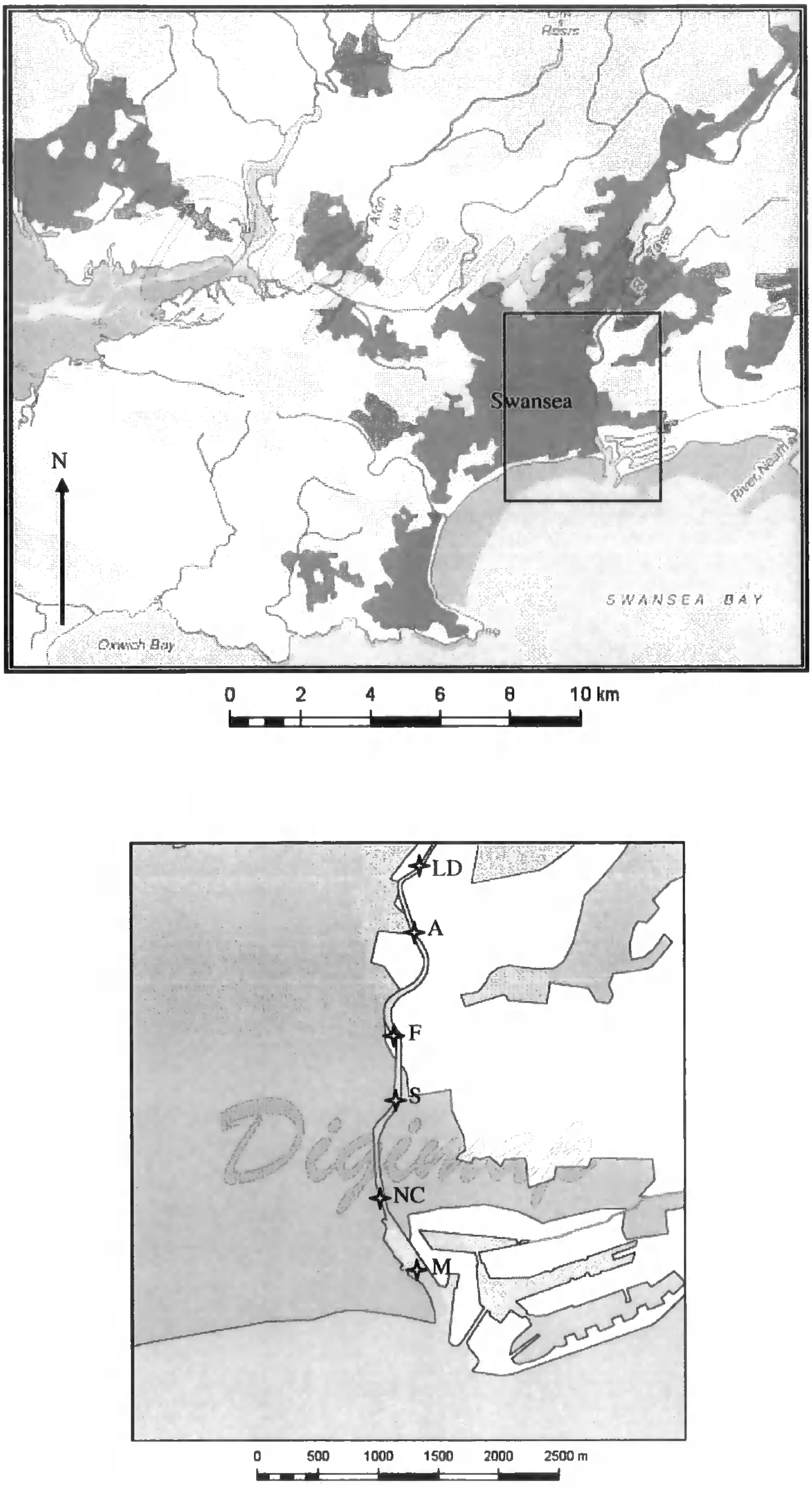


Figure 2.3. Location of the sampling sites on the Tawe estuarine impoundment.

River	Site name	Site abbreviation	Replicates	Grid reference
Tees	Low Moor	LM		NZ 3655 1050
	Low Worsall	LW	✔	NZ 3912 1034
	Above Leven	AL		NZ 4295 1264
	Leven	LV		NZ 4334 1293
	Preston Hall	PH		NZ 4308 1568
	Railway Bridge	TRB		NZ 4469 1800
	Tees Barrage	TB	✔	NZ 4616 1905
Wansbeck	Sheepwash EA	SW	✔	NZ 2565 8587
	Caravan Park	CP	✔	NZ 2610 8635
	Railway Bridge	WRB		NZ 2775 8585
	Castle Island	CI	✔	NZ 2835 8561
	Wansbeck Barrage	WB	✔	NZ 2935 8536
Tawe	Landore EA	LD		SS 6660 9620
	Addis Factory EA	A	✔	SS 6645 9530
	Foxhole EA	F		SS 6630 9430
	Steps EA	S		SS 6620 9430
	New Cut Bridge EA	NC	✔	SS 6610 9320
	Marina EA	M		SS 6640 9260
Blyth	Tidal Limit	TL		NZ 2766 8200
	Road Bridge	AB		NZ 2822 8231
	Above Sleek Burn	AS	✔	NZ 2976 8253
	Power Station	PS		NZ 3053 8272

✔ denotes replicate samples taken at sampling site.

Table 2.1. Locations and names of sampling sites on the four estuaries included in the research.

2.1.4 Depths sampled

Based on knowledge of limnological processes involving thermal or chemical stratification (Hutchinson, 1957; Strøm, 1955), and preliminary studies on the impoundments (Worrall and McIntyre, 1998; Worrall et al., 1998) it was known that water quality was likely not to be homogenous with depth in at least some of the systems. As such, it was decided to take samples for analysis at three depths at each site. These were at the surface, just (circa 10cm) above the sediment water interface, and at the mid-depth between these points. Depth was measured using an echo sounder on the RV. At shallow sites where it had been ensured that the water was well mixed enough to be homogenous (by taking DO, T and conductivity measurements), only surface samples were taken. This was always the case at sites TL on the Blyth, and SW and CI on the Wansbeck, where weirs or riffles provided turbulence to mix the water body. At LM on the Tees samples are recorded at 3 depths but can effectively be thought of as replicates since a weir provides complete mixing here. The water quality parameters measured in the field (DO, T, conductivity, pH and, when taken, Eh) were also taken at surface, mid and deep points in the water column. On several occasions profiles of these parameters were taken at a resolution of 30.5cm throughout the water column to help define vertical variations in water quality on a finer scale.

2.1.5 Replicates

As a check on random errors introduced in either sampling or analysis, duplicate samples were taken at all depths (shallow, mid and deep) at a variety of sites. The sites at which duplicates were taken are recorded in table 2.1.

2.1.6 Dates sampled and hypothesis testing

The water quality surveys were carried out with the aim of statistically testing the significance of a selection of factors as controls on water quality (hypothesis testing). The major comparisons carried out within this research using the results of the water quality surveys may be summarised:

1. Testing of the significance of season (summer vs. winter) and river stage on water quality within a total tidal exclusion impoundment (the Tees).
2. Testing of the significance of season (spring, summer, autumn (fall) and winter) and river stage on water quality within a partial tidal exclusion impoundment (the Wansbeck).
3. Testing of the significance of barrage design (partial vs. total tidal exclusion; high vs. low proportions of tides overtopping) on water quality (Tees, Tawe and Wansbeck summer surveys).
4. Testing of the significance of presence vs. absence of a barrage on water quality (Wansbeck and Blyth summer surveys).

Name of survey	Dates sampled	Days sampled	Tests
Tees summer 1999	21/07/99, 04/08/99, 11/08/99, 25/08/99, 08/09/99, 22/09/99	6	1 and 3
Tees winter 2000	02/02/00, 08/02/00, 16/02/00, 23/02/00, 29/02/00	5	1 and 3
Wansbeck spring 2000	04/03/00, 05/03/00, 07/03/00, 09/03/00, 11/03/00, 12/03/00, 13/03/00, 14/03/00, 15/03/00, 16/03/00	10	2
Wansbeck autumn 2000	25/09/00, 26/09/00, 27/09/00, 28/09/00, 29/09/00, 30/09/00, 01/10/00, 02/10/00, 03/10/00, 04/10/00, 05/10/00, 06/10/00, 07/10/00, 08/10/00, 09/10/00, 10/10/00	16	2
Wansbeck winter 2001	03/02/01, 05/02/01, 06/02/01, 07/02/01, 08/02/01, 09/02/01	6	2
Wansbeck summer 2001	04/06/01, 05/06/01, 06/06/01, 07/06/01, 08/06/01, 09/06/01, 10/06/01, 11/06/01, 12/06/01, 13/06/01, 14/06/01, 15/06/01, 16/06/01, 17/06/01, 18/06/01, 19/06/01, 20/06/01, 21/06/01, 22/06/01, 23/06/01, 24/06/01	21	2, 3 and 4
Blyth summer 2001	04/06/01, 05/06/01, 06/06/01, 07/06/01, 08/06/01, 09/06/01, 10/06/01, 11/06/01, 12/06/01	9	4
Tawe summer 2000	10/06/00, 11/06/00, 12/06/00, 13/06/00, 14/06/00, 15/06/00, 16/06/00, 17/06/00, 18/06/00, 19/06/00, 20/06/00, 21/06/00	12	3
	Total:	85	

Table 2.2. Dates sampled for each of the estuaries studied during the water quality surveys.

Seasonal effects on water quality are discussed within chapter 3, barrage design effects within chapter 4 and impoundment effects within chapter 5 of this thesis. The dates water quality sampling was carried out within the estuaries in order to carry out the tests above are shown in table 2.2. A total of 85 days of water quality surveying was completed, with sampling during summer carried out on the Tawe, Blyth, Tees and Wansbeck, winter sampling carried out for the Tees and Wansbeck, and autumn and spring sampling carried out for the Wansbeck alone.

2.2 Sampling procedure

2.2.1 Safety precautions

Precautions were taken to limit the risk to those involved during water quality sampling. Fieldwork was always completed with at least 2 people in the RV and at least one on shore, all carrying mobile telephones, on all occasions. Lifejackets and high visibility clothing were worn when on the water or when working from river banks. A first-aid kit was carried in the RV. Gloves were worn when collecting samples to avoid risk of infection, in addition to avoiding contamination of samples. All field and laboratory work carried out as part of this PhD was done so without any injury to any party.

2.2.2 Procedure

Sampling was attempted to be carried out as close as possible to midday during all of the surveys to avoid diurnal changes in water quality (e.g. changes in DO due to algal respiration with time of day (Lingeman et al., 1975)) confounding results. This was not possible for the survey of the River Blyth due to sampling needing to be carried out at high tide when depth of water was at its maximum. In this case, sampling was carried out from around 3pm at the start of the survey to around 8pm at the end of the survey. The length of time taken for each date's sampling run was on average circa 3 hours (slightly longer on the Tees and slightly shorter on the Blyth). The sequence of data and sample collection from each of the sites varied between rivers depending on the relative position at which the RV was launched. However, it is assumed that parameters did not vary significantly during the length of time taken to complete a date's sampling run.

All work was carried out from the RV (figure 2.4) except at sites SW on the Wansbeck and LM on the Tees where, at low flows, sampling was carried out by wading. Care was taken to carry out field analysis and water sampling on the upstream side of the RV and gloves were worn to minimise the risk of contamination. At each site the time, water depth and number of samples successfully taken, and the water quality parameters measured in the field (using the methods outlined in Field Analytical Methods) and the depth of their measurement, were recorded in a notebook. At the start of each run the weather conditions were noted.

Figure 2.4. The research vessel used during the water quality surveys.

Water sampling was carried out using a stainless steel depth (grab) sampler. This consists of a tube of 10cm diameter and 30cm length held in a horizontal position, oriented parallel to the flow by a fin. Two sprung-loaded flaps can be closed over the ends of the tube by dropping a messenger weight down the graduated lowering rope to enclose a sample of water from a defined depth. It was felt unlikely that the steel of the depth sampler would act as a source of metal contamination at the range of pHs encountered. Samples were transferred to the laboratory in 0.1 M nitric acid-washed 1 litre polyethylene sample bottles. These were rinsed 3 times with portions of the samples with which they were to be filled. Samples were transported to the laboratory in the dark in cool boxes at 4°C, and the time between collection and preliminary laboratory analysis and treatment was kept to less than 2 hours (ISO 1990).

Samples were taken in order of increasing depth (surface, then mid, then deep sampling). The depth sampler was lowered gently into position to avoid disturbance of any stratification, and held in position for 10 seconds prior to releasing the messenger. Care was taken when lowering the sampler to depth not to disturb the bed sediment.

Where it was noticed that sediment had been disturbed, sampling was repeated. Inclusion of non-homogenous particulates such as wood and leaves in samples was avoided.

2.3 Water quality parameters measured

2.3.1 Introduction

Water quality may be defined by a huge variety of parameters. Until relatively recently the range and type of parameters used to assess water quality has varied between countries and even regionally (Kristensen and Bøgestrand, 1996). The trend now is towards the harmonisation of water quality monitoring and assessment programmes (e.g. European Union River Network, United Nations Environment Programme (UNEP), OECD). The UNEP Global Environmental Monitoring System Freshwater Quality Programme (Meybeck et al., 1989; WHO, 1991) divides water quality parameters by the following classification:

- **Physical/Chemical:** Conductance, Suspended Solids, pH, BOD and COD.
- **Major Ions:** Alkalinity, Sodium, Magnesium, Sulphate, Chloride, Potassium, and Calcium.
- **Metals:** Aluminum, Chromium, Manganese, Iron, Nickel, Copper, Zinc, Arsenic, Selenium, Cadmium, Mercury, and Lead.
- **Nutrients:** Nitrogen, Ammonia, and Phosphorus.
- **Organic:** P,P-DDT, DDT, O,P-DDT, P,P-DDD, O,P-DDD, P,P-DDE, O,P-DDE, Lindane, Alpha - BHC, Mirex, Aldrin, Endrin, Dieldrin, PCBs, Atrazine, Methiocarb, Aldicarb, 2,4-D, P,P-DDD Olefin, and BHC.
- **Microbiology:** Total Coliforms, Faecal Coliforms, and Faecal Streptococci.

The choice of water quality parameters to measure in this research was based on the GEMS/Water programme, with the range of analytes being kept to a manageable level by excluding the organic and microbiological parameters. Thus, the focus was on the general physical and chemical parameters, major ions, metals, and nutrients. This scheme allows a suitably broad assessment of water quality, whose results may be compared internationally. To aid in comparability, standard methods of analysis were used wherever possible (American Public Health Association (Clesceri et al., 1998) or International Organisation for Standardisation (ISO, 1990)).

Due to availability of equipment, the parameters measured differed slightly from those listed above. Since the majority of metal analysis was carried out using ICP-OES/AES, the range of analytes measured in most samples excluded heavy metals (Cd, Hg, Pb) and As and Se, but included a greater range of less heavy elements (Co, Sc, Si, Sn, Ti, V). Chloride was not measured, but it was felt that in an estuarine environment chloride would almost certainly be proportional to sodium, and that sodium could be used as an alternative conservative index of mixing. Time constraints during the immediate processing of samples following sampling runs meant that BOD alone, without COD, was taken as an indicator of oxygen demand. Throughout this work, according to convention (e.g. APHA, 1998), dissolved refers to all components passing through a filter of 0.45 μm pore size.

2.3.2 Physical/chemical

2.3.2.1 Dissolved oxygen

Dissolved oxygen (DO) is probably the most fundamental parameter in the study of water quality. Chapman (1996) explains that, "...oxygen is involved in, or influences, nearly all chemical and biological processes within water bodies." Oxygen dissolves in water from the atmosphere, which contains around 21% oxygen. The solubility of oxygen in water increases non-linearly with decreasing temperature, and linearly with increasing atmospheric partial pressure (Mortimer, 1981). Salinity reduces the solubility of oxygen, and oxygen contents of seawater are around 80% relative to freshwaters under the same conditions (Green and Carritt, 1967; Weiss, 1970). The differences between observed values of DO and those expected from purely physical controls (given as a % saturation) are a reflection of the biological processes (photosynthesis and respiration) in a water body. The aerobic decomposition of organic matter in the water column or at the sediment-water interface is particularly significant in leading to dangerously low DO levels (Breuer et al., 1977). Most fish cannot survive below levels of 2 mg/l DO (Chapman, 1996), and anaerobic conditions can lead to releases of methane (CH_4), ammonium (NH_3), hydrogen sulphide (H_2S), phosphorus (P), and iron (Fe) and manganese (Mn) and associated metals, to the water column.

2.3.2.2 Biochemical oxygen demand

Since aerobic decomposition of organic matter is a major depleter of DO in water bodies, it is useful to have a measure of how much oxygen the decomposition of any organic matter will consume. The biochemical oxygen demand (BOD) gives an approximate determination of the amount of DO required by aerobic micro-organisms to break down the organic material contained within a water or wastewater sample (Velz, 1984). BOD values range from under 1 mg/l in some unpolluted waters, to around 600 mg/l for raw sewage and 25000 mg/l for paper pulping waste (Reeve, 1994). Chemical oxygen demand (COD) measures the oxygen equivalent of organic material broken down by a strong chemical oxidant, and is often used together with or instead of BOD measurements. In this project, due to time constraints during the water quality surveys, it was decided to measure BOD alone. BOD better reflects the environmental behaviour of organic material than COD. Due to the limited number of BOD bottles available and that fact that each BOD determination takes a period of 5 days, BOD values were only taken on a portion of the days of water quality sampling, and therefore the power of significance tests involving BOD are lower than for other parameters analysed (see appendix 1 for a description of power in statistical analyses).

2.3.2.3 pH

pH is defined as the negative of the logarithm to the base 10 of the hydrogen ion activity (generally the same as concentration) in a solution. Pure water dissociates weakly to H^+ and OH^- ions to give a pH of 7 defined as neutrality. In natural UK lowland waters the pH tends to be mainly controlled by the balance between carbon dioxide, carbonate and bicarbonate ions, and tends to lie between 6.0 and 8.5 (Chapman, 1996). This balance can be altered by the addition of pollutants (e.g. acid rain), by natural organic acids (e.g. in Sphagnum bogs) or inorganic acids (mainly in volcanic regions), and autochthonous production of carbon dioxide and bicarbonate on a various time-scales. Fish populations are strongly affected by low pH values, salmon decreasing below pH 6.5, perch below 6.0 and eels below 5.5, with little life below pH 5 (Reeve, 1994). pH also affects the speciation and solubility of metals in water bodies.

2.3.2.4 Alkalinity

Whilst pH is the measurement of the hydrogen ion activity in a water body, the alkalinity is the measurement of the resistance to change of the pH. Low alkalinities indicate that a water body is susceptible to a reduction of pH on the addition of an acid. Alkalinity is taken to represent the amounts of carbonate, bicarbonate and hydroxide in the water body, and tends to be given in units of mg/l $CaCO_3$ equivalent (the hypothetical value assuming all alkalinity were due to $CaCO_3$).

2.3.2.5 Eh

Eh or redox potential gives a qualitative idea of whether a water is in reducing or oxidising state. In a similar way to pH representing the behaviour of acids and bases as proton (hydrogen ion) donors and acceptors, Eh represents the behaviour of reductants and oxidants as electron donors and acceptors in a solution. Unlike protons, however, there are no free electrons: every oxidation is accompanied by a reduction (Stumm and Morgan, 1981). Eh is given as a potential, and its range in natural waters is around –500 mV to +700 mV (Chapman, 1996). It is dependent on the equilibria of all the redox systems in the water (i.e. the number of oxidised and reduced species), and is particularly influenced by the redox states of oxygen, iron and sulphur. The presence of dissolved oxygen normally gives Eh values of between +100 and +500 mV, and highly reducing conditions, characterised by the presence of hydrogen sulphide, have Eh values down to –100 mV. Under stratified conditions in the impoundments studied a fall in Eh values might be expected from the oxygenated freshwater layer to the deoxygenated saline water at depth.

2.3.2.6 Conductivity

Conductivity is the measure of the ability of water to carry an electrical current. It is dependent on the concentration and type of dissolved solids in the water. Inorganic solutes tend to be good conductors, whereas organic solutes tend not to dissociate as easily and are poor conductors. Conductivity is given in units of microsiemens per centimetre (μS/cm) in freshwaters, or millisiemens per centimetre (mS/cm) in brackish and saline waters where conductivity is several orders of magnitude higher. Conductivity can give an idea of the total dissolved solids content (mg/l) of a water sample if the ionic makeup is known. For waters in which sodium and chloride dominate:

$$mg / l = 0.67 \times \mu S / cm$$

gives an approximation of total dissolved solids (mg/l). In freshwaters, pollutants or a high proportion of land run-off tend to increase the conductivity. Conductivity was considered to be an important determinand in this study since it can indicate the amount of mixing between fresh and saline waters.

2.3.2.7 Temperature

Temperature in a water body will vary seasonally and often diurnally. In general the larger the water body the lower are its fluctuations in temperature. Changes in temperature are dependent on the amount of solar insolation, transfers of heat from sediments and the air, and condensation and evaporation of water at the water surface. The rates of physical, chemical and biological processes in water are dependent on the temperature. The solubility of gases, including oxygen and carbon dioxide, decrease with increasing temperature. In general rates of reactions increase with temperature increases. Metabolic rates, and hence rates of decomposition of organic material leading to deoxygenation, growth rates of algae, etc., increase with increased temperature.

2.3.2.8 Transparency

The transparency of a water body is a combined function of its colour and turbidity. Turbidity is controlled by the amount and concentration of suspended particulate matter in the water column. Particulates can be mineral (e.g. clay and silt) or biological (e.g. algae and cyanobacteria) in origin. Colour is imparted by dissolved components such as minerals and organic acids. Transparency will vary under a variety of conditions including flow and the growth rates of suspended organisms, and is a simple and convenient method of giving a rough comparison of these factors.

2.3.2.9 Total Suspended Solids

Total suspended solids (TSS) is the measurement of particulate matter (mineral or organic) which is suspended in the water column. Convention is to define total suspended solids as the matter which will not pass through a filter of 0.45µm pore size. TSS will affect the amount of light available for photosynthesis entering the water. Significantly for this study, fluxes in TSS may indicate the state of sedimentation or erosion in an impoundment.

2.3.3 Nutrients

The Environment Agency defines eutrophication as:

"The enrichment of waters by inorganic plant nutrients which result in the stimulation of an array of symptomatic changes. These include the increased production of algae and/or other aquatic plants, affecting the quality of the water and disturbing the balance of organisms present within it. Such changes may be undesirable and interfere with water uses." (Environment Agency, 1998; OECD, 1982).

Eutrophication is a problem in many parts of the world including the UK, and so the study of the nutrient status is key in any study of water quality. The biological productivity in a water body tends to be limited by the concentration of either nitrogen (N) or phosphorus (P) (Vollenweider, 1968). Silica can be important where diatoms are a significant part of algal production (Lund, 1954).

2.3.3.1 Nitrogen

Nitrogen is essential to organisms in the formation of proteins and DNA, and is converted by algae and aquatic plants from inorganic to organic forms. Inorganic forms of nitrogen occur in waters as nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+) and molecular nitrogen (N_2), and various processes act to convert N between its oxidation states. These can be summarised as:

a) Assimilation of inorganic forms by organisms to produce organic N, such as amino acids.
b) Nitrogen fixation: reduction by micro-organisms of $N_2 \rightarrow NH_4^+$ and organic N.
c) Heterotrophic conversions.
d) Nitrification: oxidation of $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$.
e) Ammonification: production of NH_4^+ by decomposition of organic matter.
f) Denitrification: reduction of $NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2$ (which may be lost from the system) under anoxic conditions.

Physical transfers of N occur due to the processes of sorption and sedimentation.

Ammonia

The main sources of ammonia in water bodies are from the breakdown of organic material, and industrial and sewage waste and agricultural run-off. In addition to its contribution to eutrophication, at high concentrations and higher pH conditions ammonia is highly toxic to many organisms, especially fish. At high pH the equilibrium between ammonium (NH_4^+) and toxic undissociated ammonia (NH_3) (the two dominant forms of ammonia) moves towards ammonia. Total ammonia concentrations tend to be low in natural waters (<0.1 mg/l). Higher values occur in polluted waters or where anoxic decomposition of organic material is significant.

Nitrate

Nitrate (NO_3^-) is normally the dominant form of N occurring in natural waters. Determination of nitrate tends to include nitrite (NO_2^-), but since nitrite is rapidly oxidised to nitrate its contribution is usually minor. The concentrations of nitrate in natural waters are low (<0.1 mg/l), but concentrations are usually higher due to contributions from industrial and sewage wastes, and particularly run-off of inorganic nitrate fertilisers. The Environment Agency (1996) give that the UK use of nitrogenous fertilisers increased by around 50% from 1970 to 1990, although has since remained relatively constant. Nitrate is the major form of N available to algae and aquatic plants, and therefore a significant factor in understanding eutrophication. Very high concentrations (>200 mg/l) of nitrate in drinking water have led to "blue baby syndrome" in the past, although these levels are never approached in the UK today (Porteous, 2000).

2.3.3.2 Phosphorus

Relative to N and other elements essential to biota, P is normally the least abundant in natural waters, and most commonly limits biological productivity (Sakamoto, 1966; Dillon and Rigler, 1974; Schindler, 1977), although estuaries may show N limitation at their seaward ends. P is essential to organisms as a component of nucleic acids and in intracellular molecular synthesis and transport. The majority of P is therefore contained within organic forms, the majority of this being in particulate material. Dissolved orthophosphate (phosphate) is less than 5% of total P in natural waters (Prepas and Rigler, 1982). However it is this form which is most bioavailable, with most other forms scarcely available at all (Reynolds and Davies, 2001). Levels of phosphate in water bodies are normally very low (<0.02 mg/l) since uptake of phosphate by organisms is very rapid. Significant inputs of phosphate come from sewage (particularly containing polyphosphate-based detergents), industrial effluents and agricultural run-off. Binding to sediment can act as a sink for phosphorus, but phosphorus may be recycled from sediments under anoxic conditions. In this study, both dissolved orthophosphate (SRP) and total dissolved P (TDP) were measured.

2.3.3.3 Silicon

Silicon occurs in natural waters as dissolved, colloidal or suspended forms of silica (SiO_2). Dissolved forms occur as silicilic acid and its dissociation and association products, and organic silicon compounds. In this study, total dissolved silica was measured. The majority of silica is derived from the weathering of siliceous minerals. Silica is relatively unreactive, but is essential to diatomaceous algae and may limit blooms of diatoms in spring. Seasonal variations my occur due to uptake by diatoms during cell growth, and release during decomposition. Concentrations of silica tend to be fairly high relative to other nutrients (1-30 mg/l in freshwaters (Chapman, 1996)), and higher in freshwaters than seawaters.

2.3.4 Major elements

There is a marked difference in both total concentrations and relative abundances of major elemental constituents between freshwater and seawater. The major cations in freshwater generally follow an order of abundance of $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$, whilst in seawater the order is $Na^{2+} > Mg^{2+} > Ca^{2+} > K^{+}$ (Ward, 1996). Whereas the concentration in freshwaters can vary widely between catchments, the concentration of major ions in seawater is remarkably constant around the world. The ionic strength of seawater is such that mixing of only 1% by volume with freshwaters in an estuary will give a ratio of ions which is almost identical to that in the seawater (Andrews et al., 1996). This difference has a major affect on the transport of particulate and dissolved material through estuaries, through the processes of flocculation and ion exchange. Thus, measurement of the concentration of major ions in seawater can constrain mixing and its associated processes in estuaries.

2.3.4.1 Sodium

Sodium (Na^{2+}) is the dominant cation in seawater (World mean concentration of around 10800 mg/l) and also occurs in significant concentration in freshwaters (World mean concentration in stream water of 6.1 mg/l) (Reimann and Caritat, 1998). It is highly soluble and mainly sourced from rainwater and dissolution of Na bearing minerals. Human inputs of sodium to freshwaters include sewage and industrial discharges, and run-off from road salting. High levels of sodium can cause freshwaters to be unsuitable for use for drinking or for irrigation. Sodium behaves conservatively on mixing of fresh and saline waters in an estuary, and can hence be used as an index of mixing when looking at the conservative/non-conservative behaviour of other elements (Liss, 1976).

2.3.4.2 Potassium

Potassium (K^+) is sourced from dissolution of rocks plus cation exchange but, since potassium containing minerals are generally of low solubility, concentrations are lower than for sodium in both fresh (2.3 mg/l World mean) and saline (399 mg/l World mean) waters (Reimann and Caritat, 1998). Potassium is an essential nutrient, and is applied in large quantities as a plant fertiliser. Fertiliser run-off, together with industrial discharges provide the main anthropogenic inputs of potassium. Potassium also behaves conservatively on mixing in estuaries.

2.3.4.3 Magnesium

Magnesium (Mg^{2+}) is sourced from ferromagnesium and carbonate minerals. Anthropogenic inputs are usually relatively insignificant. World average concentrations are 1290 mg/l in seawater and 4.1 mg/l in freshwater (Reimann and Caritat, 1998). Magnesium behaves conservatively on mixing in estuaries.

2.3.4.4 Calcium

Calcium (Ca^{2+}) dissolves easily from carbonate or sulphate rocks. Calcium is essential for most organisms (particularly for shells and bones), but concentrations are normally higher than would limit biological productivity. Calcium and magnesium salts cause hardness. World average concentrations are 412 mg/l in seawater and 18 mg/l in freshwater (Reimann and Caritat, 1998). Calcium behaves conservatively on mixing in estuaries.

2.3.4.5 Sulphur

Sulphur (S) exists in several oxidation states in natural waters. Under oxidising conditions sulphate (SO_4^{2-}) is the dominant form. Sulphate can be used as an oxygen source by bacteria, which convert it to hydrogen sulphide (H_2S, HS^-) under anaerobic conditions. Total dissolved sulphur was measured. Sulphur is essential for all organisms but deficiencies are rare. High concentrations of hydrogen sulphide are toxic to aquatic life and make water unsuitable for drinking. Sulphur in freshwaters is sourced from sulphur containing minerals (sulphates or sulphides), atmospheric deposition of oceanic aerosols, and significant anthropogenic atmospheric inputs from the burning of fossil fuels. World average concentrations are 905 mg/l in seawater and 4 mg/l in freshwater (Reimann and Caritat, 1998). Sulphur behaves conservatively on mixing in estuaries, although anoxia can lead to some loss of sulphur as insoluble metal sulphides and as hydrogen sulphide gas.

2.3.5 Minor and trace metals

Element	Mean World Seawater Conc. (mg/l)	Mean World Stream Water Conc. (mg/l)	Environmental Impacts or Behaviour
Al	0.002	0.3	Toxic to fish at low pH. Linked to Alzheimer's disease.
Co	0.00002	0.0002	Deficiencies more widespread than toxicity problems.
Cr	0.0003	0.0007	Cr (VI) highly toxic.
Cu	0.00025	0.003	Toxic at high doses.
Fe	0.002	0.04	Redox governed. Acid mine drainage can precipitate ferric hydroxide.
Mn	0.0002	0.004	Redox governed. Similar behaviour to Fe.
Ni	0.00056	0.0003	Some compounds toxic.
Sc	0.0000006	0.000004	Thought to be non-toxic.
Sn	0.000004	0.00001	Organic forms toxic to lower organisms.
Ti	0.001	0.003	Non-toxic.
V	0.0025	0.0009	Toxic at some oxidation states.
Zn	0.0049	0.015	Low toxicity.

Table 2.3. Mean world ocean water trace metal concentrations from Lide (1996) compiled data and mean world stream water trace metal concentrations from Koljonen (1992) compiled data, reported in Reimann and Caritat (1998).

The concentration of a variety of minor and trace elements is critical to the biological health of a water body. Several metals, such as Mn, Zn, V, Cu and Co, are essential micronutrients, but at raised concentrations may exhibit toxic effects. Trace metals are released from the weathering of minerals, and anthropogenic inputs come from sources such as mining and industrial effluents. The form in which an element occurs often controls its toxicity. Ionic forms of metals are generally the most toxic, and both mobility and toxicity may be controlled by oxidation state. Some organic metal compounds (e.g. methylmercury or tributyltin) have very high toxicities. Many metals show adsorption onto suspended sediment, and partitioning to sediment can act as a sink for metals. In this study, dissolved forms of metals were measured as part of the water quality surveys and adsorbed forms were measured in sediment surveys (see chapter 6).

The range of metals analysed was in main defined by what could be analysed for accurately with the machines available. For the majority of water samples for which analysis was by ICP-OES, a total of 12 minor and trace metals were measured. For those samples which were also analysed using ICP-MS an additional 48 (mainly ultra-trace) elements were looked at. These elements are likely not to be at high enough levels to exhibit environmental impacts, but can be used to help fingerprint water and sediment inputs to the systems. Table 2.3 summarises the average abundances, and environmental impacts and behaviour, of the 12 minor and trace elements measured in all water samples.

2.3.6 Flow

Flow in estuaries is controlled by river flow and tidal flow, and will vary dependent on the relative state of each.

River flow or discharge is generally an essential measurement in all river water quality studies as it allows:

- measurement of the amount of volume available for use
- calculation of fluxes of materials carried by the flow (e.g. suspended sediment or nutrients)
- characterisation of the origin of many water quality parameters by their relationship to flow.

Discharge regimes are controlled by, the size of catchment, climate, topography and land-use, and hydrology. Larger flows are more able to cope with inputs of effluents and wastewaters, and low water quality conditions may occur under drought conditions where flows are insufficient to dilute pollutant inputs.

A river's hydrograph (a graphical presentation of variations of flow over time) is made up of two components: baseflow and runoff (Wilson, 1990). Baseflow is the water entering a river from groundwater, which tends to be relatively constant compared to runoff, which is the portion of rainfall which flows overland to the river. Many variations in water quality can be explained by the relative influence of these two sources. Runoff will contain high TSS, organic carbon and N and P, whilst groundwater provides elements derived from rock weathering (SiO_2, Ca^{2+}, Na^+, Mg^{2+}, K^+) (Chapman, 1996). Substances entering a river at a constant rate (from groundwater or an anthropogenic point source) will be negatively correlated with discharge. Particulates and bound species such as P and some metals, and organic material, which increase with increased runoff will be positively correlated in some manner with discharge.

Data for river discharges during the sampling runs was obtained from the EA. The EA gauging stations at which discharges were measured are:

River	Name of Gauging Station	Catchment Area (square km)	Grid Reference
Tees	Low Moor	1264.0	NZ 365 105
Tawe	Ynystanglws	287.3	SS 685 998
Wansbeck	Mitford	227.7	NZ 175 858
Blyth	Hartford Bridge	269.4	NZ 243 800

Table 2.4. Gauging stations used for flow data within the research.

Discharges are reported at the approximate time of sampling (12:00). Since the freshwater contained within the impoundments may represent flow conditions prior to the time of sampling, the maximum and mean discharges over the prior 24 hour period are also included in the dataset. Discharges are given in m^3/s.

Seawater discharges were not measured directly, but rather the height of the high tide prior to sampling relative to the crest height of the barrage is given. This overtopping (measured in m) gives a relative idea of how much seawater is entering the impounded areas, although the volume will vary with the amount of freshwater discharge opposing this input. Tidal data was obtained from the UK Hydrographic Office (2000, 2001).

Seawater is of a far more constant composition than freshwater, and will not vary significantly with tidal flow at the point of entrance to mouths of estuaries, although within the estuaries the strength of tidal flow is important in the transport of sediment and bound species. Within estuaries there is a continual exchange of sediment between the suspended and bed phases due to tidal flows (Mehta and Dyer, 1990).

2.4 Analytical methods

The parameters of DO, pH, Eh, conductivity, temperature and transparency were measured *in situ* in the field. The parameters of alkalinity, TSS, BOD, nutrients, major elements and minor and trace metals and non-metals were measured in laboratories of the University of Durham and set up within Swansea City Council offices on samples transported and stored as described above.

Analytical grade reagents and Milli-Q® 18 MΩ.cm water were used in all the laboratory work described. Glassware and plasticware was acid and Decon 90® (non-ionic surfactant) washed (soaked overnight in 1% HNO_3, followed by overnight in 5% Decon 90® and rinsed in de-ionised water). Where reported, limits of detection LOD are given as:

$$LOD = S_b + 3\sigma$$

where:

S_b = the mean measured value of a series of sample blanks, and
σ = the standard deviation of the series of sample blanks

(Long and Winefordner, 1983).

2.4.1 Dissolved oxygen

Principle:

Membrane electrometric methods of DO measurement were used in all water quality surveys including the determinations of BOD. Membrane electrode methods have advantages over iodometric (Winkler) techniques due to their resistance to interferences in natural waters (McKeown et al., 1967) and ability to measure *in situ*. and are suitable for measuring DO in polluted, highly coloured and saline waters (Mancy and Okun, 1960).

Apparatus:

A Hanna Instruments HI 9143 Portable Waterproof Microprocessor Dissolved Oxygen Meter was used for all fieldwork. The probe consists of a silver chloride anode, a platinum cathode (sensor) and an oxygen permeable Teflon membrane cap. Care was taken to keep the platinum cathode untarnished and the electrolyte solution (KCl) free from bubbles of air, and the membrane was replaced if dirt or algal growth was observed. The manufacturer's specifications are:

Range: 0.00 to 19.99 mg/l O_2
0.0 to 100.0 % O_2
Resolution: 0.01 mg/l O_2
0.1 % O_2
Accuracy (@25°C): ±1.5% Full Scale
Calibration: Automatic in saturated air.
Temperature compensation: Automatic from 0 to 50°C.

The meter was easy to calibrate (at 100% saturation) in air, and was checked in solutions of 100% and 0% saturation. The response time was relatively rapid and a water movement of at least 0.3m/sec was ensured during measurements by either the flow of the rivers or manual agitation where flow was insufficient.

For laboratory measurements of DO during BOD analyses a WTW Oxi92 Dissolved Oxygen Meter of very similar design and operation to the Hanna meter was used.

2.4.2 pH

Principle:

Electrometric methods of pH measurement were used in all water quality surveys. Electrometric measurement determines the activity of the hydrogen ions within a solution by measuring the potential between a glass electrode and a reference electrode. The potential between the electrodes is in linear relation to the pH, and the meter is calibrated using standard pH buffer solutions to enable readouts directly in units of pH (Bates, 1973). pH measurements are affected by temperature (both mechanically and chemically) and meters usually include temperature probes and automatic temperature compensation features. Glass electrodes are not significantly affected by salinity (except at pH>10), or colour, turbidity or redox state (Clesceri *et al.*, 1998).

Apparatus:

For the water quality surveys on the Tees and the Tawe, and for the Wansbeck March 2000 survey, pH was measured using a Hanna Instruments HANNA Water Tester with specifications of:

Range: 0.0 to 14.0
Resolution: 0.1
Accuracy: ±0.2
Calibration: Double point calibration in neutral (pH 7.00±0.02 at 20°C phosphate) buffer solution plus an acid (pH 4.00±0.02 at 20°C phthalate) buffer solution.

This meter requires a small sample of the water for analysis to be poured into a sample compartment, and as such limited pH measurement to samples collected in the water trap and brought to the surface. It was decided, to enable pH measurement at a higher resolution over the depth of the impoundments, to use a Hanna Instruments 9023C pH meter with a length of cable between the probe and the meter for the majority of the surveys. The 9023C has the added advantage of higher resolution and accuracy:

Range: 0.00 to 14.00
Resolution: 0.01
Accuracy: ±0.01
Calibration: Automatic with 3 memorised standard buffers (4.01, 7.01 and 10.01).

2.4.3 Eh

Principle:

Eh (or oxidation-reduction potential (ORP)) is also measured electrometrically, by measurement of the potential between an inert electrode (e.g. platinum) and an indicator electrode which ideally donates or accepts electrons from oxidised and reduced species in the water being analysed. The measurement of Eh is complicated by several factors including inert redox couples, electrode poisoning, very small exchange currents, irreversible reactions and rapid changes in redox conditions on storage (Clesceri et al., 1998).

Apparatus:

Eh measurements were also made using a Hanna Instruments HANNA Water Tester in the same manner as pH. The manufacturer's specifications are:

Range: -1000 to +1000mV
Resolution: 1mV
Accuracy: ±5mV

The HANNA instrument is non-calibratable for Eh. It was found during the surveys that Eh measurements for the same samples varied between the HANNA Water Testers used (probably due to differences in the conditions of the electrodes), and thus the accuracy of the Eh data are likely to be poor. Appelo and Postma (1994) explain that, "Eh measurements are only qualitative indicators for redox comditions and should be made as sloppy as possible, so that you will not be tempted to relate them to anything quantitative afterwards." It was decided that, on dropping the HANNA Water Tester for the measurement of pH (see above), Eh measurement would not continue.

2.4.4 Conductivity

Principle:

Conductivity in a solution is measured between 2 inert electrodes applying an alternating current and measuring resistance using a Wheatstone bridge, and should be made in situ or in the field immediately after sample collection. Meters are calibrated against standard solutions of KCl to determine cell constants for the meter. Conductivity is temperature dependent (increases with increasing temperature due to increasing ionic motion) and readings are usually standardised at 25°C. Conductivity probes are fairly robust, although poor readings may be obtained from fouled electrodes or inadequate water circulation.

Apparatus:

As for pH and Eh, initial water quality surveys' conductivity readings were made using a Hanna Instruments HANNA Water Tester of specifications:

Range: 0 to 1999 μS/cm
Resolution: 1 μS/cm
Accuracy: 2% Full Scale
Calibration: Single point conductivity solution (1413 μS/cm @ 25°C)

As indicated above, the HANNA Water Tester's range is only up to 1999 μS/cm and therefore saline and brackish waters were diluted volumetrically with de-ionised water (of assumed 0 conductivity) for measurement. To avoid the errors and inconvenience introduced by these dilutions, and the general problems with the HANNA Water Tester outlined in the pH methodology, the majority of the surveys' conductivity measurements were made using a Hanna Instruments HI 9635 Portable Waterproof Multi-Range Conductivity/TDS Meter:

Range: 0.0 to 150.0 μS/cm
    150 to 1500 μS/cm
    1.50 to 15.00 mS/cm
    15.0 to 199.9 mS/cm
Resolution: 0.1 μS/cm
    1 μS/cm
    0.01 mS/cm
    0.1 mS/cm
Accuracy: ±2% Full Scale @ 20°C
Calibration: Automatic 1, 2 or 3 point calibration at 84, 1413 or 12880 μS/cm
Temperature compensation: Automatic from 0 to 60°C

This allowed measurement of conductivity *in situ* and over the whole range of values encountered in the estuaries.

2.4.5 Temperature

Principle:

Thermistor electrical thermometers were used for all water temperature measurements. Thermistors allow determinations of temperature from the principle of electrical resistance decreasing with increasing temperature, and have the advantages of rapid response and ease of *in situ* measurement.

Apparatus:

Temperatures were measured *in situ* as part of the water quality surveys using the temperature sensor of the Hanna Instruments HI9143 Dissolved Oxygen Meter (see DO method):

Range: 0.0 to 50.0°C
Resolution: 0.1°C
Accuracy: ±0.5°C

Readings were occasionally checked against those from the pH meters and taken using a mercury thermometer and were found to be in good agreement.

2.4.6 Transparency

Principle:

Transparency of the water column is measured as the depth at which a Secchi disc (first used in the Mediterranean in 1865 by Secchi) lowered into the water column disappears from view. Secchi discs are made of metal or rigid plastic, but may vary in design in terms of colour, pattern and size (Bartram and Balance, 1996).

Apparatus:

The Secchi disk used in all transparency measurements was a 30cm wide metal disc painted with black and white quadrants, suspended from a graduated rope (manufactured in the workshop of the Department of Geological Sciences, Durham University). The disk was lowered into the water from the shaded side of the RV, and the depth noted at which it disappeared from view. It was then raised and the depth at which it reappeared was noted. The average of these 2 depths (given to the nearest 5cm in this research) was recorded as the Secchi depth. The method is subject to several problems including, variations in light conditions between dates, times and sites, its inability to measure during high flow conditions, and inherent subjectivity, but gives a rough idea of variations in colour and turbidity.

2.4.6 Alkalinity

Principle:

Carbonate/bicarbonate alkalinity of a water sample is determined by titration with a strong mineral acid to a defined pH end point. The change in pH can be followed over the titration either by colour indicator solutions (phenolphthalein (pH 8.3 end point) or methyl orange (pH 4.5 end point)) or electrometrically. Colour indicators are appropriate in most cases, but electrometric methods must be used where high accuracy is essential or where high colour, turbidity or suspended solids would obscure the indicator colour change. Indicator solutions were used in this study after ensuring that there was good agreement with electrometric tests.

Method:

Samples were transported in cool boxes and stored at 4°C prior to analyses. Titrations were carried out a maximum of 3 hours after sample collection for all water quality surveys. Samples were titrated in conical flasks using 0.005 M HCl to a pH 4.5 end point using methyl orange solution as the indicator, and alkalinity T as $CaCO_3$ equivalent mg/l calculated by:

$$T = \frac{50000 \times A \times M}{V}$$

where:

A = volume of HCl (ml) used to reach the methyl orange end point,
M = concentration of HCl (M), and
V = volume of sample (ml).

Blanks of deionised water were analysed for quality control and found to give results of effectively zero. Clesceri et al. (1998) report that precision is likely to be much higher than uncertainties introduced in sampling and sample handling before the analysis.

2.4.7 Total suspended solids

Principle:

Total suspended solids (TSS) (also referred to as suspended particulate matter (SPM)) is determined by vacuum filtering a well mixed water sample through a weighed filter of defined pore size, which is then dried under specified conditions to a constant weight (Degen and Nussberger, 1956). The increase in weight of the filter over the volume of sample filtered is the TSS. Filtration volumes are adjusted according to the amount of TSS in the samples to give residues of approximately 100-200mg on each filter (to avoid clogging of the filters, leading to excessive filtration times and removal of colloidal material). Large floating particles (e.g. leaf and other vegetation material) are removed prior to filtration.

Method:

Samples were transported in cool boxes and stored at 4°C prior to analyses. Filtrations were carried out a maximum of 3 hours after sample collection for all water quality surveys. Standard Whatman® Cellulose Nitrate Membrane Filters of 0.45μm pore diameter were used in all determinations of TSS and filtering of samples for further analysis for nutrients and metals. These were stored in a desiccator prior to pre-weighing, and filters and residues were dried at 105°C overnight followed by cooling in a desiccator prior to weighing to 4 decimal places on a Mettler AJ100 electronic balance. TSS values in mg/l were calculated by:

$$TSS = \frac{(A-B)\times 1000000}{V}$$

where:

A = weight of filter + retained solids (g),
B = weight of filter (g), and
V = volume of sample filtered.

Blank (de-ionised water) samples were run to check that the weight of filters did not alter significantly on use.

2.4.8 Biochemical oxygen demand

Principle:

Biochemical oxygen demand (BOD) measures the amount of oxygen consumed during the biochemical breakdown of matter in a water or wastewater sample. It is determined by measuring the DO of a sample (either iodometrically or potentiometrically) before and after incubation in the dark in airtight bottles under defined conditions and for a specified duration. Several standard methods exist with various variations in these conditions and incubation periods (Young *et al.*, 1981; National Council of the Paper Industry, 1982; ISO, 1990), but the most commonly used methods are run over 5 days (BOD_5) and are based on the original United Kingdom Royal Commission on Sewage Disposal method. pH of samples should be between 6.5 and 8.5, and sterile samples need to be seeded with an appropriate microbial culture. The method can be subject to errors from the additional use of oxygen by nitrifying bacteria to oxidise ammonia to nitrite and nitrate, and nitrification inhibitors (e.g. allylthiourea (ATU) or 2-chloro-6-(trichloro methyl) pyridine (TCMP)) may be added to samples containing ammonia (e.g. riverwaters).

Method:

The standard method from Methods for the Examination of Waters and Associated Materials: 5 Day Biochemical Oxygen Demand (BOD_5) (HMSO 1998) was used for all BOD analyses. Samples were transported in cool boxes and stored at 4°C prior to analyses. BOD incubations were initiated a maximum of 3 hours after sample collection during all water quality surveys, and analyses were carried out on well mixed unfiltered samples. DO readings were taken potentiometrically using a WTW Oxi92 Dissolved Oxygen Meter, and ATU was used as a nitrification inhibitor. Blanks of Milli-Q® 18 MΩ.cm water were run in parallel with sample BOD_5 determinations. Bottles were incubated in a temperature controlled room (20°C ± 10%, temperature checked with a maximum/minimum thermometer) in the dark. No sample pre-treatment for the presence of algae, chlorine, ferrous iron, hydrogen sulphide or sulphur dioxide, or high TSS were deemed necessary for any of the samples.

2.4.9 Nitrate, ammonia and phosphate

Principle:

Nitrate, ammonia and phosphate were analysed by segmented continuous flow autoanalytical techniques. For continuous flow methods sample is continuously taken up together with appropriate reagents, flows through a manifold (to undergo treatment such as mixing, heating or dialysis) into a flow cell to be detected, and is ejected to waste. In segmented continuous flow techniques gas (normally air) bubbles separate the liquid stream into discrete compartments to aid sample and reagent mixing and avoid carry-over between samples. Samples are introduced to the flow using an autosampler, and responses from the detector are recorded and processed by a computer.

Methods:

2.4.9.1 Nitrate

Nitrate (or more strictly nitrate plus nitrite) analysis was carried out on a San^{plus} Segmented Flow Analyser from Skalar Analytical B.V. set-up with a Skalar Sampler 1000 autosampler. The procedure is based on the cadmium reduction method (Navone, 1964). The water sample is passed through an activated copper-cadmium column to reduce nitrate to nitrite. The nitrite then reacts with sulphanilamide and α-naphthylethylenediamine dihydrochloride to form a highly coloured diazo dye. Colour is measured at 540nm in a spectrophotometer. Sample turbidity may interfere, and so samples should be filtered before analysis (Clesceri et al., 1998).

Samples were transported in cool boxes and stored at 4°C prior to filtration within 3 hours on 0.45μm Whatman® Cellulose Nitrate Membrane Filters, before being stored frozen at -20°C in 60ml Azlon polyethylene bottles for a maximum of one month prior to analysis. Standard calibration curves were created using sodium nitrate standards at 2, 4, 6, 8 and 10mg/l $N\text{-}NO_3$ or 1, 2, 3, 4 and 5mg/l $N\text{-}NO_3$ depending on the concentration in the samples. Correlations were all $r = 0.99$ or better. The LOD from the analyses of 6 blanks (Milli-Q® 18 MΩ.cm water), is 0.02mg/l $N\text{-}NO_3$.

2.4.9.2 Ammonia

Ammonia (ammonium) determination is based on the modified Berthelot reaction (Verdouw et al., 1977). This entails the chlorination of ammonia to monochloramine, which reacts with salicylate to 5-aminosalicylate. This is oxidised to produce a green coloured complex with absorbance measured at 660nm. Ammonia analyses were carried out on the same system as nitrate and phosphate (San^{plus} Segmented Flow Analyser from Skalar Analytical B.V. set-up with a Skalar Sampler 1000 autosampler), set up to allow simultaneous determination of all three parameters from the same water sample. Sample pre-treatment and storage conditions are therefore identical for nitrate, ammonia and phosphate analyses.

Standard calibration curves were created using ammonium chloride standards at 0.2, 0.4, 0.6, 0.8 and 1.0mg/l $N\text{-}NH_3$ or 0.1, 0.2, 0.3, 0.4 and 0.5mg/l $N\text{-}NH_3$. Correlations were all r = 0.99 or better. The LOD from the analyses of 6 blanks (Milli-Q® 18 MΩ.cm water), is 0.04mg/l N-NH_3.

2.4.9.3 Phosphate

Phosphate analyses were carried out in parallel with nitrate and ammonia analyses on a San^{plus} Segmented Flow Analyser from Skalar Analytical B.V. set-up with a Skalar Sampler 1000 autosampler. Phosphate (i.e. orthophosphate or dissolved reactive phosphate) analysis is based on the reaction of acidified ammonium molybdate catalysed by potassium antimony tartrate with phosphate to form a phospho-molybdic acid complex (Boltz and Mellon, 1948). When reduced by ascorbic acid this forms an intense blue colour with absorbance measured at 880nm. The reaction is quite tolerant to interferences (salt concentrations up to 20% (w/v) cause an error of less than 1% (Clesceri et al., 1998)), but turbidity should be removed by filtration.

Standard calibration curves were created using potassium dihydrogen o-phosphate standards at 0.2, 0.4, 0.6, 0.8 and 1.0mg/l P-PO_4^{3-} or 0.1, 0.2, 0.3, 0.4 and 0.5mg/l P-PO_4^{3-}. Correlations were all r = 0.99 or better. The LOD from the analyses of 6 blanks (Milli-Q® 18 MΩ.cm water), is less than 0.00mg/l P-PO_4^{3-}.

2.4.10 Metals and non-metals by ICP-OES

Principle:

Inductively coupled plasma – optical emission spectrometry (ICP-OES), or as it is also known inductively coupled plasma – atomic emission spectrometry (ICP-AES), initially developed in the 1960s (Greenfield et al., 1964), is now established as one of the most widely used techniques of elemental analysis (Walsh, 1997). It has great advantages due to the high temperature of the plasma (breaking all chemical bonds), low background interferences, ability to create linear calibration lines over a wide range of concentrations and ability to measure a range of elements in a sample almost simultaneously.

A plasma is a high temperature (6000 to 8000°K) partially ionised gas which is a good conductor of electricity. Inductively coupled plasma (ICP) methods use a plasma source to evaporate and dissociate samples into free atoms and ions, and to excite the free atoms and ions into higher energy states. The high temperature of the plasma and the dissociation and excitation of analytes is caused by collision with free electrons.

An inductively coupled plasma is created through argon gas flowing through a quartz torch surrounded by an induction coil through which radio frequency (RF) radiation is applied. The RF field creates an intense oscillating magnetic field, which in turn induces an electric field in the gas. The plasma is "ignited" by a Tesla discharge which provides seed electrons and ions that oscillate within the electric field to form the plasma. The torch and induction coil are water cooled.

Optical emission spectrometry (OES) (also often termed atomic emission spectrometry (AES)) makes use of the fact that the excited state of the atoms and ions in the plasma is unstable. The particles lose their energy either by colliding with other particles, or by a reduction in energy level of their electrons. This reduction in energy level emits electromagnetic radiation in the optical range (an ionic emission spectra). The wavelengths of the light emitted are characteristic of the elements which are excited in the plasma flame. In the spectrometer the light is separated into discrete spectral lines by a diffraction grating, and the intensity of these lines is measured to give a quantitative measurement of analyte concentration. Spectrometers are designed to either measure several spectral lines simultaneously (polychromator) or one line at a time (monochromator). Sample is introduced to the plasma as an aerosol created by a nebuliser via a carrier gas flow (generally argon) into the centre of the flame.

Method:

A Perkin Elmer Optima 3000 Family Optima 3300RL ICP Emission Spectrometer was used for all ICP-OES work (Perkin Elmer, 1997). Calibration and reprocessing of signals was carried out using Perkin Elmer ICP WinLab™ software (Perkin Elmer, 1997). This is a dual detector system: a UV detector covers an ultraviolet wavelength range from 165 to 403nm and a VIS detector covers a visible wavelength range from 404 to 782nm. The plasma is viewed radially: i.e. the torch is positioned vertically and viewed form the side. An echelle grating is used to separate wavelengths and detection is by a polychromator. Samples were run using a Perkin Elmer AS90 autosampler.

Samples were transported in cool boxes and stored at 4°C prior to filtration within 3 hours on 0.45μm Whatman® Cellulose Nitrate Membrane Filters. Samples were then acidified to <pH 2 by adding 0.1ml of HNO_3 per 20ml of sample, and stored in 30ml polystyrene specimen containers at 4°C for a maximum of 2 months prior to analysis.

All water samples taken were analysed for the following analytes using the wavelengths indicated below (all values in nm). Intensities were also measured for at least one other wavelength for each element as a check against interferences.

Aluminium (Al 396.153)
Calcium (Ca 315.887)
Cobalt (Co 230.786)
Chromium (Cr 205.560)
Copper (Cu 324.752)
Iron (Fe 234.349)
Potassium (K 766.490)
Magnesium (Mg 279.077)
Manganese (Mn 293.305)
Sodium (Na 330.237)
Nickel (Ni 227.022)
Phosphorus (P 214.914)
Sulphur (S 181.975)
Scandium (Sc 361.383)
Silicon (Si 251.611)
Tin (Sn 235.485)
Titanium (Ti 336.121)
Vanadium (V 270.093)
Zinc (Zn 213.857)

Standard linear calibration curves were produced using standard solutions made up from analytical grade standard stock solutions of the following concentrations:

For freshwater (Tees) samples:

Standard:	**Analytes:**	**Concentration:**
Minors	Al, Co, Cu, Cr, Mn, Ni, P, S, Sc Si, Sn, Ti, V and Zn	0.5, 1.0 and 2.0mg/l
Majors	Ca, Fe, K, Mg and Na	5, 10 and 25mg/l

For Tawe, Wansbeck and Blyth samples:

Standard:	Analytes:	Concentration:
Iron	Fe	2.5, 5.0 and 10.0mg/l
Minor metals	Al, Co, Cr, Cu, Mn, Ni, Sc, Sn, Ti, V and Zn	0.05, 0.10 and 0.20mg/l
Minor non-metals	P and Si	0.5, 1.0 and 2.0mg/l
"Seawater" standard	Na	5000, 10000 and 20000mg/l
	Mg and S	250, 500 and 1000mg/l
	Ca and K	125, 250 and 500mg/l

Tables 2.5 and 2.6. Analytical standards used during metal and non-metal analysis by ICP-OES.

Different standards were used for the wholly freshwater survey samples (Tees) to the truly "estuarine" survey samples which included fresh to saline waters (Tawe, Wansbeck and Blyth) due to the different concentration ranges for the analytes involved. In addition, in latter analyses, standards for metals and non-metals (Si and P) were separated to avoid any possible complexation and precipitation of elements on storage of standard solutions.

0.1ml of 100mg/l yttrium (Y) solution was added per 10ml of sample as an internal standard (spike). High ionic strength (brackish and seawater) samples were found to have measured intensities about 20% lower than in freshwater samples (and calibration and process blanks) for Y (measured at 360.073nm). This suppression was probably due to high salt loading in the plasma decreasing the power delivered to the argon ions which maintain the plasma (Walsh, 1997). It was assumed that all wavelength intensities were suppressed by the same factor as that for the Y internal standard, and values were adjusted accordingly. Spiking also allows correction for any drift in machine sensitivity.

The viewing height within the plasma flame was 7mm. Machine sensitivity tests were carried out before each sample run using a standard 10mg/l Mn solution. Quality control included periodically analysing standard solutions as unknowns during sample runs as a check on accuracy. LOD (3s) calculated from a set of 6 blanks (Milli-Q® 18

MΩ.cm water) run as part of this study (within analysis of Blyth samples), and working detection limits (6s) data from Potts (1987) are as follows:

Analyte:	3s detection limit (data from this study) mg/l:	6s detection limit (data from Potts, 1987) mg/l:
Al	0.055	0.005-0.05
Ca	0.587	0.005-0.05
Co	0.002	0.005-0.05
Cr	0.004	0.005-0.05
Cu	0.003	0.005-0.05
Fe	0.004	0.005-0.05
K	1.085	≥0.05
Mg	1.832	≥0.05
Mn	0.004	≤0.005
Na	8.252	≥0.05
Ni	0.005	0.005-0.05
P	0.007	≥0.05
S	1.348	Not normally measurable
Sc	0.000	0.005-0.05
Si	0.013	0.005-0.05
Sn	0.033	0.005-0.05
Ti	0.002	0.005-0.05
V	0.011	0.005-0.05
Zn	0.003	0.005-0.05

Table 2.7. Analytical limits of detection for ICP-OES analyses.

2.5 Overview of data collected during the water quality surveys

2.5.1 Data handling and quality assurance

Data collected during the surveys were initially recorded in 3 ways:

1. Parameters measured in the field (depth, T, DO, pH, conductivity and Secchi depth) were recorded systematically field notebooks.
2. Parameters measured manually in the laboratory (BOD where measured, alkalinity and TSS) were recorded systematically on custom laboratory results sheets.
3. Parameters measured on automated systems in the laboratory (nutrients and metals), and flow data obtained from the EA, were recorded in personal computer (PC) data files.

Data were subsequently transferred to spreadsheets for each sampling period, in which water quality variables appear in columns and data for each sample are recorded in the rows. Care was taken to avoid transcription errors when carrying out the (somewhat arduous!) task of transferring data from paper to PC, and outlying values were double checked for any such mistakes. The automatically recorded (nutrient and metal) data had the advantage that transcription errors were avoided, but checks were carried out to ensure there were no systematic (and potentially more serious) errors in recording these data in the spreadsheets. This included checking that data fell within the ranges expected and that major ion ratios were similar for each river.

The spreadsheets for the individual sampling periods were subsequently combined to form a spreadsheet containing all data collected during the water quality surveys, which could easily be transferred between statistical and analytical software packages (from Excel to Minitab).

2.5.2 Fulfilment of experimental design

It is almost inevitable during a large water quality assessment programme that not all data planned to be collected in the experimental design will be. This can be for a variety of reasons such as spilt or missing samples, failure of equipment, or lack of access to sampling site (in the case of this study due to dangerously high flow and storm conditions). Overall, however, the vast majority of data intended to be collected were able to be, and the water quality surveying work can be considered successful (with many thanks due to those listed in the acknowledgements).

2.5.2.1 Rivers/estuaries studied

Water quality parameters in four rivers were sampled: the Tees, Wansbeck, Tawe and Blyth. For further information see section 2.1 Survey design.

2.5.2.2 Dates sampled

Water quality was sampled on a total of 11 dates on the Tees, 53 on the Wansbeck, 12 on the Tawe, and 9 on the Blyth (a combined total of 85 sample dates). Sampling was carried out during the seasons of: summer and winter for the Tees; spring, summer, autumn (fall) and winter for the Wansbeck; and summer alone for both the Tawe and Blyth. All periods intended to be sampled in the experimental designs were able to be. For further information see section 2.1.

2.5.2.3 Sites and distances sampled

Sampling was carried out at 6 sites (plus 1 site in the Leven tributary) within the Tees, 5 sites within the Wansbeck, 6 sites within the Tawe, and 4 sites within the Blyth. These sites are located with approximately equidistant spacing longitudinally within the water bodies. The length of the profiles sampled are 25.9 km within the Tees, 4.3 km within the Wansbeck, 5.6 km within the Tawe, and 3.4 km within the Blyth. All sites intended to be sampled were able to be so, with the exception of sites at which water depth was too shallow to allow access by the RV during draining of the Wansbeck impoundment. For further information see section 2.1.

2.5.2.4 Depths sampled

Water quality was sampled at 3 depths at each site (except at sites where the water depth was shallow enough for complete turbulent mixing to be observed), shallow (s), mid-depth (m) and deep (d). Actual depths varied between sites, and with river level. The maximum depths sampled were 11.6 m in the Tees, 5.5 m in the Wansbeck, 8.5 m in the Tawe, and 4.6 m in the Blyth. For further information see section 2.1 Survey design.

2.5.3 Data summary

2.5.3.1 One-way ANOVA between estuaries

Simple one-way ANOVA was carried out to test the significance of differences in the water quality variables measured between the estuaries for the periods studied. Normality of distribution of the datasets for each estuary was assumed. Graphical presentation showed this generally to be the case, although several parameters show skewed or bimodal distributions, particularly where two distinct water bodies (fresh and seawater) are involved (figures 2.5 and 2.6). There is strong argument about how suitable ANOVA and other parametric tests are when the distribution assumptions are not fully met (e.g. Bradley, 1968), although generally such tests are "remarkably unaffected by violations in distribution assumptions" (Howell, 1997). Of particular importance to this study is that ANOVA can work with multiple normal distributions within a dataset.

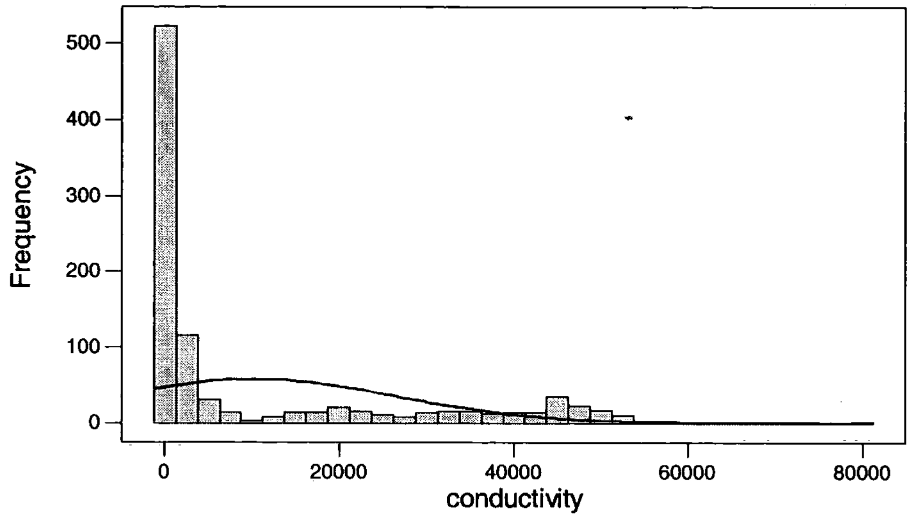


Figure 2.5. Histogram of conductivity (in μS/cm) with normal curve for all water quality surveys on the Wansbeck, showing positively skewed dataset due to the large difference in conductivity between freshwater (the larger volume of water in the impoundment) and seawater.

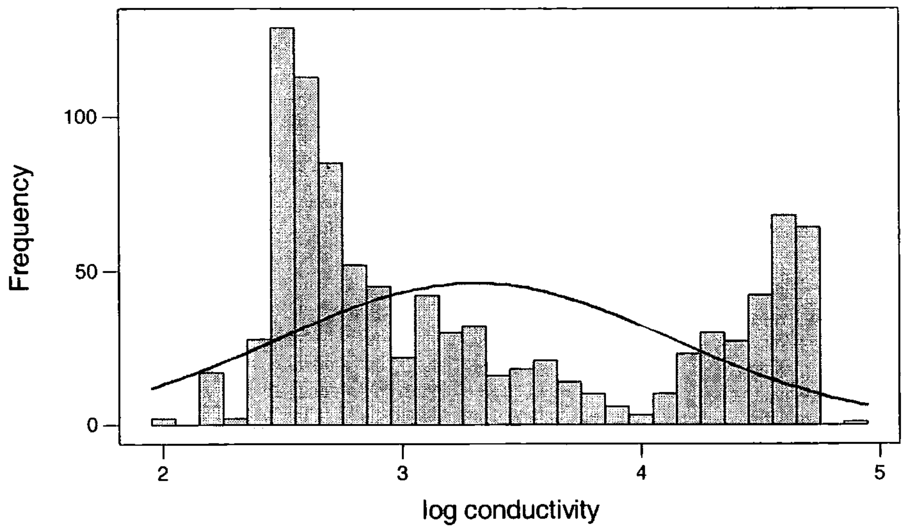


Figure 2.6. Histogram of data with from the Wansbeck estuary as figure 2.5 after log transformation of the conductivities, showing the bimodal distribution due to incompletely mixed freshwater and seawater end members.

The P-values obtained from one-way ANOVA show that during the periods of sampling there were significant (at > 99 % confidence interval) differences in all the water quality parameters measured between the 4 estuaries studied. (P-values are 0.000 for all parameters, with the exception of absolute DO concentration which gives 0.002). The differences observed between the estuaries are likely to be caused by both:

- fundamental differences between the systems (e.g. catchment sizes and characteristics, or barrage design), and
- differences in conditions during sampling periods (e.g. in temperature, flow or seasonal effects).

Subsequent comparison of the systems must take into account the multiple sources of variance within the data to enable isolation of the factors of interest (e.g. by normalisation to input values to remove catchment effects on water quality differences).

To ensure that non-normal distributions do not invalidate the use of parametric testing, Kruskal-Wallis tests (the non-parametric analogue for one-way ANOVA) were carried out in addition to ANOVA. Resulting P-values for Kruskal-Wallis tests of differences between estuaries were all 0.000 (> 99 % probability of a significant difference).

2.5.3.2 Graphical presentation of data as boxplots

The boxplots used in the subsequent data presentation were produced using the Minitab 13 statistical package, and use the following (figure 2.7) conventions:

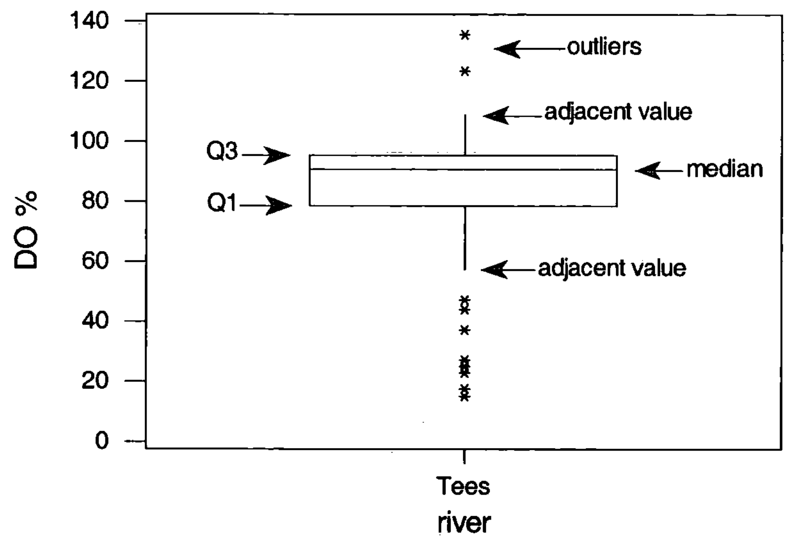


Figure 2.7. Example boxplot showing distribution characteristics shown in all boxplots presented.

Q1 = first quartile,

Q3 = third quartile, and

whiskers extend from the top and bottom of the box to the highest and lowest adjacent values within upper and lower limits defined by:

Lower Limit: Q1 - 1.5 (Q3 - Q1)

Upper Limit: Q3 + 1.5 (Q3 - Q1).

Outlying values where they occur are shown by asterisks and the mean values where shown by solid circles.

2.5.3.3 Tidal height and overtopping

Tidal heights are recorded for each sampling date for the 3 estuaries which have tidal influence. The Tees impoundment has no tidal input. For the Wansbeck and Tawe impoundments the maximum height of the high tide preceding sampling relative to the barrage crest is recorded as overtopping. For further information see section 2.1 Survey design.

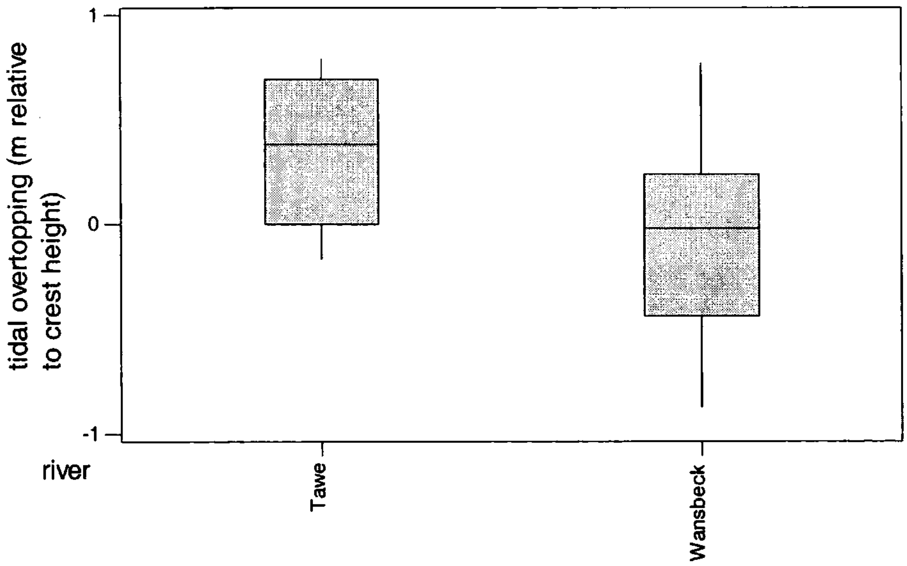


Figure 2.8. Tidal overtopping of the Tawe and Wansbeck barrages during the water quality surveys. 0 represents the barrage height. Negative values mean that seawater did not enter the impoundment with the high tide preceding sampling.

The majority of tides during the sampling period overtopped the Tawe barrage whereas the majority of tides did not overtop the Wansbeck barrage (figure 2.8). The range of overtopping values is greater for the Wansbeck since it was sampled during both spring and neap tidal cycles.

2.5.3.4 River flow

River flow for each sampling date on each river is expressed in the dataset in 3 forms: (i) the flow at midday (the approximate time of sampling) (Flow 12); (ii) the mean flow during the 24 hour period prior to sampling (Mean 24) and; (iii) the maximum flow during the 24 hour period prior to sampling (Max 24). For further information see section 2.1 Survey design. During the periods sampled these terms were strongly correlated for the whole dataset:

Mean 24 = 1.49 + 0.859 Flow 12 (P = 0.000, S = 6.846, R-Sq = 75.3%)

and,

Max 24 = 2.42 + 1.35 Flow 12 (P = 0.000, S = 9.922, R-Sq = 78.1%).

Obviously the relationship between these values will depend on when sampling takes place in relation to any high flow events (whether on the rising or the falling limb of the hydrograph). However the relatively strong linear relationships during the sampling periods of this study mean that in subsequent data analyses a single parameter may be used to represent flow.

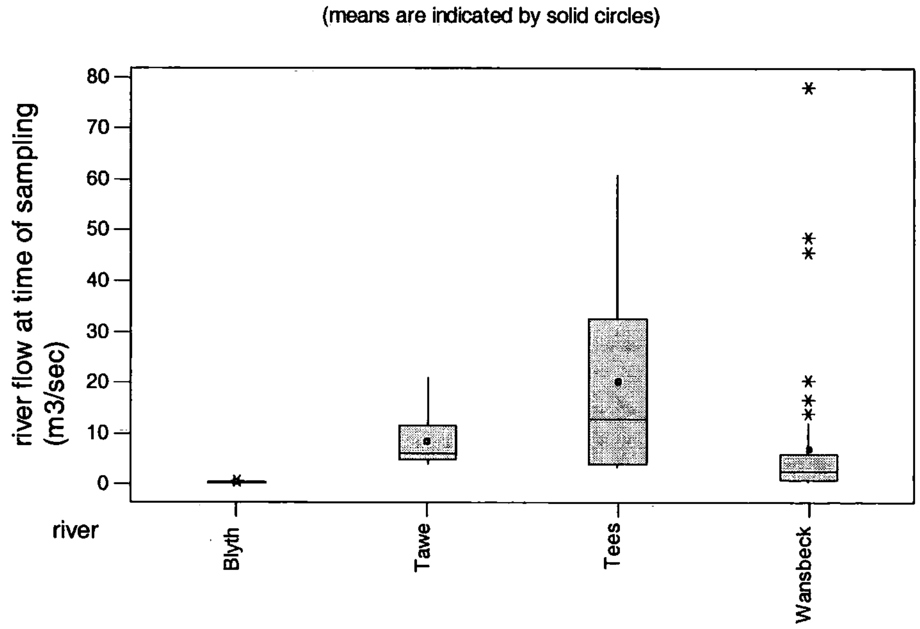


Figure 2.9. River flow in the estuaries studied during the water quality surveys.

The mean river flow varies between estuaries on the basis of the different sizes of the catchments, and seasonal and meteorological effects. The range in values of flow for the rivers during the water quality surveys represent the range of flow conditions sampled for each river (figure 2.9). Both the Tees and the Wansbeck were sampled during multiple periods, including both summer and winter flow conditions and the ranges in river flow are high. The Tawe and Blyth were only sampled for a single summer period each and have lower ranges. No flood events were sampled on the Blyth and hence its flow remained relatively constant during the sampling period.

2.5.3.5 Temperature

The water temperature was taken in situ at the three depths sampled at each site on each date sampled for each river. Temperature is likely to be dependent on meteorological conditions on the dates of sampling. The Tawe and the Blyth have higher mean temperatures since they were only sampled during summer periods. The range in temperatures is higher for the Tees and the Wansbeck, which were sampled over a range of seasons, compared with the Tawe and Blyth, which were only sampled during summers (figure 2.10). The mean temperatures (and standard deviations) measured during the sampling periods are 12.4, 14.4, 11.8 and 10.5°C (SD = 1.5, 1.7, 6.5 and 3.8°C) for the Blyth, Tawe, Tees and Wansbeck respectively.

Temperature data collection was relatively simple due to the straightforwardness of the equipment used. Almost all data intended to be collected in the experimental design was able to be. A sudden violent storm during sampling at the Tees barrage caused measurement of temperature (and DO) to be abandoned (2 datum missing). During the period in which the Wansbeck impoundment was drained, water depths were too shallow to allow the RV to access the sampling sites, and therefore some data is missing (55 datum in total for T) for these dates.

Figure 2.10. Water temperature (in °C) in the estuaries studied during the water quality surveys.

2.5.3.6 Dissolved oxygen

The dissolved oxygen concentration of the water was taken in situ at the three depths sampled at each site on each date sampled for each river. Data are reported as both absolute concentrations (mg/l) and as percentage saturations (%). The meter used included automatic temperature compensation so that the values in mg/l are not fixed to values in % saturation (solubility increases with decreasing temperature). Values were not compensated for salinity however, and % saturations in saline waters are therefore reported at lower than their true values. Hence the relationship between DO in mg/l and DO as % saturation, although good (figure 2.11, DO = - 0.169 + 0.113 DO%, S = 0.9807, R-Sq = 88.3%), shows some scatter from a straight line for the periods surveyed.

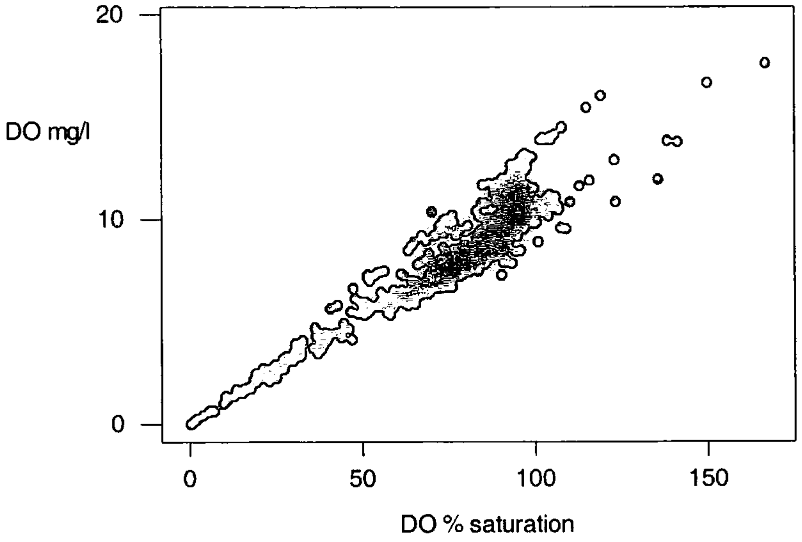


Figure 2.11. The relationship between DO concentration and % saturation for the water quality surveys.

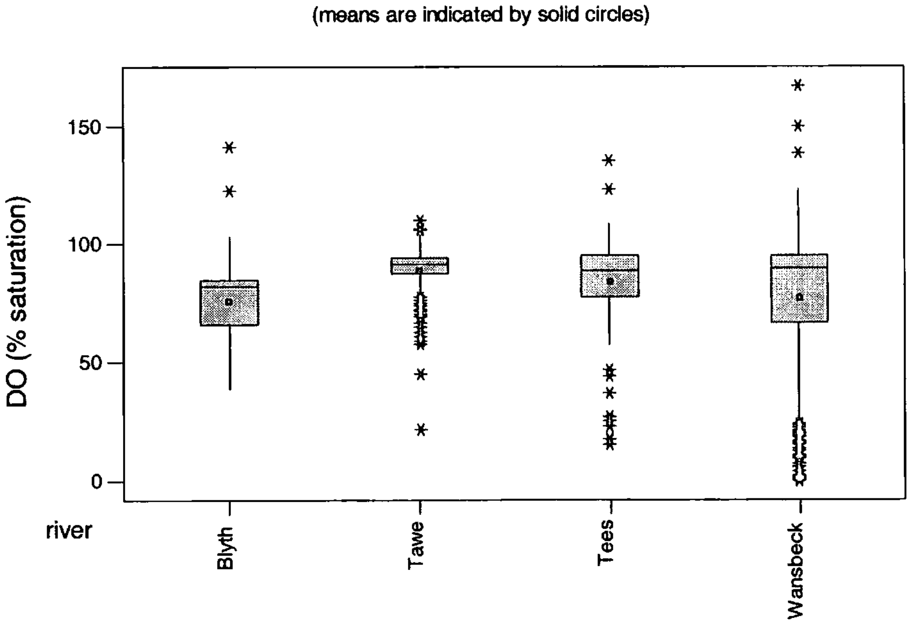


Figure 2.12. DO % saturations in the estuaries studied during the water quality surveys

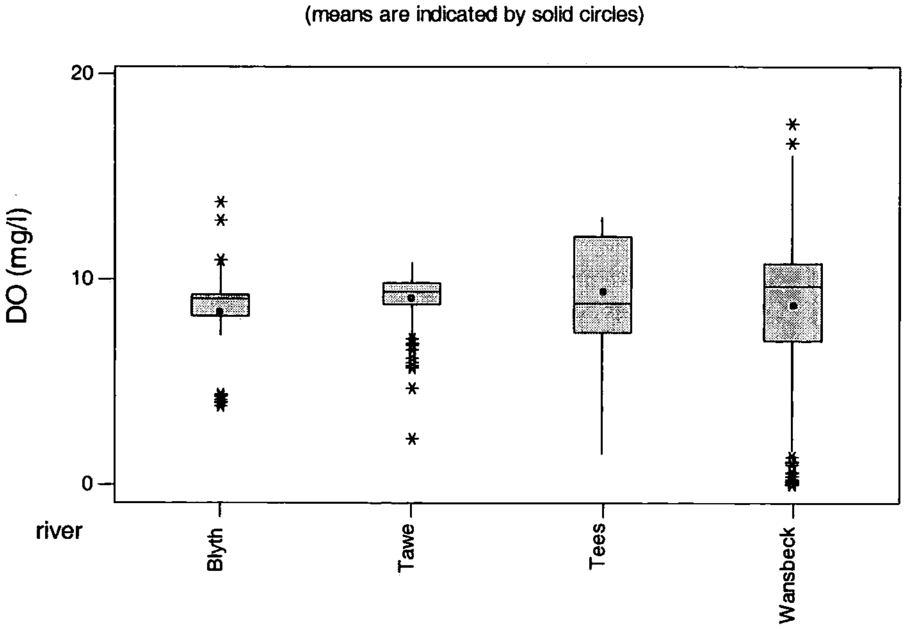


Figure 2.13. DO absolute concentrations (mg/l) in the estuaries studied during the water quality surveys.

Mean values (and SDs) for DO in the estuaries during the periods studied are 8.4, 9.1, 9.4 and 9.7 mg/l (SD = 2.1, 1.1, 2.7 and 3.3 mg/l) for the Blyth, Tawe, Tees and Wansbeck respectively (figure 2.13). In terms of saturation levels values are 75.8, 89.1, 84.1 % and 77.1 (SD = 20.0, 10.0, 16.3 and 27.9 %) respectively (figure 2.12).

The behaviour of DO in water bodies is complicated, and the variations which are seen to occur could be due to a variety of factors. The behaviour of DO is further investigated in subsequent chapters. At this stage it is worth noting however that several values are recorded at below 5 mg/l, which is the threshold Statutory Water Quality Objective (SWQO) value set by the then NRA (National Rivers Authority, 1991) for salmonid species of fishery, and on occasions the DO was below the 3 mg/l necessary for cyprinid and migratory fisheries. These low oxygen conditions were encountered at depth, and detailed depth profiles carried out on several occasions showed stratification of DO levels associated with density stratification of the water column (often as positive heterograde curves, figure 2.14).

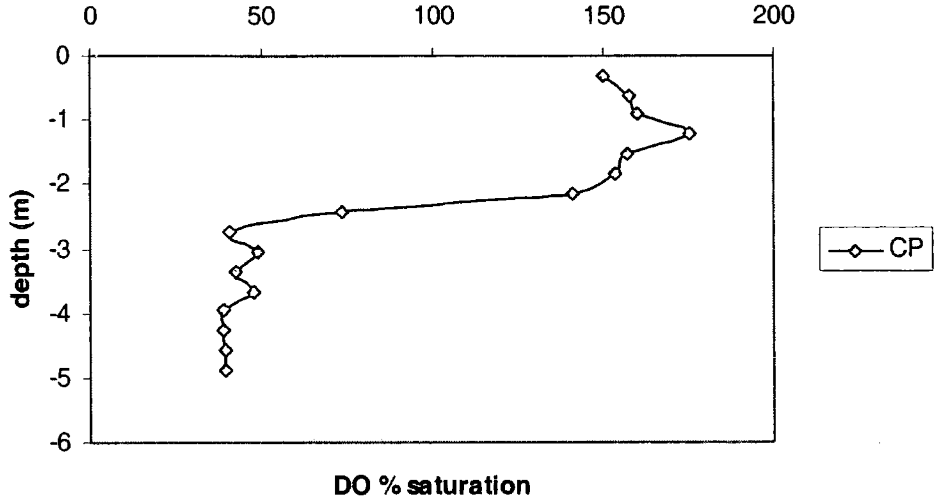


Figure 2.14. Dissolved oxygen profile from site CP from the Wansbeck from the 2nd September 2000, showing sharp decrease in DO with progression from fresh water at surface to brackish and saline water at depth. Supersaturation is observed in the surface waters due to the effects of high primary production (cyanobacterial blooms).

2.5.3.7 BOD

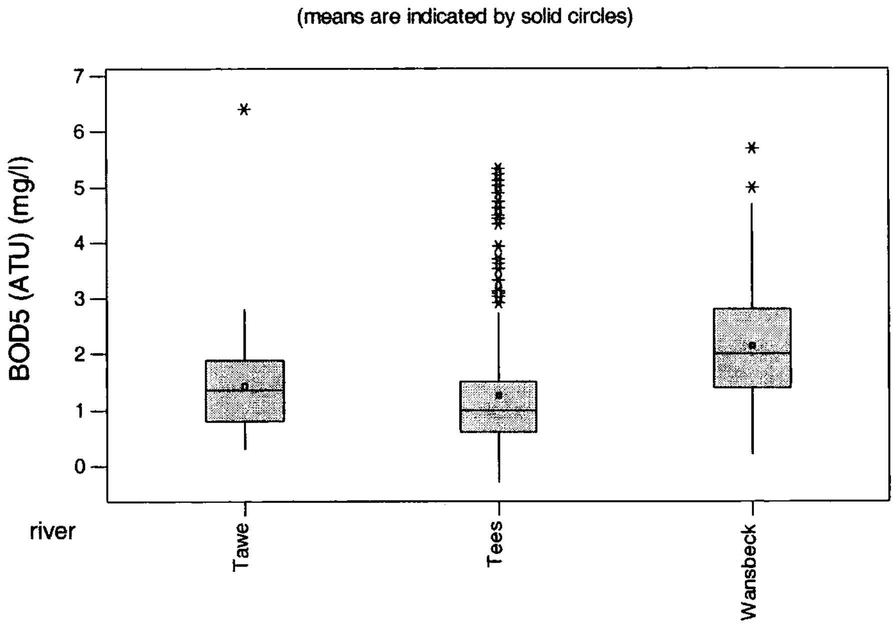


Figure 2.15. BOD values for the rivers during the water quality surveys.

Mean BOD values for the 3 estuaries in which the parameter was taken (time and equipment constraints meant that no measurements were taken from the Blyth) are 1.4, 1.3 and 2.1 mg/l of DO for the Tawe, Tees and Wansbeck respectively, implying that in general the oxygen demand of the waters was not large during the periods surveyed.

2.5.3.8 pH

Mean pH values for the estuaries studied conform to the typical values experienced in natural waters buffered by the carbonic acid, bicarbonate and carbonate system of between pH 7 and 9 (Andrews et al., 1996). The differences between mean values of pH between the estuaries (7.31, 7.35, 7.59 and 7.69 for the Blyth, Tawe, Tees and Wansbeck respectively) are small but significant, and probably reflect differences in the ionic composition of the freshwater entering the estuaries. The boxplot of pH against rivers (figure 2.16) shows several low pH outliers, particularly for the Blyth and Wansbeck (lowest value = pH 4.82). The cause of these low pH values is discussed further in subsequent sections.

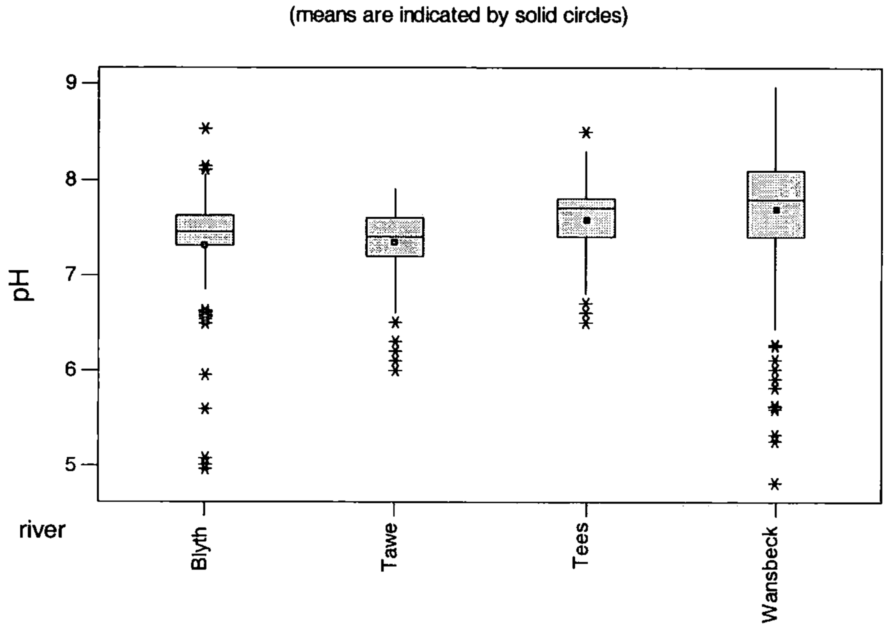


Figure 2.16. pH values for the rivers during the water quality surveys.

2.5.3.9 Alkalinity

Alkalinity mainly arises from the presence of the carbonate buffer system described above. These ions come from the atmosphere and biological respiration, plus dissolution of carbonate rocks where these occur in the watershed. The values encountered in the estuaries studied suggest that they are well buffered. All of the rivers run through solid geologies containing some carbonate (Carboniferous) and this contributes to their alkalinities. The alkalinity of the Blyth, which as discussed for conductivity below consists mainly of seawater for the dates and section sampled, has a lower average alkalinity. This is contrary to the general estuarine situation in which seawater alkalinity is higher than that of riverwater (Dyrssen and Wedborg, 1980).

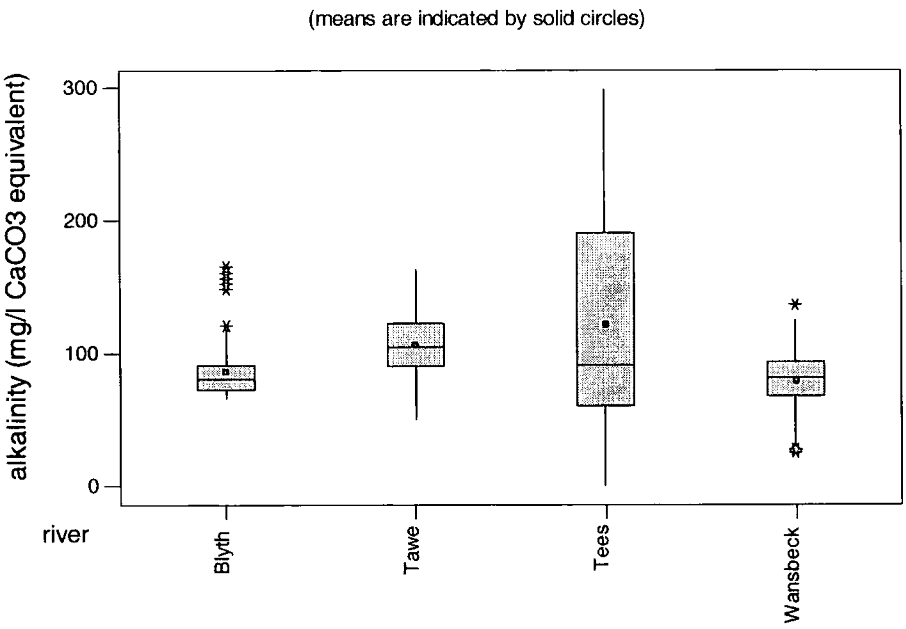


Figure 2.17. Alkalinity values for the rivers during the water quality surveys.

2.5.3.10 Conductivity

There are large differences between the conductivities of the 4 rivers (figure 2.18). The mean conductivities are related to the amount of seawater to freshwater in the systems, and reflect the differences in barrage heights to the tidal frame. The highest mean conductivity is therefore found in the Blyth where there is no impoundment (conductivities were augmented due to low freshwater flows during the sampling period on the Blyth), and lowest on the Tees where no seawater can enter the impoundment.

The median values for conductivity for the Tees, Wansbeck and Tawe (figure 2.18) are similar lower values (251, 943 and 940 μS/cm respectively), and show that most of the water sampled is fresh in these impoundments, whereas the Blyth median value of 41200 μS/cm is higher than the mean and shows that most of the water in this estuary is saline.

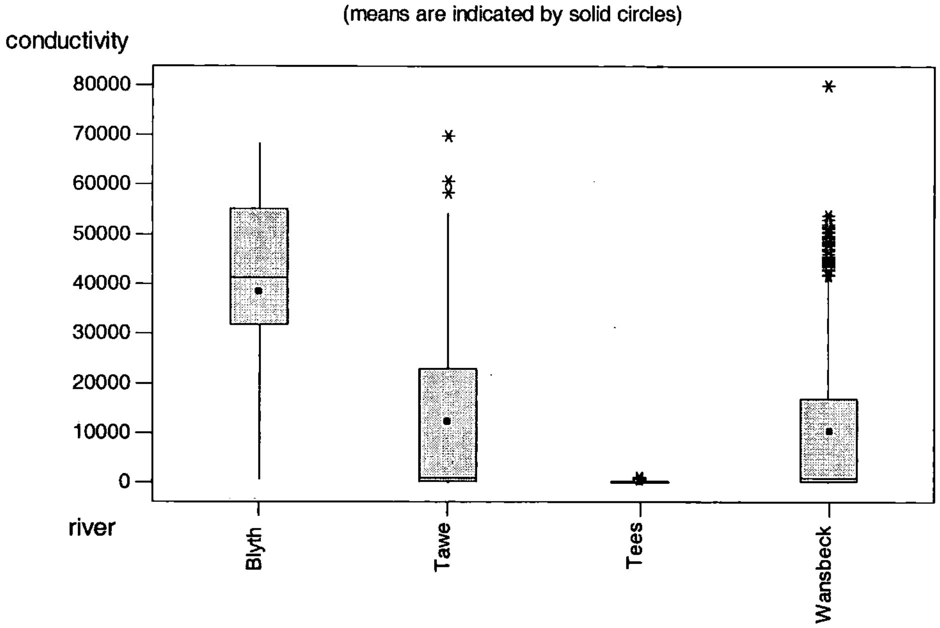


Figure 2.18. Conductivity values (in μS/cm) for the rivers during the water quality surveys, showing the difference between total exclusion (Tees), partial exclusion (Tawe and Wansbeck), and unimpounded (Blyth) estuaries.

Detailed depth profiles carried out on several occasions showed there to be a strong salinity (density) stratification in the partial tidal exclusion impoundments (e.g. figure 2.19).

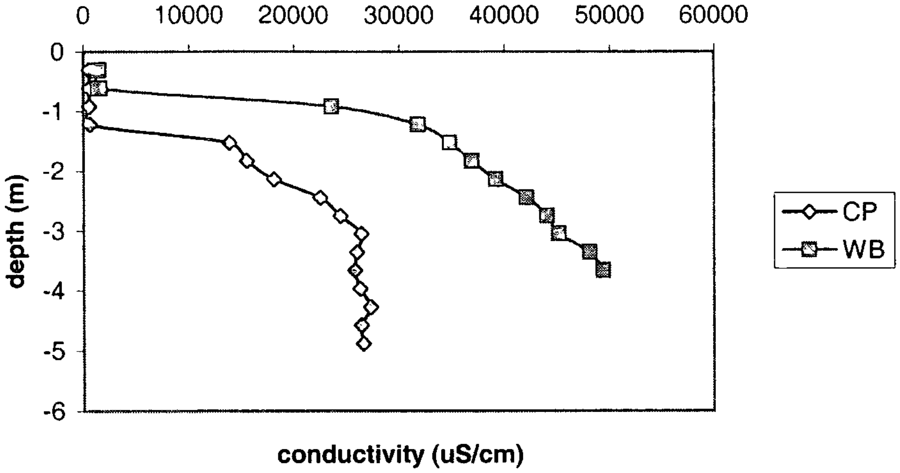


Figure 2.19. Conductivity changes with depth in the water column from two sampling sites from the Wansbeck from 2nd September 2000, showing stratification between fresh and brackish and saline waters. Site WB is immediately behind the barrage whilst CP is further upstream at the deepest point in the impoundment.

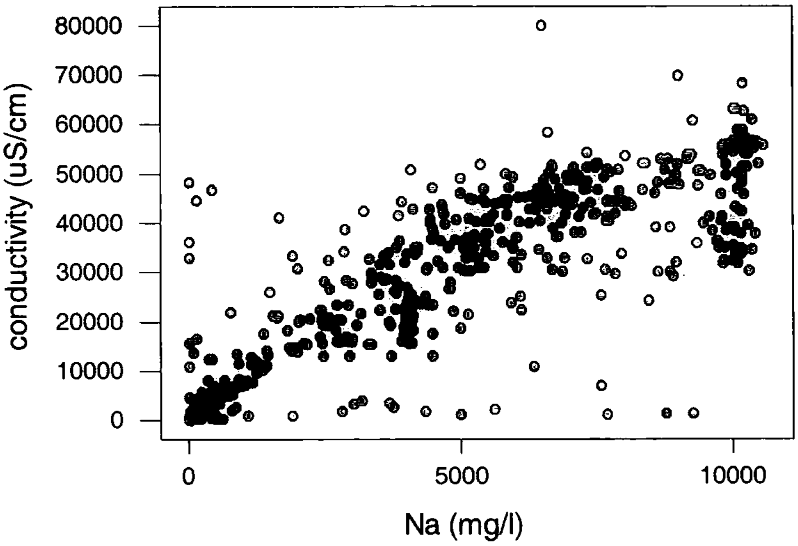


Figure 2.20. The relationship between conductivity and Na for samples taken during all water quality surveys, showing significant scatter from straight line.

In theory conductivity should be proportional to Na for the samples, assuming that seawater dominates conductivity in the systems, but a large amount of scatter from a straight line relationship is seen (figure 2.20). This implies that, although care was taken to take water samples for laboratory analysis at the same point at which in-situ parameters were measured, values from field and laboratory measurements may not represent exactly the same portion of water. This is particularly the case for samples and readings taken close to the sharp and strong halocline (the interface between seawater and freshwater stratified due to density differences) which was observed in the Tawe and Wansbeck impoundments. Small vertical variations about this interface are likely to have meant that distinct (freshwater or seawater) packages of water were sampled at the "same" point (giving outlying values on figure 2.20). Care should thus be taken when comparing field and laboratory measured parameters.

2.5.3.11 Eh

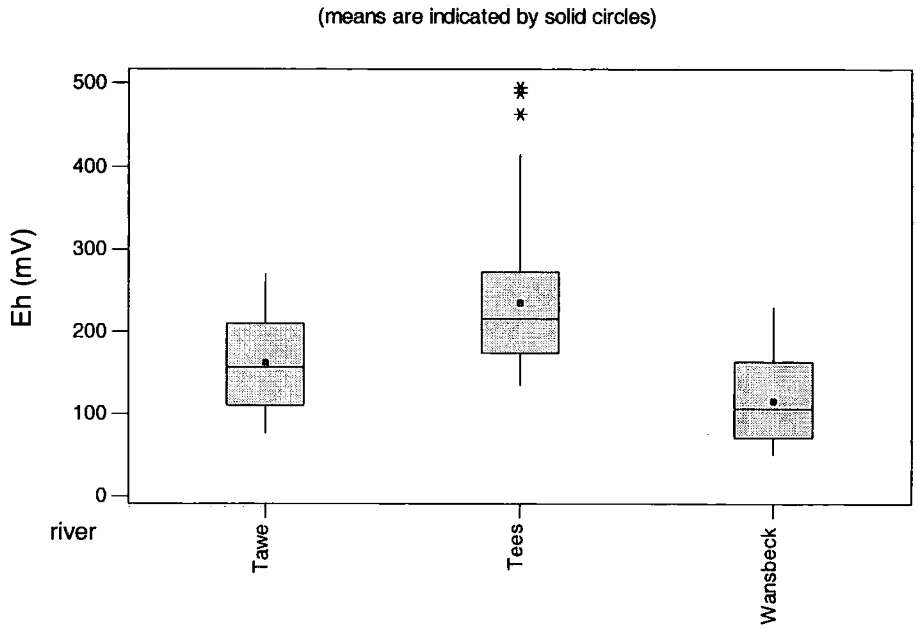


Figure 2.21. Eh values for the rivers during the water quality surveys.

Eh measurements were taken during just under half of the water quality surveys (based on equipment availability: see section on Field Analytical Methods). No Eh measurements were made on the Blyth estuary.

Strongly reducing conditions were not observed during the Eh sampling periods, although some values (below ≅ 100 mV) suggest that anoxic conditions are developed (cf. DO data). Semi-quantitive interpretation gives that reducing conditions are more likely in the Wansbeck and the Tawe than in the Tees impoundment.

2.5.3.12 Transparency

Transparency ranges from 0.05 m (following high flow in the Wansbeck) to 3.55 m (Tawe), and there are significant differences in transparencies (measured as Secchi depths) between the estuaries (figure 2.22).

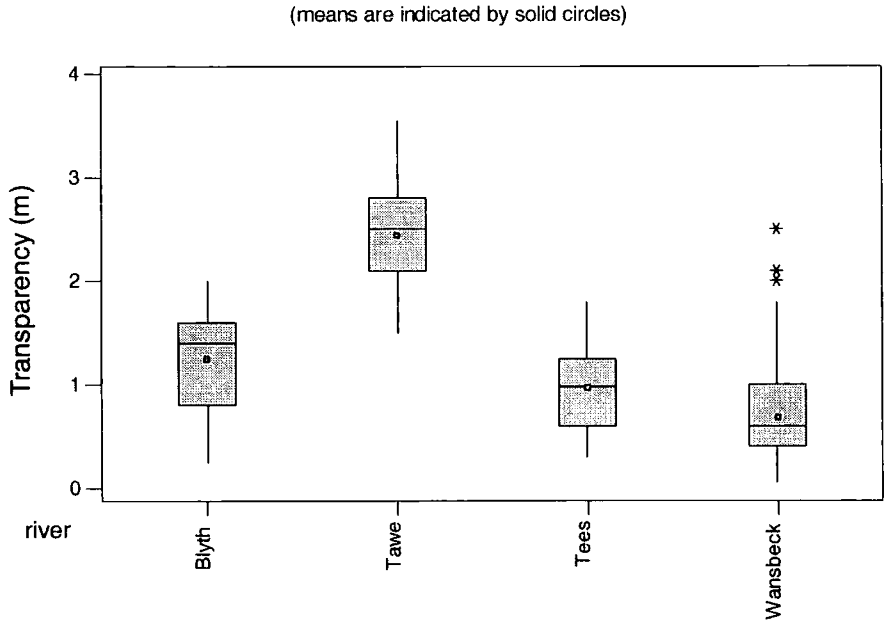


Figure 2.22. Transparency values (as Secchi depths) for the rivers during the water quality surveys.

Transparency is a combined function of colour and turbidity. The Tawe is relatively far more transparent than the estuaries in the Northeast of England. This is probably related to the low TSS of the freshwater entering the impoundment during the period sampled (related to low flow and relatively low drift deposits in the catchment). The Tees has a strong colour imparted by humic and fulvic acids (Wright and Worrall, 2001) and hence exhibits a relatively low transparency.

2.5.3.13 TSS

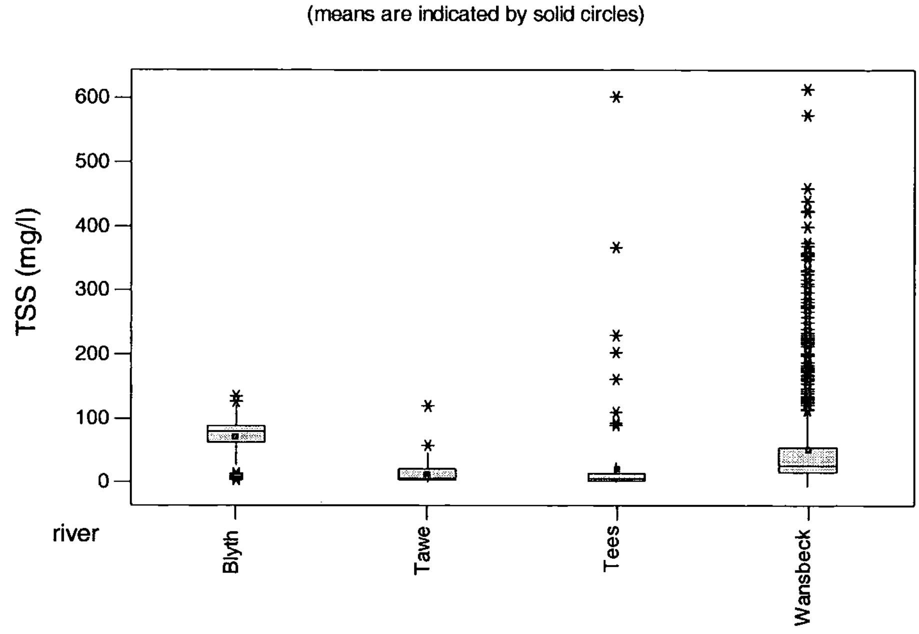


Figure 2.23. TSS values for the rivers during the water quality surveys.

TSS also varies significantly between estuaries, with the Wansbeck and Blyth showing much higher average values (50 and 72 mg/l respectively) than the Tees and Tawe (20 and 13 mg/l respectively). The Tawe was sampled under low flow conditions, and has a distinct catchment as described above. It is probable that the Tees is less turbid and has lower TSS (although, as mentioned, a low transparency due to its strong colouration) due to a lack of tidal currents acting to re-suspend settling particulates. Re-suspension of material by turbulent shearing from strong tidal currents acts to give high TSS values for the Blyth even when TSS inputs from the freshwater source (samples taken from the tidal limit) are low. Continual and rapid exchange of sediment between the bed and suspended phase due to tidal currents is described by Dyer (1995). Such tidal currents will be suppressed by the construction of a barrage. The allochthonous supply of TSS in freshwater is likely to relate to freshwater flow for each catchment.

Outlying high values observed for TSS relate to either high flow periods or samples from depth at sampling sites. Although care was taken to avoid disturbing the sediment-water interface when taking water samples at depth, it is possible that in some cases high TSS were measured due to disturbed bed sediment. Unfortunately it is impossible to assess whether this is the case, or whether "true" sediment concentrations were being recorded (e.g. sampling a fluff layer at the sediment-water column interface).

Some negative values for TSS were recorded for the initial laboratory work (mainly from the Tees) in which the cellulose nitrate filter papers used were not perfectly dry before use (and thus lost weight on subsequent oven drying and dessication). In later work care was taken that dry papers were used by storing them in a dessicator, and pre-weighing at a distance from any water samples. Additional problems occurred in several cases because filter material was lost on transfer to and from filter apparatus and the balance, due to the fragile nature of the filter papers. Negative values of TSS are excluded from data analyses.

2.5.3.14 Nutrients

Nitrate

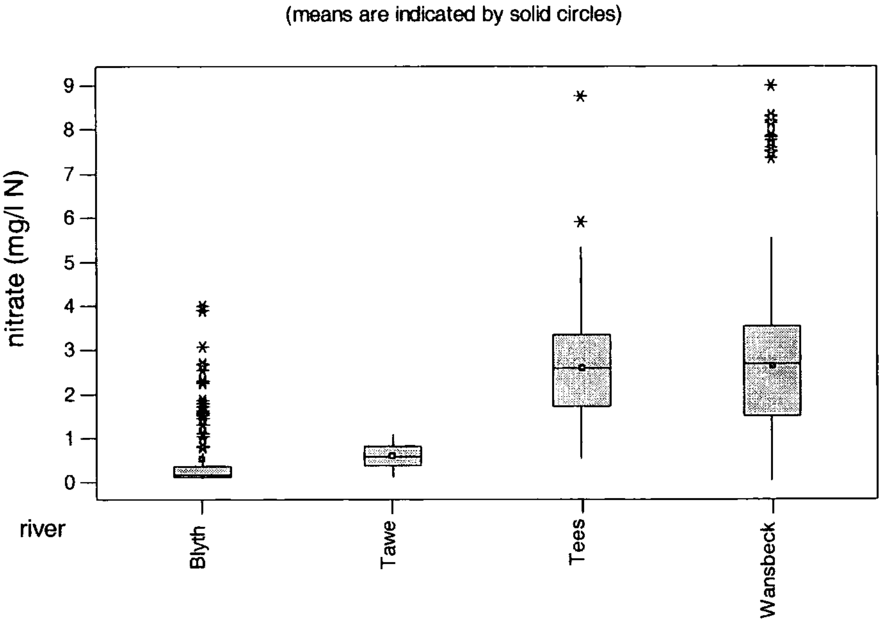


Figure 2.24. Nitrate values for the rivers during the water quality surveys.

Mean nitrate values for the periods studied are 0.53, 0.61, 2.58 and 2.64 mg/l N for the Blyth, Tawe, Tees and Wansbeck respectively (figure 2.24). The outlying values for the Blyth represent the freshwater input to the estuary, which show significantly higher nitrate than the seawater end member. The positive outliers for the Wansbeck are from sampling on the 16th June 2001. The 2 Tees outlying values are from deep sampling points and may represent sampling which disturbed the bed sediment.

Variations in nitrate concentrations occur with different land management within catchments (e.g. amount of ploughing or fertiliser application (Roberts and Marsh, 1987; Johnes and Burt, 1993)), quantities of point source inputs, and with season (peak nitrate tending to occur in spring (Heathwaite and Johnes, 1996)). The greatest range in nitrate concentrations is seen in the Wansbeck, which was sampled over the greatest range of seasons. The Blyth and Tawe were only sampled during summer periods, during which run-off and nitrogen export are likely to be at their lowest.

Ammonia

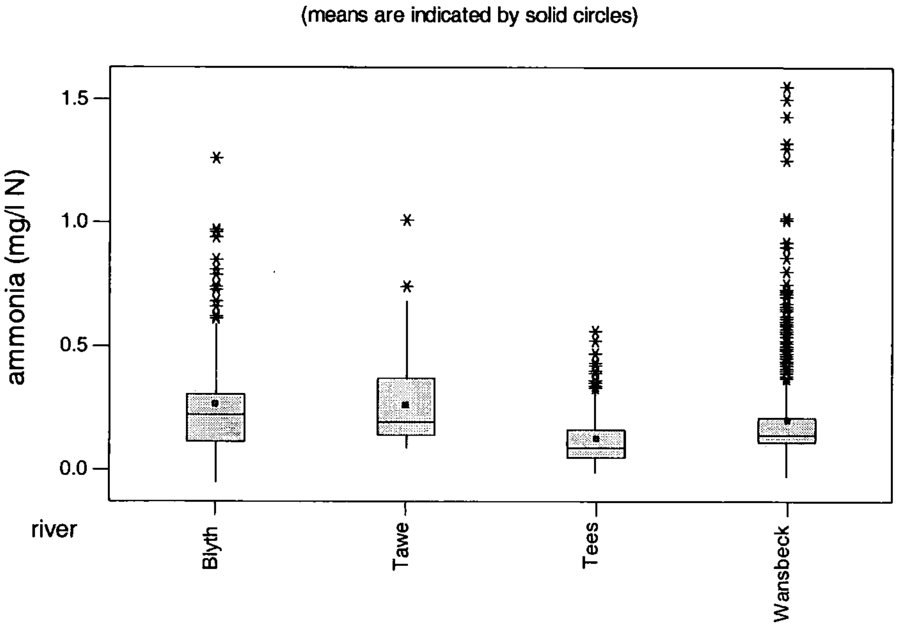


Figure 2.25. Ammonia values for the rivers during the water quality surveys.

The pattern for the relative mean values of ammonia between the estuaries is the reverse of that for nitrate. The values for the Blyth and Tawe (0.27 and 0.26 mg/l N respectively) are higher than those for the Tees and Wansbeck (0.13 and 0.20 mg/l N respectively). Ammonia is normally at low levels in unpolluted waters due to biologically mediated reactions to more oxidised states (nitrification). The values in the estuaries studies are generally low and suggest that conditions are relatively unpolluted by ammonia and are oxic. However, several outlying high values (figure 2.25) corresponding to deep samples indicate that anoxic conditions and possible release from sediments may exist in places.

Phosphate

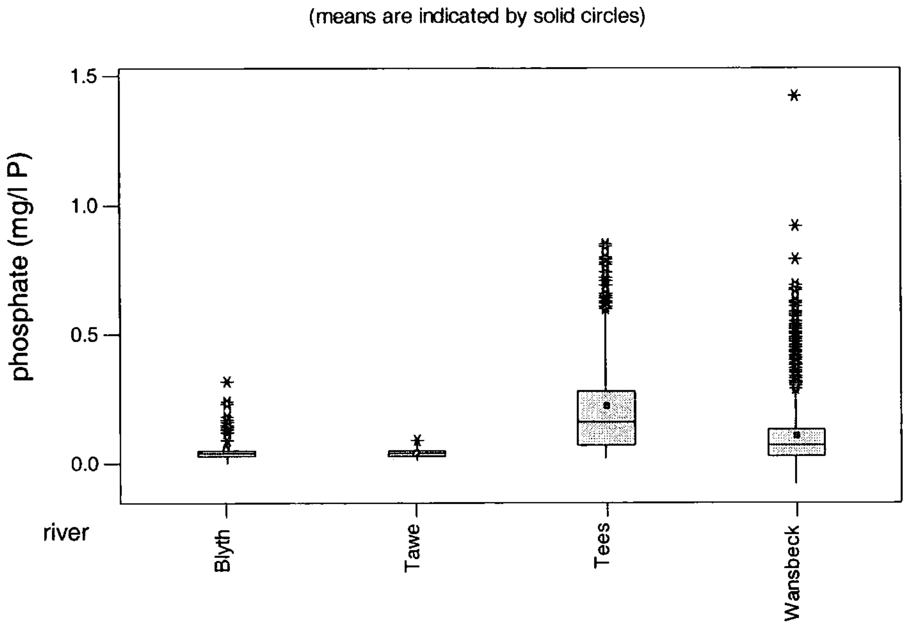


Figure 2.26. Phosphate values for the rivers during the water quality surveys.

Dissolved orthophosphate concentrations tend to be very low in natural waters since it is rapidly taken up by biota. Maybeck (1982) gives the global average river water concentration of dissolved phosphorus as 0.028 mg/l P – PO_4. The OECD threshold level for lake eutrophy is 0.035 mg/l P – PO_4 (Reynolds and Davies, 2000). The mean values encountered in the estuaries during the water quality surveys are above these levels (0.057, 0.041, 0.225 and 0.109 mg/l P for the Blyth, Tawe, Tees and Wansbeck respectively), the Tees and Wansbeck in particular having high phosphate concentrations, indicating that there are anthropogenic inputs to the systems which may lead to eutrophic behaviour. The positive outlying values for phosphate for the Tees and Wansbeck (figure 2.26) are from summer sampling dates (low flows) on the rivers.

Silica

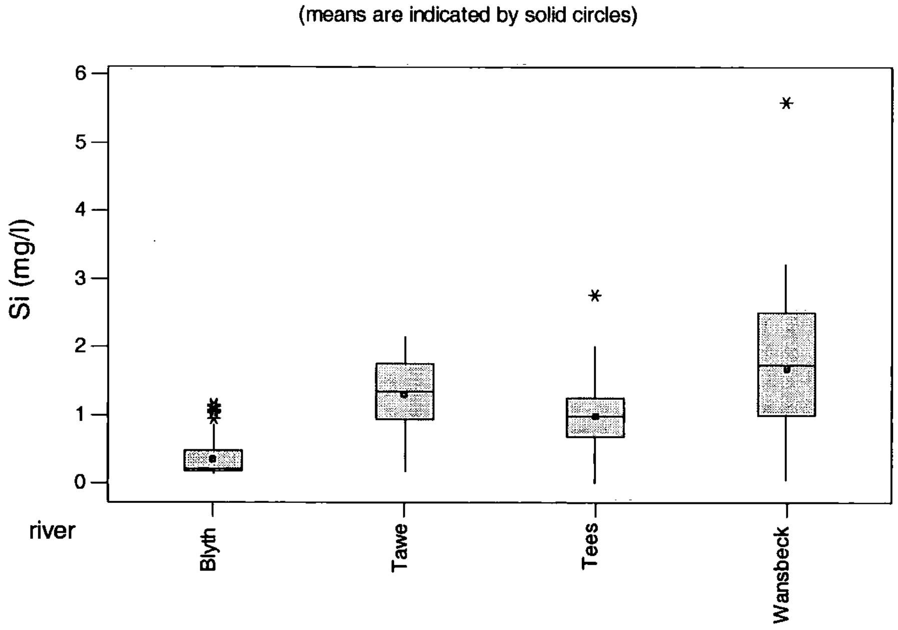


Figure 2.27. Si values for the rivers during the water quality surveys.

Mean silica values for the estuaries are 0.35, 1.30, 0.99 and 1.68 mg/l for the Blyth, Tawe, Tees and Wansbeck respectively. Silica variations between freshwater inputs are likely to be due to variations in the geologies of the catchments, and flows. Concentrations on specific dates will vary with the relative amounts of baseflow and stormflow contributing to the freshwater flow. The concentrations in freshwater are higher than those in seawater.

2.5.3.15 Major elements

The mean values for the (dissolved) major elements of Na, Mg, Ca, K and S in the impoundments show the same pattern as conductivity, being dominated by the relative amount of seawater in the system (figure 2.28 and table 2.8).

(mg/l)	Blyth	Tawe	Tees	Wansbeck
Ca	324	74	29	114
K	314	59	3	61
Mg	991	181	6	213
Na	7918	1523	24	1578
S	757	384	16	179

Table 2.8. Mean concentrations for major elements during water quality surveys.

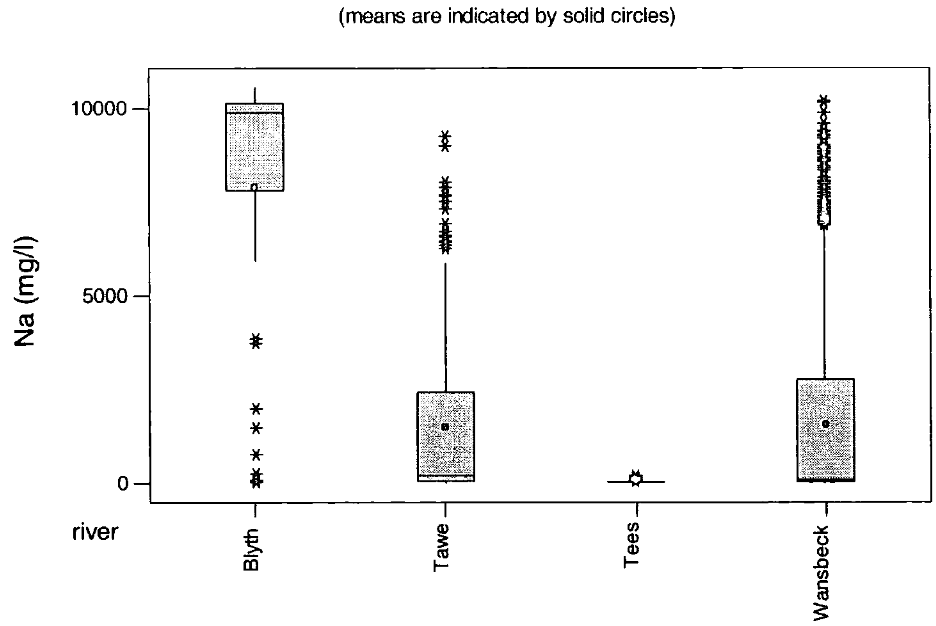


Figure 2.28. Na values for the rivers during the water quality surveys.

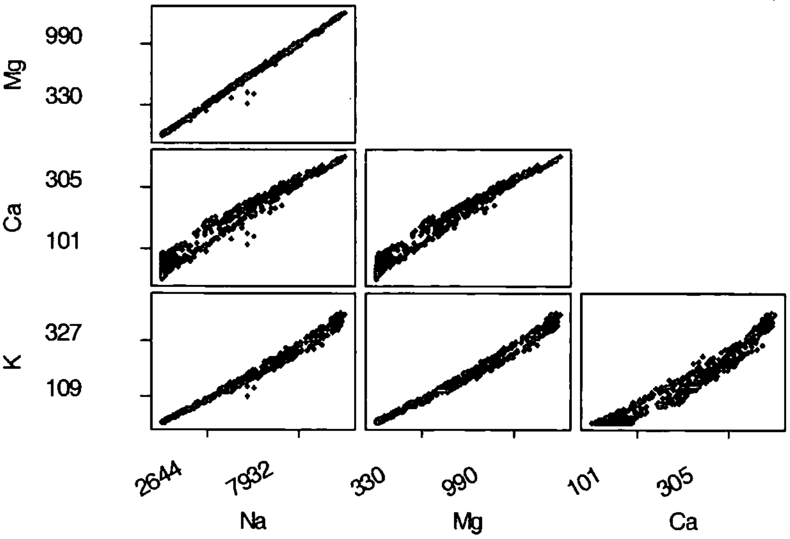


Figure 2.29. Co-linearity between major metals with conservative mixing of freshwater and seawater for the water quality surveys.

Major elements are of far higher concentration in seawater than river water and behave conservatively (Liss, 1976), and therefore represent the relative amount of seawater in an estuary. The Blyth contains the maximum amount of seawater and the Tees contains no seawater, with the Tawe and Wansbeck in intermediate positions.

Conservative mixing of the major elements can be seen in the strong co-linearity of Ca, Mg, K and Na for all data (figure 2.29):

- Ca = 42.4 + 0.0361 Na (P = 0.000, S = 20.97, R-Sq = 96.5%)
- K = 0.773 + 0.0378 Na (P = 0.000, S = 9.548, R-Sq = 99.3%)
- Mg = 3.24 + 0.125 Na (P = 0.000, S = 13.55, R-Sq = 99.9%)

S is less well correlated with Na (figure 2.30) due to analytical problems in the determination of S.

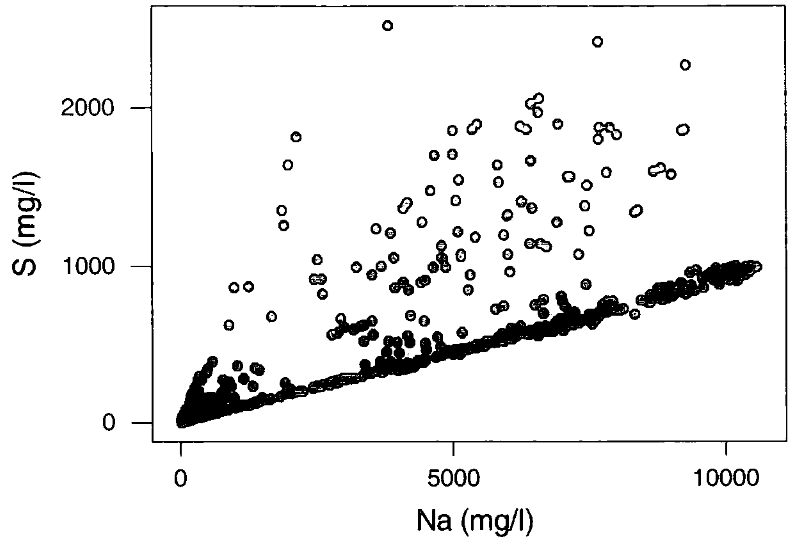


Figure 2.30 The relationship of S to Na during the water quality surveys. The scatter of points above the conservative mixing line is due to analytical error.

Whilst for the majority of analytical runs on the ICP-OES S measurement showed low error and could be seen to show conservative mixing within the impoundments, for a few runs S determination showed large random (although always positive) errors. These were identified as errors (rather than true measurements) by the observation of large fluctuations in the S values reported for the "seawater" standard included periodically in the sampling runs. These errors were unique to S and no underlying cause was able to be identified. Care is taken in interpretation of results for S which include these errors.

2.5.3.16 Minor and trace metals

Trace metal levels and LOD

A large number of the trace metal values lie close to or below the 3s limit of detections (LOD). These elements tend to have very low concentrations in dissolved forms and partition strongly to particulate phases at normal pH values, and so the low values encountered in the water quality surveys are typical. The 3s LOD represents the value at which there is 99% probability of the response being a true value (rather than analytical error). Considering values below this level entails a greater risk of responses being due to random error rather than the concentration in the sample. Hence, for many of the dissolved trace elements analysed for in the water quality surveys, interpretation may only be semi-quantitative.

mg/l	LOD	Blyth	Tawe	Tees	Wansbeck
Al	0.055	0.013	0.013	0.048	0.031
Co	0.587	0.0011	0.0013	-0.0020	-0.0001
Cr	0.004	0.0015	0.0046	-0.0026	0.0012
Cu	0.003	-0.0093	-0.0016	-0.0026	-0.0016
Fe	0.004	0.082	0.078	0.167	0.168
Mn	0.004	0.058	0.109	0.017	0.166
Ni	0.005	0.0036	0.0015	-0.0035	-0.0005
Sc	0.000	-0.0014	0.0006	0.0027	-0.0001
Sn	0.033	0.0059	-0.0382	0.0055	0.0054
Ti	0.002	-0.0015	0.0004	-0.0035	0.0003
V	0.011	0.0087	0.0615	-0.0086	0.0423
Zn	0.003	-0.0163	0.0590	0.0180	0.0017

Table 2.9. Mean concentrations and LODs (see section 2.4.10) for minor and trace elements during water quality surveys.

Fe and Mn

Both Fe and Mn occur at levels well above the 3s LOD values for the ICP-OES analysis (Fe = 0.004 mg/l, Mn = 0.004 mg/l), and show significant mean concentration differences between the estuaries. The concentration of Fe and Mn are likely to be controlled both external to (freshwater and seawater inputs to the estuaries) and within the estuaries. The behaviour of both elements is strongly controlled by redox conditions. In oxygenated water, Fe occurs as insoluble ferric hydroxide and as complexes with dissolved and colloidal organic (particularly humic) and inorganic substances. Mn behaves similarly but has a higher solubility. Under low oxygen conditions Fe and Mn are released from sediment in dissolved form to the water column. The high values of Mn observed for some of the samples taken at depth within the Wansbeck, Tawe and Tees (positive outliers on figure 2.31) suggest some release from sediments occurs in these systems. The redox conditions within the systems are discussed further in subsequent sections.

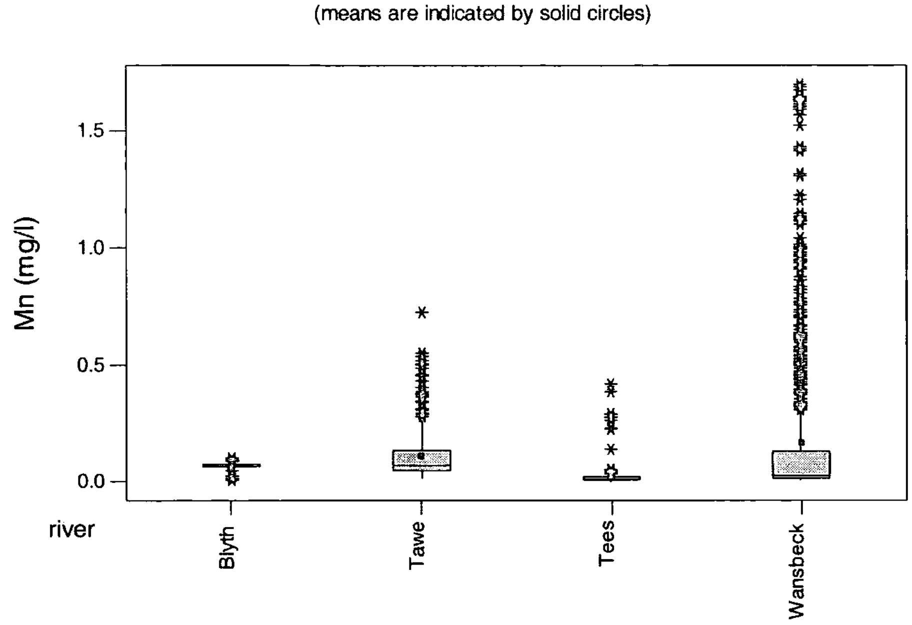


Figure 2.31. Mn values for the rivers during the water quality surveys.

Chapter 3

Seasonal Effects on Water Quality

3.1 Introduction

Differences in water quality in estuarine impoundments between seasons were examined using data collected from water quality surveys of the Tees and the Wansbeck impoundments. Firstly, differences between the summer and winter seasons in a total tidal exclusion impoundment (the Tees) were assessed using the complete range of water quality parameters measured. Secondly, the variation between spring, summer, autumn and winter in a partial tidal exclusion impoundment (the Wansbeck) were assessed using a selection of water quality parameters. General Linear Model (GLM) ANOVA was used to assess the significance of season as a factor in water quality variation.

3.2 Tees

Seasonal differences in water quality were examined using (GLM) ANOVA. For the Tees, sampling periods were summer (dates sampled: 04/08/99, 11/08/99, 25/08/99, 08/09/99 and 22/09/99), and winter (dates sampled: 02/02/00, 08/02/00, 16/02/00, 23/02/00 and 29/02/00). To create a balanced dataset (one in which factor levels (e.g. number of dates sampled or sample sites) are the same for each treatment (season, etc.), one of the dates sampled as part of the summer survey (21/07/99) was not included in the analyses.

The significant controls on the water quality parameters in the Tees impoundment were assessed using ANOVA with the factor levels of season (summer or winter), distance within the impoundment from the former tidal limit (in terms of the 6 approximately equidistant sites sampled, represented by numbers 1 to 6 with increasing distance from the upstream limit at Low Moor), and depth (shallow (s), middle (m) and deep (d)) sampled in the water column at each sampling site. The interactions between these factors (season*distance, etc.) were assessed. Analyses were carried out both with and without the inclusion of flow and temperature as covariates in the models, with the results from these analyses presented where relevant.

3.2.1 Temperature

Results

Source	F	P	σ^2	Size of Effect (ω^2)
Season	2191.19	0.000	247.9	1.00
Distance	0.16	0.977	na	na
Depth	1.01	0.366	na	na
Season*distance	0.20	0.964	na	na
Season*depth	0.68	0.509	na	na
Depth*distance	0.04	1.000	na	na
Season*distance*depth	0.07	1.000	na	na
Error			4.1	0.00

Table 3.1. Results from GLM ANOVA for seasonal effects on temperature within the Tees impoundment (na = not applicable since factor insignificant (P>0.05)).

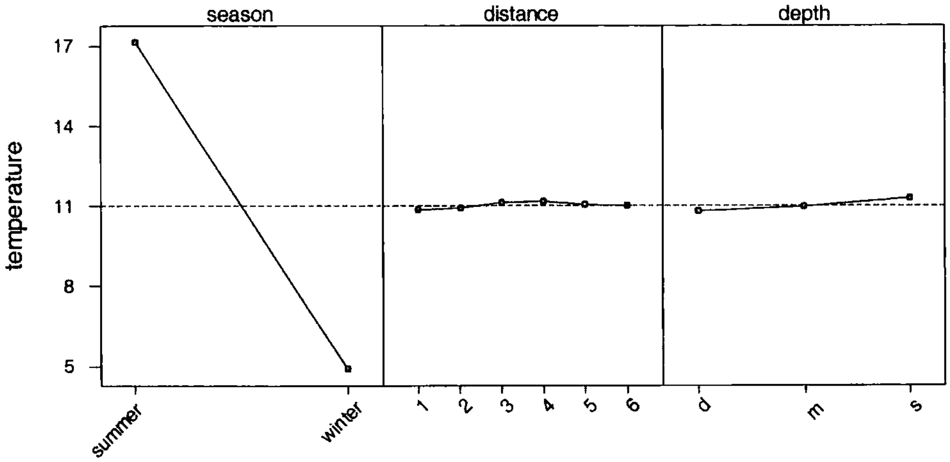


Figure 3.1. Main effects plot for temperature (in °C) in the Tees impoundment (least square (LS) means for factor levels), showing season as the only significant factor.

The results (table 3.1) show that all of the variation in temperature observed in the sampling periods can be explained by season (size of effect for season (ω^2) = 1.00). Water temperature does not vary with either distance or depth within the impoundment.

Discussion

The results show that, as might be expected, the temperature of the Tees impoundment varies significantly dependent on climatic factors (expressed as season in the model). No internal variation within the water body is seen to develop. Significantly, the system may be assumed to have sufficient mixing throughout the year that thermal stratification (as occurs in the majority of temperate lakes of > approximately 10 m depth (Wetzel 1983)) does not occur.

3.2.2 Dissolved oxygen

Results

The difference in behaviour of DO within the impoundment was analysed in terms of DO % saturation to remove the effects of solubility differences due to temperature on the concentrations. The raw DO % values were used, with no normalisation to input values (the water entering the impoundment at the upstream limit of the impoundment) being applied. Results are shown in table 3.2.

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
Season	188.75	0.000	532.0	0.41
Distance	16.82	0.000	224.2	0.17
Depth	13.49	0.000	70.8	0.05
Season*distance	16.10	0.000	213.9	0.17
Season*depth	15.05	0.000	79.6	0.06
Depth*distance	2.10	0.025	31.3	0.02
Season*distance*depth	2.20	0.019	33.9	0.03
Error			102.0	0.08

Table 3.2. Results for GLM ANOVA for DO % with season within the Tees.

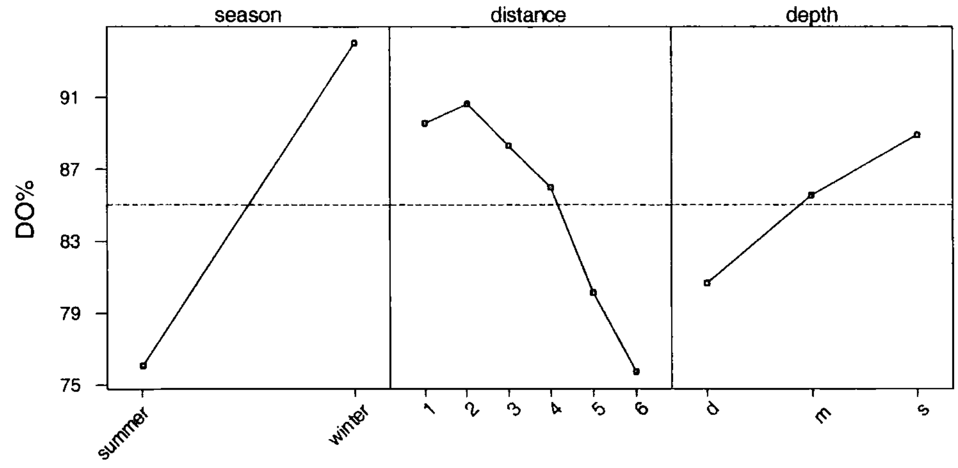


Figure 3.2. Main effects plot for DO % in the Tees impoundment (least square (LS) means for factor levels).

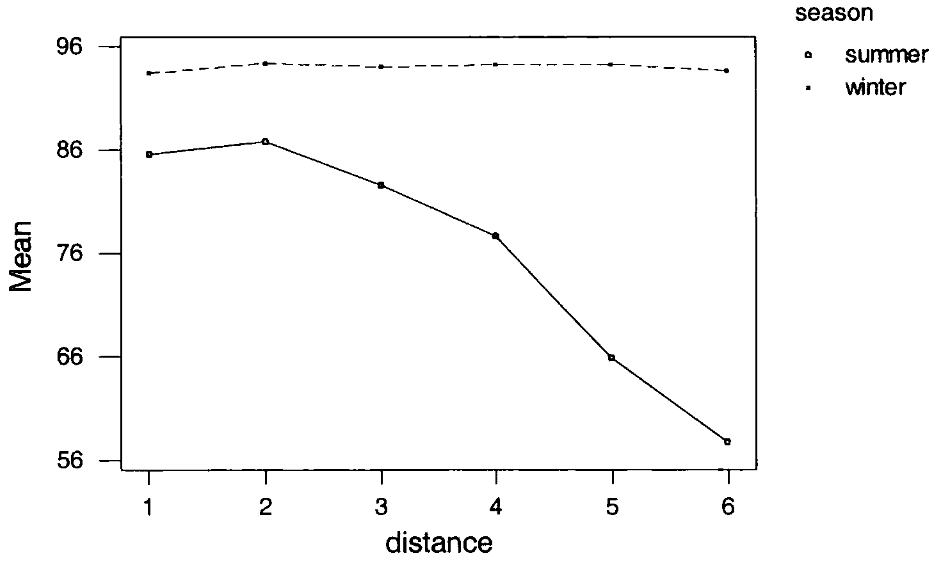


Figure 3.3. Interaction between season and distance effects on DO % (LS means) in the Tees impoundment. Summer results as solid line and winter as dashed line.

The results show that the variation in DO in the impoundment can be explained to a large (75%) extent by three parameters: season, distance, and the season*distance interaction. The largest effect in the model is that of season, which explains 41% of the variation in levels of DO in the Tees impoundment. Distance accounts for 17% of the variation, and shows a substantial (17%) interaction with season (figure 3.3). During summer, DO saturations are significantly (P = 0.000) lower (table 3.2 and figure 3.2), with a mean value of 75.4 %. The range of values of DO is also far greater than in winter (SD = 19.7 %, maximum = 135.6 % and minimum = 15.1 %). The effects of distance and depth in the impoundment only become significant during summer (figures 3.3 and 3.4). Statistically this is demonstrated by the size of experimental effects being almost identical for both distance and the distance*season interaction (ω^2 = 0.17 and 0.17 respectively), and depth and the depth*season interaction (ω^2 = 0.05 and 0.06 respectively). DO decreases with distance downstream in the impoundment and with depth at sampling sites. The depth effects, in terms of reduced DO concentrations with increasing depth in the system, also becomes slightly more pronounced with distance downstream (figure 3.5, interaction ω^2 = 0.02).

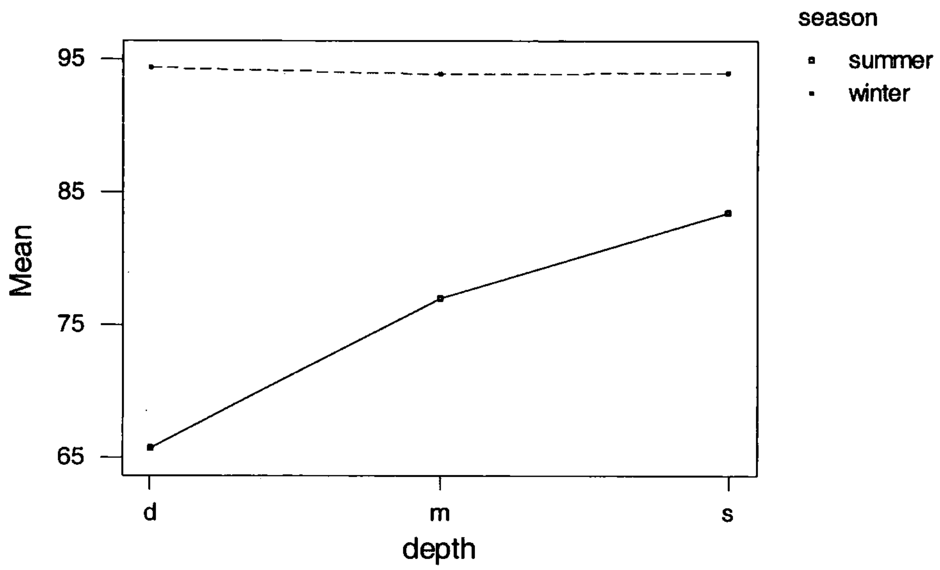


Figure 3.4. Interaction between season and depth effects on DO % (LS mean) in the Tees impoundment. Summer results as solid line and winter as dashed line.

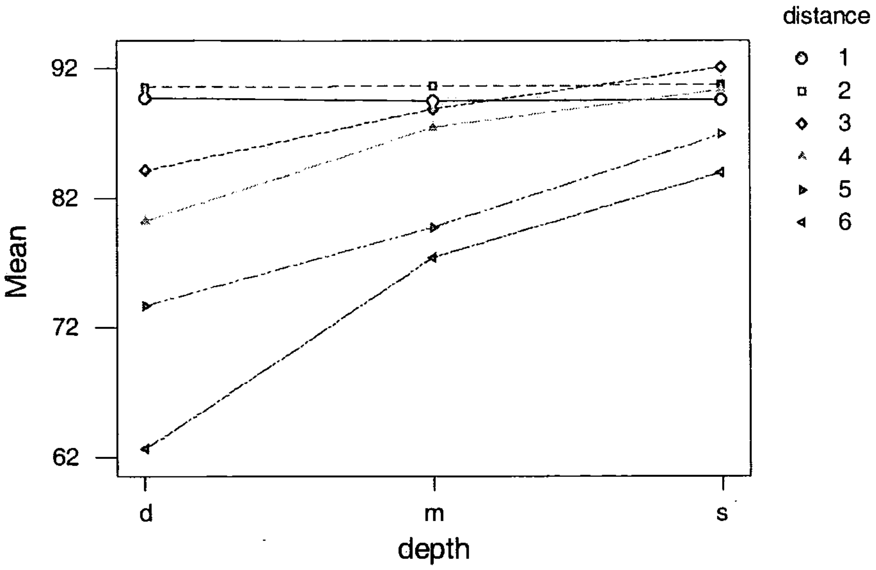


Figure 3.5. Interaction between distance and depth effects on DO % (LS mean) in the Tees impoundment.

Discussion

The Tees carries a large (particularly dissolved) organic load (Worrall et al. in press) due to its source in peat covered uplands, which is likely to exert a natural BOD to the river. The impact of this BOD will be greater during the summer period due to the higher temperatures of the water and hence the Tees, as would be expected, shows significant seasonal differences in DO %. The impacts of colour due to humic substances with seasonality on DO levels are discussed in Belanger et al. (1987) and Crisman et al. (1998). The variation in dissolved organic carbon levels with season and flow is discussed in the section on BOD below.

As mentioned temperature controls the solubility of oxygen in water (and therefore modelling was carried out using % saturations), so that absolute values (in which terms SWQOs for DO tend to be set) at a particular % saturation will be lower in warmer summer water. The mean summer water temperature during the surveys was 17.2°C and that in winter 4.9°C, both with low variation (SD = 2.5°C and 1.0°C respectively), and the temperature control on absolute DO concentration can be seen in the separation of summer and winter data when DO % and DO mg/l values are plotted (figure 3.6).

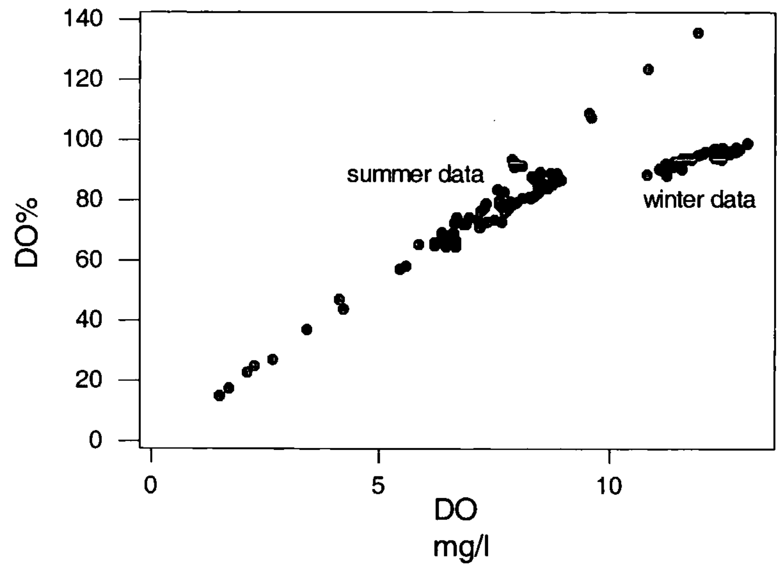


Figure 3.6. DO % and absolute DO in the Tees during summer and winter periods.

Figure 3.6 also confirms that during winter the water in the Tees is generally at 100 % saturation, irrespective of where sampling takes place in terms of distance. This is likely to be a combined effect of:

- lower rates of microbial respiration and hence oxygen demand at lower temperatures, and
- higher flows ensuring turbulent and fully mixed and aerated flow throughout the river.

The distance effect is likely to be due to the change in flow velocity which occurs as the Tees follows its course from the upstream limit of sampling at the former tidal limit 26 km above the barrage (site LM; defined in analysis as distance 1), through distances 2, 3, 4 and 5 (sites LW, AL, PH and TRB respectively) to distance 6 at the barrage (TB). The reduction in flow velocity leads to a decrease in both turbulence and re-oxygenation of the water body from the atmosphere, so that the reduction in DO due to the decomposition of organic matter remains in evidence. In addition the oxygen demand of the sediments is likely to increase with distance downstream as the bed changes in character from coarse gravel and sand, to finer and more organic rich material with decreasing flow velocity. The nature of the bed sediment of the Tees is discussed further elsewhere in the thesis. It is also possible that the there is an increased oxygen demand within the water column with the course of the river from diffuse (agricultural) or point (CSO and other wastewater) source inputs, although no evidence for this was seen in the BOD results, which remain relatively constant throughout the impoundment.

The decrease in DO levels with depth is only significant during summer periods, when flows are lower and incomplete mixing of the water column occurs. This leads to a slight stratification in DO levels which becomes more pronounced as depth in the impoundment increases and river gradient decreases (and hence flow velocity and turbulence decrease) with distance downstream. Re-oxygenation of the waters isolated from the water column-atmosphere interface cannot occur and reduced DO saturation occurs.

The error term in the ANOVA for DO % saturation has a value of ω^2 of 0.08, meaning that 8 % of the variation in DO cannot be explained by the factors included in the model. This error may include differences in external loading of oxygen demand to the water body not accounted for by seasonality, or variations in flow which are independent of season. Repeat analysis carried out with the inclusion of flow as a covariate showed this term to be insignificant, however.

An additional impact of seasonality is on primary production in the water body. Phytoplankton primary production is evident in the Tees in summer from observations of supersaturation of DO. At shallow and mid depths on the 4th August (during which water temperature was high (≅22°) and river flow low (≅3.5 m2/sec)) at sites AL and PH, oversaturation (<137 %) was measured. Assuming the normal diel effects of primary production and respiration, these values would have fallen to undersaturation during the night.

3.2.3 BOD

Results

The model used to assess DO behaviour above (with season, distance and depth as factors) was run for BOD, with both exclusion and inclusion of flow as a covariate. Although flow is generally higher in the winter than in summer, it shows a large amount of variation in and some overlap between these seasons during the Tees sampling. Without flow as a covariate, none of the 3 factor levels or their interactions showed any significant effects (at 95 % confidence interval) on BOD. Including flow (as the mean flow in the 24 hour period preceding sampling (Mean 24)) gave the following results:

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
Flow	83.3	0.000	2.15	0.45
Season	67.6	0.000	1.74	0.36
Distance	1.1	0.368	na	0.00
Depth	1.2	0.299	na	0.00
Season*distance	1.0	0.405	na	0.00
Season*depth	0.6	0.527	na	0.00
Depth*distance	0.4	0.950	na	0.00
Season*distance*depth	0.6	0.806	na	0.00
Error			0.94	0.19

Table 3.3. Results from GLM ANOVA for seasonal effects on BOD within the Tees impoundment including flow as a covariate (na = not applicable since factor insignificant (P>0.05)).

During summer BOD levels are significantly higher than in winter during the periods sampled in the Tees (table 3.3, figure 3.7). BOD does not vary significantly within the impoundment with either distance or depth during either summer or winter. The seasonal effect is independent of flow, which also shows a significant control on BOD. Together flow and season account for the majority of the variation in values of BOD measured during the sampling periods (ω^2 = 0.45 and 0.36 respectively), with an error term in the model of 19 %.

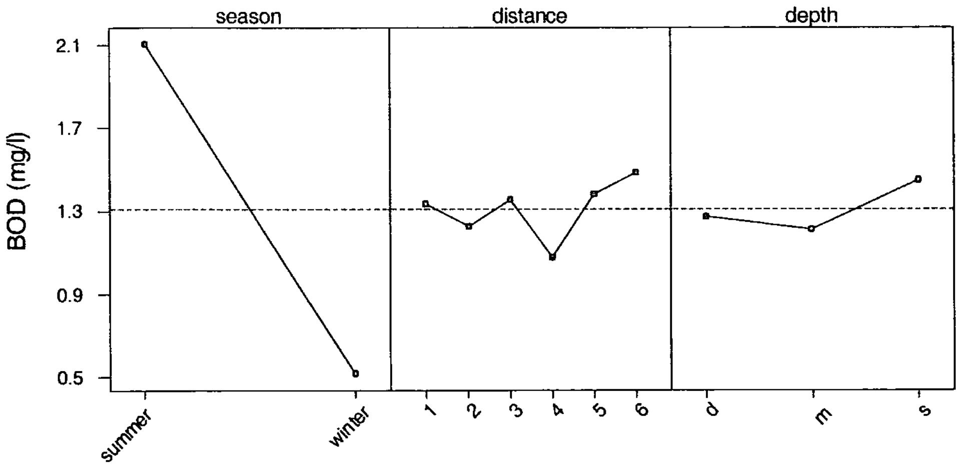


Figure 3.7. Main effects plot for BOD in the Tees impoundment (least square (LS) means for factor levels).

Discussion

BOD is externally controlled in the Tees impoundment, i.e. no significant change in BOD values occurred in the section studied during the sampling periods. Assuming this is the general case, then inputs to the river within the impounded section are not important in affecting DO levels in the system. It must be noted however that the number of sampling dates in this study was limited and may not have picked up all possible conditions in the Tees.

BOD is largely controlled by river flow in the Tees (figure 3.8). Increased oxygen demanding (organic) material is transported to the river when flows are high. The relationship between flow and BOD differs with season however. Increased flow conditions in the summer period give much greater increases in BOD than do those in the winter period. Assuming that the sources of BOD are natural, this is likely to reflect the behaviour of removal of organic material from the peat in the upland catchment of the Tees during runoff episodes. As mentioned the Tees shows a positive relationship between flow and colour (Worrall et al., in press), and this colour relates to soil humic substances (Tipping, 1987). Greater removal of this organic material has been observed during warm weather, particularly when rainfall follows a dry period (Burt et al., 1990; Grieve, 1990; Tipping et al., 1998). Hence colour and BOD levels show greater response to runoff events in summer than in winter. Dissolved organic carbon levels carried by baseflows, however, vary with season in relation to rising or falling water tables in the peat (giving lowest levels in spring as water tables fall and highest in autumn at the maximum rate of rise in water table), and baseflow levels are likely to be on average lower in summer than winter.

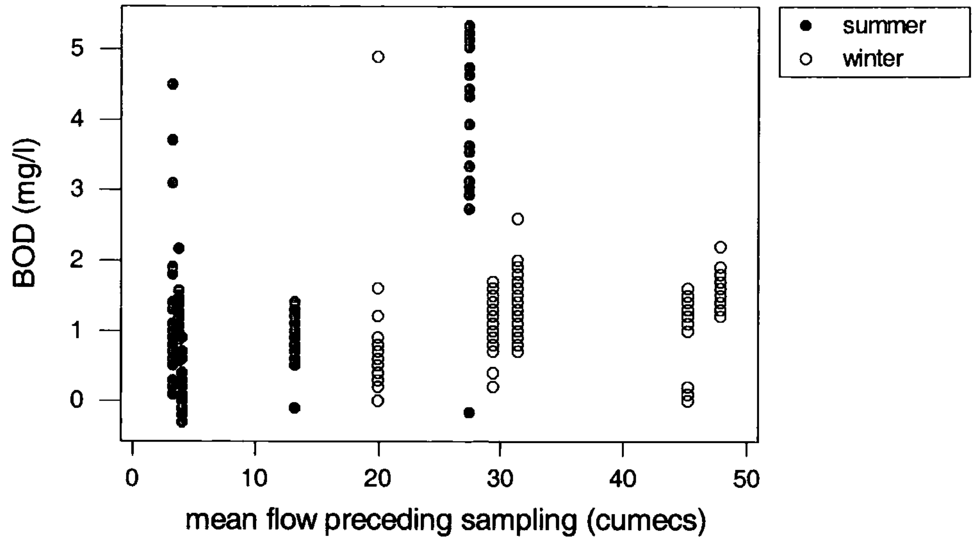


Figure 3.8. BOD values for the sampling dates against mean flow preceding sampling. Summer measurements are indicated by solid circles and winter by open circles. Note that baseflow levels in summer are lower than in winter but show a greater response to stormflow events.

BOD may also be entered to the water body from anthropogenic (point) sources within sections of the Tees upstream of those studied during the sampling programme (the city of Darlington is upstream of the sampled section). The error term in the model may for example be explained by variations in point source inputs to the system. However, assuming relatively constant rates of input, the BOD from point sources would be likely to be diluted by higher river flows. The possible impact of CSO (combined storm overflow) discharges, which come into effect only during high flow conditions, on supply of BOD (or nutrients, etc.) is not investigated as part of this study.

3.2.4 pH

Results

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
Season	104.98	0.000	0.182	0.54
Distance	4.52	0.001	0.031	0.09
Depth	1.18	0.307	na	0.00
Season*distance	8.10	0.000	0.062	0.18
Season*depth	1.20	0.302	na	0.00
Depth*distance	0.88	0.557	na	0.00
Season*distance*depth	0.48	0.903	na	0.00
Error			0.063	0.19

Table 3.4. Results from GLM ANOVA for seasonal effects on pH within the Tees impoundment (na = not applicable since factor insignificant (P>0.05)).

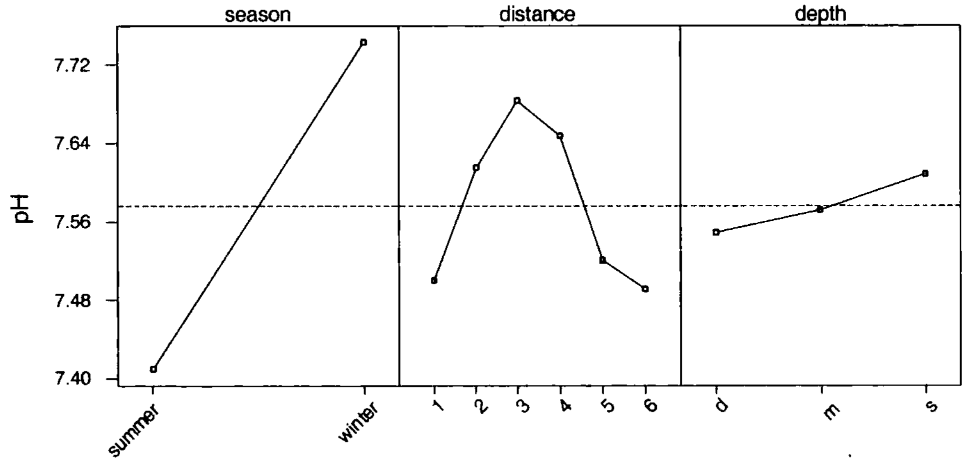


Figure 3.9. Main effects plot for pH in the Tees impoundment (least square means for factor levels).

The same model applied above to DO was used to examine the seasonal behaviour of pH within the Tees impoundment. The results are shown in table 3.4. The majority of the variance in the data (54 %) is due to the effect of season. Distance within the impoundment is also significant at the 99 % level, but accounts for only 9 % of the differences between pH values. There is a significant interaction between season and distance (figure 3.10, $\omega^2 = 0.18$), and distance is seen to be a more significant factor during the summer period. Depth is not shown to be a significant control on pH in the Tees impoundment.

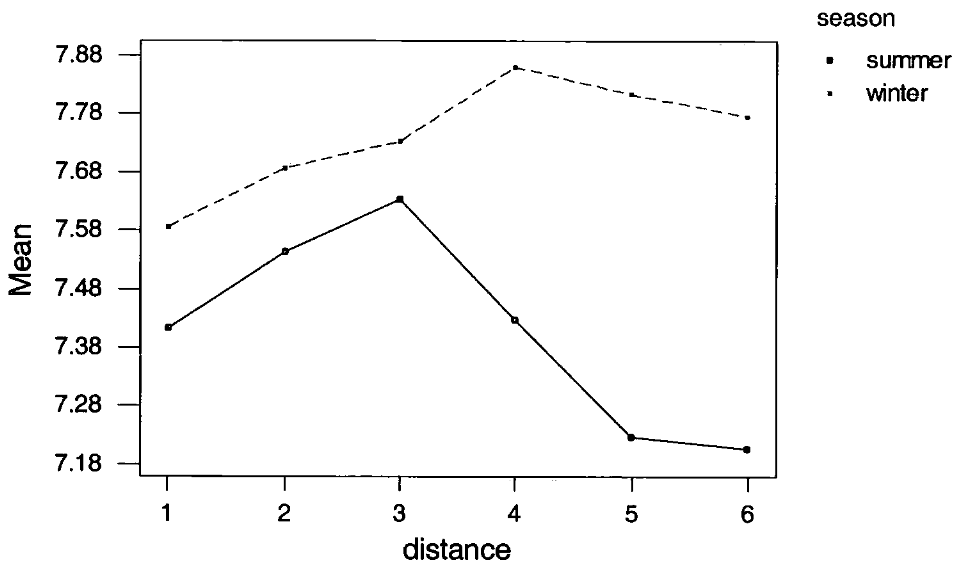


Figure 3.10. Interaction between season and distance effects on pH (LS mean) in the Tees impoundment. Summer results as solid line and winter as dashed line.

Discussion

The variations in pH observed in the Tees, although significant, are not large and, assuming the sampling periods are representative of the general situation in the river, the range of values is such that pH is not likely to be a cause any major water quality problems (such as solubilisation of metals). Low variability in pH would be expected given the well buffered nature of the water body due to carbonate dissolution (mean alkalinity during the sampling of 121 mg/l $CaCO_3$ equivalent).

pH values observed were slightly lower in summer than in winter. Within a water body primary production tends to increase pH and alkalinity by photosynthetic fixation of dissolved CO_2 together with H^+ according to:

$$106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+ \Leftrightarrow \{C_{106}H_{263}O_{110}N_{16}P_1\} + 138O_2$$

(Andrews et al., 1996). Respiration acts in the reverse direction and reduces pH. Changes in the relative amounts of photosynthesis and respiration with light availability can lead to diel cycles in pH and DO. In this study the effects of any such variations on the reporting of water quality were minimised by sampling at approximately the same time of day for each sampling date and site. Oxidation of organic matter either in the water column or the sediments also acts to reduce pH. The lower pH values encountered during the summer period could be explained by increased rates of oxidation with higher temperature.

It is also possible that change in the water source with season may have an effect on pH. Summer flows may contain a higher proportion of baseflow coming from lower pH Permo-Trias sandstones of the catchment, compared with the winter condition of flow from the upland catchment (composed of Carboniferous sediments).

The River Leven tributary, which has its major groundwater source in the Permo-Triassic geologies and enters the Tees between sites 3 and 4, may explain some of the decrease in pH seen between these points in summer, although the pattern is opposite in winter and the contribution of the Leven cannot be well quantified due to lack of flow data. It may be assumed therefore that the majority of the distance effects on pH observed are due to the relative rates of photosynthesis, respiration and oxidation. As is evident in DO values, the impact of oxidation increases with distance downstream during the summer period, and pH values also decrease in summer towards the barrage. Increasing pH with distance in the whole system in winter, and at upstream sites in summer, could correspond to increased primary production at these sites associated with decreasing flow velocities in the river. That pH values do not decrease significantly with depth (as occurs in the hypolimnion of eutrophic lakes), in addition to the low size of depth effect on DO, suggests that entrenched stratification of the water column of the Tees does not occur.

The error term in the model is relatively large (19 %), meaning that the terms included (season, distance and depth) cannot account for all of the variance in pH values seen. Including flow (as the mean flow in the 24 hours previous to sampling) as a covariate in the model reduces the error term to 13 %. Including temperature as a covariate in the model does not reduce the error term, and it can be assumed that temperature effects are adequately explained within season. It is possible that variations in the contribution to pH levels from the Leven tributatry may explain a portion of the error.

3.2.5 Alkalinity

Results

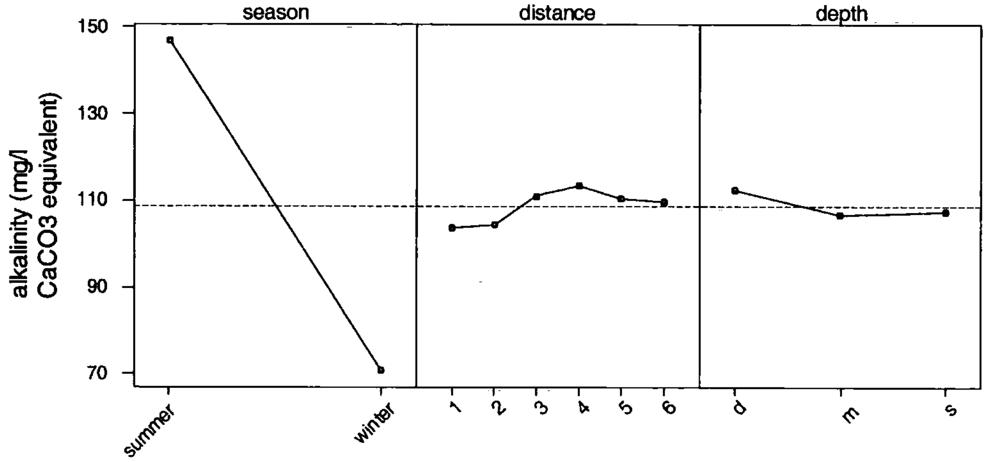


Figure 3.11. Main effects plot for alkalinity in the Tees impoundment (least square means for factor levels). Distance and depth effects are insignificant at 95 % CI.

Alkalinity is significantly lower (99 % level) in winter than in summer. Applying the ANOVA model used for DO, BOD and pH to alkalinity shows that there are no significant differences with either distance or depth in the impoundment (figure 3.11), implying that alkalinity is externally controlled. One-way ANOVA shows a magnitude of effect for season of 88 %.

Discussion

The Tees is well buffered due to dissolution of carbonate minerals in the geology of its catchment. Flow is higher in winter than summer and, given relatively constant rates of carbonate dissolution, alkalinity is diluted by these higher flows (figure 3.12, Kirschner et al. 1993) such that:

alkalinity = 270 - 135 log(Mean 24) (P = 0.000, S = 23.7413, R-Sq = 86.0 %)

where alkalinity is measured in mg/l $CaCO_3$ equivalent, and Mean 24 is the mean flow during the 24 hours prior to sampling measured in m^3/s (cumecs).

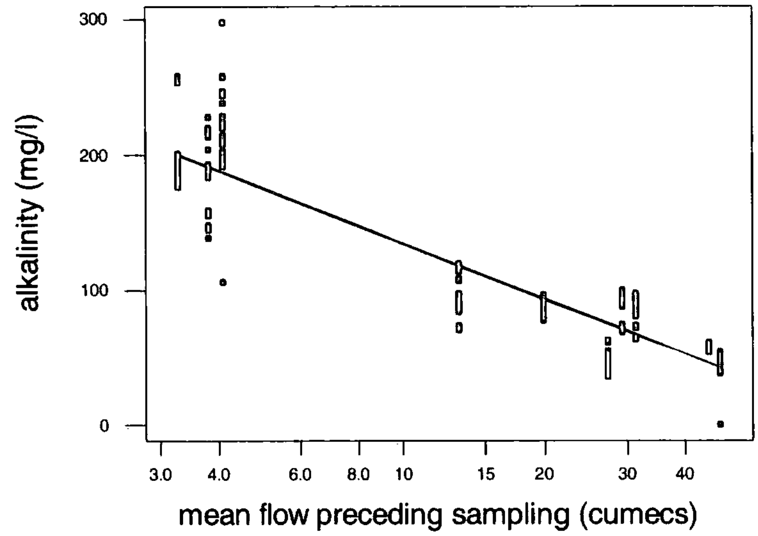


Figure 3.12. The relationship between alkalinity and flow in the Tees, showing the dilution effect with increasing flow (logarithmic scale). P = 0.000, R-Sq = 86.0 %.

3.2.6 Conductivity

Results

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
Flow	66.28	0.000	29886	0.40
Season	1.24	0.267	na	0.00
Distance	7.82	0.000	15616	0.21
Depth	3.76	0.025	2524	0.03
Season*distance	4.57	0.001	8164	0.11
Season*depth	3.86	0.027	2455	0.03
Depth*distance	1.80	0.062	na	0.00
Season*distance*depth	1.72	0.077	na	0.00
Error			16481	0.22

Table 3.5. Results from GLM ANOVA for seasonal effects on conductivity within the Tees impoundment (na = not applicable since factor insignificant ($P>0.05$)).

Using a model containing the factors of season, distance and depth shows that conductivity varies significantly with season and distance. Factoring in flow as a covariate removes any significant effects of season and gives the results shown in table 3.5 and figure 3.13. Flow and distance within the impoundment can explain the majority of variation (ω^2 = 0.40 and 0.21 respectively) in values of conductivity in the Tees. There is also a significant interaction between the distance effect and season (figure 3.14), with a general increase in conductivity values with distance downstream in the impoundment. There is also a small (ω^2 = 0.03) depth effect during the summer period, with higher conductivity values at depth (figure 3.15). Approximately 22 % of the behaviour of conductivity is not explained by terms in the model.

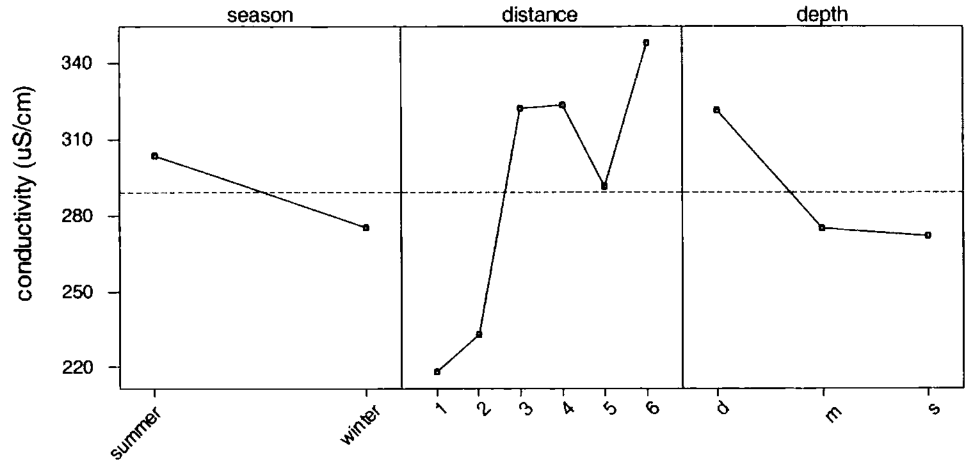


Figure 3.13. Main effects plot for conductivity in the Tees impoundment (least square means for factor levels).

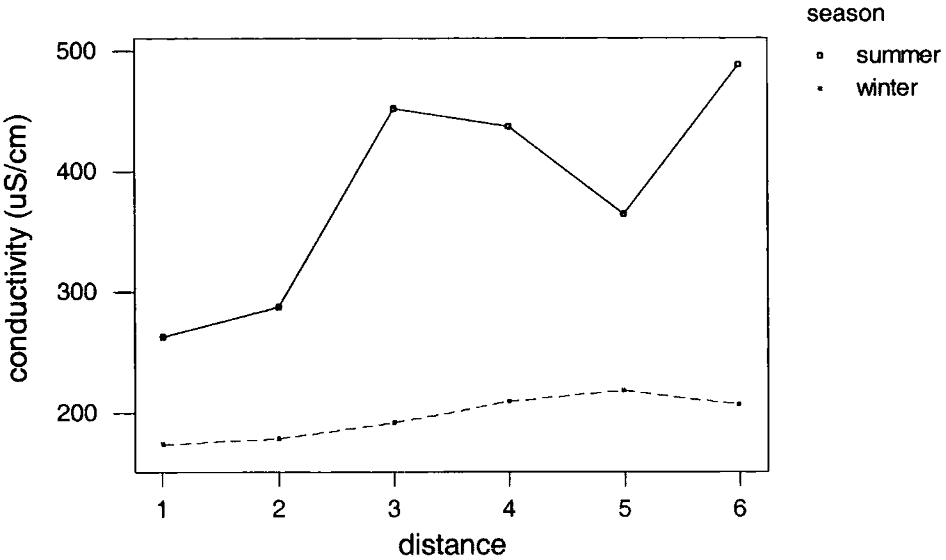


Figure 3.14. Interaction between distance and season effects on conductivity (LS mean) in the Tees impoundment. Summer results as solid line and winter as dashed line.

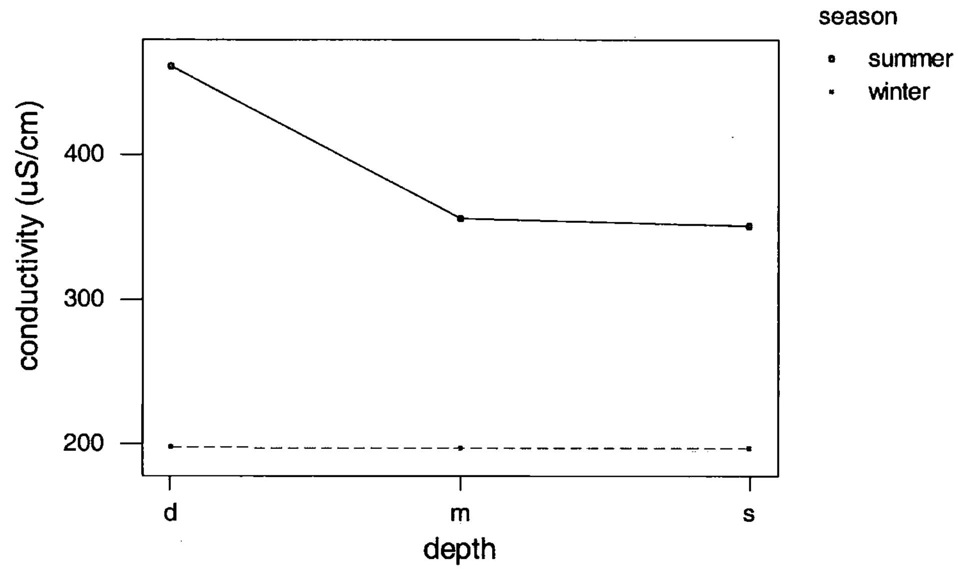


Figure 3.15. Interaction between depth and season effects on conductivity (LS mean) in the Tees impoundment. Summer results as solid line and winter as dashed line.

Discussion

As for alkalinity, conductivity is also controlled by the relative amounts of baseflow and stormflow making up the discharge of the Tees, and therefore shows a dilution effect with increased flow (figure 3.16).

conductivity = 586 - 247 log(Mean24)   (P = 0.000, S = 153.305, R-Sq = 32.9 %)

where conductivity is measured in μS/cm, and Mean 24 is the mean flow during the 24 hours prior to sampling measured in m^3/s (cumecs).

However the relationship is less strong than that for alkalinity due to several other factors showing significant control, particularly during the summer period. Whereas alkalinity is controlled almost wholly by species dissolved from the geologies of the catchment, conductivity is controlled by a variety of species of different sources showing a variety of responses to variations in discharge. For example, as mentioned, the dissolved organic input to the Tees increases with increasing flow.

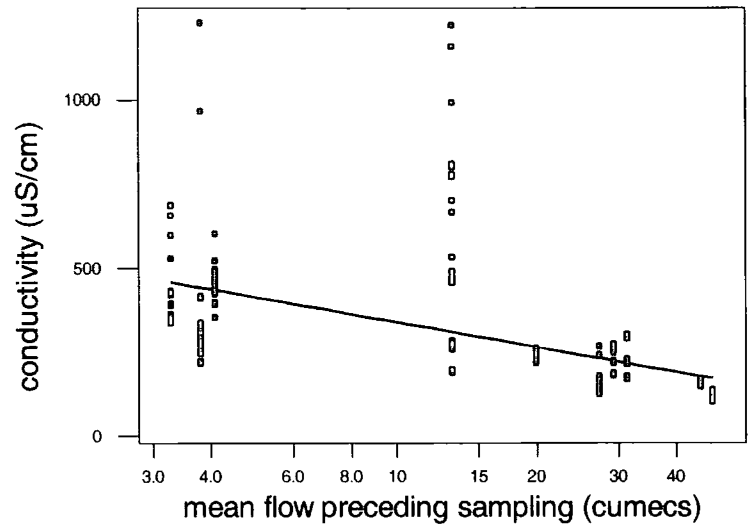


Figure 3.16. The relationship between conductivity and flow in the Tees, showing the dilution effect with increasing flow (logarithmic scale). P = 0.000, R-Sq = 32.9 %.

Additional inputs to conductivity occur with distance downstream in the river (distance effect), and possibly to a small extent from releases from bed sediment (depth effect). As mentioned for major elements below, some of the distance and depth effects on conductivity are due to the intrusion of small amounts of seawater close to the barrage, probably through the navigation lock. It is likely that there is a variable effect dependent on the relative flow of the Leven tributary which enters the Tees between distances 3 and 4 and generally has a higher conductivity (a mean value of 508 μS/cm compared to 293 μS/cm for the Tees), although in general its effects appear to be insignificant. During the winter period when flows are higher and more turbulent, the water body throughout the impounded area is more homogenous, and these "internal" inputs have less impact than during the lower flows of summer.

3.2.7 Transparency

Results

Transparency (as Secchi depth) was measured once at each site on each date sampled on the Tees, hence the ANOVA model run included the factors of season and distance. As mentioned, the amount of colour in the Tees increases with flow, as generally does turbidity in rivers, and so flow (as the mean flow in the 24 hour period prior to sampling) was included as a covariate.

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
Flow	245	0.000	1.4	0.62
Season	73	0.000	0.4	0.18
Distance	16	0.000	0.3	0.15
Season*distance	3	0.024	0.0	0.02
Error			0.05	0.03

Table 3.6. Results for GLM ANOVA for transparency with season within the Tees.

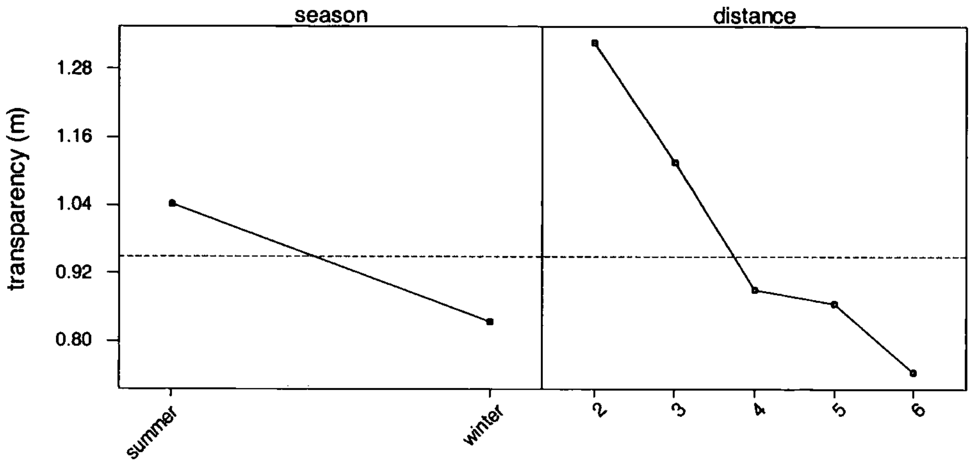


Figure 3.17. Main effects plot for transparency (as Secchi depth) in the Tees impoundment (least square means for factor levels).

The results (table 3.6, figure 3.17) show that transparency varies significantly with flow, season and distance within the impounded area. The majority of the variance in data (62 %) can be related to flow in the river. 18 % of the behaviour is explained by season, and distance accounts for 15 % of the variance. There is very little interaction between the season and distance effects (figure 3.18). Since the depth at site LM (distance 1) was too shallow to allow measurement of Secchi depth, the distance effect on transparency is only tested at 5 distances. The error term is small (3 %), and the terms included are adequate to model the behaviour of transparency in the Tees.

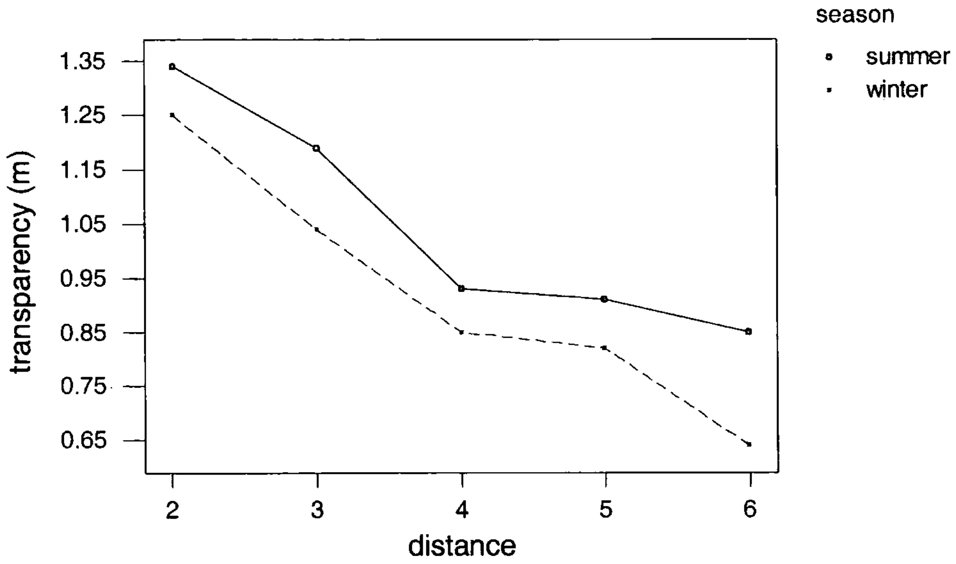


Figure 3.18. Interaction between distance and season effects on transparency (LS mean) in the Tees impoundment. Summer results as solid line and winter as dashed line.

Discussion

The effect of flow on transparency (figure 3.19) is assumed to be a combined effect of increased colour (humic organic compounds) and increased turbidity with increased flow. With the covariance with flow factored out, the seasonal effect is to reduce transparency in winter compared with summer. It is likely that this is an effect of increased turbidity in winter since the colour response to flow events is temperature dependent (Worrall et al., in press), and thus likely to be inversely greater during summer. The likely mechanism giving increased turbidity in winter is greater overland runoff due to greater saturation of the soil of the catchment. It is also possible that lesser vegetation cover of agricultural land also allows greater removal of particulate material in winter. Unfortunately ANOVA could not be run on TSS (suspended solids) data due to rank deficiency (insufficient data) associated with the problems in measurement mentioned previously.

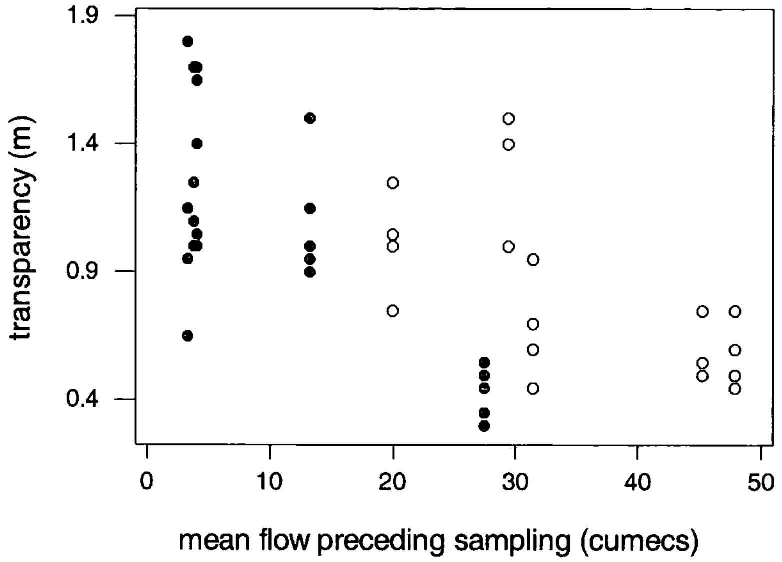


Figure 3.19. The relationship between transparency and flow in the Tees. Summer measurements are indicated by solid circles and winter by open circles. P = 0.000, R-Sq = 35.2 %.

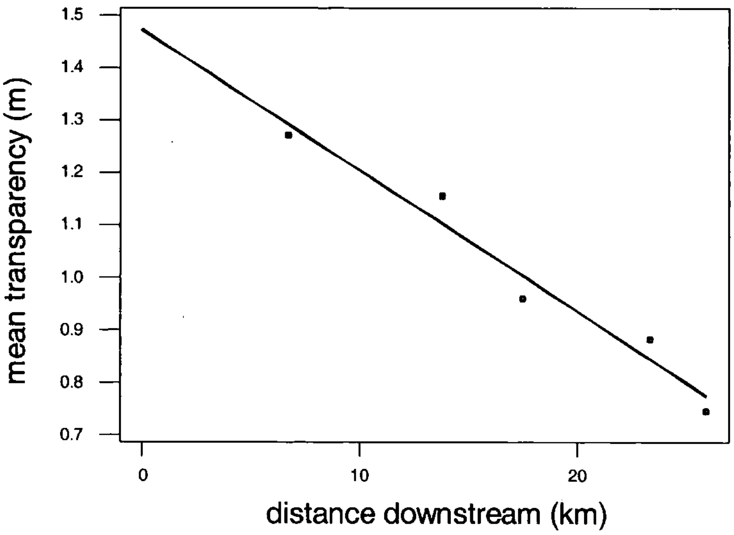


Figure 3.20. The relationship between transparency and distance downstream within the impounded area of the Tees. S = 0.0490, R-Sq(adj) = 94.6 %.

Re-suspension of bed and bank material is proposed as the mechanism by which transparency decreases with distance downstream (figure 3.20). Transparency decreases with distance downstream within the impoundment according to:

transparency = 1.47 - 0.0269 Mean24 (S = 0.0490, R-Sq(adj) = 94.6 %)

where transparency is measured as Secchi disk visibility (m) and Mean24 is the mean flow in the 24 hours preceding sampling measured in cumecs.

The lack of interaction between distance and season implies that biological productivity in the water column (assumed to be seasonal) does not impact significantly on transparencies.

3.2.8 Nutrients

3.2.8.1 Nitrate

Results

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
Flow	217.86	0.000	4.32	0.45
Season	213.72	0.000	4.24	0.44
Distance	1.78	0.119	na	0.00
Depth	0.56	0.571	na	0.00
Season*distance	3.84	0.002	0.28	0.03
Season*depth	0.74	0.479	na	0.00
Depth*distance	0.25	0.991	na	0.00
Season*distance*depth	0.41	0.940	na	0.00
Error			0.72	0.08

Table 3.7. Results from GLM ANOVA for seasonal effects on nitrate within the Tees impoundment (na = not applicable since factor insignificant (P>0.05)).

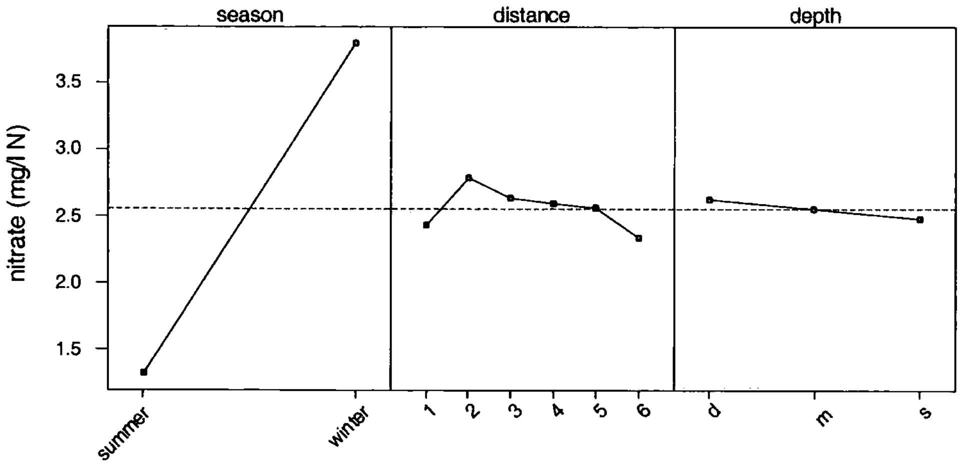


Figure 3.21. Main effects plot for nitrate in the Tees impoundment (least square means for factor levels).

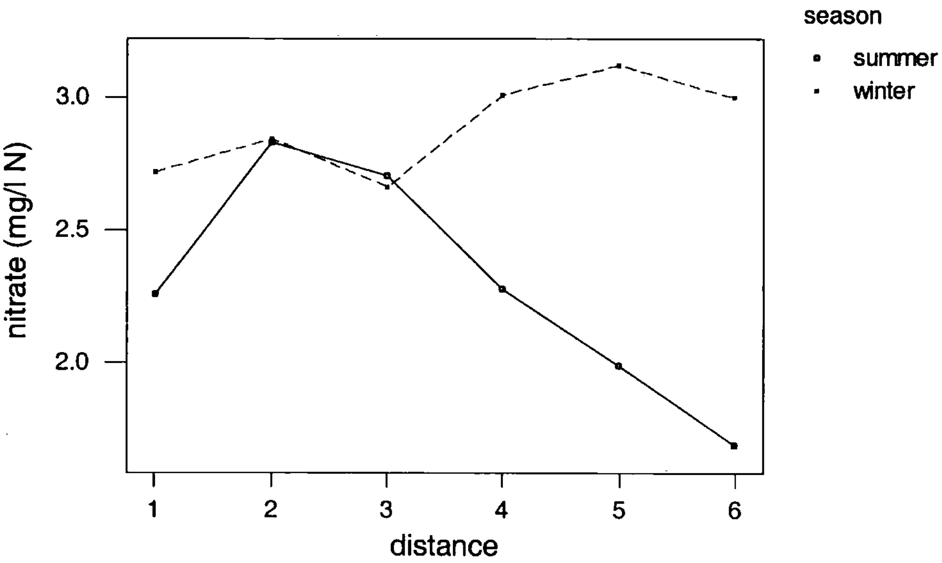


Figure 3.22. Interaction between distance and season effects on nitrate (LS mean) in the Tees impoundment. Summer results as solid line and winter as dashed line.

The majority of variance (≅ 89 %) values for nitrate in the Tees impoundment during the periods studied can be explained by flow (≅ 45 %) and by season (≅ 44 %) (table 3.7). Nitrate levels are significantly (P = 0.000) higher in winter than in summer (figure 3.21). There is a significant interaction between season and distance, with contrasting patterns of behaviour for the 2 seasons studied (figure 3.22) (hence distance on its own is not a significant factor), although the size of the effect is small (≅ 3 %). Nitrate does not vary significantly with depth in the Tees. The error term in the model is relatively small (≅ 8 %).

Discussion

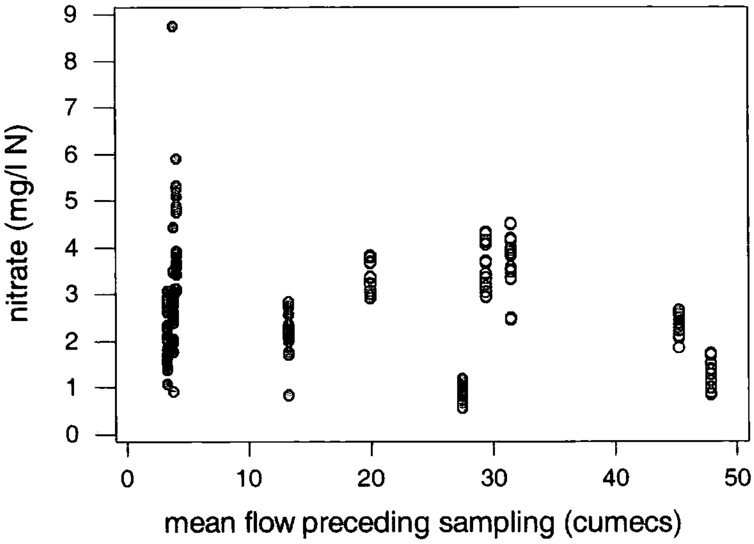


Figure 3.23. The relationship between nitrate and flow in the Tees. Summer measurements are indicated by solid circles and winter by open circles. P = 0.001, R-Sq = 3.8 %.

The increased levels of nitrate experienced in winter are assumed to relate to greater removal of nitrate from soil due to higher saturation and hence subsurface flow (Heathwaite and Johnes 1996), plus a greater amount of nitrate available in soil due to a lack of vegetation on ploughed land of the catchment and lower vegetation growth rates elsewhere. Nitrate tends to decrease with increasing flow both in summer and in winter (figure 3.23). Jarvie et al. (1998) suggest that a negative relationship between nitrate and flow occurs in urban and industrial rivers in which point sources of N dominate, and which undergo dilution with increased flow. It seems logical to suggest therefore that nitrate sources in the Tees are both diffuse (and seasonally controlled) and point (and flow controlled). The limited number of dates and flow conditions sampled however mean that more work needs to be done to confirm the sources and behaviour of nitrate in the system.

The small distance*season interaction in the model is interpreted as being due to greater assimilation of nitrate by organisms during the summer period leading to a decrease in nitrate levels on progression downstream within the less turbulent sections of the river. During winter, due to lower temperatures and insolation and P limitation, the biological impact on nitrate levels is insignificant relative to inputs to the system with distance downstream.

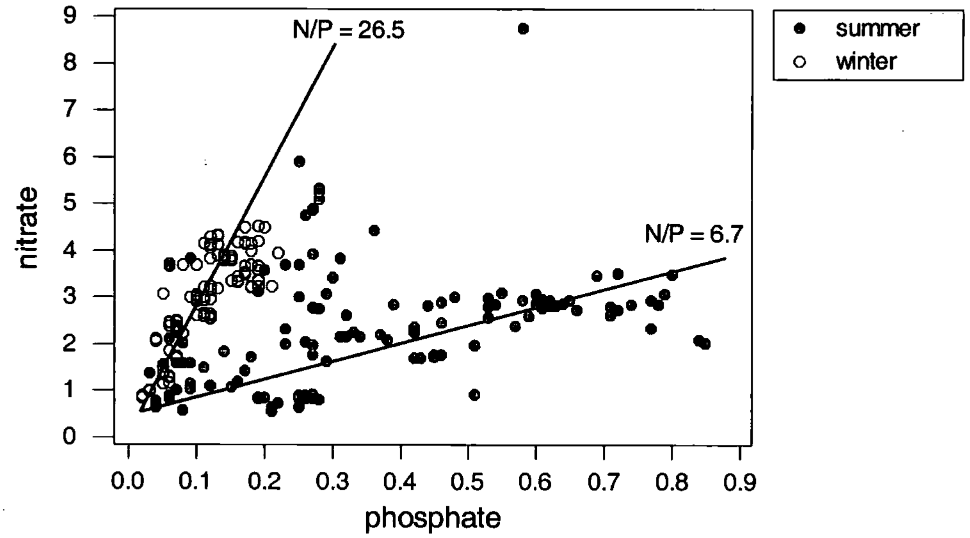


Figure 3.24. N/P in the Tees impoundment during the periods sampled showing the difference in nutrient limitation between winter and summer.

It is worth noting also that there is a distinct difference in the nutrient limitation in terms of the 'Redfield ratio' for limitation of biological primary production by either N (bioavailable nitrogen) or by P (bioavailable P) between winter and summer in the Tees. Stoichiometrically a ratio of N/P greater than 16 means that growth in a water body is limited by P, and a ratio of less than 16 means that the system is limited by N. By mass this ratio is 7.3 (Jarvie et al. 1998). Assuming that the Redfield ratio (which was developed for marine phytoplankton) can be applied to the freshwater Tees, and that total bioavailable N and total bioavailable P can be represented by nitrate and orthophosphate, respectively (Reynolds and Davies 2001), then in winter the river is generally phosphate limited (ratio of the mean values from the winter season = 26.5 by mass) and in summer it is nitrate limited (ratio of the mean values from the summer season = 6.7) (figure 3.24). It is difficult to say to what extent this change in the N/P ratio is due to a change in inputs to the river or to variation in growth rates (higher during summer) of algae, etc. with season. That the scatter of N/P values tends to be higher under low flow conditions in summer (figure 3.24) during which biological production is likely to be at its highest (as opposed to much less variable N/P ratios during winter) suggest that growth rates are significant.

3.2.8.2 Ammonia

Results

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
Season	5.75	0.017	0.002	0.07
Distance	3.69	0.003	0.004	0.20
Depth	3.27	0.040	0.001	0.07
Season*distance	2.63	0.025	0.003	0.12
Season*depth	2.68	0.071		0.00
Depth*distance	1.32	0.222		0.00
Season*distance*depth	0.77	0.653		0.00
Error			0.012	0.54

Table 3.8. Results from GLM ANOVA for seasonal effects on ammonia within the Tees impoundment (na = not applicable since factor insignificant (P>0.05)).

Using a model containing the terms of season, distance and depth plus their interactions can account for less than half of the variance in ammonia values observed in the Tees impoundment (ω^2 for error of 0.54, table 3.8). To attempt to explain more of the variance in ammonia behaviour the same model was applied with the inclusion in turn of the covariates of flow, temperature and dissolved oxygen concentration. Flow and temperature proved to have an insignificant effect on ammonia levels, but DO % was found to remove the effects of all terms in the model except for season. The data were reanalysed with only season as a factor level, and DO % as a covariate was able to account for over 90 % of the behaviour of ammonia observed (table 3.9).

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
DO %	110.50	0.000	0.50	0.91
Season	10.38	0.001	0.04	0.08
Error			0.01	0.02

Table 3.9. Results from GLM ANOVA for seasonal effects on ammonia within the Tees impoundment with the inclusion of DO % as a covariate.

There is also a significant difference between levels of ammonia between seasons, with winter levels of ammonia generally slightly higher than summer levels (figure 3.25).

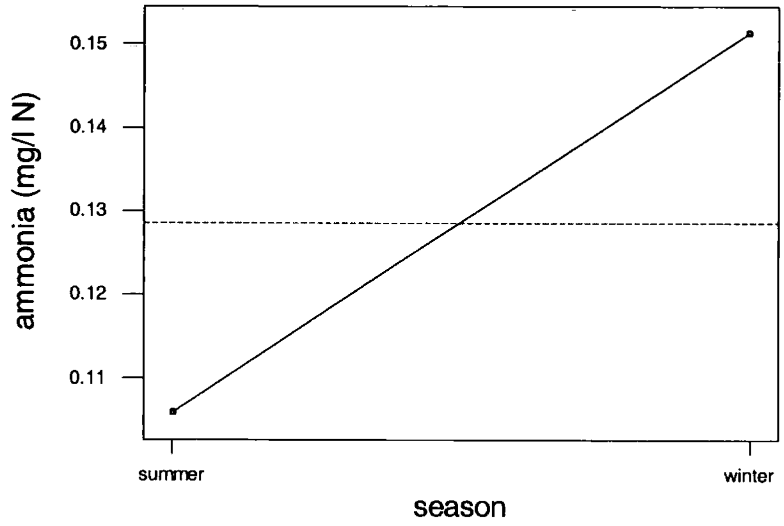


Figure 3.25. Main effects plot for ammonia by season in the Tees impoundment (least square means for factor levels), with the inclusion of DO % as a covariate.

Discussion

Relative to the effect of DO levels on ammonia in the Tees, the effects of flow, distance and depth within the impoundment are insignificant, and the impact of season is minor. The small ($\omega^2 = 0.08$) seasonal difference giving greater ammonia levels in winter are interpreted as due to greater removal (possible adsorbed onto particulates) from the catchment during the period of minimum crop cover (Heathwaite et al. 1989, Heathwaite and Johnes 1996).

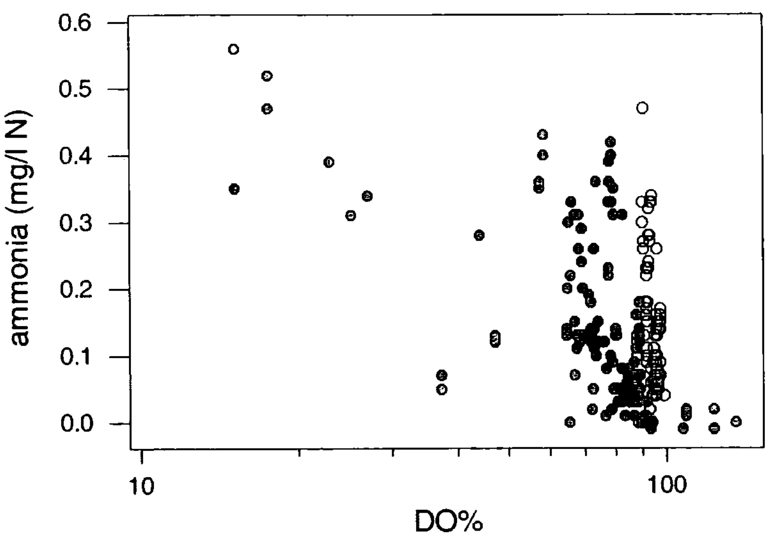


Figure 3.26. The relationship between ammonia and DO % levels (logarithmic scale) in the Tees impoundment, showing ammonification under low DO conditions. Summer measurements are indicated by solid circles and winter by open circles.

The major influence on ammonia levels in the water of the Tees impoundment is the amount of DO dissolved in the water (figure 3.26). DO % is in turn controlled by the factors of season, distance and depth described above (low DO % and high ammonia points on figure 3.26 are from sites 5 and 6 from a range of summer sampling dates). Ammonia is generated as the primary end product of the breakdown of organic material. Under low oxygen conditions the process of nitrification ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$), which normally acts to convert ammonia to nitrate, ceases and allows ammonia levels to build up. In addition the loss of an oxidised layer at the upper surface of the sediments interfacing with the water column decreases the particulate adsorptive capacity and release of ammonia may occur (Kamiyama et al. 1977).

3.2.8.3 Phosphate

Results

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
Season	142.82	0.000	0.09	0.65
Distance	6.21	0.000	0.02	0.12
Depth	0.04	0.965	na	0.00
Season*distance	3.60	0.004	0.01	0.06
Season*depth	0.03	0.973	na	0.00
Depth*distance	0.23	0.993	na	0.00
Season*distance*depth	0.18	0.998	na	0.00
Error			0.02	0.17

Table 3.10. Results from GLM ANOVA for seasonal effects on phosphate within the Tees impoundment (na = not applicable since factor insignificant (P>0.05)).

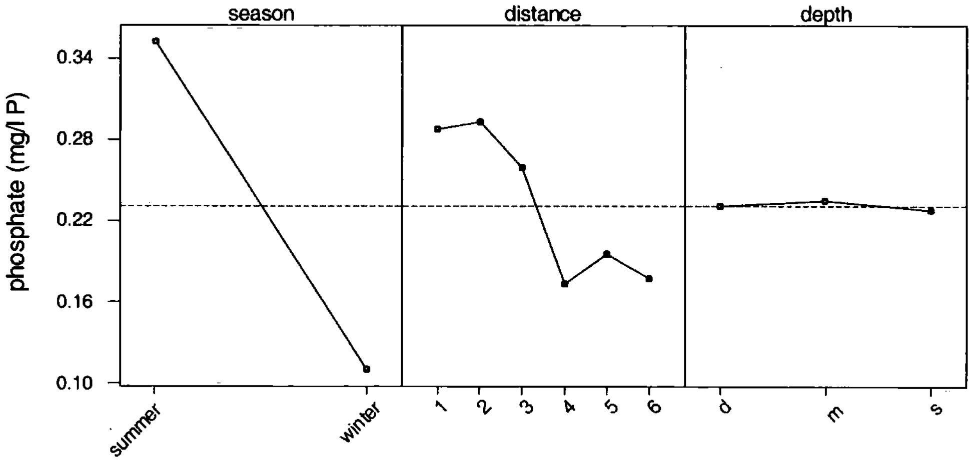


Figure 3.27. Main effects plot for phosphate in the Tees impoundment (least square means for factor levels).

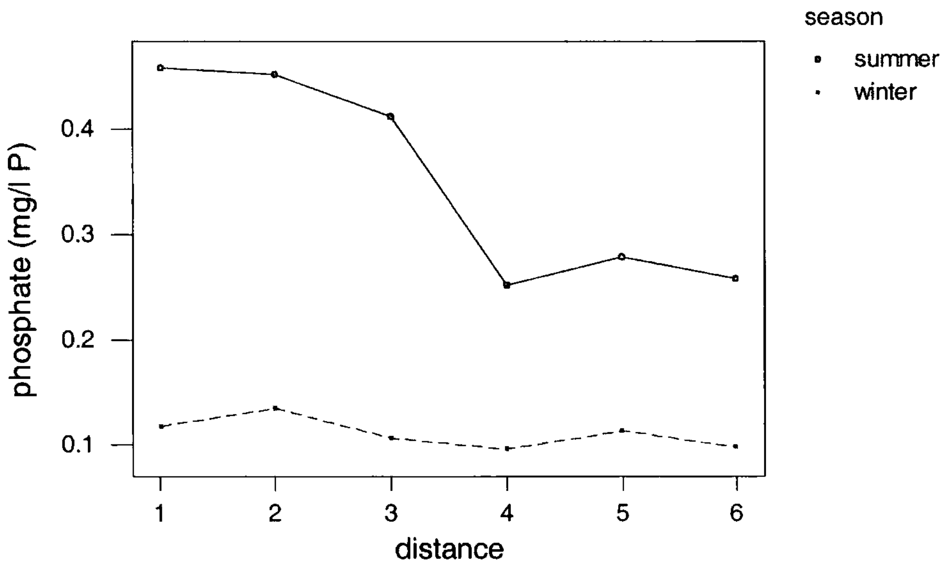


Figure 3.28. Interaction between distance and season effects on phosphate (LS mean) in the Tees impoundment. Summer results as solid line and winter as dashed line.

The results (table 3.10, figure 3.27) show that there is a distinct difference between phosphate levels in the Tees between summer and winter, which accounts for approximately 65 % of the variance of the dataset, with phosphate levels generally higher in summer than in winter. Phosphate also varies with distance, with decreasing values with distance downstream within the impounded area particularly during the summer season (figure 3.28).

Discussion

The higher levels of phosphate observed in summer than in winter are interpreted as due to point sources dominating dissolved orthophosphate (a.k.a. SRP, see Heathwaite and Johnes 1996, Jarvie et al. 1998 or Reynolds and Davies 2001 for discussion of P speciation and bioavailability) inputs to the system which undergo dilution under higher winter flows (figure 3.29). Diffuse sources of dissolved P (due to fertiliser application) are likely to be minimal due to strong adsorption to particulate material (Neal et al. 1996b). Adsorption to particulates drastically reduces the bioavailability of P (Reynolds and Davies 2001).

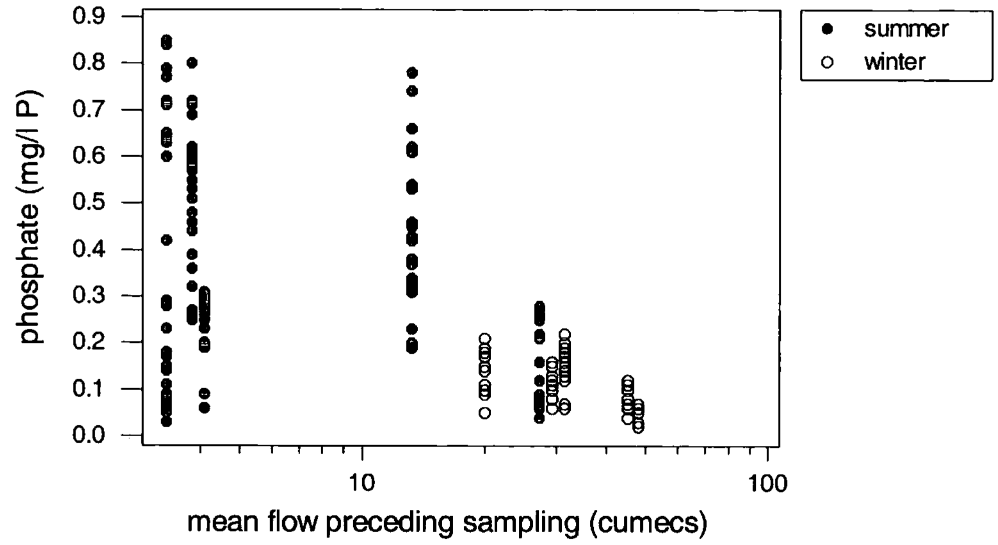


Figure 3.29. The relationship between phosphate and flow in the Tees. P = 0.000, R-Sq = 43.2 %.

There is a distinct decrease in levels of phosphate with progression downstream in the impoundment during the summer season, and a minor decrease during the winter season. The difference in behaviour between the seasons implies that this is likely to be due to utilisation in primary production in the water column (conversion from dissolved P to particulate organic P) with progression downstream to the less turbulent sections of the river. This assumption could be tested in future work including determinations of chlorophyll *a*. That phosphate levels do not generally decrease to zero during the growing season confirms that growth tends not to be phosphate limited in the impounded area of the Tees.

3.2.8.4 Silica

Results

Silica variation is explained to a large (ω^2 = 0.78) extent by season in the Tees (table 3.11, figure 3.30), with levels generally being higher in winter than in summer (the inverse of the situation for phosphate). Silica values also increase significantly with distance downstream within the impounded section, and this effect does not show any significant difference (P = 0.325 for season*distance interaction) between winter and summer. Introducing flow as a covariate to the model (P = 0.000) shows part of the seasonal effect being due to the general difference in flow between the seasons, but season remains a significant factor and the size of the error term is not reduced.

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
Season	153.46	0.000	0.45	0.78
Distance	2.41	0.037	0.02	0.04
Depth	1.52	0.222	na	0.00
Season*distance	1.17	0.325	na	0.00
Season*depth	2.27	0.106	na	0.00
Depth*distance	0.68	0.741	na	0.00
Season*distance*depth	0.57	0.839	na	0.00
Error			0.11	0.18

Table 3.11. Results from GLM ANOVA for seasonal effects on silica within the Tees impoundment (na = not applicable since factor insignificant (P>0.05)).

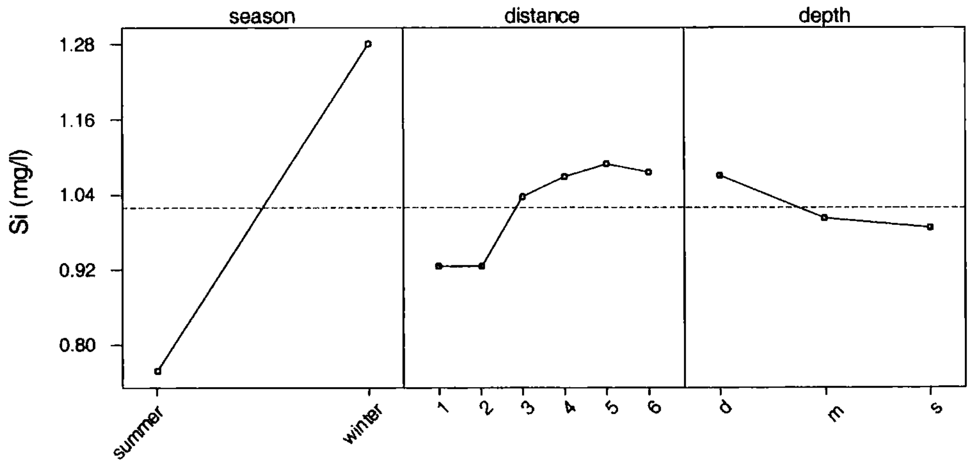


Figure 3.30. Main effects plot for silica in the Tees impoundment (least square means for factor levels).

Discussion

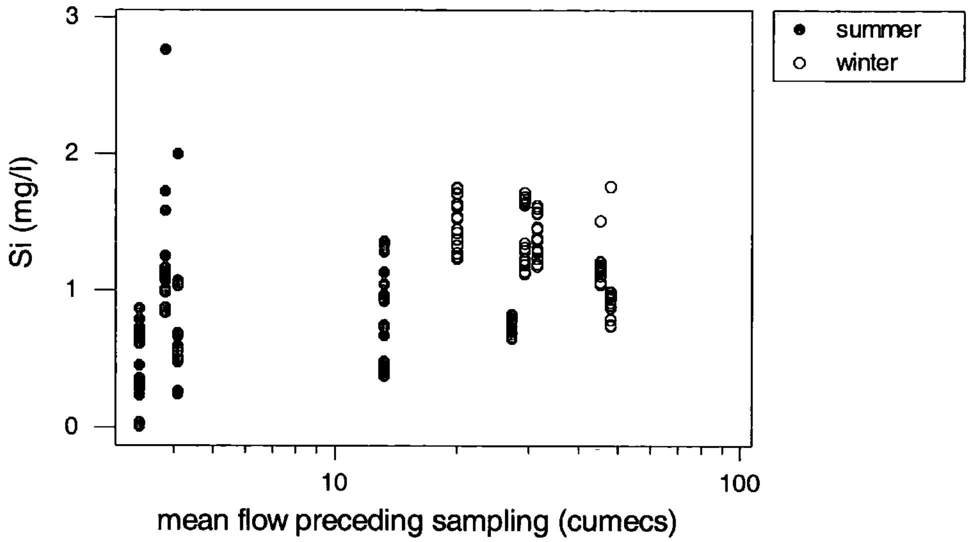


Figure 3.31. The relationship between silica and flow in the Tees (logarithmic scale for flow). P = 0.000, R-Sq = 17.6 %.

The increase in Si levels with flow (figure 3.31) is likely to be due to a diffuse catchment source for the element, with levels in baseflow lower than in surface and shallow runoff (stormflow), contrasting with for example alkalinity or Ca which show dilution with increased stormflow. There is an additional difference between summer and winter Si levels. The generally higher values in winter are interpreted as due to greater removal of Si from soils in the catchment due to lack of vegetation and generally higher levels of soil saturation. This near surface diffuse source for Si is also suggested by the increase in levels of Si with distance downstream in the river during both summer and winter. The lack of difference between the distance effects between the seasons suggests that, at least during the periods sampled, biological mediation of Si levels is insignificant (either because levels are far in excess of those required or because diatoms form a minor part of the biota during these periods (Pinder et al. (1997a) found diatom growth rates to be highest in the River Great Ouse, southeast UK, to be greatest during April)).

3.2.9 Major elements

Results

The behaviour of the major elements (Ca, Na, Mg, K and S) in the Tees was examined using an ANOVA model containing season, and distance and depth within the impoundment (and interactions between these factors), together with flow as a covariate (since assuming that rock weathering is the source of the major elements (Chapman 1996) then values are likely to be lower under high flow conditions when groundwater flow is diluted). The results are as follows:

Ca

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
Flow	357.96	0.000	361.10	0.77
Season	59.33	0.000	59.01	0.13
Distance	3.17	0.009	10.95	0.02
Depth	0.92	0.402	na	0.00
Season*distance	0.93	0.460	na	0.00
Season*depth	1.08	0.340	na	0.00
Depth*distance	0.61	0.806	na	0.00
Season*distance*depth	0.50	0.889	na	0.00
Error			36.42	0.08

Table 3.12. Results from GLM ANOVA for seasonal effects on Ca within the Tees impoundment (na = not applicable since factor insignificant (P>0.05)).

The majority of variation in Ca (77 %) is explained by variation in flow during the periods sampled on the Tees. Season also shows a significant effect (at >99 % level), with approximately 13 % of the variance being explained by reduced summer values of Ca (table 3.12, figure 3.32). There is a minor increase in Ca values with distance downstream in the impounded area, but depth is not a significant factor.

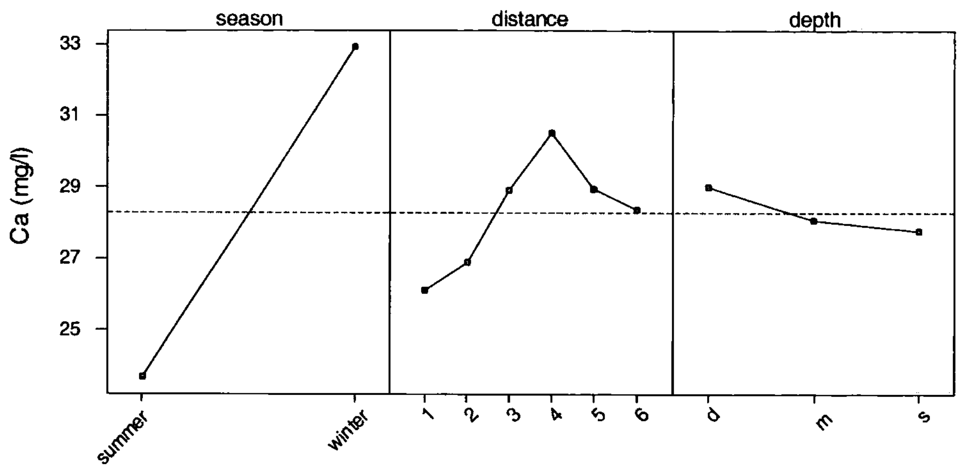


Figure 3.32. Main effects plot for Ca in the Tees impoundment (least square means for factor levels).

Na

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
Flow	20.57	0.000	193.81	0.16
Season	0.56	0.455	na	0.00
Distance	8.03	0.000	348.08	0.29
Depth	3.47	0.033	48.88	0.04
Season*distance	4.77	0.000	186.86	0.16
Season*depth	3.57	0.030	50.84	0.04
Depth*distance	1.59	0.109	na	0.00
Season*distance*depth	1.65	0.095	na	0.00
Error			356.50	0.30

Table 3.13. Results from GLM ANOVA for seasonal effects on Na within the Tees impoundment (na = not applicable since factor insignificant (P>0.05)).

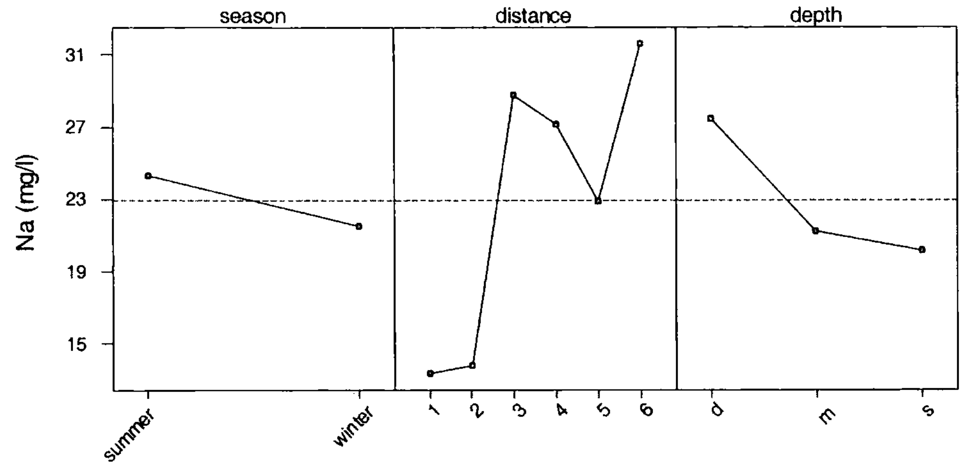


Figure 3.33. Main effects plot for Na in the Tees impoundment (least square means for factor levels).

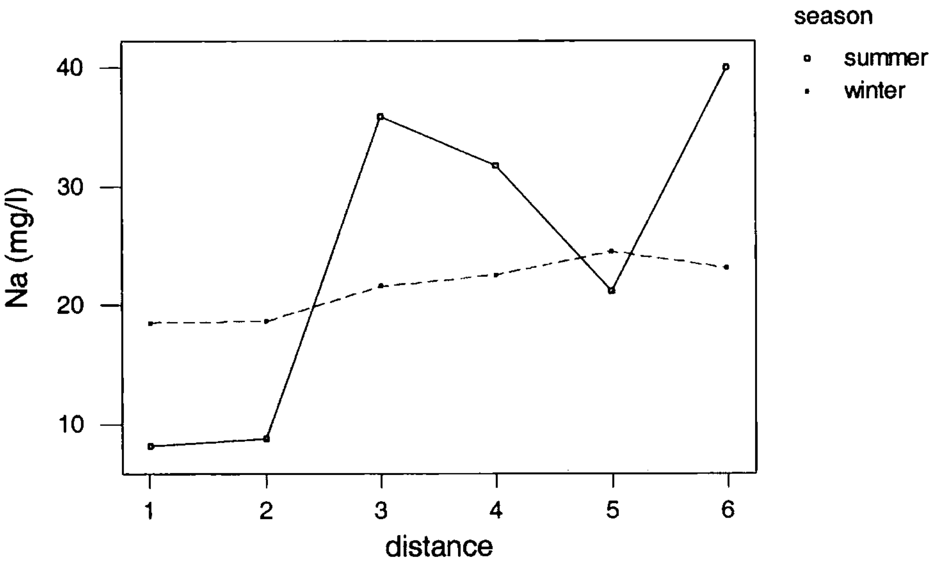


Figure 3.34. Interaction between distance and season effects on Na (LS mean) in the Tees impoundment. Summer results as solid line and winter as dashed line.

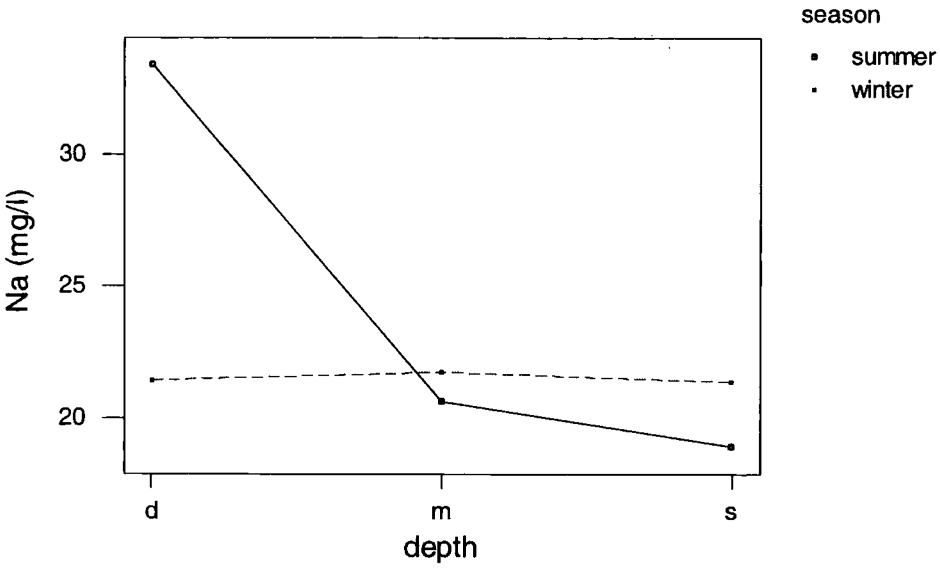


Figure 3.35. Interaction between depth and season effects on Na (LS mean) in the Tees impoundment. Summer results as solid line and winter as dashed line.

Flow is also a significant factor in controlling Na values in the Tees, although the size of effect is smaller than for Ca (table 3.13, figure 3.33). Distance explains a greater portion of the variance in Na levels ($\omega^2 = 0.29$ as opposed to 0.02), with levels increasing during both summer and winter, although to a greater extent during summer (distance*season interaction $\omega^2 = 0.16$, figure 3.34). Na levels also increase slightly with depth, but this effect is only significant during the summer season (figure 3.35). A relatively large proportion of the variance in Na levels (approximately 30 %) cannot be explained by the terms in the model.

Mg

The behaviour of Mg is very similar to that of Ca in the Tees, although with a slightly smaller effect of season, a slightly larger effect of distance (figure 3.36), and a larger error term ($\omega^2 = 0.18$ compared to 0.08, table 3.14).

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
Flow	136.25	0.000	20.11	0.69
Season	12.48	0.000	1.71	0.06
Distance	3.57	0.004	1.91	0.07
Depth	2.51	0.084	na	0.00
Season*distance	0.98	0.432	na	0.00
Season*depth	3.01	0.051	na	0.00
Depth*distance	1.24	0.264	na	0.00
Season*distance*depth	1.58	0.112	na	0.00
Error			5.35	0.18

Table 3.14. Results from GLM ANOVA for seasonal effects on Mg within the Tees impoundment (na = not applicable since factor insignificant (P>0.05)).

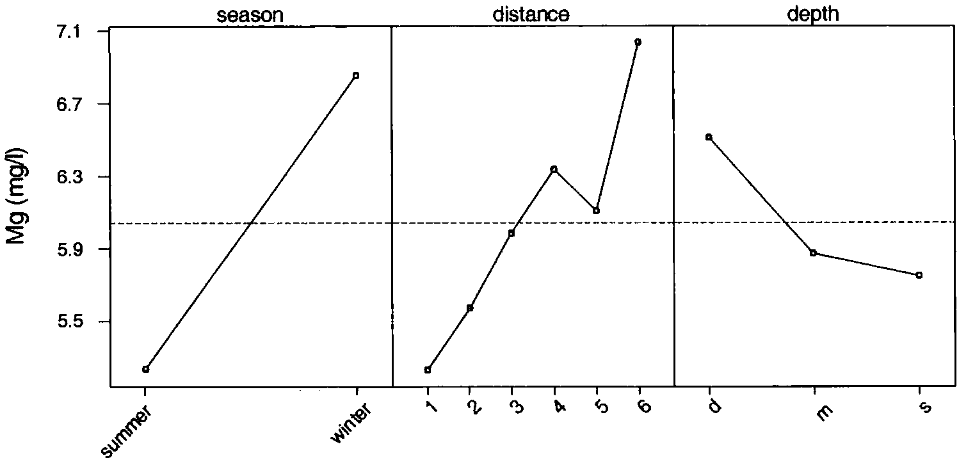


Figure 3.36. Main effects plot for Mg in the Tees impoundment (least square means for factor levels).

K

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
Flow	59.99	0.000	1.40	0.26
Season	117.98	0.000	2.77	0.51
Distance	3.21	0.008	0.26	0.05
Depth	3.98	0.020	0.14	0.03
Season*distance	0.58	0.713	na	0.00
Season*depth	2.29	0.104	na	0.00
Depth*distance	0.88	0.553	na	0.00
Season*distance*depth	1.33	0.215	na	0.00
Error			0.85	0.16

Table 3.15. Results from GLM ANOVA for seasonal effects on K within the Tees impoundment (na = not applicable since factor insignificant (P>0.05)).

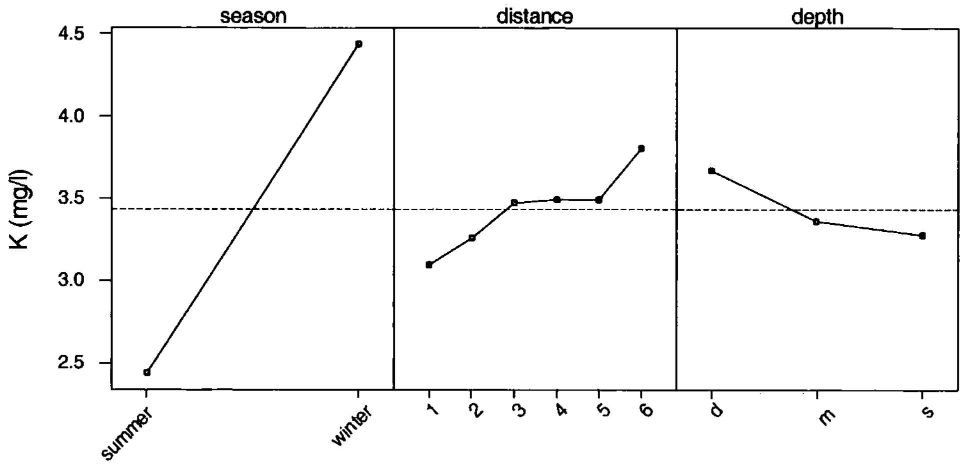


Figure 3.37. Main effects plot for K in the Tees impoundment (least square means for factor levels).

K is the least abundant of the major elements in the Tees (mean value = 3.48 mg/l). The largest effect is season which accounts for over 50 % of the variance observed. As for Ca and Mg, K is significantly higher in winter than in summer. Flow is a less significant control than season ($\omega^2 = 0.26$). There is a slight increase in K values with distance and depth within the impoundment (figure 3.37).

S

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
Flow	16.25	0.000	61.21	0.11
Season	15.23	0.000	57.11	0.10
Distance	10.39	0.000	188.56	0.34
Depth	1.67	0.191	na	0.00
Season*distance	6.05	0.000	101.29	0.18
Season*depth	1.70	0.184	na	0.00
Depth*distance	0.57	0.834	na	0.00
Season*distance*depth	0.58	0.834	na	0.00
Error			144.50	0.26

Table 3.16. Results from GLM ANOVA for seasonal effects on S within the Tees impoundment (na = not applicable since factor insignificant ($P>0.05$)).

S behaviour is similar to that for Na. The distance effect is the main factor in the model, with S values increasing with distance downstream, again more so during summer (figure 3.38). Conversely to Ca, Mg and K, the effect of season is to lower S values in winter (figure 3.39). As for Na, the error term in the model is relatively large (table 3.16).

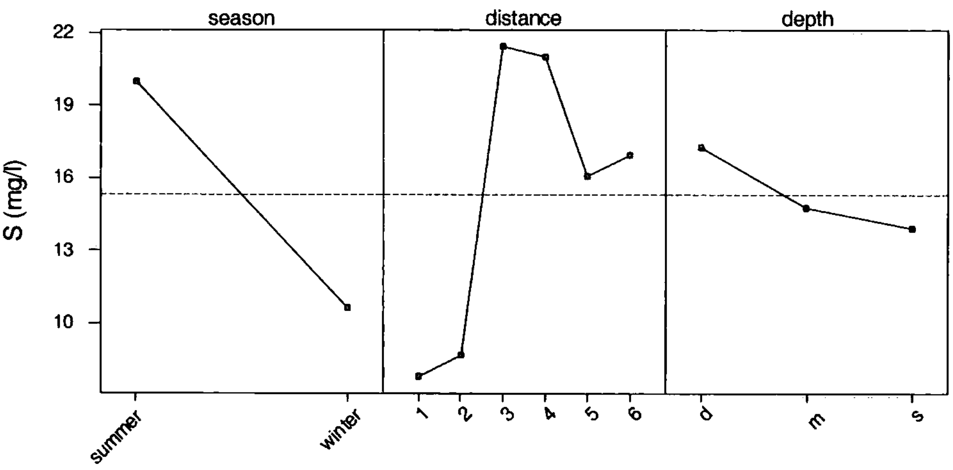


Figure 3.38. Main effects plot for S in the Tees impoundment (least square means for factor levels).

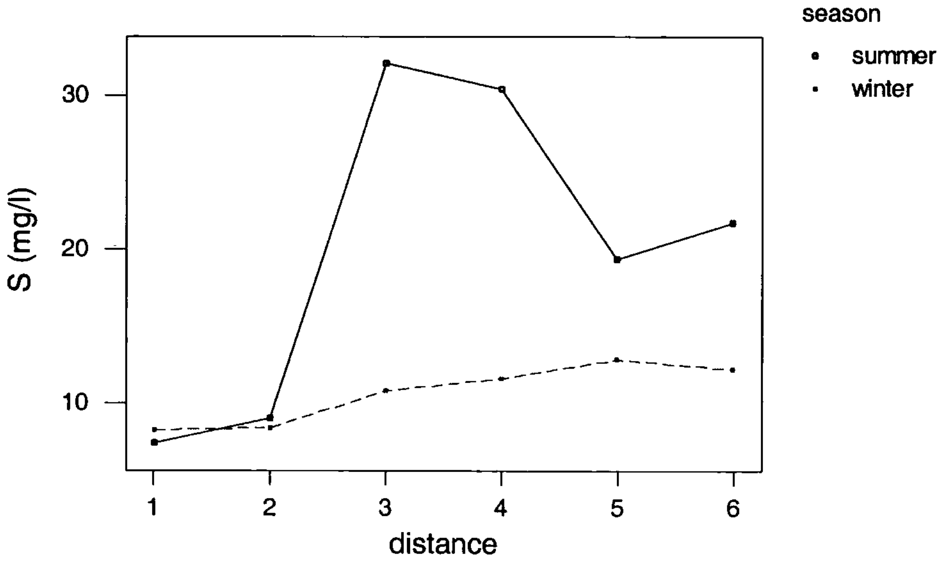


Figure 3.39. Interaction between distance and season effects on S (LS mean) in the Tees impoundment. Summer results as solid line and winter as dashed line.

Discussion

The behaviour of the major elements in the Tees shows a variety of controls including river flow (discharge), season, distance and depth. The behaviour of the individual elements differs, as might be expected given that their relationships between one another are not perfectly linear (figure 3.40).

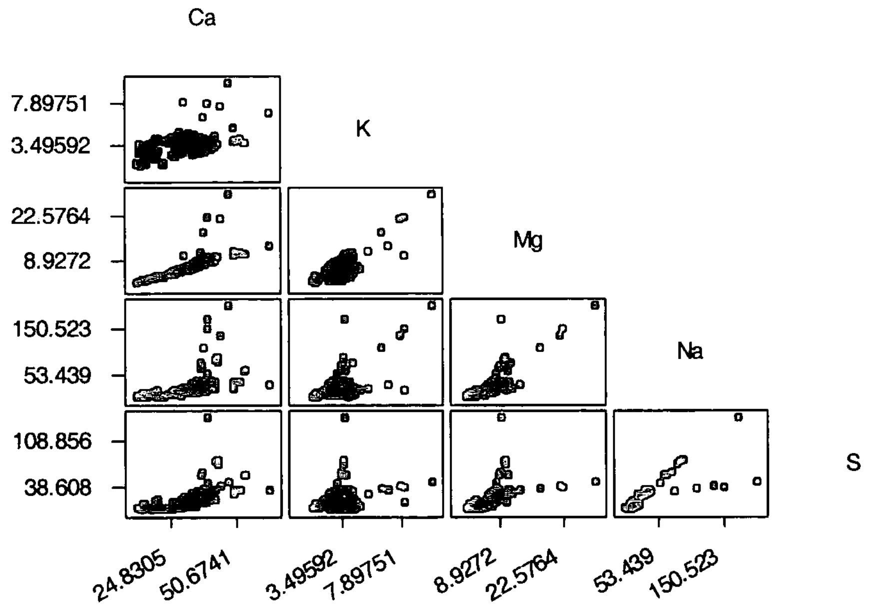


Figure 3.40. The relationships between the major elements in the Tees during the sampling periods. Values in mg/l.

The effect of flow, which is significant for all the major elements, is to give decreased concentrations with increasing river discharges (figure 3.41). For example for Ca, which shows the strongest flow effect, the relationship is:

Ca = 40 - 0.488 Mean24 (P = 0.000, S = 6.30424, R-Sq = 59.8 %)

where,

Ca = concentration of Ca in the river (mg/l), and

Mean24 = the mean flow in the 24 hour period preceding sampling.

This implies that groundwater supplies a large proportion of the major elements, via dissolution from the geologies, to the Tees. As discharge increases following rainfall, the contribution of groundwater or base flow to the river relative to surface runoff or stormflow decreases. When groundwater levels are higher, baseflows in the river are higher, and so for the same level of (summer) discharge the values for the major elements encountered in winter are likely to be higher. Neal et al. (2000) suggest that agricultural disturbance of land increases the amount of weathering at the surface, and the increase in ploughed area in winter may also impact to give reduced dilution effects.

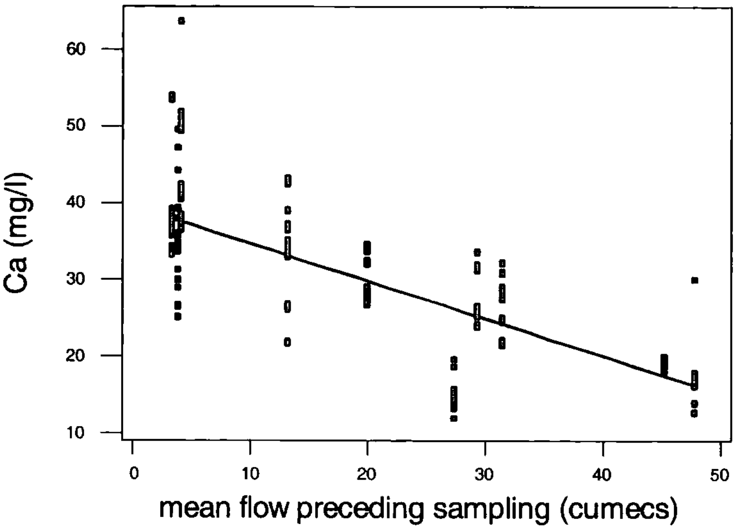


Figure 3.41. The relationship between Ca and flow on the Tees, showing dilution as the relative amount of baseflow decreases. P = 0.000, R-Sq = 59.8 %.

There is also a general increase in concentrations with distance downstream in Tees, which is also likely to relate to the relative amounts of baseflow and stormflow in the water body. Water is likely to enter the river from groundwater throughout its course, but the majority of overland flow for the Tees enters the river in the upland catchment above the section surveyed, thus there is an increase in baseflow to stormflow component with distance.

The impact of the River Leven entering the Tees between distances 3 and 4 (sites AL and PH) is seen normally to be minimal. The concentration of major elements is approximately twice as high in the Leven (a lowland river) than the Tees (table 3.17), although the discharge is generally much smaller than that in the Tees. However on the 8th September 1999 the relative and absolute levels of Na and S in the Leven are much greater (151 and 129 mg/l respectively) for unknown reasons, and the values in the Tees immediately upstream and downstream of the confluence are affected.

Major element	**Leven**	**Tees**
Ca	55	28
K	4.6	3.5
Mg	13	6.2
Na	36	23
S	30	15

Table 3.17. Mean concentration of the major elements (in mg/l) for the water quality surveys for the River Tees and its tributary the River Leven.

The third impact on levels of major element concentrations in the Tees impoundment appears to be the incursion of small amounts of seawater close to the barrage (at the downstream limit of the section surveyed) during the summer period (or specifically on the dates of 25th August and 8th September 1999). The Tees barrage height is above the level of the highest tide encountered and thus no tides overtop the barrage, and although the upstream (freshwater) section is linked to the downstream (tidal) section by a navigation lock the design does not allow seawater incursion. It is therefore assumed that small amounts of seawater were able to enter the impoundment via groundwater during this period. The large difference in ionic composition and strength of seawater means that small amounts can totally dominate the composition of the mixed water.

The effects of this are seen in the depth effects for Na, K and S described above, and in the relatively high error terms within the model.

The major element concentrations in the Tees impoundment are in summary controlled by (figure 3.42):

- the relative proportions of baseflow to stormflow making up the discharge,
- the relative discharge and composition of the Leven tributary, or
- the amount of incursion of brackish or saline water from downstream of the barrage.

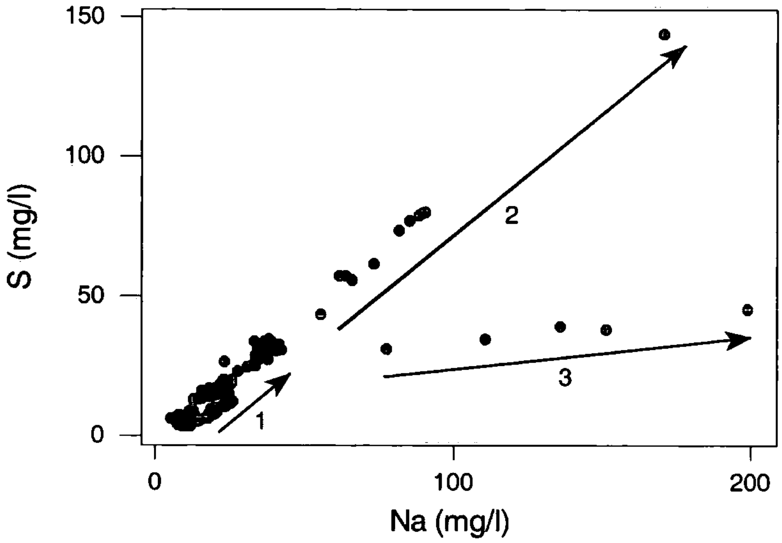


Figure 3.42. The relationship between S and Na in the Tees impoundment showing the mixing of water sources in the system. Line 1 represents the effects of flow on concentration (flow decreasing in direction of arrow) in the Tees, line 2 represents the mixing of Leven water of higher ionic strength but similar S/Na ratio with the water from 1, and line 3 represents the mixing of seawater (of higher ionic strength and different ionic composition) with the water from 1.

3.2.10 Fe and Mn

Results

Fe

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
Flow	212.19	0.000	0.027	0.49
Season	187.25	0.000	0.024	0.43
Distance	0.96	0.441	na	0.00
Depth	0.18	0.834	na	0.00
Season*distance	0.89	0.487	na	0.00
Season*depth	0.13	0.874	na	0.00
Depth*distance	0.30	0.982	na	0.00
Season*distance*depth	0.27	0.987	na	0.00
Error			0.005	0.08

Table 3.18. Results from GLM ANOVA for seasonal effects on Fe within the Tees impoundment (na = not applicable since factor insignificant (P>0.05)).

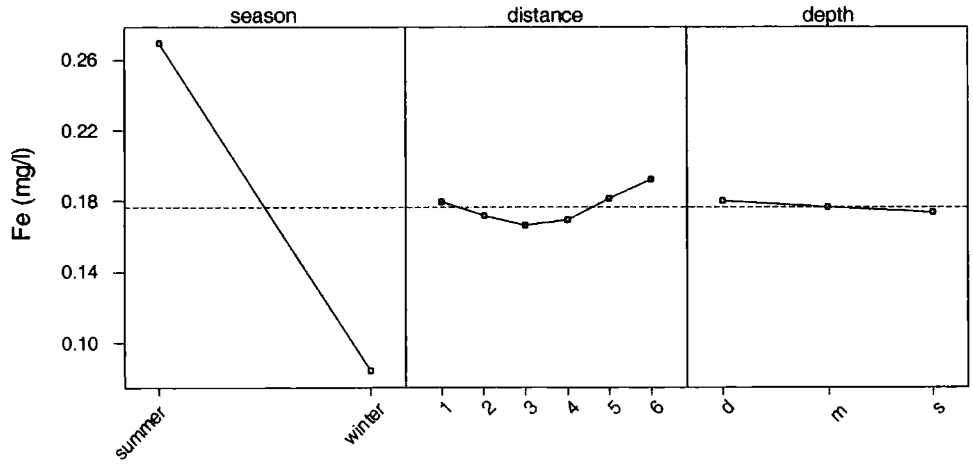


Figure 3.43. Main effects plot for Fe in the Tees impoundment (least square means for factor levels).

Approximately 92 % of the variance observed in Fe levels in the Tees during the water quality surveys is explained by flow ($\omega^2 = 0.49$) and seasonal ($\omega^2 = 0.43$) effects (table 3.18). The effect of season is to give increased Fe concentrations during summer compared to winter (at the same levels of flow). No other factors are significant, and the error term is relatively small (table 3.18, figure 3.43).

Mn

The behaviour of Mn contrasts with that of Fe. Flow as a covariate is insignificant, and seasonal effects on their own are small (table 3.19). As opposed to Fe there are significant differences in Mn levels with distance ($\omega^2 = 0.19$) and depth ($\omega^2 = 0.07$) within the impoundment, and several higher order interactions between the factors in the model (table 3.19, figure 3.44). Mn tends to increase with distance downstream, but more significantly during summer and at depth (figures 3.45, 3.46 and 3.47).

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
Season	16.57	0.000	0.0005	0.05
Distance	12.13	0.000	0.0017	0.19
Depth	11.32	0.000	0.0006	0.07
Season*distance	4.64	0.000	0.0005	0.06
Season*depth	10.79	0.000	0.0006	0.07
Depth*distance	7.60	0.000	0.0020	0.23
Season*distance*depth	7.16	0.000	0.0019	0.21
Error			0.0011	0.12

Table 3.19. Results from GLM ANOVA for seasonal effects on Mn within the Tees impoundment (na = not applicable since factor insignificant (P>0.05)).

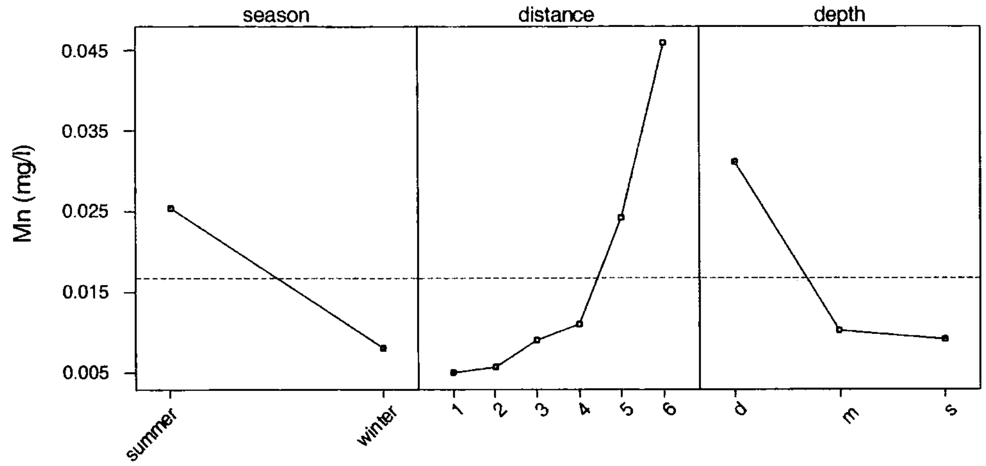


Figure 3.44. Main effects plot for Mn in the Tees impoundment (least square means for factor levels).

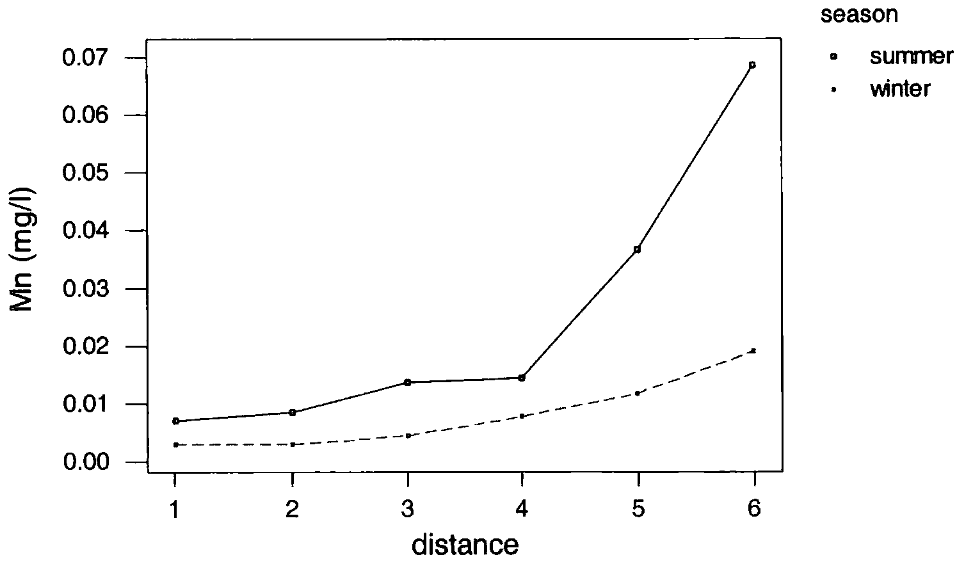


Figure 3.45. Interaction between distance and season effects on Mn (LS mean) in the Tees impoundment. Summer results as solid line and winter as dashed line.

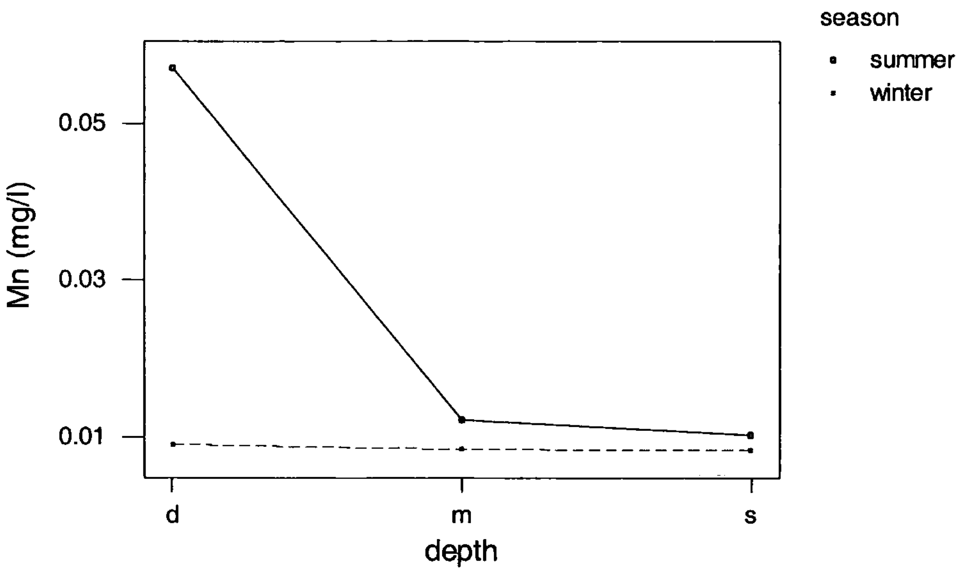


Figure 3.46. Interaction between depth and season effects on Mn (LS mean) in the Tees impoundment. Summer results as solid line and winter as dashed line.

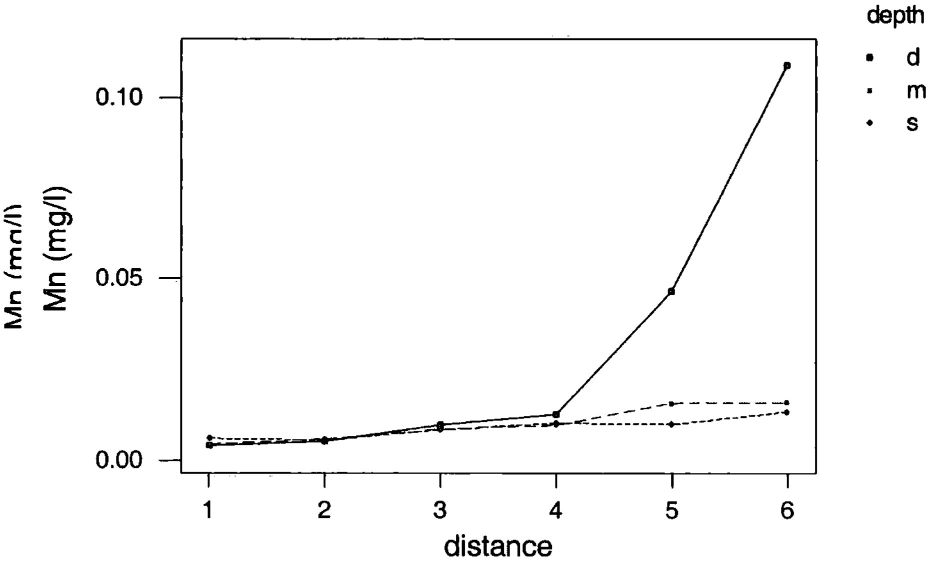


Figure 3.47. Interaction between depth and distance effects on Mn (LS mean) in the Tees impoundment.

Discussion

There is a distinct contrast between the controls on Fe and Mn in the Tees impoundment. It is likely that Fe is mainly sourced from the upland part of the Tees catchment within dissolved humic substances removed from the extensive areas of peat. As mentioned above (for BOD and colour), the removal of dissolved organic material increases with flow, but is greatest under storm events following warm and dry periods due to increased humification in the upper layers of peat (Evans et al. 1999). Therefore Fe concentrations are strongly related to both season and to discharge in the Tees (figure 3.48). During the periods sampled there appeared to be very little internal cycling of Fe relative to the external inputs.

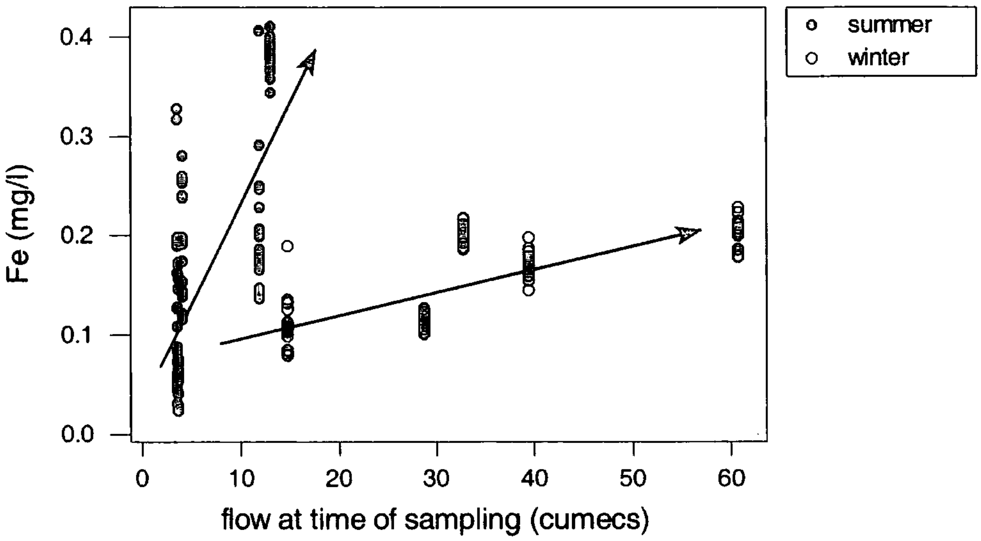


Figure 3.48. The relationship between Fe and discharge in the Tees impoundment, showing an increase in Fe concentration with increasing flow in addition to a marked seasonal difference.

In contrast the behaviour of Mn appears to be controlled totally internally within the impoundment. The concentration of Mn increases with distance downstream, particularly during summer and at depth within the impoundment. This is interpreted as an effect of diffusion of Mn from sediment, and is seen to be strongly redox controlled. Significant increases in dissolved Mn concentrations are strongly related to low (< approximately 40 %) DO conditions encountered in the impoundment (figure 3.49). No similar pattern is seen for Fe implying that either the reducing conditions which develop are insufficient to allow mobilisation of Fe from the sediment, or that the effects of mobilisation are insignificant compared to the flow and seasonal controls on concentrations.

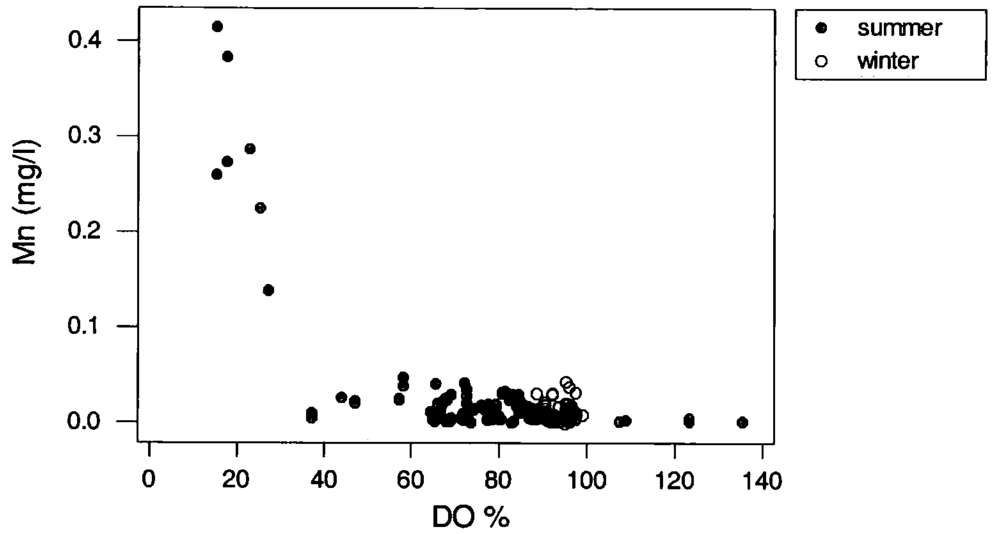


Figure 3.49. The relationship between Mn and DO in the Tees impoundment, showing release of Mn from sediment under reducing conditions. Increased Mn values at low DO % are from depth at sites 5 (RB) and 6 (TB) from 4th August, 25th August and 8th September 1999.

3.2.11 Summary and conclusions

Parameter	ω^2 for season	Covariates	Controlling processes
Temperature	1.00		Climate.
DO	0.41		Temperature controlled microbial respiration. Flow controlled stratification vs. mixing and aeration. Seasonal primary production.
BOD	0.36	Flow	Flow controlled removal of humic substances from peat. Temperature and saturation levels in peat of catchment.
pH	0.54		Temperature controlled microbial respiration. Primary production. Seasonally controlled geological sources.
Alkalinity	0.88		Flow controlled dilution (stormflow vs. baseflow).
Conductivity	Not significant with flow as a covariate	Flow	Flow controlled dilution (stormflow vs. baseflow). Relative contribution of Leven tributary. Small amounts of seawater intrusion close to barrage.
Transparency	0.18	Flow	Flow controlled colour and turbidity. Increased overland flow and less vegetation cover in winter giving greater particulate removal. Resuspension of bed and bank material with distance downstream.

Parameter	ω^2 for season	Covariates	Controlling processes
Nitrate	0.44	Flow	Increased soil nitrate export in winter. Flow controlled dilution of point sources of nitrate. Seasonal primary production.
Ammonia	0.08	DO	Increased soil ammonia export in winter. Seasonal lack of nitrification under low DO conditions.
Phosphate	0.65		Flow controlled dilution of point sources of phosphate. Seasonal primary production.
Si	0.78		Increased soil Si export in winter and with increased flow.
Ca	0.13	Flow	Flow controlled dilution (stormflow vs. baseflow). Relative contribution of Leven tributary. Small amounts of seawater intrusion close to barrage.
Na	Not significant with flow as a covariate	Flow	As Ca.
Mg	0.06	Flow	As Ca.
K	0.51	Flow	As Ca.
S	0.10	Flow	As Ca.
Fe	0.43	Flow	Flow and seasonally controlled removal with humic substances from peat (cf. BOD).
Mn	0.05		Redox controlled diffusion from sediments.

Tables 3.20 and 3.21. Summaries of seasonal effects and proposed controlling processes on water quality parameters in the Tees impoundment.

Seasonal variation in water quality behaviour is important in the Tees impoundment, and through determination of the controlling processes it can be generalised that this is likely to apply to all estuarine impoundments. Season has a significant impact on the behaviour of all of the water quality parameters measured (at above LODs) except for Na (for which any effect is overshadowed by the impact of small amounts of seawater intrusion to the impoundment), although the size of the seasonal effect varies widely between parameters (ω^2 for significant seasonal effect varies from 0.05 (for Mn) to 1.00 (for temperature)). Summaries of the results from ANOVA testing of the significance of seasonal effects, and proposed controlling processes for each of the water quality parameters are shown in tables 3.20 and 3.21.

A large amount of the seasonal variation is related to flow (river discharge), either as a dilution effect of constant point source or baseflow inputs (e.g. major metals, alkalinity and phosphate), or increased flow leading to greater export from diffuse sources (e.g. BOD, Si and Fe). Levels of saturation of the soil and peat of the catchment also vary with season, and control the amount of surface and near-surface runoff (transparency, N and Si) and the amount of humification in peat (BOD, transparency and Fe). The seasonal differences in flow have a third effect on the homogeneity of the water body, with a generally more homogenous water body being observed during the higher flows of winter, and greater variation with distance and depth during the lower flows of summer (particularly noticeable for DO). The relative impact of the River Leven tributary cannot easily be constrained, but is generally considered to be minor.

Seasonal variation is also related to temperature differences, and in particular their effects on the rates of biological processes within the catchment and water body. Rates of microbial respiration (oxidation of organic material) are higher during the summer reducing DO and pH (and in turn increasing ammonia and Mn), and increasing humification of peat in the catchment. Biological primary production relates to both temperature and light and nutrient availability, all of which show seasonal variation. Photosynthetic production affects pH, DO and the amounts of nitrate and phosphate in the water body.

In conclusion, the close links between the processes controlling water quality in the Tees to river flow and temperature mean that there are significant seasonal differences in the values of parameters. In general low water quality conditions are more likely to be encountered during the summer, and DO conditions below the SWQO for both salmonids and cyprinids (NRA 1991) and increased levels of ammonia (although below the 0.78 mg/l SWQO for salmonids) are observed in the Tees impoundment during the sampling periods. The majority of the processes discussed are involved in all of the impoundments investigated, and significant differences in water quality between seasons are likely to be universal. The strong influence that the extensive areas of blanket peat in the upper catchment have on the Tees is probably not applicable to the other (more lowland) systems studied however.

In terms of subsequent modelling and comparison between the systems, it is important that the effects of seasonality (particularly temperature and river flow) are considered. At the simplest level this involves comparing datasets collected during the same season. To enable comparison of processes occurring within the areas of study, catchment differences may be factored out by normalising to input values for the parameters of interest.

3.3 Wansbeck

Examination of seasonal differences in the behaviour of selected water quality variables was carried out for total tidal exclusion (freshwater) impoundments in section 3.2, and is discussed here for partial tidal exclusion systems using the Wansbeck as an example. Analysis concentrated on those variables which were seen to show significant internal (within impounded area) variance in the Tees impoundment. Those parameters are DO, pH, nitrate, ammonia, Fe and Mn.

A general linear model (ANOVA) including the terms of season, distance within the impounded area and depth within the impounded area plus the interactions between season and distance and season and depth was used. Interactions between distance and depth could not be assessed since at two sites (SW and CI (distances 1 and 4)) only surface samples were taken since the water depths were low (normally < 0.5 m). The Wansbeck was sampled during four periods designated as spring, summer, autumn and winter in the model. The spring sampling period includes the dates of 4th, 5th, 7th, 9th and 11th to 14th March 2000, the summer period was from the 4th to 18th June 2001, autumn sampling was from 25th September to 10th October 2000, and winter sampling was 3rd and 5th to 9th February 2001. Periods were chosen within spring tidal cycles giving a similar number of days without seawater influx for all seasons in order to factor out tidal effects and sample during the periods of lowest likely water quality. Distance downstream/sampling site were represented by numbers 1 to 5 from the former tidal limit (SW) to the barrage (WB). Depth is represented by sampling at shallow (S), mid-depth (m) and deep (d) at each sampling site. The significances of differences in water quality between seasons were tested using Tukey simultaneous tests. Analyses were carried out using both raw data and data normalised to the freshwater inputs to the impoundment to allow assessment of the differences between seasons based on catchment effects and those due to differences in behaviour within the impounded area.

3.3.1 Dissolved oxygen

Results

Due to connection problems with the DO meter during the winter sampling period the data used in the analysis are limited to the 3rd, 6th and 7th February 2001. Mean DO levels are significantly lower in summer and higher in winter than in spring and autumn (figure 3.50, table 3.22). However the most significant effect on DO % levels in the Wansbeck is depth. The decreases in DO with depth explain approximately 50 % of the variance in the dataset. The distance effect is strongly related to the depths of the sampling sites, with lowest mean values for DO at the deepest site (distance 2/site CP) (figure 3.51). The depth effects were the same for summer, spring and autumn but much smaller (and probably related solely to salinity) during the winter sampling period (figure 3.52). Approximately 16 % of the variance in DO % in the dataset cannot be explained by the terms in the model.

Source	**F**	**P**	**σ2**	**Size of Effect (ω2)**
Season	15.06	0.000	335	0.12
Distance	6.67	0.000	180	0.06
Depth	92.67	0.000	1455	0.50
Season*distance	5.27	0.000	271	0.09
Season*depth	6.43	0.000	173	0.06
Error			476	0.16

Table 3.22. Results from GLM ANOVA for DO % (raw data) between seasons in the Wansbeck impoundment.

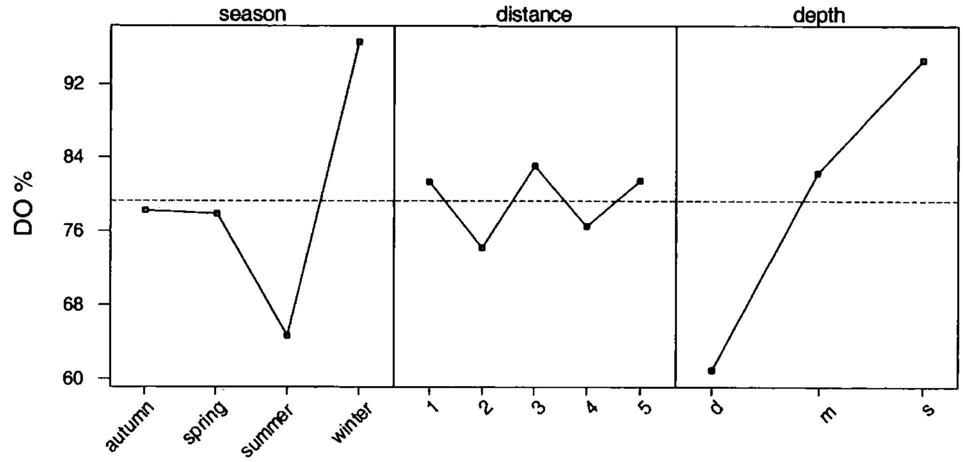


Figure 3.50. Main effects plot for the factors of season, distance and depth on DO % (raw data) in the Wansbeck impoundment (LS means for factor levels).

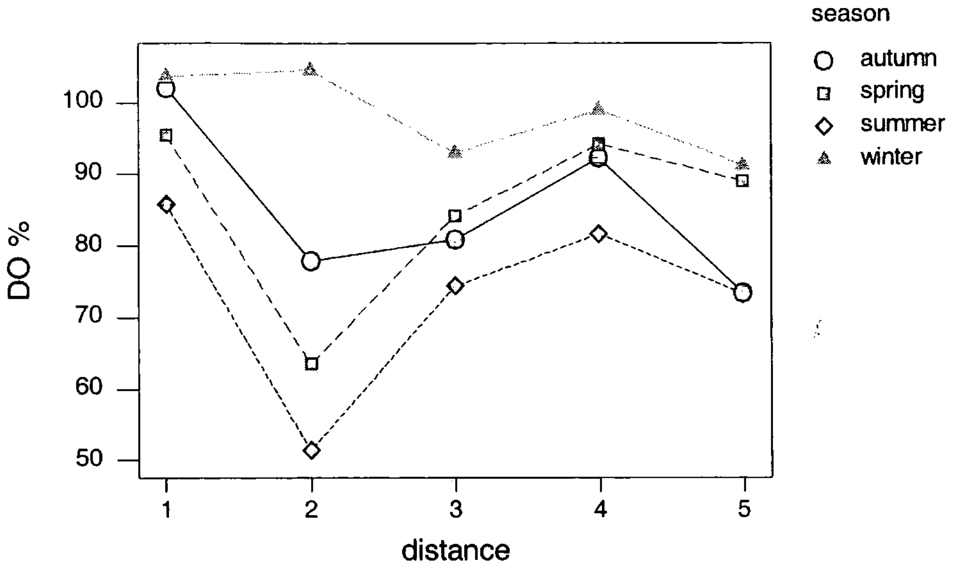


Figure 3.51. Interaction between season and distance effects on DO % (raw data) within the Wansbeck impoundment (LS means).

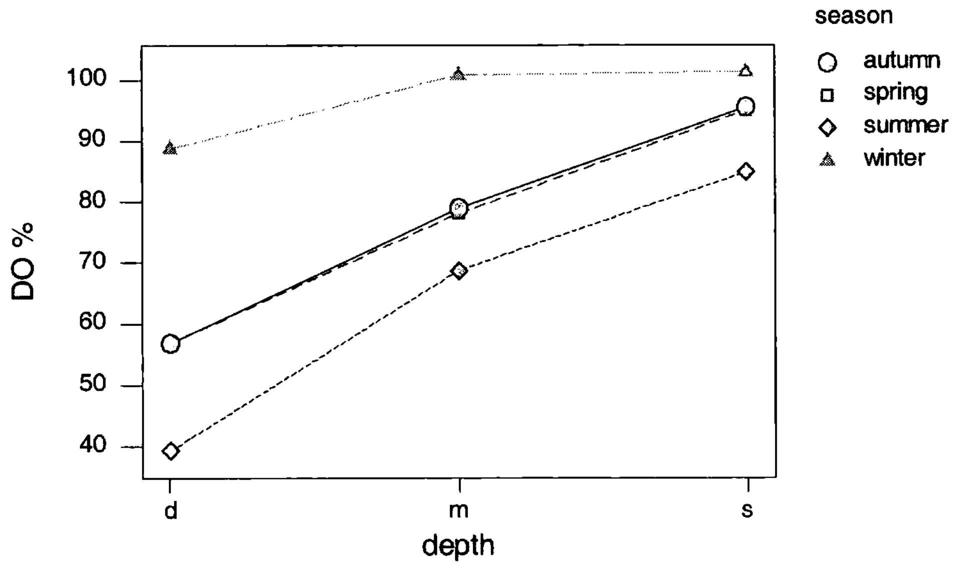


Figure 3.52. Interaction between season and depth effects on DO % (raw data) within the Wansbeck impoundment (LS means).

Factor	Pairwise comparison	Adjusted P-value
Season	Spring - Autumn	0.999
	Summer - Autumn	0.000
	Winter - Autumn	0.000
	Summer – Spring	0.000
	Winter -Spring	0.000
	Summer – Winter	0.000

Table 3.23. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for DO % (raw data) within the Wansbeck impoundment.

Since DO % levels are broadly similar within the freshwater inputs to the systems, the general pattern of results for data normalised to the freshwater inputs is similar to that for raw data (figure 3.53). The distance behaviour is very similar for spring, summer and autumn but contrasting in winter (figure 3.54). Depth remains the most significant factor and even more clearly shows that the decrease in DO with depth is similar for spring, summer and autumn but lower in winter (figure 3.55). Relative to input levels DO is lower by approximately 8 % in winter and by approximately 20 % in the impounded area in spring, summer and autumn.

Source	F	P	σ2	Size of Effect (ω2)
Season	50.58	0.000	0.17	0.33
Distance	6.02	0.000	0.02	0.05
Depth	77.95	0.000	0.17	0.35
Season*distance	5.14	0.000	0.04	0.07
Season*depth	8.32	0.000	0.03	0.07
Error			0.07	0.13

Table 3.24. Results from GLM ANOVA for DO (normalised data) between seasons in the Wansbeck impoundment.

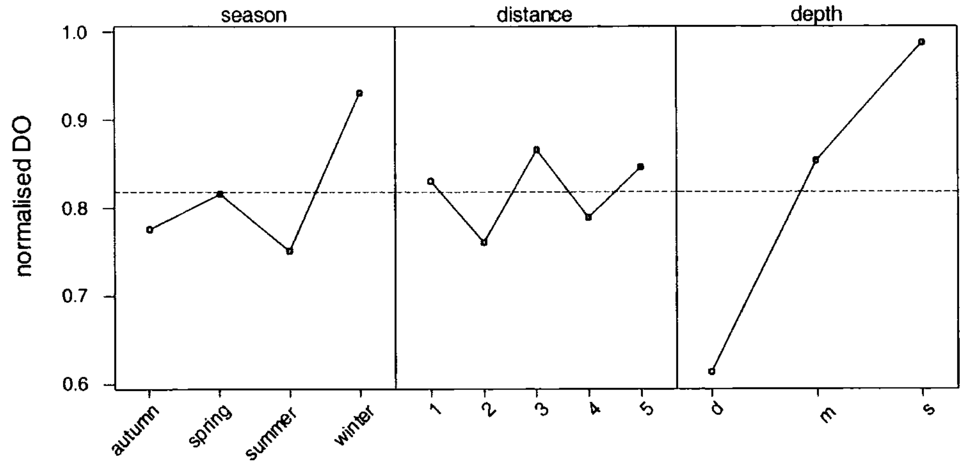


Figure 3.53. Main effects plot for the factors of season, distance and depth on DO (normalised data) in the Wansbeck impoundment (LS means for factor levels).

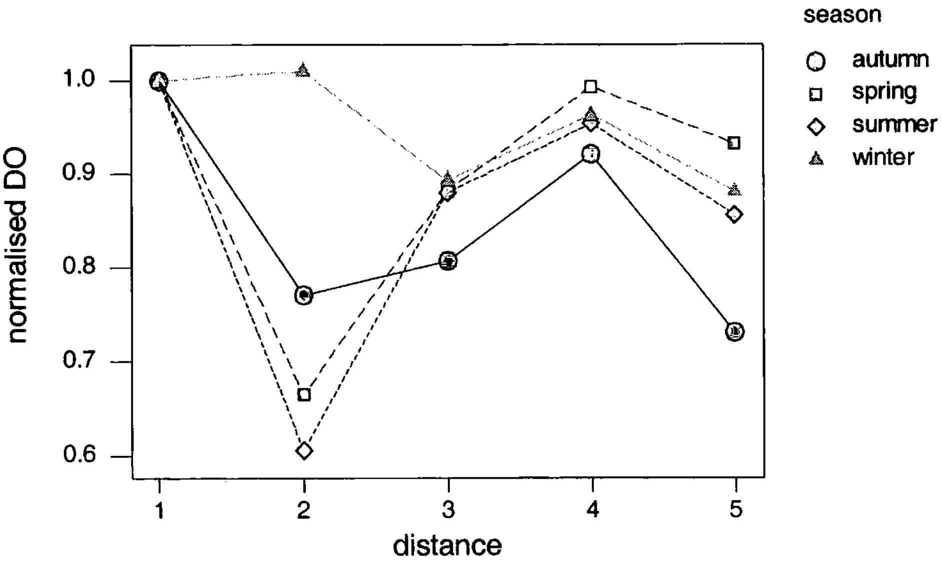


Figure 3.54. Interaction between season and distance effects on DO (normalised data) within the Wansbeck impoundment (LS means).

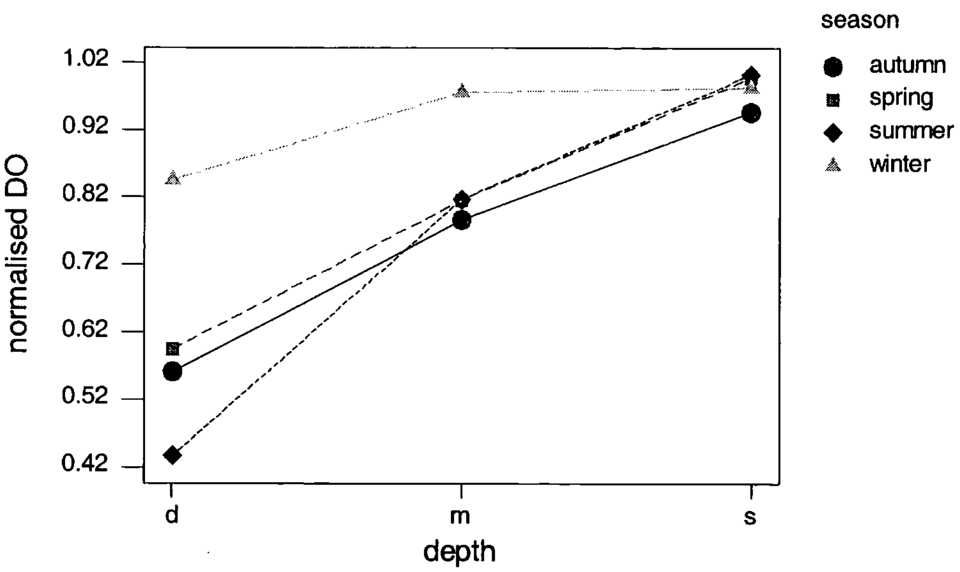


Figure 3.55. Interaction between season and depth effects on DO (normalised data) within the Wansbeck impoundment (LS means).

Factor	Pairwise comparison	Adjusted P-value
Season	Spring - Autumn	0.470
	Summer - Autumn	0.747
	Winter - Autumn	0.001
	Summer – Spring	0.101
	Winter -Spring	0.044
	Summer – Winter	0.000

Table 3.25. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for DO (normalised data) within the Wansbeck impoundment.

Discussion

The most significant control on oxygen levels in the impoundments is density stratification. Stratification isolates portions of water from sources of re-oxygenation whilst respirative processes act to consume dissolved oxygen. In comparison of barrage designs (chapter 4) it is seen that this effect is most significant in the Wansbeck impoundment.

The results above show that for the Wansbeck impoundment the effect of stratification is significant throughout the year, but to a greater extent during spring, summer and autumn periods, and only slightly greater during summer when mean temperatures are highest (mean T during the sampling periods are 11.8, 7.2, 13.1 and 3.0°C for autumn, spring, summer and winter respectively). That the lowest levels of DO are encountered during the summer period relates more to the lower DO concentrations in the water entering the impoundment than to greater impacts of stratification. During all seasons the freshwater input progresses downstream along the surface of the impoundment and is unaffected by internal processes in terms of DO concentration.

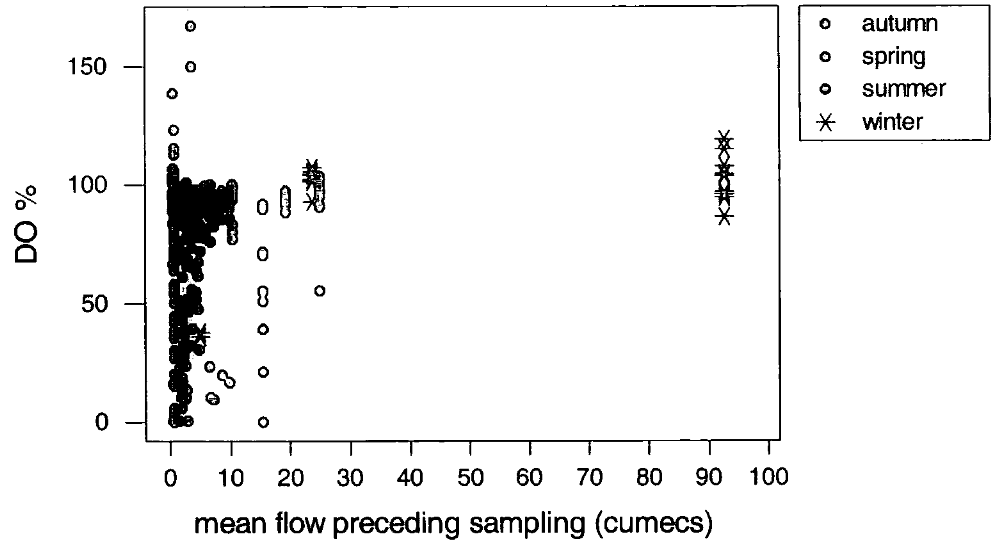


Figure 3.56. DO vs. flow for the Wansbeck impoundment showing the lack of low DO values under high flow conditions due to the removal of saline stratification of the water body.

The differences in behaviour between the seasons sampled is likely to be due to both differences in temperature and differences in freshwater discharge. During the winter period sampled flow was generally high enough to remove the majority of saline water, and particularly to remove any stratification at the deepest point (distance 2 / site CP) at which lowest DO conditions were encountered at other periods of the year (figure 3.56). Comparing the decreases in DO at depth over periods of isolation of deep saline water at site CP during the other seasons shows that the rate of de-oxygenation is virtually identical for spring and autumn (figure 3.57), but that DO is consistently at almost 0 % during summer (implying that low DO may exist over longer periods in the summer).

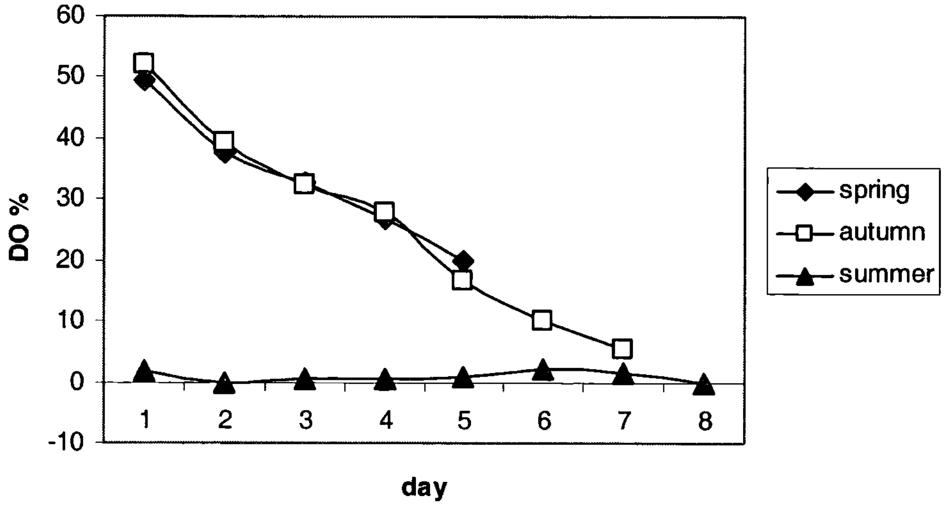


Figure 3.57. The decrease in DO concentration in deep (stratified) water from site CP on the Wansbeck during 3 sampling periods. Spring data are from 12th to 16th March 2000, autumn data are from 1st to 7th October 2000, and summer data are from 8th to 15th June 2001.

3.3.2 pH

Results

For raw pH data the majority of variance is between seasons (table 3.26). Lowest pH values occur in summer and the highest in spring and autumn, with significant differences between all pairs of season except spring and autumn (figure 3.58 and table 3.27). The distance pattern relates to the water depths at each sampling distance, such that deeper sites (especially site CP at distance 2) show lower mean pHs (figure 3.59). pH decreases with depth to a similar degree during all seasons. Approximately 14 % of the variance in the dataset cannot be explained by the terms in the model.

Source	F	P	σ2	Size of Effect (ω2)
Season	69.14	0.000	0.57	0.43
Distance	10.76	0.000	0.16	0.12
Depth	45.01	0.000	0.37	0.28
Season*distance	1.50	0.118	na	na
Season*depth	2.28	0.035	0.02	0.02
Error			0.19	0.14

Table 3.26. Results from GLM ANOVA for pH (raw data) between seasons in the Wansbeck impoundment (na = not applicable since factor insignificant at 95 % level).

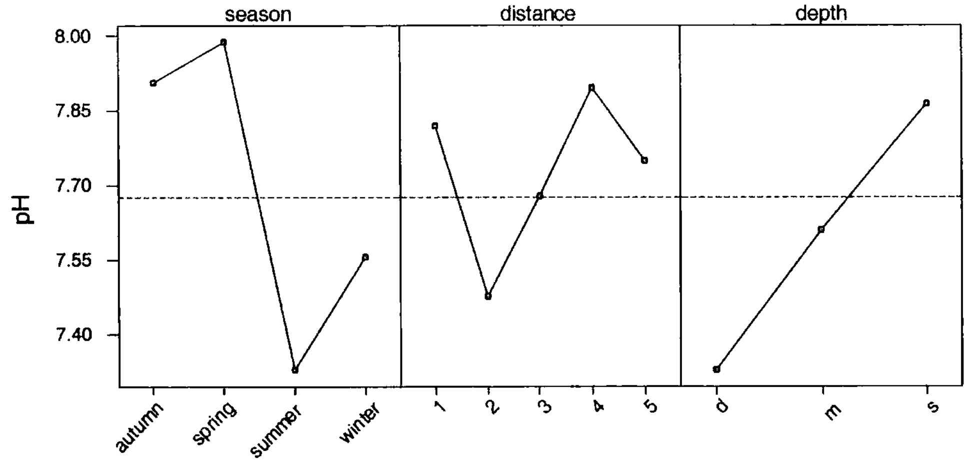


Figure 3.58. Main effects plot for the factors of season, distance and depth on pH (raw data) in the Wansbeck impoundment (LS means for factor levels).

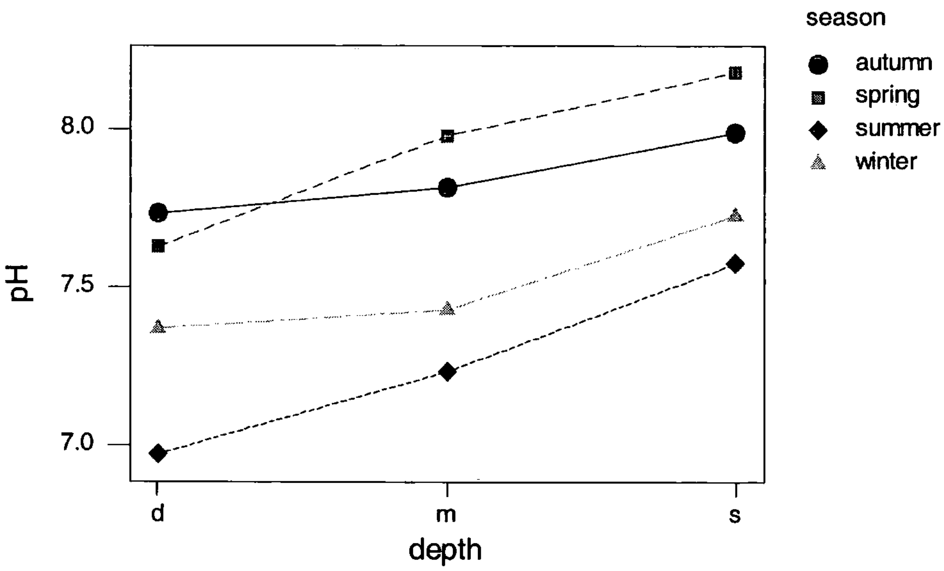


Figure 3.59. Interaction between season and depth effects on pH (raw data) within the Wansbeck impoundment (LS means).

Factor	Pairwise comparison	Adjusted P-value
Season	Spring - Autumn	0.375
	Summer - Autumn	0.000
	Winter - Autumn	0.000
	Summer – Spring	0.000
	Winter -Spring	0.000
	Summer – Winter	0.001

Table 3.27. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for pH (raw data) within the Wansbeck impoundment.

Normalising the data to the freshwater input values for each of the days sampling almost totally removes the effect of season, implying that within impoundment variation in values of pH is relatively constant throughout the year (table 3.28, figure 3.60). Approximately 74 % of the variance within the impounded area is with depth or distance, pH values being approximately 5 % lower at depth than in surface waters and the distance pattern relating to the actual water depths at each sampling site (with lowest pH being found at the deepest site (CP) at distance 2) (figure 3.61). The reduction in pH with depth is slightly higher in summer than in the other seasons (figure 3.62).

Source	**F**	**P**	**σ2**	**Size of Effect (ω2)**
Season	5.43	0.001	0.00	0.03
Distance	20.88	0.000	0.00	0.24
Depth	83.57	0.000	0.01	0.50
Season*distance	2.88	0.001	0.00	0.05
Season*depth	4.50	0.000	0.00	0.04
Error			0.00	0.14

Table 3.28. Results from GLM ANOVA for pH (normalised data) between seasons in the Wansbeck impoundment.

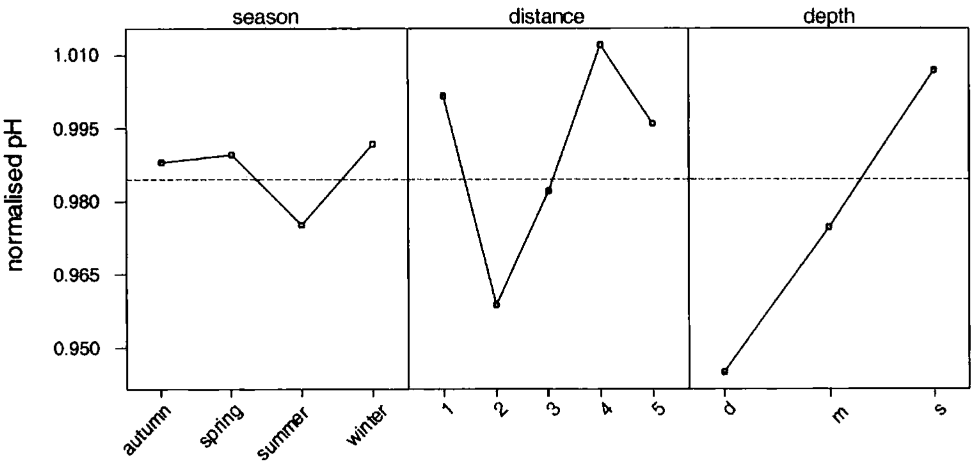


Figure 3.60. Main effects plot for the factors of season, distance and depth on pH (normalised data) in the Wansbeck impoundment (LS means for factor levels).

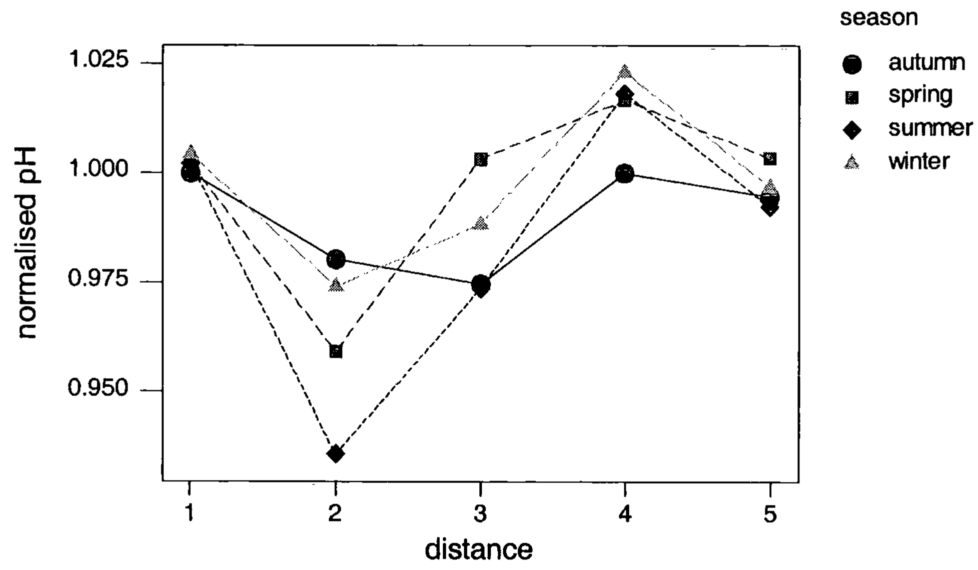


Figure 3.61. Interaction between season and distance effects on pH (normalised data) within the Wansbeck impoundment (LS means).

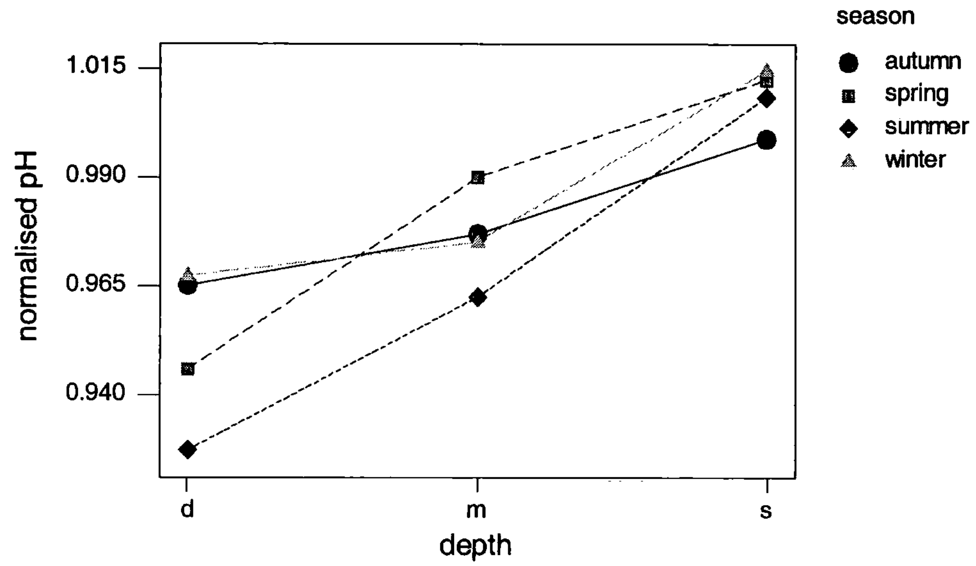


Figure 3.62. Interaction between season and depth effects on pH (normalised data) within the Wansbeck impoundment (LS means).

Factor	Pairwise comparison	Adjusted P-value
Season	Spring - Autumn	0.948
	Summer - Autumn	0.026
	Winter - Autumn	0.894
	Summer – Spring	0.007
	Winter -Spring	0.996
	Summer – Winter	0.012

Table 3.29. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for pH (normalised data) within the Wansbeck impoundment.

Discussion

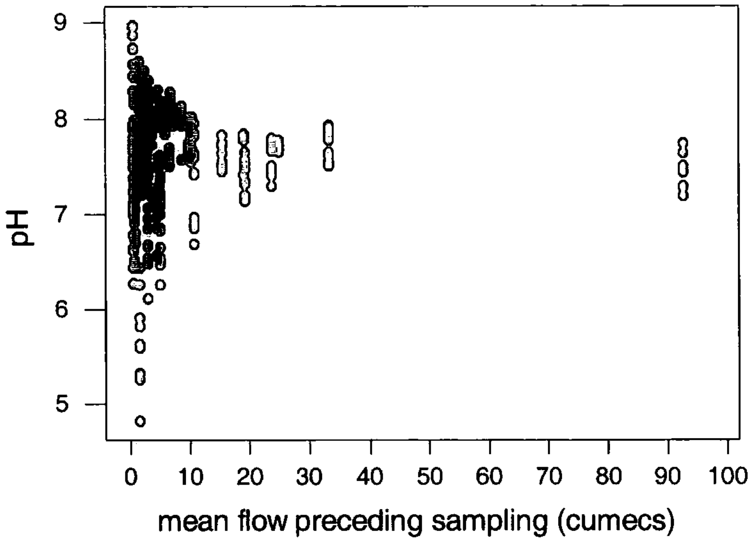


Figure 3.63. pH vs. flow in the Wansbeck impoundment, showing greater variation in pH under low flow conditions due to stratification and production/respiration effects. Under high flows stratification of the water body is removed and pH values are more homogenous.

The majority of the variation in pH between seasons is explained by the differences in the freshwater entering the impounded areas at their upstream limits. Variation in the pH of the freshwater inputs is independent of flow (although, as for DO, at higher flows pH shows less variance due to a lack of stratification (figure 3.63)), and therefore is likely to relate to biological effects. On this basis primary production relative to respiration in the water column is greatest in the spring and autumn periods of sampling.

Within the impounded areas the variation in pH is with depth in the water column and relates to both the lower pH in seawater than river water and the greater amount of respiration in deep water in a stratified water column. The decreases in pH with depth are similar throughout the year implying that lower pHs in seawater are more important than biological processing, although the slightly greater decreases in summer (in addition to a slight increase in alkalinity (figure 3.64) suggest that respiration effects on pH are more significant in this season.

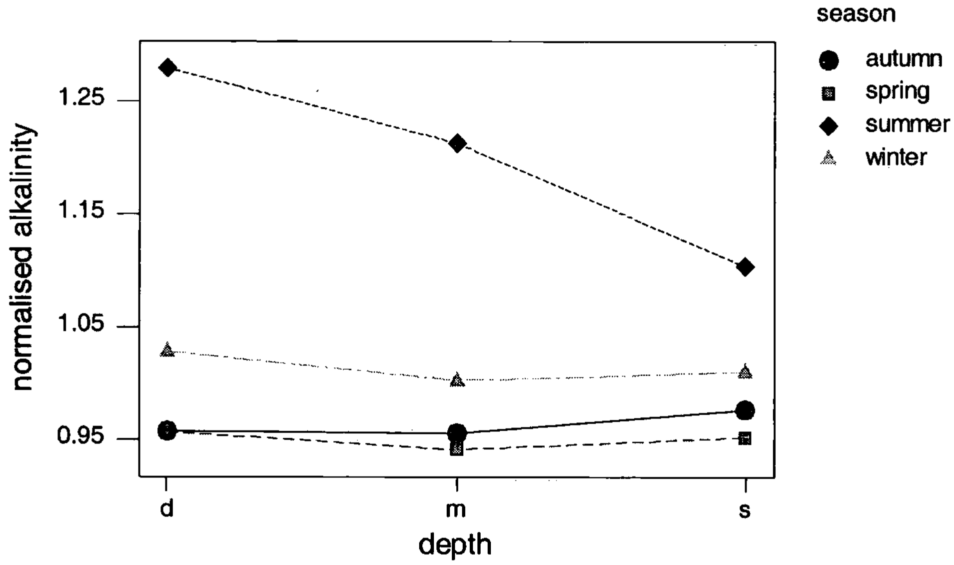


Figure 3.64. Interaction between season and depth effects on alkalinity (normalised data) within the Wansbeck impoundment (LS means).

3.3.3 Nitrate

Results

The seasonal effects on nitrate are small relative to internal variation within the Wansbeck impoundment (table 3.30, figure 3.65). Actual nitrate concentrations are significantly lower in autumn than during the other seasons. Variation with depth accounts for 61 % of the behaviour of nitrate. Nitrate values decrease significantly with depth during all seasons, but to a greater degree during spring, summer and autumn than during winter (figure 3.66).

Source	**F**	**P**	**σ2**	**Size of Effect (ω2)**
Season	12.90	0.000	0.7	0.09
Distance	4.64	0.001	0.5	0.06
Depth	80.81	0.000	5.0	0.61
Season*distance	1.10	0.360	na	na
Season*depth	5.33	0.000	0.5	0.07
Error			1.4	0.17

Table 3.30. Results from GLM ANOVA for nitrate (raw data) between seasons in the Wansbeck impoundment (na = not applicable since factor insignificant at 95 % level).

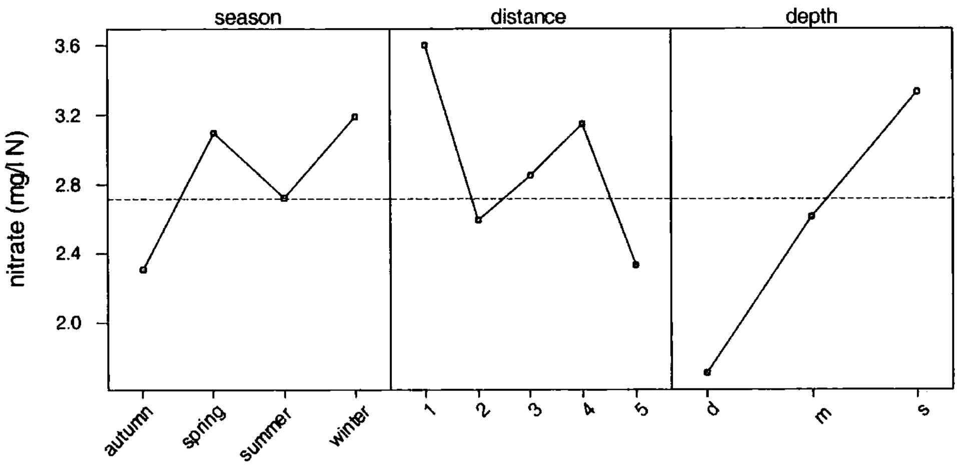


Figure 3.65. Main effects plot for the factors of season, distance and depth on nitrate (raw data) in the Wansbeck impoundment (LS means for factor levels).

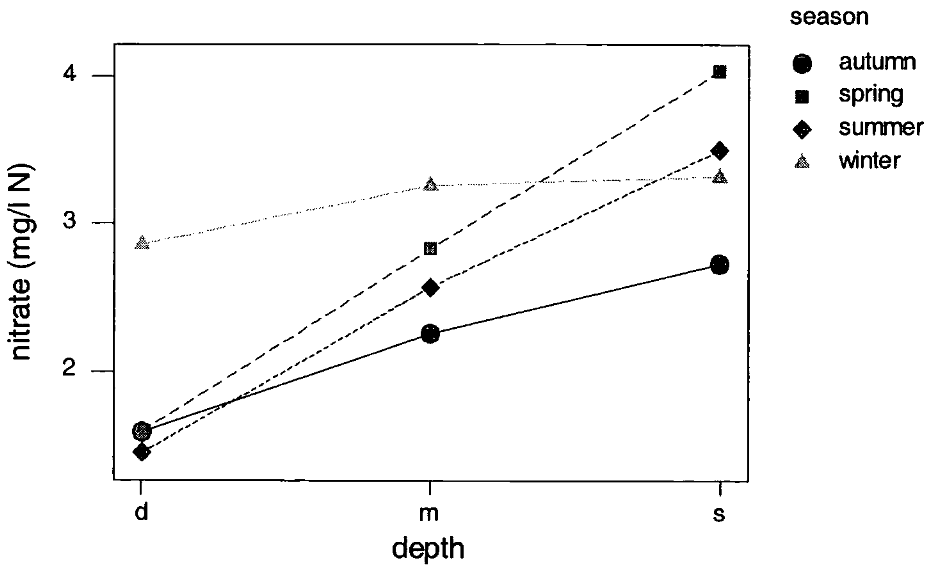


Figure 3.66. Interaction between season and depth effects on nitrate (raw data) within the Wansbeck impoundment (LS means).

Factor	Pairwise comparison	Adjusted P-value
Season	Spring - Autumn	0.000
	Summer - Autumn	0.010
	Winter - Autumn	0.000
	Summer – Spring	0.209
	Winter -Spring	0.609
	Summer – Winter	0.013

Table 3.31. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for nitrate (raw data) within the Wansbeck impoundment.

As might be expected given the small amount of difference between season for raw data, analysis using normalised data (figures 3.67 and 3.68) shows a similar pattern to that presented above for raw nitrate data. Nitrate values at depth in the water column are on average approximately 50 % lower than those at the surface. Surface water nitrate values are generally at the same level as those in the freshwater inputs to the impoundment. The least difference between mean nitrate levels in the impoundment and those entering in freshwater is during the winter season.

Source	**F**	**P**	**σ2**	**Size of Effect (ω2)**
Season	22.90	0.000	0.09	0.14
Distance	3.92	0.004	0.02	0.04
Depth	98.68	0.000	0.39	0.64
Season*distance	0.98	0.462	na	na
Season*depth	3.92	0.001	0.02	0.04
Error			0.09	0.15

Table 3.32. Results from GLM ANOVA for nitrate (normalised data) between seasons in the Wansbeck impoundment (na = not applicable since factor insignificant at 95 % level).

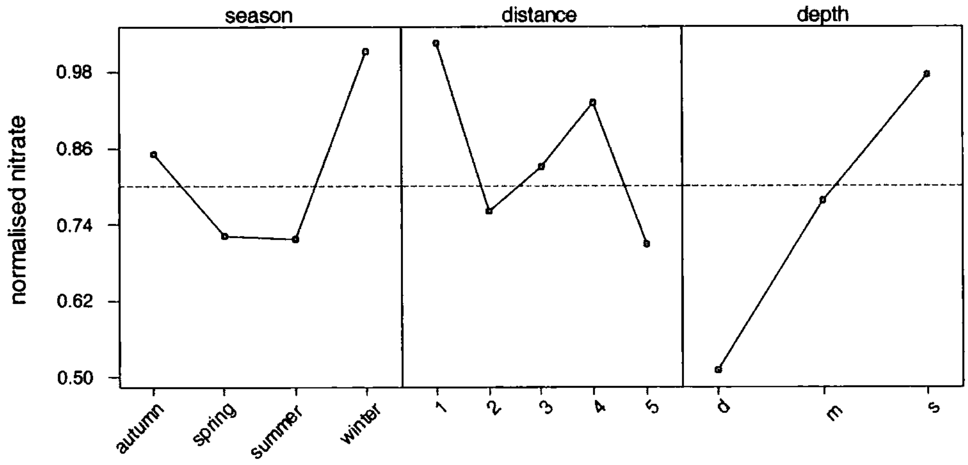


Figure 3.67. Main effects plot for the factors of season, distance and depth on nitrate (normalised data) in the Wansbeck impoundment (LS means for factor levels).

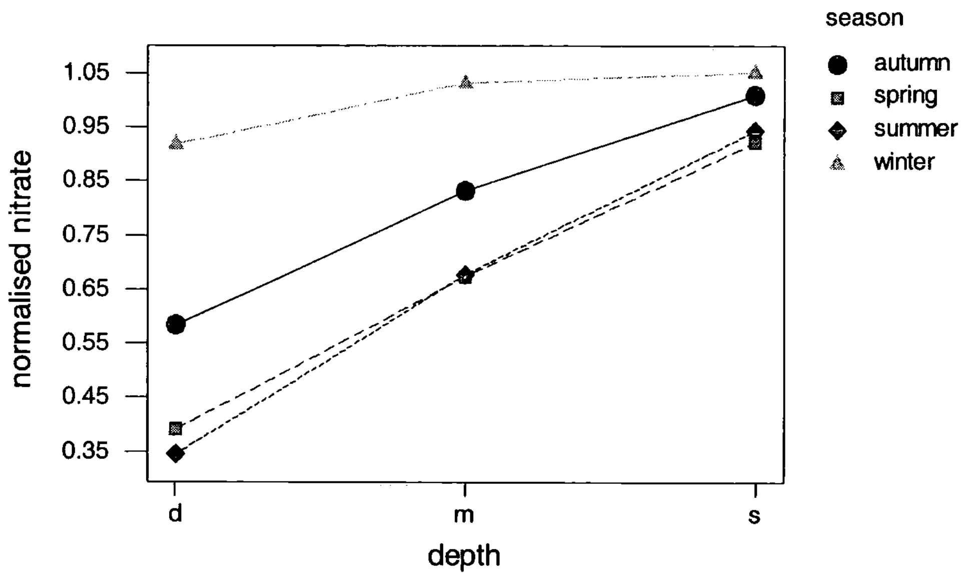


Figure 3.68. Interaction between season and depth effects on nitrate (normalised data) within the Wansbeck impoundment (LS means).

Factor	Pairwise comparison	Adjusted P-value
Season	Spring - Autumn	0.001
	Summer - Autumn	0.000
	Winter - Autumn	0.000
	Summer – Spring	1.000
	Winter -Spring	0.000
	Summer – Winter	0.000

Table 3.33. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for nitrate (normalised data) within the Wansbeck impoundment.

Discussion

It was shown during comparison of barrage designs that the largest control on internal (within impounded area) variation of nitrate concentrations in partial tidal exclusion impoundments is the difference in nitrate concentrations between fresh and seawater in the systems. For the whole of the data from the Wansbeck included in the analyses presented above the mean nitrate value in freshwater (conductivity < 500 μS/cm) was

3.56 mg/l N and in saline water (conductivity < 500 μS/cm) it was 2.20 mg/l N (a difference of approximately 40 %). The mean difference between (generally saline) water at depth and (generally fresh) water at the surface during the periods studied was 50 % implying that the majority of variation with depth throughout the year is due to this difference.

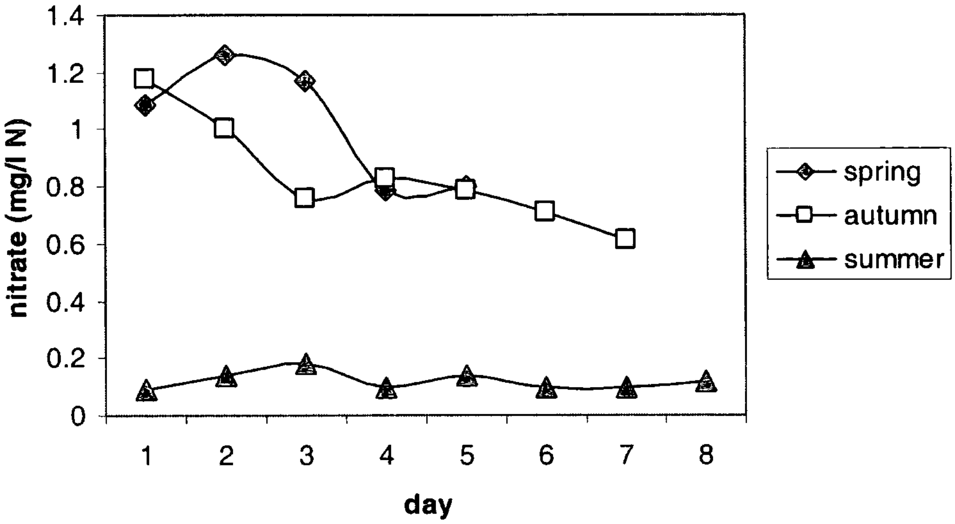


Figure 3.69. The decrease in nitrate concentration in deep (stratified) water from site CP on the Wansbeck during 3 sampling periods. Spring data is from 12th to 16th March 2000, autumn data is from 1st to 7th October 2000, and summer data is from 8th to 15th June 2001.

It was also seen that nitrate generally behaved conservatively on mixing of fresh and seawater. Some loss of nitrate through denitrification and reduction to ammonia was observed at depth (particularly at site CP) during autumn in the Wansbeck. For the periods over which decreasing DO concentrations are presented above, the patterns of nitrate decrease are similar for spring and autumn (as was DO % decrease) but had already reduced to a minimum level at the start of sampling in summer (figure 3.69), meaning that no comparison of rates can be carried out. It is likely that rates of all of the biologically mediated processes are increased at higher temperatures, but since conditions in terms of flow (and hence amount of time in which the water column is stratified) vary markedly between periods this is difficult to assess.

3.3.4 Ammonia

Results

Source	**F**	**P**	**σ2**	**Size of Effect (ω2)**
Season	13.17	0.000	0.015	0.11
Distance	0.97	0.421	na	na
Depth	63.17	0.000	0.075	0.58
Season*distance	2.09	0.015	0.005	0.04
Season*depth	3.56	0.002	0.006	0.05
Error			0.027	0.21

Table 3.34. Results from GLM ANOVA for ammonia (raw data) between seasons in the Wansbeck impoundment (na = not applicable since factor insignificant at 95 % level).

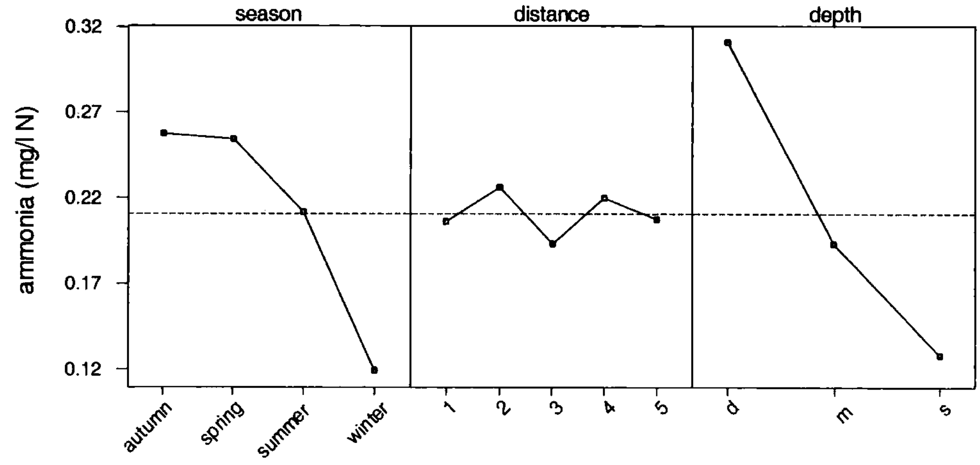


Figure 3.70. Main effects plot for the factors of season, distance and depth on ammonia (raw data) in the Wansbeck impoundment (LS means for factor levels).

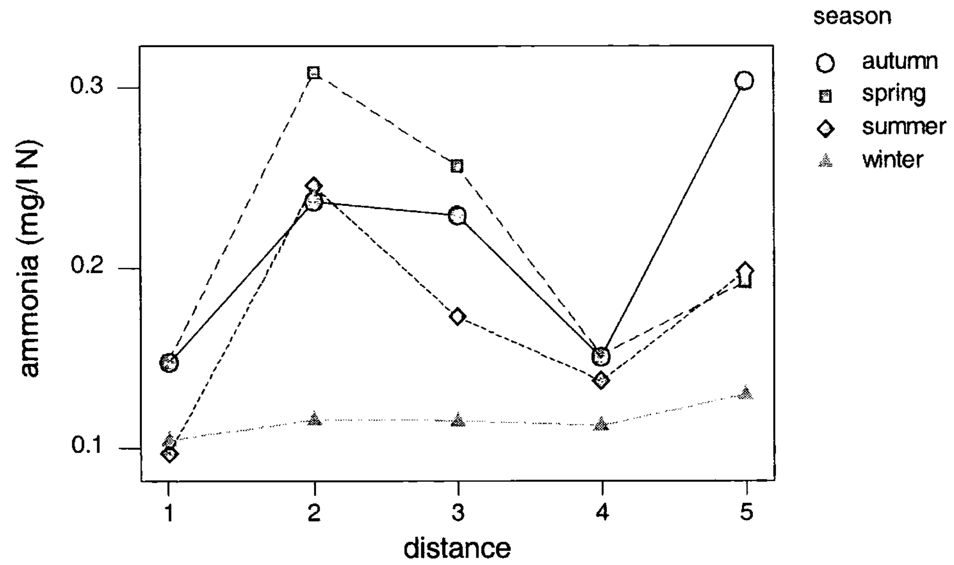


Figure 3.71. Interaction between season and distance effects on ammonia (raw data) within the Wansbeck impoundment (LS means).

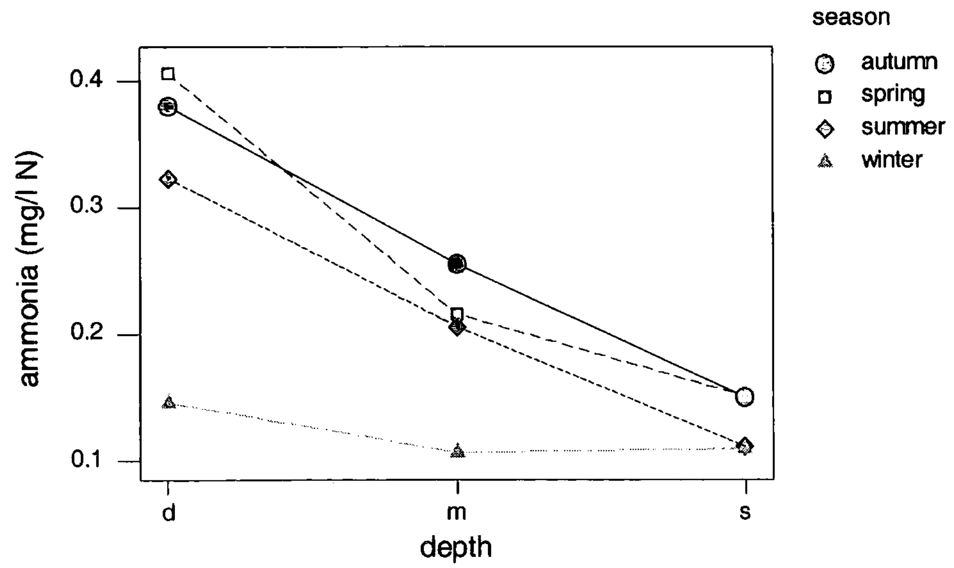


Figure 3.72. Interaction between season and depth effects on ammonia (raw data) within the Wansbeck impoundment (LS means).

Factor	Pairwise comparison	Adjusted P-value
Season	Spring - Autumn	0.998
	Summer - Autumn	0.046
	Winter - Autumn	0.000
	Summer – Spring	0.164
	Winter -Spring	0.000
	Summer – Winter	0.001

Table 3.35. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for ammonia (raw data) within the Wansbeck impoundment.

The seasonal differences in ammonia levels are minor (table 3.34, figure 3.70) and relate almost totally to the differences between seasons in the distance and depth behaviour (figures 3.71 and 3.72). The depth effect explains over half of the variance in the dataset, with ammonia values increasing with depth in the water column in all seasons except winter. The distance effect, as for DO, relates to the actual water depth at each sampling site with maximum ammonia levels at the deepest site (CP). The relatively large error is likely to be due to random analytical error (and hence error is magnified when data is normalised).

Source	F	P	σ2	Size of Effect (ω2)
Season	8.67	0.000	5.4	0.16
Distance	0.78	0.535	na	na
Depth	15.66	0.000	10.3	0.30
Season*distance	0.97	0.472	na	na
Season*depth	2.75	0.012	2.5	0.07
Error			15.8	0.47

Table 3.36. Results from GLM ANOVA for ammonia (normalised data) between seasons in the Wansbeck impoundment (na = not applicable since factor insignificant at 95 % level).

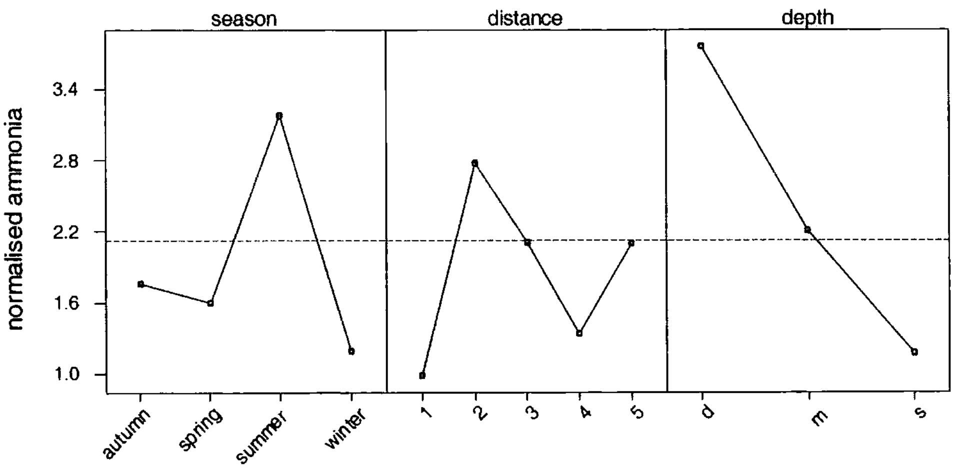


Figure 3.73. Main effects plot for the factors of season, distance and depth on ammonia (normalised data) in the Wansbeck impoundment (LS means for factor levels).

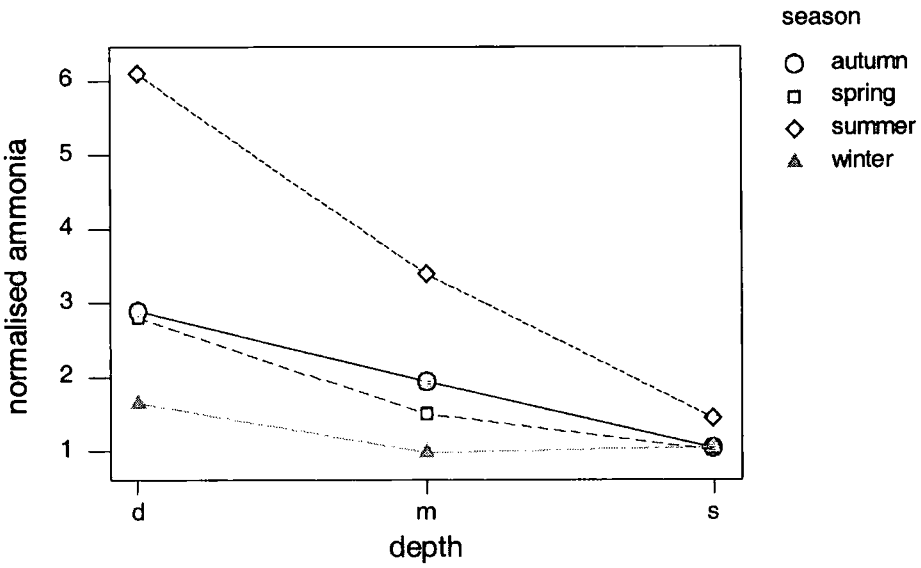


Figure 3.74. Interaction between season and depth effects on ammonia (normalised data) within the Wansbeck impoundment (LS means).

Factor	Pairwise comparison	Adjusted P-value
Season	Spring - Autumn	0.985
	Summer - Autumn	0.001
	Winter - Autumn	0.604
	Summer – Spring	0.001
	Winter -Spring	0.829
	Summer – Winter	0.000

Table 3.37. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for ammonia (normalised data) within the Wansbeck impoundment.

Analysis using normalised data (table 3.36, figure 3.73) shows a similar pattern as that for raw data since the majority of variation in ammonia levels is related to within impoundment processing. Ammonia increases with depth to the greatest degree in summer (by approximately 6 times the input concentration), by approximately 3 times in spring and autumn, and only to a very small extent in winter (figure 3.74).

Discussion

Ammonia levels in the freshwater inputs to the Wansbeck are low (mean concentration is 0.13 mg/l N for all sampling periods), and the major controls on ammonia occur within the impounded area. Ammonia levels build up through decomposition of organic material and reduction of nitrate under low redox conditions. These processes particularly affect water at depth in a stratified water column, and therefore ammonia levels are significantly greater at depth than at the surface in the Wansbeck impoundment. As for DO and nitrate there is a contrast between the behaviour during the winter sampling period and the spring, summer and autumn sampling periods. During winter the water body tends to be far more homogenous due to a combination of higher flows acting to remove stratification and presumably lower temperatures causing lower rates of biological processing. As for DO and nitrate, during the sustained periods for which water at depth at site CP in the Wansbeck was isolated the rate of change (increase) in ammonia was very similar during spring and autumn but showed a constant (high) level during summer (figure 3.75).

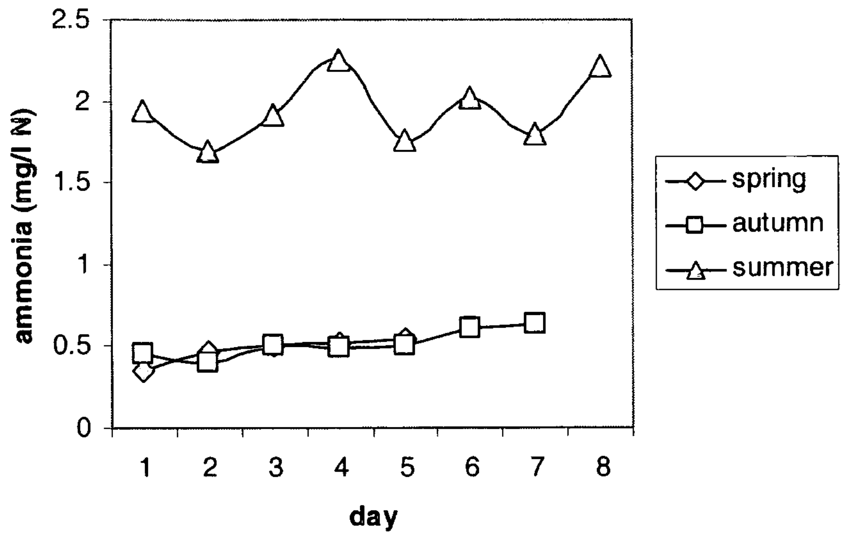


Figure 3.75. The increase in ammonia concentration in deep (stratified) water from site CP on the Wansbeck during 3 sampling periods. Spring data is from 12th to 16th March 2000, autumn data is from 1st to 7th October 2000, and summer data is from 8th to 15th June 2001.

3.3.5 Fe

Results

Source	**F**	**P**	**σ2**	**Size of Effect (ω2)**
Season	103.61	0.000	0.054	0.66
Distance	9.66	0.000	0.009	0.11
Depth	1.97	0.140	na	na
Season*distance	1.78	0.047	0.002	0.02
Season*depth	6.01	0.000	0.005	0.06
Error			0.012	0.14

Table 3.38. Results from GLM ANOVA for Fe (raw data) between seasons in the Wansbeck impoundment (na = not applicable since factor insignificant at 95 % level).

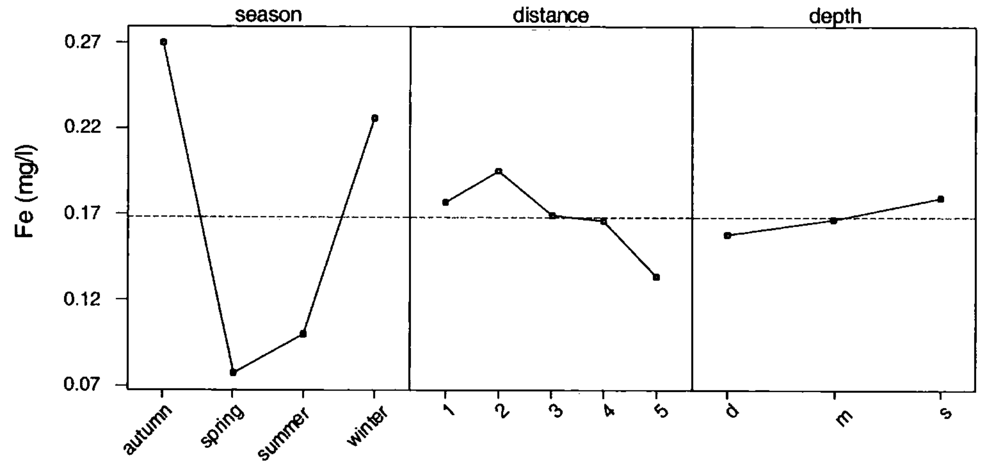


Figure 3.76. Main effects plot for the factors of season, distance and depth on Fe (raw data) in the Wansbeck impoundment (LS means for factor levels).

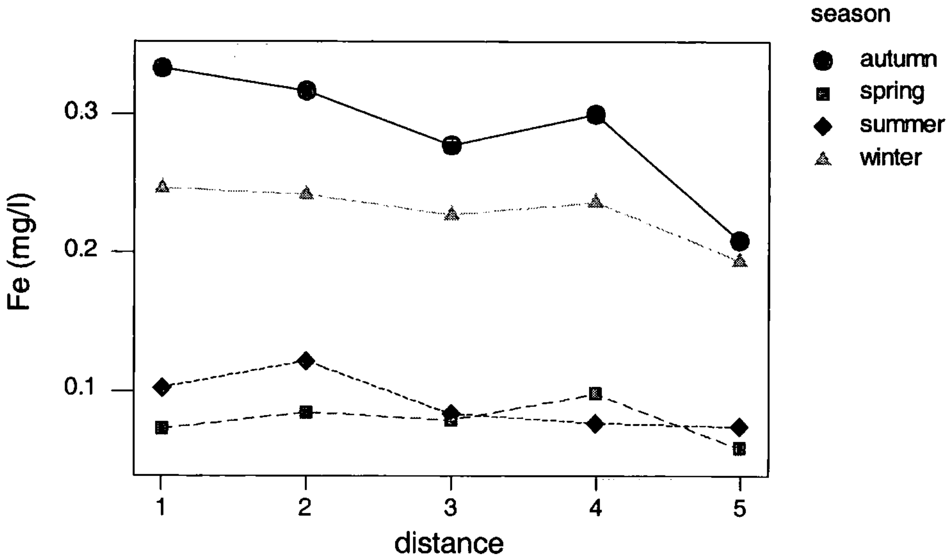


Figure 3.77. Interaction between season and distance effects on Fe (raw data) within the Wansbeck impoundment (LS means).

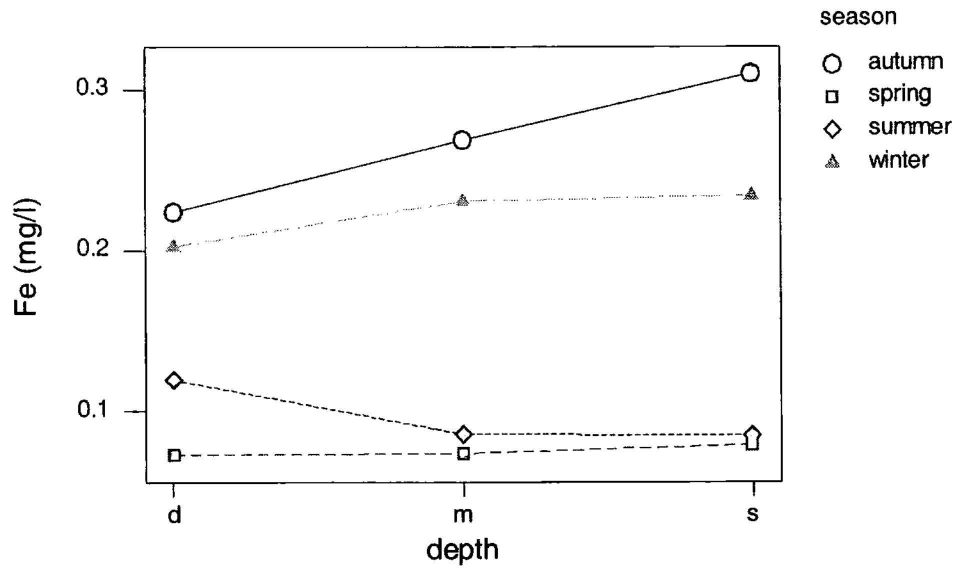


Figure 3.78. Interaction between season and depth effects on Fe (raw data) within the Wansbeck impoundment (LS means).

Factor	Pairwise comparison	Adjusted P-value
Season	Spring - Autumn	0.000
	Summer - Autumn	0.000
	Winter - Autumn	0.026
	Summer – Spring	0.343
	Winter -Spring	0.000
	Summer – Winter	0.000

Table 3.39. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for Fe (raw data) within the Wansbeck impoundment.

Fe shows a large variation between seasons with significant differences between all pairs of season except summer and spring (tables 3.38 and 3.39). Mean Fe levels within the Wansbeck were highest during the autumn sampling period, slightly lower during winter, and lowest during spring and summer (figure 3.76). Distance is also a significant factor, with Fe decreasing slightly downstream particularly during autumn (figure 3.77). Contrasting depth effects are shown between seasons (figure 3.78).

During summer Fe concentrations at depth are higher than those in surface water, but during the other seasons Fe shows no variation or a slight decrease with depth.

Source	F	P	σ2	Size of Effect (ω2)
Season	23.33	0.000	0.73	0.29
Distance	8.56	0.000	0.50	0.20
Depth	2.08	0.126	na	na
Season*distance	1.90	0.031	0.12	0.05
Season*depth	7.44	0.000	0.42	0.17
Error			0.739	0.29

Table 3.40. Results from GLM ANOVA for Fe (normalised data) between seasons in the Wansbeck impoundment (na = not applicable since factor insignificant at 95 % level).

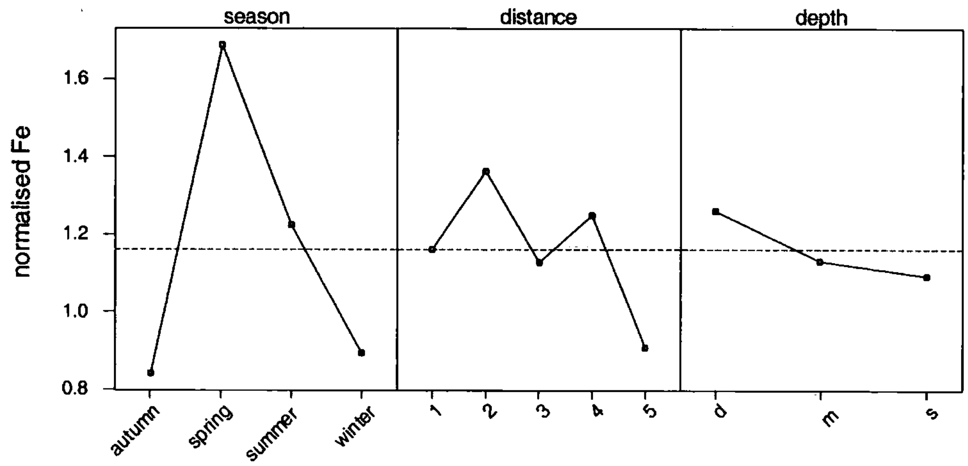


Figure 3.79. Main effects plot for the factors of season, distance and depth on Fe (normalised data) in the Wansbeck impoundment (LS means for factor levels).

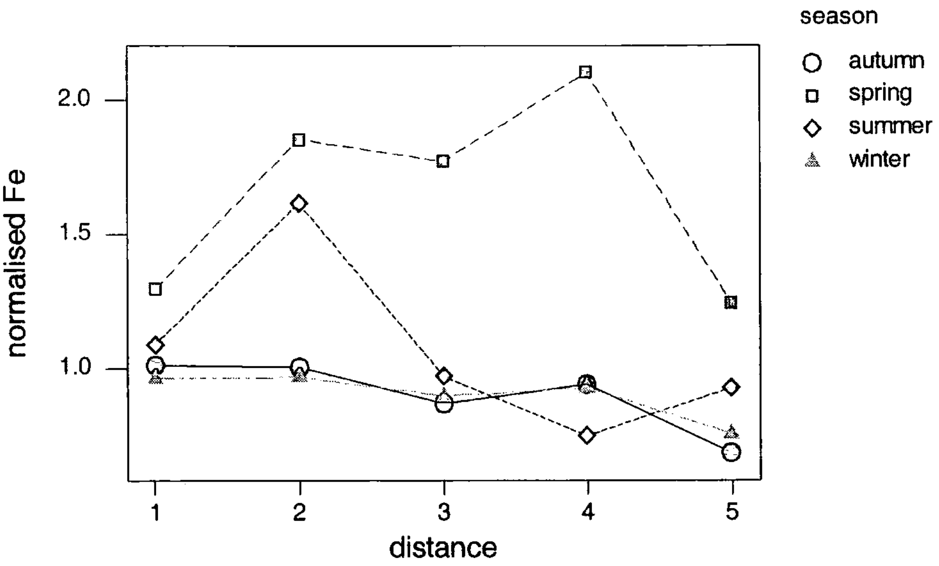


Figure 3.80. Interaction between season and distance effects on Fe (normalised data) within the Wansbeck impoundment (LS means).

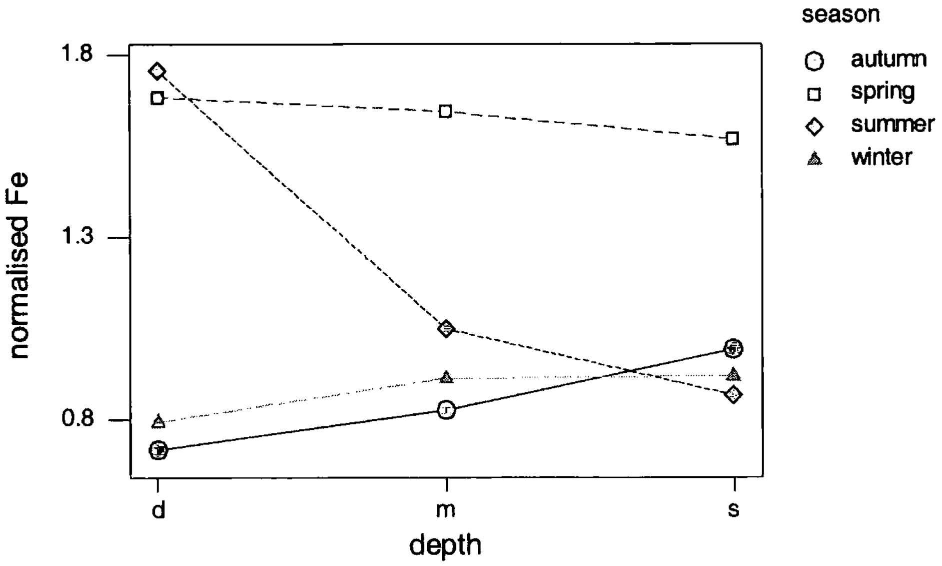


Figure 3.81. Interaction between season and depth effects on Fe (normalised data) within the Wansbeck impoundment (LS means).

Factor	Pairwise comparison	Adjusted P-value
Season	Spring - Autumn	0.000
	Summer - Autumn	0.000
	Winter - Autumn	0.976
	Summer – Spring	0.000
	Winter -Spring	0.000
	Summer – Winter	0.034

Table 3.41. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for Fe (normalised data) within the Wansbeck impoundment.

Season is a less significant factor for analysis using data normalised to the freshwater inputs compared to analysis with raw data (approximately 29 % as opposed to 66 % of the variance in the dataset). This implies that much of the variation in Fe concentrations in the Wansbeck with season are due to effects external to the impounded area. Relative to input values Fe levels are higher in spring and summer and lower in winter and autumn in the impounded area (figure 3.79). There is a general decrease in Fe with distance, although during spring and summer the distance pattern relates to the depth of the water column (i.e. is elevated at distance 2) (figure 3.80). As for raw data the pattern for depth effects is contrasting between the seasons (figure 3.81). During winter and autumn Fe decreases with depth, during summer Fe increases with depth and during spring it remains constant with depth.

Discussion

A large amount of the variation in concentrations of Fe is related to freshwater flow in the Wansbeck. There is a positive correlation between Fe concentration and flow, but the exact nature of this correlation differs between the seasons (figure 3.82). The greater rate of increase in Fe concentrations with flow during spring, summer and autumn relative to winter (as was observed for the Tees) suggests that temperature is important in controlling the near-surface availability of Fe (through humification and weathering processes). The higher flows experienced during autumn and winter sampling explain the higher average Fe concentrations in the Wansbeck impoundment during these periods. The maximum rate of increase of Fe concentration with flow in autumn probably relates to the flushing of dissolved organic carbon following the summer period (Evans et al., 1999).

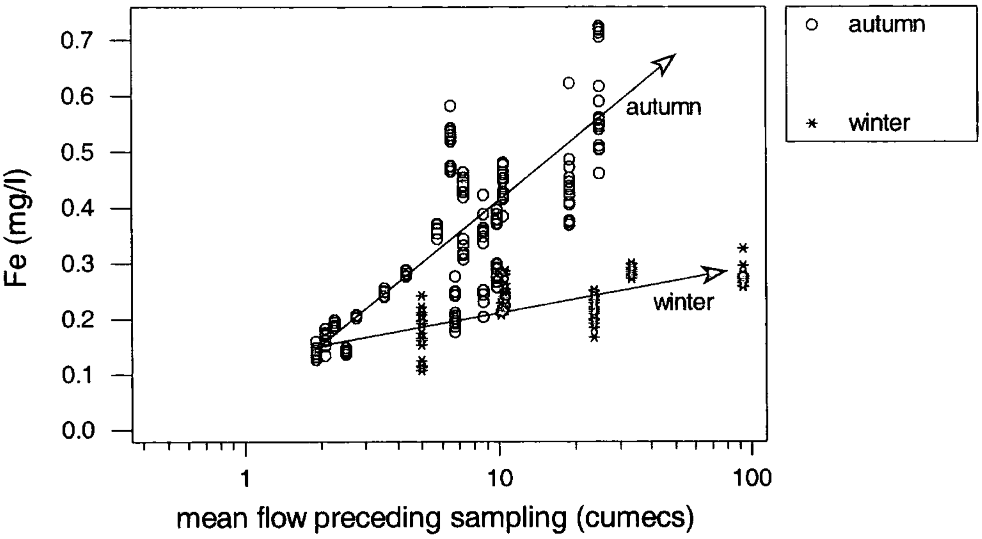


Figure 3.82. The differing relationships between Fe and flow in the Wansbeck impoundment between seasons.

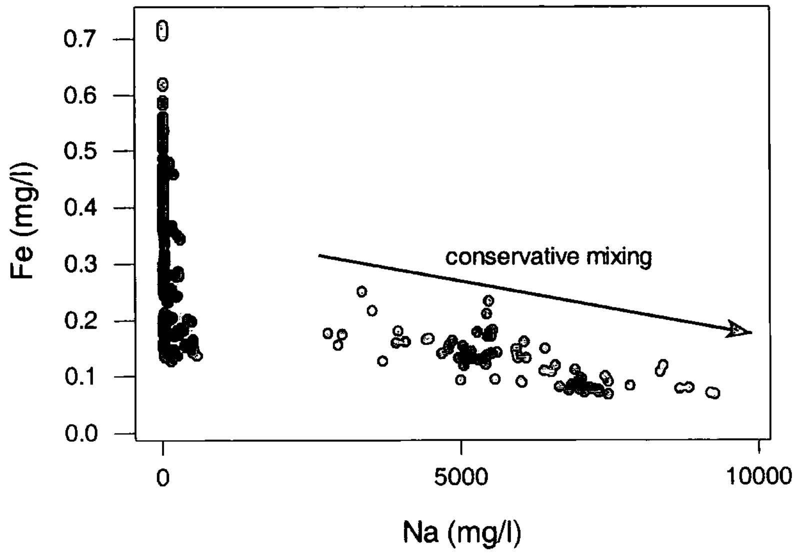


Figure 3.83. Conservative mixing behaviour of Fe in the Wansbeck impoundment during the autumn sampling period.

The internal variation in Fe concentrations also differs between seasons. Mean Fe levels in seawater are on average slightly lower than in freshwater (0.10 and 0.21 mg/l respectively for all sampling), and during winter and autumn the decrease in Fe levels with distance downstream and depth in the impoundment follows the pattern of seawater mixing (figure 3.83). During spring and summer under lower flow conditions the Fe concentration of the freshwater inputs to the impoundment relative to the concentration in seawater are lower, and release of Fe from sediment under anoxic conditions at depth (particularly at site CP), causes mean Fe concentration to increase with depth (figure 3.84).

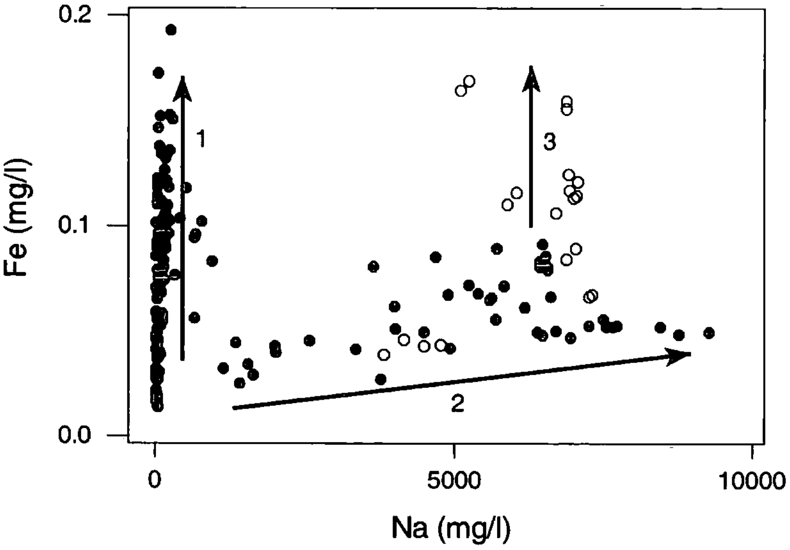


Figure 3.84. The controls on Fe during the spring sampling period in the Wansbeck impoundment. 1 represents the freshwater flow control, 2 represents the conservative mixing between seawater and freshwater, and 3 represents the release of Fe under anoxia from sediment. Open circles are samples collected at depth from site CP (distance 2).

3.3.6 Mn

Results

Source	F	P	σ2	Size of Effect (ω2)
Season	23.20	0.000	0.06	0.12
Distance	11.88	0.000	0.06	0.11
Depth	77.28	0.000	0.22	0.40
Season*distance	6.83	0.000	0.07	0.12
Season*depth	14.39	0.000	0.08	0.14
Error			0.06	0.12

Table 3.42. Results from GLM ANOVA for Mn (raw data) between seasons in the Wansbeck impoundment.

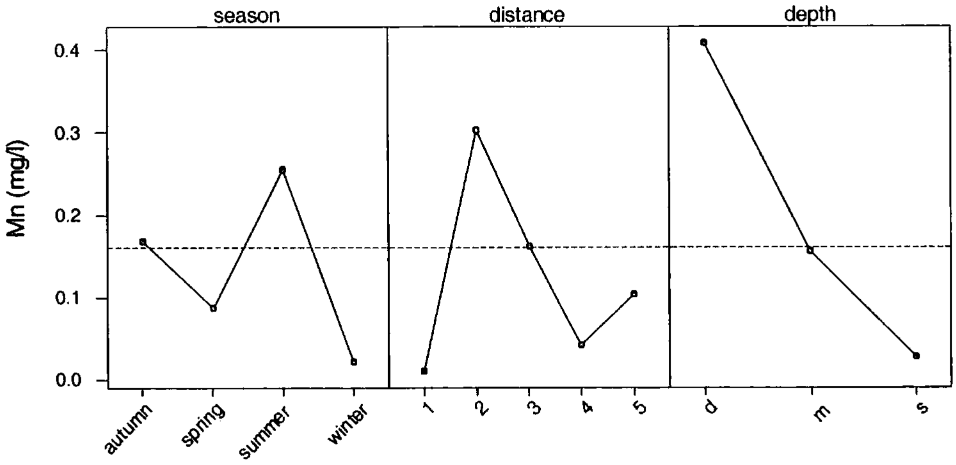


Figure 3.84. Main effects plot for the factors of season, distance and depth on Mn (raw data) in the Wansbeck impoundment (LS means for factor levels).

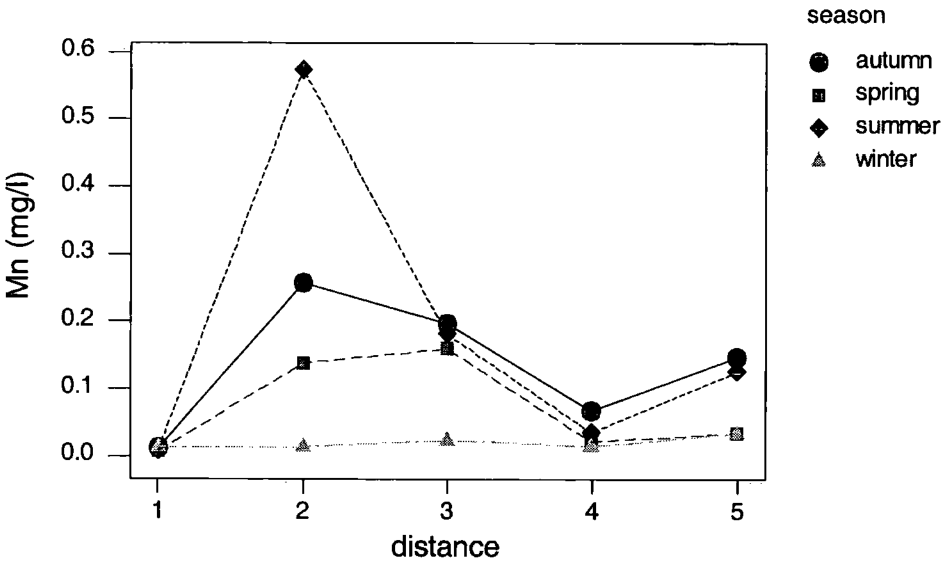


Figure 3.85. Interaction between season and distance effects on Mn (raw data) within the Wansbeck impoundment (LS means).

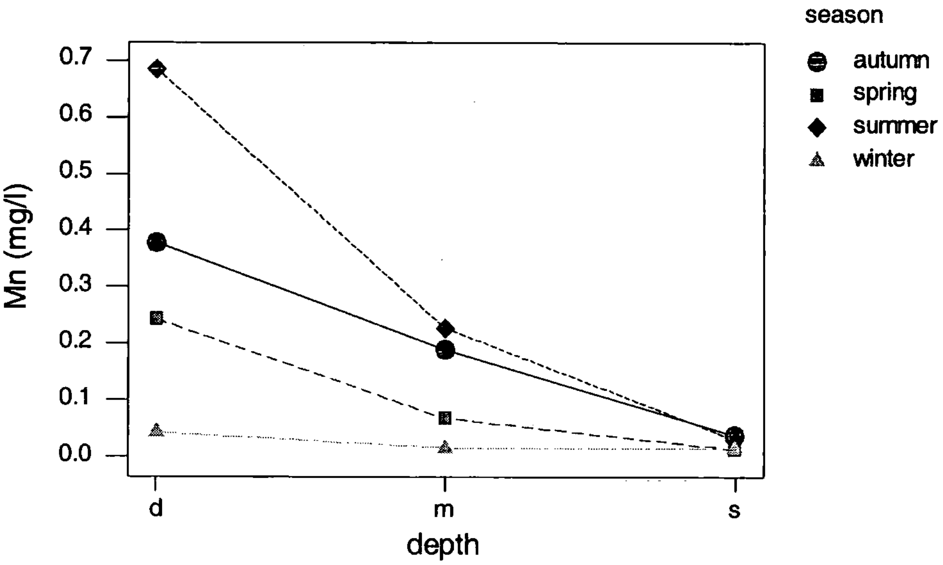


Figure 3.86. Interaction between season and depth effects on Mn (raw data) within the Wansbeck impoundment (LS means).

Factor	Pairwise comparison	Adjusted P-value
Season	Spring - Autumn	0.019
	Summer - Autumn	0.003
	Winter - Autumn	0.000
	Summer – Spring	0.000
	Winter -Spring	0.131
	Summer – Winter	0.000

Table 3.43. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for Mn (raw data) within the Wansbeck impoundment.

Mn levels in the Wansbeck impoundment are highest in summer and lowest in winter for the periods sampled (figure 3.84). The largest effect is that of depth, with Mn levels being significantly higher at depth than at the surface, and a distance pattern which reflects the true depths at each sampling site. The increase in Mn with depth is dependent on season, and is greatest in summer and least in winter (figures 3.85 and 3.86).

Source	F	P	σ2	Size of Effect (ω2)
Season	25.75	0.000	1402	0.13
Distance	11.66	0.000	1208	0.11
Depth	69.44	0.000	3879	0.35
Season*distance	8.31	0.000	1657	0.15
Season*depth	16.33	0.000	1738	0.16
Error			1275	0.11

Table 3.44. Results from GLM ANOVA for Mn (normalised data) between seasons in the Wansbeck impoundment (na = not applicable since factor insignificant at 95 % level).

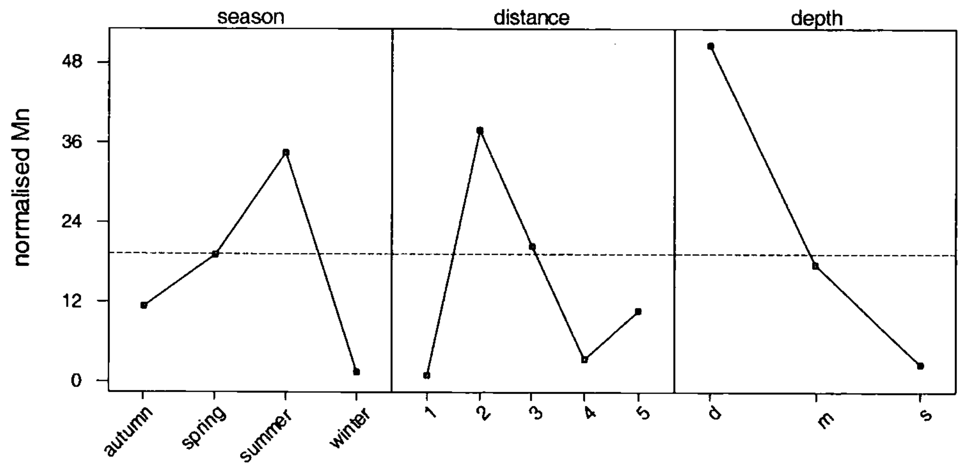


Figure 3.87. Main effects plot for the factors of season, distance and depth on Mn (normalised data) in the Wansbeck impoundment (LS means for factor levels).

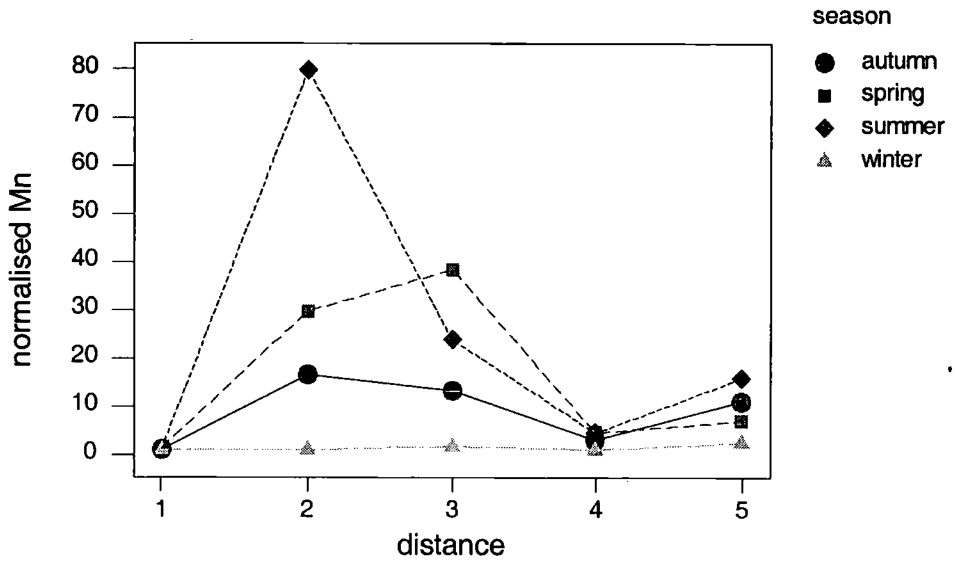


Figure 3.88. Interaction between season and distance effects on Mn (normalised data) within the Wansbeck impoundment (LS means).

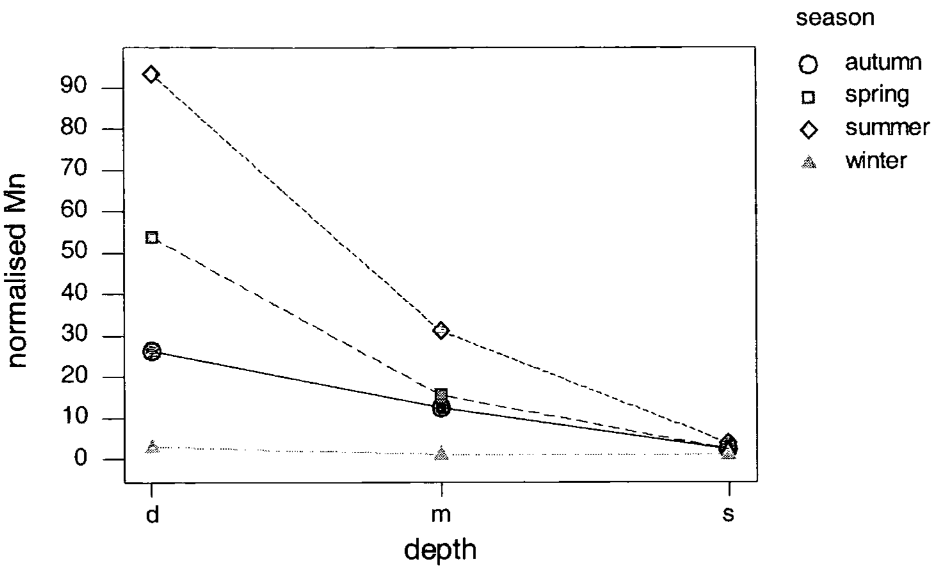


Figure 3.89. Interaction between season and depth effects on Mn (normalised data) within the Wansbeck impoundment (LS means).

Factor	Pairwise comparison	Adjusted P-value
Season	Spring - Autumn	0.051
	Summer - Autumn	0.000
	Winter - Autumn	0.096
	Summer – Spring	0.003
	Winter -Spring	0.000
	Summer – Winter	0.000

Table 3.45. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for Mn (normalised data) within the Wansbeck impoundment.

Since the freshwater input Mn values are consistently low the relative increases within the impounded area are large. The pattern of results using normalised data is similar to that using raw data (figures 3.87 and 3.88). Depth is the most significant factor and shows interaction with season (figure 3.89). Mn shows the maximum increase with depth in the summer sampling period, less in the spring, even less in the autumn, and virtually no increase with depth during the winter sampling period.

Discussion

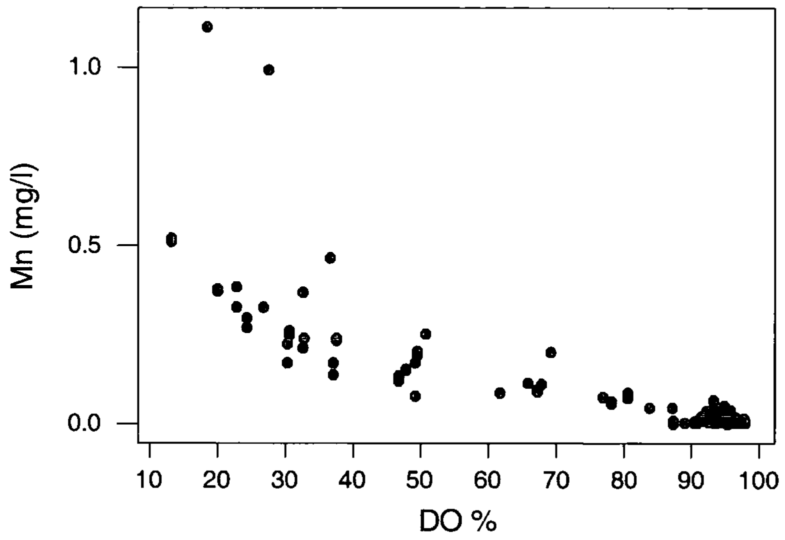


Figure 3.90. Mn vs. DO % from the spring sampling period on the Wansbeck.

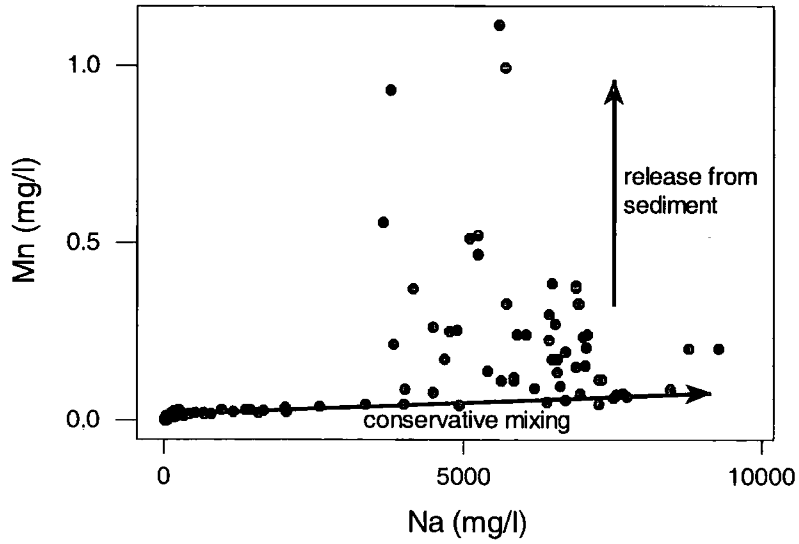


Figure 3.91. Mn vs. Na from the spring sampling period on the Wansbeck, showing the far greater impact of release of Mn from sediment on Mn concentrations than seawater

mixing. The points above the conservative mixing line are from depth at sites CP, RB and WB (distances 2, 3 and 5 in general linear model).

It is seen during comparison of barrage designs (chapter 4) that Mn release from sediment takes place during summer under redox conditions corresponding to approximately 50 % DO concentration in the water body (figure 3.90). Mn is also related to DO concentration during the other seasons, although Mn release is seen to take place at higher (< 90 %) DO % saturations. The Mn concentration in seawater is higher than in freshwater, but it can be seen that the difference is small relative to that of sediment releases (figure 3.91). Corresponding to the degree of oxygen depletion observed during the sampling periods, Mn releases are greatest during summer, lower in spring and autumn, and almost zero during winter (figure 3.92) when high flows act to remove the density stratification which allows low oxygen conditions to develop.

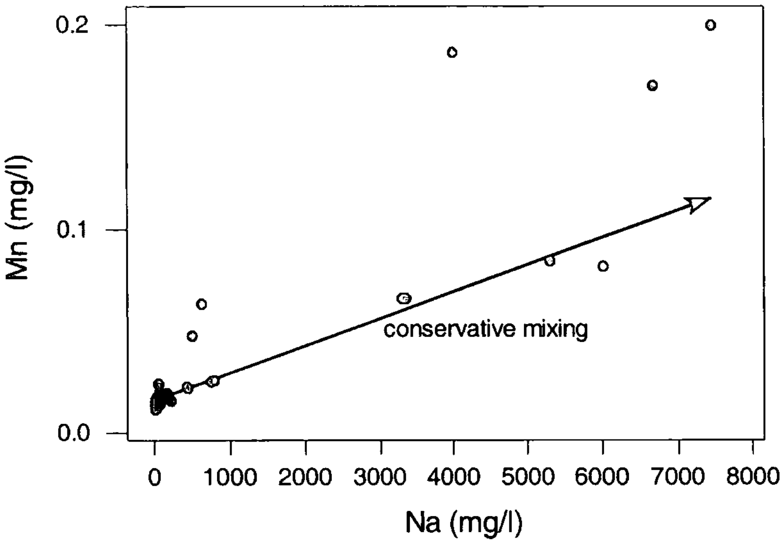


Figure 3.92. Mn vs. Na from the winter sampling period on the Wansbeck, showing that the majority of water sampled was fresh (and of very low Mn concentration) and that mixing between freshwater and seawater is generally conservative. A small amount of release of Mn from sediment occurs at sites RB and WB (points above the conservative mixing line).

3.3.7 Summary and conclusions

For all of the parameters assessed there are significant differences between seasons in the Wansbeck impoundment (table 3.46). Through comparison of the significance of seasonal differences for analysis carried out with raw data and data normalised to the freshwater inputs these differences were determined to be either mainly due to processing taking place internal or external to the impounded area (i.e. seasonal differences which may be affected by the construction of an estuarine barrage and those which are independent of the presence of a barrage). As discussed previously parameters which show variation internal to the impounded area are strongly related to density stratification of the water body. The impact of impoundment on saline stratification and the subsequent processing of water quality are explored in the following section of this chapter.

Parameter	**Varies with season**	**Major seasonal control (internal/external)**	**Major internal process**
DO	√	Internal	Respiration relative to re-oxygenation
pH	√	External	
Nitrate	√	Internal	Seawater/freshwater mixing
Ammonia	√	Internal	Decomposition of organic material and nitrate reduction
Fe	√	External	
Mn	√	Internal	Redox controlled release from sediment

Table 3.46. Summary of seasonal variation and controlling processes in the Wansbeck impoundment.

For the Wansbeck impoundment it is found that lowest water quality conditions (lowest DO, highest ammonia, maximum redox controlled release of Fe and Mn (and associated metals) from sediment, etc.) occur in summer, during which temperatures (and hence rates of reactions) tend to be highest and freshwater discharges (which may act to remove stratification of the water column) lowest. However, sampling shows that low water quality conditions may be encountered during the majority of the year in the Wansbeck impoundment (observed during both the March (spring) and September/October (autumn) sampling periods in addition to summer). This has important implications for management and remediation of partial tidal exclusion systems. Significantly any use of aerators (such as are installed in the Tawe impoundment) would need to function over most of the year. Only during winter are good water quality conditions generally maintained throughout the impounded area of the Wansbeck (in main due to high freshwater discharges acting to remove density stratification, although also temperature related).

In section 3.2 it was shown that for the (freshwater) Tees lower water quality conditions are also likely to be encountered during summer. Comparison of barrage design however showed there to be contrast between the behaviour of water quality within the impounded areas which did not relate to type of impoundment (in terms of partial or total tidal exclusion). It is likely therefore that the seasonal effects on water quality are also differ between individual impoundments, and it is recommended that assessments of the probable periods of low water quality are made on a case by case basis.

Chapter 4

Barrage Design and Water Quality

4.1 Introduction

An important question in the design and management of impounded estuaries is what differences in behaviour there are between systems which totally exclude any tidal intrusion and maintain a freshwater impounded area, and those which allow a proportion of high tides to overtop the barrage crest and whose impounded areas contain both fresh and saline water. The crucial question is which design maintains higher impounded water quality.

4.2 Identification of controlling factors through PCA

Initial determination that differences exist in the behaviour between total and partial exclusion impoundments, and preliminary identification of major controls on water quality, was carried out using principal components analysis (PCA).

Results

Initial PCA was carried out using a correlation matrix (as opposed to a covariance matrix) since parameters were measured on different scales, and included the water quality parameters of DO % saturation, pH, conductivity, alkalinity, nitrate, ammonia, phosphate, Ca, Fe, Mn, TSS and temperature. The strong covariance between Na, Ca, Mg, K and S (related to conservative mixing of fresh and seawater) meant that a single major ion (Ca) was used to represent the 5 ions. The minor and trace metals which were measured close to or below their LODs were excluded from the analysis. To ensure that a lack of data on TSS for some of the samples (due to the problems outlined in the section Overview of Data Collected) did not significantly affect the results, analysis was also carried out using transparency instead of TSS and found to give a similar pattern. The results are summarised in table 4.1 and 4.2 and figure 4.1.

Principal component	Eigenvalue	Proportion of variance	Cumulative proportion of variance
1	3.8125	0.318	0.318
2	1.7115	0.143	0.460
3	1.4186	0.118	0.579
4	1.1471	0.096	0.674
5	0.9136	0.076	0.750
6	0.7531	0.063	0.813
7	0.6268	0.052	0.865
8	0.5217	0.043	0.909
9	0.4109	0.034	0.943
10	0.3496	0.029	0.972
11	0.2649	0.022	0.994
12	0.0696	0.006	1.000

Table 4.1. Eigenvalues and proportions of variance for the principal components calculated for PCA carried out for all data collected from the impounded estuaries studied.

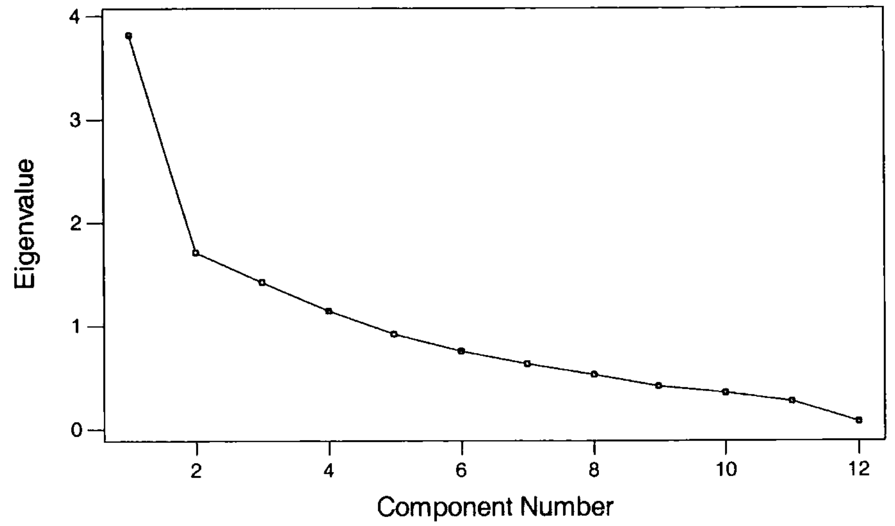


Figure 4.1. Scree plot of eigenvalues for principal components calculated for PCA carried out for all data collected from the impounded estuaries studied, showing a large amount of variance explained by the 1^{st} principal component relative to subsequent components.

As can be seen in table 4.1 and figure 4.1, the 1st principal component (PC1) contains a large amount of the variance in the dataset (32 %) relative to subsequent components. The subsequent decrease in eigenvalues for components is gradual, implying that several processes are acting to control the water quality parameters or that parameters behave independently. A weakness of PCA, however, is that no tests of significance are applied to the principal components, and so assessment of the importance of components is subjective.

Variable	PC1	PC2	PC3	PC4
DO %	**-0.366**	0.091	0.066	-0.391
pH	-0.219	0.163	**0.572**	-0.112
conductivity	**0.442**	-0.016	0.181	-0.123
alkalinity	0.080	**0.427**	**0.499**	-0.038
nitrate	**-0.297**	-0.050	0.297	**0.545**
ammonia	**0.373**	-0.019	0.152	-0.031
phosphate	-0.009	**0.422**	-0.174	**0.626**
Ca	**0.439**	-0.014	0.243	-0.015
Fe	-0.150	**-0.335**	-0.104	-0.120
Mn	**0.388**	-0.105	-0.040	0.137
TSS	0.062	**-0.509**	0.138	0.293
temperature	0.141	**0.468**	-0.393	-0.099

Table 4.2. Coefficients for water quality parameters for the first 4 principal components calculated for PCA carried out for all data collected from the impounded estuaries studied.

Coefficients for the first 4 principal components (accounting for 67 % of the variance in the dataset) are shown in table 4.2. Only the principal components with eigenvalues > 1 are selected for discussion. PC1 contrasts the levels of DO and nitrate with conductivity, Ca, ammonia and Mn (the coefficients for these two sets of parameters have opposite sign and are not close to zero). As mentioned, the size of PC1 in terms of the amount of variance it explains is much greater than the subsequent components. PC2 contrasts alkalinity, phosphate and T to Fe and TSS. PC3 shows a range in values for the coefficients between parameters, with pH and alkalinity showing strong positive relation to this component. PC4 also shows a range of coefficients, with nitrate and phosphate showing the strongest correlation. The smaller amount of variance (eigenvalues < 1) explained by subsequent components means that consideration of their relationships and interpretation is not carried out.

Discussion

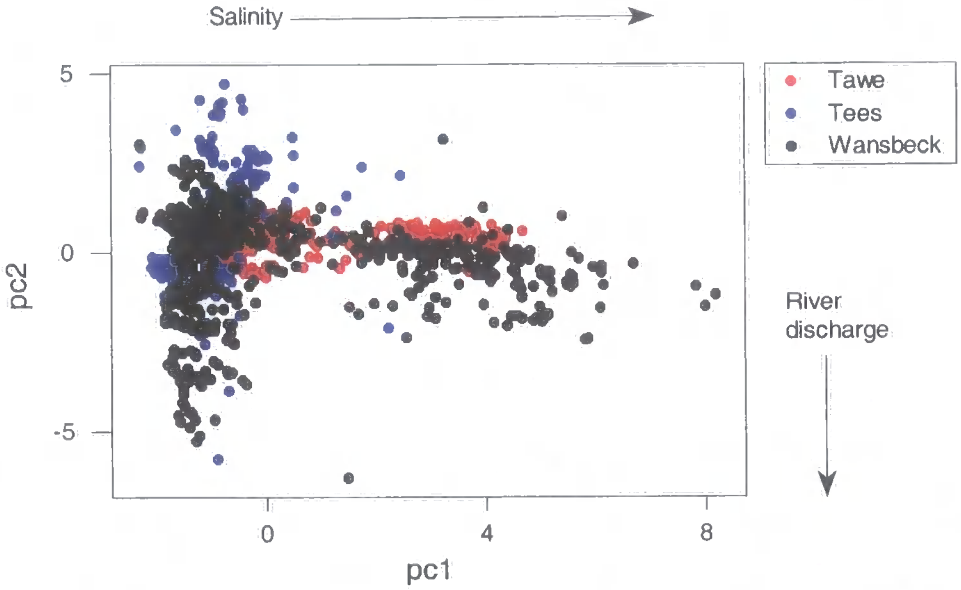


Figure 4.2. Principal component scores for 1st and 2nd principal components showing contrasting control of saline stratification and river discharge on the Tees, Tawe and Wansbeck impoundments.

Plotting scores for PC2 against PC1 (figure 4.2) shows that the 3 impoundments studied show both similar and contrasting behaviours. PC1 contrasts the levels of DO and nitrate with conductivity, Ca, ammonia and Mn, and can be interpreted as representing both the amount of and the processes associated with saline intrusion to the impounded area. Conductivity and Ca are fairly well correlated (Ca = 42.5784 + 0.0054213 conductivity; S = 38.3142, R-Sq = 82.7 %) and, due to the large difference in the ionic strength between fresh and seawater, can be taken as a measure of salinity of the water sample. The salinity of the water shows a subsequent control (through stratification) on

DO and ammonia/nitrate as discussed below. Hence data from the Tawe and Wansbeck (partial exclusion) impoundments show a spread of values along this axis due to the saline water entering the system, whilst Tees data generally plots at below zero and does not trend along PC1. Since PC1 relates to the input of seawater to the systems it understandably explains a much larger amount of the variance in the whole dataset than the subsequent components. The Tawe and Wansbeck data also group slightly into positive and negative scores along this axis, which may be interpreted as distinct saline and freshwater bodies respectively. Detailed conductivity depth profiles carried out on several occasions showed there to be strong salinity (density) stratification in the partial exclusion water bodies.

In addition to showing relative amounts of seawater in the impoundments, PC1 includes variance in parameters due to processes associated with seawater intrusion. For example DO was observed to be generally at near 100 % saturation in the fresh/surface waters of the Wansbeck impoundment, but was often depleted at depth in saline water (down to 0.0 %), associated with isolation from the atmosphere (the source of re-oxygenation) and contact with oxygen demanding sediments of the bed. Low DO concentrations in turn control the amount of ammonia vs. nitrate in the water, and the release of Mn from the sediment, as noted for summer in the Tees in the section on Seasonal Effects. The high coefficients for these parameters on PC1 are likely to represent this series of relationships. Indeed the scatter of points from the Tees impoundment (which contains virtually no seawater) above 0 on the PC1 axis is of values of low (< 30 %) DO, and increased ammonia (> approximately 0.30 mg/l) and Mn (> approximately 0.10 mg/l).

PC2 contrasts alkalinity, phosphate and T with Fe and TSS, such that increasing values of PC2 relate to increased alkalinity, phosphate and T, and decreased Fe and TSS. As can be seen on figure 4.2, there is a large amount of scatter in the scores for the water samples on this component, particularly in freshwater samples (low scores on PC1). The spread of data along PC2 is seen to relate quite closely to freshwater flow (discharge) for each of the impoundments, such that higher discharges give lower scores on this component. PC2 is therefore interpreted as relating to the freshwater flow controlled water quality parameters in the impoundments. For example, alkalinity is seen to decrease with increasing freshwater flow into the impoundments (figure 4.3), and Fe is seen to increase (figure 4.4).

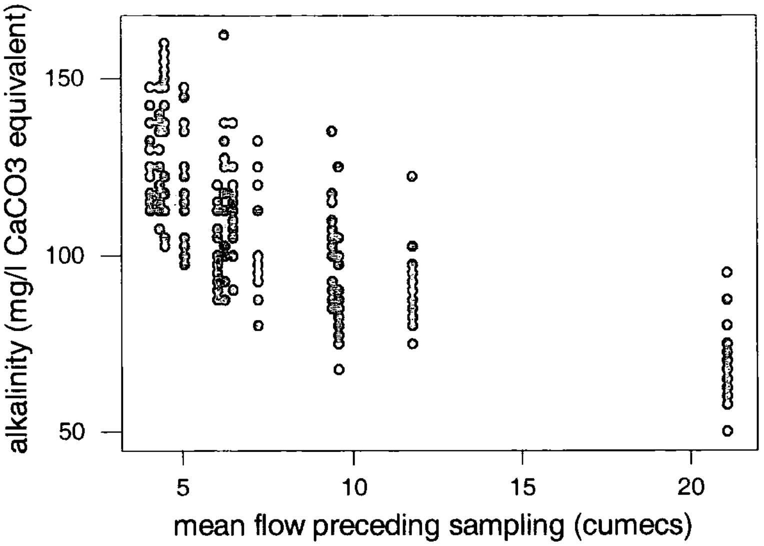


Figure 4.3. Decreasing alkalinity with increasing freshwater flow for the Tawe impoundment, related to dilution of baseflow component by increasing stormflow.

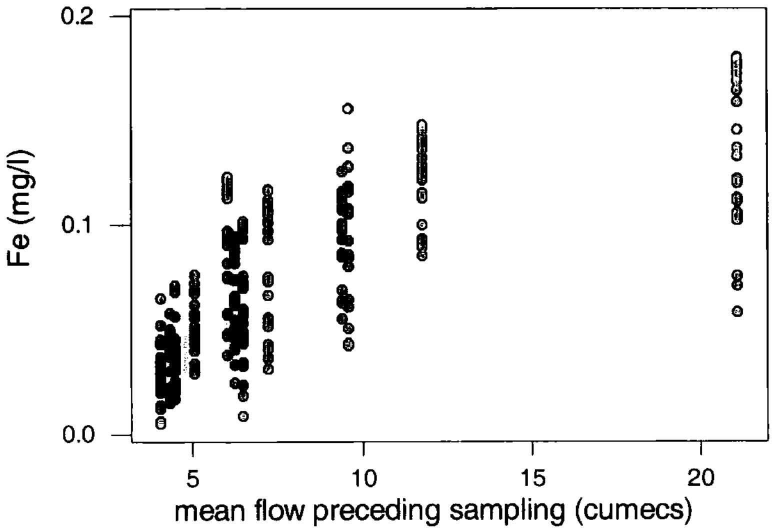


Figure 4.4. The positive relationship between Fe concentrations and freshwater flow in the Tawe impoundment. Fe is assumed to have a diffuse/surface or near-surface source (perhaps organic associated)

The two main controls on the water quality parameters included in the PCA can thus be interpreted as the amount of saline water and/or stratification and internal processing in the systems (by a long way the largest control), and the flow-controlled freshwater (external or catchment controlled) inputs to the systems. The Tees shows lower variation in scores on PC1 than the two other impoundments since it is an entirely freshwater impoundment, and the Tawe shows lower variation on PC2 since it was sampled under a lower range of flow conditions (for a 12 day period in summer only).

Scores for the 3rd and 4th principal components are shown in figure 4.5. The 3rd principal component shows high coefficients for pH and alkalinity (0.572 and 0.499 respectively). Water samples from all of the impoundments show a general relationship between higher scores on this component and higher pH or alkalinity. This is an interesting pattern to observe, since the pH and alkalinity variation are assumed to be independently sourced. Regression analysis for the relationship between pH and alkalinity for the whole dataset included in the PCA reveals that these two parameters are not strongly related (R-Sq = 7.1 %), implying independent relationships to PC3 (i.e. PC3 is related to either pH variations at similar levels of alkalinity, or alkalinity variations at similar pHs). On specific dates and at specific sites in which significant amounts of organic decomposition are taking place, alkalinity and pH are seen to be negatively correlated (figure 4.6). pH is largely controlled by the partial pressure of carbon dioxide in the water, such that an increase in CO_2 concentration due to respiration leads to an increase in hydrogen ion concentration and hence decreased pH (Mortimer, 1971; Maberly, 1996; Neal et al., 2002). As noted previously, the majority of variance in alkalinity is related to variation in freshwater flow. Additional variance may be sourced from, in addition to biological effects, difference between the alkalinity of freshwater and seawater inputs to the impoundments, and variations in freshwater source based on distribution and pattern of rainfall within the catchment, variations in contribution from groundwater based on height of the piezometric surface, etc.

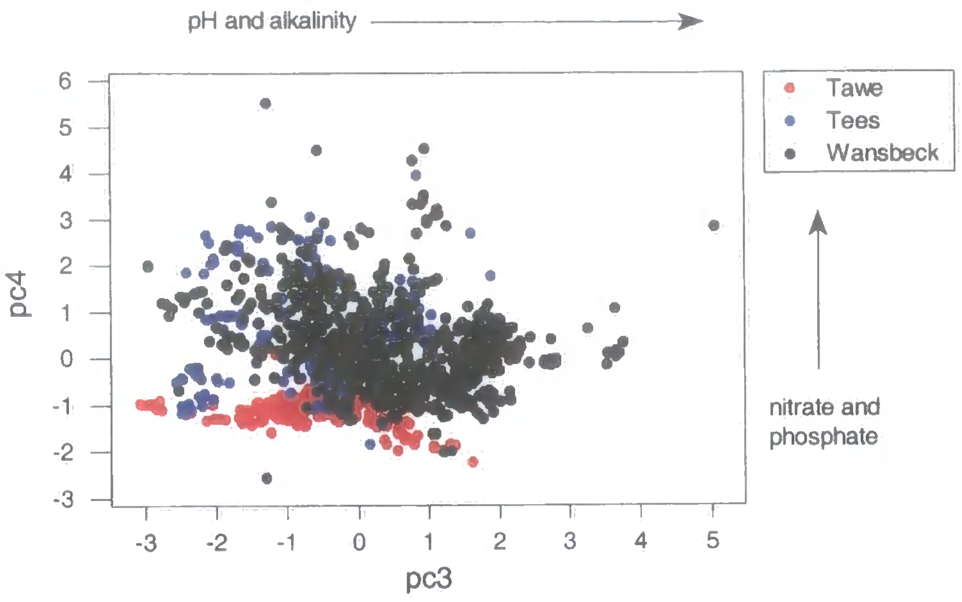


Figure 4.5. Principal component scores for 3rd and 4th principal components, showing internal (respirative) control on pH and alkalinity within all the impoundments, and a contrast between nutrient levels and behaviours between the impoundments.

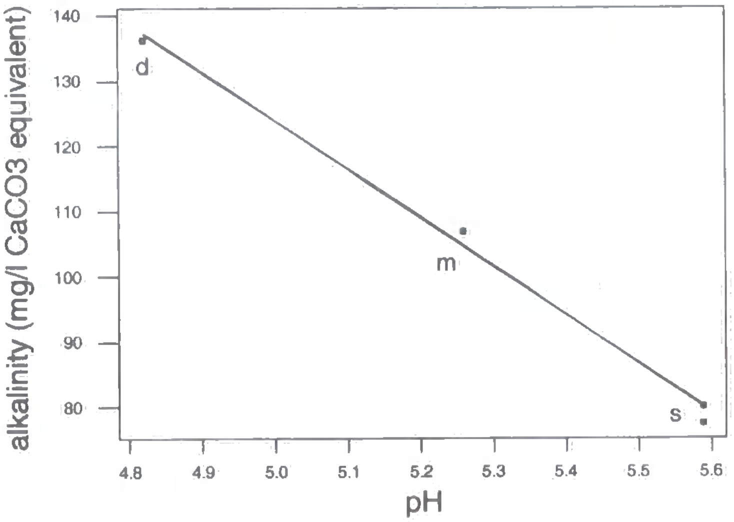


Figure 4.6. pH and alkalinity at site CP (deepest point) in the Wansbeck impoundment from 11th June 2001. The relative amounts of production vs. respiration in the water column, and sediment-water exchanges, at different depths within the stratified water column lead to variations in the pH and alkalinity of the water samples. s = shallow, m

= mid-depth, and d = deep water sampling (corresponding to depths of 0.00, 2.44 and 4.88 m depth in the water column). Replicates were taken and are plotted at each depth. (R-Sq = 99.4 %, R-Sq(adj) = 99.3 %).

The 4th principal component has strong coefficients for nitrate and phosphate. Generally an increase in score on this component relates to an increase in levels of these nutrients in the water sample. This component is interpreted as representing the general level of nutrient input to the systems. Nutrient values show a large amount of variation due to a combination of factors which probably include freshwater flow, seawater vs. freshwater concentrations, seasonal variations in catchment vegetation and fertiliser application, variation in point source inputs including CSOs, and a range of differences between the rivers. Whilst PCA can give a general grouping of variables and imply similar underlying controls, it does not lend itself to the identification of or the breakdown of the significance of controls. As for PC2 the Tawe, which was sampled over a lower range of conditions, shows less variation in its scores on this component than do the Tees and Wansbeck impoundments.

4.3 Behavioural differences between impoundments

The PCA carried out above suggests a number of factors act to control water quality in the impoundments, including the influence of seawater and stratification in the water body, flow related freshwater inputs, internal biological controls, etc. In addition PCA has allowed qualitative comparison of the extent of these factors in each of the impoundments, and enabled suggestion of the groups of underlying processes acting to control water quality parameters. More detailed investigation of the differences in behaviour between the impoundments, and quantitative testing of the significance of factors is carried out through ANOVA.

The significance of the factors of river (used interchangeably with the term impoundment), distance (as sampling sites at 5 distances in each of the impounded areas), and depth in the water column sampled (shallow (s), mid-depth (m) and deep (d)) were determined for a selection of water quality variables using general linear modelling (GLM) ANOVA. Note that both distance (1 to 5) and depth (s, m and d) vary in real (km and m) terms between the impoundments (e.g. the Tees is a bigger river in terms of length and depth of impounded area than the Tawe and Wansbeck). For the Tees and the Tawe data from one of the sampling sites from each (site LM and S respectively, see chapter 2) was excluded from the analyses to give an equal number of sample distances (5 distances) for all impoundments. The interactions between river and depth and river and distance were also examined to determine whether distance and depth effects varied between impoundments. Season was not included as a factor since the seasons sampled differed between impoundments (the Wansbeck was sampled in spring, summer, autumn and winter, the Tees in summer and winter, and the Tawe in summer alone). Only data from the summer periods of sampling on each river were included in the analyses. For the Tees the dates included were 21st July, 4th 11th and 25th August and 8th and 22nd September 1999, for the Wansbeck the dates included were the 4th to 18th June 2001, and for the Tawe the 10th to 21st June 2000. Although a longer period was sampled in summer in the Wansbeck (up to 24th June), during the latter part of this period the impoundment was drained by opening the navigation lock gates in the barrage in an attempt to remove bed sediment and so this data is not included in the modelling. The effects of draining and refilling on water quality are discussed elsewhere (Lamping, PhD Thesis). The seasonal variations in water quality in total and partial tidal exclusion impoundments are discussed in chapter 3. A crossed model was specified. Size of effects are calculated and reported, and the significance of differences between means (hypothesis testing) for the factor level of was carried out using the Tukey method of multiple comparisons.

To enable comparison of the importance of external (catchment) controls and internal (within the impounded areas) processing on water quality, several analyses were carried out using both raw data and data normalised to the values entering the impounded areas at the upstream limits. For those parameters showing markedly different values for fresh and seawater (conductivity, Na, Si, etc.) analysis was with raw data only.

4.3.1 Dissolved oxygen

Results

Initial ANOVA was carried out on raw data for levels of DO % saturation in the impoundments during the periods of water quality survey. % saturations as opposed to mg/l values were used to normalise against the effects of temperature changes within the sampling periods. The results show that all factors included in the model have a significant effect on DO % levels (table 4.3). The effect of river explains approximately 31 % of the variation in DO levels, with significant differences between all 3 impoundments. Mean levels are highest in the Tawe and lowest in the Wansbeck (figure 4.7). There are significant differences in DO with depth in the impoundments accounting for 28 % of the variance, with levels generally decreasing with depth. However the depth effect varies between impoundments (river*depth interaction (ω^2 = 0.17)), with greater depth effects in the Wansbeck than in the Tawe or Tees (figure 4.8). Distance shows a small but significant effect and shows contrasting behaviour between the impoundments, with a consistent decrease with distance in the Tees (figure 4.9).

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
River	89.69	0.000	1250	0.31
Distance	4.66	0.001	103	0.03
Depth	81.61	0.000	1136	0.28
River*distance	11.24	0.000	577	0.14
River*depth	25.59	0.000	693	0.17
Error			317	0.08

Table 4.3. Results from GLM ANOVA for DO % (raw data) in partial and total tidal exclusion impoundments.

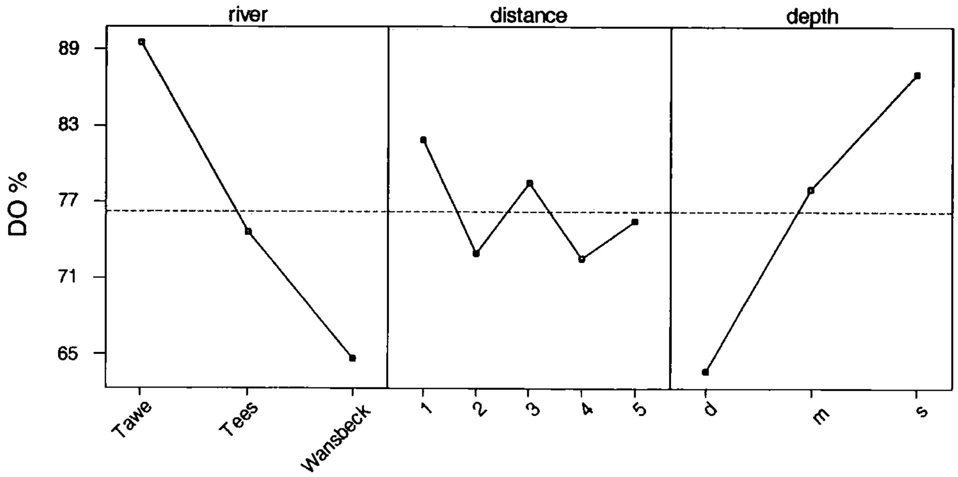


Figure 4.7. Main effects plot for the factors of impoundment (river), distance and depth on DO % (raw data) (LS means for factor levels).

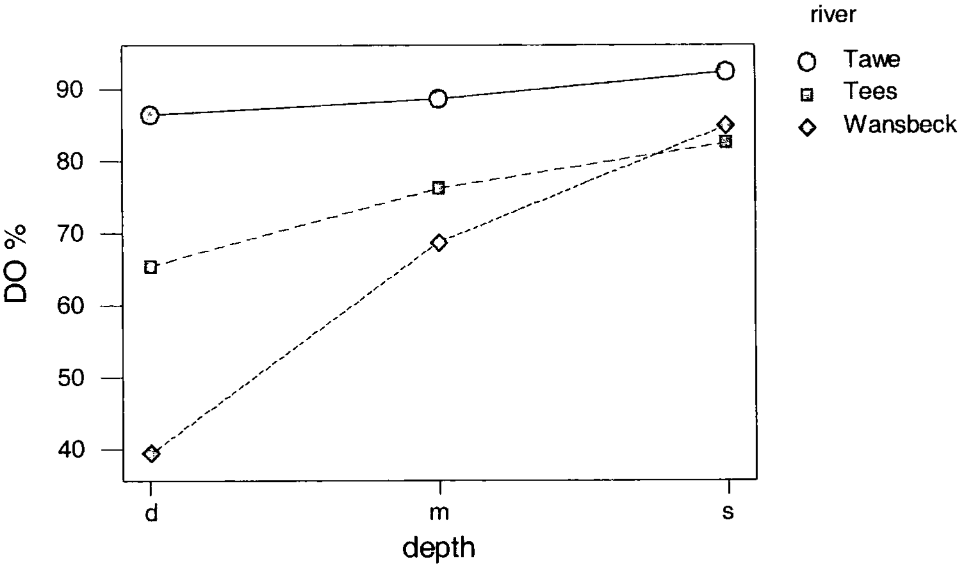


Figure 4.8. Interaction between river and depth effects on DO % (LS means).

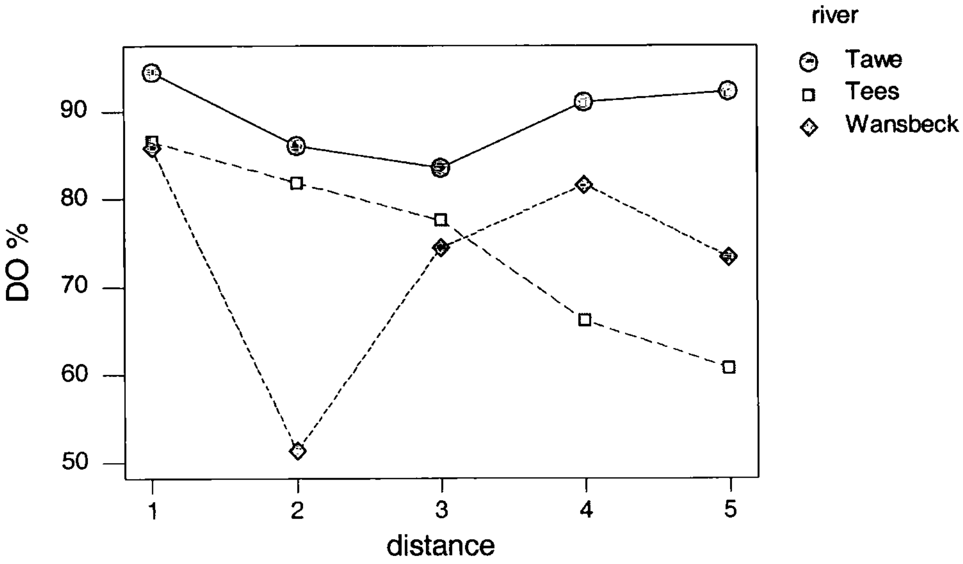


Figure 4.9. Interaction between river and distance effects on DO % (LS means).

Factor	Pairwise comparison	Adjusted P-value
River	Tees - Tawe	0.000
	Wansbeck - Tawe	0.000
	Wansbeck - Tees	0.000

Table 4.4. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for DO % (raw data) in partial and total tidal exclusion impoundments.

The results reported above for ANOVA carried out on the raw DO % values show that the largest effect is that of river. They do not however distinguish between the impact that is related to, for example, differences in catchment and those which relate to internal (within the impounded area) processing of DO. In order to aid in this distinction, ANOVA was repeated for DO % values normalised to the values of DO % in the freshwater samples entering the impounded areas at the upstream ends for each of the sampling dates (i.e. results were divided by the upstream input value for that days sampling). Thus, DO is given as a proportion of these input values (such that a value greater than 1 represents an increase in DO and a value of less than 1 represents a decrease).

Source	F	P	σ^2	Size of Effect (ω^2)
River	48.55	0.000	0.078	0.16
Distance	5.17	0.000	0.014	0.03
Depth	103.00	0.000	0.168	0.34
River*distance	13.10	0.000	0.080	0.16
River*depth	36.78	0.000	0.118	0.24
Error			0.037	0.07

Table 4.5. Results from GLM ANOVA for DO % (data normalised to freshwater inputs) in partial and total tidal exclusion impoundments.

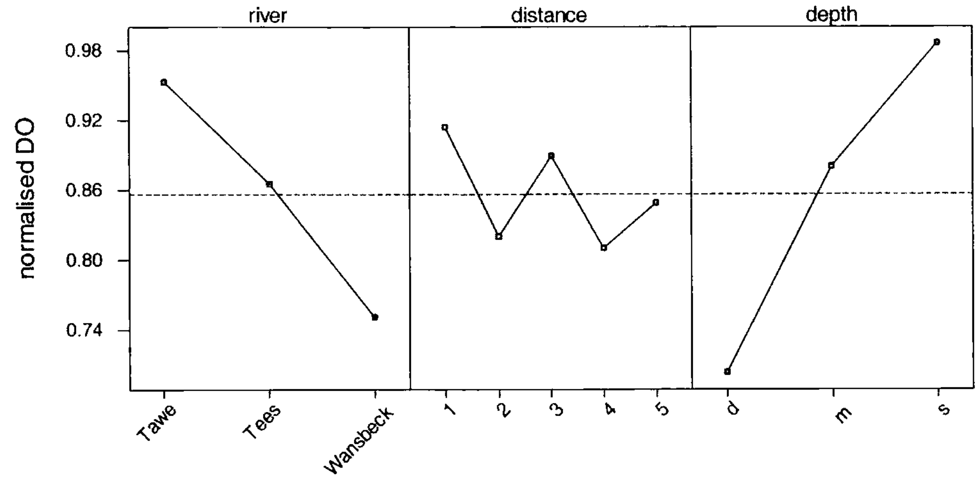


Figure 4.10. Main effects plot for the factors of impoundment (river), distance and depth on DO % (data normalised to freshwater inputs) (LS means for factor levels).

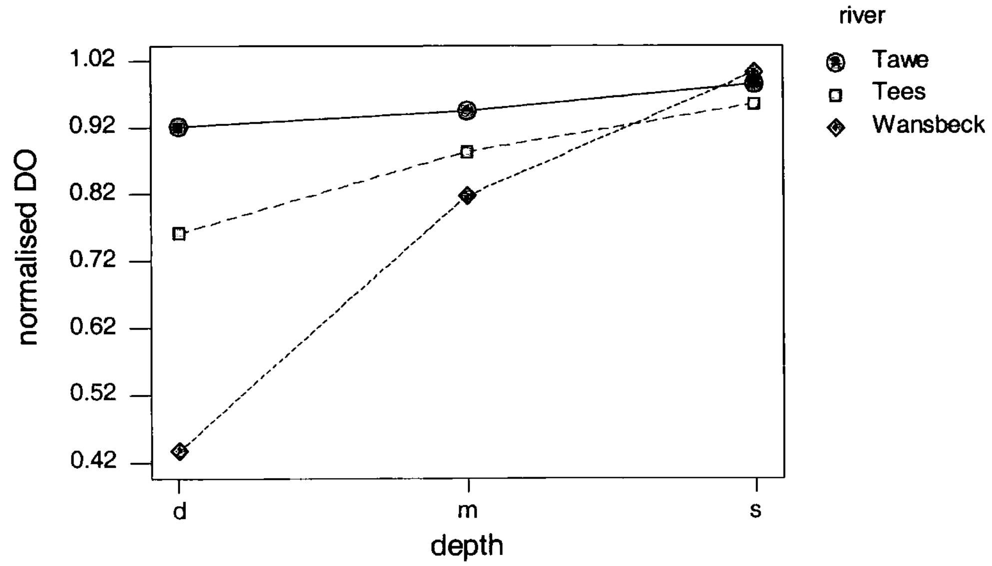


Figure 4.11. Interaction between river and depth effects on DO % (data normalised to input values) (LS means).

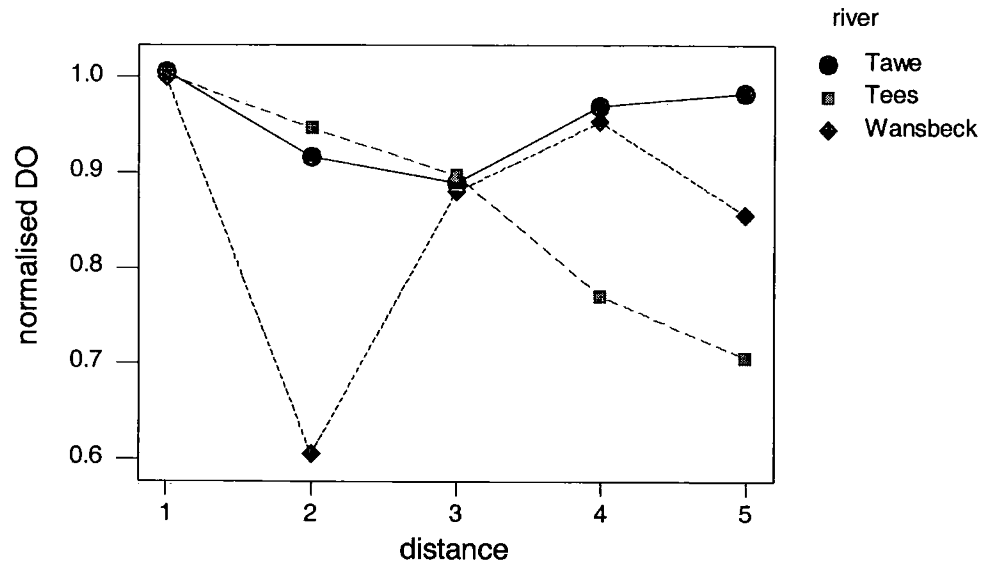


Figure 4.12. Interaction between river and distance effects on DO % (data normalised to input values) (LS means).

The results (tables 4.5) show that river is a less significant effect when data are normalised to input values. The depth and river*depth and river*distance interactions show very similar sizes of effect and patterns of interaction for both raw and normalised data (figures 4.10, 4.11 and 4.12; i.e. DO levels decrease with depth, to a greater extent in the Wansbeck than the Tees or Tawe). Generally the results for DO are similar for raw and normalised data since the input values were relatively consistent (around 90 % saturation) for all rivers and sampling dates.

Discussion

The effect of river on levels of DO in the impoundments can be looked at in two ways. Firstly there is the difference in levels of DO relating to differences in DO concentration in the waters (fresh and saline) entering the impounded areas. Secondly there is the difference in levels of DO relating to differences between systems in the amount of internal processing within the impounded areas. Both of these effects are important in allowing prediction of water quality in estuarine impoundments, although in a sense the internal processes are of greater interest since they show the effect of construction of a barrage and the difference between designs of impoundment. The comparison of results from ANOVA carried out on both raw and normalised DO data is an approach (albeit a simplified one in that it only takes into account variation in the freshwater entering the impoundments) to distinguish the two effects of river.

For the analysis of raw DO data, there is a significant difference between all three rivers, with higher mean DO % in the Tawe than the Tees than the Wansbeck (mean values during the summer sampling periods are 89.2, 74.8 and 68.8 % respectively (note % saturations are based on freshwater saturation values and no salinity corrections are applied). Since there is no significant difference between input values of DO between the 3 impoundments (mean values of 93.9, 86.3 and 85.9 % respectively (one-way ANOVA gives $P = 0.574$)), and the pattern of depth and distance effects similar for raw and normalised data, it is clear that internal (within the impounded area) variation in DO is more important than external (upstream of the impounded area) variation. Mean DO in the Tawe is approximately 95 % of the input value, in the Tees it is 87 % of the input value, and in the Wansbeck it is 81 % of the input value. Therefore, higher water quality in terms of DO is maintained in the Tawe than the Tees than the Wansbeck. It is interesting to note the difference in behaviour does not depend on barrage design in terms of partial or tidal exclusion.

It is important to emphasise that results are in terms of mean levels of DO and do not show (apart from in their effect on the means) the outlying low values of DO which occur in all three impoundments. Minimum values for DO encountered in the impoundments (all in deep samples) are 21.5, 15.1 and 0.0 % (or 2.26, 1.49 and 0.00 mg/l) for the Tawe, Tees and Wansbeck respectively. Of particular note is that although the Tawe shows a high mean DO level, the low values encountered at depth have been considered important enough for Swansea City Council to install a series of aerators to re-oxygenate and mix the water. The success of remediation schemes on dissolved oxygen levels in the Tawe are analysed in detail as another topic of the SIMBA project (Lamping, 2003).

The distance effect is small relative to other factors, and the DO variation with distance in the impounded area varies between impoundments. The Tees shows a clear relationship between DO concentrations and distance downstream in the impounded area (see chapter 3 and figure 4.13). In winter DO % does not vary significantly with distance, but in summer there is a decrease in mean DO levels according to:

$$\text{Mean DO \%} = 85.9 + 0.508\ \text{distance} - 0.0573\ \text{distance}^2$$

(S = 0.422017 R-Sq = 99.9 % R-Sq(adj) = 99.8 %).

This decrease in DO during summer is related to the amount of de-oxygenation by decomposition of organic matter exceeding the amount of re-oxygenation from the atmosphere, associated with a decrease in flow velocities and possibly the change in nature of the bed sediments to more organic rich material with distance downstream. As mentioned previously, no evidence is seen of an increase in the levels of BOD with distance downstream. No oxygen depletion occurs in winter since rates of biological respiration are lower and higher flows ensure turbulence and re-oxygenation of the water column. Neither the Wansbeck nor the Tawe shows any significant correlation between DO and distance (figure 4.14, R-Sq(adj) = 0.0 %), although it must be noted that the length of river sampled (the impounded section) is much shorter than for the Tees, and the differences in mean DO levels with distance relate to the depth effects discussed below.

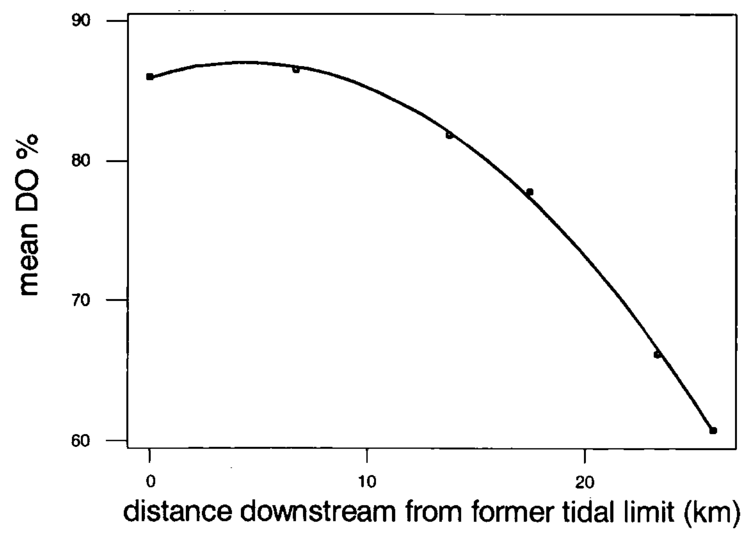


Figure 4.13. Fitted line plot for the quadratic relationship between DO % and distance downstream in the Tees impoundment (summer data only).

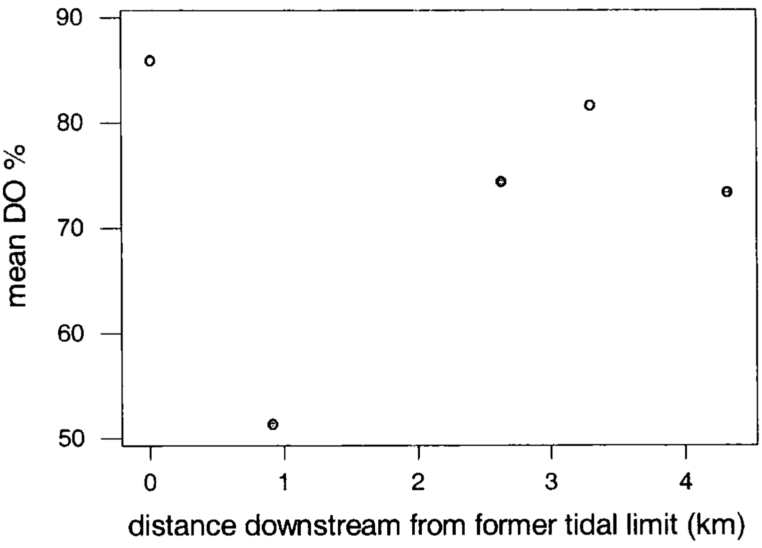


Figure 4.14. DO % and distance downstream in summer in the Wansbeck impoundment. Variation in mean DO % levels with distance relates to differences in depth between sampling sites.

There are significant differences in DO between the three depths sampled in each of the impoundments. It was noted during the PCA and within the section on seasonal effects that DO internal processing is depth related. This internal processing is related to thermal or salinity stratification of the water bodies, leading to isolation from the atmosphere and prolonged contact with oxygen demanding bed sediments. The presence of stratification and low DO conditions over the majority of the year is demonstrated statistically in this project for the Wansbeck, and has also been recorded in the Tawe (Swansea City Council, pers. com.), more research is needed to determine the proportion of time the Tees is subject to stratification. It is felt that since stratification in the Tees is solely due to thermal density differences then the periods of stratification are likely to be shorter and the energy (freshwater flow) required to mix the water body lower. The density of pure water is at a maximum of 1.000 g/ml at approximately 4°C and decreases non-linearly with increasing temperature to 0.998 g/ml at approximately 20°C (Vallentyne, 1957), whilst density increases linearly with increasing salt content to a mean seawater (35 ‰) value of 1.028 g/ml at 4°C (Ruttner 1963).

The interactions between river and depth (again very similar for raw and normalised data) show that the amount of stratification is similar for the Tees and Tawe and greater for the Wansbeck during the periods of sampling. Mean DO levels are reduced to about 90 % of input values at depth in the Tees and Tawe, and 60 % in the Wansbeck, whilst the surface water in all the impoundments shows no reduction in DO in any of the impoundments. There are several possible reasons for the difference in stratification behaviour between the rivers including differences in depths in real terms between impoundments, length of time deep water is isolated from 'fresh' (oxygenated) seawater, length of time between overturning by high freshwater flows, amount of oxygen demand in the water (BOD), and oxygen demand from the sediment. Analysis shows that the length of time water is isolated from sources of re-oxygenation is an important factor:

The maximum oxygen depletion with depth is encountered at site CP (distance 2, 0.92 km downstream from the tidal limit in the Wansbeck). In addition to being the point of maximum depth in the Wansbeck impoundment (approximately 5 m), this site allows ponding of saline water introduced by the highest tides overtopping the barrage crest behind shallower downstream sections of the impoundment (shown schematically in figures 4.15 and 4.16). This saline water at depth becomes isolated from both the atmosphere and 'fresh' (oxygenated seawater) saline water during non-overtopping and lower high tides, and subsequently dissolved oxygen levels decrease.

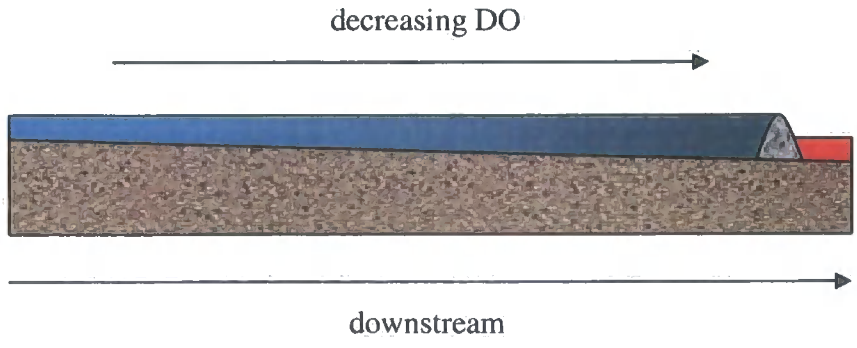


Figure 4.15. Schematic of internal DO control in profile along the impounded section of the Tees in summer, showing the general decrease in DO with progression downstream from the former tidal limit to the barrage. Freshwater is shown in blue and saline water in red. Not to scale.

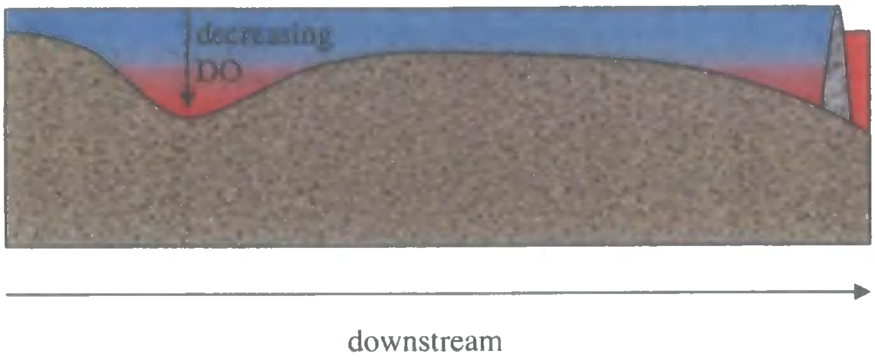


Figure 4.16. Schematic of internal DO control in profile along the impounded section of the Wansbeck in summer, showing the decrease in DO with depth relating to saline stratification in the water body. Freshwater is shown in blue and saline water in red. Not to scale.

Modelling the rate of decrease in oxygen levels in the Wansbeck in terms of average behaviour is complicated by the fact that, during the periods studied, on a few occasions high freshwater flows acted to overcome the density difference between the saline and fresh water and removed low oxygen water (see Lewis, 1997 for a detailed description of mixing of stratified flows by the development of internal waves). As such, an example showing the development of almost complete anoxia (the period 1st to 7th October 2000) is used to show the typical rate of de-oxygenation (figure 4.17):

$$\text{DO } \% = 56.7 - 7.62 \text{ day}$$

$$(S = 2.4 \qquad \text{R-Sq} = 98.3\ \% \qquad \text{R-Sq(adj)} = 97.9\ \%)$$

where,

DO % = dissolved oxygen % saturation at depth at site CP in the Wansbeck impoundment, and

day = the time in days following isolation from sources of re-oxygenation.

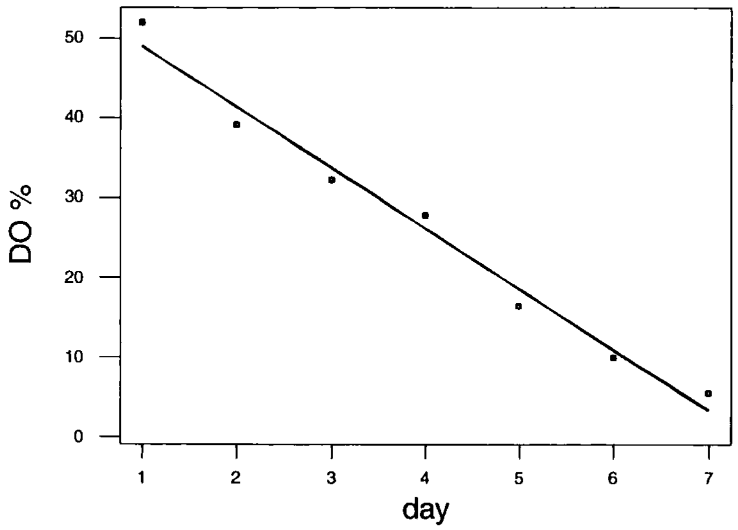


Figure 4.17. The decrease in DO concentration in deep (stratified) water from the Wansbeck impoundment between the dates of 1st and 7th October 2000.

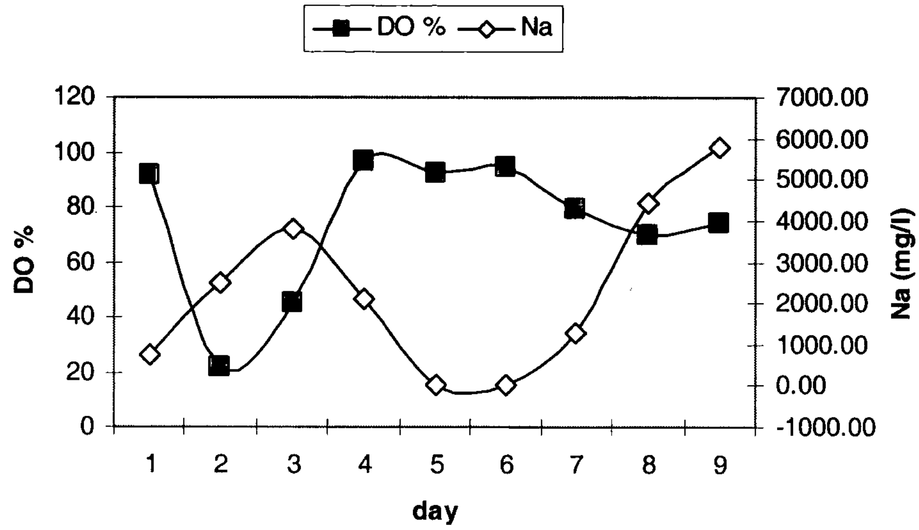


Figure 4.18. DO and Na concentrations over 10th to 18th June 2000 in deep water at site F in the Tawe.

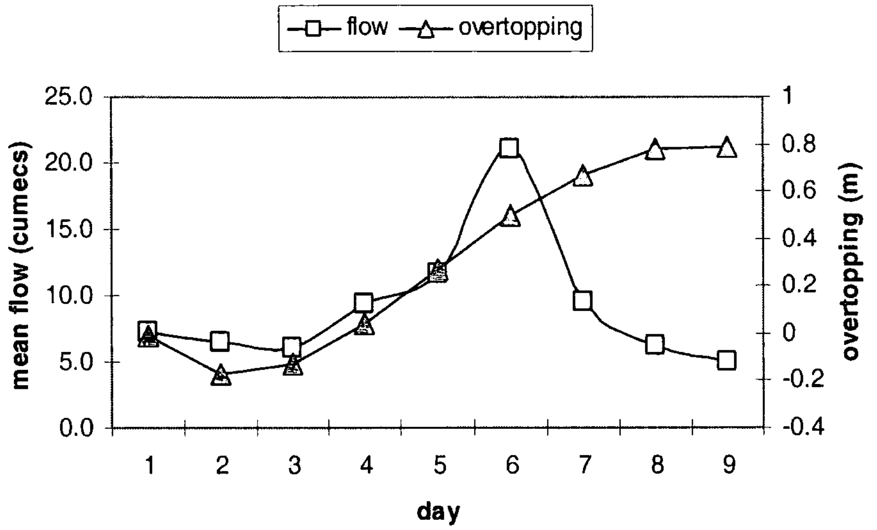


Figure 4.19. Mean freshwater discharge and tidal overtopping preceding sampling over the same period as figure 4.18 above (overtopping = tidal height – barrage height).

It is noteworthy that DO absolute concentrations at depth decreased in the Wansbeck to below the SWQO of 5 mg/l for salmonid species on approximately the 2nd day and the 3 mg/l for cyprinid species on the 4th day. The tidal height at which seawater was able to progress upstream to site CP was approximately 5 m (30 cm higher than the crest height of the Wansbeck barrage).

That DO concentrations at depth in the Tawe are not generally as low as in the Wansbeck during the periods studied is not due to the rate of de-oxygenation being any less in the Tawe than in the Wansbeck, but due to the shorter periods of isolation encountered by waters in the Tawe. Over a 9 day period of sampling from a site (F) in the Tawe where ponding of saline water is often encountered (Swansea City Council, pers. comm.) a complex relationship between DO concentration and salinity and freshwater discharge and tidal overtopping height is seen (figures 4.18 and 4.19). DO is generally maintained at close to 100 % over the majority of the period either by 'fresh' seawater progressing upstream to this point or by sufficient freshwater discharge to provide mixing and removal of saline stratification, but falls rapidly (from 91.7 to 21.5 % over 1 day) on isolation of brackish water (between day 1 and 2 on figure 4.18). The relationship between overtopping, freshwater discharge and DO in the Tawe impoundment is explored further using a larger dataset by Lamping (2003).

4.3.2 BOD

Results

Applying the model used above for DO % for ANOVA on BOD gave no significant effects for any of the factors included, although no comparisons can be made for the Wansbeck since due to time constraints no BOD measurements were taken during the summer sampling period.

During examination of seasonal effects on the Tees it was identified that BOD in this river is mainly from natural sources and shows a strong control by freshwater flow. It was also shown that for the Tees there were no significant internal (with depth or distance) variations in BOD during the periods studied. Initial examination of the Wansbeck and Tawe shows that BOD is also flow related in these rivers (figure 4.20):

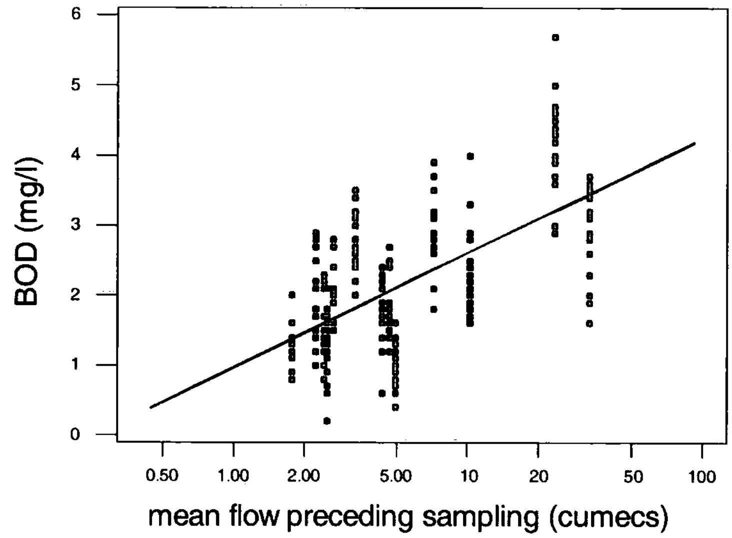


Figure 4.20. The relationship between BOD and flow for the Wansbeck (data from spring, autumn and winter sampling periods).

For the Wansbeck:

BOD = 0.969 + 1.64 log(Mean24) (P = 0.000, S = 0.809, R-Sq = 37.8 %)

For the Tawe:

BOD = -0.721 + 2.42 log(Mean24) (P = 0.000, S = 0.450, R-Sq = 48.1 %)

where BOD is measured in mg/l and Mean24 is the mean flow in the 24 hours preceding sampling measured in cumecs.

Discussion

BOD increases with increasing flow implying a diffuse source in all 3 rivers studied. The mean BOD measured was higher in the Wansbeck than the Tees or Tawe (2.1, 1.3 and 1.4 mg/l respectively) for all sampling, although BOD in the water column is fairly low in all 3 impoundments. The higher value of BOD for the Wansbeck is likely to relate to the lowland and more heavily farmed nature of its catchment. There is a relatively large amount of unexplained variation in the dataset for BOD. The measurement of BOD is a fairly imprecise technique, and often 2 mg/l is given as the LOD (Clesceri et al., 1998). For future work the use of COD as a measure of oxygen demand is recommended due to its greater precision and repeatability. The random variance due to the analytical technique makes it difficult to draw any conclusions about any within impoundment control on BOD, although for the data collected no significant effects can be shown. This implies that much of the oxygen demand within the systems causing the reductions in DO described above is from the organic rich bed sediments.

4.3.3 pH

Results

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
River	5.07	0.007	0.041	0.06
Distance	1.14	0.334	na	na
Depth	23.17	0.000	0.223	0.31
River*distance	4.97	0.000	0.159	0.22
River*depth	4.26	0.002	0.066	0.09
Error			0.226	0.32

Table 4.6. Results from GLM ANOVA for pH (raw data) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant at 95 % level).

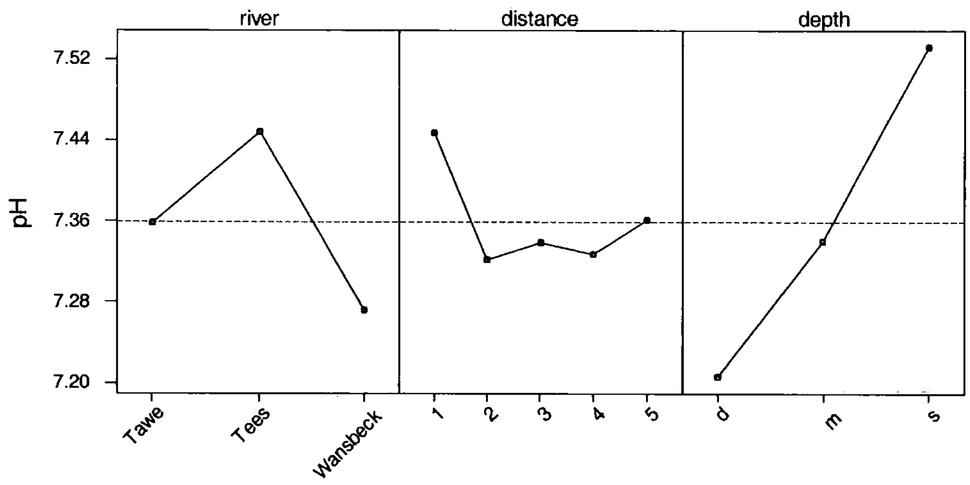


Figure 4.21. Main effects plot for the factors of impoundment (river), distance and depth on pH (raw data) (LS means for factor levels).

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
River	32.85	0.000	0.003	0.24
Distance	1.80	0.127	na	na
Depth	38.47	0.000	0.004	0.28
River*distance	8.18	0.000	0.003	0.22
River*depth	6.93	0.000	0.001	0.09
Error			0.002	0.17

Table 4.7. Results from GLM ANOVA for pH (data normalised to freshwater input values) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant at 95 % level).

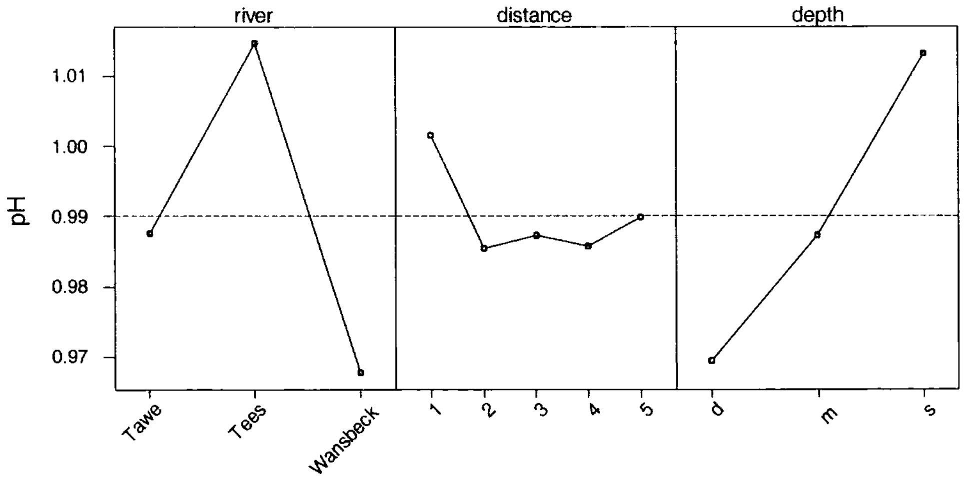


Figure 4.22. Main effects plot for the factors of impoundment (river), distance and depth on pH (data normalised to freshwater inputs) (LS means for factor levels).

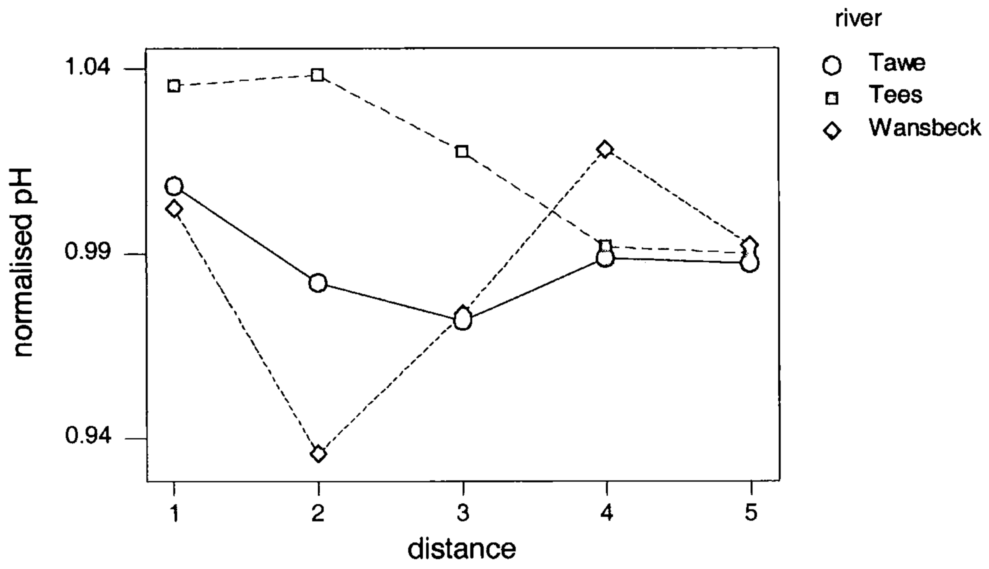


Figure 4.23. Interaction between river and distance effects on pH (data normalised to input values) (LS means).

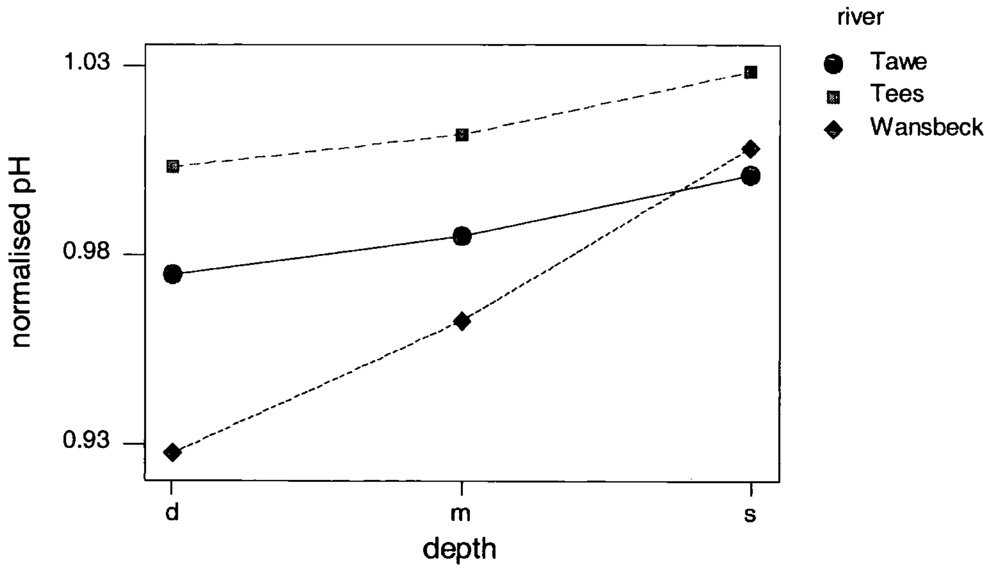


Figure 4.24. Interaction between river and depth effects on pH (data normalised to input values) (LS means).

Factor	Pairwise comparison	Adjusted P-value
River	Tees - Tawe	0.000
	Wansbeck - Tawe	0.000
	Wansbeck - Tees	0.000

Table 4.8. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for pH (data normalised to freshwater inputs) in partial and total tidal exclusion impoundments.

Analysis of pH was done using values normalised to the pH values of the freshwater inputs to the systems for each days sampling in order to assess the processes affecting pH within the impounded areas. Analysis carried out using raw data (table 4.6 and figure 4.21) showed a very similar pattern although with lesser variance due to river (implying that differences between rivers are more due to internal than external variation). One-way ANOVA gave no significant difference between the input values of pH between rivers during the summer sampling period (P = 0.602). The factors included in the model were as used with DO above.

24 % of the internal variation in pH in the dataset is due to differences between the impoundments (table 4.7). The three systems show significantly different levels of pH change between them, with the Tees showing a small increase in pH, the Tawe a small decrease in pH and mean pH in the Wansbeck decreasing by a slightly larger amount (figure 4.22). Variation in pH with distance is very different between impoundments (figure 4.23) with only the Tees showing an obvious trend. Depth effects account for approximately 37 % of the variance, and pH decreases with depth in all impoundments but to a greater extent in the Wansbeck than the Tees or Tawe (figure 4.24). Approximately 17 % of the variation in pH internal change cannot be explained by the terms included in the model.

Discussion

In general changes in pH are small, and pH remains within a range that is not detrimental to aquatic life. Changes in pH in the impoundments are likely to be biologically mediated. Primary production leads to increased pH, and respiration reactions decrease pH. In this light, in the Wansbeck and Tawe impoundments respiration is in excess of production, and in the Tees production is in excess of respiration. Interpretation of pH changes are complicated however by the differences in pH between freshwater and seawater inputs to the impoundments. Burton (1976) suggests that river water is often of lower pH than seawater. In the estuaries included in this study the opposite appears to be true. In the Blyth estuary the mean value for freshwater inputs is pH 7.6 and for the rest of the estuary (which is interpreted as seawater relatively unaffected by biological processes) the mean pH is 7.2. Samples in the other estuaries which are composed of saline water also tend to have lower pHs than the freshwater inputs although, as will be discussed, the pHs of these waters may have been affected by respiration processes.

The decreases in pH are greater in deep water due to contact with the organic rich bed sediments. The depth effects are greater in the Wansbeck implying that, as for DO processing, more stable stratification (due to salinity as opposed to temperature differences) gives greater periods in which respiration may take place, although some of this difference is probably due to the initial difference in pH values between seawater and freshwater inputs.

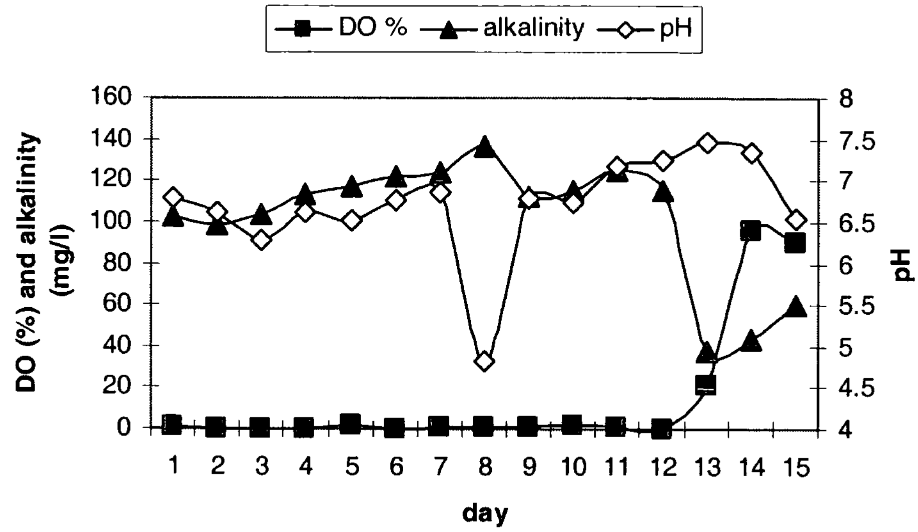


Figure 4.25. DO, pH and alkalinity over the period 4th to 18th June 2001 in deep water at site CP in the Wansbeck impoundment.

The lowest values of both DO and pH are encountered in the Wansbeck impoundment. As described for DO above, the difference between the Wansbeck and Tawe impoundments in the development of low pH conditions at depth in stratified water is likely to be due more to the greater length of time that water is 'ponded' in the Wansbeck rather than differences in the rates of DO and pH decrease. Unfortunately for the period analysed above to determine the rate of DO % decrease in deep stratified water no pH data was collected due to the cable supplied by the manufacturer for the pH probe being to short to reach the depth of sampling. The cable was lengthened for subsequent sampling periods on the Wansbeck, but unfortunately a similar period showing the progression from 'fresh' to 'stagnant' (reduced DO and pH, etc.) water was not sampled. Figure 4.25 shows pH, alkalinity and DO at depth over the longest period of anoxia sampled on the Wansbeck, and the subsequent removal of the saline water between day 12 and 13 of sampling by high freshwater discharge. It can be seen that pH remains relatively constant (buffered) between days 1 and 7 whilst alkalinity increases slightly. No reason can be determined for the drop in pH and increase in alkalinity on day 8, although perhaps sampling on this day disturbed the bed sediment. On mixing with freshwater (day 13) DO increases, pH increases slightly, and alkalinity drops markedly. The subsequent decrease in pH and increase in alkalinity may relate to the breakdown in suspended organic material transported to the impoundment with the high (maximum 50.2 m^3/s) discharge. TSS for day 13 is 310 mg/l compared with <100 mg/l for all other days.

The maximum rate of pH decrease at site F in the Tawe over the period for which DO is discussed above is from 7.7 to 6.5 over 1 day (figure 4.26). Alkalinity over this period follows the proportion of seawater (Na concentration) in the deep water quite closely (R-Sq = 69.2 %). For both the Tawe and the Wansbeck the biological effects on alkalinity appear to be minor relative to the proportion of seawater (higher alkalinity) to river water (lower alkalinity).

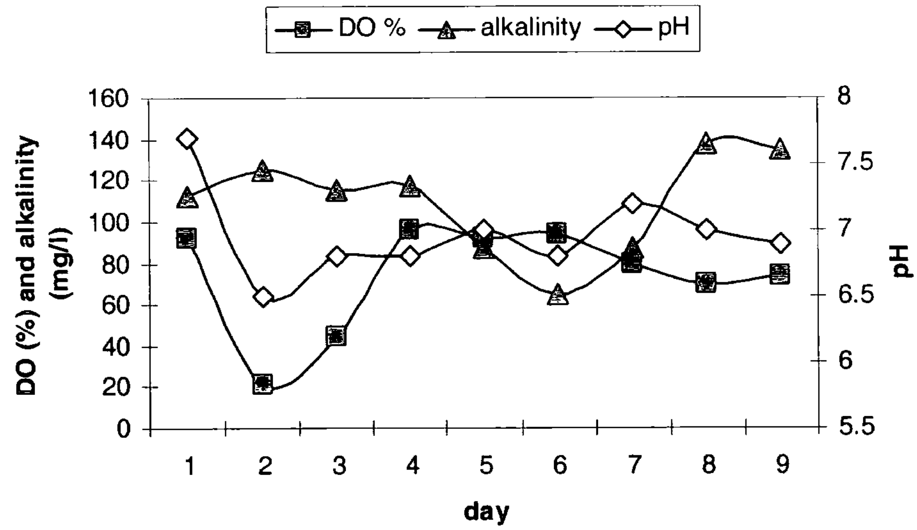


Figure 4.26. DO, pH and alkalinity over the period 10th to 18th June 2000 in deep water at site F in the Tawe impoundment.

4.3.4 Alkalinity

Results

PCA showed that alkalinity was strongly aligned with a principal component interpreted as a freshwater discharge factor, and that alkalinity shows a dilution effect with increasing flow. For the periods studied (data from all seasons sampled) on the 3 impoundments the relationships are:

For the Tees:

alkalinity = 270 - 135 log(Mean 24) (S = 23.7, R-Sq = 86.0 %)

For the Tawe:

alkalinity = 180 - 86.3 log(Mean24) (S = 14.1, R-Sq = 60.3 %)

For the Wansbeck:

alkalinity = 92.1 - 26.1 log(Mean24) (S = 13.5, R-Sq = 53.4 %)

where alkalinity is measured in mg/l $CaCO_3$ equivalent and Mean24 is the mean flow in the 24 hours preceding sampling measured in cumecs. P = 0.000 for each relationship.

ANOVA carried out on raw alkalinity data gives significant differences between rivers, but no significant variation in alkalinity with distance and only a very small effect of depth (table 4.9). The Tees has significantly higher alkalinity than the Tawe, and the Tawe has significantly higher alkalinity than the Wansbeck (P = 0.000 for Tukey simultaneous tests). 12 % of the variance in alkalinity cannot be explained by the factors in the model, and probably relates to within river variation in alkalinity with variation in freshwater flow.

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
River	159.63	0.000	10704	0.86
Distance	2.26	0.061	na	na
Depth	3.38	0.034	161	0.01
River*distance	0.62	0.763	na	na
River*depth	0.42	0.797	na	na
Error			1518	0.12

Table 4.9. Results from GLM ANOVA for alkalinity (raw data) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant (P>0.05)).

To determine the within impoundment controls on alkalinity the ANOVA applied above to raw data was repeated with data normalised to the values of alkalinity in the freshwater inputs to the impoundments for each of the sampling dates. The importance of river as a factor is much smaller when looking at internal changes compared with the overall variation in alkalinity (i.e. comparing input normalised and raw data results). Alkalinity is higher within the impounded areas than in the freshwater inputs in all the systems, but to a greater extent in the Tawe and Wansbeck (which show no statistical difference between them). Alkalinity increases with distance downstream and with depth in all 3 impoundments to a similar degree. The error term when using normalised data is relatively large (44 %) and probably relates in part to random analytical error relating to the precise identification of the end-point (methyl orange indicator colour change) in the alkalinity titrations, and in part to variation in the amount of seawater entering the systems.

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
River	7.48	0.001	0.018	0.13
Distance	6.88	0.000	0.032	0.23
Depth	11.39	0.000	0.028	0.20
River*distance	1.28	0.248	na	na
River*depth	0.93	0.445	na	na
Error			0.062	0.44

Table 4.10. Results from GLM ANOVA for alkalinity (data normalised to freshwater input values) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant ($P>0.05$)).

Factor	**Pairwise comparison**	**Adjusted P-value**
River	Tees - Tawe	0.001
	Wansbeck - Tawe	0.875
	Wansbeck - Tees	0.006

Table 4.11. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for alkalinity (data normalised to input values) in partial and total tidal exclusion impoundments.

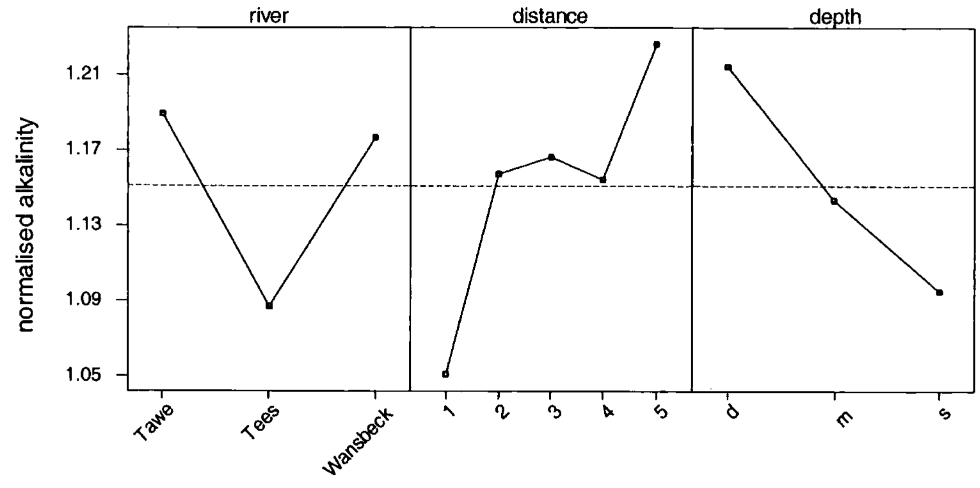


Figure 4.27. Main effects plot for the factors of impoundment (river), distance and depth on alkalinity (data normalised to freshwater inputs) (LS means for factor levels).

Discussion

The majority of variation in levels of alkalinity is due to differences in freshwater inputs which relate to differences between the catchments of the rivers (geological effects) and with the relative proportion of baseflow to stormflow components of river discharge. In relation to these variations, the variation within the impounded areas of the estuaries is small, and therefore the effect on alkalinity of barrage construction minor.

The difference between rivers when examining data normalised to the freshwater inputs to the systems is in part an effect of the difference in volumes of seawater entering the systems. In general the alkalinity of seawater is higher than that of freshwater (Dryssen and Wedborg, 1980), and alkalinity behaves conservatively on mixing (figure 4.28). For the three impoundments studied the mean value for alkalinity in brackish and saline water (arbitrarily defined as Na > 100 mg/l) is 99 mg/l $CaCO_3$ equivalent compared with 88 mg/l $CaCO_3$ equivalent in fresh (Na < 100 mg/l) water (mean pHs are 7.53 and 7.66 respectively). The Tawe and Wansbeck have similar amounts of tidal overtopping of the barrage crest and seawater entering the impoundment, and so in general show a greater increase in alkalinity from freshwater inputs than the Tees.

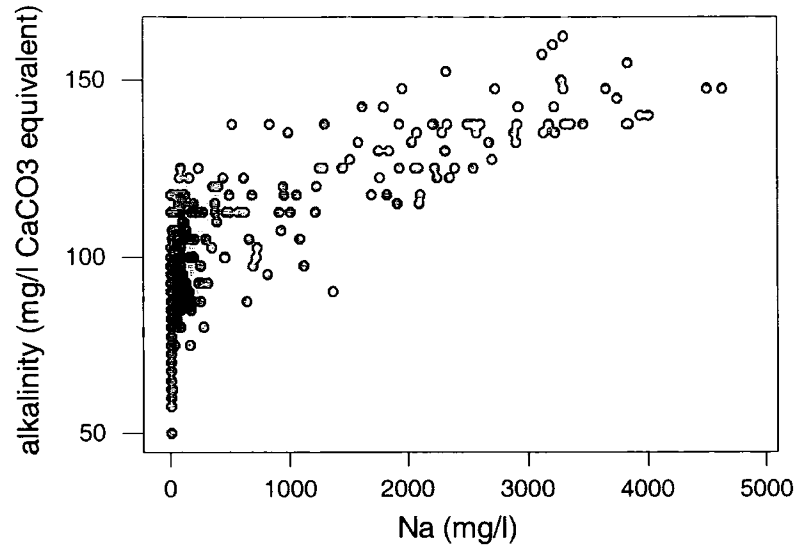


Figure 4.28. Conservative behaviour of alkalinity on mixing between fresh and saline water. Data shown from the Tawe impoundment. Variation in freshwater samples relates to river flow.

Since the behaviour is similar for all impoundments (i.e. no interactions are significant) the distance and depth effects on alkalinity within the impoundments are likely to be due in part to the biological controls of production (acting to decrease alkalinity by removing CO_2) and respiration (acting to increase alkalinity by releasing CO_2). The relationship between alkalinity and pH with depth was identified during PCA above. At depth there is a significant increase in alkalinity due to respiration in excess of production (mirroring the behaviour of pH as described above). The general increase in alkalinity with distance downstream may relate to biological effects, inputs of groundwater, dissolution of CO_2 from the atmosphere or, for the partial exclusion systems, greater seawater contribution closer to the barrages.

4.3.5 Conductivity

Results

Conductivity relates to the amount of seawater entering the impounded areas. The pattern of its distribution in time and space relates to density stratification and the mixing and removal of saline water by freshwater flow. ANOVA carried out on all conductivity data collected during the water quality surveys of the impoundments shows that there is (as would be expected) significantly higher conductivity in the partial tidal exclusion impoundments (Tawe and Wansbeck) than the total exclusion impoundment (Tees). There is no significant difference between the Tawe and Wansbeck for the periods sampled. Conductivity increases with distance downstream (proximity to the barrage) in the partial exclusion systems (figure 4.29). A larger effect (34 %) is shown by depth, with conductivity increasing with depth in the partial exclusion systems.

Source	**F**	**P**	σ^2	**Size of Effect** (ω^2)
River	49.96	0.000	248151315	0.23
Distance	9.53	0.000	86486241	0.08
Depth	71.98	0.000	359760731	0.34
River*distance	5.94	0.000	100172092	0.09
River*depth	16.82	0.000	160346308	0.15
Error			114046936	0.11

Table 4.12. Results from GLM ANOVA for conductivity (raw data) in partial and total tidal exclusion impoundments.

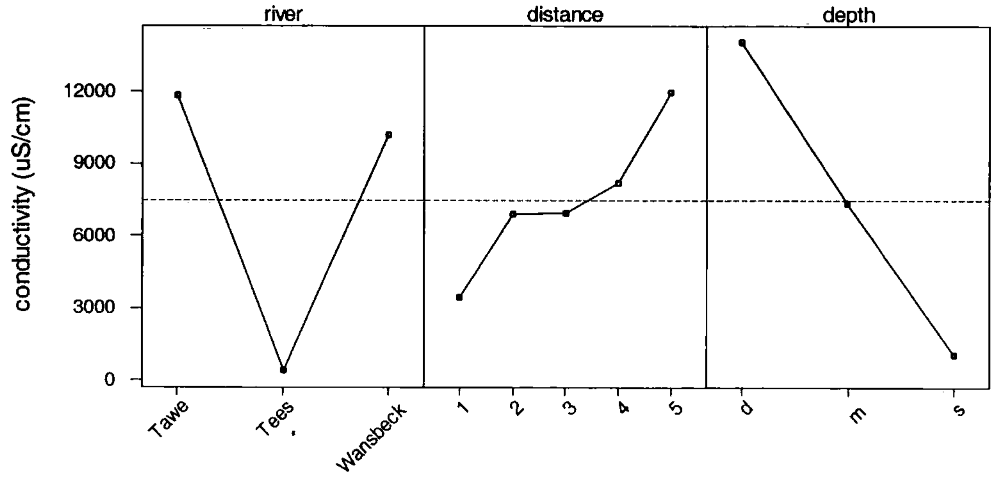


Figure 4.29. Main effects plot for the factors of impoundment (river), distance and depth on conductivity (raw data) (LS means for factor levels).

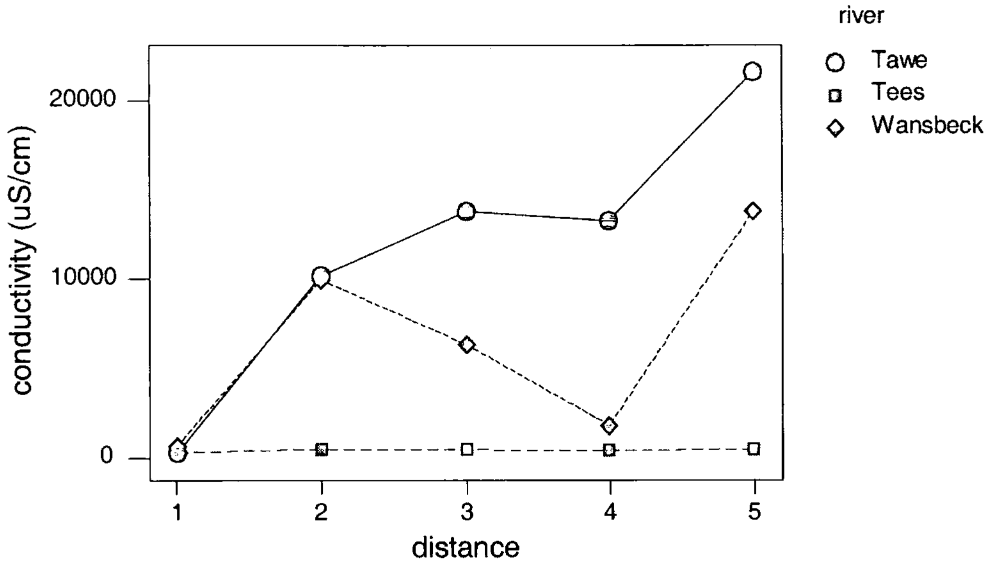


Figure 4.30. Interaction between river and distance effects on conductivity (raw data) (LS means).

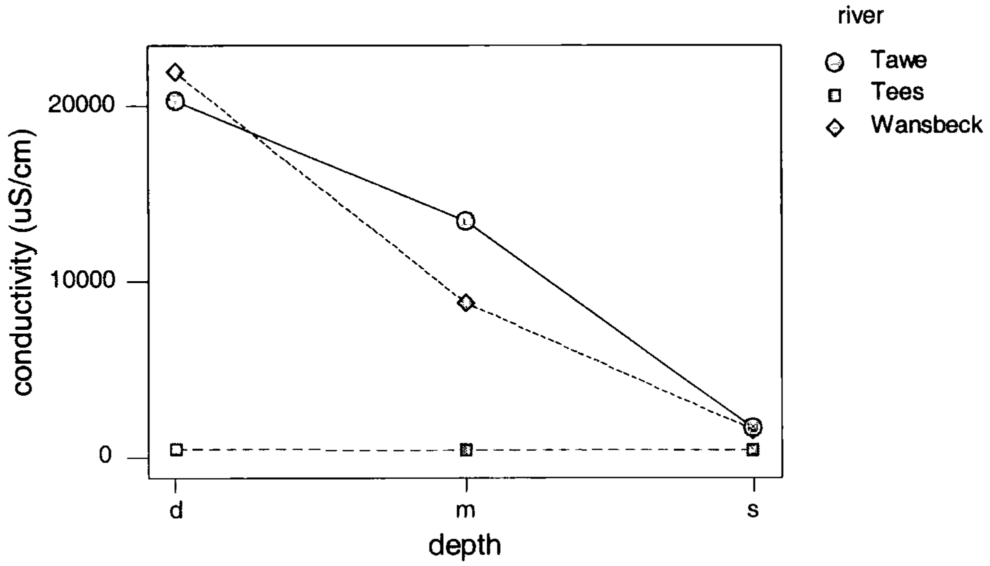


Figure 4.31. Interaction between river and depth effects on conductivity (raw data) (LS means).

Factor	Pairwise comparison	Adjusted P-value
River	Tees - Tawe	0.000
	Wansbeck - Tawe	0.284
	Wansbeck - Tees	0.000

Table 4.13. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for conductivity (raw data) in partial and total tidal exclusion impoundments.

Discussion

The behaviour of conductivity in the impoundments was discussed above during the PCA and in relation to the variation in DO. In systems that allow seawater to overtop the barrage crest and enter the impounded area, density stratification occurs between the less dense river water and denser saline water through large parts of the impoundment. The removal of saline water is by mixing upwards through internal waves at the density interface (Lewis, 1997), and is dependent on freshwater flow velocity. At low flow velocities creation of waves is dependent on bed shear (which may not have an effect if the distance to the density interface is large) and at high velocities interfacial shear becomes significant. As such, stratification persists over longer periods in deeper sections of the impoundments (e.g. sites CP in the Wansbeck and F in the Tawe discussed above).

In the ANOVA model used above significant variation is seen between total and partial tidal exclusion impoundments, with depth (stratification) in partial exclusion impoundments, and with distance (proximity to the source of seawater). The size of the difference between the conductivity of the saline water and the freshwater in the systems (given as water of conductivity <500 μS/cm and >500 μS/cm respectively in this thesis) means that no processes other than the amount of seawater/freshwater mixing can be identified within the whole dataset. For the (freshwater) Tees it was shown that conductivity shows a dilution effect with increased discharges, and separating the Wansbeck and Tawe freshwater samples (samples with conductivity < 500 μS/cm) from samples that have mixed with saline water (samples with conductivity > 500 μS/cm) shows similar flow relationship for these rivers.

In the Wansbeck impoundment the removal of saline water shows a progressive increase with increased flow, and the mixing upwards effect is shown by the relatively constant conductivity of the deep saline water through all ranges of flow at which it is encountered (figure 4.32). The removal of saline water is demonstrated by the decrease in the number of points at which it is encountered, and commences at flows greater than approximately 5 cumecs (m^3/s). Total removal of saline water does not occur until somewhere between 40 and 100 cumecs, with saline water being found at depth behind the barrage up to this point.

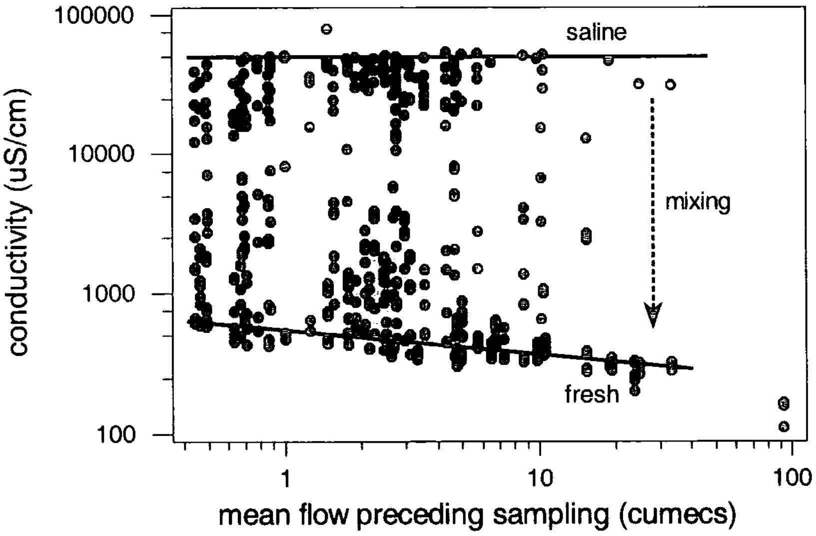


Figure 4.32. Conductivity and freshwater flow in the Wansbeck impoundment. Saline water conductivity is independent of flow but the number of sampling sites at which saline water is encountered decreases with increasing flow. High conductivity samples are almost all from depth. Freshwater conductivity decreases with increasing flow.

The behaviour of density stratification with flow is similar for the Tawe impoundment (figure 4.33). The removal of saline water (shown by the decrease in number of samples of high conductivity) commences at approximately 7 cumecs. The slightly higher discharge for the Tawe compared with the Wansbeck is probably due to the greater water depth (mean depths 2.15 and 1.39 m respectively) meaning that bed shear has less impact in the creation of internal waves and hence mixing for the same discharge.

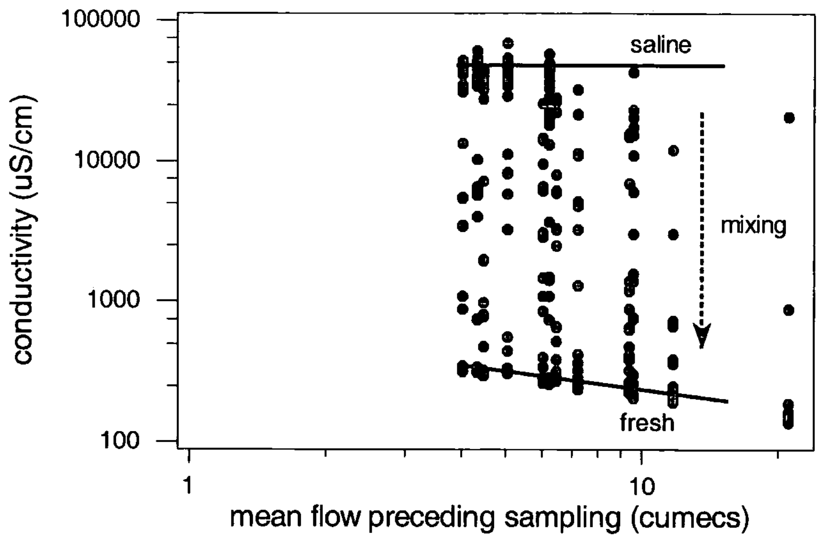


Figure 4.33. Conductivity and freshwater flow in the Tawe impoundment. The behaviour is very similar to the Wansbeck (above). Removal of saline water commences at approximately 7 cumecs.

For both rivers, the freshwater samples (taken as those with conductivities lower than 500 μS/cm) show a decrease in conductivity with increasing freshwater flow, interpreted as due to dilution of baseflow component by increasing stormflow (figure 4.34). The relationships between freshwater conductivities and freshwater flow within the impoundments are:

For the Wansbeck:

conductivity = 621 - 231 log(Mean24) (S = 124, R-Sq = 51.8 %)

For the Tawe:

conductivity = 515 - 272 log(Mean24) (S = 51.5, R-Sq = 55.2 %)

For the Tees:

conductivity = 586 - 247 log(Mean24) (S = 153, R-Sq = 32.9 %)

where conductivity is measured in μS/cm, and Mean24 is the mean flow in the 24 hours preceding sampling measured in cumecs. P = 0.000 for each relationship.

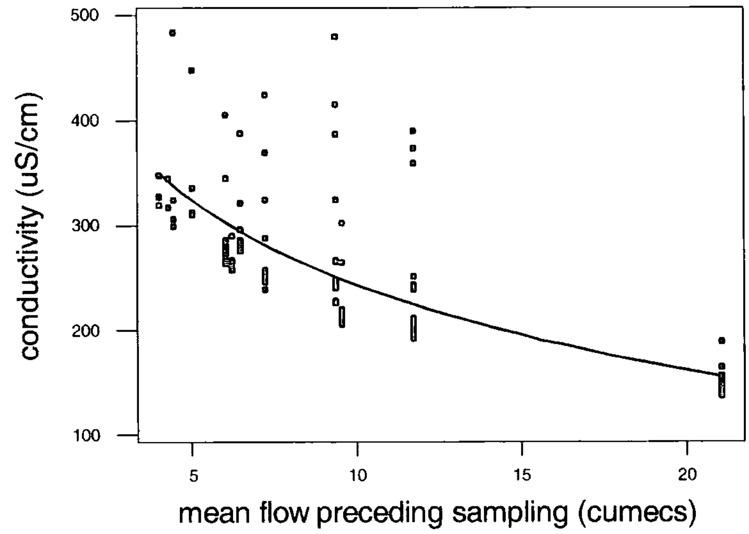


Figure 4.34. The relationship between freshwater (taken as conductivity < 500 μS/cm) and flow in the River Tawe. The scatter of points above the regression line are due to the mixing of freshwater with seawater.

4.3.6 Transparency

Results

Since transparency (measured using a Secchi disk) was measured once at each site on each date sampled, the ANOVA model used excluded depth as a factor. On several occasions the water depth at the former tidal limit sites (which were used to represent the freshwater inputs to the systems for data normalisation) was too shallow to allow transparency measurements to be taken, and so analysis is carried out on raw data only.

The results show that there are large differences in transparency between the impoundments, explaining 91 % of the variance in raw transparencv values. Transparency is greater in the Tawe than the Tees, and in the Tees than the Wansbeck (table 4.14). Transparencies show a small but significant amount of decrease with distance downstream in all of the impoundments (figures 4.35 and 4.36). Very little of the variance in the dataset (approximately 1 %) cannot be explained by the terms included in the model.

Source	**F**	**P**	σ^2	**Size of Effect** (ω^2)
River	854.66	0.000	13.8	0.91
Distance	14.22	0.000	0.9	0.06
River*distance	4.99	0.000	0.3	0.02
Error			0.194	0.01

Table 4.14. Results from GLM ANOVA for transparency (raw data) in partial and total tidal exclusion impoundments.

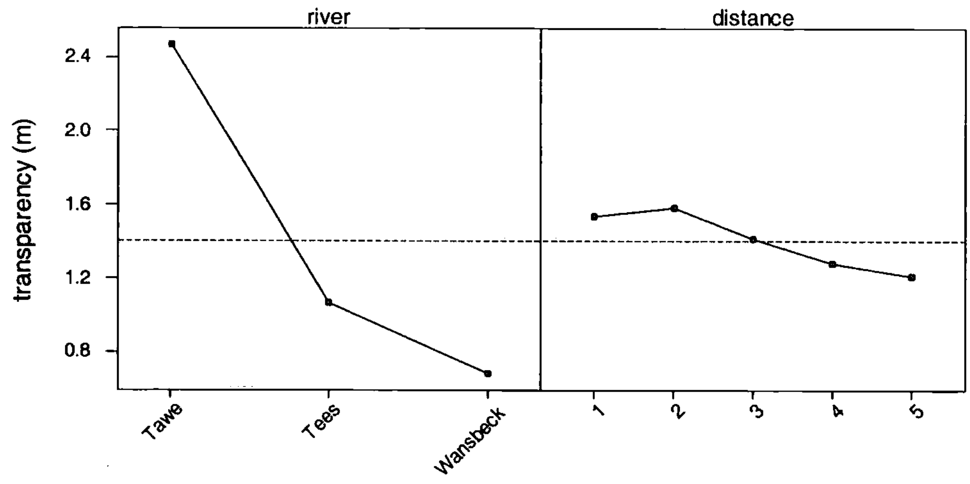


Figure 4.35. Main effects plot for the factors of impoundment (river) and distance on transparency (raw data) (LS means for factor levels).

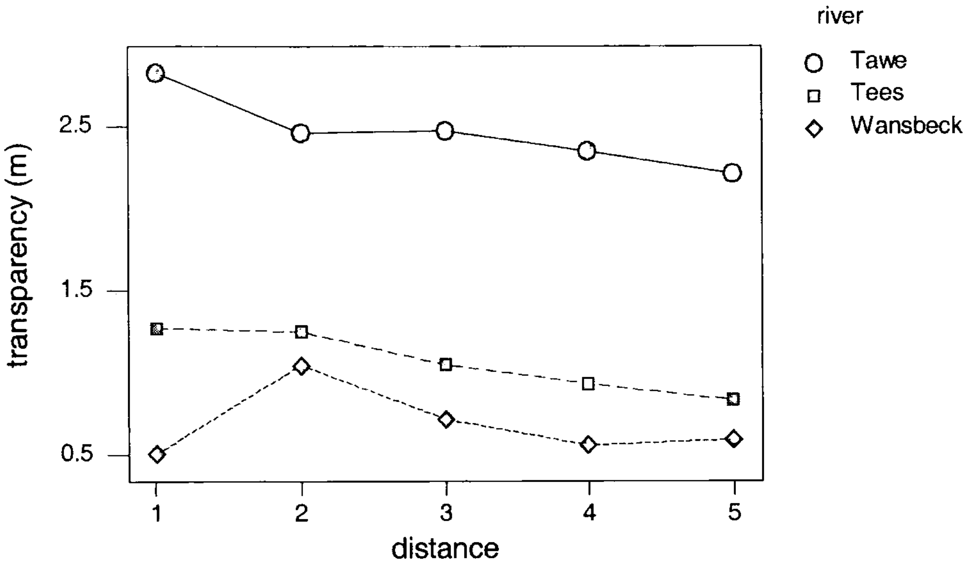


Figure 4.36. Interaction between river and distance effects on transparency (raw data) (LS means).

Discussion

Within the River Tees it was seen that a large amount of variation in transparency was due to increased turbidity with increased discharge. However, the small amount of variance unexplained in the model above when comparing the 3 impoundments studied suggests that flow is a minor effect compared to the size of the differences in transparency between the rivers. If it is assumed that transparencies relate to turbidity in all the systems, then this large difference has implications in terms of the relative amounts of sediment and possible sediment build-up in the impounded areas. The Tees and the Wansbeck have the potential for more rapid sedimentation than does the Tawe. Sedimentation, and in particular sediment quality, are discussed in chapter 6.

The decrease in transparency with distance downstream was interpreted as due to the re-suspension of bed material in the Tees, and this is also likely to be the case in the partial exclusion systems although in these tidal currents may also act to re-suspend material. Note that for the Wansbeck the transparency at distance 1 is unrepresentatively low since the low water depth at this point meant that measurement could only take place under low transparency conditions. Un-impounded estuaries often show turbidity maxima due to tidal pumping (Dyer, 1988), but no maxima appear to be present (in terms of transparency peaks) in the impounded estuaries studied, although tidal inputs and currents may explain some of the downstream decrease in transparencies in the Tawe and Wansbeck.

4.3.7 TSS

Results

The data for TSS collected in summer 1999 on the Tees is suspect due to variation in the amount of moisture in the filter papers used in the measurements, and therefore only the Tawe and Wansbeck impoundments are compared in the ANOVA. Analysis is initially carried out using raw TSS data to examine the overall differences between the rivers, and then using data normalised to the freshwater input values to assess the internal variation in TSS.

Analysis using raw data shows that (as for transparency) differences between rivers account for the majority of the variance in the dataset (table 4.15), with suspended solids approximately 5 times higher in the Wansbeck than the Tawe during the sampling periods (figure 4.37). Compared to this variance the effect of distance and the river*distance interaction is insignificant. There are significant differences between the 3 factor levels of depth in the impoundments, and depth accounts for approximately 16 % of the variance. TSS increase with depth, and to a greater extent (in absolute terms) in the Wansbeck than the Tawe. It is likely that much of the unexplained variance in TSS is related to variation in freshwater flow.

Source	F	P	σ^2	Size of Effect (ω^2)
River	96.40	0.000	7412	0.58
Distance	0.12	0.974	na	na
Depth	27.81	0.000	2083	0.16
River*distance	1.04	0.385	na	na
River*depth	10.36	0.000	1455	0.11
Error			1748	0.14

Table 4.15. Results from GLM ANOVA for TSS (raw data) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant).

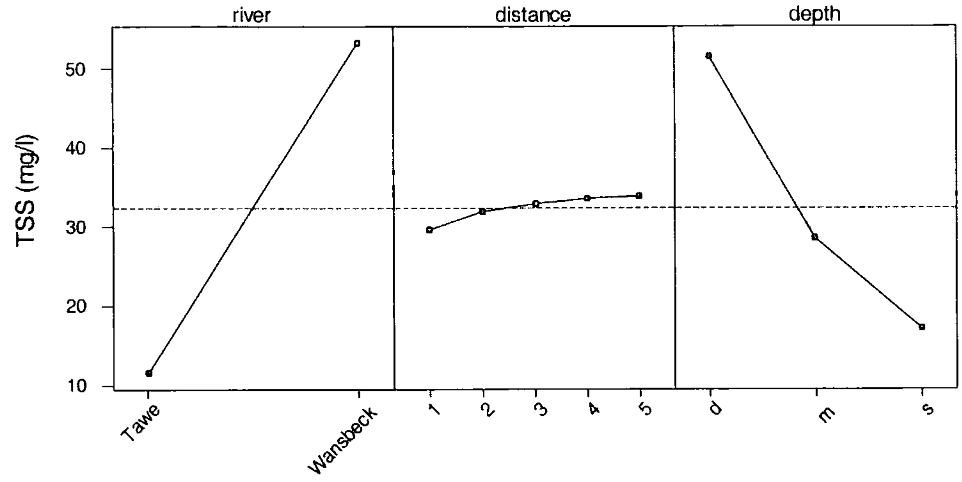


Figure 4.37. Main effects plot for the factors of impoundment (river), distance and depth on TSS (raw data) (LS means for factor levels).

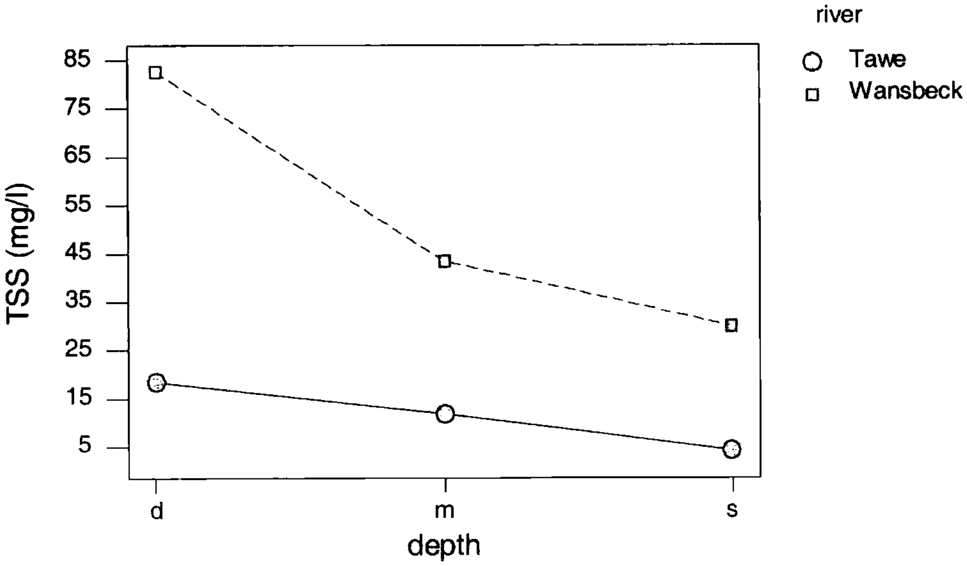


Figure 4.38. Interaction between river and depth effects on TSS (raw data) (LS means).

Source	F	P	σ^2	Size of Effect (ω^2)
River	2.08	0.150	na	na
Distance	8.54	0.000	14.1	0.16
Depth	49.96	0.000	45.8	0.51
River*distance	3.43	0.009	9.1	0.10
River*depth	0.84	0.433	na	na
Error			21.0	0.23

Table 4.16. Results from GLM ANOVA for TSS (data normalised to freshwater input values) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant).

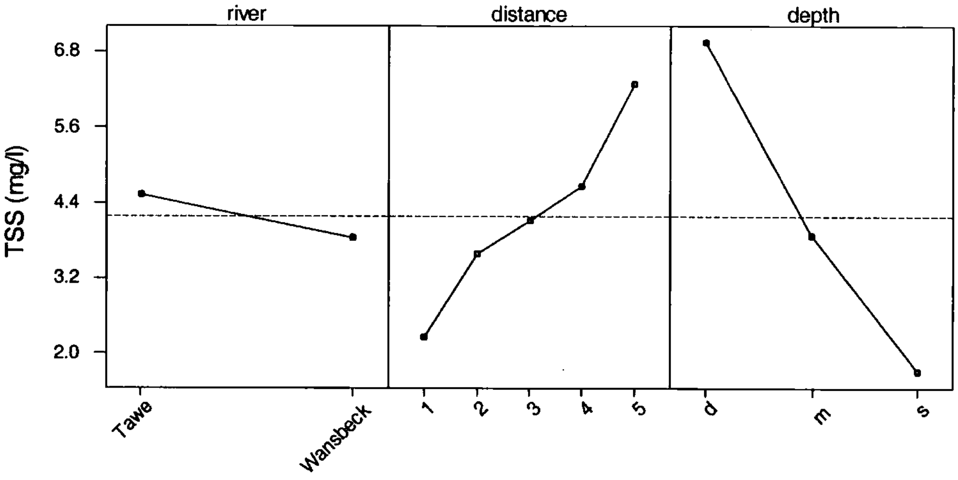


Figure 4.39. Main effects plot for the factors of impoundment (river), distance and depth on TSS (data normalised to freshwater inputs) (LS means for factor levels).

Repeating the ANOVA using normalised data (results in table 4.16) shows no significant effect for river, therefore differences between the rivers are generally due to differences in the amount of TSS entering the systems rather than any differences in the behaviours within the impounded areas. Removing the variance in TSS entering the impounded areas allows distance to show a significant effect with values of TSS increasing with distance downstream (figure 4.39), and by a greater degree in the Tawe than the Wansbeck (figure 4.40). The biggest within impoundment variation in TSS is with depth ($\omega^2 = 0.51$), with TSS increasing with depth by exactly the same degree in both impoundments.

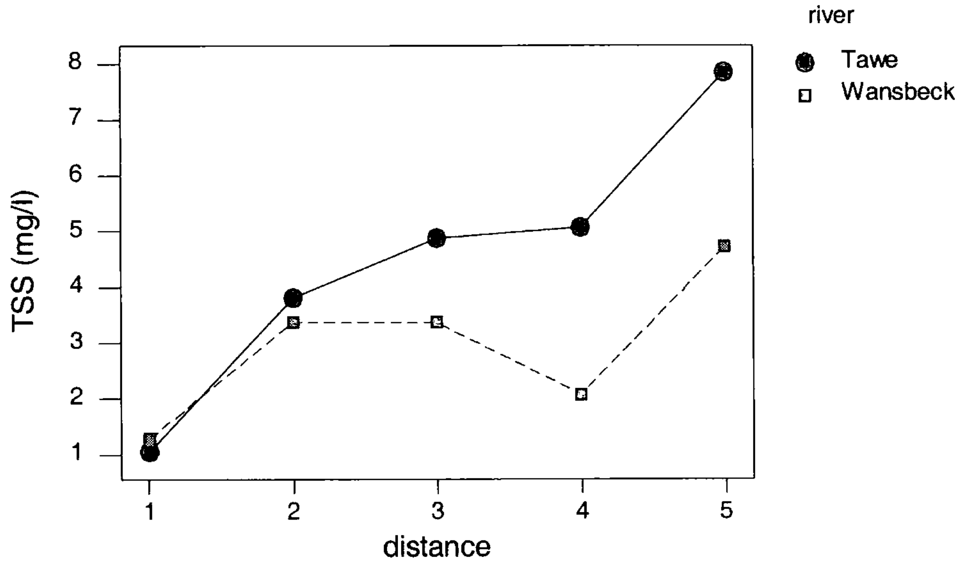


Figure 4.40. Interaction between river and distance effects on TSS (raw data) (LS means).

Discussion

The major controls on the amount of suspended material in the impoundments' water columns are external to (i.e. upstream of) the impounded areas. These controls on sediment load relate to the catchments (e.g. land use) and river discharge. Modelling of sediment transport (Beavers, 2003) and an attempt at fingerprinting sediment sources to the impoundment (Neilson, 2003) are carried out as specific tasks of the SIMBA Project.

Relative to these external effects, internal variance in the concentration of suspended particulate material is low, but demonstrates some important behaviour. Firstly, both the Tawe and the Wansbeck show the same relative increase in TSS with depth in the impounded area, with deep samples containing approximately 3 times the concentration of suspended material as surface samples. This suggests that sediment may be settling through the water column from the surface water down to the bed at similar rates in both systems. It may also be that the saline water at depth shows higher TSS concentrations due to inputs from downstream of the barrages, or re-suspension of unconsolidated bed material by tidal currents (as is common in estuaries of unrestricted tidal circulation (Dyer, 1988). The greater relative increase in TSS concentrations downstream in the Tawe, which is subject to higher tidal overtopping, may also be due to the effect of tidal currents resuspending bed material. The TSS results, as might be expected, mirror the transparency results for the Tawe and Wansbeck suggesting that the assumption that transparency relates to turbidity in these rivers is correct. The pattern of sediment transport and build-up within the impounded areas is discussed further in chapter 6.

4.3.8 Nutrients

4.3.8.1 Nitrate

Results

The majority of the variance (67 %) in nitrate in the systems studied is between the rivers. The Tees and the Wansbeck have significantly higher mean nitrate levels than the Tawe (figure 4.41 and table 4.17). Nitrate levels decrease slightly with distance downstream in all 3 impoundments, but there are contrasting depth effects. The Tees and the Tawe show no depth effects but the Wansbeck shows a significant decrease in levels of nitrate with increasing depth (figure 4.42).

Source	F	P	σ^2	Size of Effect (ω^2)
River	162.94	0.000	9.86	0.67
Distance	7.32	0.000	0.77	0.05
Depth	13.82	0.000	0.78	0.05
River*distance	1.40	0.195	na	na
River*depth	16.55	0.000	1.89	0.13
Error			1.37	0.09

Table 4.17. Results from GLM ANOVA for nitrate (raw data) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant).

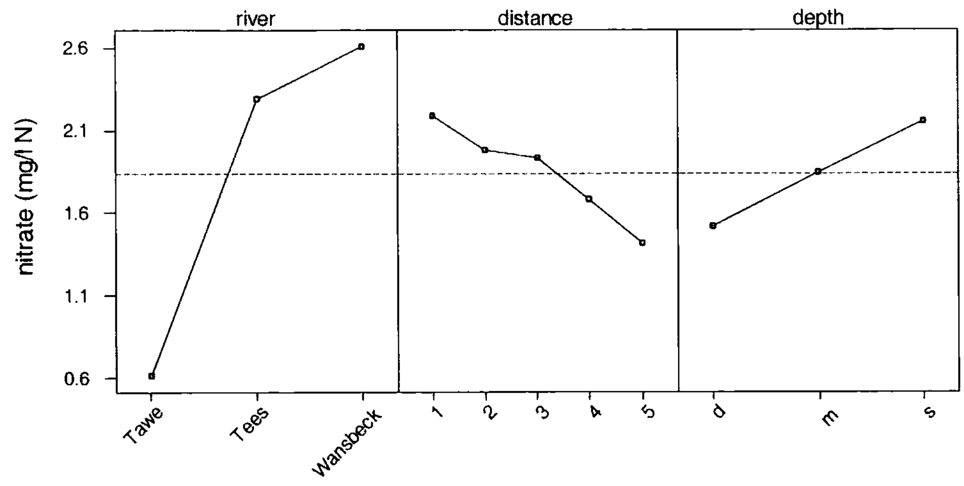


Figure 4.41. Main effects plot for the factors of impoundment (river), distance and depth on nitrate (raw data) (LS means for factor levels).

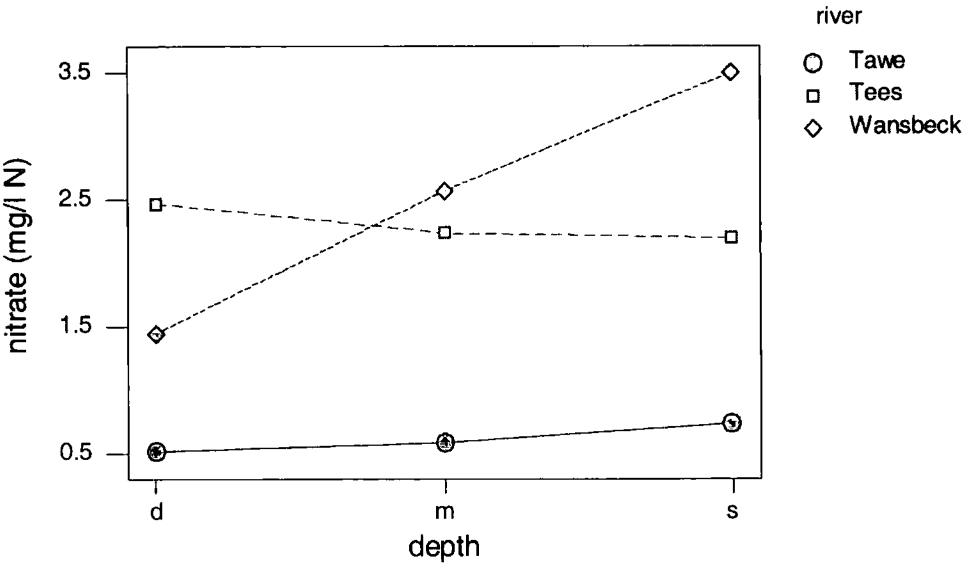


Figure 4.42. Interaction between river and depth effects on nitrate (raw data) (LS means).

Factor	Pairwise comparison	Adjusted P-value
River	Tees - Tawe	0.000
	Wansbeck - Tawe	0.000
	Wansbeck - Tees	0.065

Table 4.18. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for nitrate (raw data) in partial and total tidal exclusion impoundments.

Applying the same model to data normalised to the upstream freshwater input values for nitrate gives the following results (table 4.19). Difference between the rivers remains the most important effect (explaining 58 % of the variance), however the pattern differs from that shown by raw data. Mean levels of nitrate in the Tees are approximately 30 % higher than those entering the impoundment at the upstream limit. The distinct increase in nitrate concentrations takes place between site LM and site LW in the Tees. In the Tawe and the Wansbeck mean levels of nitrate are lower than in the freshwater input values, and to a significantly greater extent in the Wansbeck. The size and pattern for the distance and depth effects is similar for both raw and normalised data. Nitrate levels increase slightly with distance downstream in all 3 impoundments, but show contrasting depth effects. Nitrate decreases with depth in the partial tidal exclusion systems and increases slightly in the Tees.

Source	F	P	σ^2	Size of Effect (ω^2)
River	83.13	0.000	0.70	0.58
Distance	4.41	0.002	0.06	0.05
Depth	13.97	0.000	0.11	0.09
River*distance	0.88	0.529	na	na
River*depth	9.95	0.000	0.15	0.13
Error			0.19	0.16

Table 4.19. Results from GLM ANOVA for nitrate (data normalised to freshwater input values) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant).

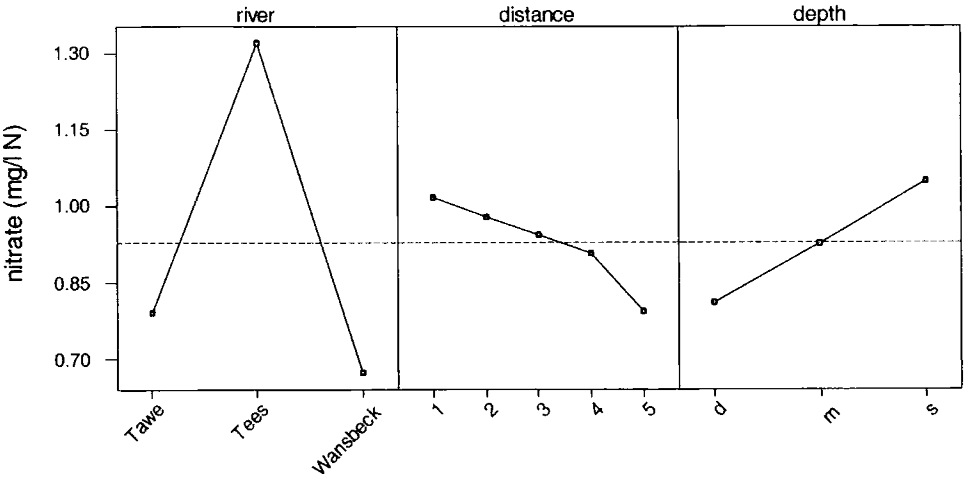


Figure 4.43. Main effects plot for the factors of impoundment (river), distance and depth on nitrate (data normalised to input values) (LS means for factor levels).

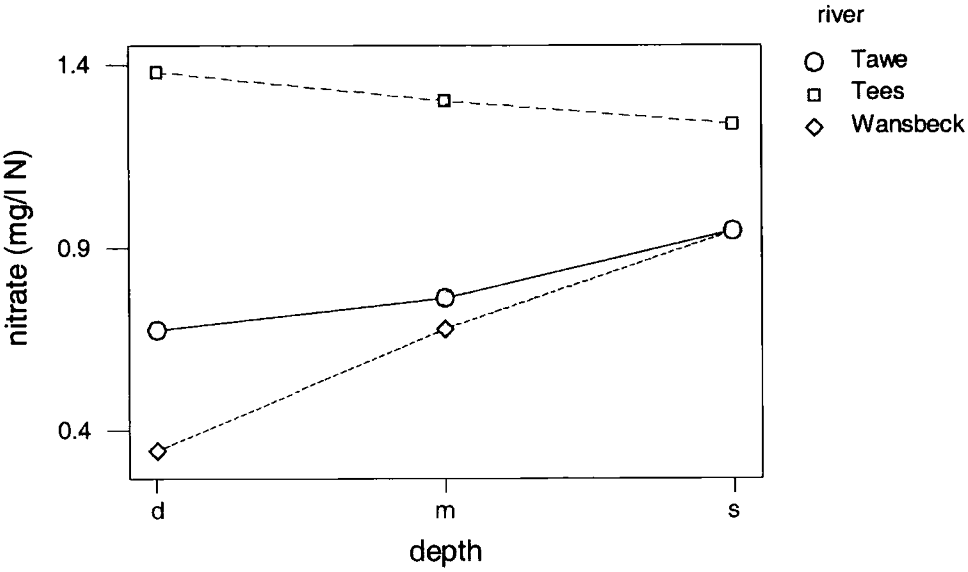


Figure 4.44. Interaction between river and depth effects on nitrate (data normalised to input values) (LS means).

Factor	Pairwise comparison	Adjusted P-value
River	Tees - Tawe	0.000
	Wansbeck - Tawe	0.020
	Wansbeck - Tees	0.000

Table 4.20. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for nitrate (data normalised to input values) in partial and total tidal exclusion impoundments.

Discussion

A large amount of the difference in levels of nitrate within the impoundments can be explained by differences between the amount of nitrate input to the systems from the rivers. During the periods included in the analysis above, mean nitrate levels in the freshwater inputs to the systems were 3.85, 2.16 and 0.79 mg/l N for the Wansbeck, Tees and Tawe, respectively, and this is reflected in the relative mean values for the whole impoundments. Differences in nitrate levels in the rivers are due to a combination of catchment (land-use), flow and point-source effects. As mentioned, nitrate in the Tees shows an approximate dilution with increasing flows (R-Sq = 39.1 % for summer data; R-Sq = 56.8 % for winter data) and is therefore possibly point-source (urban) dominated in this river, with seasonal differences controlled by diffuse sources. However, high flow events in the Tees are generally due to rainfall on the upland (Pennines) part of the catchment which is a poorer nitrate source than the more intensively farmed lowlands, and it is difficult to separate this contribution to the dilution effect. Carrying out regression analysis on nitrate vs. flow for the freshwater nitrate values in the Wansbeck and Tawe during the summer periods shows nitrate to be inversely related to flow (and therefore predominantly of point source) in the Tawe (R-Sq = 62.2 %, figure 4.45), but that nitrate is proportional to flow (and therefore of diffuse source) in the Wansbeck (R-Sq = 23.8 %, figure 4.46).

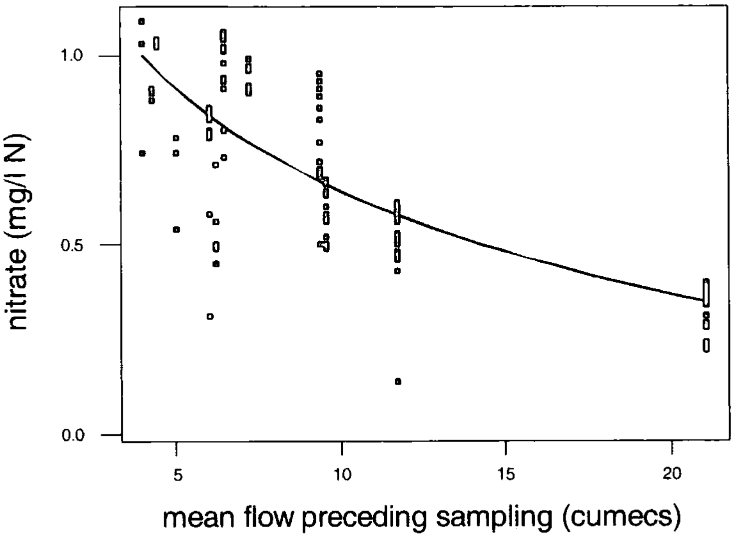


Figure 4.45. The relationship between nitrate concentration in freshwater (conductivity < 500 μS/cm) samples and river flow in the Tawe.

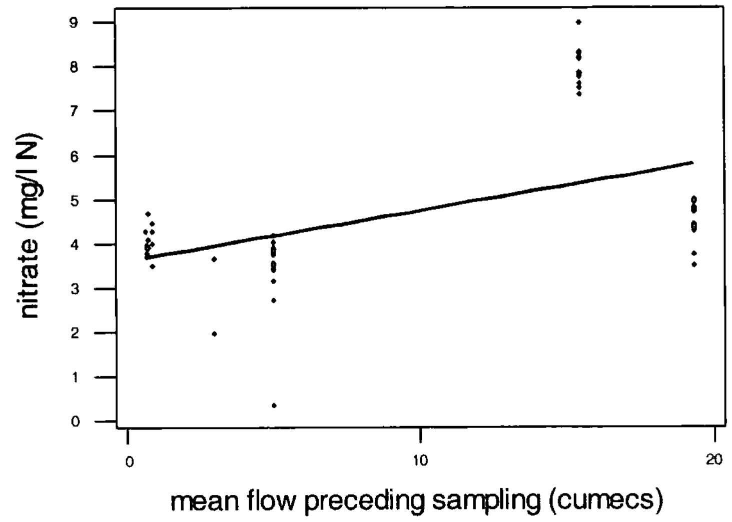


Figure 4.46. The relationship between nitrate concentration in freshwater (conductivity < 500 μS/cm) samples and river flow in the Wansbeck.

For the Tawe:

nitrate = 1.55 - 0.907 log(Mean24) (S = 0.148725 R-Sq = 62.2 %)

For the Wansbeck:

nitrate = 3.61 + 0.113 Mean24 (S = 1.54373 R-Sq = 23.8 %)

where,

nitrate = nitrate concentration in mg/l N in freshwater (conductivity < 500 μS/cm) in the Tawe impoundment,

Mean24 = the mean river flow in the 24 hour period preceding sampling, and

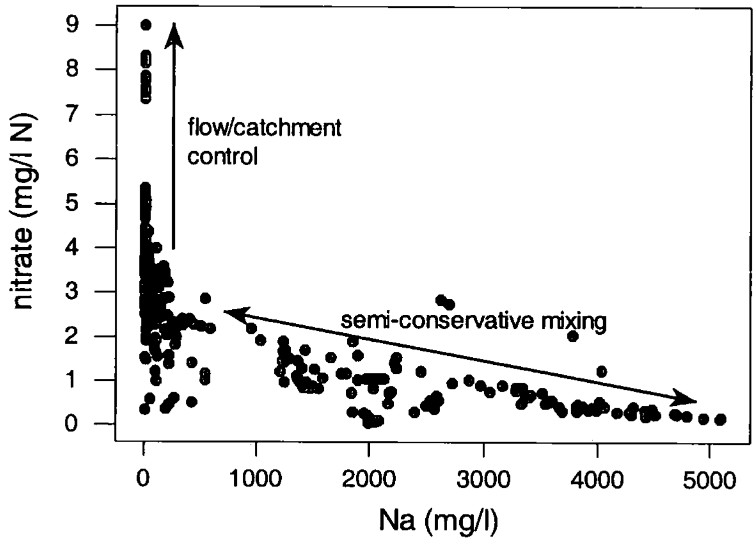


Figure 4.47. The two major controls on nitrate concentration in partial tidal exclusion impoundments: Freshwater nitrate levels relate to river discharge and catchment characteristics, and nitrate levels in saline samples to the mixing of seawater and freshwater inputs. The term semi-conservative is used to describe this mixing since reduction processes can act to reduce nitrate levels in stratified saline water. Data shown are from Wansbeck summer sampling.

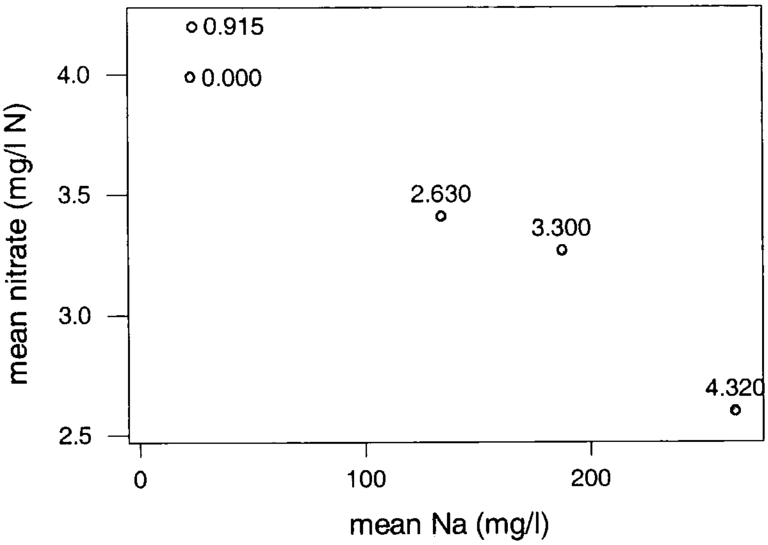


Figure 4.48. Mean nitrate levels vs. mean Na levels in surface water samples at each sampling site in the Wansbeck (summer data), showing mixing of fresh and saline water with progression downstream. Data labels are distance (km) from the tidal limit for the sampling sites.

The second difference between systems is related to the relative amounts of seawater and freshwater within the impounded areas. Nitrate levels in river water tend to be higher than those in seawater. For example, for the Tawe during the summer sampling period the mean level in freshwater samples (conductivity < 500 μS/cm) was 0.68 mg/l N whereas in saline (conductivity > 500 μS/cm) water it was 0.56 mg/l N. For the Wansbeck the difference is even greater at 4.75 and 2.10 mg/l N for fresh and saline water respectively. The decrease in nitrate levels due to seawater inputs is seen in the ANOVA for normalised data as the lower mean nitrate values in the partial exclusion systems relative to the freshwater inputs, and in the decrease in nitrate with depth and distance in these impoundments. The relative decreases in nitrate concentration with mixing are lower for the Tawe than the Wansbeck since the freshwater inputs for this system are of lower nitrate concentration, but the amount of seawater mixing is (based on conductivity and Na data) assumed to be similar for both impoundments.

The mixing of fresh and seawater is generally conservative in relation to nitrate levels (figures 4.47 and 4.48), although in stratified saline water a gradual decrease in nitrate is seen as anoxic conditions develop and nitrate reduction processes (denitrification and reduction to ammonia) take place (figures 4.49 and 4.50). For the Wansbeck the same period over which DO levels were seen to decrease in the deep water at site CP is used to determine a rate of nitrate reduction. As mentioned above for DO, a similar period of deep saline water isolation is not seen during the sampling period on the Tawe due to replacement by new saline water or removal by high freshwater flow. For the same period at site F over which DO was described above, nitrate follows DO levels in the water (which are in turn related to length of time of isolation from sources of DO) quite closely (figure 4.51). Relative to the variance in nitrate levels associated with changes in the freshwater inputs to the system or the amount of seawater mixing, the effect of nitrate reduction is small, but may be important in removal of N from the systems and/or in the build-up of ammonia levels in the water column. The behaviour of ammonia is explored further below.

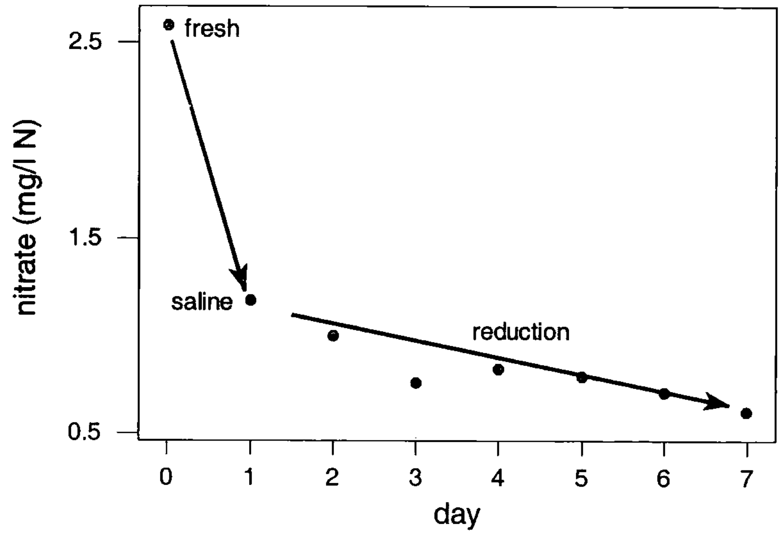


Figure 4.49. The changes in nitrate concentration through change from fresh to saline water followed by reductive processes in deep (stratified) water from the Wansbeck impoundment between the dates of 30th September and 7th October 2000.

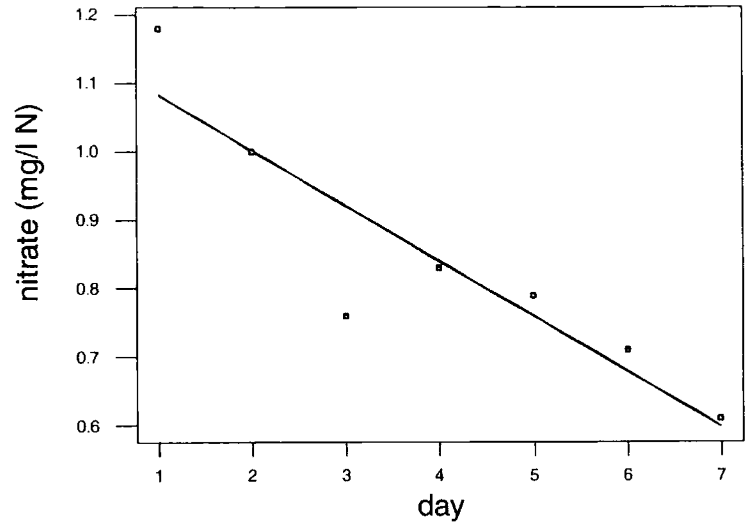


Figure 4.50. The decrease in nitrate concentration through reductive processes in deep (stratified) water from the Wansbeck impoundment between the dates of 1st and 7th October 2000.

Apart from the small decrease in nitrate levels with distance downstream in the Tees, which is interpreted as due to biological uptake, no other processes could be identified as important in controlling nitrate levels in the impounded areas. The importance of sediment as a possible nutrient source and sink is examined further in the sediment chapters of this thesis.

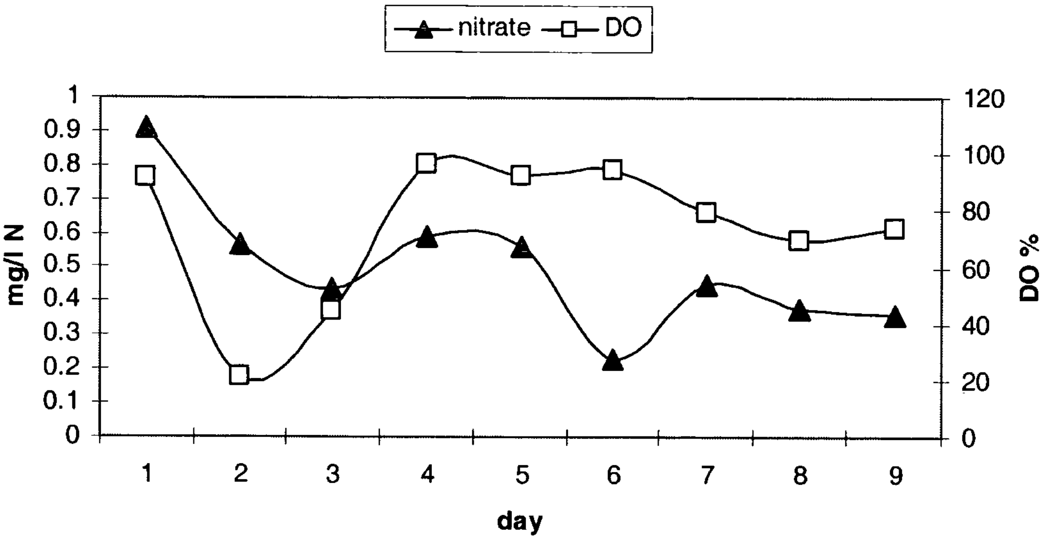


Figure 4.51. Nitrate and DO at depth at site F in the Tawe impoundment over the period 10th to 18th June 2000. Nitrate levels generally follow DO levels. DO levels vary with river flow and tidal overtopping.

4.3.8.2 Ammonia

Results

During analysis of the seasonal effects on the Tees it was shown that DO was the major influence on ammonia levels in the water. Initial analysis is carried out here first on raw and normalised data without the inclusion of DO as a covariate, and subsequently on normalised data including DO as a covariate.

Results using raw data (tables 4.20 and 4.21, figures 4.52 and 4.53) show that there are significant differences between the Tees and the Tawe, and the Wansbeck and the Tees in mean ammonia levels. Ammonia levels are highest in the Tawe and lowest in the Tees. Distance is also a significant factor, but the response varies between rivers, and the distance effect is assumed to relate to increased depths with distance downstream. Ammonia tends to increase with distance downstream in the Tawe and Tees and show an irregular pattern (relating to the highly variable site depths) in the Wansbeck. Depth is the most significant factor explaining approximately 41 % of the variance, and ammonia increases with depth in all 3 impoundments to the same degree in real terms. The error term is quite large and probably relates to analytical error. Several values (particularly from the Tees) are measured at close to the 3s LOD (0.04 mg/l N), and in general the baseline during the colorimetric determination of ammonia was subject to noise (and drift, although a drift standards were used to correct for this).

Source	**F**	**P**	σ^2	**Size of Effect** (ω^2)
River	11.47	0.000	0.015	0.13
Distance	4.63	0.001	0.011	0.09
Depth	34.27	0.000	0.048	0.41
River*distance	2.75	0.005	0.010	0.09
River*depth	1.67	0.155	na	na
Error			0.033	0.28

Table 4.20. Results from GLM ANOVA for ammonia (raw data) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant).

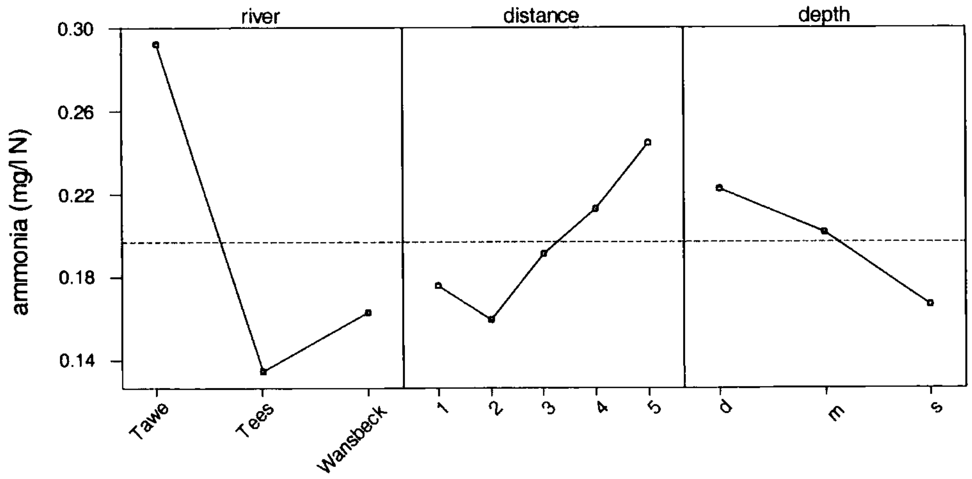


Figure 4.52. Main effects plot for the factors of impoundment (river), distance and depth on ammonia (raw data) (LS means for factor levels).

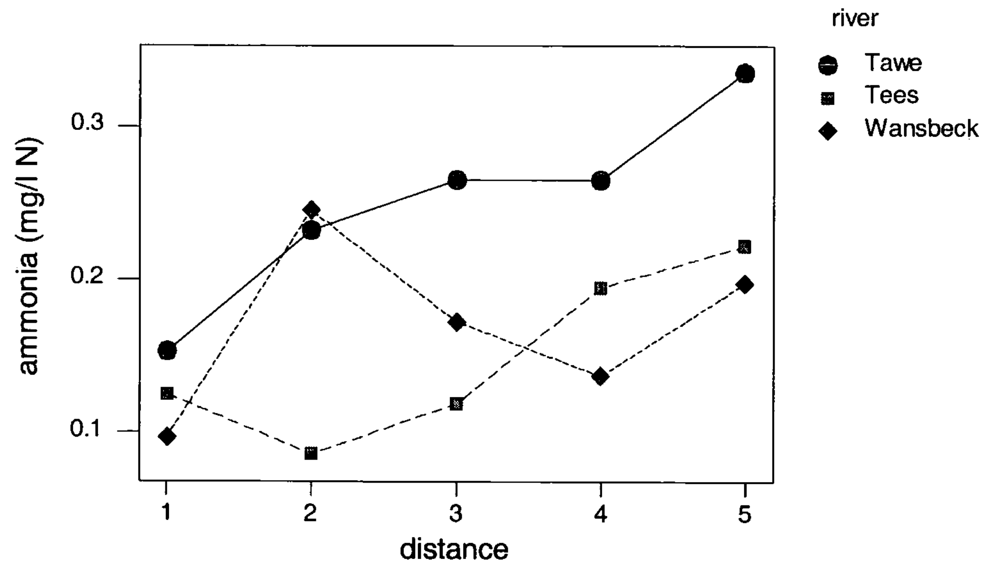


Figure 4.53. Interaction between river and distance effects on ammonia (raw data) (LS means).

Factor	**Pairwise comparison**	**Adjusted P-value**
River	Tees - Tawe	0.000
	Wansbeck - Tawe	0.090
	Wansbeck - Tees	0.013

Table 4.21. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for ammonia (raw data) in partial and total tidal exclusion impoundments.

Results for analysis using data normalised to freshwater inputs to the impoundments (tables 4.22 and 4.23, figures 4.54 and 4.55) show that ammonia levels in all 3 impoundments are significantly higher than in the water entering at the upstream limits. The increase in the Wansbeck is higher than in the Tees and Tawe. The Tees and Tawe show no statistical difference between them in the overall level of increase in ammonia. The size of effect for the factor of river is greater using normalised data (18 %) than for raw data (13 %) implying that the majority of variation in ammonia levels is within the impounded areas. Whilst in real terms the increase in ammonia with depth is the same in all 3 impoundments, as a proportion of the input values the increase is greater in the

Wansbeck (levels approximately 6 times greater than input values in deep samples) than in the Tees or Tawe (2 to 3 times greater).

Source	**F**	**P**	σ^2	**Size of Effect** (ω^2)
River	9.47	0.000	7.93	0.18
Distance	1.13	0.340	na	na
Depth	13.93	0.000	12.10	0.27
River*distance	1.69	1.69	na	na
River*depth	3.24	3.24	4.20	0.09
Error			21.05	0.46

Table 4.22. Results from GLM ANOVA for ammonia (data normalised to freshwater inputs) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant).

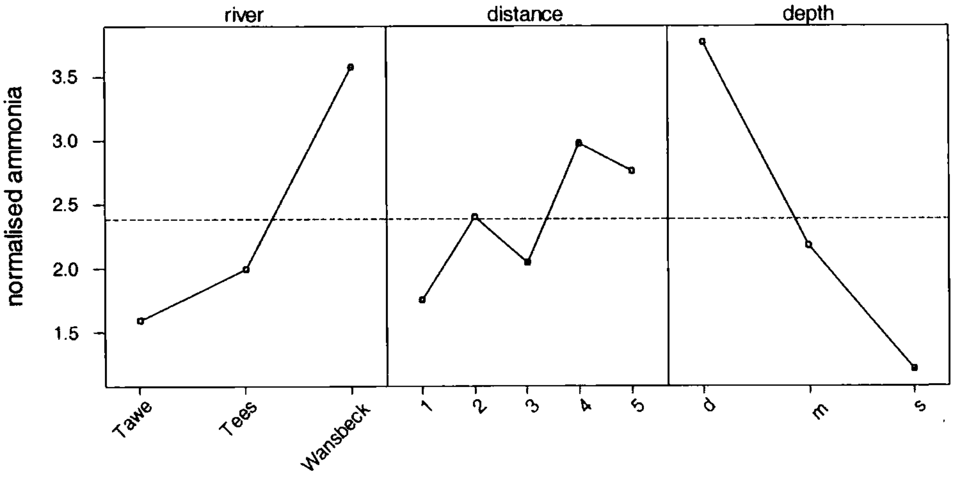


Figure 4.54. Main effects plot for the factors of impoundment (river), distance and depth on ammonia (data normalised to freshwater inputs) (LS means for factor levels).

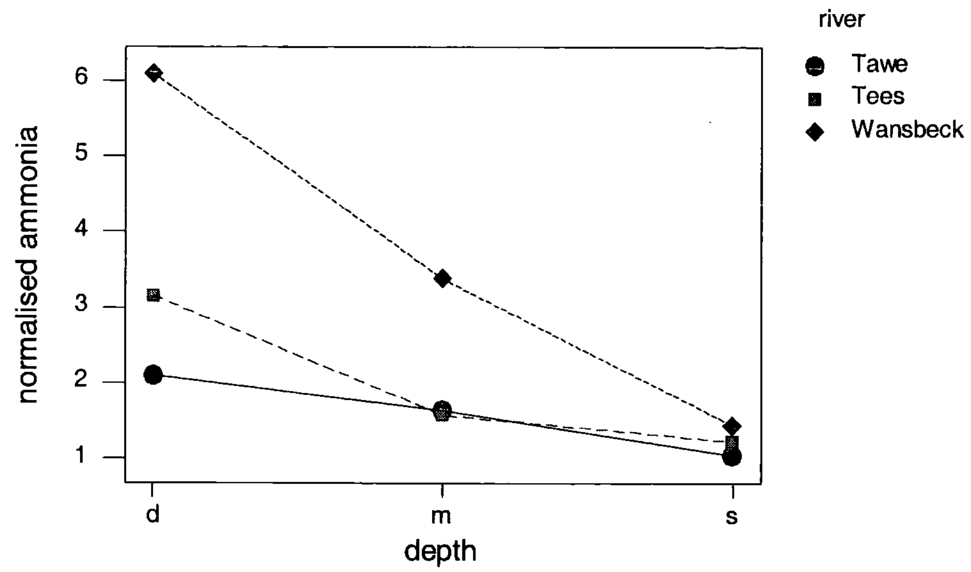


Figure 4.55. Interaction between river and depth effects on ammonia (data normalised to freshwater inputs) (LS means).

Factor	Pairwise comparison	Adjusted P-value
River	Tees - Tawe	0.742
	Wansbeck - Tawe	0.000
	Wansbeck - Tees	0.015

Table 4.23. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for ammonia (data normalised to freshwater inputs) in partial and total tidal exclusion impoundments.

Including normalised DO as a covariate in the model shows that a large amount of the depth effects relate to oxygen levels being lower in deeper water. Even accounting for the effects of oxygen depletion on ammonia build-up, the increase relative to input values is greater in the Wansbeck, and there is an increase downstream in all impoundments. Inclusion of DO as a covariate does not help to reduce the amount of unexplained variance in the model, which is in contrast to the behaviour of the Tees, implying that the relationship between DO and ammonia levels differs between the impoundments.

Source	F	P	σ^2	Size of Effect (ω^2)
Normalised DO	20.88	0.000	3.23	0.22
River	4.26	0.014	1.06	0.07
Distance	3.37	0.010	1.54	0.11
Depth	5.31	0.005	1.40	0.10
River*distance	0.76	0.639	na	na
River*depth	1.43	0.223	na	na
Error			7.31	0.50

Table 4.24. Results from GLM ANOVA for ammonia (data normalised to freshwater inputs) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant). Model including DO as a covariate.

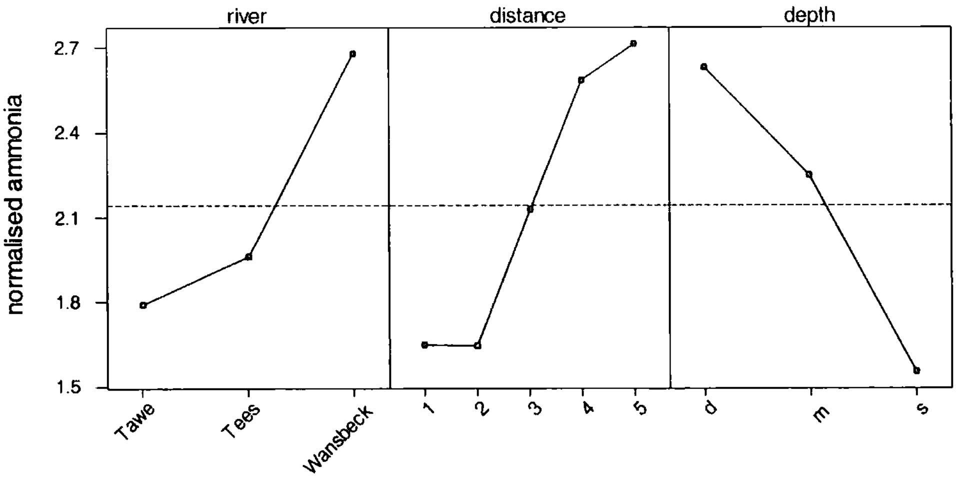


Figure 4.56. Main effects plot for the factors of impoundment (river), distance and depth, and DO as a covariate, on ammonia (data normalised to freshwater inputs) (LS means for factor levels).

Factor	Pairwise comparison	Adjusted P-value
River	Tees - Tawe	0.856
	Wansbeck - Tawe	0.012
	Wansbeck - Tees	0.104

Table 4.25. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for ammonia (data normalised to freshwater inputs) in partial and total tidal exclusion impoundments. Model including DO as a covariate.

Discussion

The mean values of ammonia in the freshwater entering the impoundments is low (mean values of 0.16, 0.11 and 0.09 mg/l N for the Tawe, Tees and Wansbeck respectively) and shows relatively little variation (standard deviations are 0.04, 0.13 and 0.08 mg/l N). The mean values for the whole impoundments are higher (0.25, 0.15 and 0.19 mg/l N for the Tawe, Tees and Wansbeck respectively) with greater variation (standard deviations are 0.15, 0.14 and 0.25 mg/l N). In all except the Wansbeck levels are below the SWQO for salmonid and cyprinid species. In the Wansbeck the SWQO for salmonids (0.78 mg/l N) is exceeded in 12 samples (all from deep water at site WB or CP) from 6 dates, and that for cyprinids (1.5 mg/l N) is exceeded on the 13th and 14th of June at site CP.

The ratios of mean ammonia/mean nitrate in the freshwater inputs to the impoundments help constrain the dominant sources of N in the rivers (Royal Society, 1983). For the Tawe the ratio was 0.206 ammonia/nitrate suggesting, together with the dilution effect for nitrate noted above, that point-sources (sewage) are dominant in this river. For the Wansbeck the ratio is 0.024, and it was seen that nitrate levels are proportional with flow, therefore diffuse (agricultural) sources dominate this river. For the Tees it was suggested that since a negative relationship exists between flow and nitrate concentrations, but that nitrate levels are generally higher in winter than summer, N is both point and diffuse sourced. The ammonia/nitrate ratio is therefore intermediate at 0.050. The differences between the riverine inputs are however small relative to the differences in ammonia levels within the impounded areas, and the differences in behaviour between the impoundments.

Ammonia levels build up in the deep water of all three impoundments studied due to the decomposition of organic material particularly in the sediments (figure 4.57). Concentrations of ammonia are also related to DO levels since under low redox conditions the process of nitrification ceases and dissimilatory nitrate reduction to ammonia can take place at (particularly at summer (>17°C) temperatures (Kelly-Gerreyn et al., 2001)).

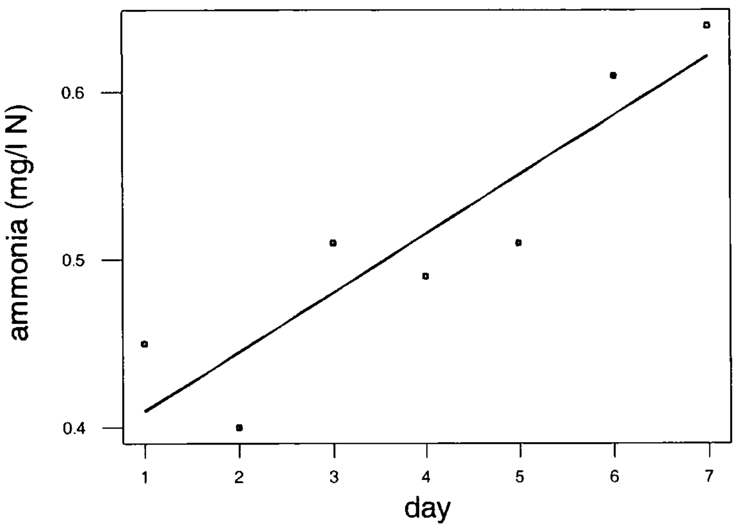


Figure 4.57. The increase in ammonia concentration in deep (stratified) water from the Wansbeck impoundment between the dates of 1st and 7th October 2000.

ammonia = 0.37 + 0.035 day (S = 0.039 R-Sq = 81.8 % R-Sq(adj) = 78.2 %)

where,

ammonia = ammonia concentration (mg/l N) at site CP in the Wansbeck impoundment, and

day = the time in days following isolation from sources of re-oxygenation.

The rate for nitrate reduction over the same period was determined as 0.0807 mg/l N/day and so, assuming that all ammonia is derived from nitrate reduction, applying a simple mass balance in terms of N suggests that N is being removed from the saline water, either by reduction to gaseous forms or by exchange with the overlying freshwater element:

decrease in nitrate N – increase in ammonia N = N loss from system

0.081 - 0.035 = 0.46 mg/l N/day lost.

Nitrate, ammonia and DO all show zero-order rate equations within isolated deep water (i.e. the rates of change of these parameters are independent of their concentrations).

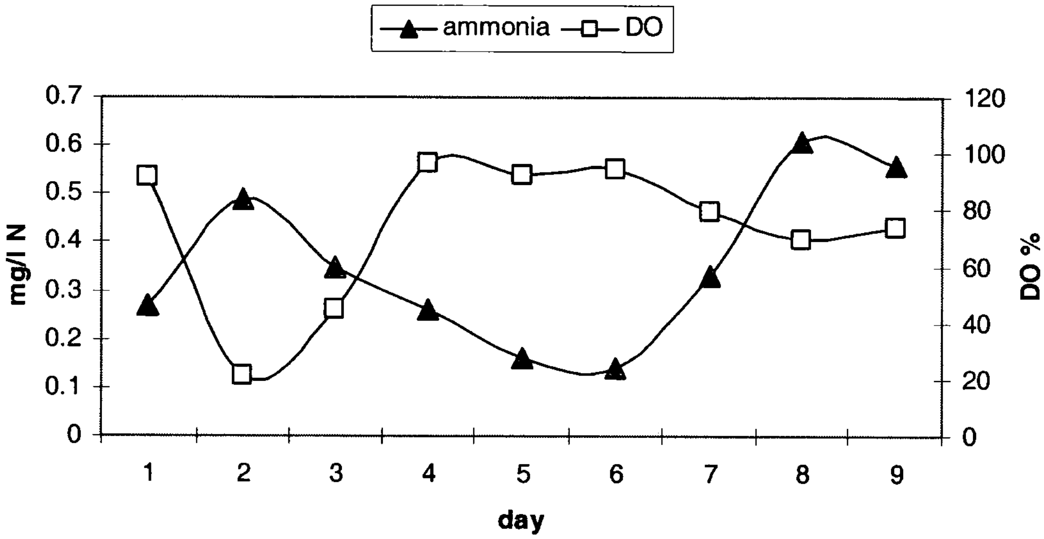


Figure 4.58. Ammonia and DO at depth at site F in the Tawe impoundment over the period 10th to 18th June 2000. Ammonia levels generally mirror DO levels. DO levels vary with river flow and tidal overtopping.

For the Tawe the rate of increase in ammonia concentrations is higher than in the Wansbeck at an equivalent 'ponded' site (figure 4.58) at approximately 0.2 mg/l N per day of isolation of deep water. Care must be taken however since the majority of this increase is due to the change in water composition from lower ammonia (mean = 0.15 mg/l N over sampling period) freshwater (conductivity < 500 μS/cm) to higher ammonia (mean = 0.35 mg/l N over sampling period) saline water (conductivity > 500 μS/cm). The mixing of fresh and seawater is generally conservative, although additions of ammonia to the mixing water body (from respiratory processes) can be seen (figure 4.59). A dataset that captured a longer period of isolation of deep stratified water would be necessary to determine the rate of change in ammonia (and DO and nitrate) excluding the effects of mixing in the Tawe. Since the mixing of seawater is also important in determining ammonia levels, the inclusion of DO as a covariate in the general linear model described above shows a worse fit for all impoundments than was seen for the Tees which has only one water source.

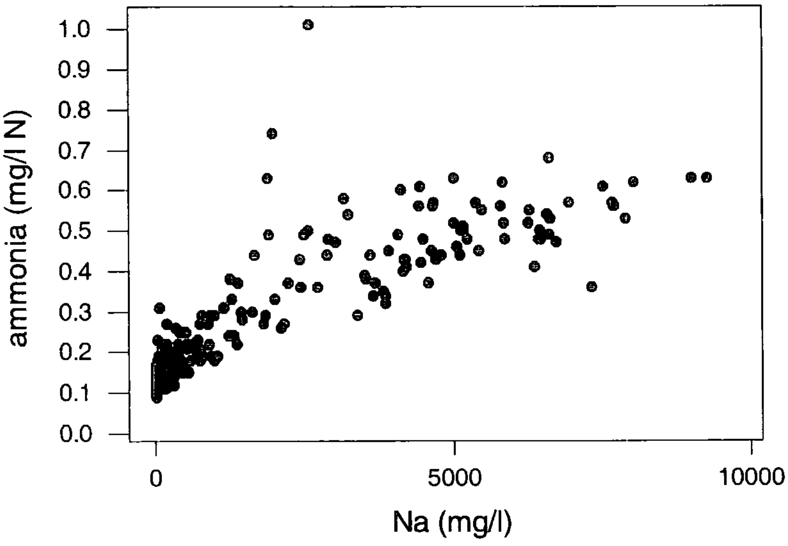


Figure 4.59. Ammonia vs. Na in the Tawe impoundment. Ammonia levels are raised above the conservative mixing line by additions from organic decomposition within sediments. The positive outlying values for ammonia are from the 11th, 12th and 13th June 2000 from site S.

4.3.8.3 Phosphate

Results

Most (74 %) of the variance in phosphate levels in the dataset can be explained by the differences between the rivers. Phosphate levels are significantly higher in the Tees than the Wansbeck than the Tawe. Internal variation in levels of phosphate in the impoundments is minor, with only small decreases with distance in the Wansbeck and Tees being important. Repeat analysis using data normalised to the freshwater input values showed that there are no significant differences (hence results are not presented) between the impoundments other than in terms of their freshwater input values and the small contrast in behaviour with distance.

Source	F	P	σ^2	Size of Effect (ω^2)
River	140.57	0.000	0.141	0.74
Distance	8.65	0.000	0.015	0.08
Depth	1.38	0.252	na	na
River*distance	3.92	0.000	0.012	0.06
River*depth	1.78	0.132	na	na
Error			0.023	0.12

Table 4.26. Results from GLM ANOVA for phosphate (raw data) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant).

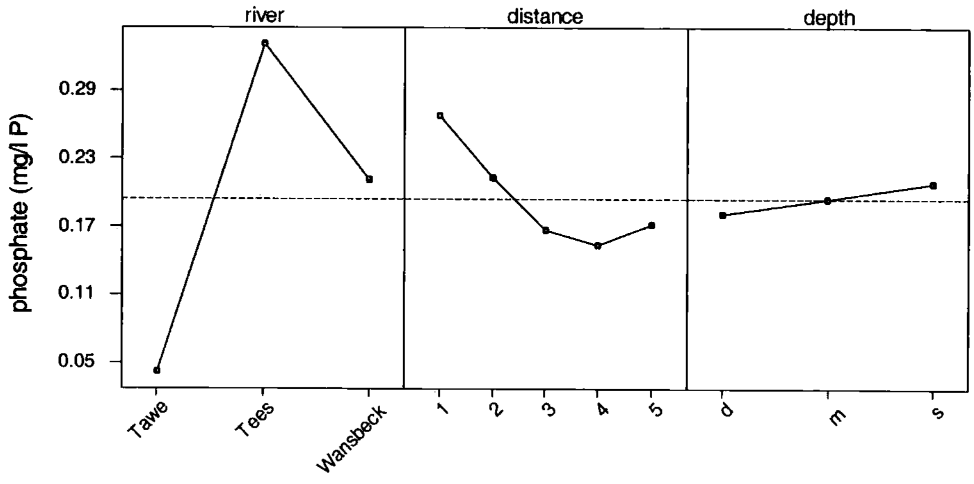


Figure 4.60. Main effects plot for the factors of impoundment (river), distance and depth on phosphate (raw data) (LS means for factor levels).

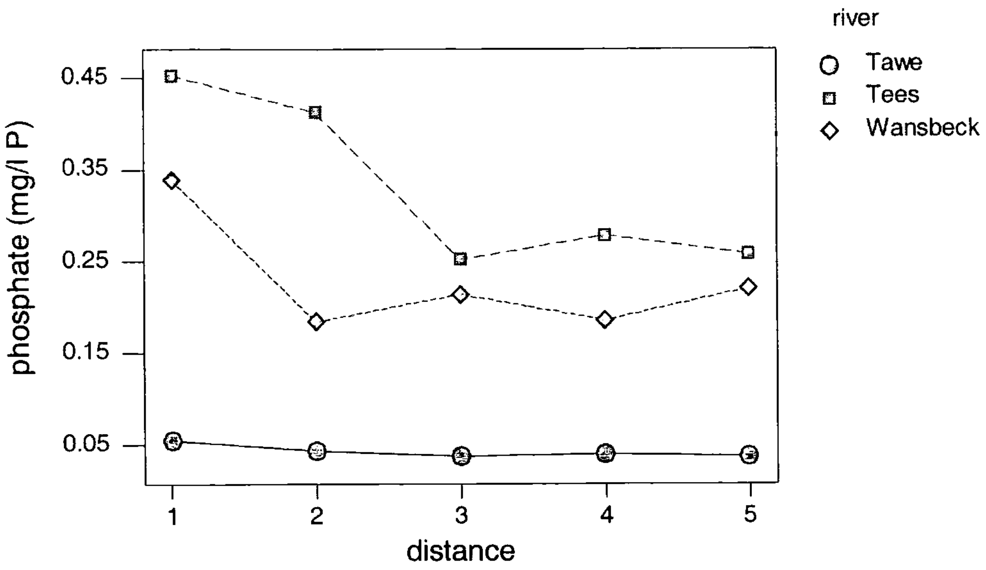


Figure 4.61. Interaction between river and distance effects on phosphate (raw data) (LS means).

Factor	Pairwise comparison	Adjusted P-value
River	Tees - Tawe	0.000
	Wansbeck - Tawe	0.000
	Wansbeck - Tees	0.000

Table 4.27. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for phosphate (raw data) in partial and total tidal exclusion impoundments.

Discussion

Dissolved P shows a dilution by increasing freshwater flows (figures 4.62 and 4.63) and therefore the majority of phosphate entering the rivers is likely to be from point-sources.

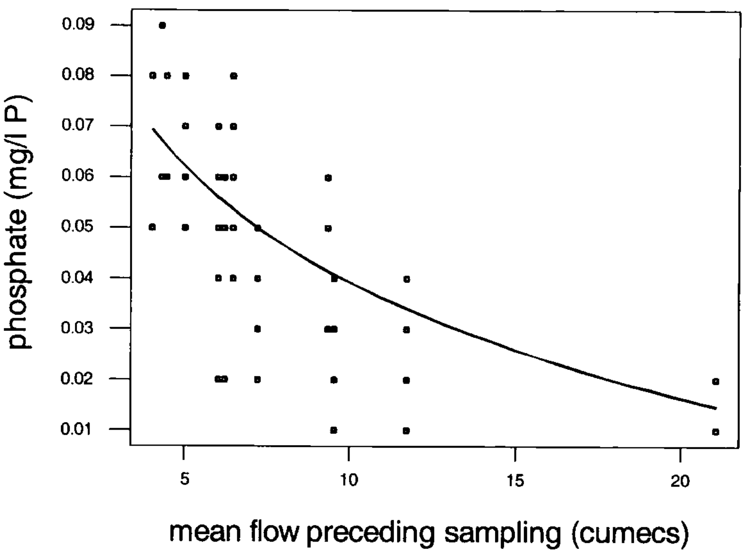


Figure 4.62. The relationship between phosphate and flow in freshwater (conductivity < 500 μS/cm) samples in the Tawe.

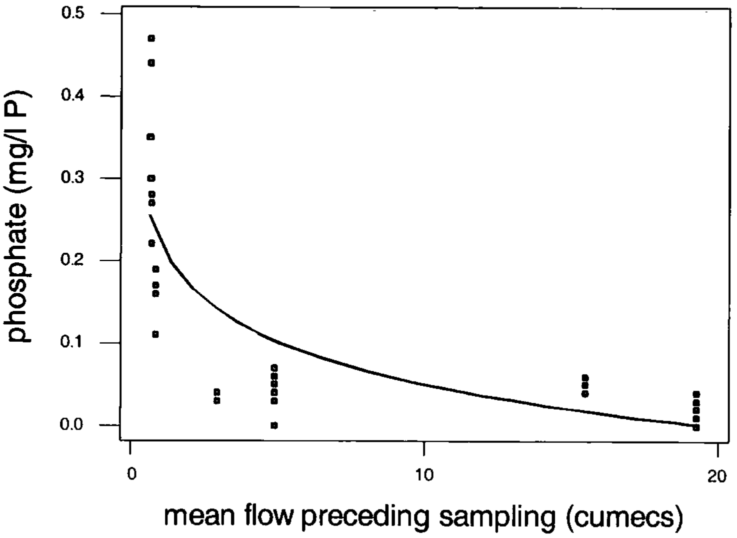


Figure 4.63. The relationship between phosphate and flow in freshwater (conductivity < 500 μS/cm) samples in the Wansbeck.

For the Tawe:

phosphate = 0.12 - 0.076 log(Mean24) (S = 0.012 R-Sq = 62.5 %)

For the Wansbeck:

phosphate = 0.22 - 0.17 log(Mean24) (S = 0.063 R-Sq = 68.4 %)

where,

phosphate = dissolved orthophosphate concentration (mg/l P) in freshwater (conductivity < 500 μS/cm) samples, and

Mean24 = the mean freshwater flow in the 24 hours preceding sampling.

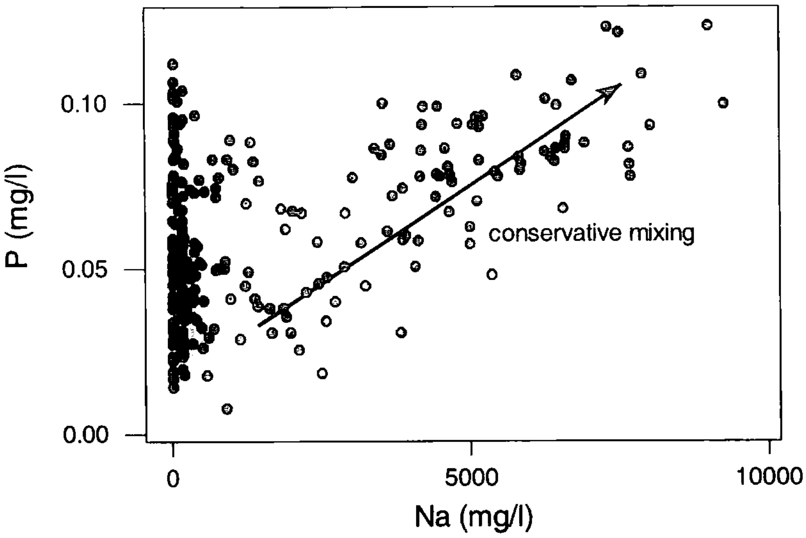


Figure 4.64. Conservative mixing behaviour of P. Data from the Tawe impoundment. P as total dissolved P.

Within the dataset no internal variation in phosphate levels could be identified apart from a small decrease in levels with distance downstream in the Tees and Wansbeck impoundments. During the periods studied no depth effects were encountered, i.e. there were no significant exchanges of phosphate between the sediment and the water columns. P behaved conservatively on mixing between fresh and seawater (figure 4.64). The distance effect is interpreted as due to the utilisation of phosphate in primary production within the water bodies. On several occasions at site SW on the Wansbeck (distance 1) large developments of *Enteromorpha intestinalis* were observed, causing the drop in phosphate levels between distances 1 and 2. Similar blooms were not seen further downstream in the saline parts of the impoundment. In terms of nutrient limitation, as was noted in the discussion of seasonal effects, the Tees has an N/P ratio below the Redfield ratio and thus biological productivity is limited by the availability of bioavailable (dissolved) N. For the Wansbeck and the Tawe the by mass ratios of the mean nitrate to mean phosphate levels are 12.5 and 14.7 respectively. By mass the Redfield ratio is 7.3 and therefore primary production in both the Wansbeck and the Tawe is in general limited by P during the summer periods.

4.3.8.4 Silica

Results

Analysis was carried out on raw Si data only since the levels in seawater are distinctly lower than in freshwater. The majority of the variance (61 %) in the dataset is explained by differences between the 3 rivers. Tukey simultaneous testing gives significant differences between each of the impoundments, with levels in general highest in the Tawe and lowest in the Tees (figure 4.65). There is a small but significant decrease in Si levels with distance downstream in the systems (the interaction, although not significant at the 95 % confidence interval, shows Si levels increasing with distance in the Tees however). The Tawe shows a small decrease in Si with depth in the water column, the Tees a small increase, and the Wansbeck a small decrease then increase.

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
River	49.84	0.000	0.57	0.61
Distance	3.00	0.018	0.05	0.05
Depth	2.32	0.099	na	na
River*distance	1.83	0.068	na	na
River*depth	3.41	0.009	0.06	0.06
Error			0.26	0.28

Table 4.28. Results from GLM ANOVA for silica (raw data) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant).

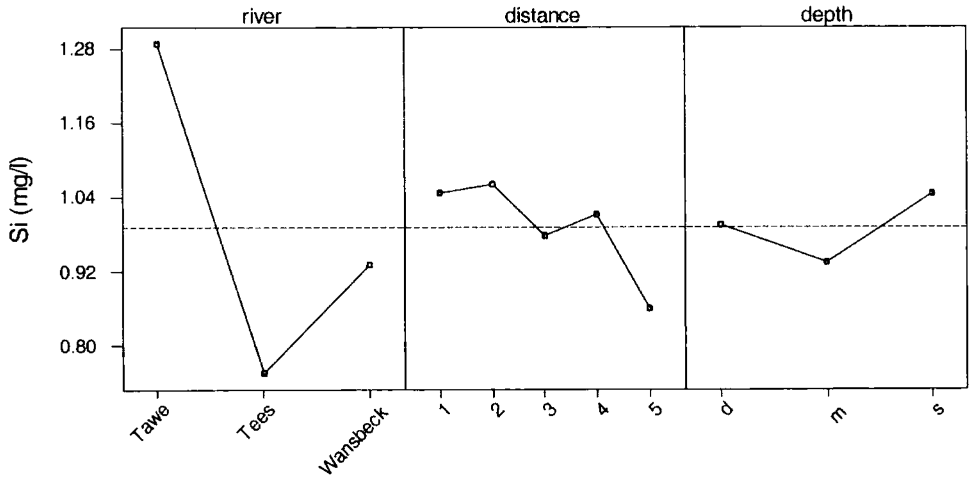


Figure 4.65. Main effects plot for the factors of impoundment (river), distance and depth on Si (raw data) (LS means for factor levels).

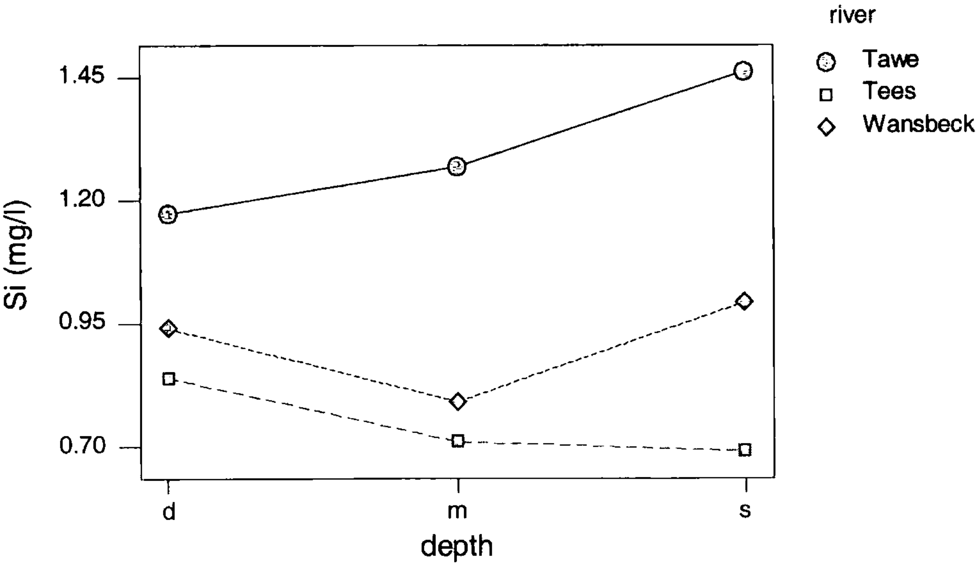


Figure 4.66. Interaction between river and depth effects on Si (raw data) (LS means).

Factor	Pairwise comparison	Adjusted P-value
River	Tees - Tawe	0.000
	Wansbeck - Tawe	0.000
	Wansbeck - Tees	0.010

Table 4.29. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for Si (raw data) in partial and total tidal exclusion impoundments.

Discussion

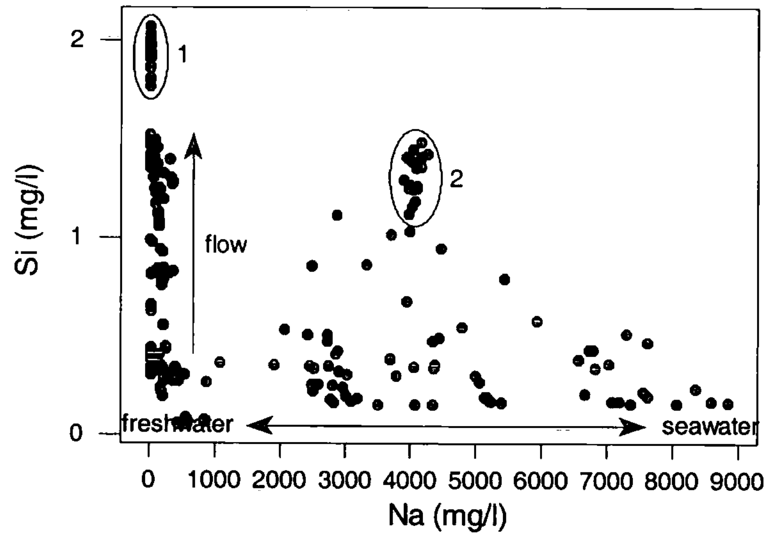


Figure 4.67. The behaviour of Si in the Wansbeck impoundment (summer data). Freshwater Si concentration is controlled by freshwater flow, and concentration in saline water is generally controlled by conservative mixing with seawater. Points within 1 are from the 16th, 17th and 18th June when high freshwater flows removed all saline water from the impounded area. Points within 2 are from deep water at site CP and show increased Si concentrations due to release from sediment.

The majority of the variation in Si levels relates to differences between the rivers entering the impounded areas. Si levels vary between rivers in relation to the geologies and land-uses of the catchments. It was noted for the Tees that Si levels increase with increased river discharge, implying a near-surface diffuse source for the element. This also appears to be the case for the Wansbeck although the relationship is not strong (R-squared = 21.7 % for linear regression between Si and flow in freshwater (conductivity < 500 μS/cm) samples). For the Tawe the opposite appears to be the case (figure 4.68), implying that the Si source is groundwater/baseflow dominated (probably relating to the greater amount of silicate (Triassic sandstones) and less intensive agriculture in the catchment).

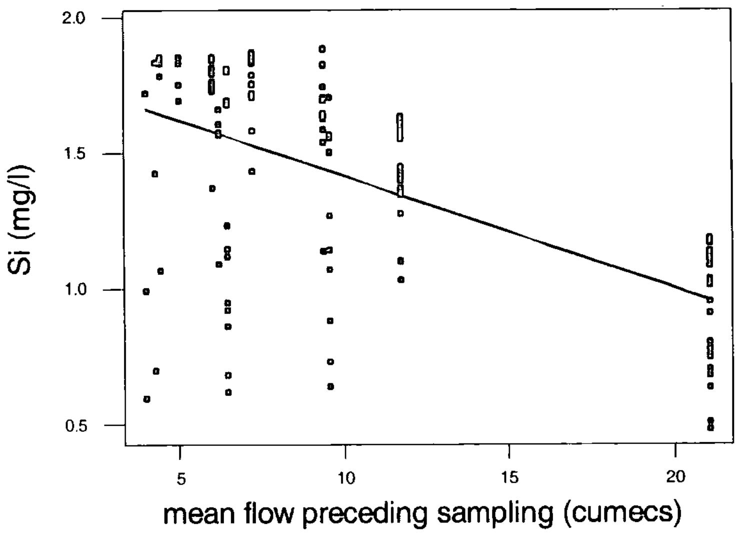


Figure 4.68. The relationship between Si and freshwater flow in the Tawe (R-squared = 32.2 %).

The mixing between fresh and seawater is of lesser importance in controlling Si levels than the riverine controls. Mixing is generally conservative in the Tawe and Wansbeck impoundments (figures 4.67 and 4.69). Figure 4.69 shows three component mixing between low flow freshwater (top left), high flow freshwater (bottom left) and seawater (bottom right) end-members. Levels of Si are lower in seawater than in the river waters (removal of Si in the marine environment is thought to take place through both biological and non-biological processes (e.g. DeMaster, 1981)).

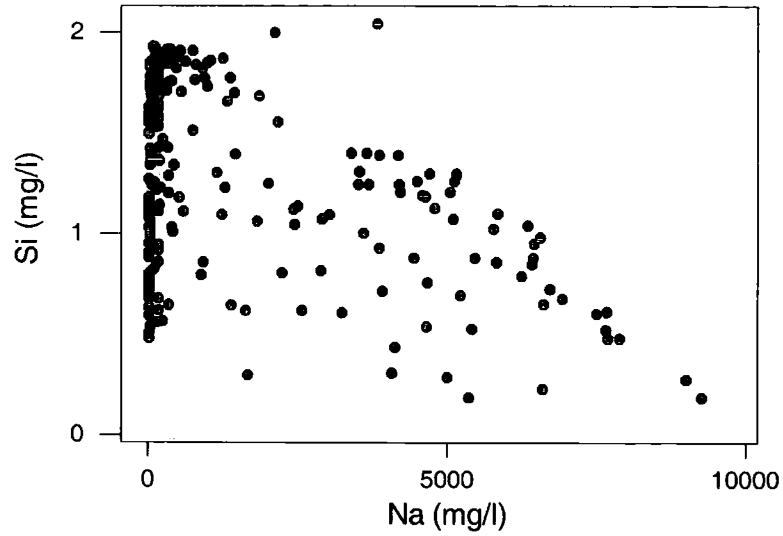


Figure 4.69. Si and Na concentrations in the Tawe, showing three component (triangular) mixing between low flow freshwater, high flow freshwater and seawater.

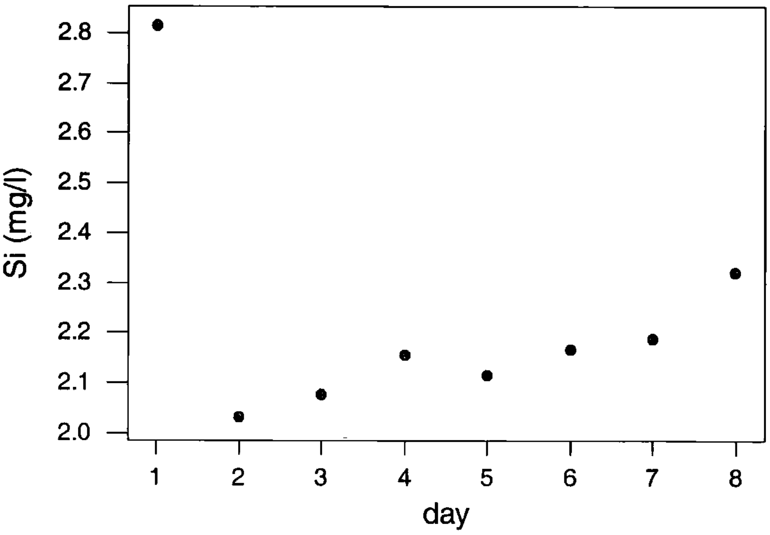


Figure 4.70. The changes in Si concentration through change from fresh to saline water followed by release from sediment in deep (stratified) water from the Wansbeck impoundment between the dates of 30th September and 7th October 2000.

Some increased values of Si were seen in deep isolated saline samples (site CP in the Wansbeck and sites F and S in the Tawe) due to release from sediment or possible remineralisation of diatomic algae. For the Wansbeck the rate of increase in Si levels in deep water is determined for the period 1st to 7th October 2000 (figures 4.70):

$$\text{Si} = 1.99 + 0.0392\ \text{day} \qquad (\text{S} = 0.0406 \quad \text{R-Sq} = 83.9\ \% \quad \text{R-Sq(adj)} = 80.7\ \%)$$

where,

Si = Si concentration in mg/l at depth at site CP in the Wansbeck, and

day = number of days following isolation of deep water.

In general, for all the nutrients studied (N, P and Si) impounded estuaries behave in the same manner as un-impounded estuaries (Kaul and Froelich, 1984; Edmond et al., 1981 and 1985) in terms of general conservative behaviours and export of the majority of the riverine inputs to the coastal shelf (with the exception of some loss of N through denitrification). A small amount of removal of P was identified for the partial exclusion systems which may relate to primary biological production or interaction with particulate material (which is at increased concentrations in the impounded areas relative to the upstream sections). The possible interactions between sediment and water are explored elsewhere in this thesis (chapter 7). The differences between impounded and un-impounded estuaries are explored further in chapter 5 through comparison of the Wansbeck and the Blyth.

4.3.9 Major elements

Results

Since the major elements (Ca, Mg, K and Na) show co-linearity due to conservative mixing between fresh and seawater, results are presented for Na only. The results for Na (major elements) are, as might be expected, very similar to those for conductivity given above. Conductivity and Na are interpreted as proportional to the ratio of seawater/freshwater in a sample. Na is significantly higher in the partial than the total exclusion impoundment. There is no significant difference in Na levels (the amount of seawater) between the two partial tidal exclusion impoundments during the periods studied. The distance and depth effects relate, as has been noted, to saline stratification in the systems, and the patterns of distribution vary with the topography of the partial exclusion impoundment beds (e.g. distance 2 (site CP) from the Wansbeck is a deep site and 'ponds' saline water, whereas distance 4 (site CI) is very shallow (< 1 m) and stratification does not develop).

Source	**F**	**P**	σ^2	**Size of Effect** (ω^2)
River	47.78	0.000	1240283	0.21
Distance	7.55	0.000	347357	0.06
Depth	82.80	0.000	2168751	0.37
River*distance	4.43	0.000	363595	0.06
River*depth	22.27	0.000	1127764	0.19
Error			596527	0.10

Table 4.30. Results from GLM ANOVA for Na (major metals) (raw data) in partial and total tidal exclusion impoundments.

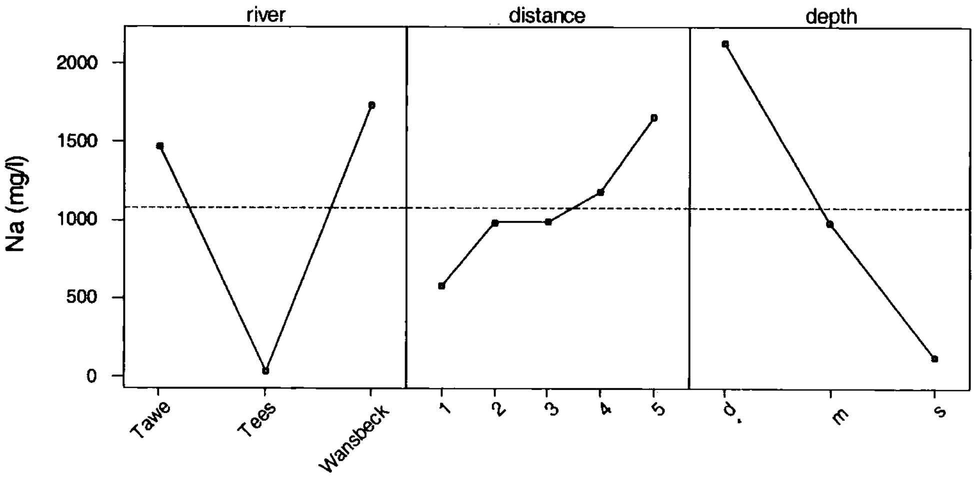


Figure 4.71. Main effects plot for the factors of impoundment (river), distance and depth on Na (raw data) (LS means for factor levels).

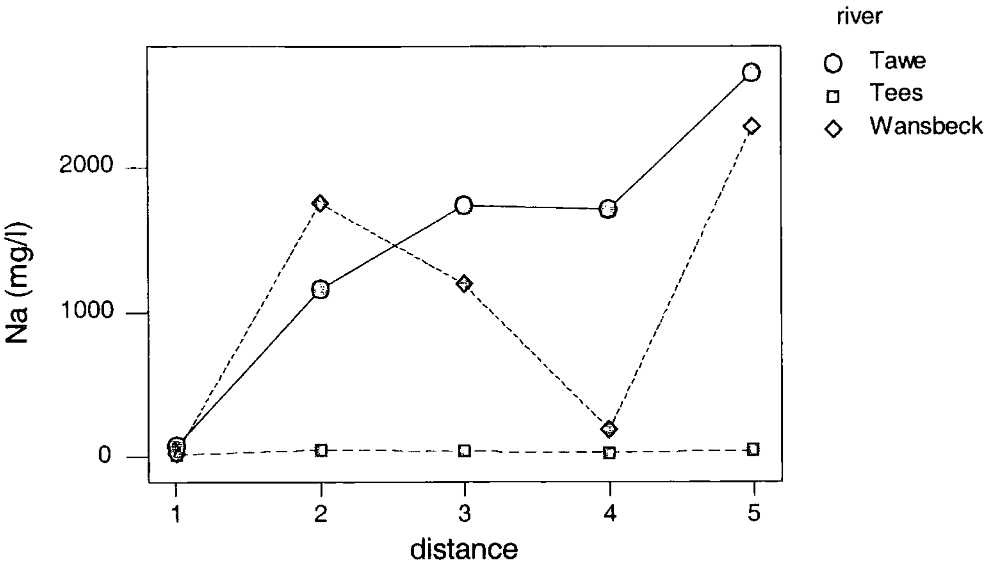


Figure 4.72. Interaction between river and distance effects on Na (raw data) (LS means).

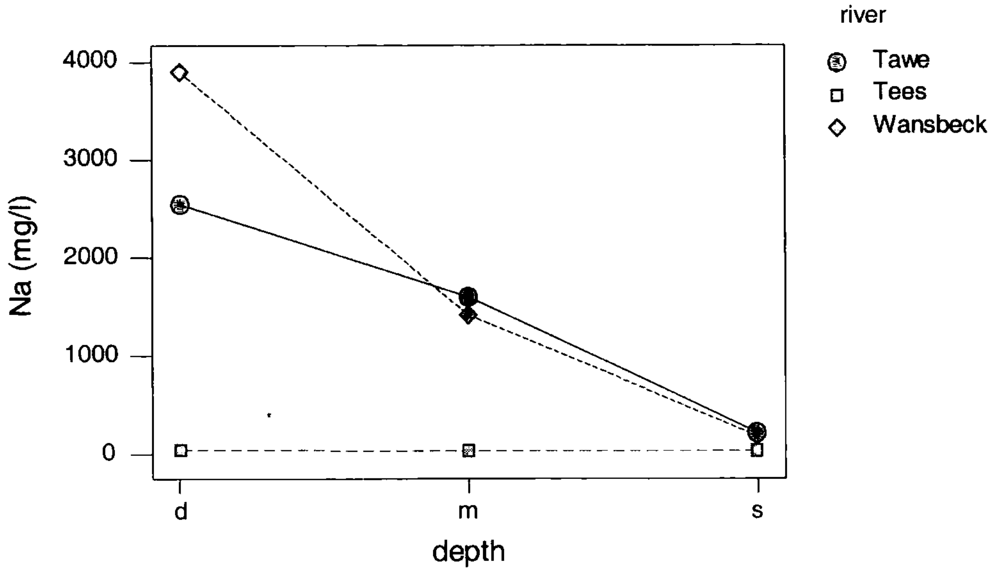


Figure 4.73. Interaction between river and depth effects on Na (raw data) (LS means).

Factor	Pairwise comparison	Adjusted P-value
River	Tees - Tawe	0.000
	Wansbeck - Tawe	0.207
	Wansbeck - Tees	0.000

Table 4.31. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for Na (raw data) in partial and total tidal exclusion impoundments.

Discussion

The distribution and concentration of major elements is (as for conductivity) dominated in the partial tidal exclusion systems by the amount of seawater mixing. The impoundments are subject to saline (density) stratification which is only broken down under conditions of high freshwater flow. The major elements behave conservatively on mixing (c.f. Liss, 1976). Ratios of major elements in world mean seawater and those in the impoundments show good comparison, and the range of major element concentrations in the impoundments extends almost up to seawater concentrations (table 4.32). For S data from the Tawe (which showed significant analytical error) is excluded.

	Estuarine impoundments	World mean seawater
Mg/Na	0.124	0.119
K/Na	0.0366	0.0369
Ca/Na	0.0375	0.0381
S/Na	0.0859	0.0838
Na (mg/l)	9271	10800
Mg (mg/l)	1124	1290
K (mg/l)	357	399
Ca (mg/l)	358	412
S (mg/l)	787	905

Table 4.32. Ratios and maximum concentrations of major elements in the impoundments (during the summer sampling periods) and World mean seawater (data from Reimann and Caritat, 1998).

The predominant species of S in natural waters is sulphate (SO_4^{2-}), but decomposition of organic matter releases toxic hydrogen sulphide (H_2S). Hydrogen sulphide is normally at low concentrations since it is either oxidised to sulphate under oxic conditions or reacts with Fe^{2+} to form FeS under reducing conditions. Analysis by ICP-OES does not allow speciation of S (or any other element) and gives the total (dissolved and colloidal) elemental concentration, but it may be assumed that levels of H_2S in the water column are low. H_2S was identified within the bed sediments during sediment coring by smell.

4.3.10 Fe and Mn

Results

Fe

Analysis of the behaviour of Fe was carried out using both raw data and data normalised to the freshwater inputs to the impoundments. The results for raw data (tables 4.32 and 4.33 and figures 4.74 and 4.75) show that there are significant differences in Fe levels between all of the impoundments. Fe concentrations are generally highest in the Tees and much lower (about half) in the Tawe and Wansbeck. Relative to the variance due to the effect of river the other factors in the model are insignificant, apart from a small amount of variance due to the difference in behaviour with distance downstream between the impoundments. Most noticeably distance 2 (site CP) on the Wansbeck (the deepest site) shows increased Fe concentration. The error term is fairly large and probably relates to variance due to change in freshwater discharge within the rivers (the flow effect accounted for approximately half of the variance in Fe in the Tees when comparing summer and winter data).

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
River	71.29	0.000	0.017	0.72
Distance	1.05	0.382	na	na
Depth	2.10	0.123	na	na
River*distance	2.22	0.025	0.001	0.05
River*depth	1.94	0.102	na	na
Error			0.005	0.23

Table 4.32. Results from GLM ANOVA for Fe (raw data) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant).

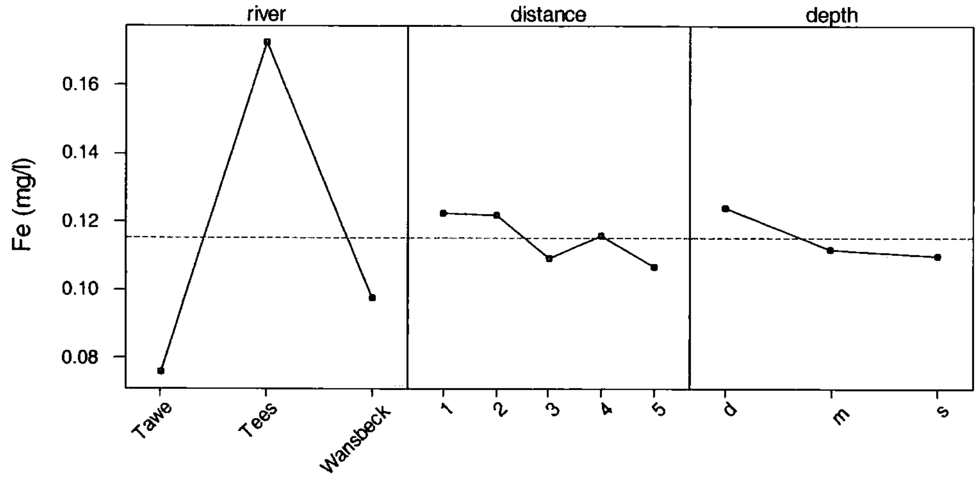


Figure 4.74. Main effects plot for the factors of impoundment (river), distance and depth on Fe (raw data) (LS means for factor levels).

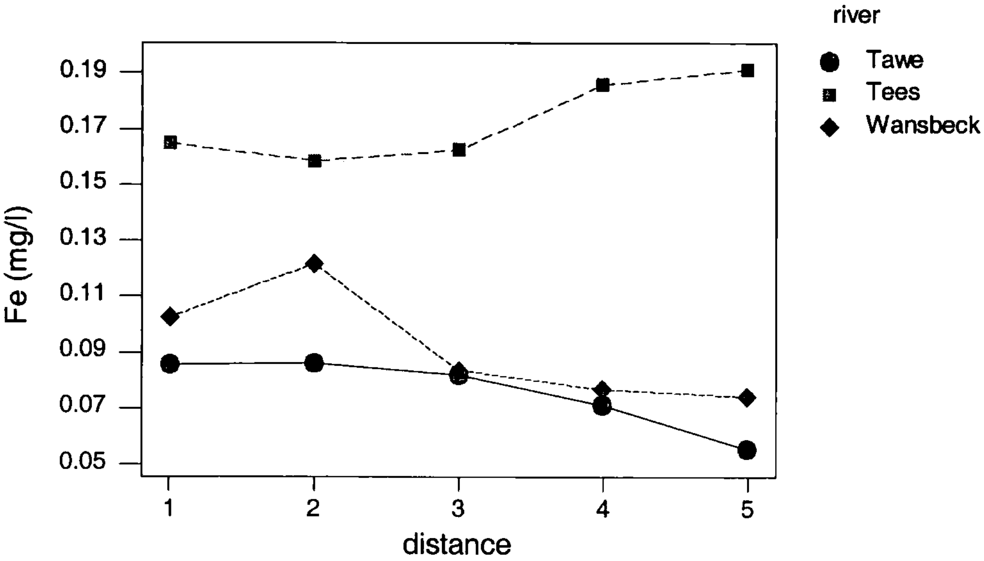


Figure 4.75. Interaction between river and distance effects on Fe (raw data) (LS means).

Factor	Pairwise comparison	Adjusted P-value
River	Tees - Tawe	0.000
	Wansbeck - Tawe	0.012
	Wansbeck - Tees	0.000

Table 4.33. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for Fe (raw data) in partial and total tidal exclusion impoundments.

Repeating the analysis using data normalised to input values (i.e. removing the variation in inputs to the systems) shows contrasting results to those from analysis of raw data. All factors in the model show significant effects. The Tees and the Tawe behave in the same manner and show no overall increase in Fe concentrations relative to the freshwater input levels, whereas within the Wansbeck mean Fe concentration is increased (by approximately 22 %) relative to that entering in the freshwater input. Also within the Wansbeck Fe levels are approximately 80 % higher in deep water than in surface water. The river*distance interaction suggests that (ignoring the depth effects for the Wansbeck) Fe decreases downstream in the partial exclusion systems (seawater Fe levels are lower than those in freshwater), and increases slightly with distance downstream in the Tees.

Source	F	P	σ^2	Size of Effect (ω^2)
River	6.50	0.002	0.138	0.08
Distance	1.79	0.129	na	na
Depth	9.50	0.000	0.213	0.12
River*distance	4.74	0.000	0.375	0.22
River*depth	9.90	0.000	0.447	0.26
Error			0.564	0.32

Table 4.34. Results from GLM ANOVA for Fe (data normalised to input values) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant).

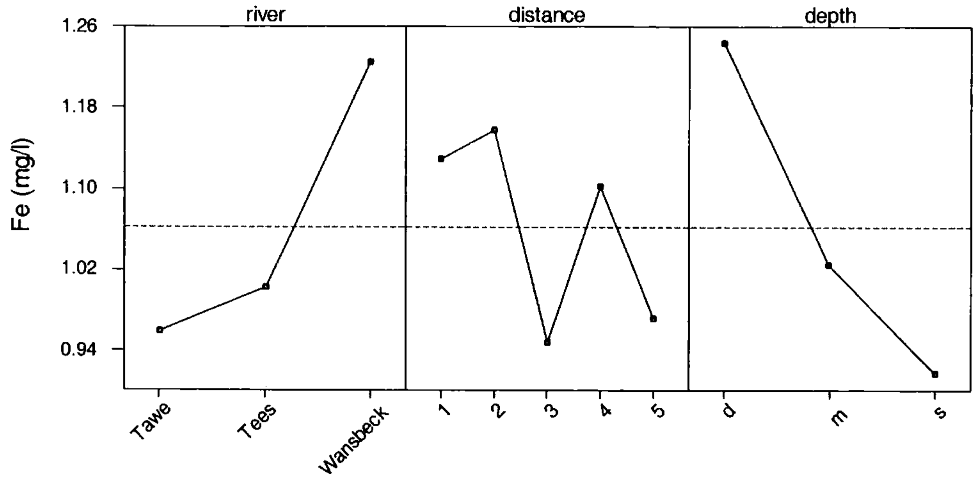


Figure 4.76. Main effects plot for the factors of impoundment (river), distance and depth on Fe (data normalised to input values) (LS means for factor levels).

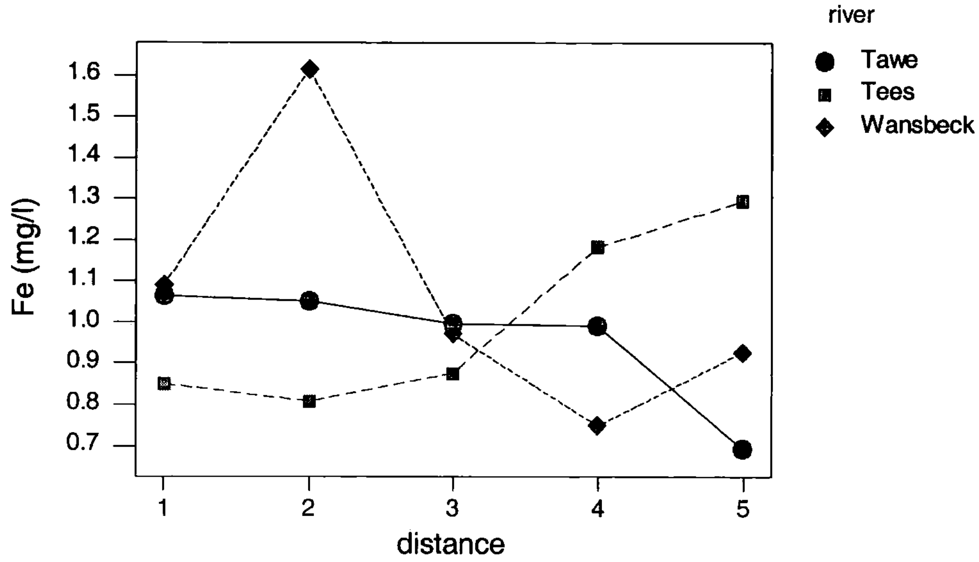


Figure 4.77. Interaction between river and distance effects on Fe (data normalised to input values) (LS means).

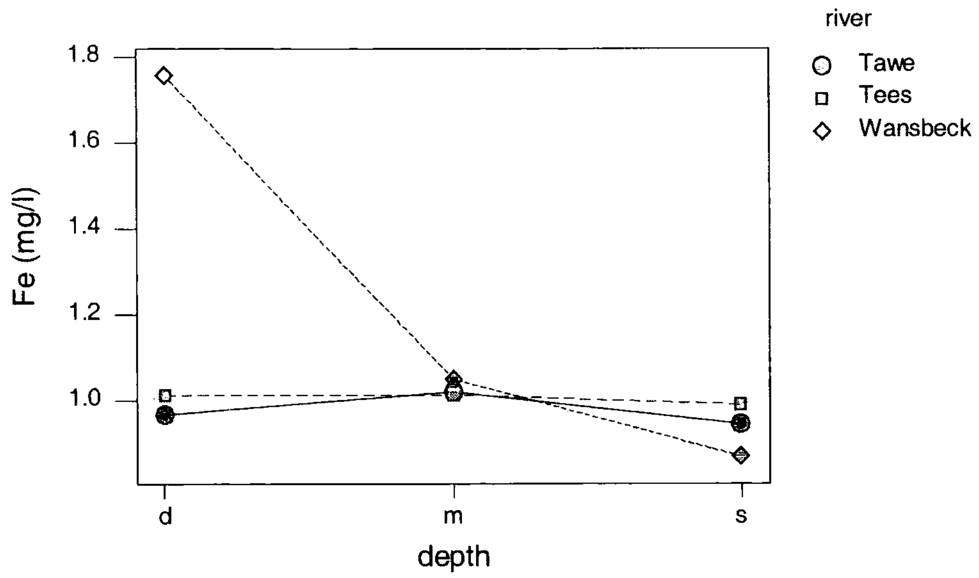


Figure 4.78. Interaction between river and depth effects on Fe (data normalised to input values) (LS means).

Factor	**Pairwise comparison**	**Adjusted P-value**
River	Tees - Tawe	0.859
	Wansbeck - Tawe	0.001
	Wansbeck - Tees	0.031

Table 4.35. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for Fe (data normalised to input values) in partial and total tidal exclusion impoundments.

Mn

Results for Mn using both raw and normalised data are very similar since levels in the inputs are close to zero (< 0.1 mg/l) in all three impoundments. Results for raw data are presented. Mean Mn levels are highest in the Wansbeck and lowest in the Tees. The distance pattern shows a small increase in Mn in the Tees (as was identified during examination of seasonal effects in the Tees), and depth related patterns in the other impoundments. Depth is the most significant factor and there are small increases in Mn with depth in the Tees and Tawe, and much larger increases in the Wansbeck.

Source	F	P	σ^2	Size of Effect (ω^2)
River	62.46	0.000	0.14	0.21
Distance	7.68	0.000	0.03	0.05
Depth	68.89	0.000	0.15	0.23
River*distance	12.28	0.000	0.10	0.15
River*depth	42.45	0.000	0.18	0.28
Error			0.05	0.08

Table 4.36. Results from GLM ANOVA for Mn (raw data) in partial and total tidal exclusion impoundments (na = not applicable since factor insignificant).

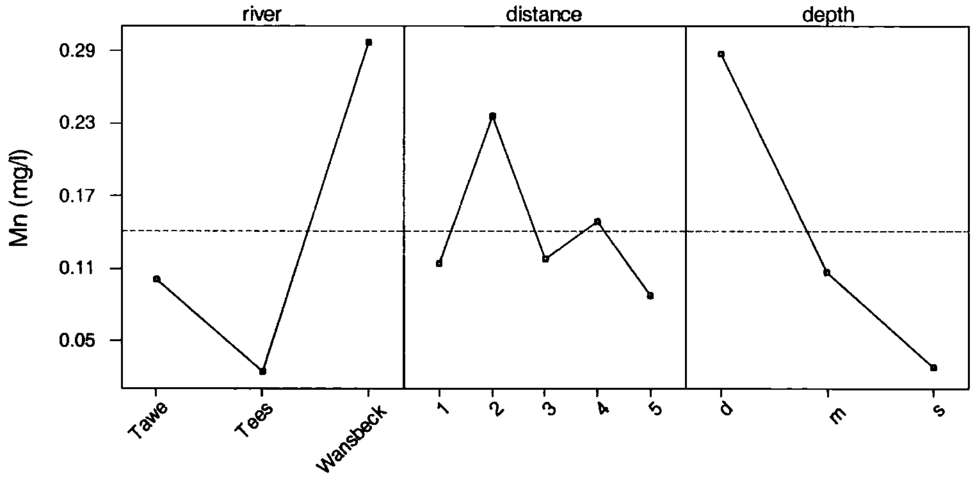


Figure 4.79. Main effects plot for the factors of impoundment (river), distance and depth on Mn (raw data) (LS means for factor levels).

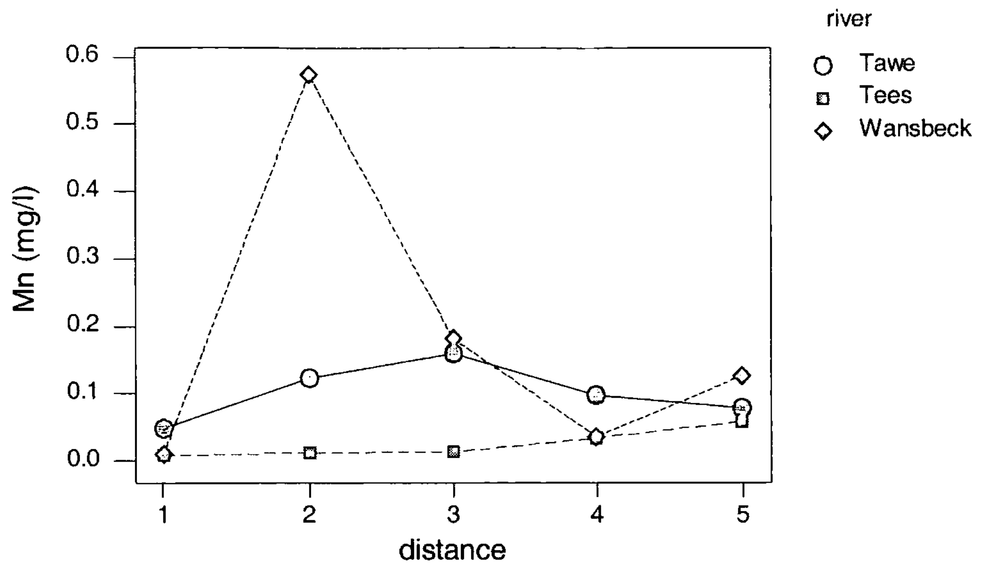


Figure 4.80. Interaction between river and distance effects on Mn (raw data) (LS means).

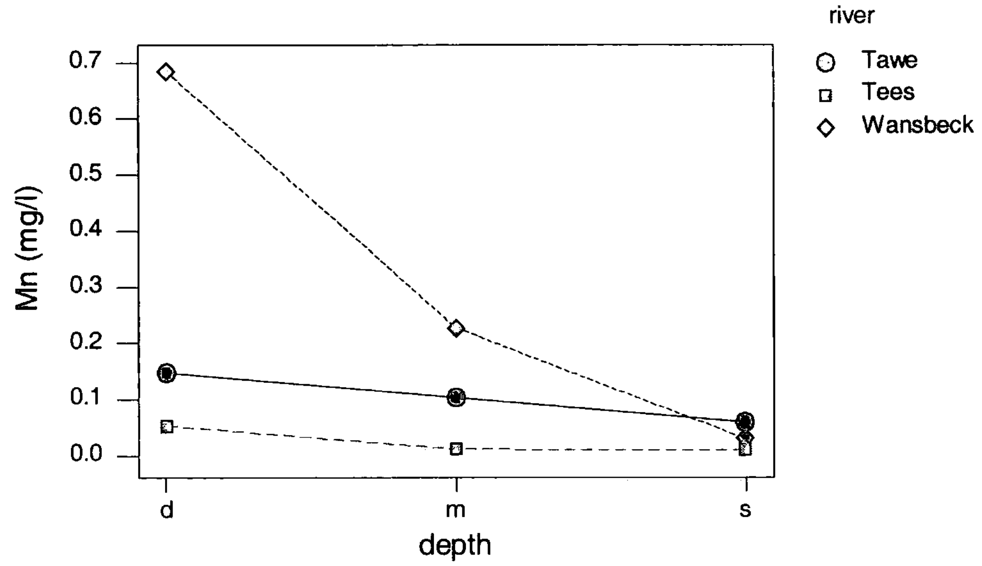


Figure 4.81. Interaction between river and depth effects on Mn (raw data) (LS means).

Factor	Pairwise comparison	Adjusted P-value
River	Tees - Tawe	0.006
	Wansbeck - Tawe	0.000
	Wansbeck - Tees	0.000

Table 4.37. Results from Tukey simultaneous tests on the significance of differences between the means of factor levels used in the ANOVA for Mn (raw data) in partial and total tidal exclusion impoundments.

Discussion

For the Tees it was noted that Fe increased with flow (to a greater degree in summer than winter), and a humic source (peat uplands) and transport mechanism were suggested. Assuming this to be the case, then the extensive areas of peat present in the Tees catchment (but not in the catchments of the Tawe or Wansbeck) explains the difference between the impoundments in their overall Fe concentrations. For the partial exclusion systems flow is also a major control on Fe concentrations in freshwater (figure 4.82), and both the Tawe and the Wansbeck show positive correlations between Fe concentration and freshwater discharge (R-Sq = 52.6 % and 68.3 % respectively).

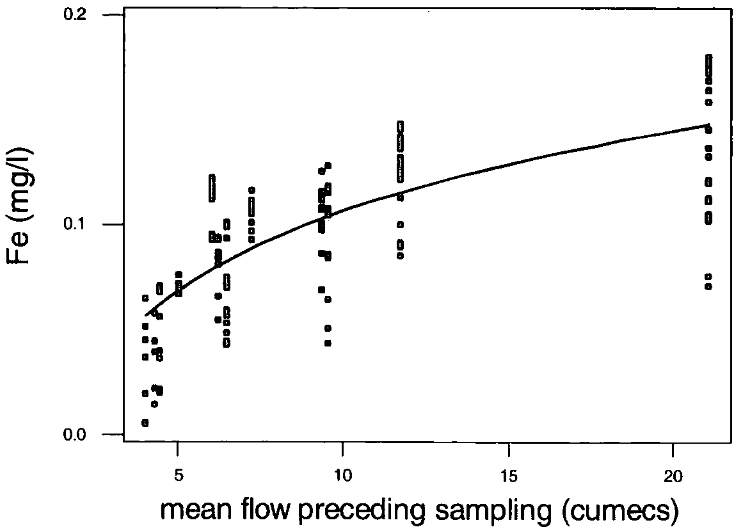


Figure 4.82. The semi-log relationship between Fe in freshwater (Na < 300mg/l) and flow in the Tawe impoundment (R-Sq = 52.6 %).

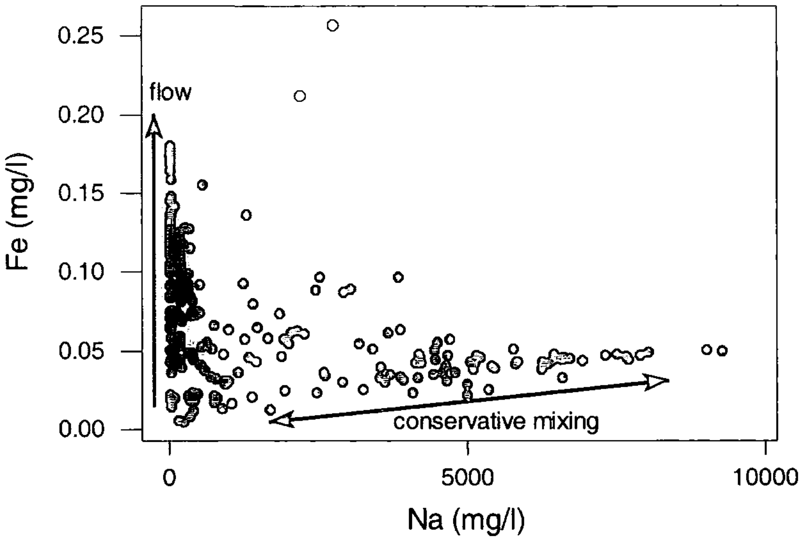


Figure 4.83. The freshwater flow and conservative mixing controls of Fe in the Tawe impoundment. Open circles represent sampling which disturbed bed sediment.

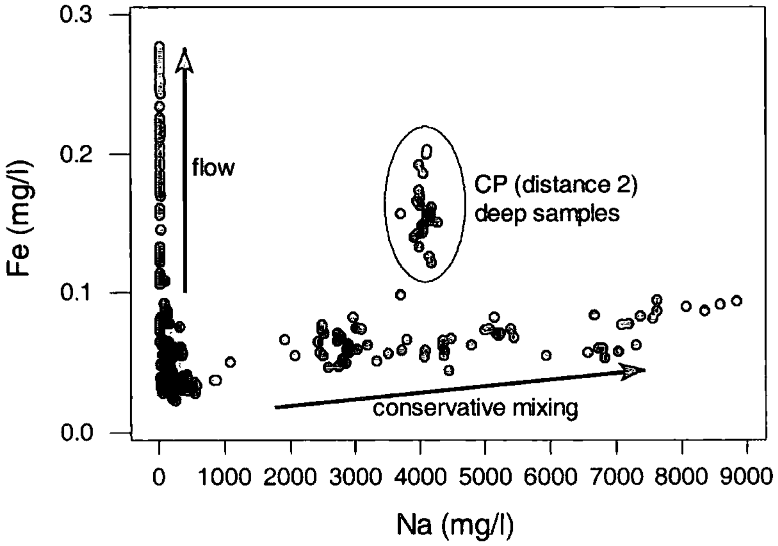


Figure 4.84. The freshwater flow and conservative mixing controls of Fe in the Wansbeck impoundment. Increased Fe concentrations are measured in deep samples from site CP due to sedimentary release under reducing conditions.

The mixing between fresh and seawater in both the Tawe and Wansbeck impoundments is conservative (figures 4.83 and 4.84) and, since over the sampling periods the mean level in the seawater end-member was lower than the mean freshwater levels, the distance effect in the ANOVA is of decreasing Fe with distance downstream (increasing seawater mixing). A significant depth effect is shown for the Wansbeck impoundment however, and increased Fe concentrations are measured at depth at site CP (distance 2) within the impounded area (figure 4.84).

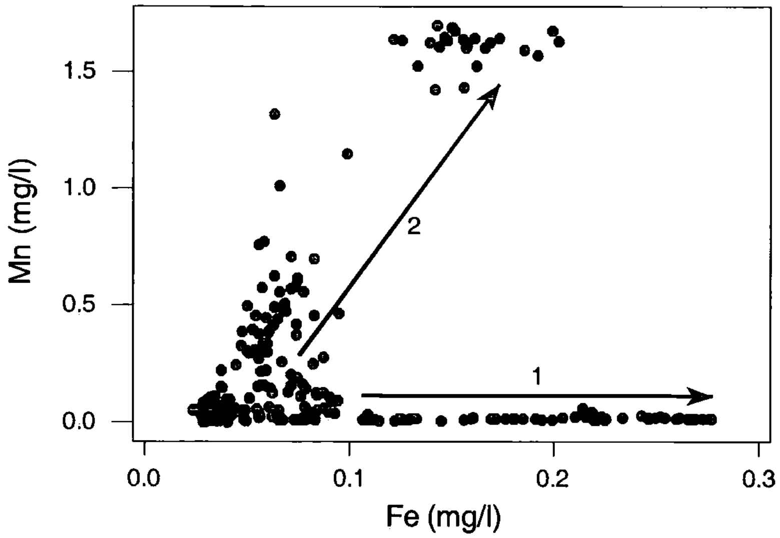


Figure 4.85. The main controls on Fe and Mn in the impoundments (data from Wansbeck summer sampling). Fe concentration in shallow water is controlled by freshwater discharge (1). Fe concentration in deep (saline) water and Mn concentration are controlled by release from sediment under low DO conditions (2).

The solubility of Fe is redox dependent. Under normal oxygenated conditions dissolved Fe is normally found mainly associated with organic colloids. Under reducing conditions (< 250 mV) Fe^{2+} (ferrous iron) diffuses from sediments to increase dissolved Fe concentrations. Whereas for the Tees and Tawe these reducing conditions were not reached, entrenched stratification of the water body in the Wansbeck impoundment at site CP allows Fe^{2+} to build-up in deep water. As mentioned above, under very low redox conditions (< 100 mV) H_2S is produced and reacts with Fe^{2+} to precipitate FeS. Observational sedimentary evidence from sediment coring on the Wansbeck (i.e. the presence of a pale oxidised microzone above black (sulphide rich) sediment) suggests that these conditions are not reached in the water column but are just below the surface of the bed sediments.

The behaviour of Mn is similar to that of Fe in terms of redox control. Mn is mobile at slightly higher redox potentials (less reducing conditions) than Fe, and Mn will remain soluble in waters in which DO < approximately 50 % (Burns and Nriagu, 1976; figure 4.86). The external controls on Mn are seen to be minor compared to the redox controls taking place within the impounded areas.

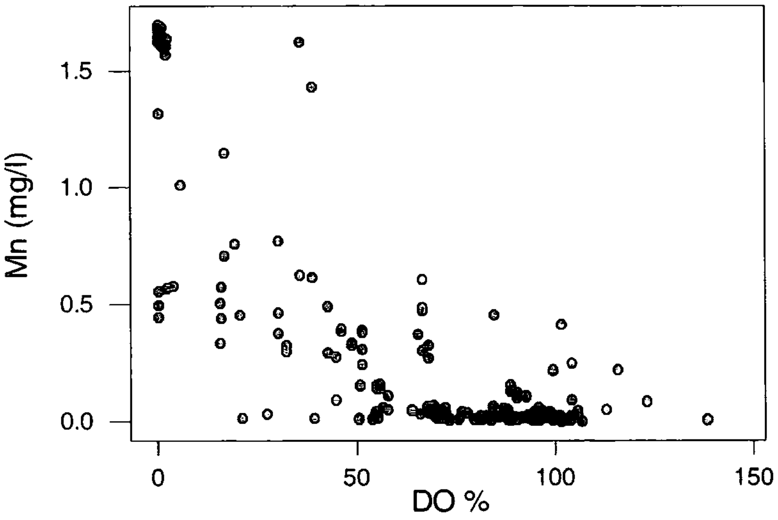


Figure 4.86. Mn vs. DO % in the Wansbeck impoundment (summer data). Mn is insoluble at DO greater than approximately 50 %. The scatter of points of increased Mn at higher DO concentrations and low Mn at low DO concentrations are from sampling at mid-depths and are interpreted as due to the problems of sampling close to a sharp density interface.

As might be expected given the release of Fe from the sediment to the water column at depth noted above, the Wansbeck shows increased levels of Mn in deep water samples. Mn concentration in freshwater and in "new" seawater are close to zero and increase to a maximum of approximately 1.5 mg/l at depth at site CP (at which significant release of Fe is observed). The rate of release of Mn can be determined over the same period (1st to 7th October 2000) for which DO, etc. were modelled above (figure 4.87):

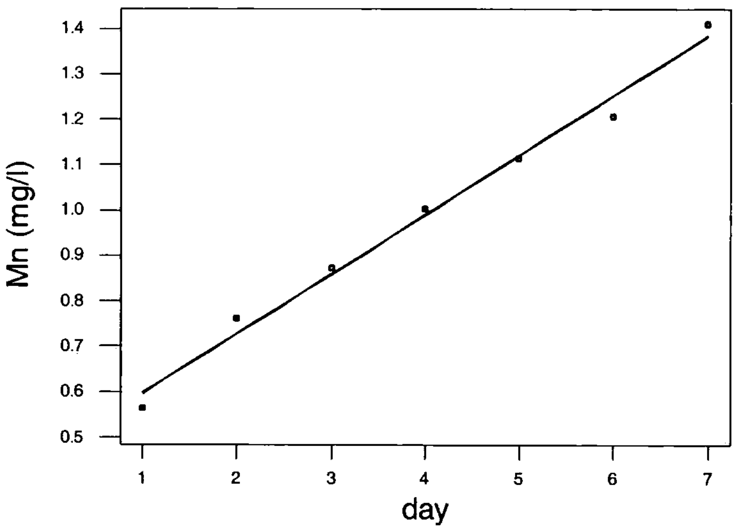


Figure 4.87. Rate of release of Mn from sediment under anoxic (DO < 50 %) conditions at depth at site CP in the Wansbeck.

$$\text{Mn} = 0.467 + 0.131\ \text{day} \qquad (S = 0.0335 \quad \text{R-Sq} = 98.8\ \% \quad \text{R-Sq(adj)} = 98.6\ \%)$$

where,

Mn = concentration of Mn in mg/l, and

day = number of days following reduction of DO to below approximately 50 %.

The amounts of release of Mn in the Tawe and Tees impoundments are significant but lower than in the Wansbeck due to the less frequent occurrence of low oxygen (< 50 %) conditions at depth (see comparison of DO behaviour above).

4.3.11 Fe and P

It is well established that there is a strong affinity between P and particulate $Fe(OH)_3$ in sediments in water bodies, and thus that P mobility may be redox mediated (Mortimer, 1941 and 1942). For the Wansbeck it has been shown that anoxic conditions can develop in the water column which allow the reduction of Fe^{3+} to Fe^{2+}, and it is possible that release of P is associated with this (figure 4.88), although relative to the variation in

P in the riverine inputs to the impoundments the impact is minor. In addition, any increase in the amount of dissolved (bio-available) P will occur under reducing conditions at depth and is therefore not likely to contribute to an increase in primary production in the systems. Upon mixing with surface waters $Fe(OH)_3$ will re-precipitate and scavenge dissolved P, thus removing any effects of redox controlled sedimentary P release on biota.

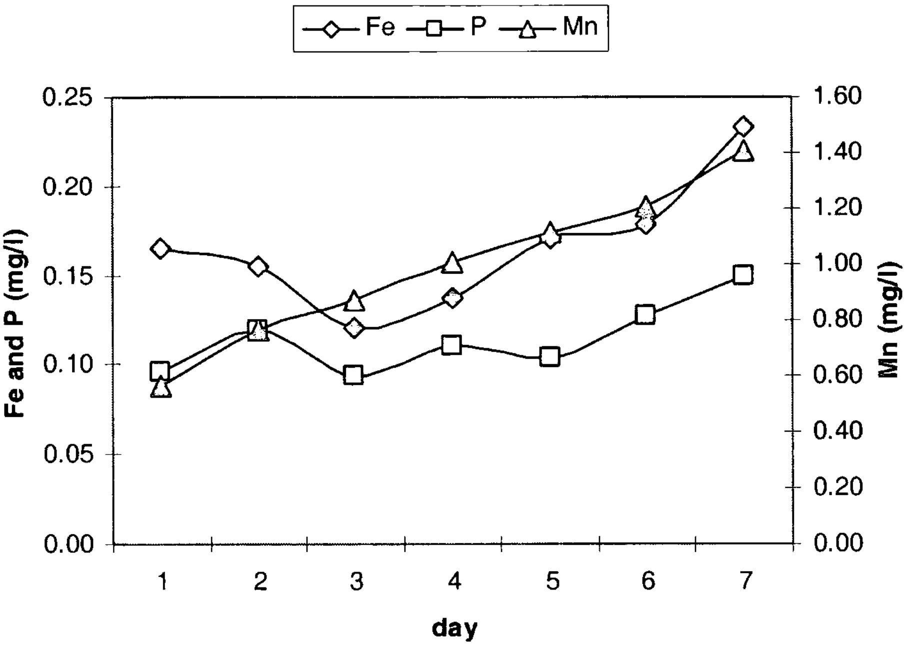


Figure 4.88. Mn, Fe and P over the period 1st to 7th October 2000 in deep water at site CP in the Wansbeck impoundment during the development of anoxia, showing the possible relationship between release of Fe and release of P from sediment to the water column.

4.4 Summary and conclusions

Within this chapter the three impounded estuaries included in this research have been compared in terms of the summer behaviour of a range of 18 water quality variables. Initially principal components analysis (PCA) was used to identify the correlation structure of the multivariate dataset, and through this to identify likely controlling processes on these groups of variables. Subsequently, general linear modelling was used to statistically assess the differences between the impoundments and the importance of processing within the impounded areas relative to the external controls on water quality. During discussion of the results obtained regression was carried out between a variety of the water quality variables and their underlying controls.

The first 2 principal components produced by PCA were interpreted as representing significant controls on a variety of variables, whilst the 3rd and 4th principal components showed less clear relationships to any single controlling process:

- PC1 = salinity control (variables showing different levels in saline and fresh water in the impoundments: conductivity, Ca, nitrate, ammonia, Mn and DO).
- PC2 = freshwater flow control (variables showing variation with discharge in the freshwater inputs to the impoundments: alkalinity, phosphate, T, Fe and TSS).
- PC3 = pH and alkalinity score strongly (probably representing a baseflow or geological control rather than a biological control on these parameters since coefficients are of the same sign).
- PC4 = nitrate and phosphate score strongly (representing a similar overall source for these nutrients).

PCA allowed only simple and qualitative comparison of the three impoundments, and so more detailed investigation was carried out using general linear modelling (ANOVA).

Significant differences of varying degrees were shown between the impoundments for all of the water quality parameters assessed, with the exception of BOD (for which limited data was available). By comparing analyses carried out using raw data and carried out using data normalised to the freshwater inputs to the impounded areas, the amount of variation external to the impounded areas relative to the variation within the impounded areas was assessed. The external variation can be thought of as independent of the construction of a barrage, whereas the internal variation may be affected by impoundment. The processes identified as important in the control of the water quality parameters are listed in table 4.38 in approximate order of significance.

Parameter	**ω^2 for river (if significant)**	**Controlling processes**
DO	0.31 (raw) 0.16 (norm)	Microbial respirative utilisation of DO relative to re-oxygenation (strongly related to density stratification).
BOD	Not significant (data for Tees and Tawe only)	Flow controlled removal of organic material in catchments.
pH	0.06 (raw) 0.24 (norm)	Amount of seawater mixing (conservative). Microbial respiration (strongly related to density stratification).
Alkalinity	0.86 (raw) 0.13 (norm)	Catchment geology. Flow controlled dilution of baseflow. Amount of seawater mixing (conservative). Microbial respiration (strongly related to density stratification).
Conductivity	0.23 (raw)	Density stratification (breakdown in stratification and conservative mixing between seawater and freshwater related to freshwater flow). Flow controlled dilution of baseflow (freshwater conductivities).
Transparency	0.91 (raw)	Catchment controls on particulate availability. Flow controlled turbidity. Re-suspension of bed material within the impounded areas.
TSS	0.58 (raw) Not significant (norm)	Catchment controls on particulate availability. Flow controlled turbidity. Re-suspension of bed material within the impounded areas.

Nitrate	0.67 (raw) 0.58 (norm)	Catchment, point-source and flow effects on river inputs. Amount of seawater mixing (conservative). Denitrification and reduction to ammonia (strongly related to density stratification).
Ammonia	0.13 (raw) 0.18 (norm) 0.22 (norm + DO as covariate)	Point source inputs to the rivers. Amount of seawater mixing (conservative). Microbial respiration and reduction of nitrate (strongly related to density stratification).
Phosphate	0.74 (raw)	Point-source and flow effects on river inputs. Biological utilisation. Possible release from sediment (strongly related to density stratification) in Wansbeck only.
Si	0.61 (raw)	Catchment geology, land-use and flow effects on river inputs. Amount of seawater mixing (conservative). Release from sediment (strongly related to density stratification) in Wansbeck only.
Major elements	0.21 (raw)	Amount of seawater mixing (conservative).
Fe	0.72 (raw) 0.08 (norm)	Catchment (amount of peat) and flow effects on river inputs. Amount of seawater mixing (conservative). Redox controlled release from sediment (strongly related to density stratification) in Wansbeck only.
Mn	0.21 (raw)	Redox controlled release from sediment (strongly related to density stratification), maximum in Wansbeck but significant in all impoundments.

Table 4.38. Summary of the effects of river (impoundment) and proposed important controlling processes on water quality within the Tees, Tawe and Wansbeck impoundments. raw = results from analysis of raw data. norm = results from analysis of data normalised to freshwater inputs.

Four types of control on water quality are identified. These can be summarised as:

1. Catchment controls on external inputs.
2. Flow controls on external inputs.
3. Internal mixing of seawater and freshwater.
4. Internal processing related to density stratification.

4.4.1 Catchment controls

Difference between the rivers entering the impoundments is the most important factor in controlling the levels of alkalinity, transparency and TSS, phosphate, Si and Fe in the impoundments, and is a significant factor for several other variables. The catchments vary in terms of size, geology, relief and precipitation, land-use, etc. and in the point-source inputs within them. Whilst some suggestion has been made of how catchment relates to water quality parameters, the study of catchment processes is generally beyond the scope of this thesis. However, it is important to note that for all impoundments, for several of the parameters, catchment management is the key to controlling water quality. This is particularly significant for phosphate and for suspended solids (TSS), both of which are identified as of major importance in impounded water quality. Both the Tawe and the Wansbeck have been identified as P limited in terms of primary productivity, and therefore any control of the eutrophic behaviour of these impoundments must be by reduced P inputs to the rivers entering the impoundments. Equally control of sedimentation within the impoundments should focus on the sediment sources to the rivers. Identification of sediment sources and transport form specific themes of the SIMBA project (Nelson, 2003; Beavers, 2003).

4.4.2 Freshwater flow controls

Several parameters show strong relationships to levels in freshwater and river discharge. The sign and nature of the correlations varies according to the sources within the catchments of the parameters:

1. Negative correlation = dilution effect (alkalinity, conductivity, nitrate (Tawe and Tees), phosphate and major elements).
2. Positive correlation = diffuse source (BOD, TSS, nitrate (Wansbeck) and Fe).

The exact relationships vary between the catchments, and are dependent on the catchment factors discussed above (e.g. geology, land-use, quantity of sewage inflows). Generally higher flows also act to remove stratification and so reduce the probability of the development of low water quality conditions at depth. However, the majority of sediment transport within systems takes place during conditions of peak flow, particularly in the Tees where bank erosion provides a major source of fine material (S. Anderton, pers. com.). For Devon rivers, Webb and Walling (1982a) give that 90 % of the TSS transport takes place in 10 % or less of the time. High flow conditions, and the associated sediment transport and deposition within the impounded areas, are therefore important in assessing the long term sustainability of estuarine barrage systems.

4.4.3 Mixing controls

Several parameters show markedly different levels between the two main water sources (i.e. seawater and freshwater) which enter partial tidal exclusion impoundments:

1. Higher in seawater: Alkalinity, conductivity, major elements (Na, Mg, Ca, K and S), ammonia and P.
2. Higher in freshwater: DO (absolute concentration), pH, Si and nitrate.

The mixing of major elements and conductivity is conservative between fresh and seawater. The mixing of the majority of other parameters is generally conservative, but may show alteration within the impoundments through a variety of processes related to density stratification.

4.4.4 Stratification controls

Impounded water bodies may become stratified due to density differences in the water column based on salinity or temperature differences. This stratification can lead to water at depth which is isolated from the atmosphere and in contact with oxygen demanding organic rich bed sediments. Respiration (organic decomposition) in excess of re-oxygenation cause a reduction in DO, and a simultaneous decrease in pH and increase in alkalinity. Under these reducing conditions a lack of denitrification and nitrate reduction leads to a decrease in nitrate and increase in ammonia concentrations in the deep water. Under sustained isolation of the deep water redox conditions decrease to levels at which Mn and subsequently Fe and associated P are released from the sediment to the water column.

Stratification is stronger in partial than total tidal exclusion impoundments since the density differences based on salinity differences are much greater than those due to temperature differences alone. The effects of the processes associated with stratification are particularly significant at deep locations within the impoundments upstream of more shallow sections since only the highest tides are able to replace the "stagnant" deep waters with "fresh" (oxygenated) seawater. The length of the periods of isolation of these "ponded" waters is therefore greatest at these points. The Tawe barrage allows a larger proportion of tides to enter the impoundment and therefore has shorter periods of isolation of deep water and better water quality than the Wansbeck. Stratification may also be removed under conditions of high freshwater discharge through the development of internal waves and mixing upwards of the saline water.

Chapter 5

Barrage Presence and Water Quality

5.1 Introduction

The study of the effects of barrage construction on estuaries is limited by the lack of good water quality data pre-dating impoundment. However, understanding the difference between estuaries in their natural state and those that are impounded is fundamental in planning and policy for estuarine barrage construction. To aim to answer this question, comparison of two equivalent estuaries – one impounded and one un-impounded – was carried out.

The Wansbeck impounded estuary has already been examined for seasonal differences in water quality and in comparison with the Tees and Tawe impounded estuaries (chapter 3 and chapter 4). Here results for comparison of the Wansbeck with the River Blyth un-impounded estuary are presented. As described in chapter 1, the Blyth runs parallel to the Wansbeck to enter the North Sea approximately 5 km to the south of the mouth of the Wansbeck, and is of almost identical size (both 339.4 km^2), geology, relief and land-use of catchment (Archer 1992). Both estuaries were sampled daily during the period 4th to 12th June 2001, with sampling on the Blyth following that on the Wansbeck by not more than 2 hours.

A general linear model (ANOVA) including the terms of river, distance downstream within the estuary and depth within the estuary plus the interactions between river and distance and river and depth was used. Distance/sampling site were represented by numbers 1 to 4 from the former tidal limit (SW) on the Wansbeck or the tidal limit (TL) on the Blyth, downstream to the barrage (WB) for the Wansbeck or a similarly distanced site (PS) on the Blyth. In order to give the same number of distances for both estuaries, data from site CI on the Wansbeck is excluded from the analyses. Depth is represented by sampling at shallow (S), mid-depth (m) and deep (d) at each sampling site (with the exception of the tidal limit or former tidal limit at which only surface samples were taken). For practical reasons sampling was carried out approximately 2 hours before high tide on the Wansbeck and at high tide on the Blyth. The tidal heights during the sampling period were such that the barrage on the Wansbeck was overtopped by seawater on the majority of sampling dates compared, with only the first day (4th June 2001) following a period of 8 days of non-overtopping and the final 3 days (10th, 11th and 12th June 2001) sampling days 1, 2 and 3 of the subsequent non-overtopping period. Analyses were carried out using both raw data and data normalised to the freshwater inputs to the estuaries to allow assessment of the differences between estuaries based on catchment effects and those due to differences in behaviour due to the presence of a barrage. Results are presented for those parameters that show significant internal (within estuary) variation (DO, pH, TSS, nitrate, ammonia, phosphate, Na/major elements, Fe and Mn).

5.2 Results and discussion

5.2.1 Dissolved oxygen

Results

There is very little difference between the results for raw data and the results for normalised data since freshwater input DO concentrations are similar between days and between rivers (implying that the choice of the Blyth as a comparable estuary to the Wansbeck was justified). DO concentrations are significantly lower in the Wansbeck than the Blyth (table 5.1 and figure 5.1), and this difference is due to variation within the impounded area of the Wansbeck (table 5.2). Depth has a significant effect and shows significant interaction with river. DO concentrations decrease with depth in both estuaries but to a far greater extent in the Wansbeck (figure 5.3). There is a similar slight decrease in DO with distance downstream in both estuaries but this is compounded by a large reduction in DO at distance 2 (site CP) at the deepest point of the Wansbeck (figure 5.2).

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
River	20.97	0.000	257	0.09
Distance	7.63	0.000	255	0.09
Depth	41.70	0.000	1046	0.36
River*distance	12.99	0.000	462	0.16
River*depth	23.08	0.000	568	0.20
Error			308	0.11

Table 5.1. Results from GLM ANOVA for DO % (raw data) between the Blyth estuary and the Wansbeck impounded estuary.

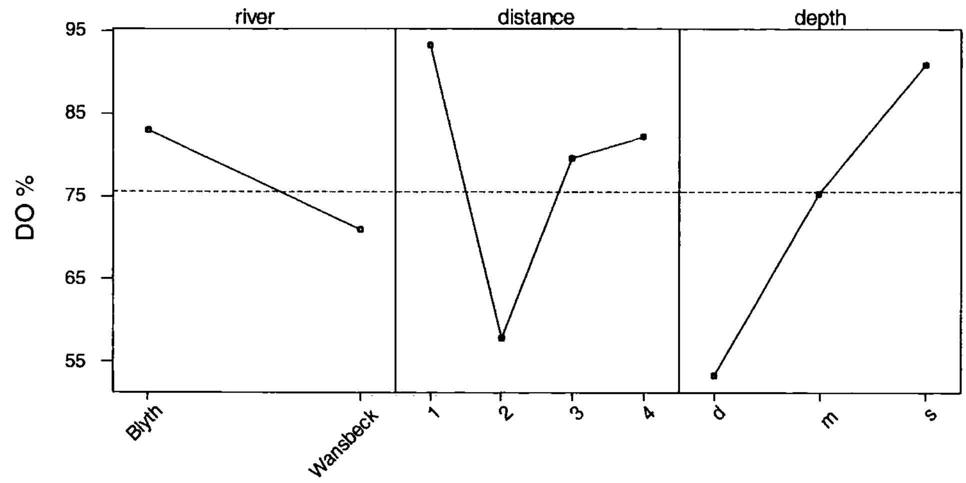


Figure 5.1. Main effects plot for the factors of river, distance and depth on DO % (raw data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

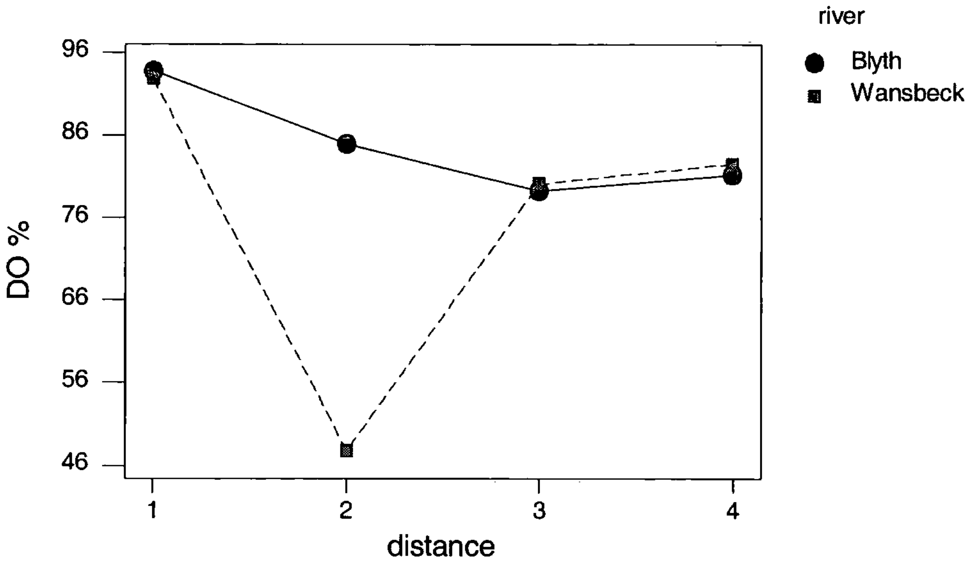


Figure 5.2. Interaction between river and distance effects on DO % (raw data) for the Blyth and Wansbeck estuaries (LS means).

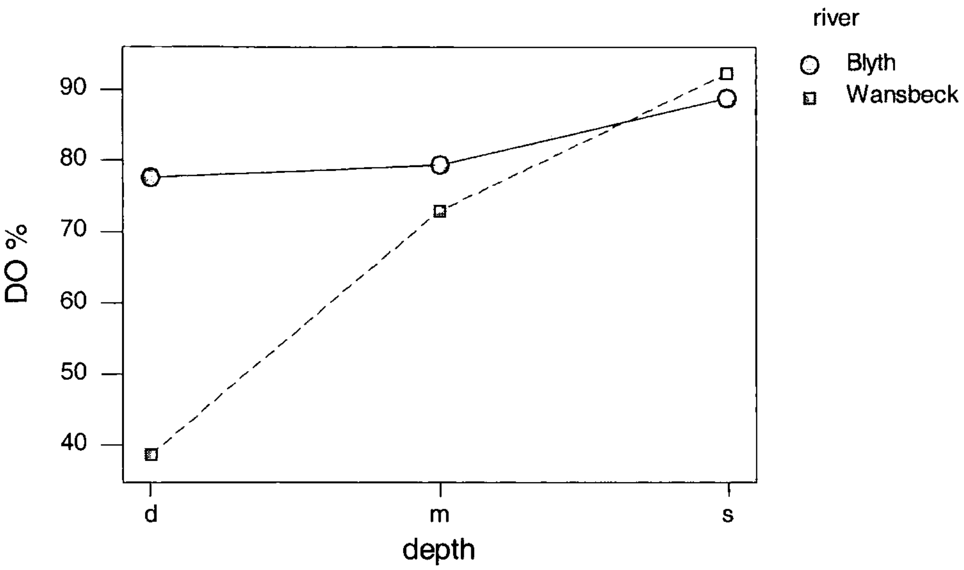


Figure 5.3. Interaction between river and depth effects on DO % (raw data) for the Blyth and Wansbeck estuaries (LS means).

Source	**F**	**P**	σ^2	**Size of Effect** (ω^2)
River	30.06	0.000	0.037	0.09
Distance	11.02	0.000	0.038	0.10
Depth	57.19	0.000	0.143	0.36
River*distance	15.35	0.000	0.055	0.14
River*depth	36.87	0.000	0.091	0.23
Error			0.031	0.08

Table 5.2. Results from GLM ANOVA for DO % (normalised data) between the Blyth estuary and the Wansbeck impounded estuary.

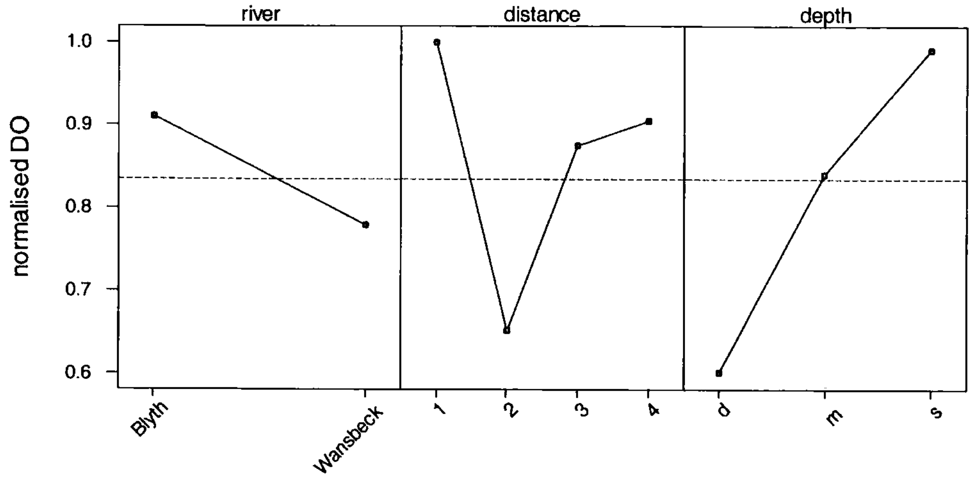


Figure 5.4. Main effects plot for the factors of river, distance and depth on DO % (normalised data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

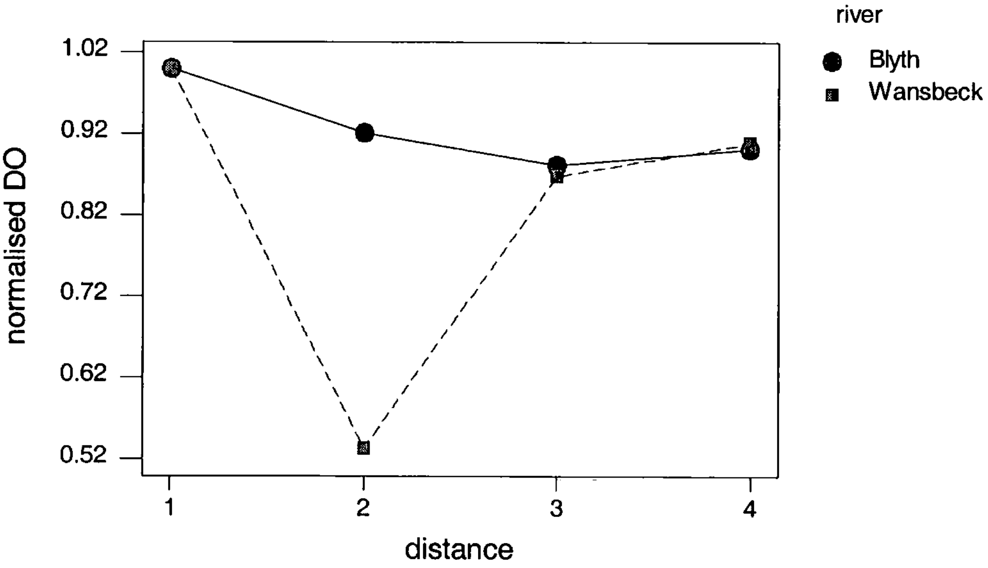


Figure 5.5. Interaction between river and distance effects on DO % (normalised data) for the Blyth and Wansbeck estuaries (LS means).

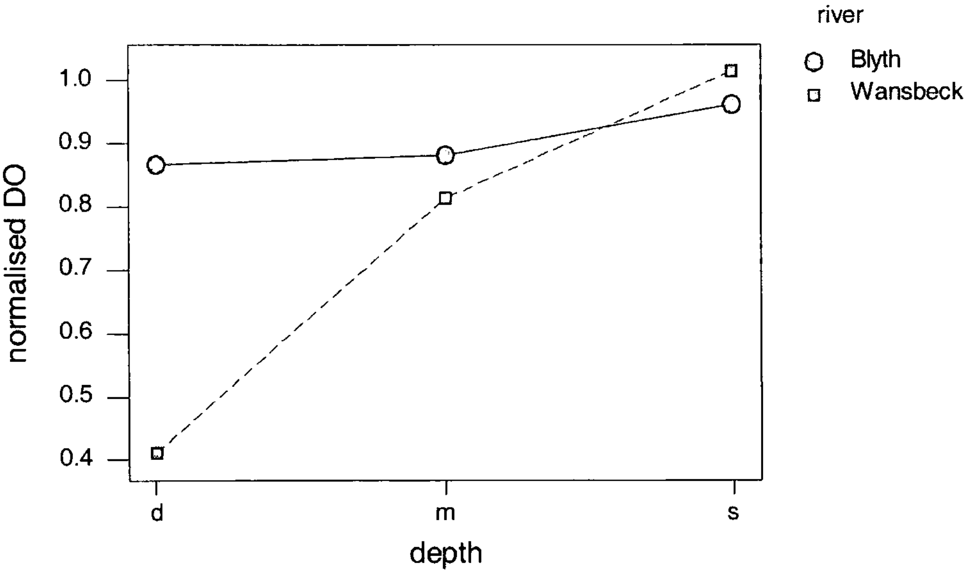


Figure 5.6. Interaction between river and depth effects on DO % (normalised data) for the Blyth and Wansbeck estuaries (LS means).

Discussion

The Blyth and the Wansbeck estuaries behaved significantly differently in terms of DO during the periods sampled. The major difference was the greater degree of oxygen depletion at depth within the Wansbeck, and this was in particular affected by the low DO conditions encountered almost throughout the sampling period at depth at site CP. As has been discussed site CP is the deepest point of the Wansbeck and shows long periods of isolation of saline water, which is only removed under conditions of high freshwater discharge or replaced when the highest (> 4.9 m) tides force new saline water upstream to this point. For the Blyth no similar sites of dramatically reduced DO at depth were encountered, and it is suggested that the unrestricted tidal circulation, along with the generally shallower depth, means that such "ponding" of saline water at depth does not occur. The minimum DO concentration encountered in the Blyth was 53.5 % compared with 0.00 % over a sustained period in the Wansbeck.

5.2.2 pH

Results

Freshwater input values for the two rivers are similar and hence, as with DO, results are similar for both raw and normalised data. There are no significant differences between the two estuaries overall (tables 5.3 and 5.4) (power of detecting a significant difference using data collected calculated as 1.000 for one-way ANOVA). Both systems are well buffered and show low pH variation. Both depth and distance are significant effects however, and both show interaction with river. pH decreases with depth and to a greater extent in the Wansbeck, and shows a decrease followed by an increase with distance downstream in both estuaries, and a large drop in value at distance 2 (site CP) in the Wansbeck. For both analyses a relatively large amount of variance is unexplained and may relate to varying amounts of biological productivity and respiration spatially and temporally.

Source	**F**	**P**	σ^2	**Size of Effect** (ω^2)
River	2.82	0.094	na	na
Distance	3.58	0.015	0.16	0.14
Depth	6.88	0.001	0.25	0.21
River*distance	3.33	0.020	0.15	0.12
River*depth	4.21	0.016	0.14	0.11
Error			0.51	0.42

Table 5.3. Results from GLM ANOVA for pH (raw data) between the Blyth estuary and the Wansbeck impounded estuary (na = not applicable since factor insignificant at 95 % level).

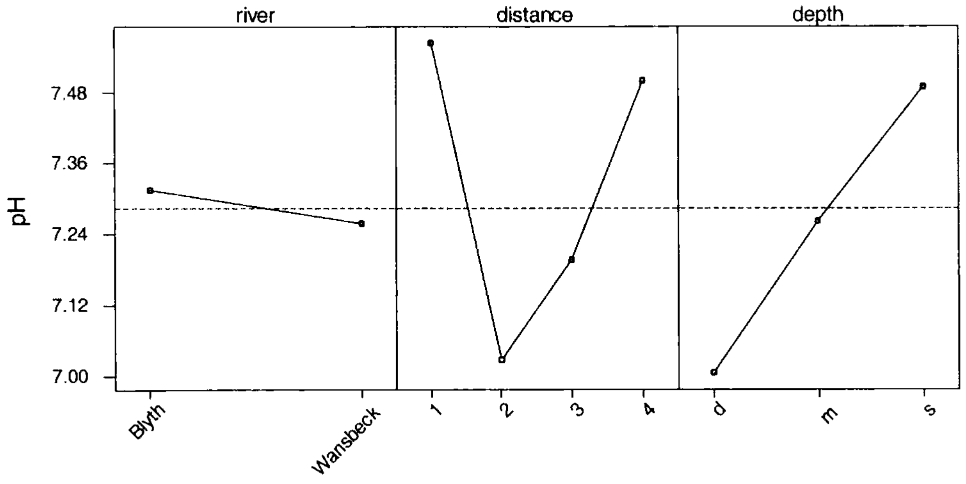


Figure 5.7. Main effects plot for the factors of river, distance and depth on pH (raw data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

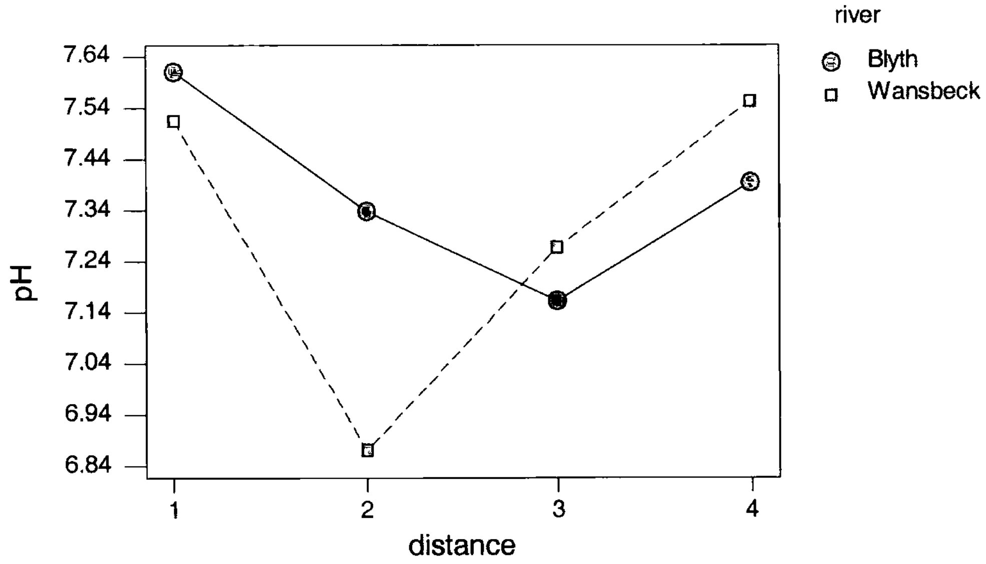


Figure 5.8. Interaction between river and distance effects on pH (raw data) for the Blyth and Wansbeck estuaries (LS means).

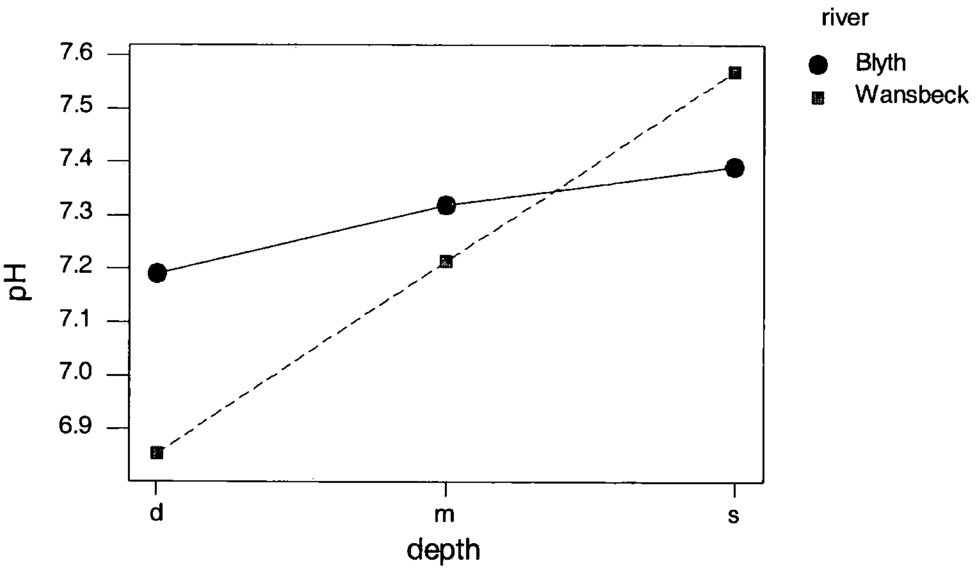


Figure 5.9. Interaction between river and depth effects on pH (raw data) for the Blyth and Wansbeck estuaries (LS means).

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
River	0.62	0.431	na	na
Distance	8.24	0.000	0.0035	0.19
Depth	16.10	0.000	0.0049	0.27
River*distance	7.64	0.000	0.0032	0.18
River*depth	9.74	0.000	0.0028	0.15
Error			0.0039	0.21

Table 5.4. Results from GLM ANOVA for pH (normalised data) between the Blyth estuary and the Wansbeck impounded estuary (na = not applicable since factor insignificant at 95 % level).

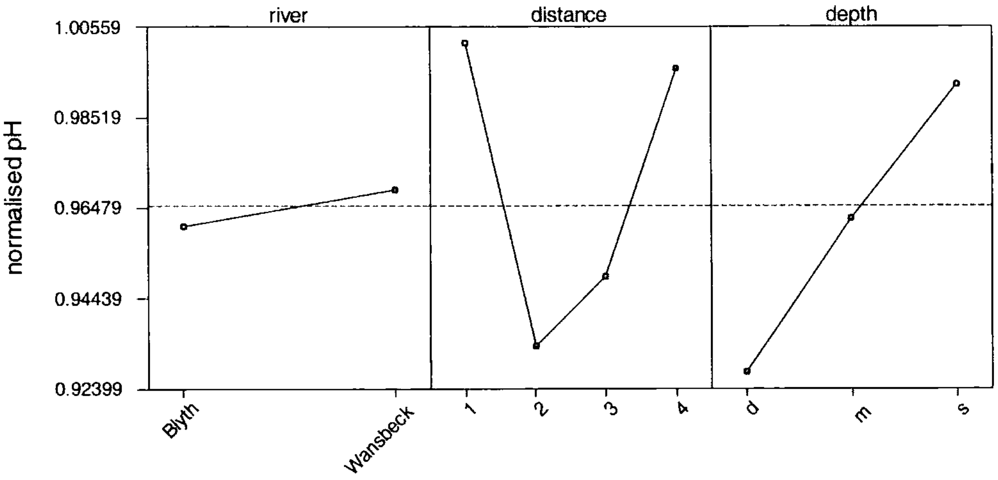


Figure 5.10. Main effects plot for the factors of river, distance and depth on pH (normalised data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

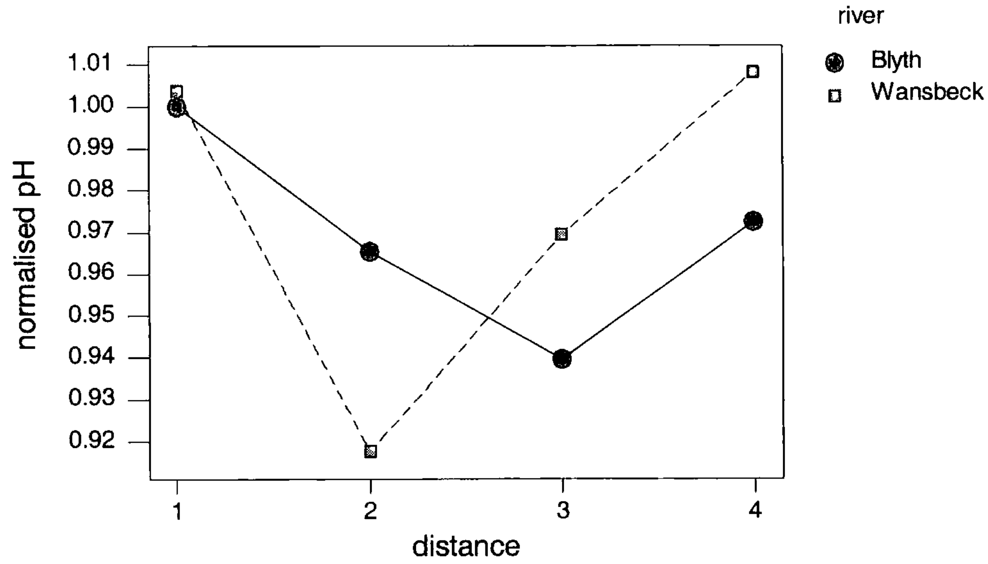


Figure 5.11. Interaction between river and distance effects on pH (normalised data) for the Blyth and Wansbeck estuaries (LS means).

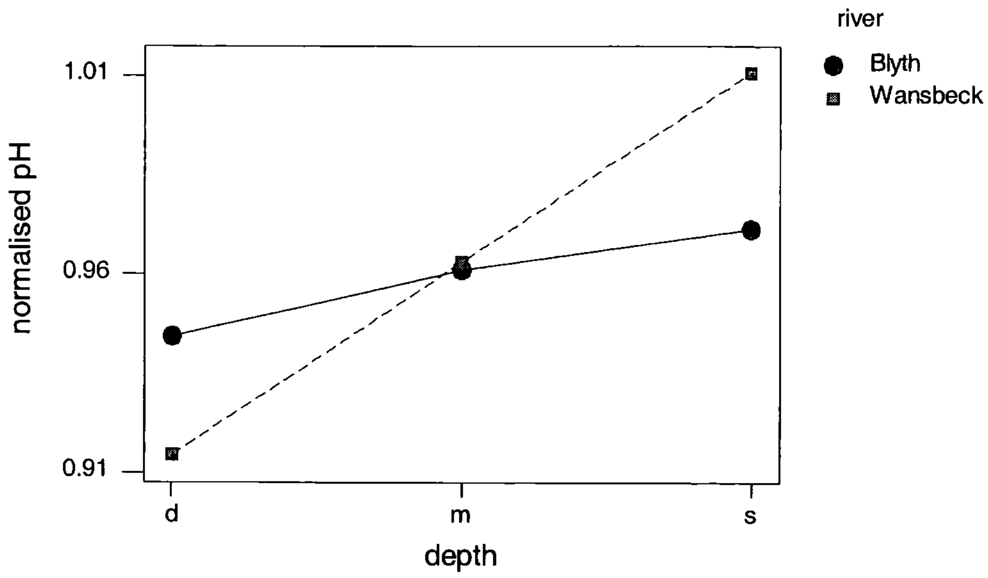


Figure 5.12. Interaction between river and depth effects on pH (normalised data) for the Blyth and Wansbeck estuaries (LS means).

Discussion

Variation in pH within the estuaries relates to both the lower pH in seawater than river water and the greater amount of respiration in deep water in a stratified water column. For the period sampled the two rivers showed very similar pH values in their freshwater inputs, and therefore the differences in pH values encountered relate to differences between the estuaries. A greater decrease in mean pH with depth is encountered in the Wansbeck due to high respiration in contact with bed sediments in deep stratified water. The distance pattern for the Wansbeck reflects the reduced pH at site CP along with the general downstream decrease with increased mixing with seawater. The Blyth does not show as large decrease in pH with depth and the depth and distance effects are likely to relate solely to the relative proportion of freshwater and seawater in each sample. The increase in pH between distances 3 and 4 on the Blyth is probably due to an increased proportion of (higher pH) freshwater from the Sleek Burn tributary which enters the estuary between these points.

5.2.3 TSS

Results

Again, as for DO and pH, results are very similar for analyses using raw and normalised data since the freshwater input values are similar and the majority of variance in the dataset is within the estuaries. Mean concentration of TSS is significantly higher in the Blyth than in the Wansbeck. TSS increases with distance downstream and depth in both estuaries (figure 5.13). The increase in TSS with distance is greater in the Blyth than the Wansbeck (figure 5.14). The depth effect also varies between the estuaries, with the Blyth showing maximum increase in TSS between shallow and mid-depths and the Wansbeck showing maximum increase between mid-depth and deep samples (figure 5.15). Overall TSS levels are approximately 4 times higher in the estuary than in the river input in the Wansbeck during the sampling period and 9 times greater in the Blyth estuary (figure 5.16).

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
River	109.85	0.000	1509	0.21
Distance	32.78	0.000	1322	0.18
Depth	81.35	0.000	2228	0.31
River*distance	26.29	0.000	1052	0.15
River*depth	29.86	0.000	800	0.11
Error			333	0.05

Table 5.5. Results from GLM ANOVA for TSS (raw data) between the Blyth estuary and the Wansbeck impounded estuary.

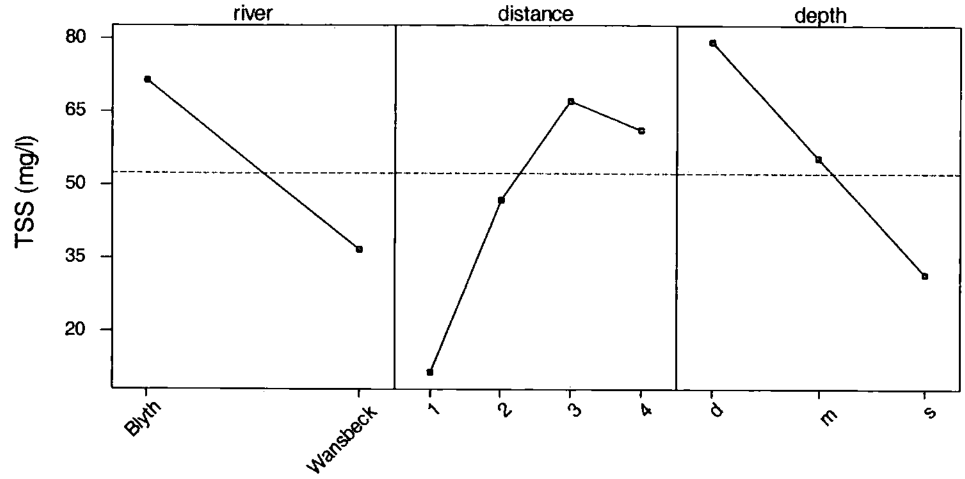


Figure 5.13. Main effects plot for the factors of river, distance and depth on TSS (raw data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

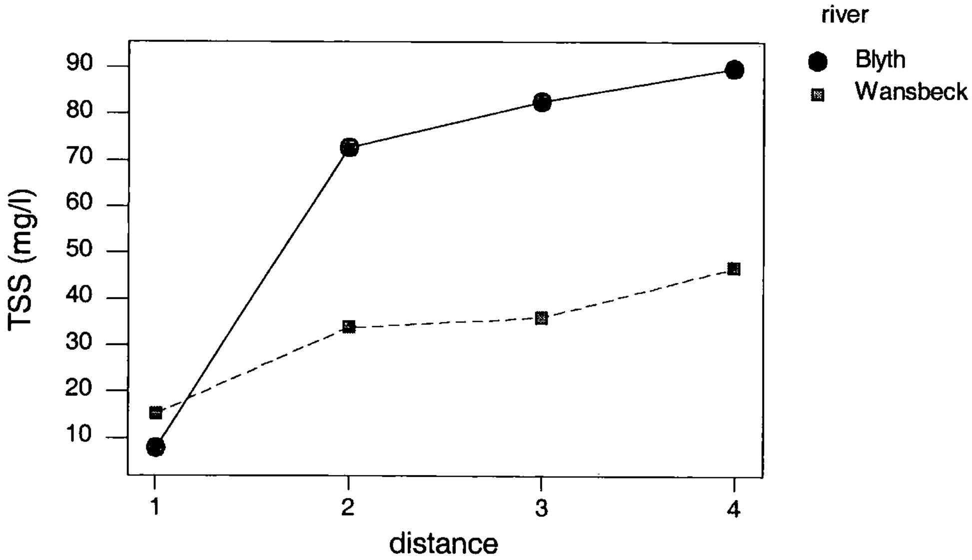


Figure 5.14. Interaction between river and distance effects on TSS (raw data) for the Blyth and Wansbeck estuaries (LS means).

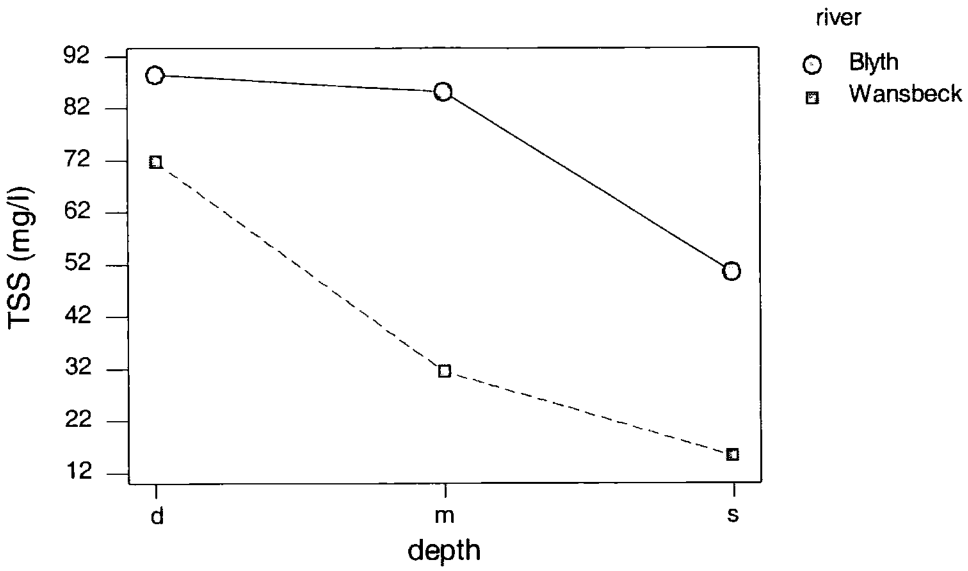


Figure 5.15. Interaction between river and depth effects on TSS (raw data) for the Blyth and Wansbeck estuaries (LS means).

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
River	34.20	0.000	27.3	0.24
Distance	10.41	0.000	23.2	0.20
Depth	16.41	0.000	25.3	0.22
River*distance	6.15	0.000	12.7	0.11
River*depth	4.80	0.009	6.2	0.05
Error			19.7	0.17

Table 5.6. Results from GLM ANOVA for TSS (normalised data) between the Blyth estuary and the Wansbeck impounded estuary.

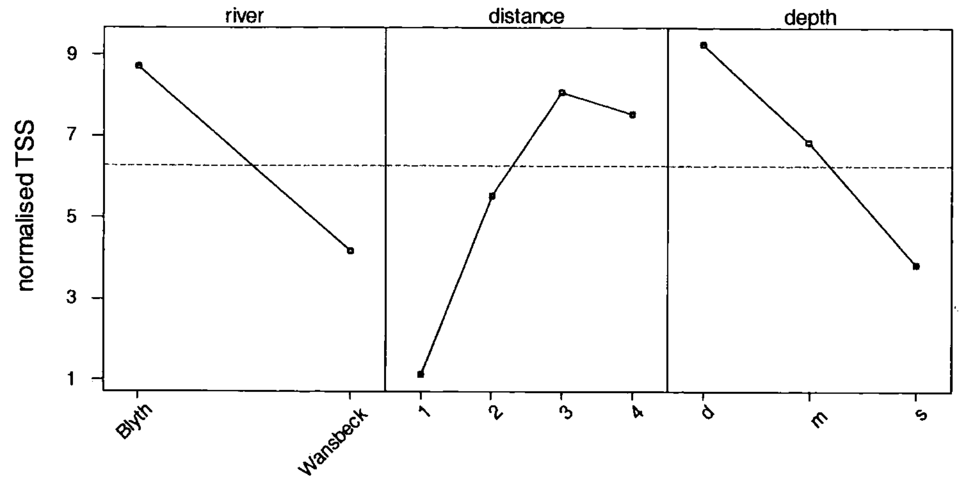


Figure 5.16. Main effects plot for the factors of river, distance and depth on TSS (normalised data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

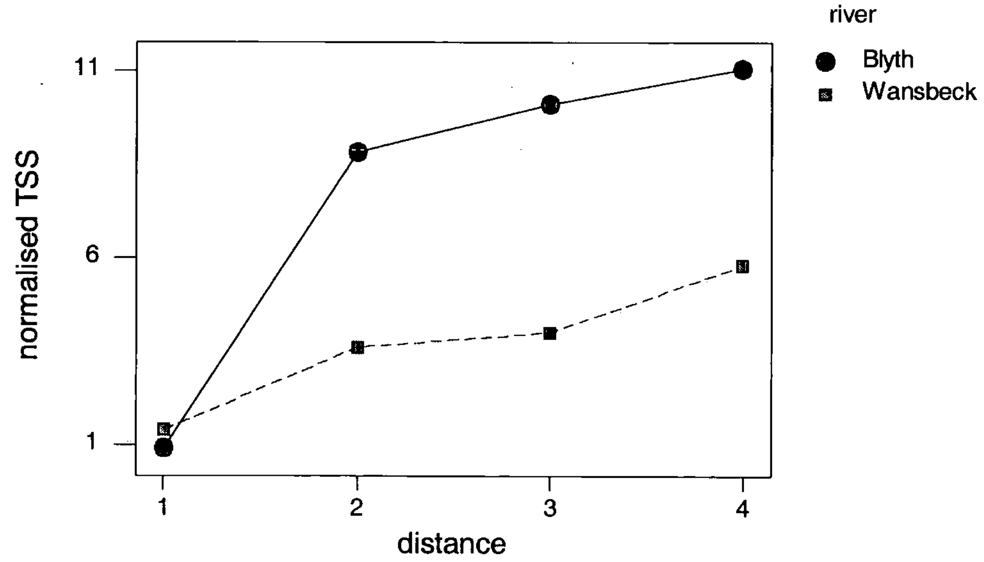


Figure 5.17. Interaction between river and distance effects on TSS (normalised data) for the Blyth and Wansbeck estuaries (LS means).

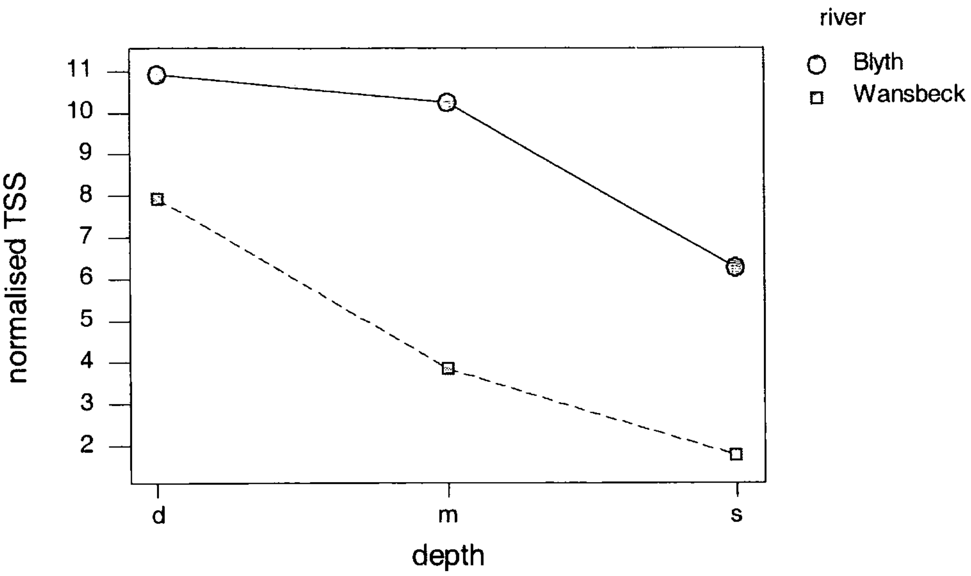


Figure 5.18. Interaction between river and depth effects on TSS (normalised data) for the Blyth and Wansbeck estuaries (LS means).

Discussion

The freshwater sediment inputs to the Blyth and the Wansbeck estuaries were similar during the period studied, which is in contrast with the comparison of impoundments in which it was shown that the major variation is due to differences between the concentrations of TSS carried by the rivers. For the Blyth and the Wansbeck the major difference in TSS behaviour is due to differences within the estuaries. These differences are interpreted as due to the effect of barrage construction on tidal circulation and mixing in the systems.

For the Wansbeck, sampling of the seawater entering the impounded area during overtopping showed that the majority of sediment within the impounded area is delivered in the freshwater inputs. Potsma (1980) gives that most TSS in strongly stratified estuaries is of fluvial source and is transported downstream in the freshwater layer. No estimation can be made of the contribution from the sea by tidal pumping for the Blyth, and it is suggested that further sediment fingerprinting work is carried out to determine the relative contributions in impounded compared with un-impounded systems. However, assuming that the sediment contribution from the sea is also low in the Blyth, then the greater TSS concentrations encountered in this estuary are due to greater tidal flows and higher bed shear stresses acting to cycle bed sediment and create a "turbidity maxima" (Dyer 1997). For the Wansbeck tidal circulation is reduced and re-suspension of bed sediment is lower, and its effects limited to deeper water. The effect of the combined discharge from the Blyth and Cramlington Sewage Treatment Works (STW) into the middle of the Blyth estuary (NZ 2950 8249; 11,664 m^3/day of 30 mg/l solids dry weather maximum and 9,600 m^3/day of 80 mg/l solids respectively) appears to have no effect on the distribution of TSS.

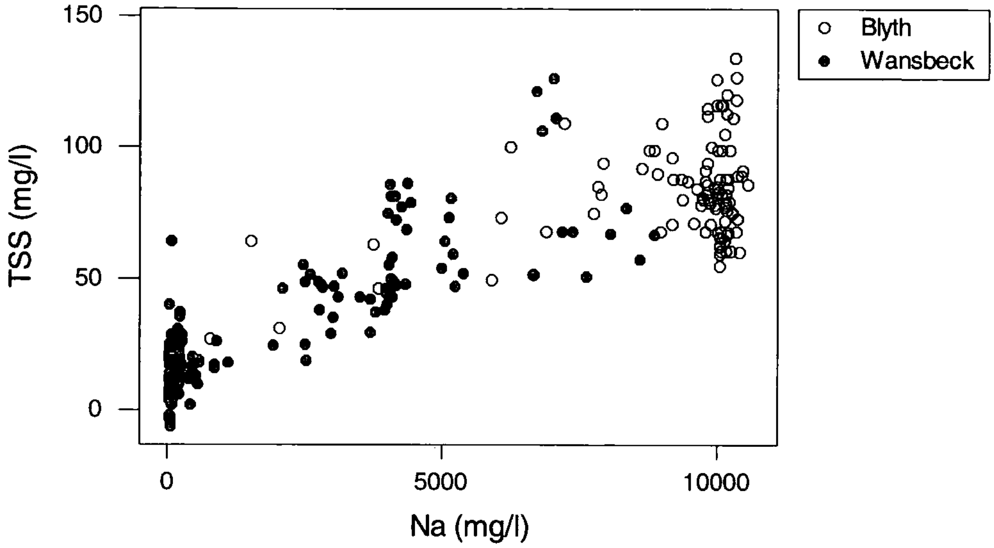


Figure 5.19. TSS vs. Na concentrations in the Blyth and Wansbeck estuaries. The greater TSS values in the Blyth which has higher seawater influence are interpreted as due to greater tidal currents and cycling of bed material rather than a seaward source of material.

Observational evidence (often in relation to contact between the RV outboard motor and the sediment!) suggests that the bed sediment is far coarser grained in the Blyth than the Wansbeck, supporting the suggestion that tidal currents are lower and hence sedimentation rates higher in the Wansbeck. The effectiveness of impounded estuaries as sediment traps in relation to current velocities is modelled as a specific task of the SIMBA project (Beavers, 2003).

5.2.4 Nitrate

Results

The freshwater input values for nitrate vary between the Rivers Blyth and Wansbeck, and hence the effect of river is larger for raw data than for normalised data (approximately 37 % compared with approximately 14 %). Nitrate levels in both the freshwater inputs to the Wansbeck and the estuary are higher than those in the Blyth (figure 5.20). Results for normalised data show that it is not the difference in freshwater input concentrations alone that explains the difference in nitrate levels and that internal effects are significant. Nitrate decreases with distance downstream and depth in both estuaries. The decrease with distance is larger in the Blyth than the Wansbeck (figure 5.21) although the depth effect in the Blyth is smaller (figure 5.22).

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
River	179.10	0.000	3.9	0.37
Distance	24.52	0.000	1.6	0.15
Depth	56.96	0.000	2.5	0.23
River*distance	7.10	0.000	0.4	0.04
River*depth	38.60	0.000	1.7	0.16
Error			0.5	0.05

Table 5.7. Results from GLM ANOVA for nitrate (raw data) between the Blyth estuary and the Wansbeck impounded estuary.

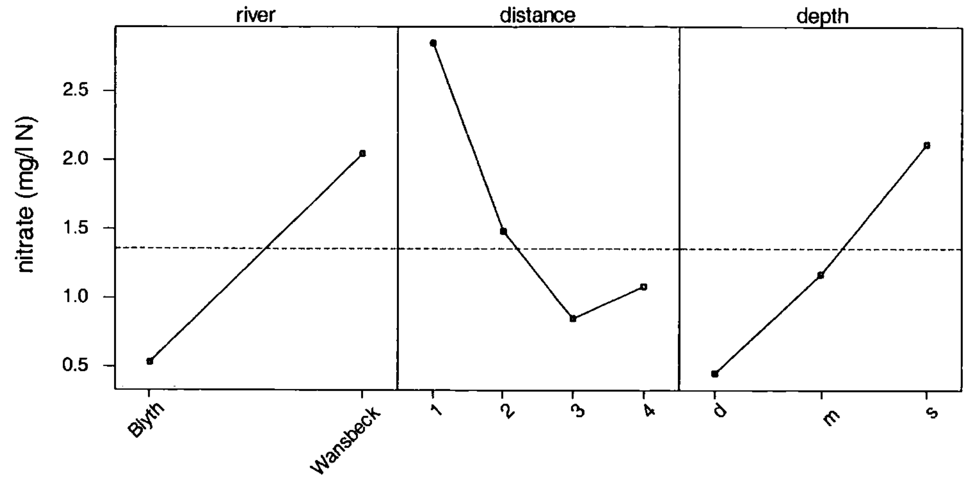


Figure 5.20. Main effects plot for the factors of river, distance and depth on nitrate (raw data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

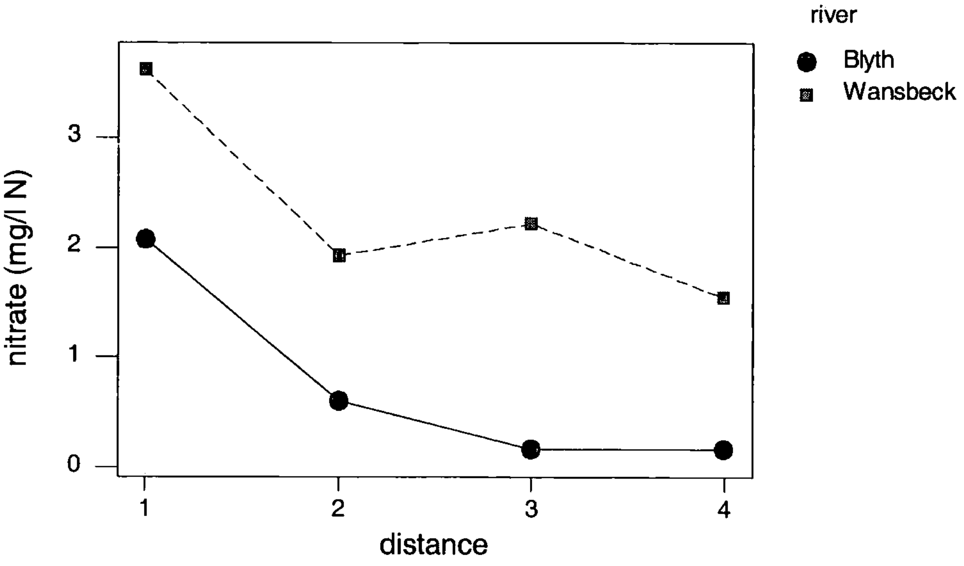


Figure 5.21. Interaction between river and distance effects on nitrate (raw data) for the Blyth and Wansbeck estuaries (LS means).

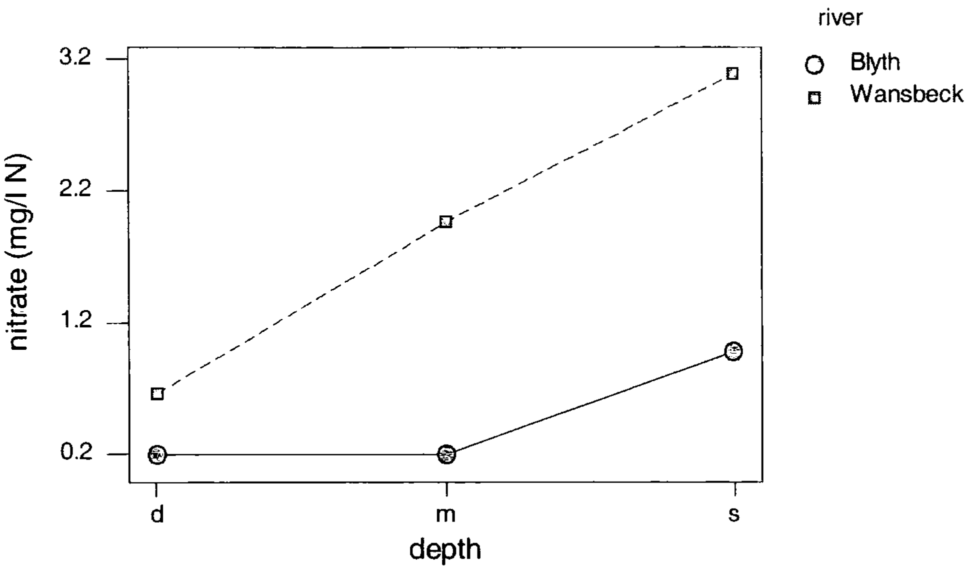


Figure 5.22. Interaction between river and depth effects on nitrate (raw data) for the Blyth and Wansbeck estuaries (LS means).

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
River	39.07	0.000	0.15	0.14
Distance	21.21	0.000	0.24	0.23
Depth	35.07	0.000	0.28	0.26
River*distance	12.10	0.000	0.13	0.13
River*depth	20.77	0.000	0.16	0.15
Error			0.10	0.09

Table 5.8. Results from GLM ANOVA for nitrate (normalised data) between the Blyth estuary and the Wansbeck impounded estuary.

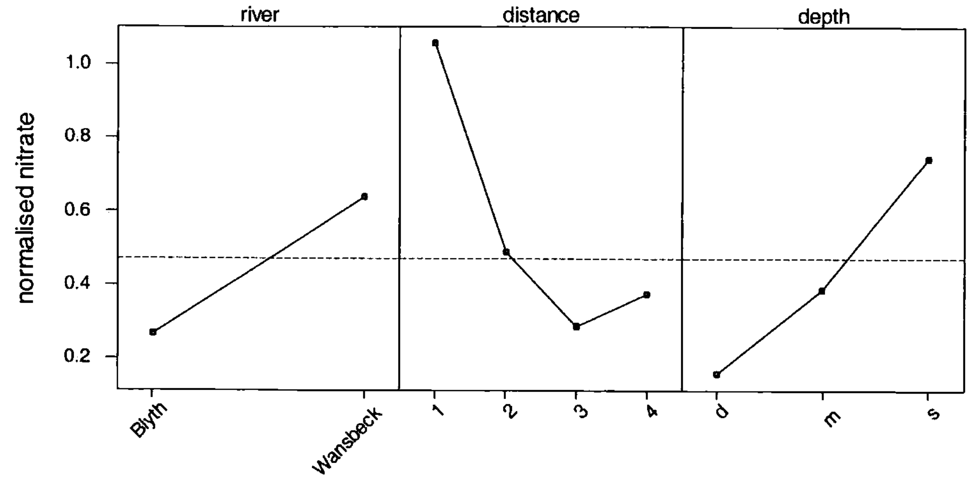


Figure 5.23. Main effects plot for the factors of river, distance and depth on nitrate (normalised data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

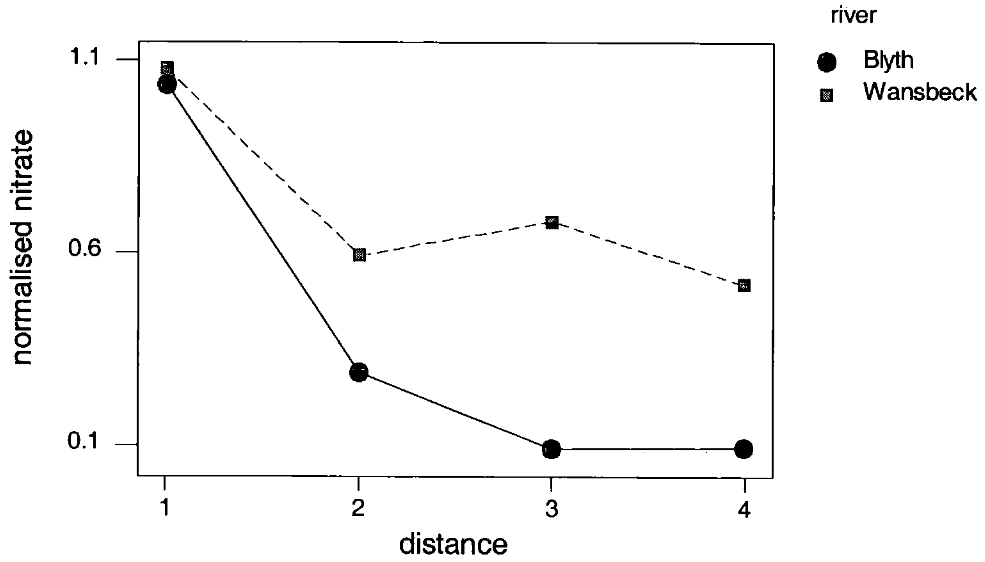


Figure 5.24. Interaction between river and distance effects on nitrate (normalised data) for the Blyth and Wansbeck estuaries (LS means).

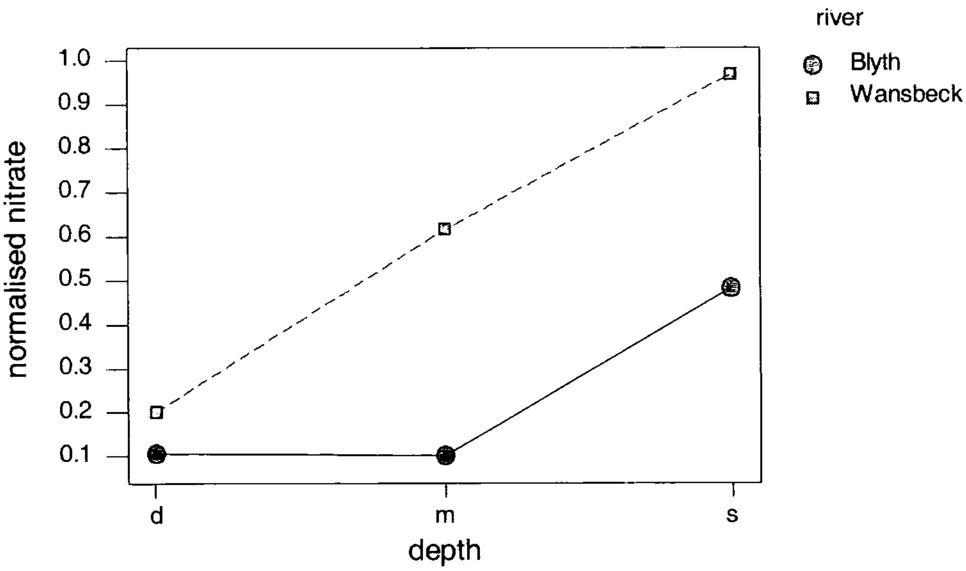


Figure 5.25. Interaction between river and depth effects on nitrate (normalised data) for the Blyth and Wansbeck estuaries (LS means).

Discussion

Nitrate within the estuaries generally behaves conservatively on mixing of freshwater and seawater (figure 5.27). (A consistent pattern of lower nitrate values at depth at site CP suggests that reducing conditions lead to some denitrification at this point, although it is difficult to assess the amount of N lost from the system.) The pattern of nitrate concentrations in the estuaries therefore reflects the relative amounts of freshwater to seawater in the water samples analysed. Nitrate is generally lower in the Blyth since this estuary is seawater dominated (see analysis for Na). The lower depth effect for nitrate in the Blyth reflects the greater degree of vertical mixing than in the Wansbeck. Within the Wansbeck surface water samples show little change in nitrate concentrations from those in the freshwater inputs since this water moves along the surface of the impoundment with little interaction with the underlying saline water. In terms of denitrification the behaviour of the estuaries studied is somewhat counter-intuitive, i.e. the system showing the development of reducing conditions and potential for denitrification shows the greatest nitrate levels since these processes only take place in saline water which is of low initial nitrate concentration, with the freshwater (high initial nitrate concentrations) not exposed to denitrifying (reducing) conditions.

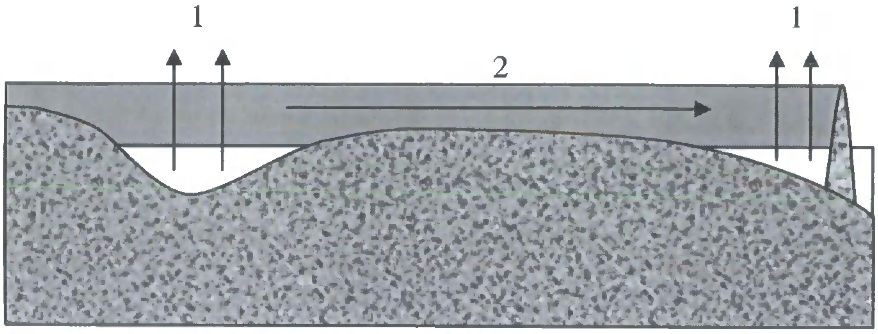


Figure 5.26. Schematic of denitrification in impounded estuaries subject to strong stratification. Reducing conditions and denitrification processes only affect saline water (of low initial nitrate concentration) at depth in the impoundment (1), whilst freshwater (of high initial nitrate concentration) progresses downstream at shallow depth and is not exposed to denitrifying conditions (2).

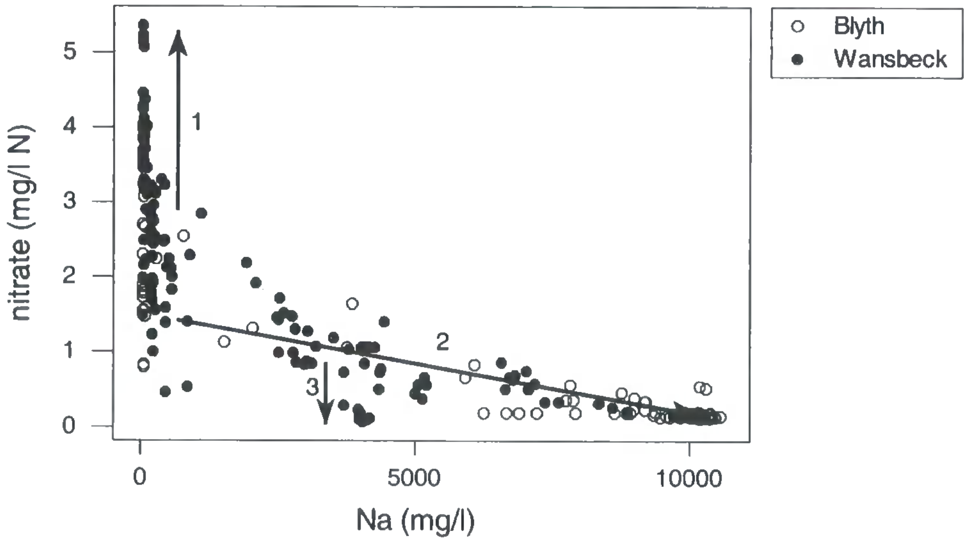


Figure 5.27. Nitrate vs. Na for the Blyth and Wansbeck estuaries. 1 represents the freshwater flow control, 2 represents conservative mixing of nitrate between freshwater and seawater, and 3 represents denitrification under low redox conditions at depth (only significant at site CP on the Wansbeck).

5.2.5 Ammonia

Results

Overall ammonia levels are higher in the Blyth than in the Wansbeck (figure 5.28). Relative to freshwater input values the changes in ammonia levels are the same within both estuaries (no significant effect for river using normalised data, table 5.10). For both estuaries the main effect (approximately 37 % of variance) is distance, which shows a pattern of sharp increase between distances 1 and 2 on both impoundments followed by a decrease with distance downstream. This effect is less pronounced in the Wansbeck (figure 5.29), although almost identical if data are normalised to the freshwater input values. The depth effects contrast between the estuaries (i.e. the depth effect alone is not significant but the river*depth interaction is), with an increase in ammonia levels with depth in the Wansbeck but far less variation with depth in the Blyth (figures 5.30 and 5.32).

Source	**F**	**P**	σ^2	**Size of Effect** (ω^2)
River	9.40	0.002	0.015	0.09
Distance	11.78	0.000	0.059	0.37
Depth	2.08	0.127	na	na
River*distance	5.21	0.002	0.023	0.14
River*depth	5.49	0.005	0.016	0.10
Error			0.044	0.27

Table 5.9. Results from GLM ANOVA for ammonia (raw data) between the Blyth estuary and the Wansbeck impounded estuary (na = not applicable since factor insignificant at 95 % level).

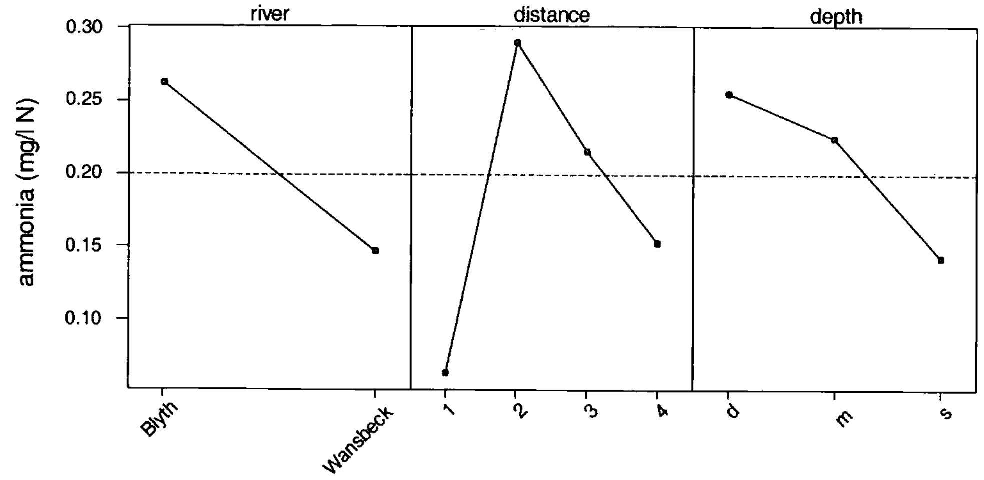


Figure 5.28. Main effects plot for the factors of river, distance and depth on ammonia (raw data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

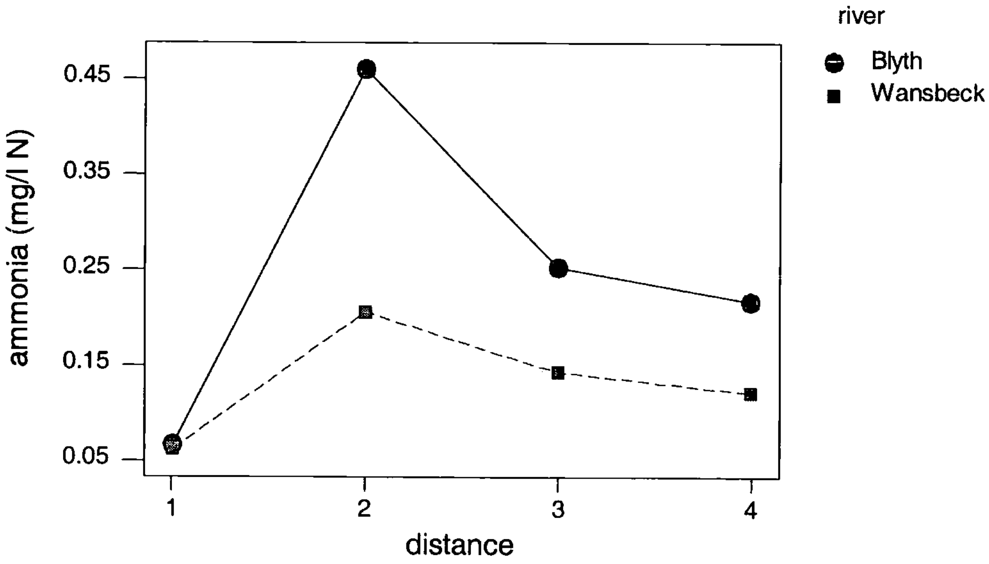


Figure 5.29. Interaction between river and distance effects on ammonia (raw data) for the Blyth and Wansbeck estuaries (LS means).

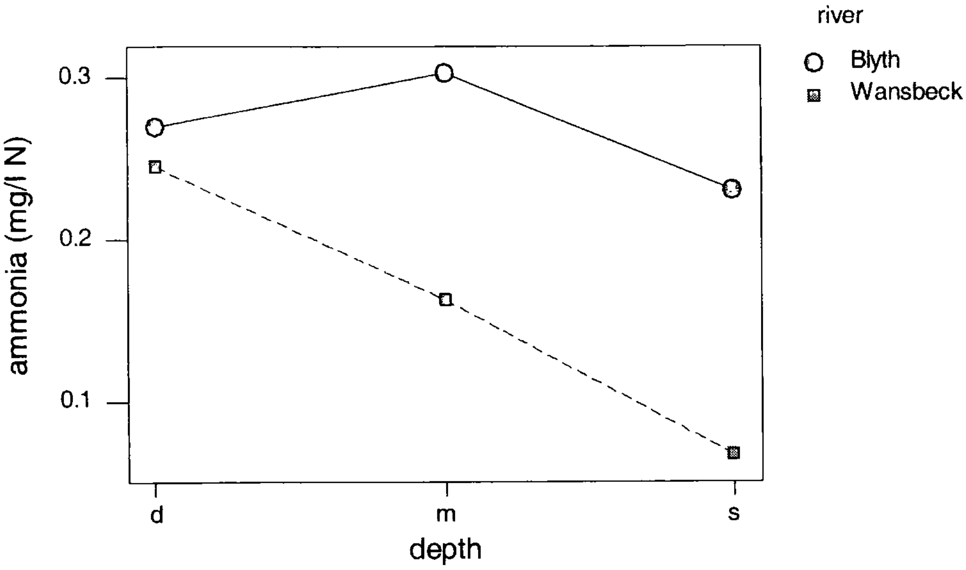


Figure 5.30. Interaction between river and depth effects on ammonia (raw data) for the Blyth and Wansbeck estuaries (LS means).

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
River	0.30	0.587	na	na
Distance	5.99	0.001	32	0.29
Depth	3.31	0.035	10	0.09
River*distance	0.78	0.506	na	na
River*depth	4.51	0.012	15	0.14
Error			51	0.47

Table 5.10. Results from GLM ANOVA for ammonia (normalised data) between the Blyth estuary and the Wansbeck impounded estuary (na = not applicable since factor insignificant at 95 % level).

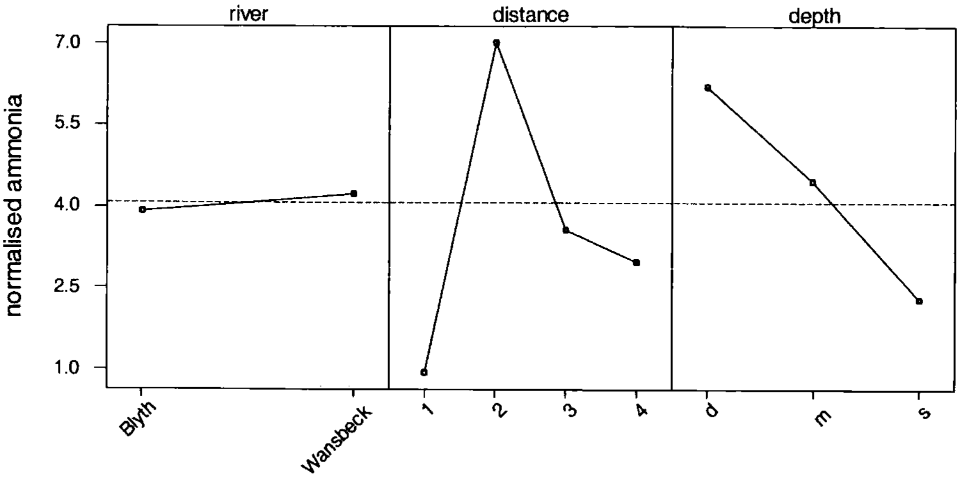


Figure 5.31. Main effects plot for the factors of river, distance and depth on ammonia (normalised data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

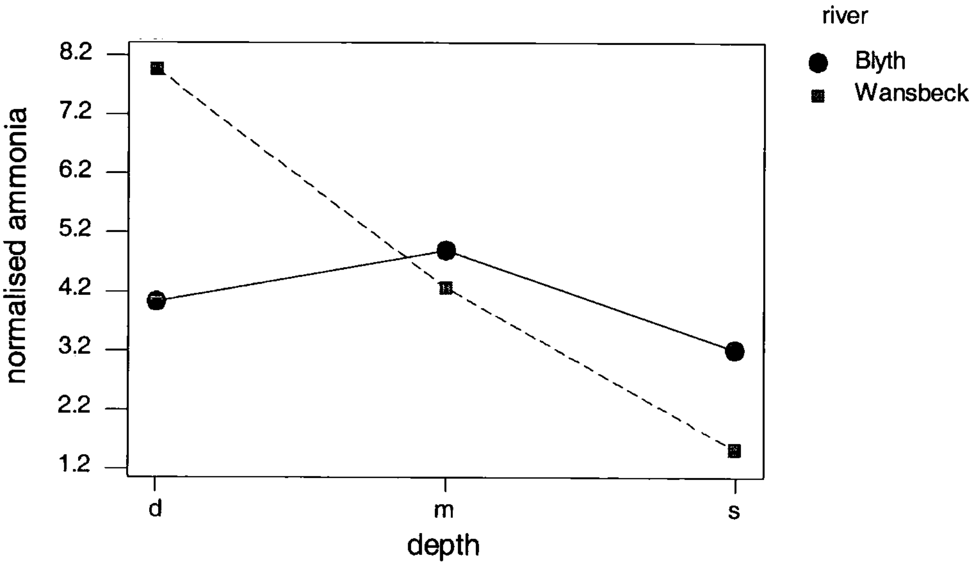


Figure 5.32. Interaction between river and depth effects on ammonia (normalised data) for the Blyth and Wansbeck estuaries (LS means).

Discussion

Whilst the ammonia concentrations in the seawater and freshwater end-members are relatively constant and the same for both the Blyth and the Wansbeck estuaries, the concentrations in intermediate (mixing) water shows a large amount of variation (figure 5.33). Ammonia levels are increased particularly at depth in the Wansbeck at site CP (distance 2) due to the processes of organic decomposition and nitrate reduction described in section 5.2.5. The within estuary increases in ammonia in the Blyth are due to a point source input to the centre of the estuary between sites AB and AS (distances 2 and 3 (NZ 2950 8249)) of (secondary) treated sewage from the Cramlington and Blyth STWs which, since sampling always immediately followed the flood tide, causes highest ammonia concentrations (throughout the water column) at site AB (figure 5.34). The Blyth shows no depth effects for ammonia since, as described above for DO, for similar tidal range, freshwater discharge and estuary morphology the lack of a barrage allows greater tidal circulation and mixing within the estuary and avoids the density stratification which leads to low DO reducing conditions.

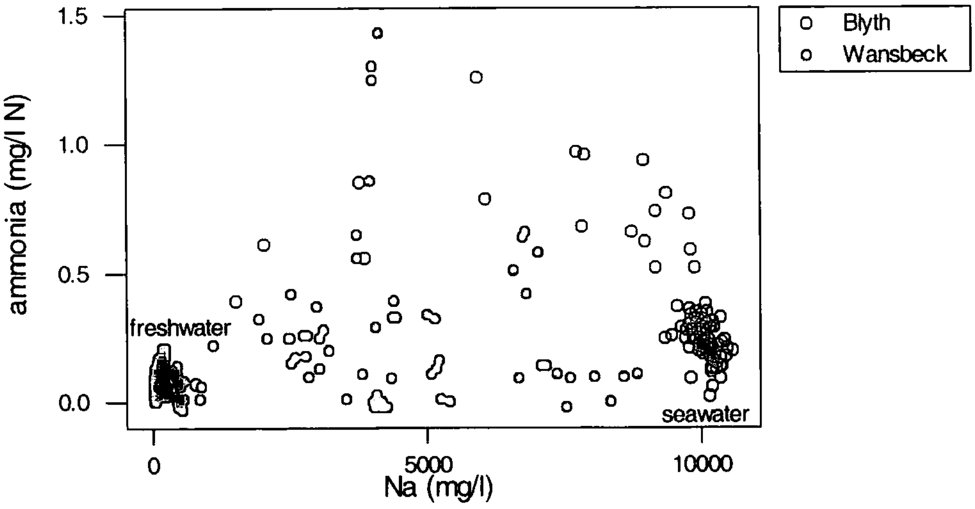


Figure 5.33. Ammonia vs. Na in the Blyth and Wansbeck estuaries, showing relatively constant ammonia concentrations in the freshwater and seawater end-members but a larg amount of variation in mixing water.

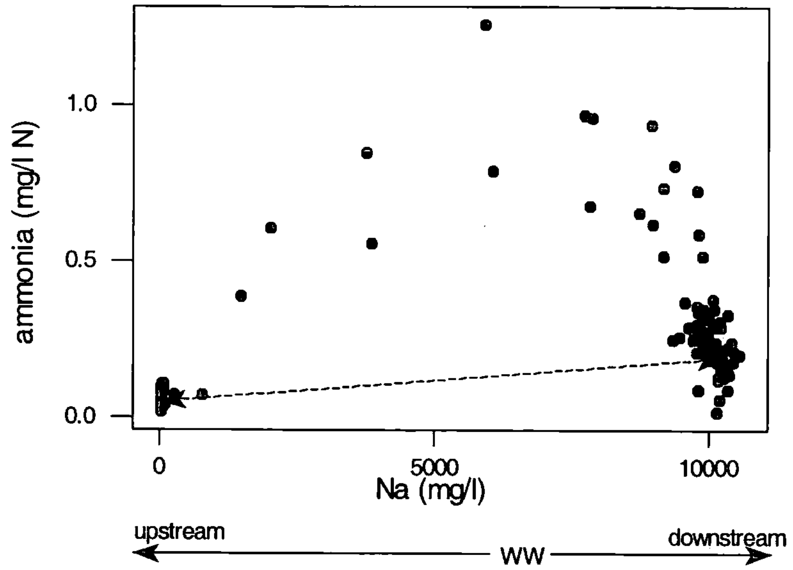


Figure 5.34. Ammonia vs. Na in the Blyth estuary. The impact of the wastewater discharge (WW) on ammonia levels with longitudinal distance and salinity within the estuary is shown as a marked departure from the conservative mixing line. A comparable pattern is shown for both P and Mn (figures 5.42 and 5.62).

5.2.6 Phosphate

Results

The large amount of variation between rivers relates to differences between the freshwater inputs to the systems ($\omega^2 = 0.53$ for raw data results and 0.14 for normalised data results). The pattern of variation is different for actual values (raw data) to that for normalised data. The variation in raw data is related to the high freshwater input values in the Wansbeck impoundment relative to both seawater and to the level in the Blyth. Hence phosphate decreases with depth in the Wansbeck but not in the Blyth (figure 5.37) and the overall distance effect is of a general decrease downstream. For normalised data the maximum amount of variation relative to the freshwater input values is within the Blyth, and is dominated by variation with distance (approximately 40 % of the variance) which shows a contrasting pattern to that of raw data.

Source	F	P	σ^2	Size of Effect (ω^2)
River	135.50	0.000	0.090	0.53
Distance	2.76	0.042	0.025	0.15
Depth	13.68	0.000	0.017	0.10
River*distance	4.95	0.002	0.008	0.05
River*depth	10.95	0.000	0.013	0.08
Error			0.016	0.09

Table 5.11. Results from GLM ANOVA for phosphate (raw data) between the Blyth estuary and the Wansbeck impounded estuary.

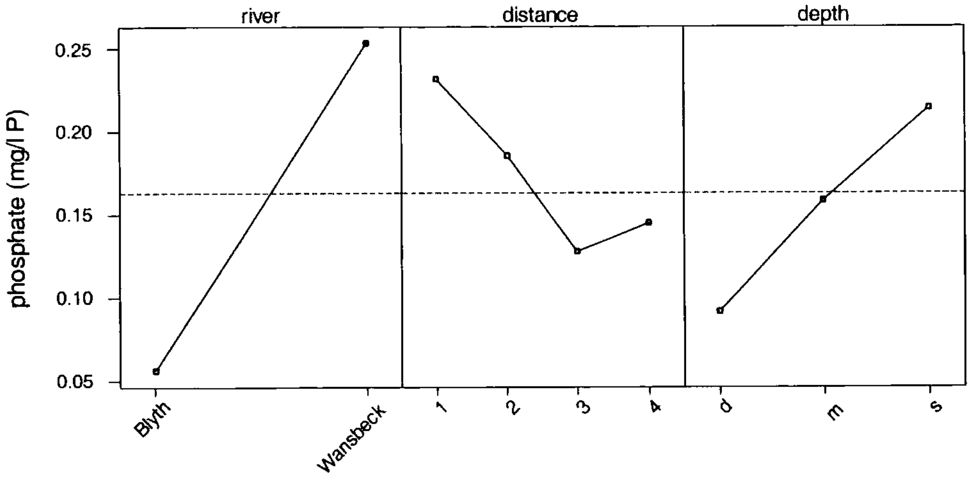


Figure 5.35. Main effects plot for the factors of river, distance and depth on phosphate (raw data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

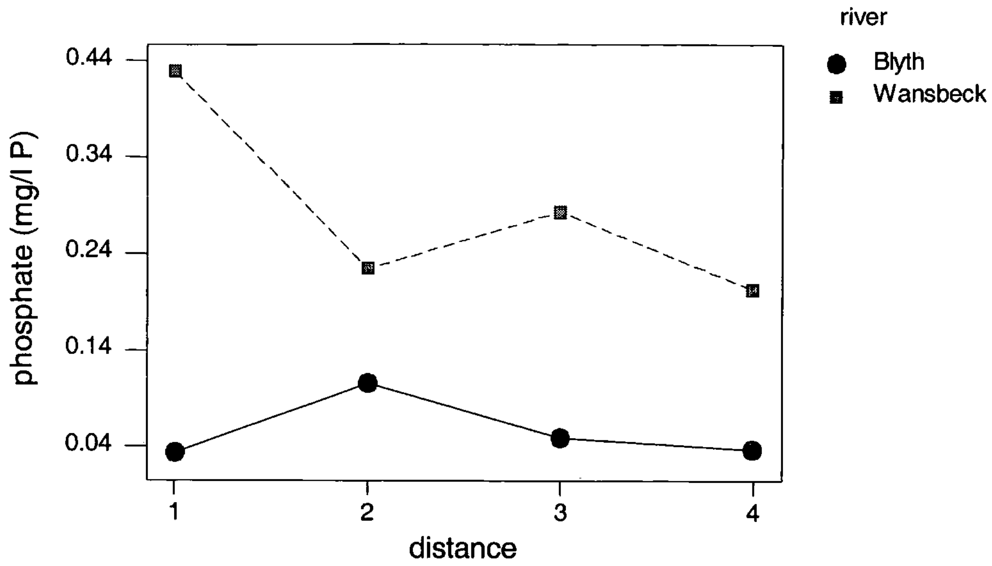


Figure 5.36. Interaction between river and distance effects on phosphate (raw data) for the Blyth and Wansbeck estuaries (LS means).

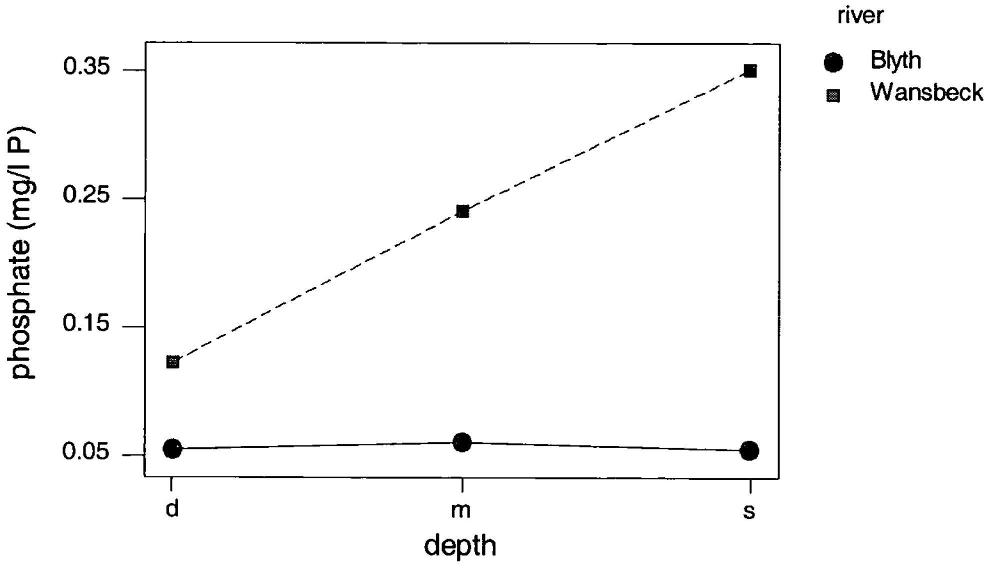


Figure 5.37. Interaction between river and depth effects on phosphate (raw data) for the Blyth and Wansbeck estuaries (LS means).

Source	**F**	**P**	σ^2	**Size of Effect** (ω^2)
River	10.77	0.001	1.91	0.14
Distance	3.98	0.005	1.74	0.13
Depth	1.03	0.357	na	na
River*distance	10.32	0.000	5.46	0.40
River*depth	0.31	0.733	na	na
Error			4.69	0.34

Table 5.12. Results from GLM ANOVA for phosphate (normalised data) between the Blyth estuary and the Wansbeck impounded estuary (na = not applicable since factor insignificant at 95 % level).

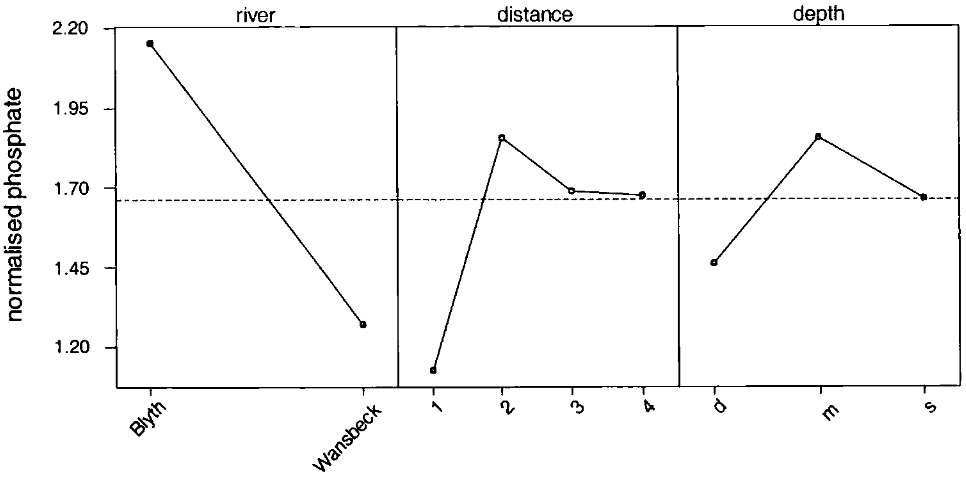


Figure 5.38. Main effects plot for the factors of river, distance and depth on phosphate (normalised data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

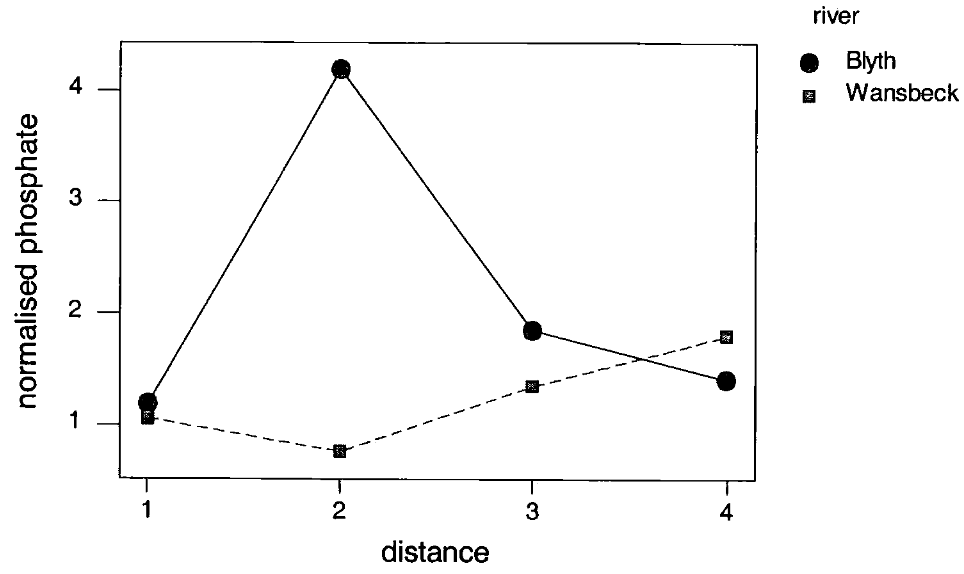


Figure 5.39. Interaction between river and distance effects on phosphate (normalised data) for the Blyth and Wansbeck estuaries (LS means).

Discussion

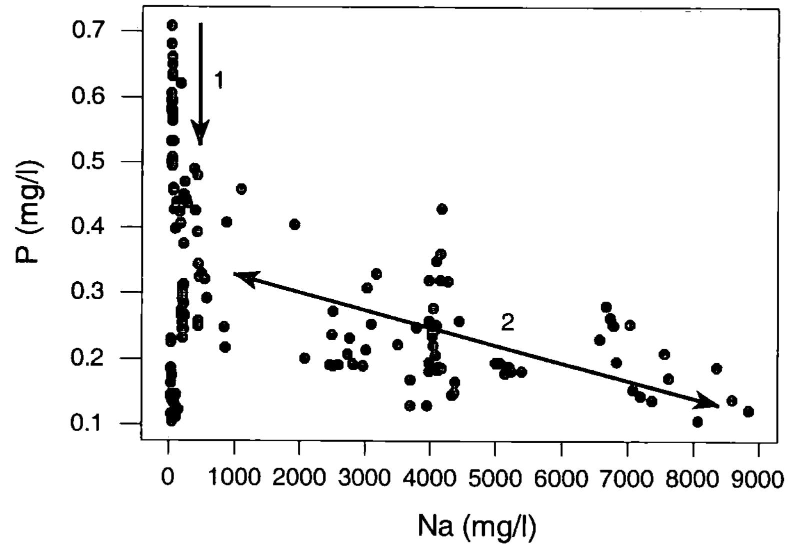


Figure 5.40. P (as dissolved orthophospate) vs. Na in the Wansbeck impoundment showing control by freshwater flow (1) and conservative mixing between freshwater and seawater (2).

Phosphate levels in the Wansbeck are higher than in the Blyth due to higher mean inputs from the freshwater entering the estuary. As stated in chapter 3, management of phosphate within the impoundments studied needs to be focussed on the inputs to the rivers. The variation in freshwater inputs is discharge related. Phosphate behaves conservatively on mixing of seawater and freshwater in the Wansbeck (figure 5.40) and hence, as for nitrate, shows a pattern of distribution related to mixing (or rather lack of) within the impoundment (i.e. a general decrease with distance downstream and a contrast between surface and deep water). For the Blyth the variation in phosphate (which represents virtually all of the dissolved phosphorus in this estuary (figure 5.41)) is, as for ammonia, related to the point source input of treated sewage between distances 2 and 3 (figure 5.42). The ratio of ammonia to phosphorous in the discharge was constant throughout the sampling period at N (as ammonia):P of approximately 5:1 by mass (figure 5.43).

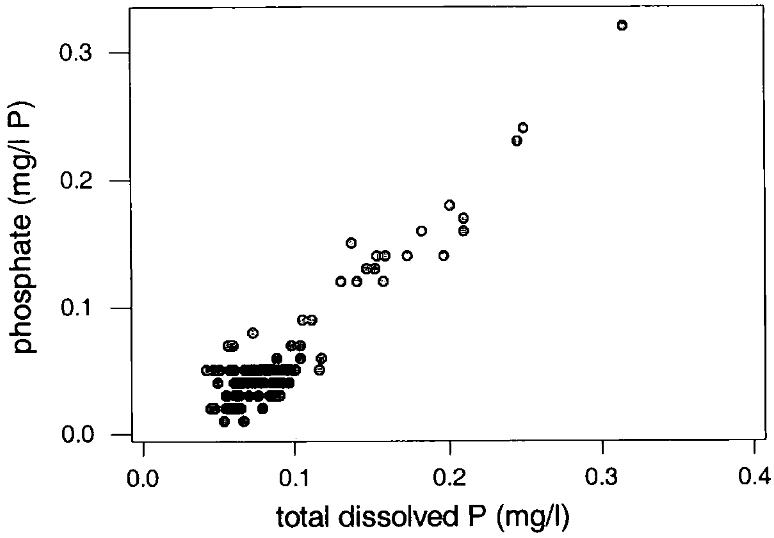


Figure 5.41. The relationship between dissolved orthophosphate (phosphate) and total dissolved P in the Blyth estuary. Virtually all P is as phosphate from wastewater within the Blyth.

The presence of the wastewater discharge to the Blyth, and its impacts on ammonia and phosphate levels in the estuary mean that it is difficult to make a direct comparison with the Wansbeck. On the basis of a lack of depth effect and the constant ratio of ammonia/P through mixing it is assumed however that no processes other than physical mixing of the water sources are significant. In particular in contrast to the Wansbeck impoundment the lack of stratification means that no reducing conditions and ammonia build-up can take place within the Blyth estuary.

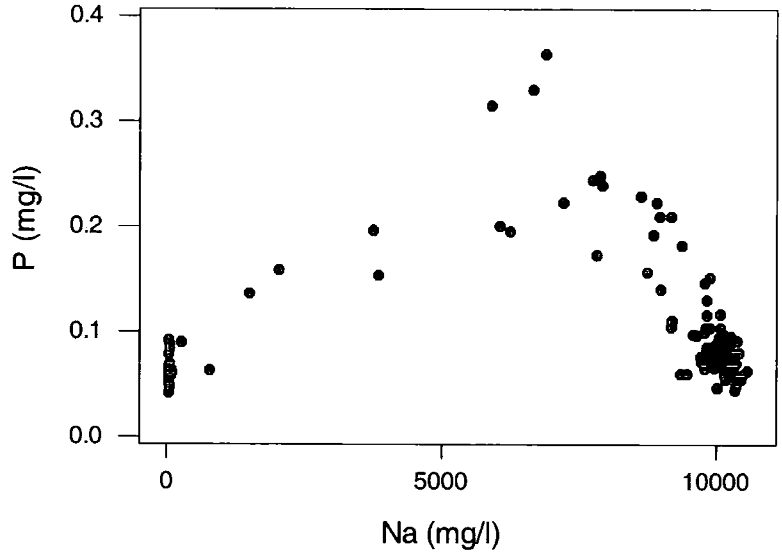


Figure 5.42. P vs. Na in the Blyth estuary, showing the impact of the wastewater discharge to the estuary (cf. figure 5.34).

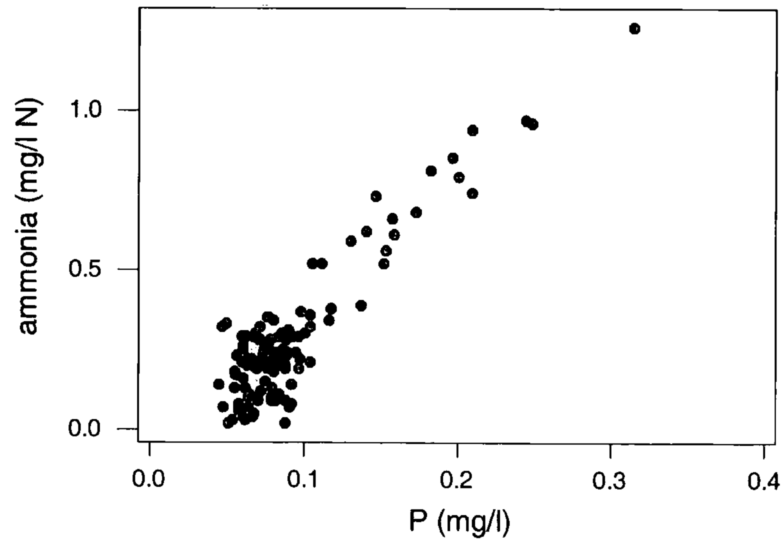


Figure 5.43. Co-linearity between ammonia and P in the Blyth estuary due to the wastewater source for these nutrients.

5.2.7 Na

Results

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
River	602.32	0.000	49161207	0.43
Distance	96.96	0.000	23537037	0.21
Depth	91.17	0.000	14744540	0.13
River*distance	87.04	0.000	21102772	0.18
River*depth	27.15	0.000	4275517	0.04
Error			1962144	0.02

Table 5.13. Results from GLM ANOVA for Na (raw data) between the Blyth estuary and the Wansbeck impounded estuary.

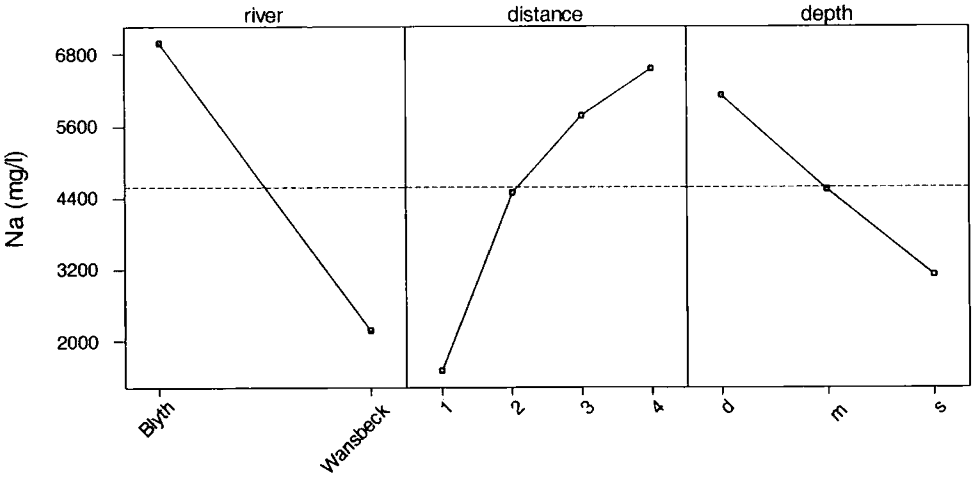


Figure 5.44. Main effects plot for the factors of river, distance and depth on Na (raw data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

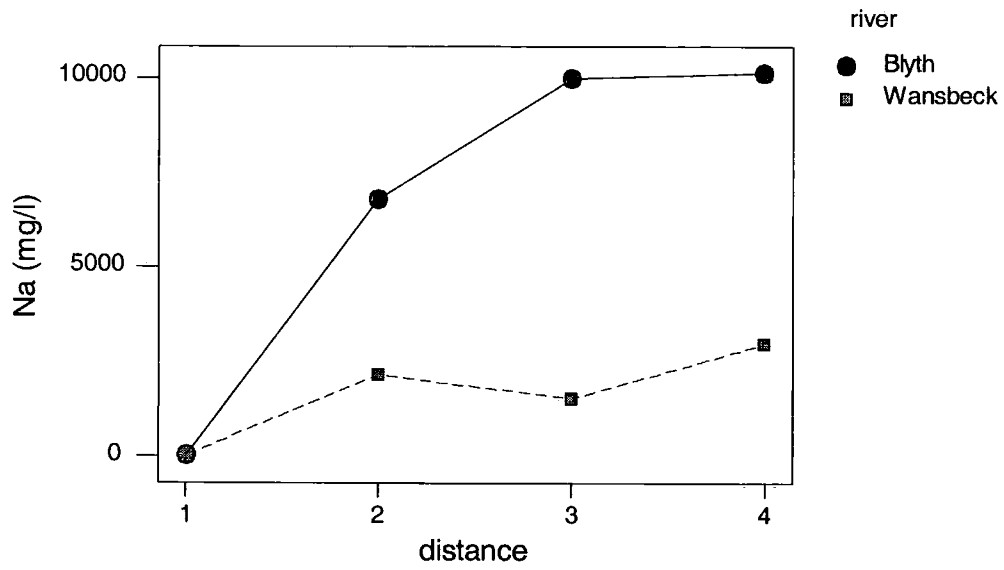


Figure 5.45. Interaction between river and distance effects on Na (raw data) for the Blyth and Wansbeck estuaries (LS means).

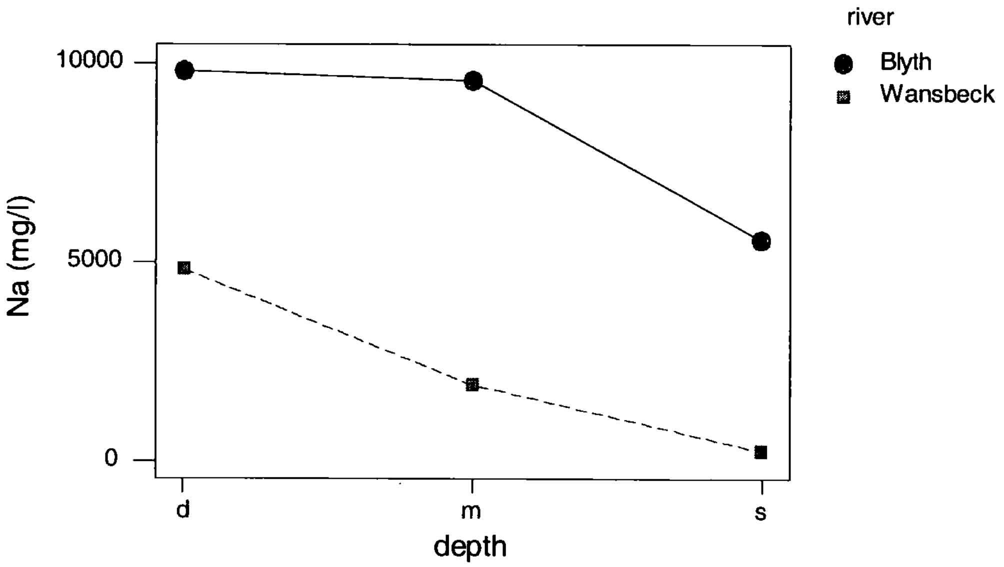


Figure 5.46. Interaction between river and depth effects on Na (raw data) for the Blyth and Wansbeck estuaries (LS means).

Na concentrations show a large difference between the two estuaries, with mean level being over three times greater in the Blyth (mean Na = 7924 mg/l) than the Wansbeck (mean Na = 2094 mg/l during the same sampling period). Na shows a general increase with distance downstream, but this is more pronounced and regular in the Blyth estuary (figure 5.45). Na increases with depth in the water column, but concentrations tend to be the same for mid-depths and deep sampling in the Blyth whereas they show difference between all depths of sampling in the Wansbeck (figure 5.46). Very little of the variance (approximately 2 %) is unexplained by terms in the model.

Discussion

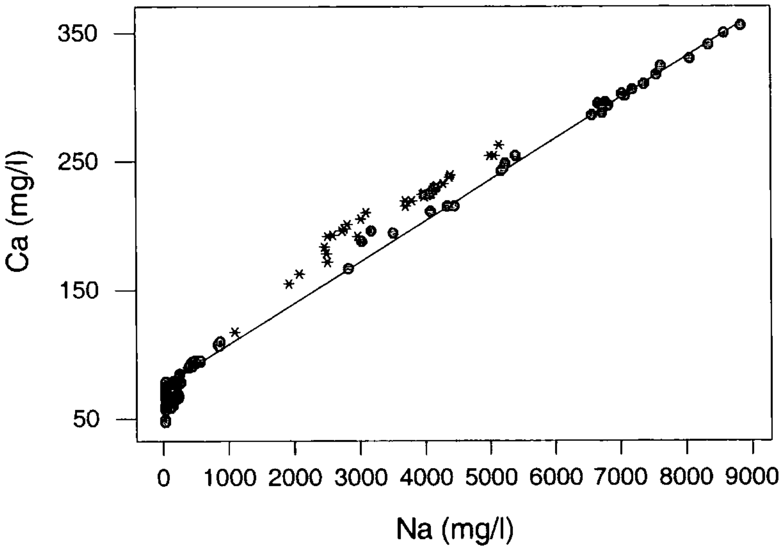


Figure 5.47. Ca vs. Na for summer sampling in the Wansbeck impoundment, showing release of Ca from sediment to deep water samples. Samples from depth at sites RB and CP and mid-depth at site CP are indicated by asterisks. All other sites are represented by solid circles.

Na is a conservative tracer of seawater/freshwater physical mixing in estuaries and as such shows a distinct contrast between the impounded and the un-impounded estuary. Seawater access is unrestricted to and therefore dominates in the Blyth whereas the majority of the water in the Wansbeck is fresh due to the reduced hydraulic heads of tidal water by impoundment. The reduction in tidal circulation, as has been observed for several parameters that are largely controlled by physical mixing, also allows long-term density stratification to develop in the Wansbeck. Within the Blyth estuary freshwater is rapidly mixed with seawater to produce a more homogenous and freely circulating water body. Na, Mg, K and S are co-linear within both the Blyth and the Wansbeck estuaries during the summer periods. Ca however shows some evidence of non-conservative behaviour during summer within the Wansbeck, where Ca concentrations above the conservative mixing line are observed in samples from depth at sites CP and RB (figure 5.47). These increases may relate to increased sedimentary carbonate solubility under the reduced pH conditions described above, and may allow mobilisation of other elements held in the carbonate phase. The elemental speciation within the sediments of the Wansbeck is discussed in chapter 6.

5.2.8 Fe

Results

The size of the variation in mean Fe between the estuaries is small (size of effect for raw data is approximately 1 %). Fe concentrations in the freshwater inputs to the two systems are similar and so the results from analyses using both raw and normalised data show similar patterns. The largest effect in both cases is that of the river*distance interaction (figures 5.49 and 5.52). The Blyth shows a continuous increase in Fe concentration with distance downstream whilst the Wansbeck show a peak in concentration at distance 2. The general effect of depth is of an increase in Fe with sampling depth. In the Blyth the mid-depth and deep samples tend to show the same Fe concentration whereas in the Wansbeck concentrations are greatest in deep water and water at the surface remains little changed from the freshwater input concentration.

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
River	5.30	0.022	0.0001	0.01
Distance	8.42	0.000	0.0005	0.07
Depth	42.74	0.000	0.0019	0.26
River*distance	44.79	0.000	0.0030	0.40
River*depth	30.72	0.000	0.0013	0.18
Error			0.0005	0.07

Table 5.14. Results from GLM ANOVA for Fe (raw data) between the Blyth estuary and the Wansbeck impounded estuary.

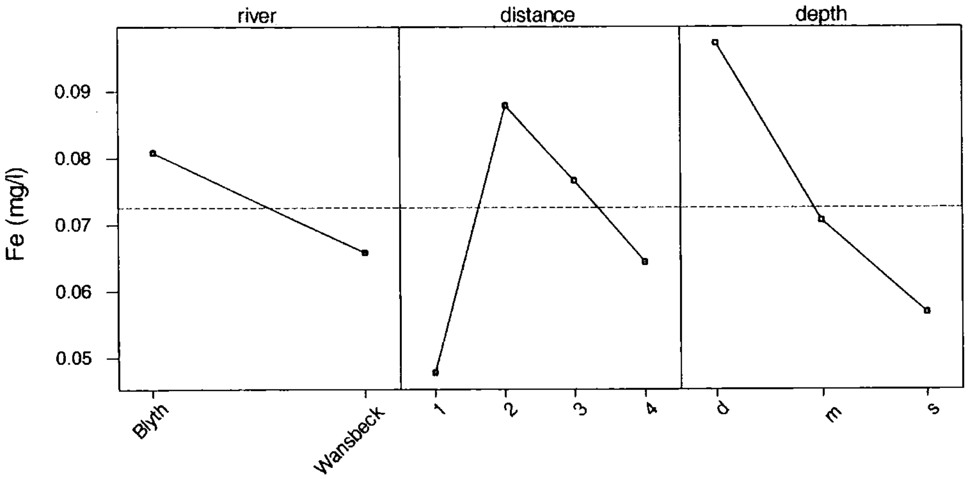


Figure 5.48. Main effects plot for the factors of river, distance and depth on Fe (raw data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

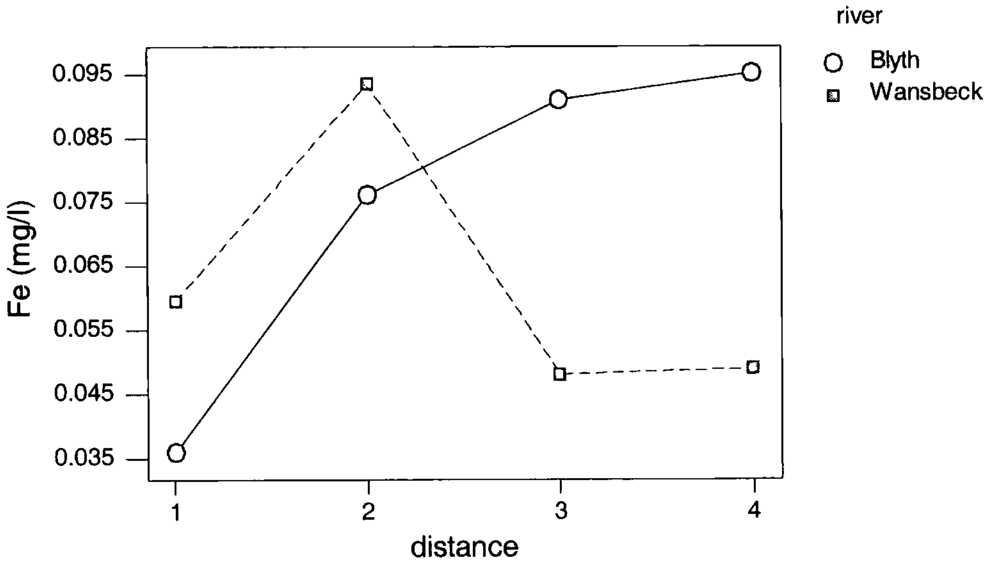


Figure 5.49. Interaction between river and distance effects on Fe (raw data) for the Blyth and Wansbeck estuaries (LS means).

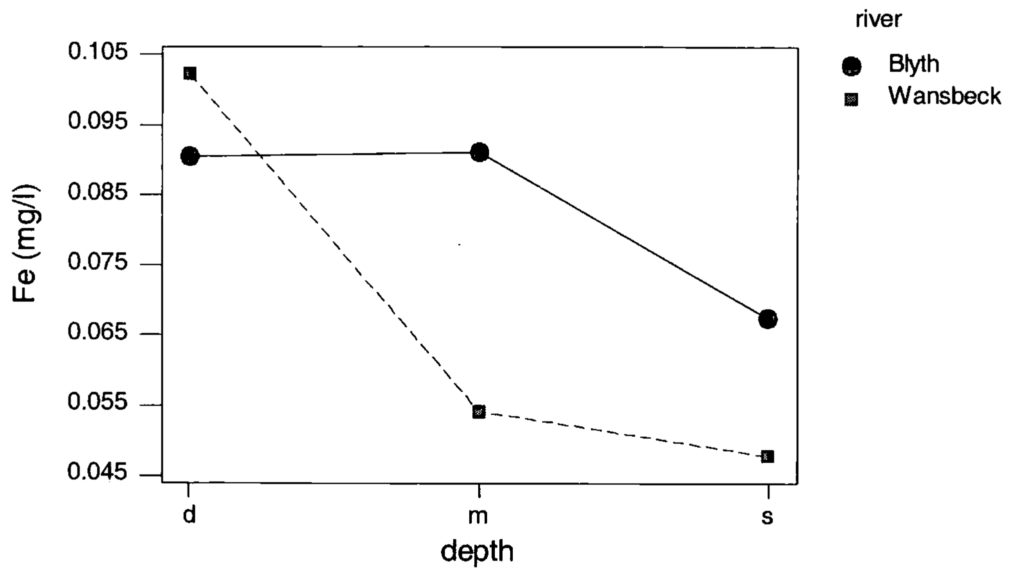


Figure 5.50. Interaction between river and depth effects on Fe (raw data) for the Blyth and Wansbeck estuaries (LS means).

Source	F	P	σ^2	Size of Effect (ω^2)
River	23.74	0.000	0.56	0.11
Distance	5.05	0.002	0.30	0.06
Depth	25.14	0.000	1.20	0.24
River*distance	22.72	0.000	1.62	0.33
River*depth	14.47	0.000	0.67	0.14
Error			0.60	0.12

Table 5.15. Results from GLM ANOVA for Fe (normalised data) between the Blyth estuary and the Wansbeck impounded estuary.

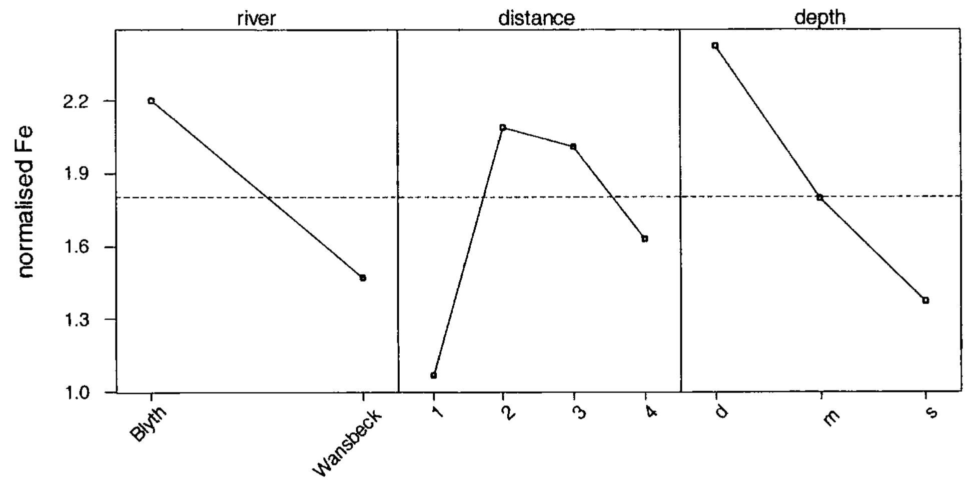


Figure 5.51. Main effects plot for the factors of river, distance and depth on Fe (normalised data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

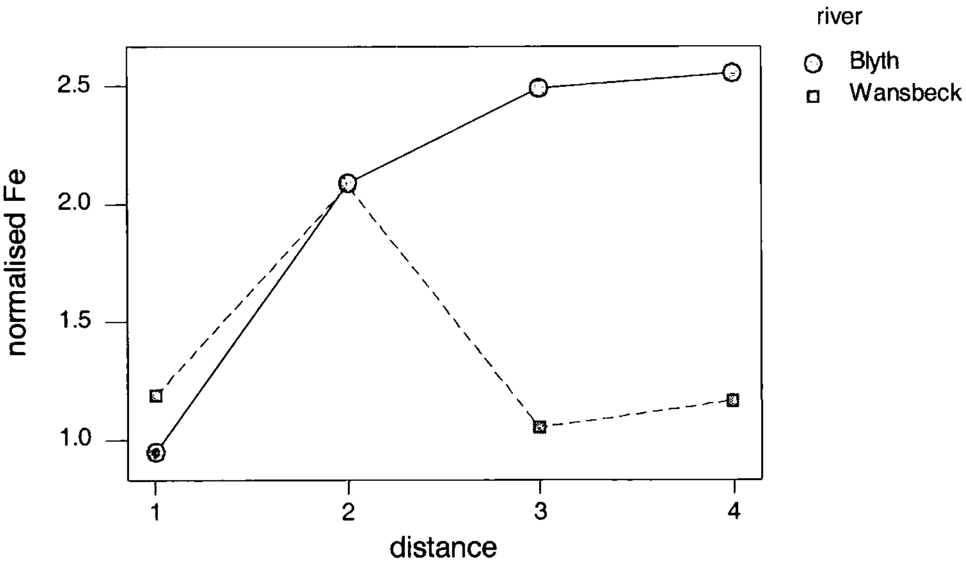


Figure 5.52. Interaction between river and distance effects on Fe (normalised data) for the Blyth and Wansbeck estuaries (LS means).

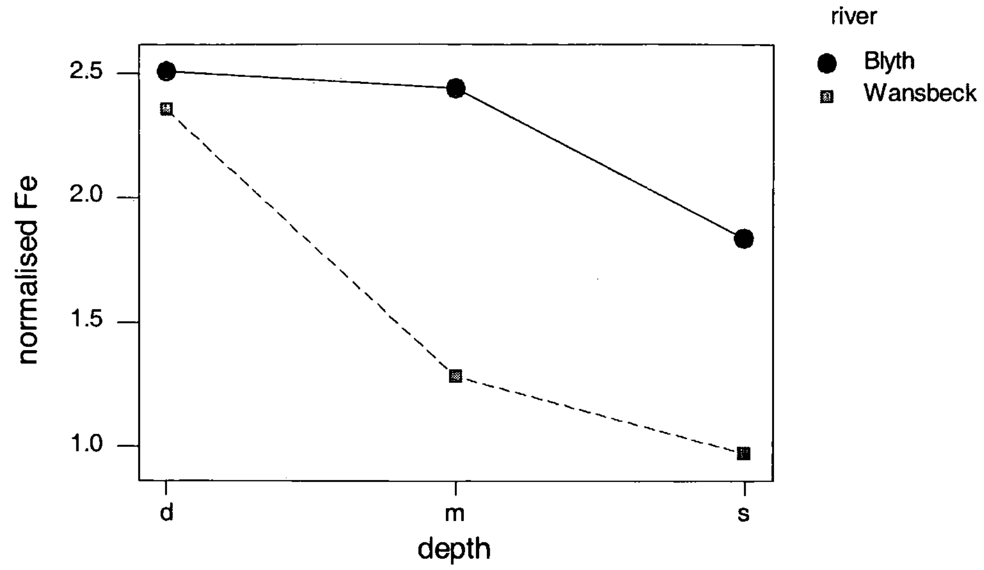


Figure 5.53. Interaction between river and depth effects on Fe (normalised data) for the Blyth and Wansbeck estuaries (LS means).

Discussion

Fe shows a very similar distribution in the estuaries to Na since the major control is conservative mixing between freshwater (which tends to show a lower Fe concentration during the period studied) and seawater (which shows a higher Fe concentration) (figure 5.54), i.e. Fe concentrations tend to be higher and more homogenous in the Blyth. Conservative mixing behaviour is in contrast with the majority of (major) estuaries which show removal of Fe at low salinities by coagulation of humic substances associated with Fe (Figueres et al. 1978), and probably relates to smaller size, reduced mixing (if impounded) and low freshwater Fe concentrations in the estuaries studied.

Variation in Fe concentration in freshwater is flow dependent, with concentrations increasing with increasing discharge for both rivers (figure 5.5.4). The Wansbeck shows greater freshwater Fe variation due to greater flow variation during the period studied. Generally Fe concentrations in freshwater during the summer period studied were very low.

Elevated Fe concentrations are shown at depth at site CP (the deepest point of the Wansbeck) relating to release of Fe^{2+} from sediment under the reducing conditions which develop in the isolated saline water (figure 5.54). Within the Blyth no redox controlled mobilisation of Fe is seen since, as described for DO, etc., greater tidal circulation causes greater mixing of the water body.

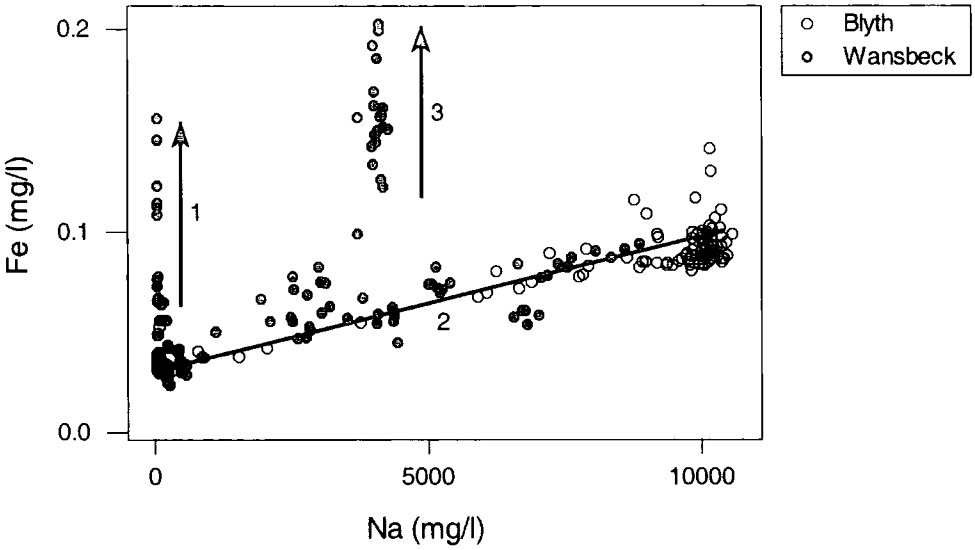


Figure 5.54. Fe vs. Na for the Blyth and Wansbeck estuaries. 1 represents the freshwater flow control, 2 represents conservative mixing of Fe between freshwater and seawater, and 3 represents the release of Fe under low redox conditions at depth (only significant for the Wansbeck).

5.2.9 Mn

Results

Since Mn values in freshwater inputs to both systems are so low relative to the values within the estuaries, results for analyses using both raw and normalised data are very similar. Mean levels of Mn are higher in the Wansbeck than the Blyth estuary. The distance effect differs between estuaries, with a small increase with distance downstream in the Blyth and a large peak in Mn concentrations at distance 2 (site CP) in the Wansbeck (figures 5.56 and 5.59). The depth effect also shows interaction with estuary. Relative to shallow water Mn concentrations those at depth within the Wansbeck are almost two orders of magnitude higher. Within the Blyth estuary Mn shows no significant difference between depths in the water column.

Source	F	P	σ^2	Size of Effect (ω^2)
River	77.07	0.000	0.17	0.17
Distance	24.40	0.000	0.16	0.15
Depth	57.08	0.000	0.25	0.25
River*distance	22.47	0.000	0.14	0.14
River*depth	55.96	0.000	0.25	0.24
Error			0.05	0.05

Table 5.16. Results from GLM ANOVA for Mn (raw data) between the Blyth estuary and the Wansbeck impounded estuary.

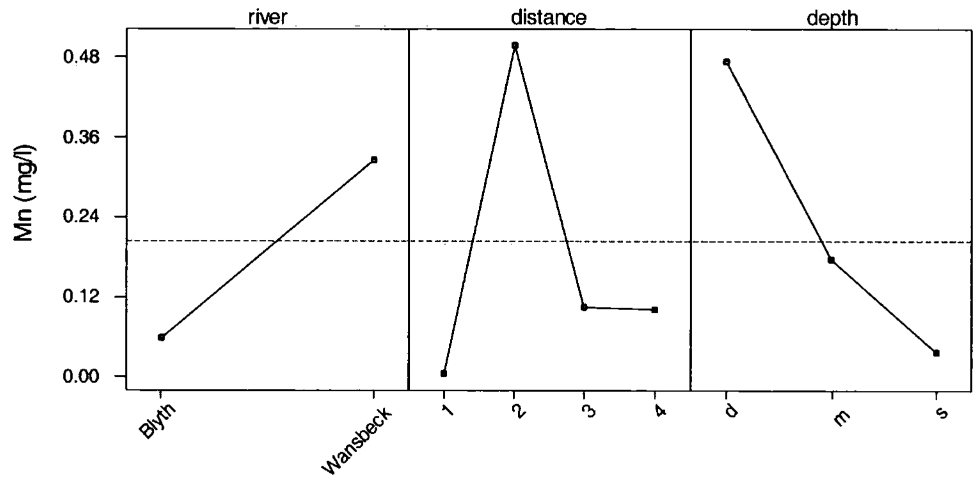


Figure 5.55. Main effects plot for the factors of river, distance and depth on Mn (raw data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

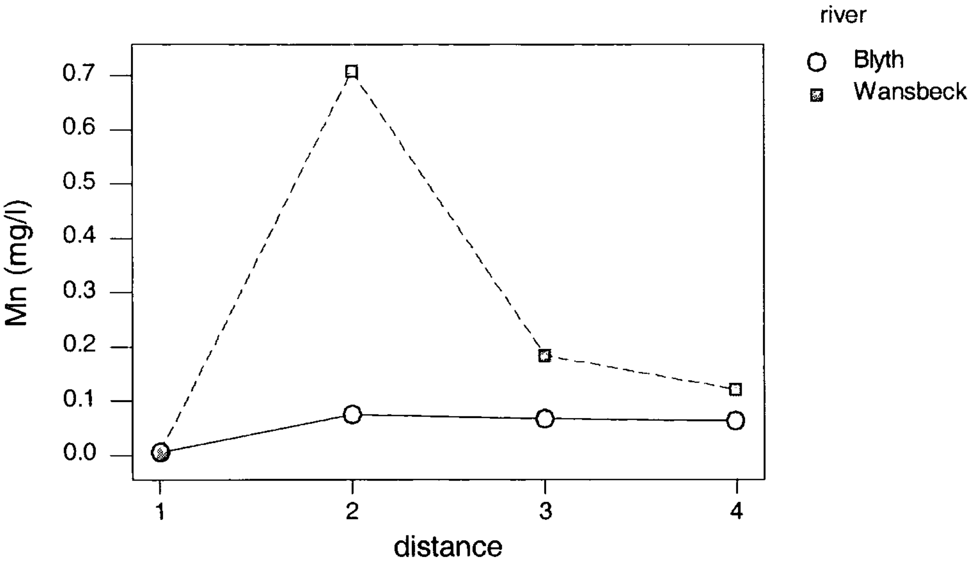


Figure 5.56. Interaction between river and distance effects on Mn (raw data) for the Blyth and Wansbeck estuaries (LS means).

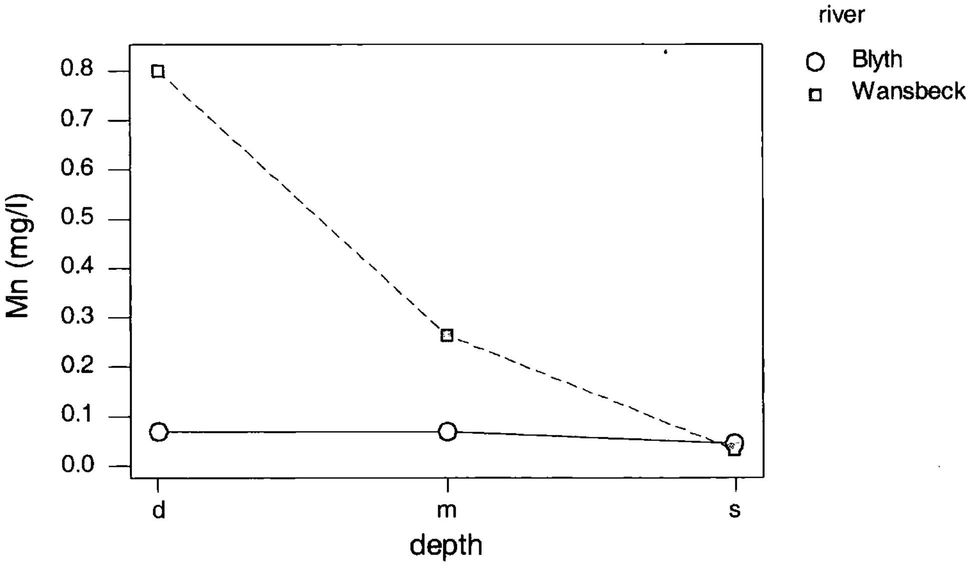


Figure 5.57. Interaction between river and depth effects on Mn (raw data) for the Blyth and Wansbeck estuaries (LS means).

Source	**F**	**P**	σ^2	**Size of Effect (ω^2)**
River	58.98	0.000	3657	0.15
Distance	20.62	0.000	3713	0.15
Depth	48.42	0.000	5982	0.25
River*distance	18.34	0.000	3281	0.14
River*depth	47.39	0.000	5852	0.24
Error			1514	0.06

Table 5.17. Results from GLM ANOVA for Mn (normalised data) between the Blyth estuary and the Wansbeck impounded estuary.

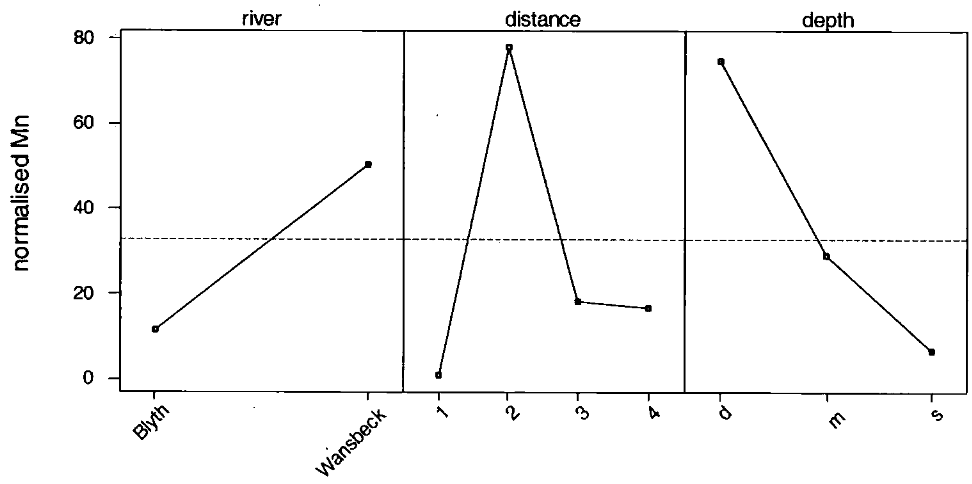


Figure 5.58. Main effects plot for the factors of river, distance and depth on Mn (normalised data) in the Blyth and Wansbeck estuaries (LS means for factor levels).

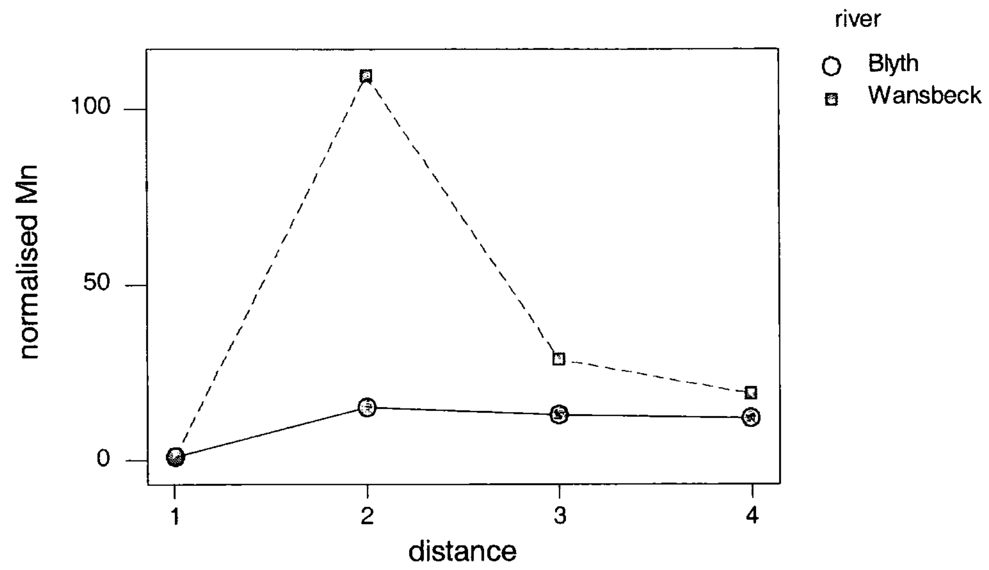


Figure 5.59. Interaction between river and distance effects on Mn (normalised data) for the Blyth and Wansbeck estuaries (LS means).

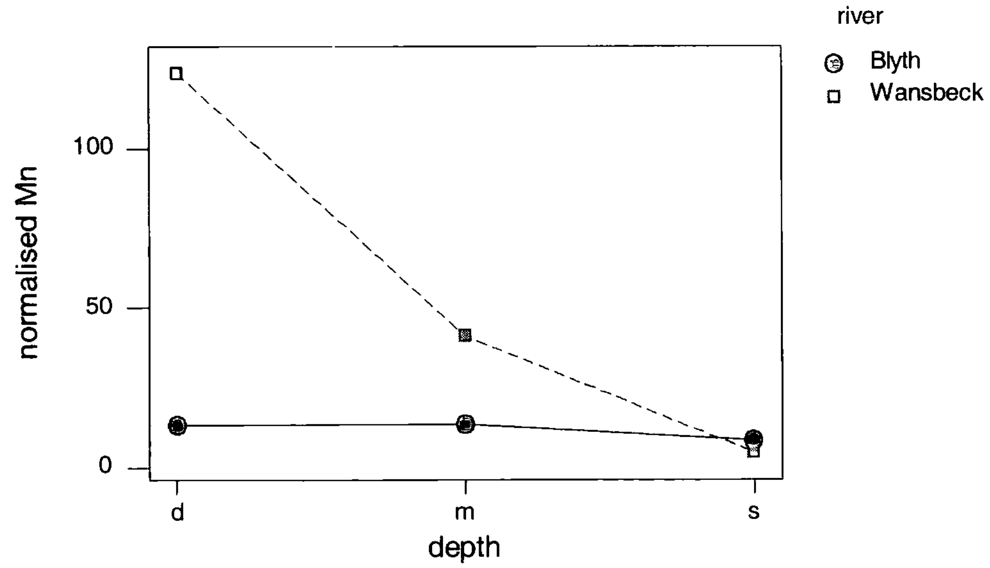


Figure 5.60. Interaction between river and depth effects on Mn (normalised data) for the Blyth and Wansbeck estuaries (LS means).

Discussion

In contrast to Fe which shows conservative behaviour in the estuaries for the periods studied, Mn show distinctly non-conservative patterns (figures 5.61 and 5.62). As described in chapter 4, Mn^{2+} may be released from bottom sediment to the water column under low redox conditions. Within the Wansbeck this process is the major control on Mn concentrations, and the distribution of Mn relates to the distribution of reducing conditions in the density stratified water column. The increase in Mn concentrations within the mixing zone of the Blyth estuary is much smaller than that shown from bed sediment release in the Wansbeck, and is due to wastewater input to the estuary (figure 5.62). Due to higher oxygen levels, release of Mn^{2+} from bed sediment does not occur within the Blyth estuary.

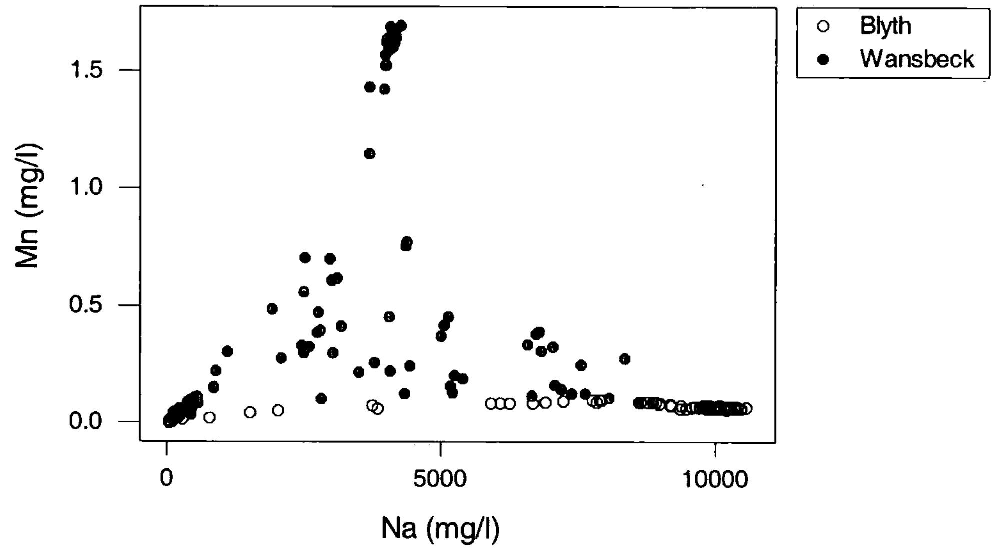


Figure 5.61. Mn vs. Na in the Blyth and Wansbeck estuaries (summer sampling), showing large release of Mn from sediment under low redox conditions within the Wansbeck.

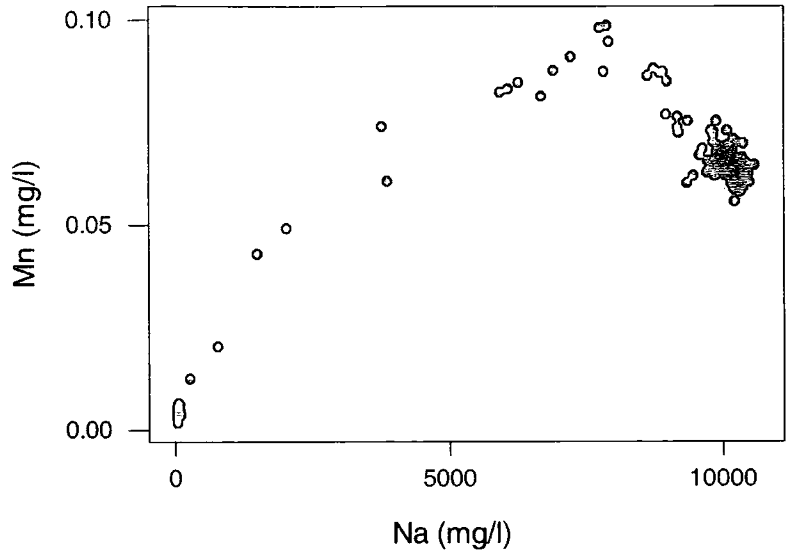


Figure 5.62. Mn vs. Na in the Blyth estuary (summer sampling). The departure from the conservative mixing line between the freshwater and seawater end members is due to wastewater input to the estuary (cf. figures 5.34 and 5.42).

5.3 Summary and conclusions

The presence or absence of a barrage has a significant effect on all of the parameters assessed (table 5.18). For all parameters which may cause or relate to detrimental effects in water bodies, the effect of barrage construction is to potentially reduce water quality. The changes in behaviour relate to three main effects of barrage construction. All three effects are due to the decrease in tidal intrusion to impounded compared with equivalent un-impounded estuaries:

1. Changes in the relative amount and distribution of freshwater and seawater in the estuary.
2. Increased stratification leading to isolation of portions of the water column.
3. Decreased tidal currents and mobilisation of bottom sediment.

Parameter	**Affected by impoundment**	**Water quality reduced by impoundment**	**Main affecting process**
DO	√	√	Increased stratification of water column
pH	√	√	Increased stratification of water column
TSS	√	×	Reduced tidal circulation and re-suspension of bed sediment
Nitrate	√	√	Reduced seawater to freshwater ratio (physical mixing control)
Ammonia	√	√	Increased stratification of water column
Phosphate	√	√	Reduced seawater to freshwater ratio (physical mixing control)
Na	√	×	Reduced seawater to freshwater ratio (physical mixing control)
Fe	√	√	Increased stratification of water column
Mn	√	√	Increased stratification of water column

Table 5.18. Summary of the impact of barrage construction on water quality.

Nitrate, phosphate and the major elements (modelled using Na) show concentrations and distributions which relate mainly to the difference in concentration between seawater and freshwater and the effects of barrage construction on the relative volumes of these two end-members. This physical mixing control is also a significant factor for several other parameters analysed, and has implications for any pollutants which are transported in either the fluvial or tidal component. The concentrations of nitrate and phosphate tend to be higher in the freshwater inputs than in seawater, and therefore, since barrage construction reduces the proportion of seawater, impounded estuaries are likely to show greater concentrations of these nutrients. Nitrate and phosphate are marked as having a potential detrimental effect on water quality in the impoundment in terms of their potential impacts on eutrophication, although whether a biological response is encountered will depend on a variety of factors (e.g. N/P limitation, turbidity, turbulence, etc.). As mentioned, eutrophic behaviour is encountered within the Wansbeck impoundment.

Reduced tidal influence on impoundment also allows changes the nature of the estuary towards a more stratified water body. In the Wansbeck the effects of this stratification are particularly dramatic due to the irregular topography of the estuarine profile which allows saline water to “pond” within deeper sections. This deep “ponded” water undergoes a series of changes following isolation from the atmosphere and contact with organic rich bottom sediments including reduction in DO and pH, and increase in ammonia and Fe and Mn (and associated metals). Although most pronounced in the Wansbeck, these effects are observed in all of the impoundments studied and may be assumed to be a major negative impact of barrage construction.

Finally, the reduction of tidal circulation has an impact on the behaviour of sediment within the estuaries. Estuaries are effective sediment traps in their formative stages but reach an equilibrium between sediment deposition and scour by currents over time (Dyer 1997). Construction of a barrage reduces the scour by currents and sedimentation will take place within the impounded area until a new equilibrium is reached. In the Blyth estuary higher tidal currents were evident in the development of a turbidity maxima due to re-suspension of bottom sediments and the general coarser grained nature of the bed.

Chapter 6

Sediment Quality and Speciation

6.1 Introduction

The objectives of the sediment surveys were multifold:

1. To assess the current state of the sediment quality in the impoundments and enable appropriate design of more detailed surveying.
2. To determine the possibility of, and conditions under which, internal cycling may lead to release of elements from the sediment to the water column of the impoundments.
3. To determine the trends in sediment quality following impoundment.
4. Together with data supplied from sedimentological studies of the SIMBA Project, to determine the flux of sediment and associated elements to the impoundments, to enable prediction of the long-term sustainability of the systems.

In order to perform these objectives bed sediment coring on the Wansbeck and Tees impoundments was carried out.

6.2 Sediment survey design

Sediment coring was carried out to give vertical profiles of sediment quality, with the aim of assessing trends in deposition and sediment quality over the lifetime of the impoundments. The coring experiments were also designed to assess the differences in sediment quality and deposition between types and ages of impoundments. The scope of this project allowed the comparison of sediment between 2 estuaries.

6.2.1 Estuaries studied

The estuaries chosen for sediment coring surveys were the Wansbeck and the Tees. The Wansbeck was impounded in 1975 and is a partial tidal exclusion system. The Tees was impounded in 1994 and is a total tidal exclusion (freshwater) system. Both estuaries are located in the Northeast of England within 1 hours drive of the University of Durham. Whilst additional sampling from the Tawe would have allowed more rigorous testing of the factors of age and design on the sediment quality, time and equipment constraints meant that this was not possible within this project.

6.2.2 Sampling sites and dates

2 sites from each impoundment were chosen as representing the most stable sedimentary environments, which had undergone the least physical mixing of sediment and were likely to give the least disturbed sediment profiles (table 6.1). These sites were chosen based on preliminary longitudinal grab-sample profiles of the impoundments, with field examination of the particle size and colour (as a rough proxy for organic content) of the sediment being used to estimate the lowest energy environments (finest particle size and highest organic content). These surveys also gave an indication of when the nature of the sedimentary behaviour changed from riverine to lacustrine typology. An additional sample was taken from the emerging island next to site RB (site SM), to assess the significant sedimentation observed to be occurring at the margins of the Wansbeck impoundment. Sampling was carried out on the 23/07/01 for the Wansbeck and 24/07/01 for the Tees.

River	Site name	Site abbreviation	Grid reference
Tees	Opposite Kvaerner Building	KV	NZ 4570 1905
Tees	Tees Barrage	TB	NZ 4616 1905
Wansbeck	Railway Bridge	RB	NZ 2775 8585
Wansbeck	Barrage	WB	NZ 2935 8536
Wansbeck	Railway Bridge Island	SM	NZ 2935 8536

Table 6.1. Sediment coring sampling sites.

6.2.3 Replicates

In order to assess local variations in sediment quality, and allow statistical testing of the significance in differences with depth in the profiles relative to random variation, duplicate cores were taken within 1 m of each other at sites WB and TB.

6.3 Sediment sampling procedure

6.3.1 Safety precautions

Precautions were taken to limit the risk to those involved during sediment sampling. Fieldwork was always completed with at least 2 people in the RV and at least one on shore, all carrying mobile telephones, on all occasions. Lifejackets and high visibility clothing were worn when on the water or when working from river banks. A first-aid kit was carried in the RV. Gloves were worn when collecting samples to avoid risk of infection, in addition to avoiding contamination of samples. All field and laboratory work carried out as part of this PhD was done so without any injury to any party.

6.3.2 Procedures

All work (except Dutch auger coring) was carried out from the RV, normally with a crew of 3 people. Sampling was carried out where possible with plastic or stainless steel equipment, and gloves were worn at all times, to minimise the risk of contamination. The date, location and time of sampling, plus any additional relevant information were recorded in a notebook for each sample taken.

6.3.3 Coring

Sediment cores were taken using either a Dutch auger coring device for the sample taken from the newly formed island at RB, or a pneumatically driven Mackereth coring device for all other sediment coring work.

6.3.3.1 Dutch auger

The Dutch auger consists of 1 m length of metal split tube, which is manually turned and driven into the sediment before being retrieved vertically with the sediment sample. The section retrieved may then be subsampled at defined depths from the sediment. The Dutch auger is effective for relatively well consolidated (low moisture content) silts and clays, such as are found on the emerged ground at RB in the Wansbeck impoundment. The 1 m core taken from the island at RB was subsampled in the field at 5 cm intervals with a stainless steel palette knife, and transferred to labelled polythene sample bags. Samples were transported to the laboratory in the dark in cool boxes at 4°C, before being stored frozen for a maximum of 1 month at -20°C prior to drying and sequential extraction, and other analyses.

6.3.3.2 Mackereth corer

The pneumatically driven Mackereth corer consists of a 1 m by 10 cm diameter perspex sampling tube which is driven vertically into the bed sediment by compressed air. The sampler and core are then brought back to the water surface, with the sediment being held in place by a plunger at the top of the perspex sample tube creating a "suction" force on the sediment. The base of the sampling tube is then capped before removal from the water, and the tube and sample removed from the sampling device on the RV and capped at the top end. Mackereth corers are appropriate for obtaining undisturbed cores from relatively unconsolidated (high moisture content) sediments such as are found in the beds of lakes and estuaries. 3 cores were taken from the RV from the bed of the Wansbeck impoundment (1 from site RB and 2 (replicates) from WB), and 3 cores from the Tees impoundment (1 from site KV and 2 (replicates) from TB). Visibly disturbed cores were discarded and sampling repeated. The length of core retrieved ranged from 40 to 70 cm, with shorter cores being retrieved from the Tees due to sandy material (which was not retained in the sample tubes) being encountered at approximately 60 cm sediment depth. The cores were transported with minimum disturbance in the dark to the laboratory, and within 1 hour were placed in a freezer. Once frozen, the sediment cores were extruded from the perspex sampling tubes using a steel plunger, and subsampled at 3 cm intervals using a stainless steel palette knife. Sample that had been in contact with the steel plunger was discarded. These discs of frozen sediment were then split into two semi-circles of material using a palette knife, to give one portion for sequential extraction experiments and one portion for trace organic analysis. Subsamples were transferred to labelled polythene bags (or wrapped in fired aluminium foil for samples to be used for trace organic analysis), and stored frozen for a maximum of 1 month at -20°C prior to drying and sequential extraction, and other analyses.

6.4 Sediment parameters measured

The focus of the sediment quality surveys was on the metal and nutrient contents and speciation in this phase. Parameters were measured using, as far as possible, similar techniques to those carried out in the water quality surveys to allow comparison of the metal and nutrient contents between the water and sediment phases.

6.4.1 Sequential extraction

Since the design of the sediment survey was to assess sediment quality in the impoundments in terms of possible environmental impact, determination of elemental speciation was considered important. Information about the physiochemical forms of elements is required to understand their environmental mobility, pathways and bioavailability (Tack and Verloo 1993). The Commission of the European Communities, Community Bureau of Reference (BCR), defines speciation as either (a) the process of identification and quantification of defined species, forms or phases in a material or (b) the description of the amounts of these species, forms or phases present (Ure et al. 1993a). Many speciation techniques have been developed with varying degrees of success and acceptance (McBride 1989). For the solid phase these include single reagent leaching, sequential extractions and ion exchange resins. Although controversial due mainly to arguments over its operationally defined and non-selective nature, sequential extraction is the most commonly applied.

Tessier et al. (1979)			**Ruttenberg (1992)**		
Step	Extractant	Extracted	Step	Extractant	Extracted
1	NaOAc (pH 8.2), or $MgCl_2$ (pH 7)	Exchangeable	1	$MgCl_2$ (pH 8)	Exchangeable
2	NaOAc (pH 5)	Acid-soluble (carbonate bound)	2	Na-citrate, Na-HCO_3, Na-dithionite (pH 7.6)	Reducible (Fe and Mn oxide bound)
3	Na-dithionite, Na-citrate and H-citrate, or $NH_2OH.HCl$ and HOAc	Reducible (Fe and Mn oxide bound)	3	NaOAc (pH 4)	Acid soluble at moderately low pH (carbonate bound plus authigenic and biogenic apatite)
4	H_2O_2, HNO_3	Oxidisable (organically bound)	4	1 M HCl	Acid soluble (detrital apatite plus other inorganic P)
5	HF-$HClO_4$	Residual (silicate bound)	5	Ash at 550°C followed by 1 M HCl	Oxidisable (organically bound)

Table 6.2. The sequential extraction procedures of Tessier et al. (1979) and Ruttenberg (1992).

There are a large number of wet chemical sequential extraction techniques applied to the problem of determining elemental speciation in sediments (Pickering 1995). The general procedure involves applying the least aggressive reagents first, with subsequent extraction steps using progressively more aggressive and lower pH solutions. Examples of commonly used sequential extraction techniques include those of Tessier et al. (1979), Salomons and Förstner (1984), and Ure et al. (1993b) for metal extraction, and Williams et al. (1976) and Ruttenberg (1992) for phosphorus. Techniques differ in terms of their number of extraction stages (species determined), the order of extraction, and the exact reagents used. Generally most techniques are based on the protocol of Tessier et al. (1979) and differ only in minor operational detail (Kersten and Förstner 1995). Although there is a movement towards harmonisation of sequential extraction procedures to allow comparability of results based on a simple three step extraction procedure (Whalley and Grant 1994, Quevauviller et al. 1996 and Quevauviller 1998), the Tessier scheme is still widely used. In this project it was felt that the environmental conditions likely to be encountered in the impoundments could most closely be modelled by the extraction steps of the Tessier sequential extraction procedure. To determine whether the Tessier scheme could also be used to quantify the speciation and hence likely release of phosphorus in the sediments, a selection of samples also underwent extraction by the procedure of Ruttenberg (1992). A summary of the two procedures is given in table 6.2.

6.4.2 Moisture content

Drying of sediments is necessary since analyses are based on dry weight of samples. Deposited sediments contain high water contents (30 to 95 %) (Loring and Rantala 1992), depending on the depositional environment, mineralogy and depth within the sedimentary sequence. A measurement of moisture content allows the effect of interstitial water composition (salinity) on the geochemical analyses to be accounted for.

6.4.3 Organic matter

Particulate organic matter has a very high specific area and therefore a very high adsorption capacity. Contaminants entering water bodies are very often adsorbed onto organic particulates (Chapman and Wang 2001), and so the determination of organic matter content of sediment is therefore necessary to assess the environmental behaviour of elements.

6.4.4 Particle size distribution

Contaminants are often associated with the fine particles of sediments due to an exponential increase in specific surface area with decreasing grain size and an increase in surface charge (Förstner et al. 1982 and Birch and Taylor 2000). As mentioned, organic matter is also often associated with contaminants, and tends to be associated with fine grained particles. This "grain size effect" must be eliminated to allow inter-comparison of results between different sampling sites or with depth within cores. This can be done either by: (a) separation and analysis of only the fine grained (generally taken as silt and clay (<64 μm)) fraction of the sediment or, (b) by analysis of bulk samples followed by the normalisation of results to the either grain size or a chemical proxy for grain size or mineralogy (e.g. Al, Si, Cs, Sc, Li). The first approach does not account for variations in grain size within the fine fraction (i.e. relative amounts of silt and clay), and so normalisation is the recommended approach. Hence, particle size analysis was necessary as part of the sediment quality surveys of the impoundments.

6.5 Sediment analytical methods

6.5.1 Moisture content

Principle:

Moisture content or water content is determined by conventional oven-drying (BS 1377 1990) or microwave oven-drying (Bentley and Carter 1987) of a sample of soil or sediment. The sample is carefully weighed before and after drying, and the difference in weights in relation to the original weight of sample is the moisture content. The microwave oven-drying is unsuitable for sediments containing a high proportion of organic material.

Method:

Percentage moisture content of approximately 50 g wet weight sediment samples was determined by oven-drying at 105°C for 24 hours and cooling in a desiccator, according to BS 1377 (1990). Percentage moisture content (M) was calculated by:

$$M = \frac{W_1 - W_2}{W_1 - W_b} \times 100\%$$

where:

W_1 = weight of beaker and wet sediment sample (g),
W_2 = weight of beaker and dried sediment sample (g), and
W_b = weight of beaker (g).

Dried samples were then gently crushed and homogenised in an agate mortar for use in subsequent analyses and sequential extraction experiments.

6.5.2 Loss on ignition

Principle:

Loss on ignition (LOI%) is determined by heating a sample of soil or sediment (that has previously been dried at 105°C) in a furnace to burn off any organic matter. The sample is carefully weighed before and after ignition, and the difference in weights in relation to the original weight of sample is the LOI. The temperature and timing of ignition can vary (Ball 1964). LOI% is not necessarily a true representation of the organic C content of a soil since weight loss can also occur due to loss of CO_2 from carbonates, and loss of structural water from clays.

Method:

Percentage loss on ignition was determined from preweighed 2-3 g subsamples of sediment, which had previously been dried at 105°C and homogenised. Samples were held at 900°C for at least 10 hours (overnight), before cooling in a dessicator and weighing to 4 decimal places on a Mettler AJ100 electronic balance. LOI% was calculated by:

$$LOI\% = \frac{W_1 - W_2}{W_1 - W_c} \times 100\%$$

where:

W_1 = weight of crucible and sediment sample prior to ignition (g),
W_2 = weight of crucible and sediment sample following ignition (g), and
W_c = weight of crucible (g).

6.5.3 Organic carbon

Principle:

Organic carbon can be estimated by LOI% or determined by methods involving wet or dry oxidation of organic matter. Dry oxidation techniques generally involve measurement of liberated CO_2 by infrared CO_2 spectrometry or gas chromatography. Modern CHNS analysers allow simultaneous determination of C, H, N and S in organic material. Wet oxidation techniques determine by titration the amount of dichromate which reacts with organic matter in a strongly acid solution.

Method:

Organic carbon content of the sediments was determined by the modified Walkley-Black (1934) titration method of Gaudette et al (1974). This is based on oxidation of organic material in the sediment by 1 N (0.167 M) $K_2Cr_2O_7$ and concentrated H_2SO_4, and the titration of excess $K_2Cr_2O_7$ with 0.5 N (0.5 M) $Fe(NH_4)_2(SO_4)_2$ with diphenylamine indicator to a sharp 1 drop end-point.

Approximately 0.25 g sediment samples which had previously been dried at 105°C and homogenised were used, together with 10 ml of $K_2Cr_2O_7$. A standardisation blank was run with each new batch of samples. % organic carbon (C) was calculated by:

$$C = 0.03 \times \left(1 - \frac{T}{S}\right) \times \left(\frac{100}{W}\right)$$

where:

W = weight of sediment sample (g),

T = sample titration volume (ml 0.5 M $Fe(NH_4)_2(SO_4)_2$), and

S = blank titration volume (ml 0.5 M $Fe(NH_4)_2(SO_4)_2$).

6.5.4 Particle size distribution

Principle:

Particle size distributions (PSD) can be determined by sieving, by sedimentation or by laser diffraction. PSD information is usually given as the % by weight or volume of material finer than defined diameters. Initial PSD determinations in this study were carried out by a combination sieving and sedimentation analysis. The majority of PSD analyses were carried out by laser diffraction.

Sieving may be used to determine the PSD down to fine sand size, and is carried out by passing sediment through a stack of sieves of descending size order, and weighing the material retained at each diameter. Dry sieving may be used for coarse grained material, but wet sieving (with a dispersant) is more accurate for materials containing any clay fraction. Sedimentation analysis is carried out on particles finer than 63 μm (i.e. the silt and clay fraction of a sediment), and is based on the velocity of settling of spherical particles in a suspension (Stokes' law): larger particles settle more rapidly. Samples from a settling suspension of material removed by pipette at a defined depth and time represent a specific particle size fraction, with the PSD being determined by the weight of the residues. Alternatively, the sedimentation can be followed by measuring the change in specific gravity of the suspension over time using a hydrometer.

The traditional methods of PSD determination of sieving and suspension are time-consuming. Modern instrumentation uses diffraction to allow much more rapid PSD analysis. When a particle is placed in a laser beam, light is diffracted by the particle over a pattern of angles and intensities (Fraunhofer diffraction pattern) which is specific to the particle size. The scattering pattern due to the diffraction from an ensemble of particles can be measured by an array of detectors and interpreted to a PSD (given in terms of volume of material). Diffraction data can determine PSD from around 2000 μm to 0.4 μm. Analysis of particles smaller than 0.4 μm is carried out by some machines based on the interaction of very small particles with polarised light of wavelength greater than the diameter of the particles.

Sieving method:

The dry sieving test described in BS 1377 (1990) was used. Test sieves were of 1800, 1200, 710, 420, 300, 150 and 63 μm. Approximately 500 g of oven dried and gently crushed and homogenised sediment were poured into the largest size sieve, and mechanically shaken for at least 10 minutes. Retained masses were weighed in g to 1 decimal place. The material passing the 63 μm sieve was retained for subsequent sedimentation analysis.

Sedimentation method:

The standard method described in BS 1377 (1990) was used. Samples had previously been oven dried and crushed and homogenised, and were pretreated with hydrogen peroxide according to BS 1377 to digest organic material. Removal of portions of suspension by pipette at 10cm depth were carried out at 4 minutes 10 seconds, 47 minutes 30 seconds, and 7 hours 7 minutes after the start of the sedimentations, equivalent to particle diameters of 20, 6 and 2 μm. Sodium hexametaphosphate (2%) solution was used as a dispersant.

Laser diffraction method:

The majority of PSD analyses were carried out using a Coulter® LS 230 laser granulometer. This uses both diffraction and PIDS (Polarisation Intensity Differential of Scattered light) to give a 116 channel PSD from 0.04 μm to 2000 μm. Calgon (sodium hexametaphosphate with sodium bicarbonate) solution was used as the dispersant. Approximately 0.3 - 0.5 g of sample was used dependent on the clay fraction of the sediment (in order to maintain a PIDS obscuration of 40-60%). Obscuration of the diffraction optics was generally around 20%. Sediment samples had previously undergone drying at 105°C and crushing and homogenisation, but no other pretreatment (i.e. no removal of organic material). Samples were left in 20 ml of Milli-Q® 18 MΩ.cm water plus 2 ml dispersant solution overnight, followed by sonification in a sonic bath for 15 minutes prior to introduction to the sampling module. A variable speed fluid module was used (Coulter® 1994).

6.6 Sequential extractions

Analytical grade reagents and 18 MΩ.cm ultra-high purity water were used in all the laboratory work described. Equipment was acid and Decon 90® (non-ionic surfactant) washed (soaked overnight in 1% HNO_3, followed by overnight soaking in 5% Decon 90® and rinsed in de-ionised water). Prior to chemical extraction, loss on ignition (LOI), and particle size distribution (PSD) analysis, sediment samples were dried at 105°C overnight, and carefully crushed and homogenised in an agate mortar. Since all sediment samples analysed contained no particulate fraction >2mm in diameter (i.e. all particles were sand sized or finer (Craig 1992)) no sieving was deemed necessary. Dried and crushed samples were stored at room temperature in polythene bags for a maximum of 2 weeks prior to analyses or extractions.

6.6.1 Sequential extraction method (after Tessier et al., 1979)

Sediment extractions were carried out using a methodology based on the sequential extraction procedure of Tessier et al. (1979). Due to safety and equipment issues, the methodology used excluded the final (5th) step of the Tessier scheme, which uses 5:1 $HF:HClO_4$ to digest the silicate lattices in the residual minerals remaining after the previous 4 extraction stages. Under normal environmental conditions this breakdown of minerals never occurs, and the metals contained within lattice positions are not bioavailable or released to the water column. The second significant modification to the Tessier procedure was that the supernatants from the wash steps between extraction stages were retained for analysis in this study, whereas in the original procedure they are discarded. It was felt that discarding the wash solution could result in an underestimation of the metal concentrations. For the initial (exchangeables) extraction step the Tessier method gives the choice of using either NaOAc or $MgCl_2$ as the reagent. For this work it was decided to use NaOAc to allow analysis of Mg from the sediments.

Initial extractions were carried out in borosilicate glassware, and with vacuum filtration on standard Whatman® Cellulose Nitrate Membrane Filters of 0.45 μm pore diameter between extraction stages and washes. The retained material on the filters was rinsed off for use in the subsequent stage following each filtration, with the weight change in the filters being used to calculate the weight of sediment used at the start of each step. Due to concerns about the preferential loss of fine sediment on the filters, and to improve time efficiency, the majority of sequential extractions were carried out using centrifuging between each extraction and wash stage. These sequential extractions were carried out in polyethylene sample bottles, which posed less risk of loss of elements (particularly P) by adsorption to container surfaces than glassware.

The sequence used for the Tessier centrifugation method follows (the sequence for the initial (filtration) method was exactly the same but with vacuum filtration at the steps where centrifuging is noted):

Stage 1 (exchangeable or loosely sorbed)

1. 2.500 ± 0.001 g dry weight of sediment was transferred using a stainless steel spatula into a 60 ml polyethylene sample bottle.
2. 20ml 1M NaOAc was added to the sample.
3. The sample was agitated for 1 hour at room temperature on a shaker table.
4. The sample was centrifuged at 4000 rpm for 30 min.
5. The supernatant was decanted to a 30 ml polystyrene specimen container (all extracts and washes were acidified to < pH 2 by adding 0.1 ml of HNO_3, and stored in at 4°C for a maximum of 2 months prior to analysis by ICP-OES or ICP-MS).
6. 20 ml H_2O was added as a wash to the residual sample and agitated briefly.
7. The sample was centrifuged at 4000 rpm for 30 min.
8. The wash supernatant was decanted to a 30 ml polystyrene specimen container.

Stage 2 (carbonate bound)

1. 20 ml 1 M NaOAc buffered to pH 5 with acetic acid was added to the residual sample from Stage 1.
2. The sample was agitated for 5 hours at room temperature on a shaker table.
3. The sample was centrifuged at 4000 rpm for 30 min.
4. The supernatant was decanted to a 30 ml polystyrene specimen container.
5. 20 ml H_2O was added as a wash to the residual sample and agitated briefly.
6. The sample was centrifuged at 4000 rpm for 30 min.
7. The wash supernatant was decanted to a 30 ml polystyrene specimen container.

Stage 3 (Fe and Mn bound)

1. 20 ml of a solution of 0.3 M $Na_2S_2O_4$, 0.175 M Na-citrate and 0.025 M citric acid was added to the residual sample from Stage 2.
2. The sample was agitated for 8 hours at room temperature on a shaker table.
3. The sample was centrifuged at 4000 rpm for 30 min.
4. The supernatant was decanted to a 30 ml polystyrene specimen container.
5. 20 ml H_2O was added as a wash to the residual sample and agitated briefly.
6. The sample was centrifuged at 4000 rpm for 30 min.
7. The wash supernatant was decanted to a 30 ml polystyrene specimen container.

Stage 4 (organically bound)

1. 7.5 ml 0.02 M HNO_3 then 12.5 ml 30% H_2O_2 (adjusted to pH 2 with HNO_3) was added to the residual sample from Stage 3.
2. The sample was left for 2 hours at 85°C with occasional agitation.
3. A further 7.5 ml aliquot of H_2O_2 (pH 2) was added.
4. The sample was left for a further 3 hours at 85°C with occasional agitation.
5. The sample was centrifuged at 4000 rpm for 30 min.
6. The supernatant was decanted to a 30 ml polystyrene specimen container.
9. 20 ml H_2O was added as a wash to the residual sample and agitated briefly.
10. The sample was centrifuged at 4000 rpm for 30 min.
11. The wash supernatant was decanted to a 30 ml polystyrene specimen container.

Reagent blanks were taken in duplicate from each batch of each reagent, with the group of extractions corresponding to each batch being noted. The mean concentration values of the appropriate blanks were subtracted from the corresponding extractants' values. Elemental concentrations are reported as mg/kg of dry sediment.

6.6.2 SEDEX method (after Ruttenburg, 1992)

A selection of sediment samples underwent sequential extraction by the SEDEX method of Ruttenberg (1992) in addition to the Tessier method, to allow comparision of the selectivity for the elemental phases (particularly P) of each. The SEDEX work was completed prior to the purchase of a centrifuge, and was therefore carried out in acid washed borosilicate glassware with vacuum filtration on standard Whatman® Cellulose Nitrate Membrane Filters of 0.45 μm pore diameter between extraction phases and washes.

0.500 ± 0.001 g dry weight of sediment was used. Extractant volumes were 50 ml except in stage 2 where it was 45 ml citrate bicarbonate + 1.125 g of $Na_2S_2O_4$. Extraction by the principal extractants is followed by successive $MgCl_2$ washes which desorb any secondarily adsorbed elements. Agitation was provided at each step by a shaker table. Extraction steps were carried out at British room temperature (20°C) in a temperature controlled laboratory, as opposed to the American room temperature (25°C) defined by Ruttenberg.

The sequence used for the SEDEX extraction method follows:

Stage 1 (exchangeable or loosely sorbed)

1. 0.500 ± 0.001 g dry weight of sediment was transferred using a stainless steel spatula to a 100 ml conical flask.
2. 50 ml 1 M $MgCl_2$ was added to the sample.
3. The sample was agitated for 2 hours at room temperature on a shaker table.
4. The sample was vacuum filtered.
5. The filtrate was transferred to a 30 ml polystyrene specimen container (all extracts and washes were acidified to $<$ pH 2 by adding 0.1 ml of HNO_3, and stored in at 4°C for a maximum of 2 months prior to analysis by ICP-OES or ICP-MS).
6. The residue was washed from the filter with 50 ml 1 M $MgCl_2$ into a 100 ml conical flask.
7. The sample was agitated for 2 hours at room temperature on a shaker table.
8. The sample was vacuum filtered.
9. The filtrate was transferred to a 30 ml polystyrene specimen container.
10. The residue was washed from the filter with 50 ml H_2O into a 100 ml conical flask.
11. The sample was agitated for 2 hours at room temperature on a shaker table.
12. The sample was vacuum filtered.
13. The filtrate was transferred to a 30 ml polystyrene specimen container.
14. The residue was washed from the filter with 50 ml H_2O into a 100 ml conical flask.
15. The sample was agitated for 2 hours at room temperature on a shaker table.
16. The sample was vacuum filtered.
17. The filtrate was transferred to a 30 ml polystyrene specimen container.

Stage 2 (Fe and Mn bound)

1. The residue from Stage 1 was washed from the filter with 45 ml (0.30 M Na_3-citrate 1.0 M $NaHCO_3$) into a 100 ml conical flask and 1.125g $Na_2S_2O_4$ was added.
2. The sample was agitated for 8 hours at room temperature on a shaker table.
3. The sample was vacuum filtered.
4. The filtrate was transferred to a 30 ml polystyrene specimen container.

5. The residue was washed from the filter with 50 ml 1 M $MgCl_2$ into a 100 ml conical flask.
6. The sample was agitated for 2 hours at room temperature on a shaker table.
7. The sample was vacuum filtered.
8. The filtrate was transferred to a 30 ml polystyrene specimen container.
9. The residue was washed from the filter with 50 ml H_2O into a 100 ml conical flask.
10. The sample was agitated for 2 hours at room temperature on a shaker table.
11. The sample was vacuum filtered.
12. The filtrate was transferred to a 30 ml polystyrene specimen container.

Stage 3 (carbonate bound (+ P in authigenic and biogenic apatite))

1. The residue from Stage 2 was washed from the filter with 50 ml 1 M NaOAc buffered to pH 4 with acetic acid into a 100 ml conical flask.
2. The sample was agitated for 6 hours at room temperature on a shaker table.
3. The sample was vacuum filtered.
4. The filtrate was transferred to a 30 ml polystyrene specimen container.
5. The residue was washed from the filter with 50 ml 1 M $MgCl_2$ into a 100 ml conical flask.
6. The sample was agitated for 2 hours at room temperature on a shaker table.
7. The sample was vacuum filtered.
8. The filtrate was transferred to a 30 ml polystyrene specimen container.
9. The residue was washed from the filter with 50 ml 1 M $MgCl_2$ into a 100 ml conical flask.
10. The sample was agitated for 2 hours at room temperature on a shaker table.
11. The sample was vacuum filtered.
12. The filtrate was transferred to a 30 ml polystyrene specimen container.
13. The residue was washed from the filter with 50 ml H_2O into a 100 ml conical flask.
14. The sample was agitated for 2 hours at room temperature on a shaker table.
15. The sample was vacuum filtered.
16. The filtrate was transferred to a 30 ml polystyrene specimen container.

Stage 4 (P as detrital apatite)

1. The residue from Stage 3 was washed from the filter with 50 ml 1 M HCl into a 100 ml conical flask.
2. The sample was agitated for 16 hours at room temperature on a shaker table.
3. The sample was vacuum filtered.
4. The filtrate was transferred to a 30 ml polystyrene specimen container.

Stage 5 (organically bound)

1. The residue from Stage 4 was transferred to a crucible.
2. The sample was ashed at 550°C.
3. The residue was washed from the crucible with 50 ml 1 M HCl into a 100 ml conical flask.
4. The sample was agitated for 16 hours at room temperature on a shaker table.
5. The sample was vacuum filtered.
6. The filtrate was transferred to a 30 ml polystyrene specimen container.

Process blanks were carried out in duplicate for each stage. The mean concentration values of the appropriate blanks were subtracted from the corresponding extractants' values. Elemental concentrations are reported as mg/kg of dry sediment.

6.6.3 ICP-OES analysis of extracts

The extracts produced by each of the stages of both the sequential extraction procedures were analysed by inductively coupled plasma – optical emission spectrometry (ICP-OES). The same methodology and standards were used as described in chapter 2 for analysis of metals within brackish and saline water samples (section 2.4.10). Y was used as an internal standard to correct for suppression of signal due to the high ionic strength of the extracts. A total of 17 elements were analysed for. Data were collected for Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Sc, Si, Ti and Zn. Sn and V were at levels below the analytical LOD. P was unable to be measured in stage 4 extracts due to analytical problems.

6.7 Results and discussion

Sediment quality data are presented for the sediment coring surveys and analyses carried out for the Tees and Wansbeck impoundments. As described in section 6.2, seven cores in total were collected during the sediment sampling. From the Tees one core was collected from site KV and two cores from within 1 m of each other from site TB (cores TB1 and TB2). From the Wansbeck one core was collected from site RB and two cores from within 1 m of each other from site WB (cores WB1 and WB2), with an additional core taken (for which data is not reported in detail) from the emerging island alongside the bridge pier next to RB (site SM).

6.7.1 Errors

Replicate extractions and analyses were carried out for samples taken at 15 cm intervals within each core (i.e. at 1.5, 16.5, 31.5, etc. cm depth in the sediment). Sources of variation in the measurements obtained from these pairs of samples are analytical error, variation in extraction and pre-treatment conditions, and heterogeneity within the samples used. All analytes except Sn and V were recorded at significantly higher levels than their analytical LODs (reported in chapter 2), and analytical errors are considered minor. Appropriate care was taken in carrying out the extraction procedures to ensure repeatability of the processes (procedure outlined in section 6.5). A significant proportion of variation may be due to actual differences between the replicate sediment based on sub-sampling at each depth, and reflect local heterogeneity within the sediment.

The differences between measurements for replicate pairs were calculated as percentages of the mean value for each pair. The means of these percentage differences (from all replicate pairs from all bottom sediment cores) are reported as the error for each analysis (table 6.3). Within profiles the initial replicate analysed is plotted at those depths at which replicates were taken.

Parameter	**Extraction stage 1**	**Extraction stage 2**	**Extraction stage 3**	**Extraction stage 4**
Sand	11.4	11.4	11.4	11.4
Silt	2.0	2.0	2.0	2.0
Clay	10.7	10.7	10.7	10.7
Organic matter	0.8	0.8	0.8	0.8
Al	44.8 *(16)*	3.3 *(44)*	4.0 *(791)*	21.5 *(511)*
Ca	1.7 *(3323)*	1.2 *(4548)*	2.0 *(1166)*	10.2 *(736)*
Co	13.8 *(0)*	2.2 *(1.4)*	3.5 *(2)*	44.8 *(1)*
Cr	34.3 *(0)*	4.5 *(1)*	3.7 *(8)*	3.7 *(21)*
Cu	9.1 *(1)*	3.5 *(1)*	47.3 *(12)*	21.4 *(10)*
Fe	25.0 *(37)*	2.5 *(406)*	4.5 *(11976)*	25.4 *(3163)*
K	2.1 *(873)*	1.8 *(156)*	7.1 *(55)*	6.1 *(64)*
Mg	2.1 *(1645)*	2.4 *(856)*	3.9 *(364)*	7.5 *(843)*
Mn	2.3 *(61)*	1.4 *(181)*	3.8 *(106)*	12.7 *(59)*
Ni	11.0 *(0)*	3.8 *(1.6)*	3.1 *(4.8)*	18.1 *(3)*
P	4.0 *(21)*	3.2 *(20.1)*	2.0 *(640)*	-
Sc	183.0 *(0)*	5.4 *(0)*	5.0 *(4)*	49.8 *(0)*
Si	19.4 *(57)*	1.7 *(195)*	3.7 *(407)*	7.4 *(540)*
Ti	164.8 *(0)*	100.3 *(0.1)*	4.7 *(14.4)*	37.8 *(1)*
Zn	11.0 *(3)*	1.6 *(61.4)*	3.6 *(71)*	27.5 *(15)*

Table 6.3. Mean % variation between replicate samples for each of the sequential extraction stages. Mean concentrations (mg/kg) for all samples from each extraction stage are given in italics.

6.7.2 Particle size distribution

Tees

The grain size distributions in terms of % volume of sand, silt and clay with depth for each of the cores collected in the Tees impoundment are presented in figures 6.1, 6.2 and 6.3. All three cores collected in the Tees impoundment show relatively consistent grain size distribution with depth in the sediment, and similar mean proportions of sand (63 – 2000 μm), silt (2 - 63 μm) and clay (< 2 μm) fractions (table 6.4).

Particle size	Core	Mean	Median	StDev
% sand	KV	26	24	10
% sand	TB1	24	12	26
% sand	TB2	23	25	7
% silt	KV	66	68	9
% silt	TB1	61	70	21
% silt	TB2	68	68	6
% clay	KV	8	8	1
% clay	TB1	15	15	6
% clay	TB2	9	8	3

Table 6.4. Basic statistics for particle size in cores collected within the Tees impoundment. Similar mean particle sizes for the cores suggests a similar pattern of deposition within the lower impoundment. The greater standard deviation for all particle size fractions TB1 relates to sampling of pre-impoundment sediment in this core.

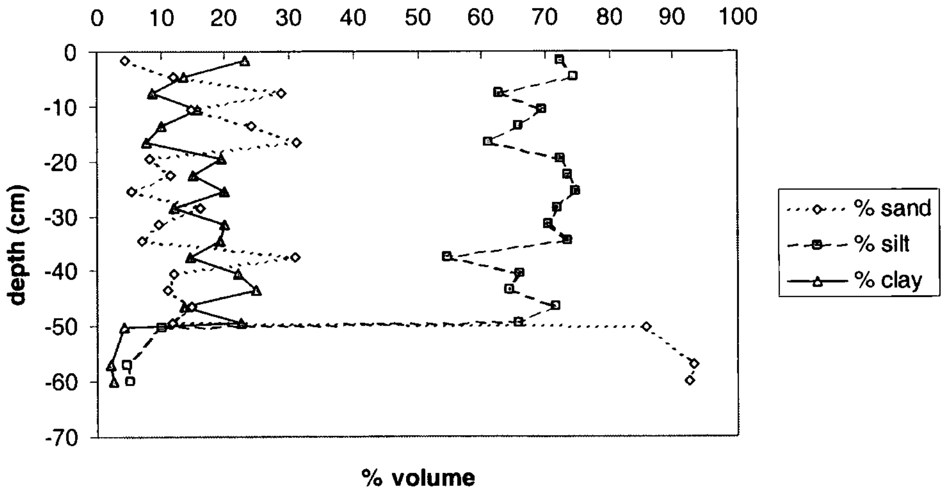


Figure 6.1. Particle size distribution with depth in the sediment for core TB1.

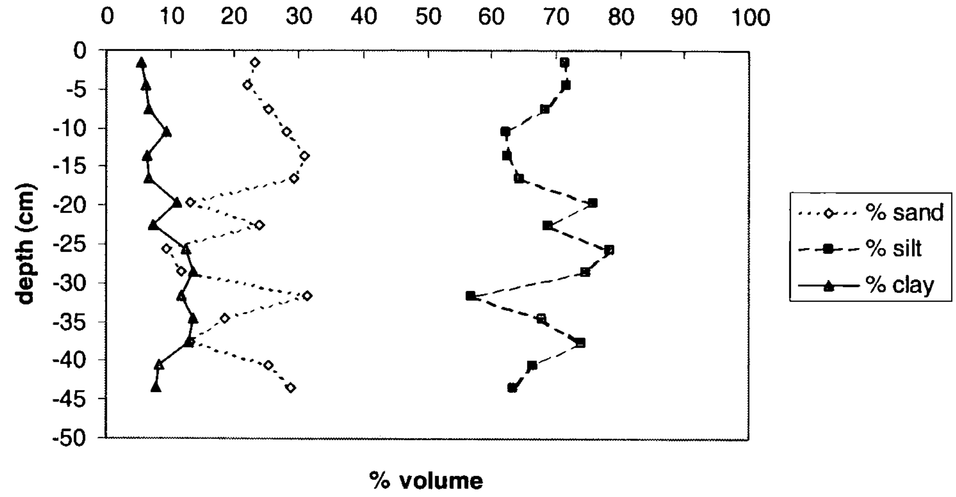


Figure 6.2. Particle size distribution with depth in the sediment for core TB2.

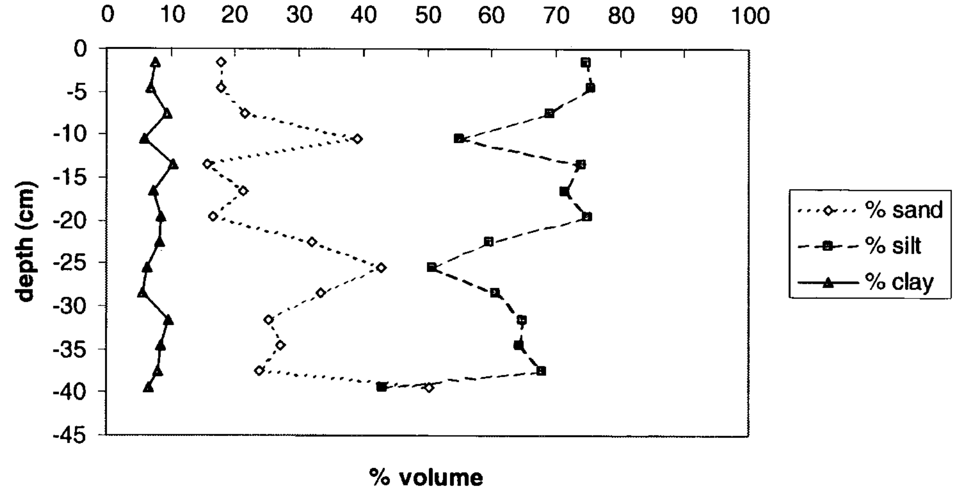


Figure 6.3. Particle size distribution with depth in the sediment for core KV.

The sediment in the lower impoundment of the Tees is dominated by silt-sized particles, with all three cores composed mainly of silt throughout their lengths. Sand-sized material makes up approximately a quarter of the volume of the sediment, and the clay fraction generally less than 10 %. No material of grain size coarser than sand (> 2 mm) was collected in any of the core samples taken. The sediment is somewhat coarser than that reported downstream of the Tees barrage (median silt and clay content of 62 and 24 % respectively (Jones and Turki 1997) or > 95 % clay + silt (Shillabeer and Tapp 1990)), which probably relates to a lack of salinity induced flocculation and subsequent settling of clay-sized particles within the impoundment.

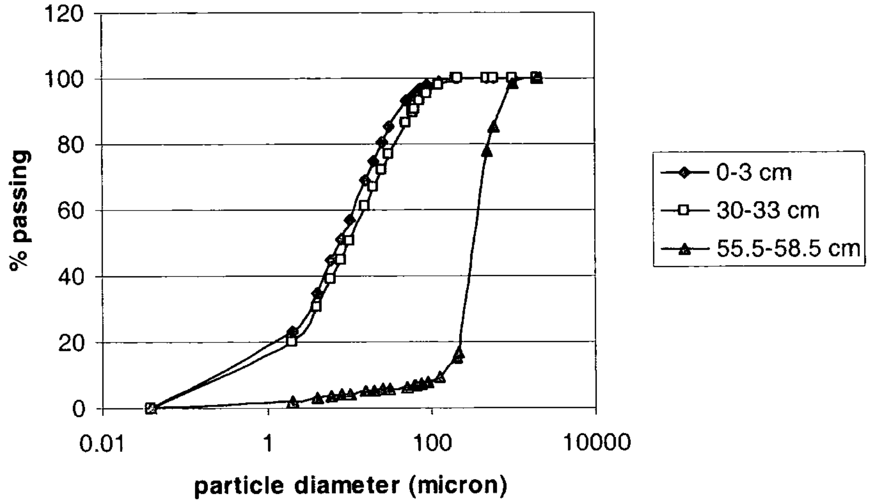


Figure 6.4. Particle size distribution curves for selected depths of sediment from core TB1, showing contrast in sedimentation between pre and post-impoundment of the Tees estuary.

No trend in fining or coarsening upwards can be seen in the bottom sediment of the lower Tees impoundment, but sequences of coarser and finer material are present. It is likely that these relate to periods of high and low river flow (and coarser and finer sediment supply), and may follow an approximately annual cycle, although without sediment dating this is difficult to confirm. Without dating of sediment it is also difficult to determine rates of sedimentation within the impoundment, however the sharp contrast between sand dominated sediment below and silt and clay dominated sediment above 50 cm depth is interpreted as representing the change in sedimentological regime on impoundment of the estuary. On this basis net sediment deposition at this site in the impoundment has been approximately 7 cm/annum (50 cm in 7 years). Detailed determination of sediment supply and flux, and modelling of patterns of deposition are specific tasks of the SIMBA project (Beavers, 2003).

Wansbeck

The grain size distributions in terms of % volume of sand, silt and clay with depth for each of the cores collected in the Wansbeck impoundment are presented in figures 6.5, 6.6, 6.7 and 6.8. The two bottom sediment cores collected at site WB in the Wansbeck impoundment show relatively consistent grain size distribution with depth in the sediment, and similar mean proportions of sand, silt and clay fractions (table 6.5). Core RB is of similar particle size distribution to sediment from WB but shows a possible coarsening upwards. The core taken from the emergent sand bar (core SM) also shows a possible coarsening upwards, and is generally of coarser material than the bottom sediment.

Particle size	Core	Mean	Median	StDev
% sand	RB	37	38	8
% sand	WB1	38	38	7
% sand	WB2	30	29	7
% sand	SM	66	66	8
% silt	RB	56	55	6
% silt	WB1	57	57	6
% silt	WB2	62	62	6
% silt	SM	31	31	7
% clay	RB	7	6	3
% clay	WB1	5	5	2
% clay	WB2	8	8	2
% clay	SM	4	3	1

Table 6.5. Basic statistics for particle size in cores collected within the Wansbeck impoundment. Cores RB, WB1 and WB2 are from bottom sediment and core SM is from an exposed sand bar.

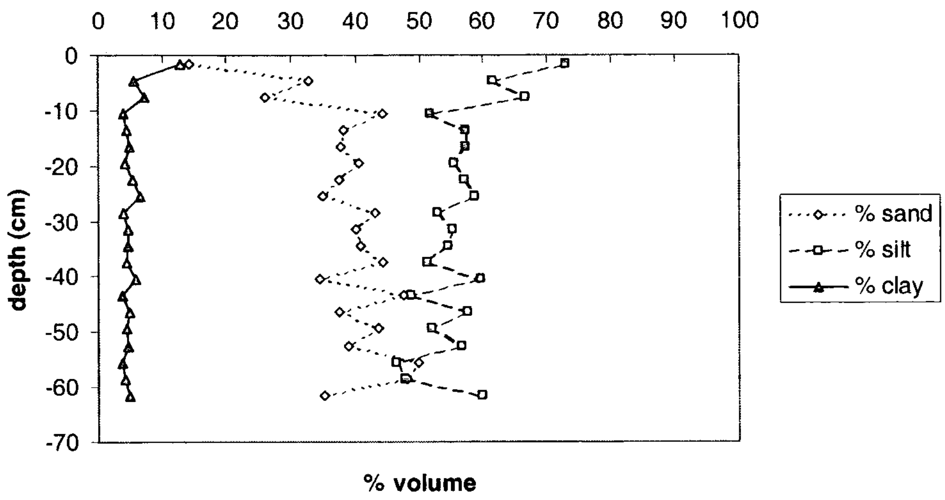


Figure 6.5. Particle size distribution with depth in the sediment for core WB1.

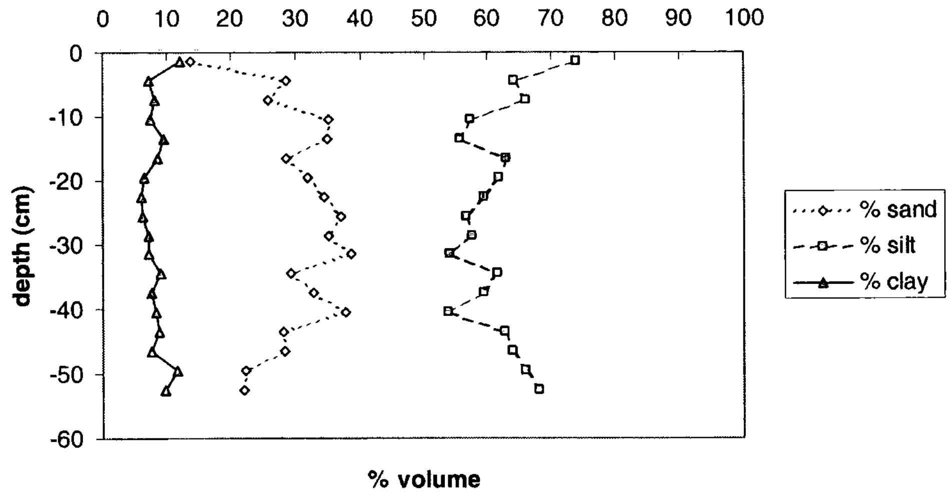


Figure 6.6. Particle size distribution with depth in the sediment for core WB2.

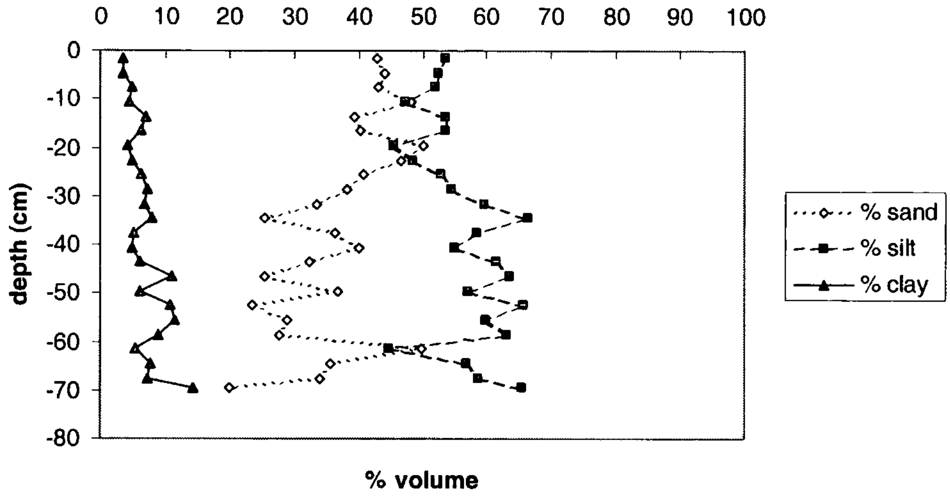


Figure 6.7. Particle size distribution with depth in the sediment for core RB.

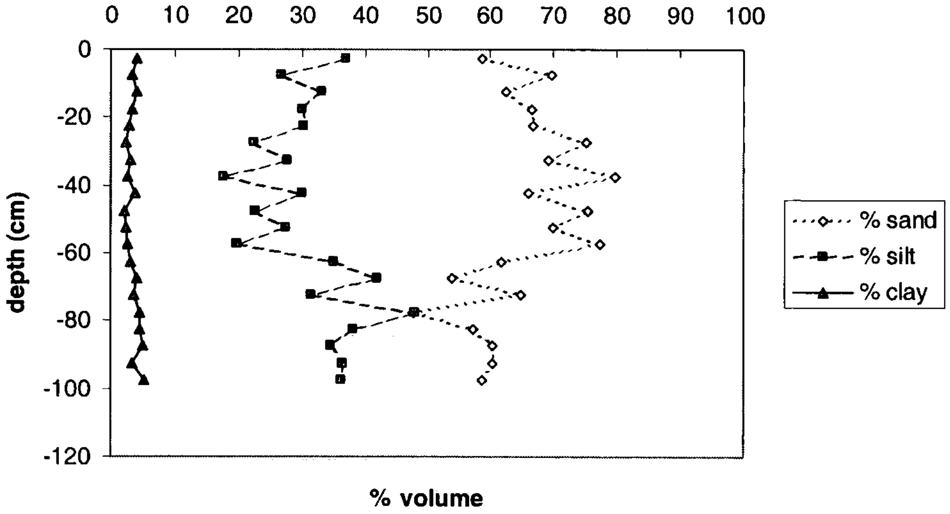


Figure 6.8. Particle size distribution with depth in the sediment for core SM.

The bottom sediment of the Wansbeck impoundment is all sand-sized and finer (< 2 mm diameter), and is predominantly of the silt-sized fraction. The bottom sediment in the Wansbeck is generally slightly coarser than that in the lower Tees impoundment, with lower sand and greater silt and clay fractions. The sediment making up the exposed sand bar from which core SM was taken is predominantly sand-sized. As suggested for the Tees, the variance in particle size with depth in the Wansbeck may relate to high flow (coarser material) and low flow (finer grained material) events.

Unlike sampling within the Tees, no distinct changes in sediment grain-size with depth were observed in the Wansbeck and it is assumed that the pre-impoundment sediment surface was not encountered. This means that no rate of sediment accumulation may be suggested for the Wansbeck impoundment, and it is therefore recommended that any future sediment sampling within the impoundments includes dating (by measurement of the vertical distribution of ^{210}Pb and ^{210}Po (Goldberg 1963) or ^{137}Cs).

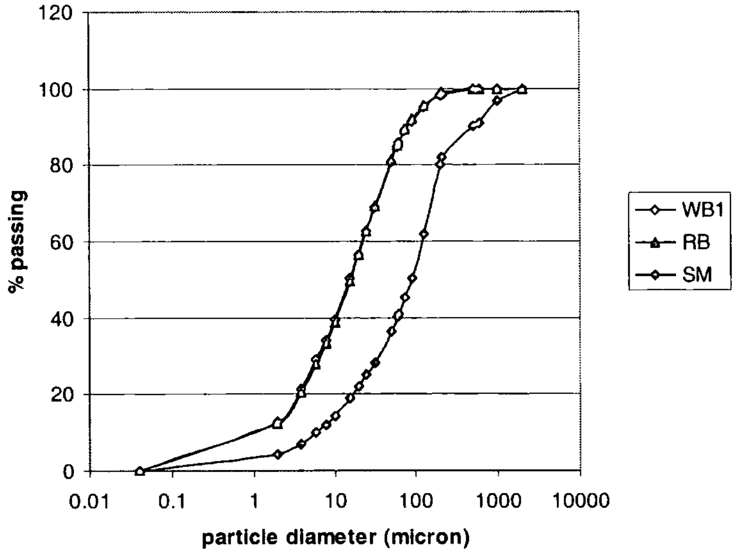


Figure 6.9. Particle size distribution curves for surficial component of the bottom sediment (WB1 and RB) and emergent sand bar (SM) of the Wansbeck impoundment.

The difference in particle size distributions between the impoundments may relate to both the nature of the sediment supply and the depositional environment. The length of river affected by impoundment is shorter in the Wansbeck meaning that the sampling sites are more proximal to the riverine sediment inputs. In addition, the Wansbeck impoundment is shallower (in part due to more mature sediment fill) and, hence, the scouring effects of river flow is greater. Both these effects are likely to be significant in causing the sediment of the Wansbeck to be coarser grained than that of the Tees. The coarsening upwards in cores RB and SM may be due to a decrease in deposition of finer sediment as water depth decreased at these sites, although the lack of a general coarsening upwards sequence implies that there remains capacity for sediment deposition within the Wansbeck to date.

Impoundment	% sand	% silt	% clay	% organic
Tees	24	65	11	17
Wansbeck	35	58	7	22

Table 6.6. Mean % grain-size fractions and % organic matter for bottom sediment cores from the Tees and Wansbeck impoundments.

6.7.3 Organic matter

Organic matter contents of the sediment were determined as loss on ignitions (LOI) for all samples. Organic carbon was determined through dichromate oxidations for 32 samples to check that LOI could be taken as an appropriate measure of organic content. As shown in figure 6.10, there is a strong relationship ($r^2 = 89.4$ %, $n = 32$) between the two methods of organic determination:

$$\text{LOI } \% = 3.78 \text{ organic carbon}$$

This conversion value between organic carbon and organic matter content is higher than that of 1.72 typically used (SSSA 1996), although several studies (e.g. Broadbent 1953) have suggested that this conversion factor is too low for high organic sediments since dichromate oxidation does not breakdown all organic components. In addition LOI techniques tend to overestimate organic matter contents through loss of structural water from hydrated aluminosilicates (particularly from clay lattices) and breakdown of carbonates (a significant component of the Tees and Wansbeck sediments). The organic matter contents reported are therefore likely to give good, if somewhat slightly too high, representations of the organic material in the sediment samples.

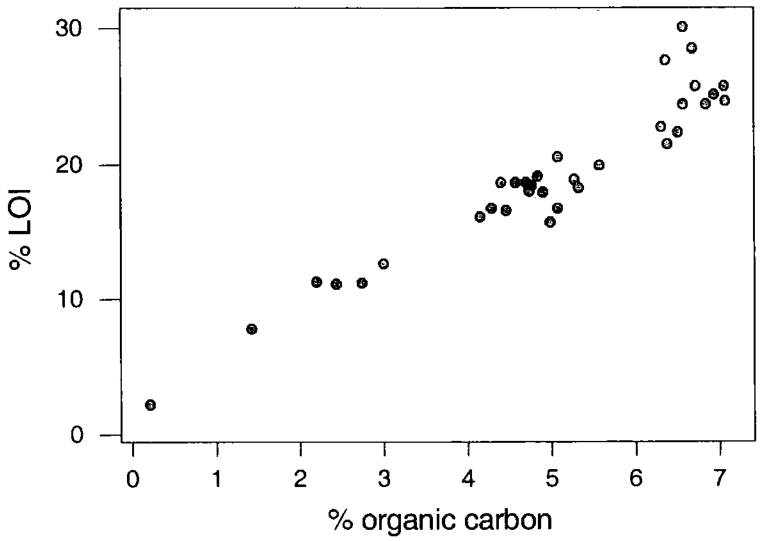


Figure 6.10. The relationship between % loss on ignition at 900°C and % organic carbon determined by dichromate oxidation for a selection of samples representing all cores collected. Organic matter contents determined by LOI are approximately 3.8 times those determined by wet oxidation.

Tees

The mean organic matter content within the lower Tees impoundment sediment is 17.5 %. The mean organic carbon content is 4.5 %. This value is comparable with the median value of 5.36 % organic carbon given by Jones and Turki (1997) for Tees estuary sediment downstream of the barrage. Organic content shows no trends with depth but a large scatter (figure 6.11), assumed to relate to variation in input of organic particulates (either allochthonous or autochthonous). Organic matter is associated with the silt-sized fraction of the sediment in the Tees (figure 6.12), and shows an inverse relationship with sand content. The proportion of organic matter (as with the silt-sized fraction) in the sediment increased dramatically on the impoundment of the estuary (from < 5 to > 15 %).

Core	Mean	Median	StDev
TB1	16.6	18.4	5.7
TB2	18.2	18.6	2.9
KV	17.9	17.9	4.4

Table 6.7. Basic statistics for % organic matter content in cores collected within the Tees impoundment.

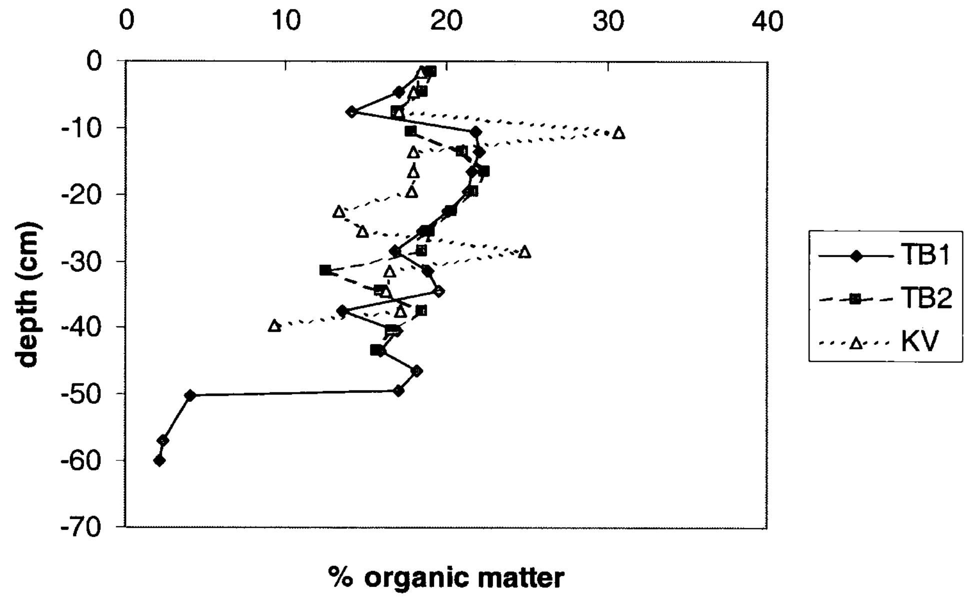


Figure 6.11. Organic matter profiles for the sediment cores taken from the Tees impoundment. Organic matter as % LOI at 900°C. A sharp increase in organic matter content occurred on impoundment of the estuary (at 50 cm depth within the sediment core TB1).

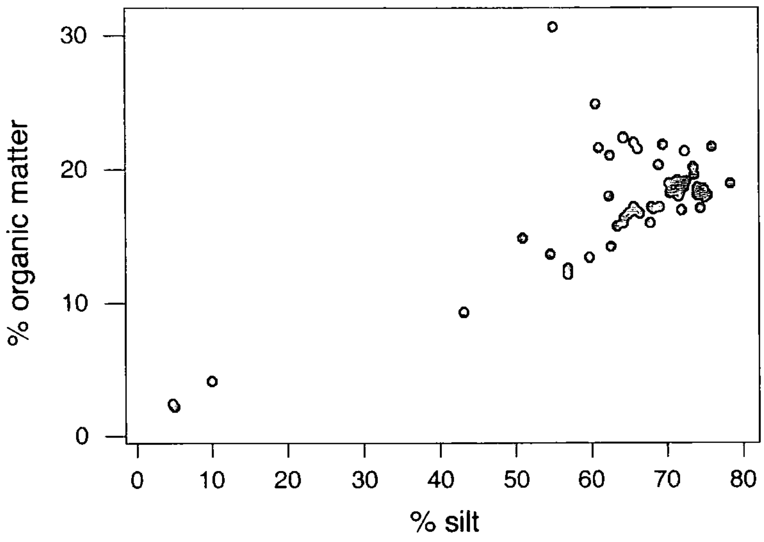


Figure 6.12. The relationship between organic matter and silt content in bottom sediment of the lower Tees impoundment.

Wansbeck

The bottom sediment (all sites cored except SM) of the Wansbeck impoundment is significantly richer in organic material than the lower Tees impoundment (22.3 % compared with 17.5 % organic matter; P = 0.000). This difference may in part be due to greater flocculation of organic material in the saline Wansbeck compared with the freshwater Tees (Sholkovitz 1978), and may in part be due to tidal input of coal waste material from the former mining operations around Ashington (noticeable coal particles of a range of sizes were identified in all cores collected from the Wansbeck). Proximity to the source of this material may explain the higher organic contents of the cores taken immediately behind the barrage compared with those taken further upstream (table 6.8). In addition less oxic conditions in the sediment of the Wansbeck than the Tees are likely to allow better preservation of organic material in this impoundment. No relationship between organic matter content and any particle size parameter is shown for the Wansbeck impoundment sediments. Organic content shows a relatively large amount of scatter but no noticeable trends with depth (figure 6.13).

Core	Mean	Median	StDev
WB1	24.9	24.7	1.7
WB2	25.6	25.6	2.2
RB	17.4	16.7	2.5
SM	11.7	11.1	4.4

Table 6.8. Basic statistics for % organic matter content in cores collected within the Wansbeck impoundment. Cores RB, WB1 and WB2 are from bottom sediment and core SM is from an exposed sand bar.

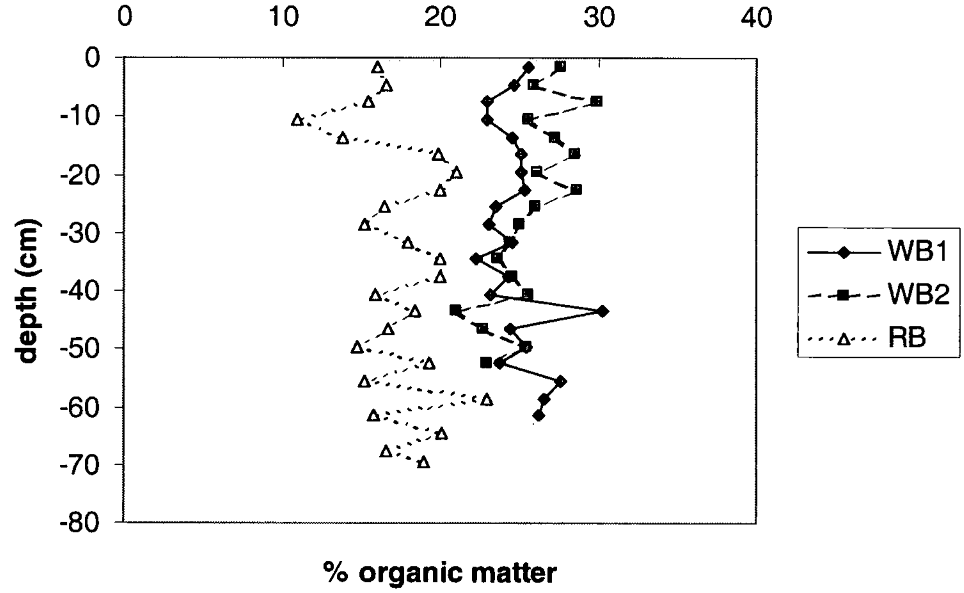


Figure 6.13. Organic matter profiles for the sediment cores taken from the Wansbeck impoundment. Organic matter as % LOI at 900°C.

6.7.4 Metals and non-metals concentration and speciation

Results are presented for both the concentrations and speciations of the metals and non-metals analysed within the bottom sediments of the Tees and Wansbeck impoundments. These elements are Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Sc, Si, Ti and Zn. Results from the sand bar in the Wansbeck (core SM) are not discussed. All results are reported in mg/kg dry weight of sediment and are in raw form (no particle size correction applied). Sn and V were below the analytical LOD within all samples and data are therefore not presented. During the stage 4 extractions vigorous reaction caused material to be lost from 7 of the samples (core KV 21-40 cm) and these data are excluded from the results. In addition no stage 4 extraction data are available for P due to analytical problems during ICP-OES.

6.7.4.1 Al

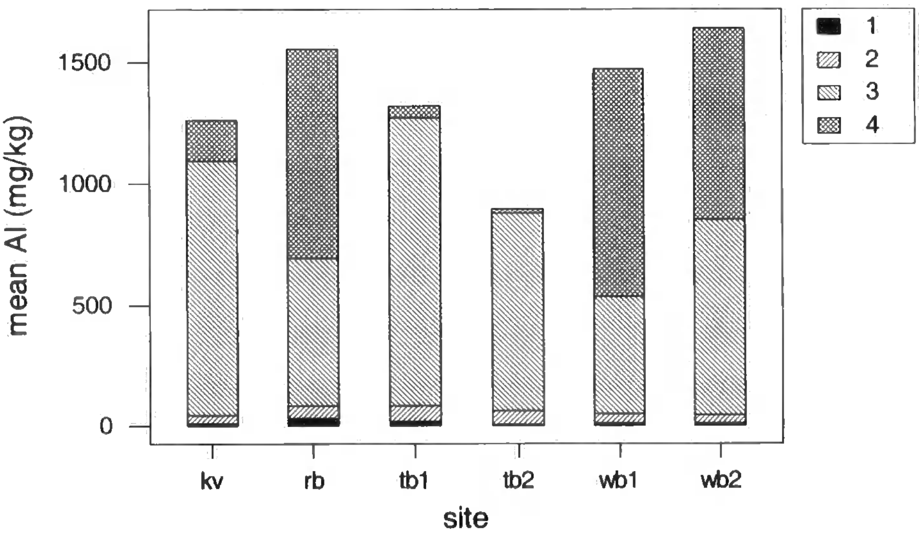


Figure 6.14. Al concentration and speciation within the bottom sediments of the Tees and Wansbeck impoundments. Cores KV, TB1 and TB2 are from the Tees and cores RB, WB1 and WB2 are from the Wansbeck. Stages 1, 2, 3 and 4 of the sequential extraction scheme used represent exchangeable, carbonate bound, Fe and Mn bound and organic bound forms respectively.

Sediment	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Total available**
Tees impoundment	13	53	1031	76	1173
Wansbeck impoundment	18	43	624	861	1547
Organic stream sediment (Finland)					11400

Table 6.9. Average Al concentrations in sediment (mg/kg) from the Tees and Wansbeck impoundments (stage 1 to 4 plus sum of stages of Tessier extraction scheme) and organic stream sediment (concentrated HNO_3 extraction; data from Lahermo et al. 1996).

Total potentially mobile Al levels are similar in the two impoundments but the phases in which it is held differ (table 6.9, figure 6.14). Al is associated with the stage 3 extraction step within the Tees sediments. Within the Wansbeck sediment Al is associated with both the stage 3 and the stage 4 extraction steps. (Stage 3 of the extraction scheme is designated as corresponding with Fe and Mn oxide associated elements, and stage 4 removes organic and sulphide bound elements (Tessier et al. 1979, Kersten and Förstner 1989)). Åström (1998) gives that available (released on oxidation) Al is from 0.2 to 0.8 % of the total Al concentration in sulphide rich sediments.

Profiles for stage 3 and stage 4 extractable Al within the sediments of the Tees and Wansbeck impoundments show no clear trends but a large amount of fluctuation with depth (figures 6.15, 6.16, 6.17 and 6.18). Stage 4 extractable Al shows a possible slight decrease towards the surface of the sediment in the Wansbeck (figure 6.18), and a clear change between pre and post-impoundment sediment in the Tees barrage cores (figure 6.17).

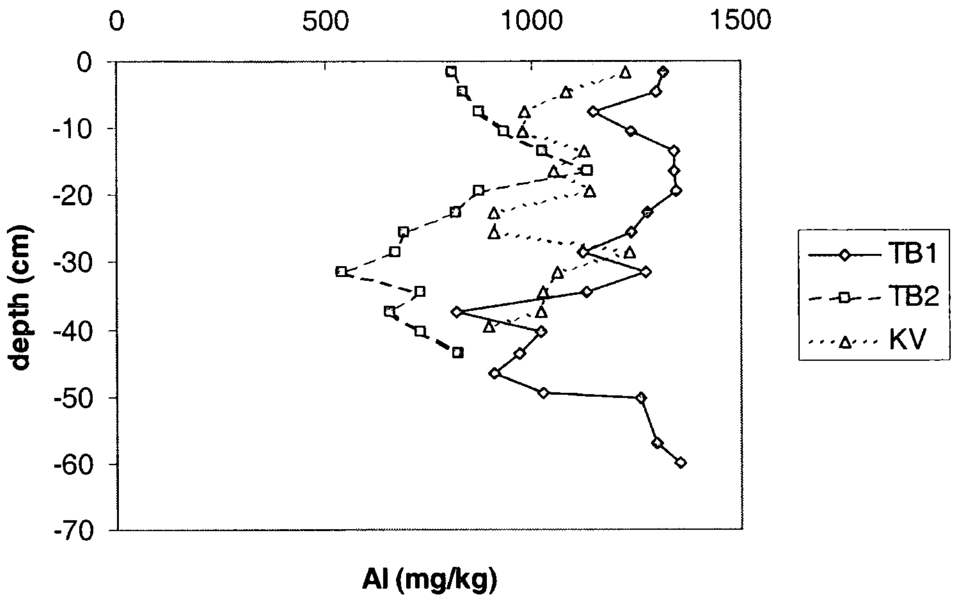


Figure 6.15. Stage 3 extractable Al with depth in cores TB1, TB2 and KV from the Tees impoundment.

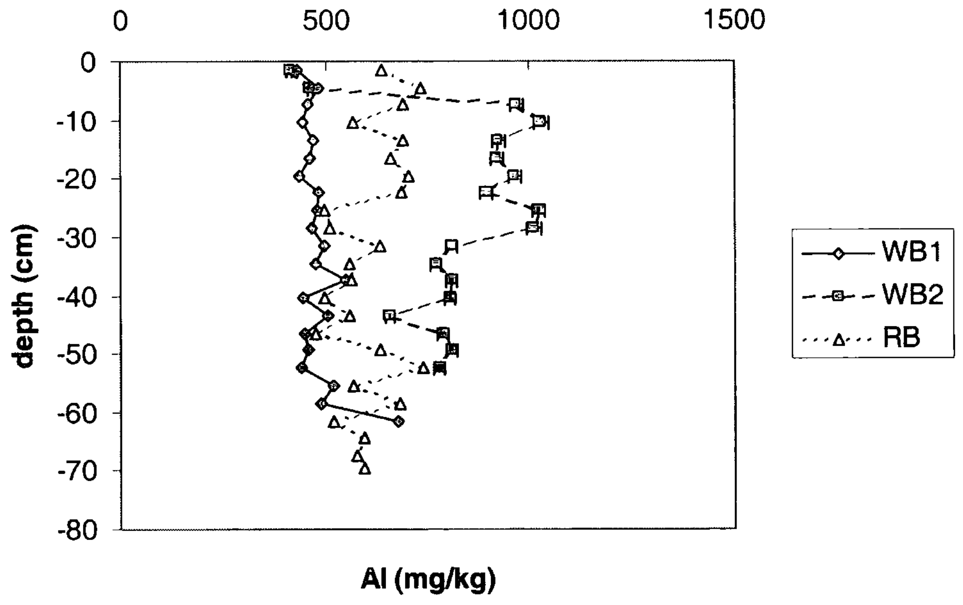


Figure 6.16. Stage 3 extractable Al with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

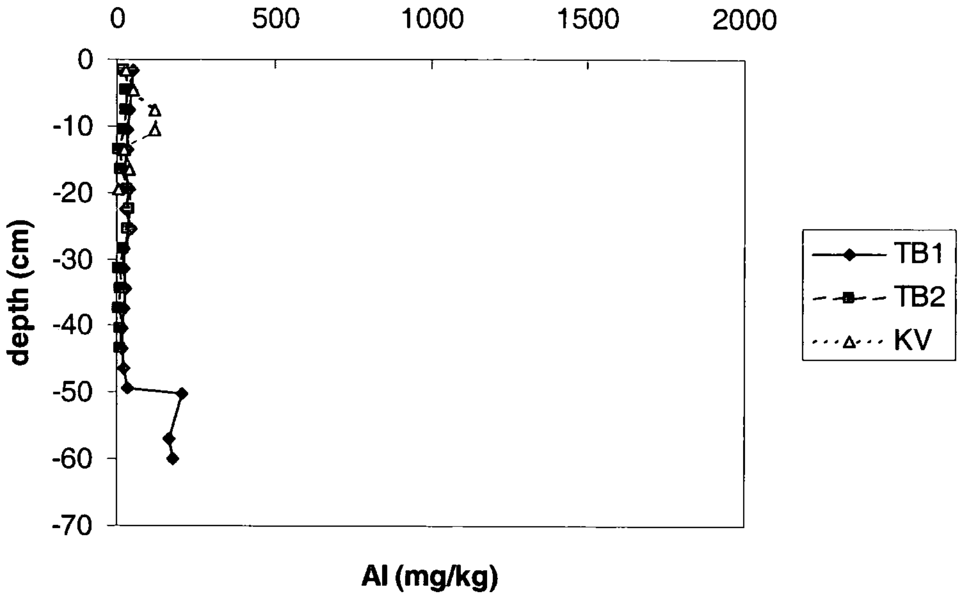


Figure 6.17. Stage 4 extractable Al with depth in cores TB1, TB2 and KV from the Tees impoundment.

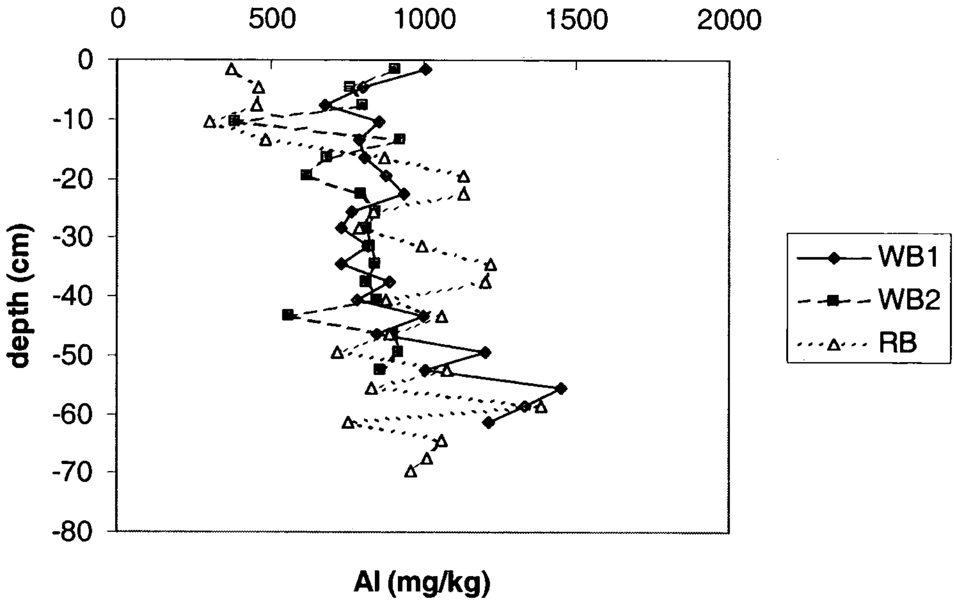


Figure 6.18. Stage 4 extractable Al with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

6.7.4.2 Ca

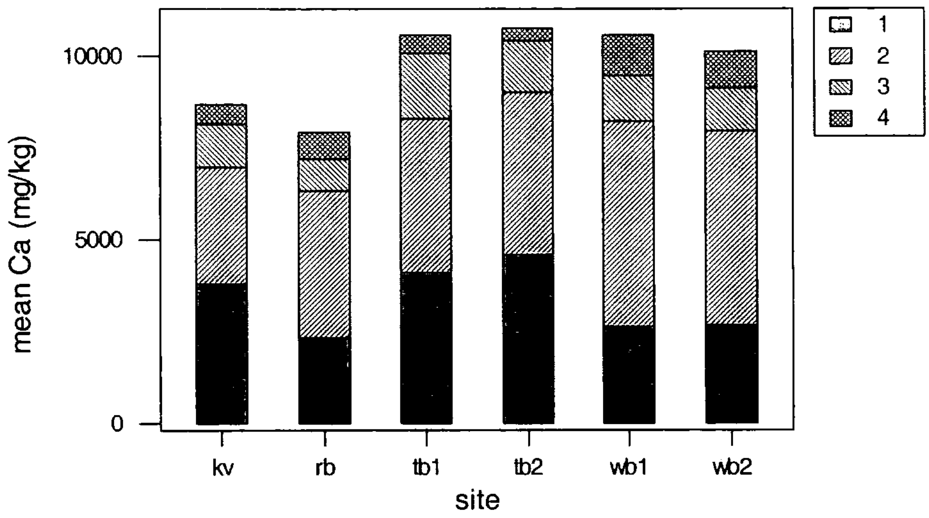


Figure 6.19. Ca concentration and speciation within the bottom sediments of the Tees and Wansbeck impoundments. Cores KV, TB1 and TB2 are from the Tees and cores RB, WB1 and WB2 are from the Wansbeck. Stages 1, 2, 3 and 4 of the sequential extraction scheme used represent exchangeable, carbonate bound, Fe and Mn bound and organic bound forms respectively.

Sediment	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Total available**
Tees impoundment	4164	3975	1476	555	10170
Wansbeck impoundment	2537	4886	1085	936	9444
Organic stream sediment (Finland)					5600

Table 6.10. Average Ca concentrations in sediment (mg/kg) from the Tees and Wansbeck impoundments (stage 1 to 4 plus sum of stages of Tessier extraction scheme) and organic stream sediment (concentrated HNO_3 extraction; data from Lahermo et al. 1996).

Significant amounts of Ca are held in all phases modelled by the extraction procedure and total available concentrations are comparable for the two impoundments (table 6.10 and figure 6.19). Perhaps surprisingly, considering that the Tees is a freshwater impoundment (and no pore water corrections are applied), exchangeable (stage 1 extractable) Ca levels are higher in Tees sediment than in the Wansbeck (which periodically contains seawater). It is possible that ion exchange with the seawater input to the Wansbeck impoundment has removed Ca from exchangeable sites in the sediment. However, stage 1 is likely to be partially dissolving carbonates present, and thus estimations of cation exchange capacities for the sediments are impossible. Not surprisingly, given that the catchments of both rivers are composed in part of carbonate geologies, the carbonate bound phase (stage 2 extraction) is a major source of Ca within the sediments of both impoundments. Stage 3 extractable Ca is on average higher and stage 4 extractable Ca lower in the Tees than in the Wansbeck sediments.

Profiles for exchangeable Ca (figures 6.20 and 6.21) show that for the Tees the concentration within the sand dominated pre-impoundment sediment is much lower than in the silt dominated (and higher pore-water content) post-impoundment sediment. Within the post-impoundment sediment at the barrage sampling site there is a slight increase in exchangeable Ca with depth in the sediment. Within the Wansbeck sediment exchangeable Ca is relatively constant with depth in the sediment. Carbonate input to the sediment went up significantly for a period following impoundment of the Tees (figure 6.22), and may be due to increased inputs of carbonate material from the catchment during the high flow periods of 1995. Within the Wansbeck sediment carbonate bound Ca shows a large amount of variation and a possible slight increase with depth (figure 6.23). The amount of Ca associated with stage 3 of the extraction procedure is relatively constant with depth for both impoundments (figures 6.24 and 6.25) with the only significant feature being much greater concentrations within the pre-impoundment sediment, possibly associated with Fe oxide coating on the sand-sized particles. Stage 4 extractable Ca also shows a distinct decrease between pre and post-impoundment sediment (figure 6.26). As with Al, stage 4 extractable Ca shows no identifiable pattern but is of higher concentration in Wansbeck than Tees sediment (figure 6.27).

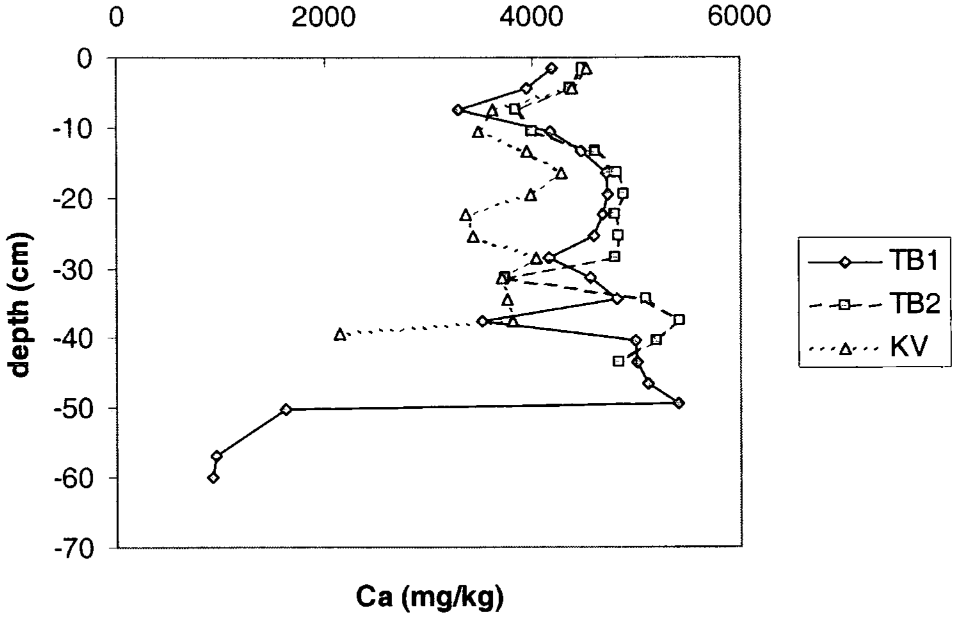


Figure 6.20. Stage 1 extractable Ca with depth in cores TB1, TB2 and KV from the Tees impoundment.

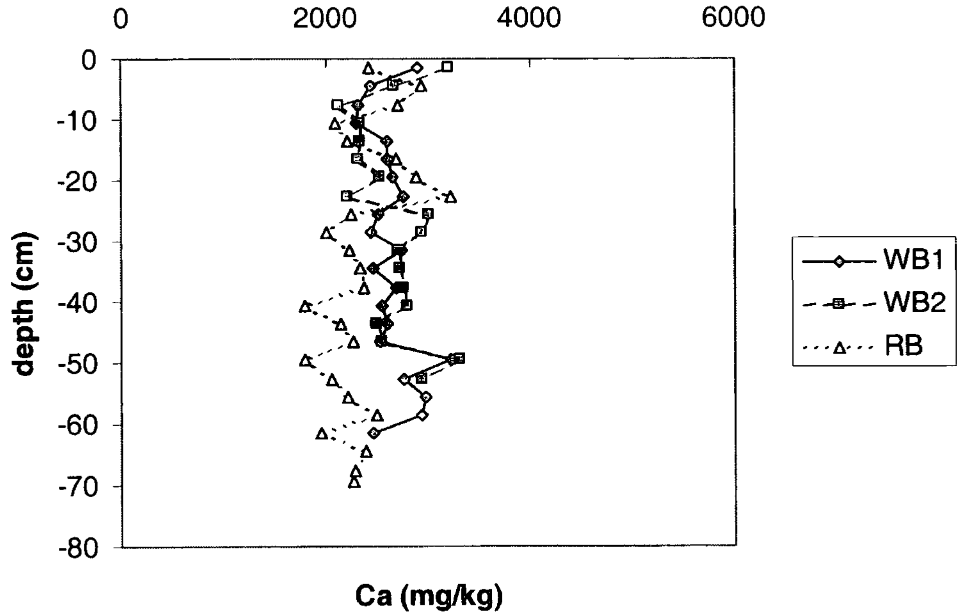


Figure 6.21. Stage 1 extractable Ca with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

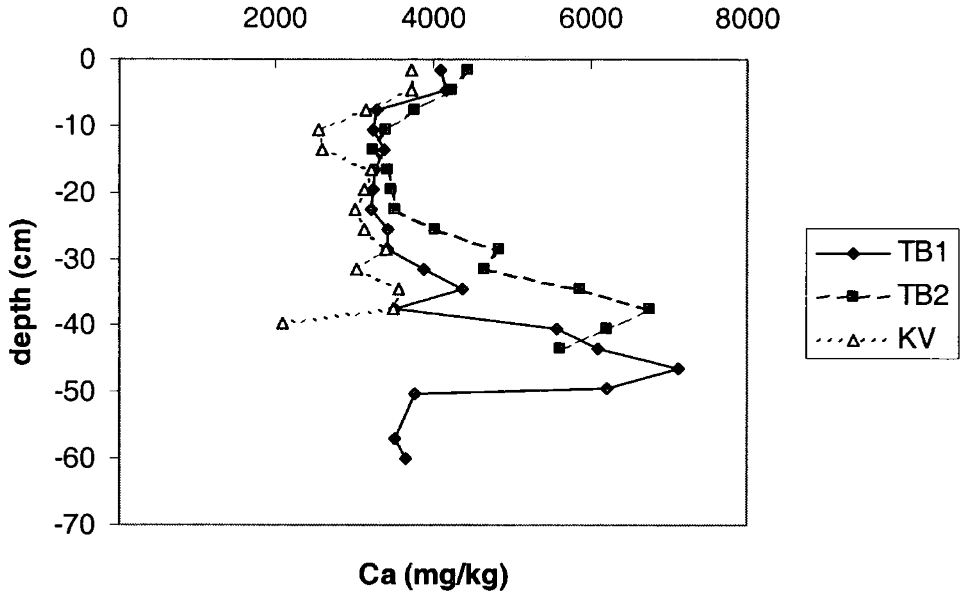


Figure 6.22. Stage 2 extractable Ca with depth in cores TB1, TB2 and KV from the Tees impoundment.

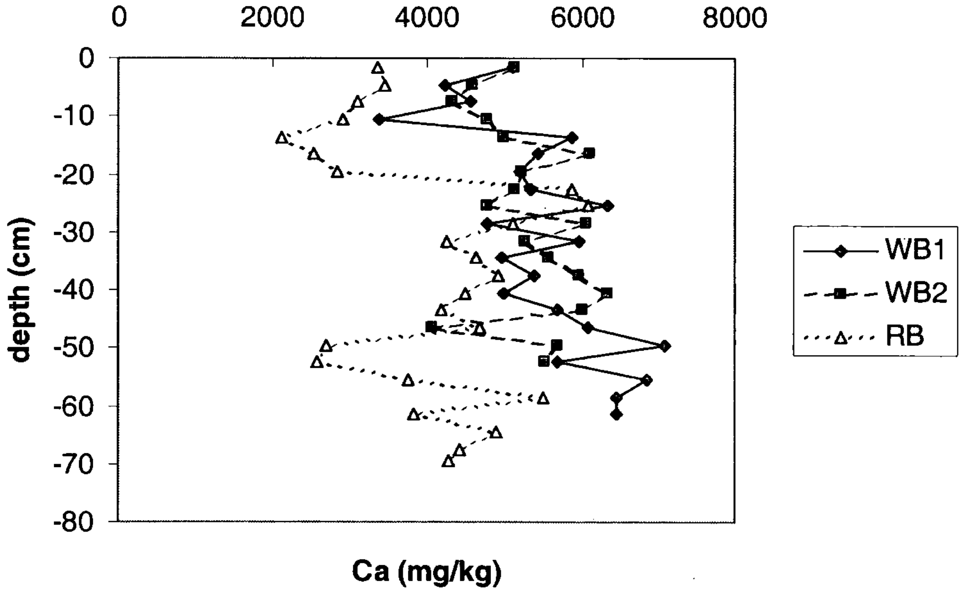


Figure 6.23. Stage 2 extractable Ca with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

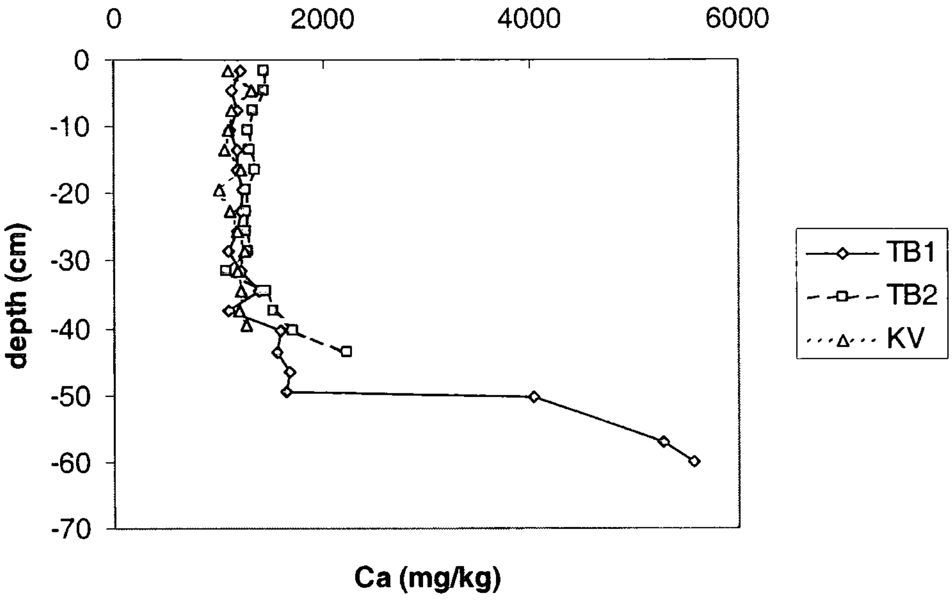


Figure 6.24. Stage 3 extractable Ca with depth in cores TB1, TB2 and KV from the Tees impoundment.

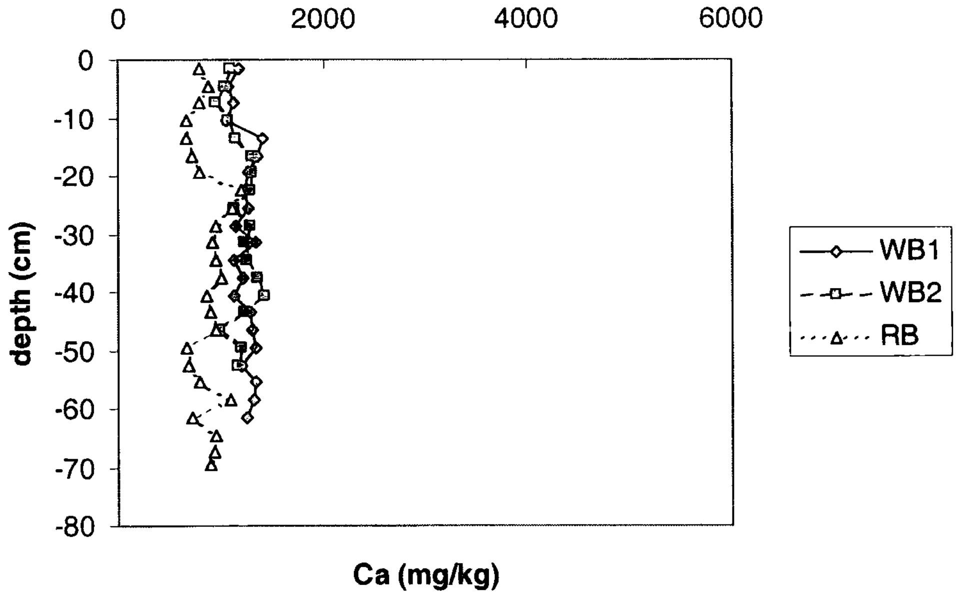


Figure 6.25. Stage 3 extractable Ca with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

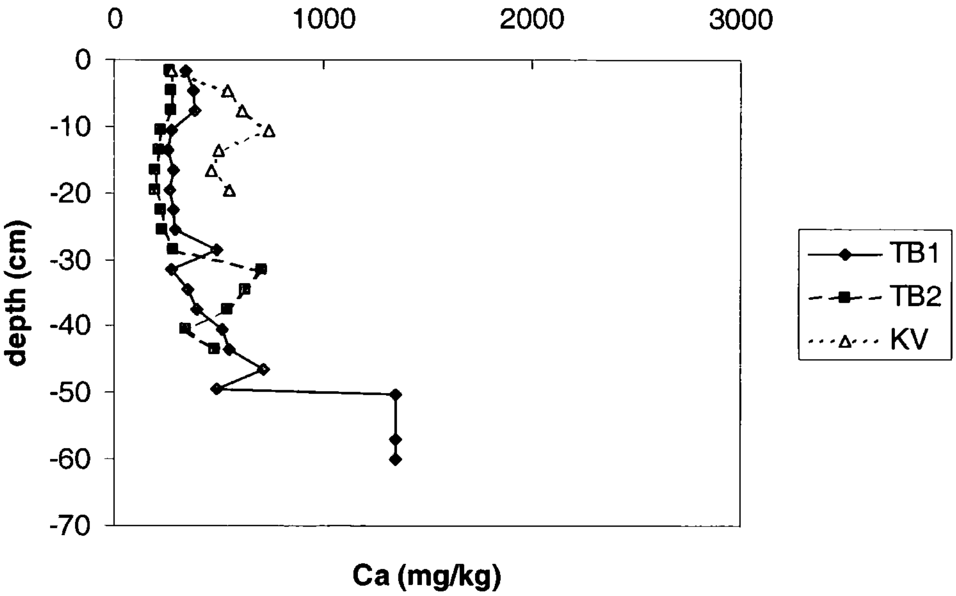


Figure 6.26. Stage 4 extractable Ca with depth in cores TB1, TB2 and KV from the Tees impoundment.

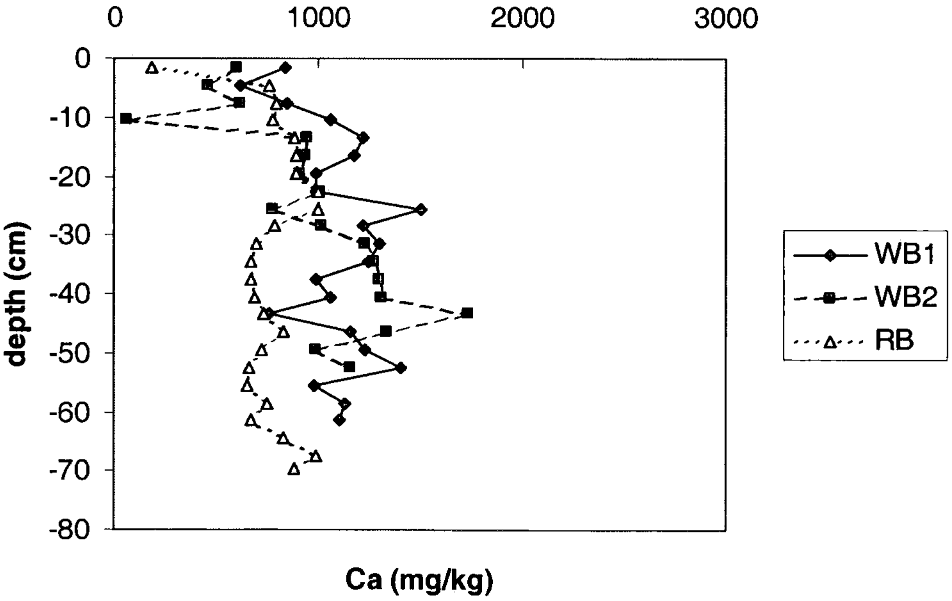


Figure 6.27. Stage 4 extractable Ca with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

6.7.4.3 Co

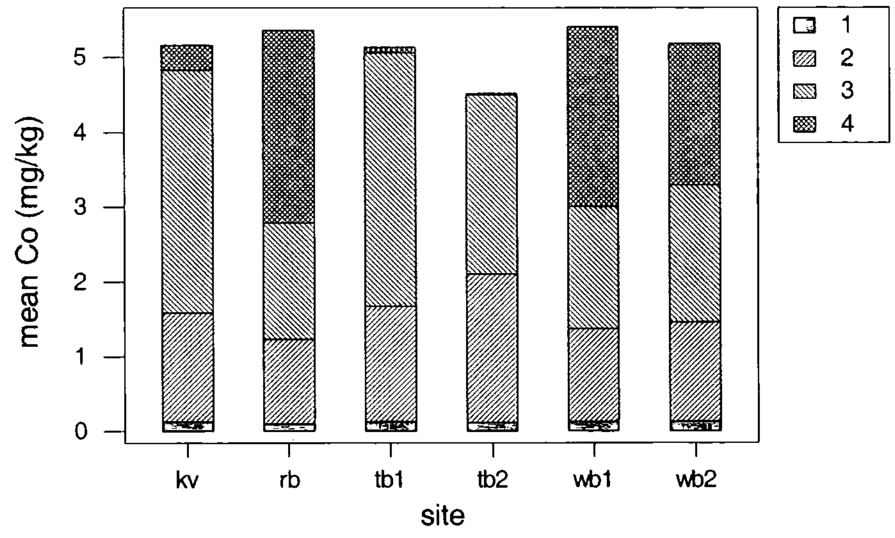


Figure 6.28. Co concentration and speciation within the bottom sediments of the Tees and Wansbeck impoundments. Cores KV, TB1 and TB2 are from the Tees and cores RB, WB1 and WB2 are from the Wansbeck. Stages 1, 2, 3 and 4 of the sequential extraction scheme used represent exchangeable, carbonate bound, Fe and Mn bound and organic bound forms respectively.

Sediment	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Total**
Tees impoundment	0.12	1.65	3.04	0.13	4.94
Wansbeck impoundment	0.12	1.23	1.66	2.30	5.31
Organic stream sediment (Finland)					10.5
Tees estuary downstream of barrage					34
Humber estuary					16

Table 6.11. Average Co concentrations in sediment (mg/kg) from the Tees and Wansbeck impoundments (stage 1 to 4 plus sum of stages of Tessier extraction scheme), organic stream sediment (< 2 mm fraction, concentrated HNO_3 extraction; data from Lahermo et al. 1996), Tees estuary sediment from downstream of barrage (total extraction; data from Jones and Turki 1997), and Humber estuary (< 100 μm fraction, concentrated HNO_3 extraction: data from Bryan and Langston 1992).

Levels of Co reported in this study are much lower than those determined for bottom sediment downstream of the Tees barrage (Jones and Turki, 1997; table 6.11), although the data are not directly comparable due to the difference between extraction techniques employed (potentially environmentally mobile vs. total concentrations). Jones and Turki state that the Co is dominantly held in the residual minerals (silicates), and most Co is therefore not available for exchange with the water column or biota.

Total available Co levels are similar for sediment from the Tees and the Wansbeck impoundments but their pattern of speciation differs. Very little Co is held exchangeably within sediments from either of the impoundments. Carbonate bound Co is slightly higher in the Tees than the Wansbeck sediment. The major difference between the impoundments is in terms of stage 3 and stage 4 extractable phases for Co, and the pattern shown is similar to that of Al. Within the Tees sediment the majority of Co is held in the reducible phase (stage 3), with very little Co in the oxidisable phase (stage 4). In Wansbeck sediment Co is held in both phases, with the greatest proportion removed during extraction 4 (table 6.11, figure 6.28).

Stage 2 extractable Co shows, as for Ca, a significant peak within the sedimentation following impoundment of the Tees estuary (figure 6.29). Stage 3 extractable Co concentration fluctuates with depth in the Tees but shows no determinable trend (figure 6.31). Stage 2 and 3 extractable Co is relatively constant with depth within the Wansbeck (figures 6.30 and 6.32). As is seen repeatedly for a variety of elements within the Tees sediment, the pattern for stage 4 extraction is of very low concentrations at all depths, with slightly higher levels in pre-impoundment sediment (figure 6.33). Sediment in the Wansbeck shows a significant decrease towards the sediment surface from circa 4 mg/kg at 70 cm depth to circa 1 mg/kg at the surface (figure 6.34).

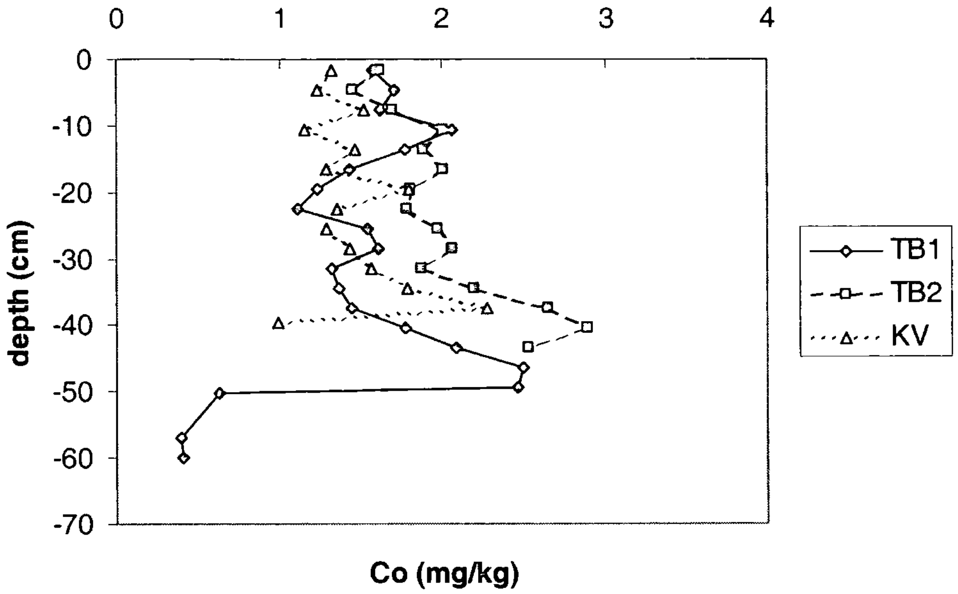


Figure 6.29. Stage 2 extractable Co with depth in cores TB1, TB2 and KV from the Tees impoundment.

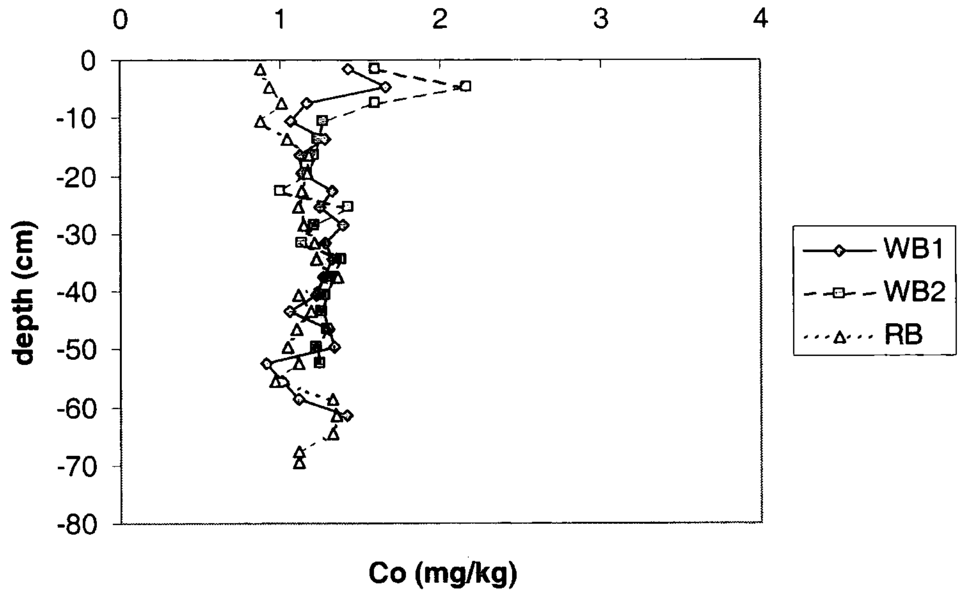


Figure 6.30. Stage 2 extractable Co with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

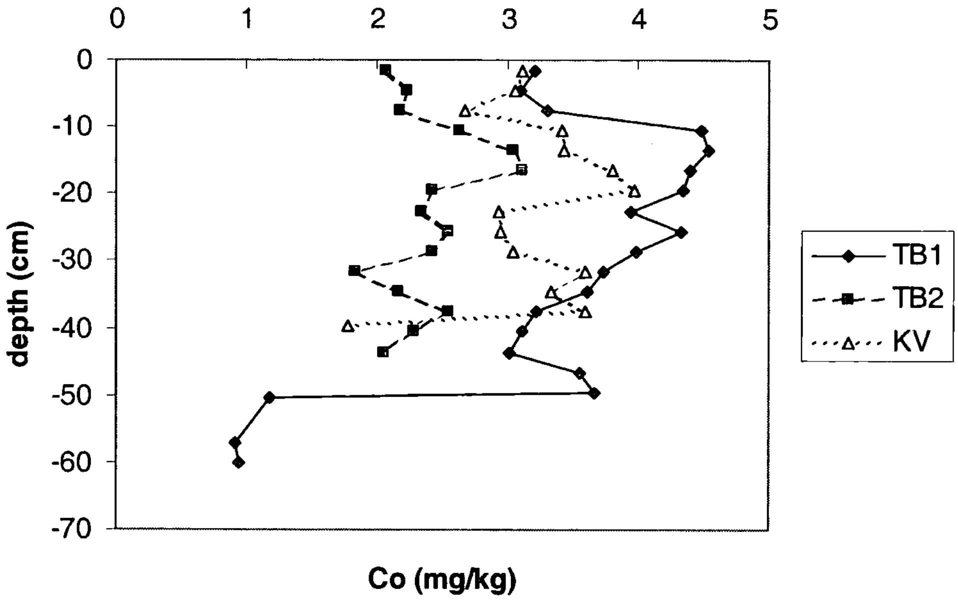


Figure 6.31. Stage 3 extractable Co with depth in cores TB1, TB2 and KV from the Tees impoundment.

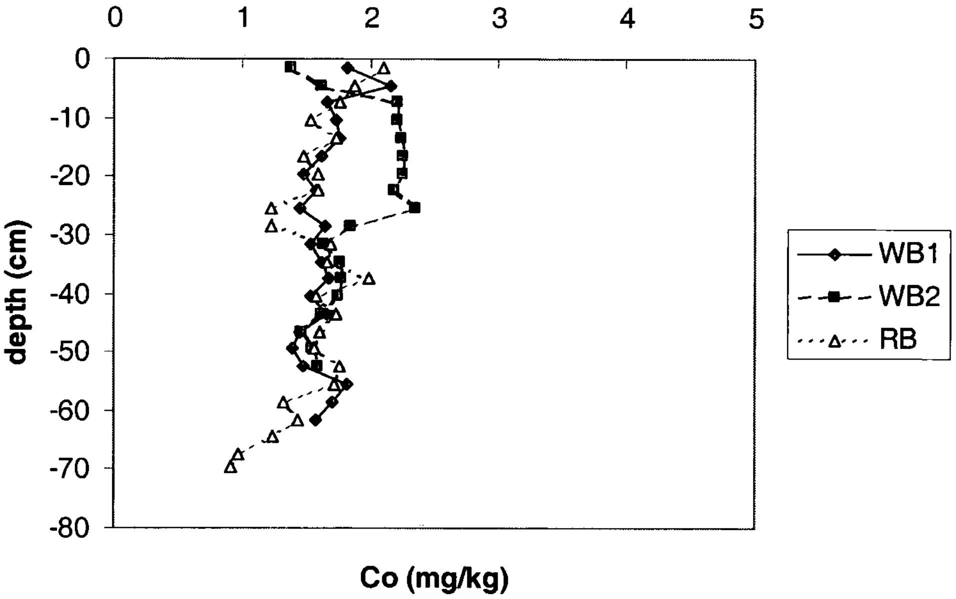


Figure 6.32. Stage 3 extractable Co with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

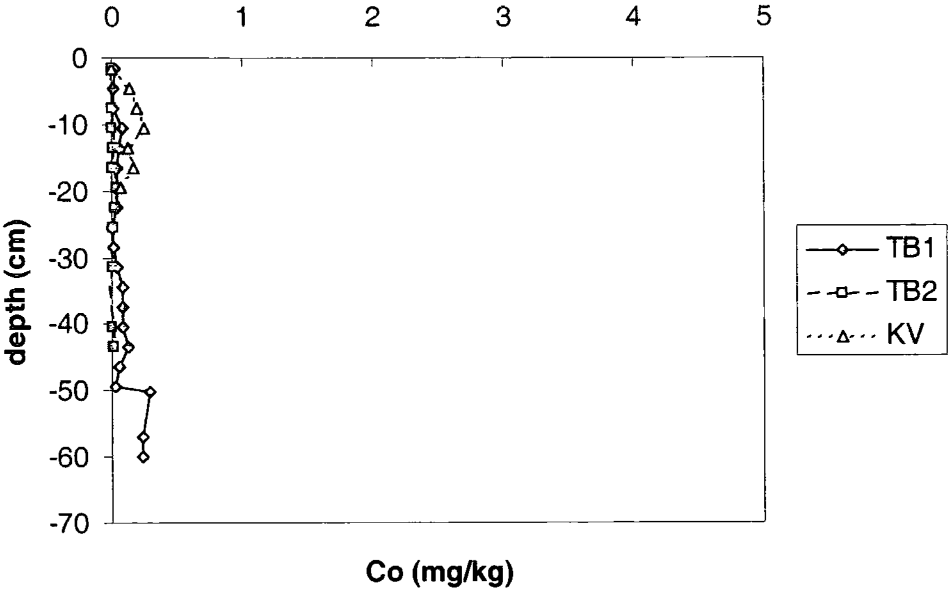


Figure 6.33. Stage 4 extractable Co with depth in cores TB1, TB2 and KV from the Tees impoundment.

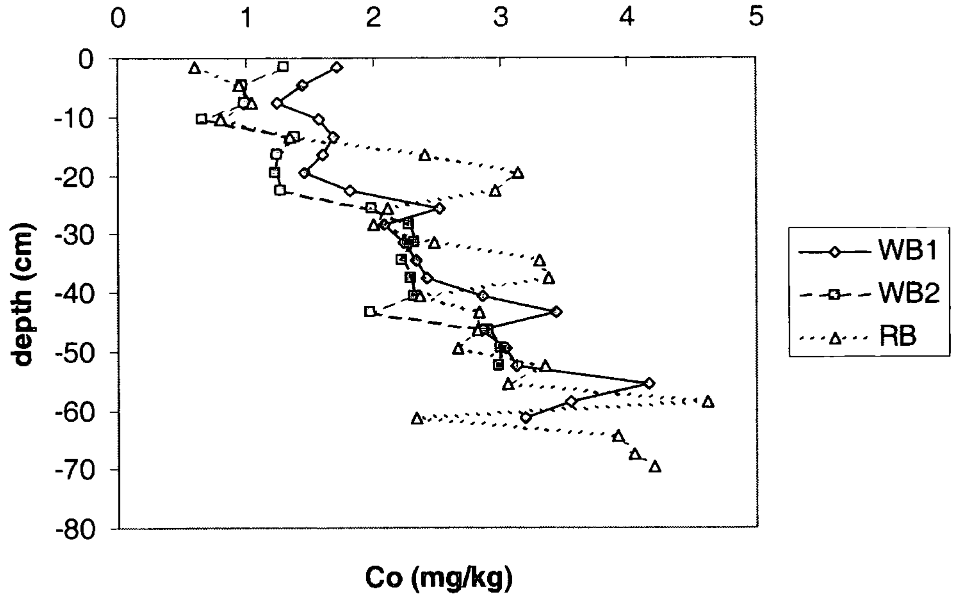


Figure 6.34. Stage 4 extractable Co with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

6.7.4.4 Cr

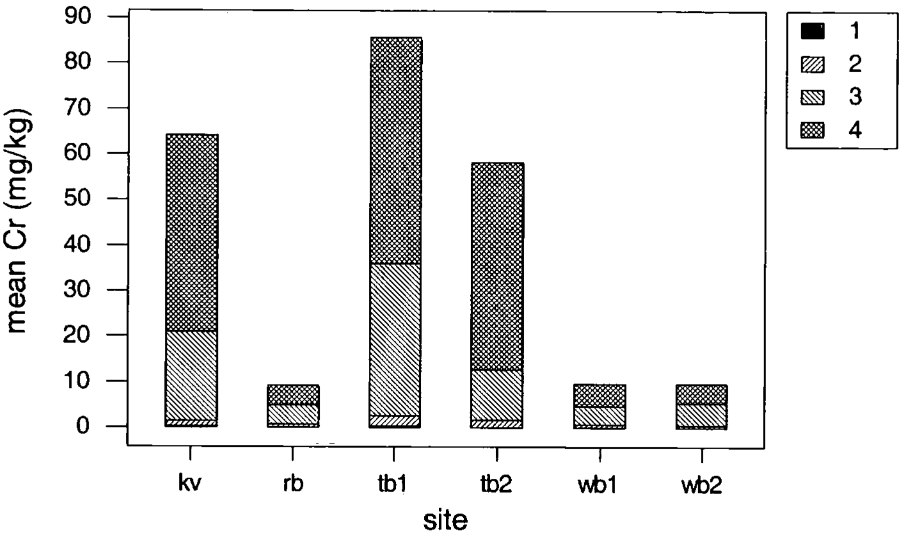


Figure 6.35. Cr concentration and speciation within the bottom sediments of the Tees and Wansbeck impoundments. Cores KV, TB1 and TB2 are from the Tees and cores RB, WB1 and WB2 are from the Wansbeck. Stages 1, 2, 3 and 4 of the sequential extraction scheme used represent exchangeable, carbonate bound, Fe and Mn bound and organic bound forms respectively.

Sediment	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Total**
Tees impoundment	0.14	1.78	22.78	46.46	71.16
Wansbeck impoundment	0.08	0.61	4.34	4.50	9.53
Organic stream sediment (Finland)					31.3
Tees estuary downstream of barrage					224
River Tees upstream of impoundment					64
Humber estuary					77

Table 6.12. Average Cr concentrations in sediment (mg/kg) from the Tees and Wansbeck impoundments (stage 1 to 4 plus sum of stages of Tessier extraction scheme), organic stream sediment (< 2 mm fraction, concentrated HNO_3 extraction; data from Lahermo et al. 1996), Tees estuary sediment from downstream of barrage (total extraction; data from Jones and Turki 1997), River Tees sediment upstream of

impoundment (< 63 μm fraction, total extraction; data from EA), and Humber estuary (< 100 μm fraction, concentrated HNO_3 extraction; data from Bryan and Langston 1992).

Cr occurs in distinctly different concentration in the two impoundments, with levels higher in the Tees through all speciations (figure 6.35 and table 6.12) likely to be due to industrial input from Cr works at Eaglescliffe (upstream of barrage). Levels in the Tees impoundment are lower however than those encountered downstream of the barrage (where available forms generally exceed 150 mg/kg (Jones and Turki 1997)), which reflects greater sewage and industrial inputs in the downstream section of the estuary. Bryan and Langston (1992) report available Cr levels reaching a maximum in UK estuaries studied of 800 mg/kg in the Loughor estuary (South Wales) which is subject to pollution from tinplate production.

The speciation pattern is similar within sediment from both impoundments. Very little Cr is held exchangeably of bound to carbonates, and the stage 3 and stage 4 extractable species are the main available forms (figure 6.35).

The pattern of stage 3 extractable (Fe and Mn oxide bound) Cr with depth in the Tees is of relatively constant concentration with depth within the post-impoundment sediment, but significantly higher Cr within the pre-impoundment sediment (> 50 cm depth) (figure 6.36). Within the Wansbeck Cr increases slightly with depth in the sediment, although there is much scatter (figure 6.37). The pattern of stage 4 extractable (sulphide and organic bound) Cr is similar to that for stage 3 extractable Cr for both impoundments, with higher concentrations in pre-impoundment sediment in the Tees (figure 6.38) and much lower concentrations but a small increase with depth in the Wansbeck (figure 6.39).

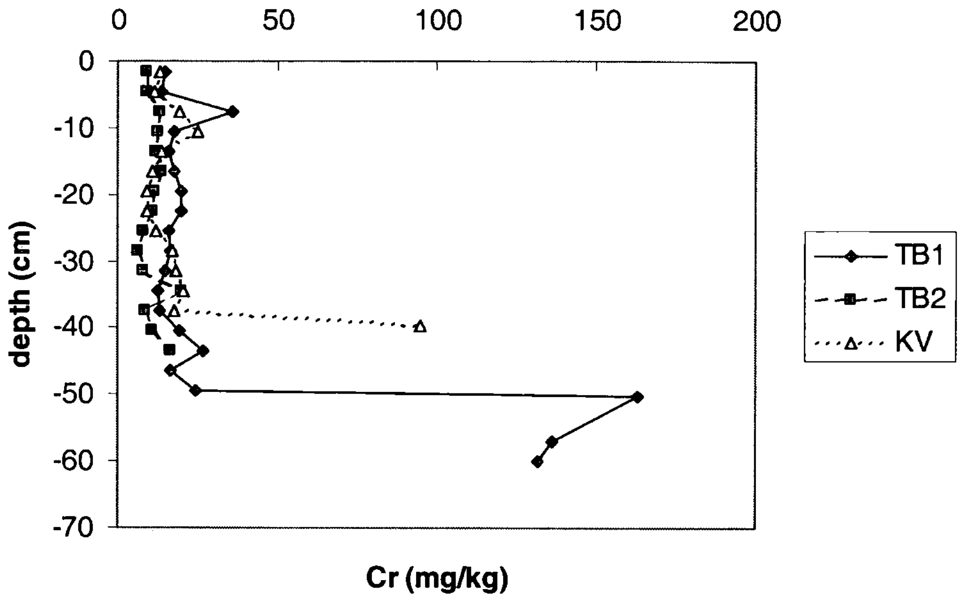


Figure 6.36. Stage 3 extractable Cr with depth in cores TB1, TB2 and KV from the Tees impoundment.

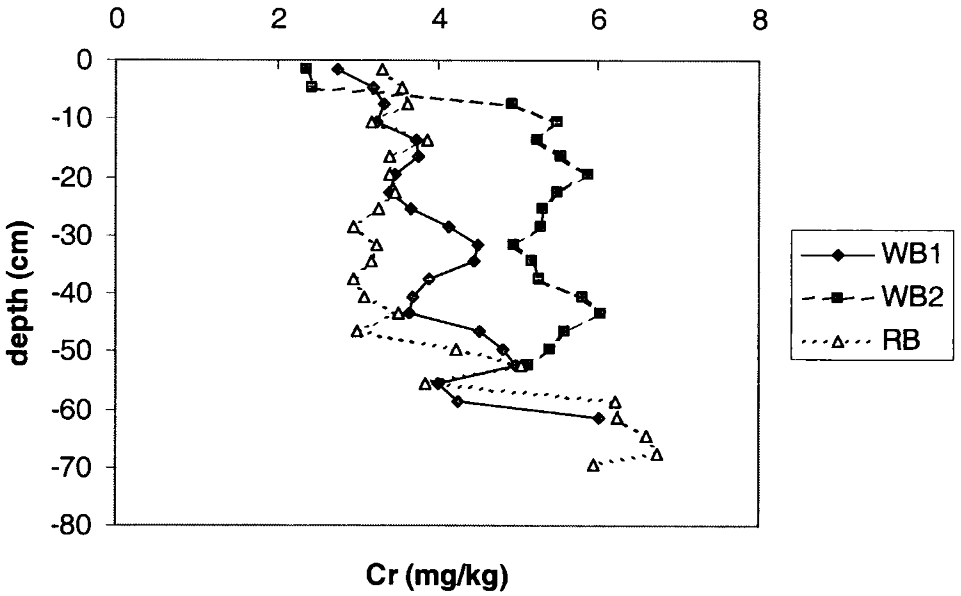


Figure 6.37. Stage 3 extractable Cr with depth in cores WB1, WB2 and RB from the Wansbeck impoundment (note different concentration scale to figure 6.36 above).

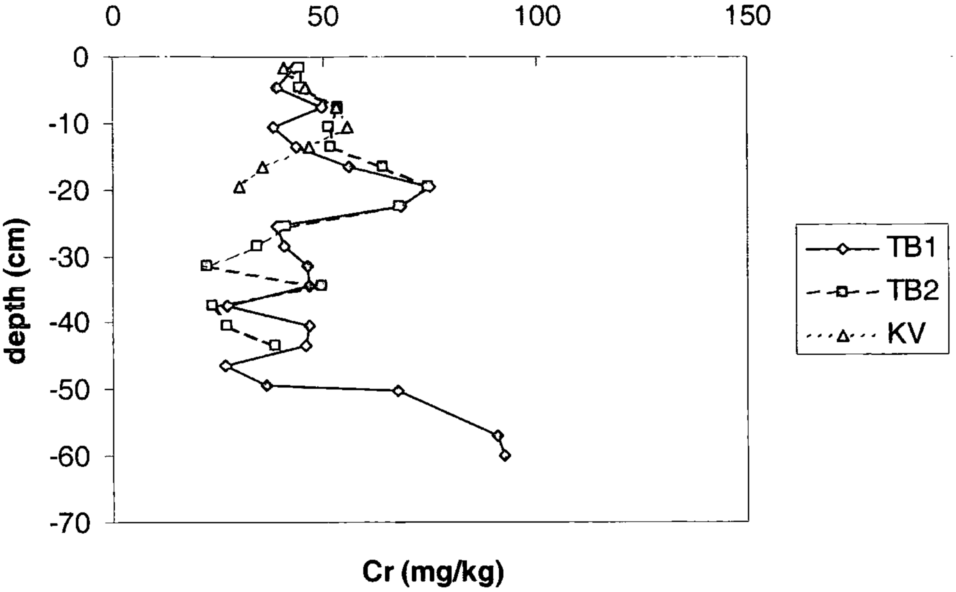


Figure 6.38. Stage 4 extractable Cr with depth in cores TB1, TB2 and KV from the Tees impoundment.

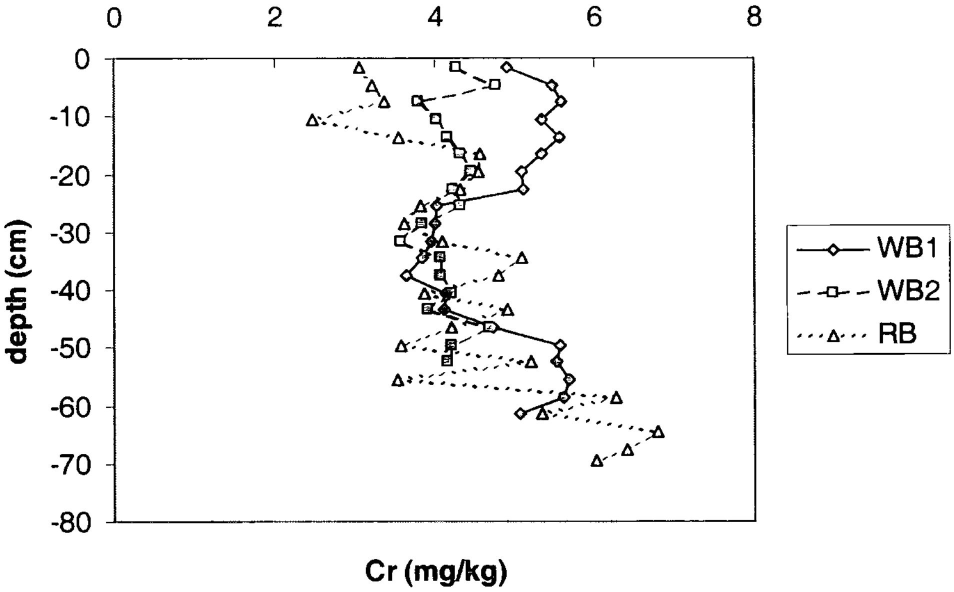


Figure 6.39. Stage 4 extractable Cr with depth in cores WB1, WB2 and RB from the Wansbeck impoundment (note different concentration scale to figure 6.38 above).

6.7.4.5 Cu

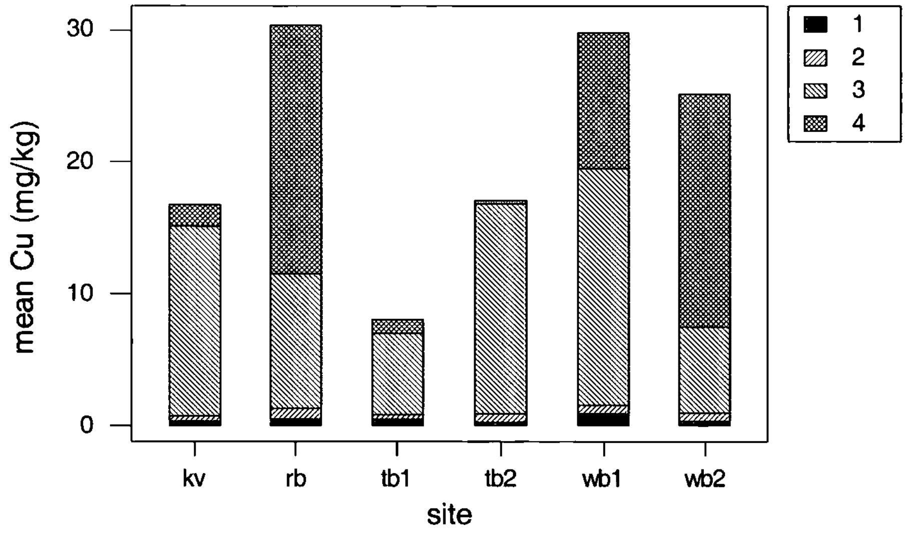


Figure 6.40. Cu concentration and speciation within the bottom sediments of the Tees and Wansbeck impoundments. Cores KV, TB1 and TB2 are from the Tees and cores RB, WB1 and WB2 are from the Wansbeck. Stages 1, 2, 3 and 4 of the sequential extraction scheme used represent exchangeable, carbonate bound, Fe and Mn bound and organic bound forms respectively.

Sediment	Stage 1	Stage 2	Stage 3	Stage 4	Total
Tees impoundment	0.41	0.44	11.54	0.92	13.31
Wansbeck impoundment	0.62	0.69	11.80	15.57	26.68
Organic stream sediment (Finland)					12.4
Tees estuary downstream of barrage					103
River Tees upstream of impoundment					56
Humber estuary					54

Table 6.13. Average Cu concentrations in sediment (mg/kg) from the Tees and Wansbeck impoundments (stage 1 to 4 plus sum of stages of Tessier extraction scheme), organic stream sediment (< 2 mm fraction, concentrated HNO_3 extraction; data from Lahermo et al. 1996), Tees estuary sediment from downstream of barrage

(total extraction; data from Jones and Turki 1997), River Tees sediment upstream of impoundment (< 63 µm fraction, total extraction; data from EA), and Humber estuary (< 100 µm fraction, concentrated HNO_3 extraction; data from Bryan and Langston 1992).

Cu levels in sediment in the Wansbeck are approximately double those in the Tees impoundment (table 6.13). Levels are slightly higher than in organic stream sediment, but lower than those reported for sediment collected in the Tees estuary downstream of the barrage.

A similar pattern of speciation to that of Al, Fe, Ni, Sc, Zn, and to an extent Co and Mn, is shown in the sediment of the impoundments by Cu: i.e. the majority of Cu is held in stage 3 extractable form (Fe and Mn oxides). Hydrous oxides of Fe and Mn are major trace metal hosts in several estuaries (Calmano and Forstner 1983; Luoma and Davies 1983; Peterson et al. 1995). In the Tees virtually no Cu is held in the oxidisable/stage 4 phase, but in the Wansbeck this phase is significant (figure 6.40). Very little Cu is held exchangeably or bound with carbonates.

Extraction stage 3 is subject to very large errors for Cu (47 %) for unknown reasons, and the irregular profiles for both impoundments reflect this error, with no patterns discernible (figures 6.41 and 6.42). The profile for stage 4 extractable Cu in the Tees shows very low levels through the post-impoundment sediment and higher levels in pre-impoundment sediment (figure 6.43), and in the Wansbeck there is a relatively steady increase with depth in the sediment column (figure 6,44).

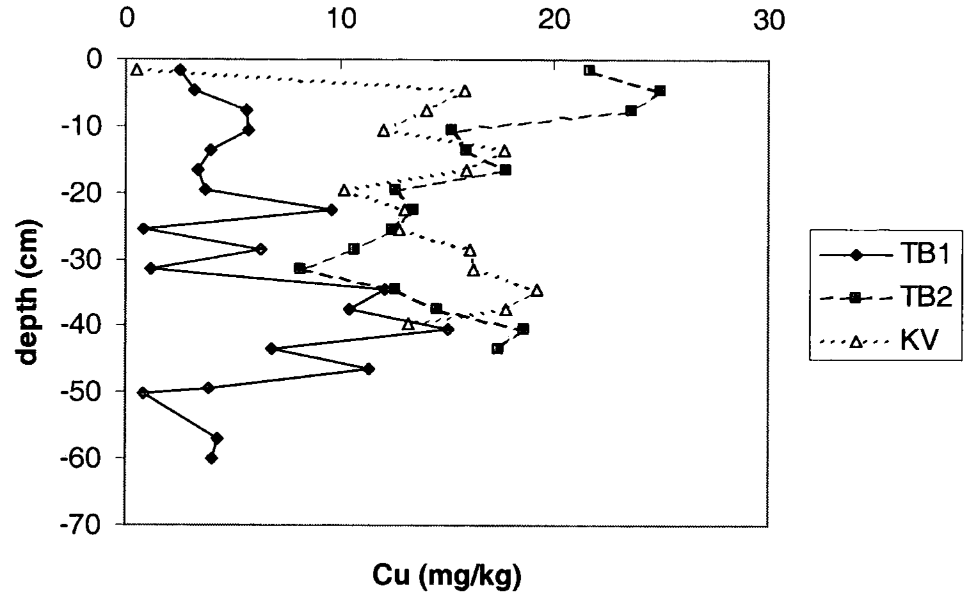


Figure 6.41. Stage 3 extractable Cu with depth in cores TB1, TB2 and KV from the Tees impoundment.

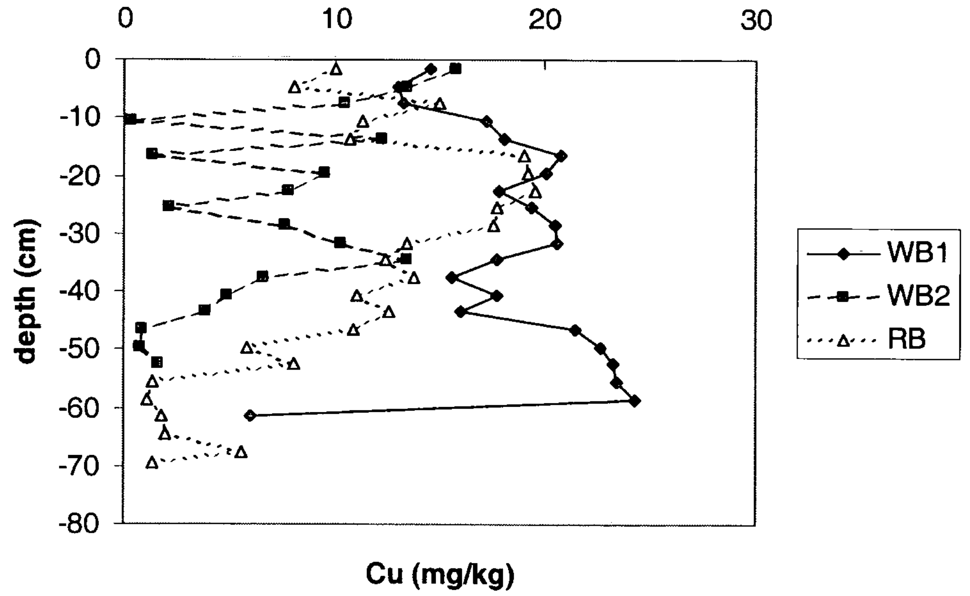


Figure 6.42. Stage 3 extractable Cu with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

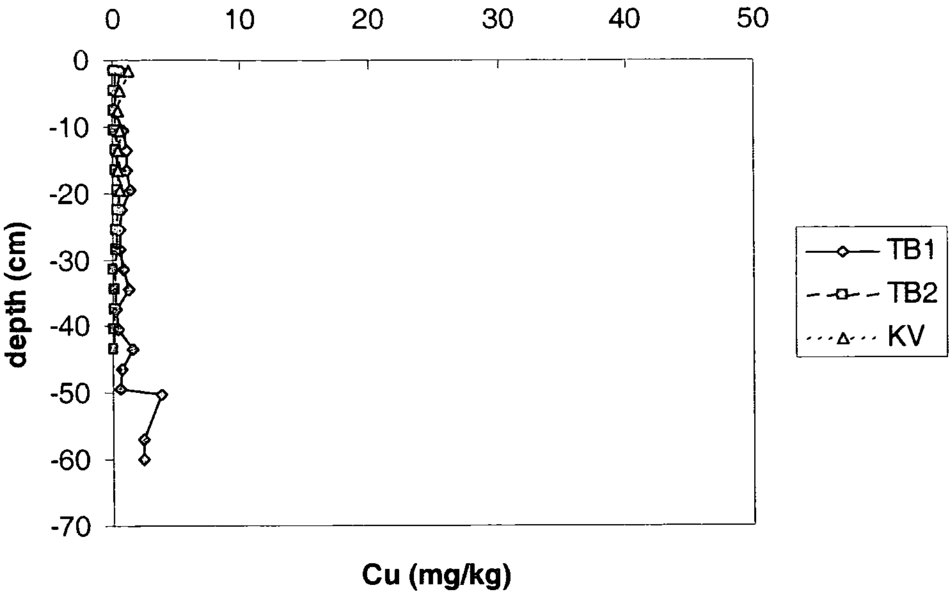


Figure 6.43. Stage 4 extractable Cu with depth in cores TB1, TB2 and KV from the Tees impoundment.

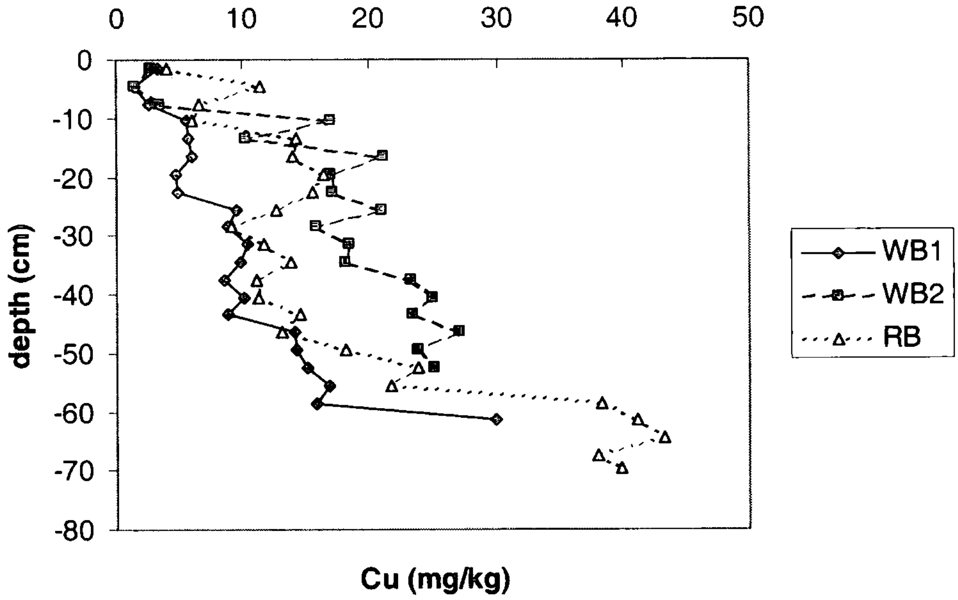


Figure 6.44. Stage 4 extractable Cu with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

6.7.4.6 Fe

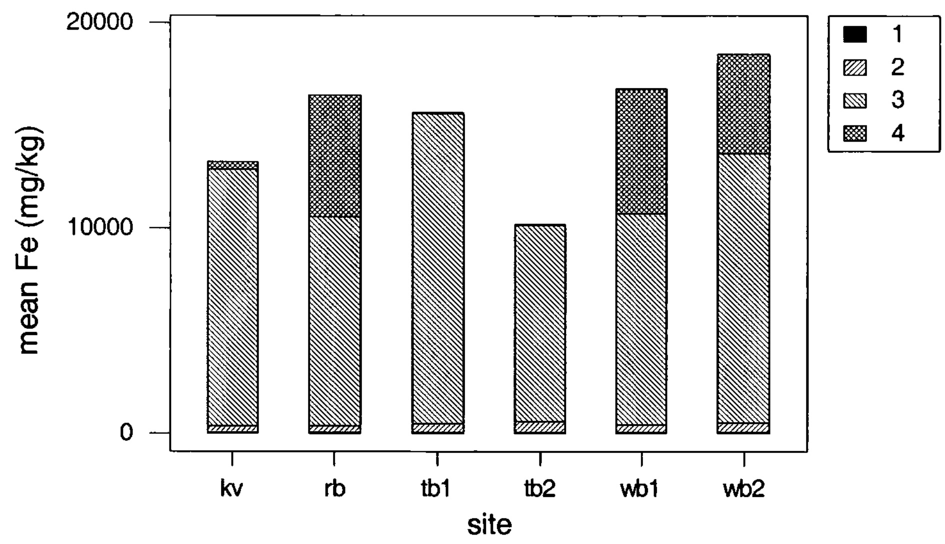


Figure 6.45. Fe concentration and speciation within the bottom sediments of the Tees and Wansbeck impoundments. Cores KV, TB1 and TB2 are from the Tees and cores RB, WB1 and WB2 are from the Wansbeck. Stages 1, 2, 3 and 4 of the sequential extraction scheme used represent exchangeable, carbonate bound, Fe and Mn bound and organic bound forms respectively.

Sediment	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Total**
Tees impoundment	37	432	12694	141	13304
Wansbeck impoundment	40	397	11083	5635	17155
Organic stream sediment (Finland)					26000
Humber estuary					35203

Table 6.14. Average Fe concentrations in sediment (mg/kg) from the Tees and Wansbeck impoundments (stage 1 to 4 plus sum of stages of Tessier extraction scheme), organic stream sediment (< 2 mm fraction, concentrated HNO_3 extraction; data from Lahermo et al. 1996), and Humber estuary (< 100 μm fraction, concentrated HNO_3 extraction; data from Bryan and Langston 1992).

Total available Fe levels are slightly higher in the sediments of the Wansbeck than the Tees impoundment (table 6.14). That levels are lower than those reported for organic stream sediment or for the Humber estuary probably relates to difference in the extraction technique and grain-size fraction analysed rather than large differences in Fe behaviour.

The speciation of Fe shows the same pattern as a number of heavy metals (Cu, Ni, Zn, etc.) in the sediments of the impoundments. Very little Fe is held in either exchangeable (stage 1 extractable) or carbonate bound (stage 2 extractable) in either estuary. Within the Tees almost all Fe is held in the reducible (Fe oxide) phase. In the Wansbeck sediments Fe is held in both the reducible and oxidisable (Fe sulphides and organic bound) phases (figure 6.45).

Fe in oxides (stage 3 extractable) shows variation but no identifiable trends with depth in the sediment of the Tees (figure 6.46), and shows a slight increase (but with much scatter) in the Wansbeck (figure 6.47). There is effectively no stage 4 extractable Fe in the Tees impoundment, apart from within the deep (pre-impoundment) sediment encountered within core TB1 (figure 6.48). Fe within sulphide (and organic bound) shows an increase with depth in sediment within the Wansbeck with concentrations at approximately 2000 mg/kg at the sediment-water column interface and almost 10000 at a depth of 60 cm (figure 6.49).

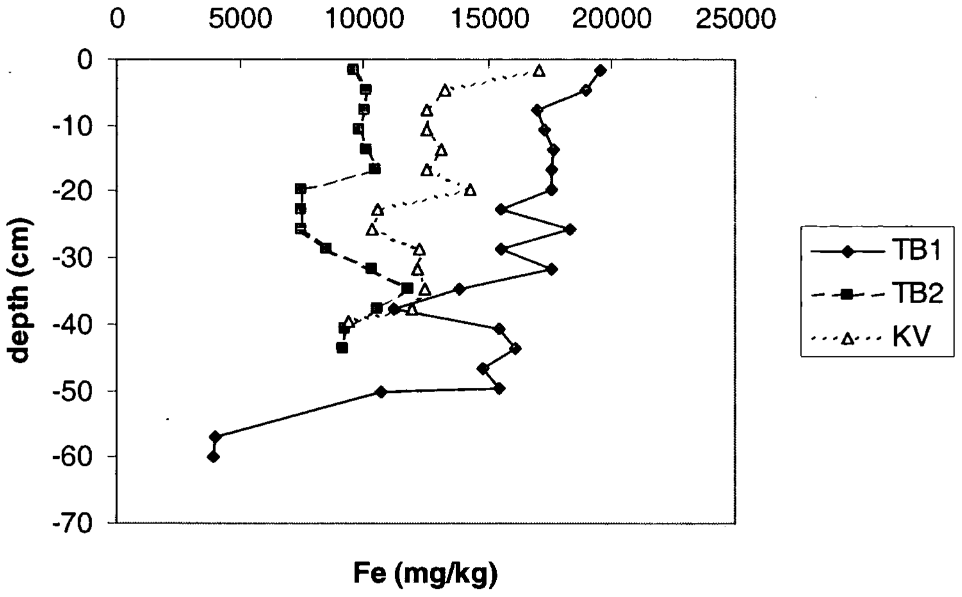


Figure 6.46. Stage 3 extractable Fe with depth in cores TB1, TB2 and KV from the Tees impoundment.

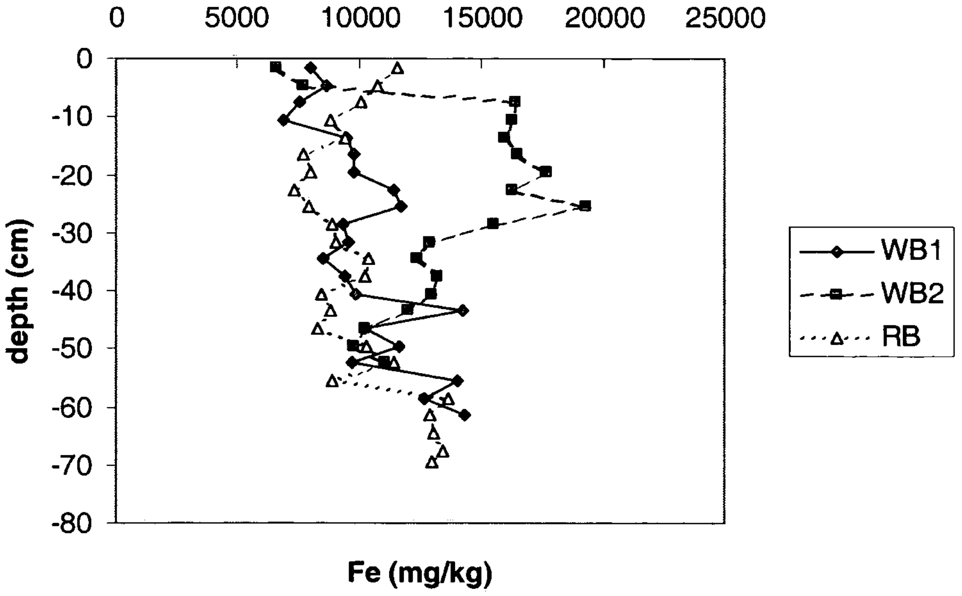


Figure 6.47. Stage 3 extractable Fe with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

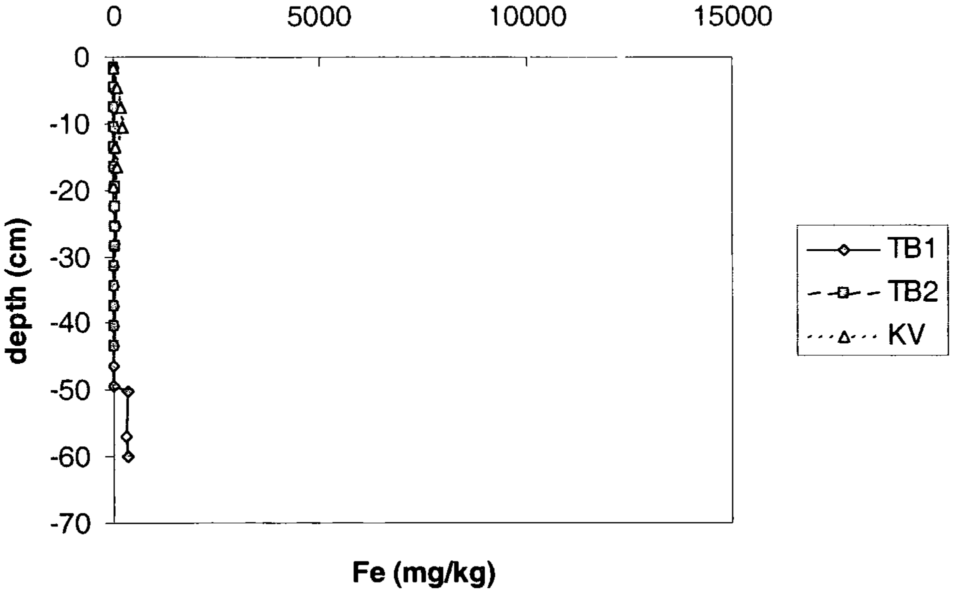


Figure 6.48. Stage 4 extractable Fe with depth in cores TB1, TB2 and KV from the Tees impoundment.

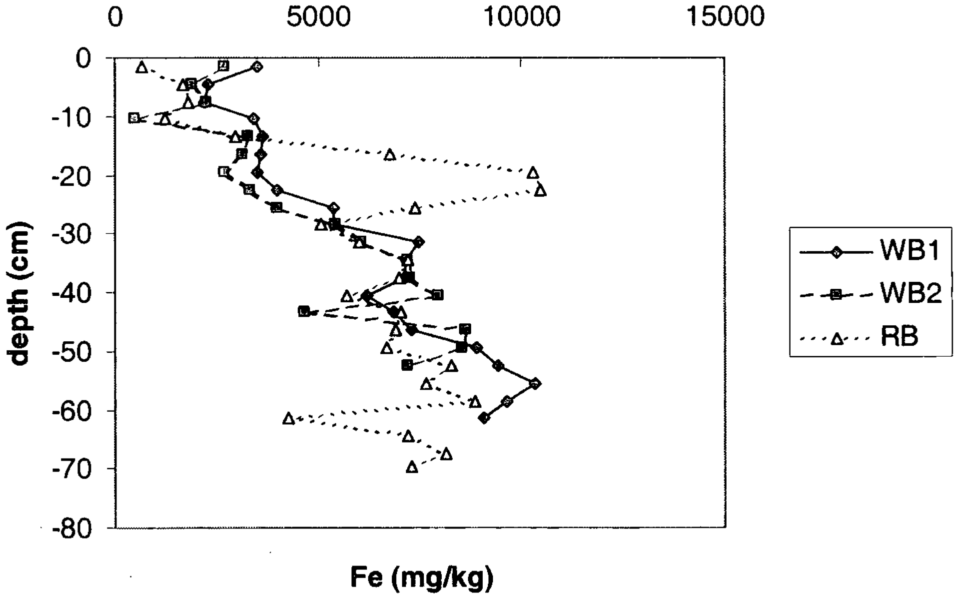


Figure 6.49. Stage 4 extractable Fe with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

6.7.4.7 K

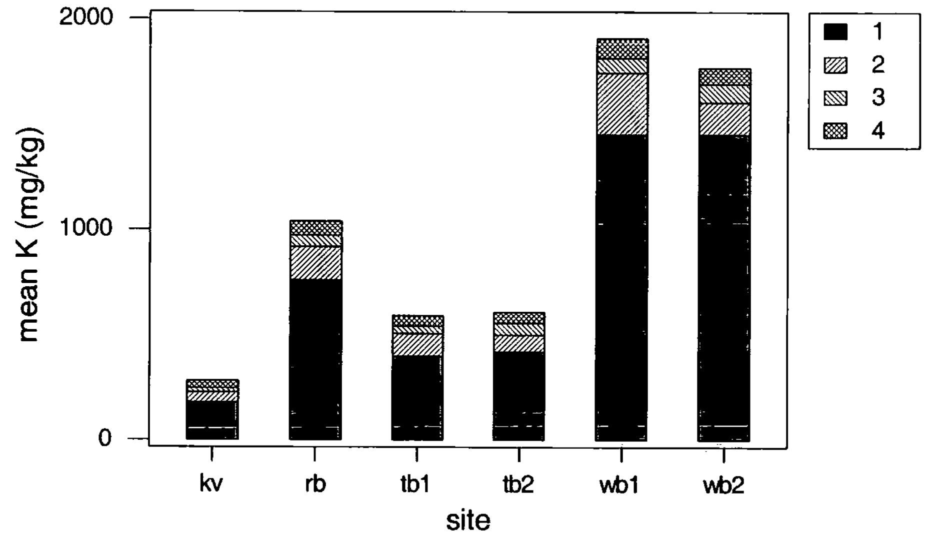


Figure 6.50. K concentration and speciation within the bottom sediments of the Tees and Wansbeck impoundments. Cores KV, TB1 and TB2 are from the Tees and cores RB, WB1 and WB2 are from the Wansbeck. Stages 1, 2, 3 and 4 of the sequential extraction scheme used represent exchangeable, carbonate bound, Fe and Mn bound and organic bound forms respectively.

Sediment	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Total**
Tees impoundment	341	81	38	47	507
Wansbeck impoundment	1193	202	69	77	1541
Organic stream sediment (Finland)					1600

Table 6.15. Average K concentrations in sediment (mg/kg) from the Tees and Wansbeck impoundments (stage 1 to 4 plus sum of stages of Tessier extraction scheme), and organic stream sediment (< 2 mm fraction, concentrated HNO_3 extraction; data from Lahermo et al. 1996).

Available K concentrations are higher in the sediment of the Wansbeck than the Tees impoundment, with the main difference being in the concentrations between exchangeable and carbonate bound phases (table 6.15 and figure 6.50). The difference is assumed to be due to the difference in K content of the overlying water columns in the impoundments (freshwater in the Tees as opposed to seawater in the Wansbeck). The higher K contents within the cores taken immediately upstream of the barrages in both impoundments is likely to be due to greater seawater influence at these points (even the "freshwater" Tees is observed to occasionally undergo seawater intrusion (see chapter 3)).

Within the sediments of both estuaries K is mainly held in the exchangeable phase, but the stage 2, and to a degree 3 and 4, extractable forms are also significant (figure 6.50).

Core KV from the Tees shows a relatively constant level of exchangeable K with depth in the sediment, whereas site TB shows an almost linear increase with depth down to the depth at which sand-dominated (and both lower moisture and clay content) pre-impoundment sediments are encountered where exchangeable K drops sharply (figure 6.51). This may be either a diffusion of mobile K at depth in the sediment towards the low (mean 3 mg/l) K water column or an ion exchange effect (see Mg below). Within the Wansbeck sediments a similar but smaller diffusion gradient is seen, but since sampling was during a period in which the seawater was overlying the sediment, a distinct increase in exchangeable K is seen close to the sediment surface (figure 6.52). Carbonate bound K in the Tees shows a very similar pattern to that of Ca and is likely to relate to the relative proportion of (flow controlled) carbonate inputs from the catchment to the sediment (figure 6.53). The profile for carbonate bound K in the Wansbeck shows a large amount of scatter but no significant trends with depth in the sediment (figure 6.54).

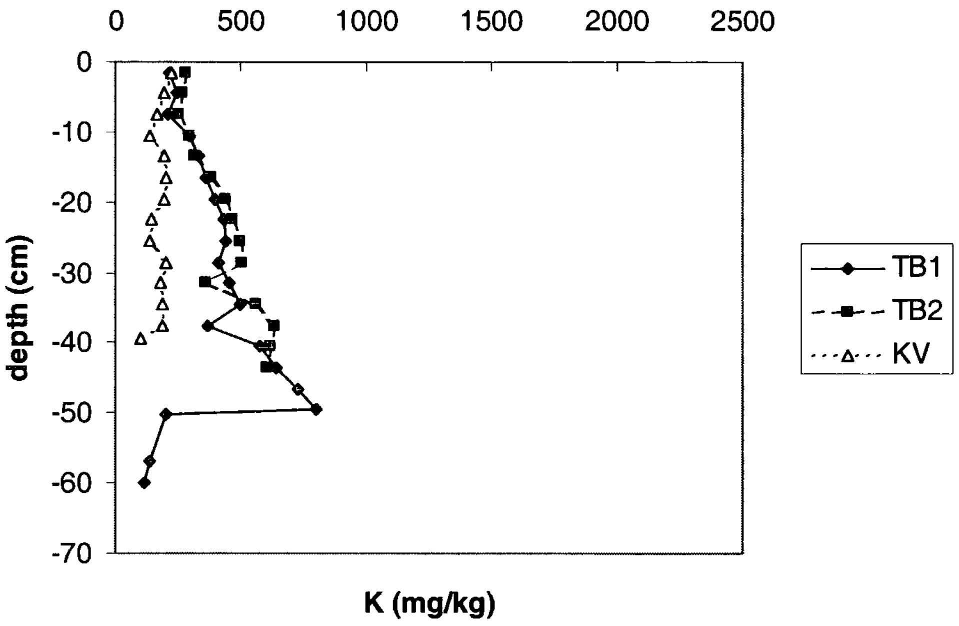


Figure 6.51. Stage 1 extractable K with depth in cores TB1, TB2 and KV from the Tees impoundment.

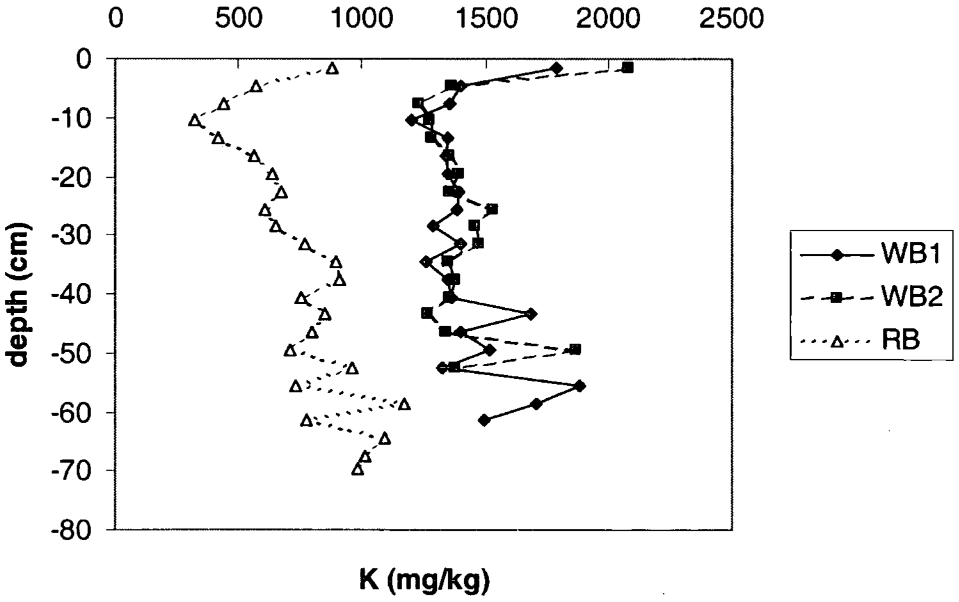


Figure 6.52. Stage 1 extractable K with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

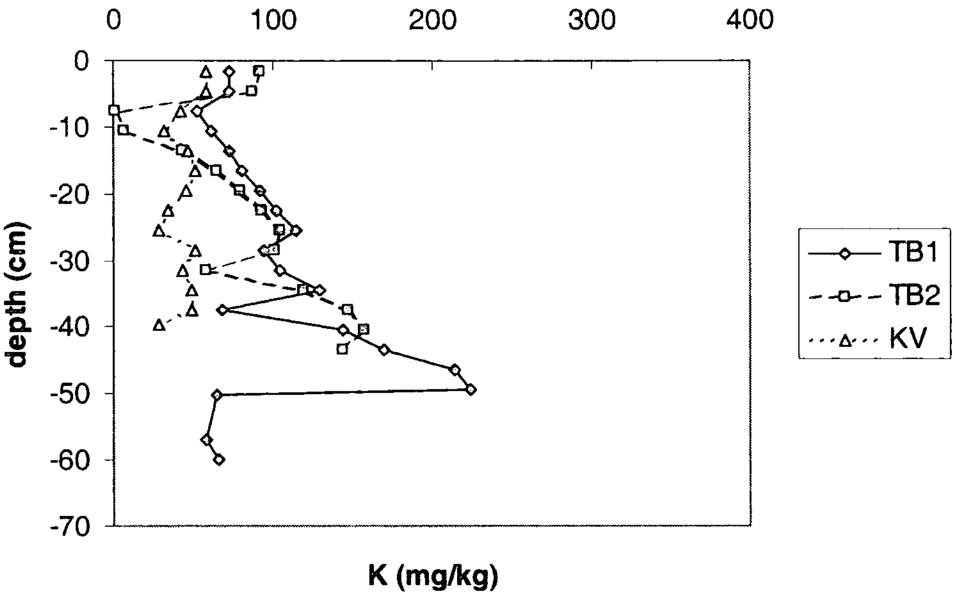


Figure 6.53. Stage 2 extractable K with depth in cores TB1, TB2 and KV from the Tees impoundment.

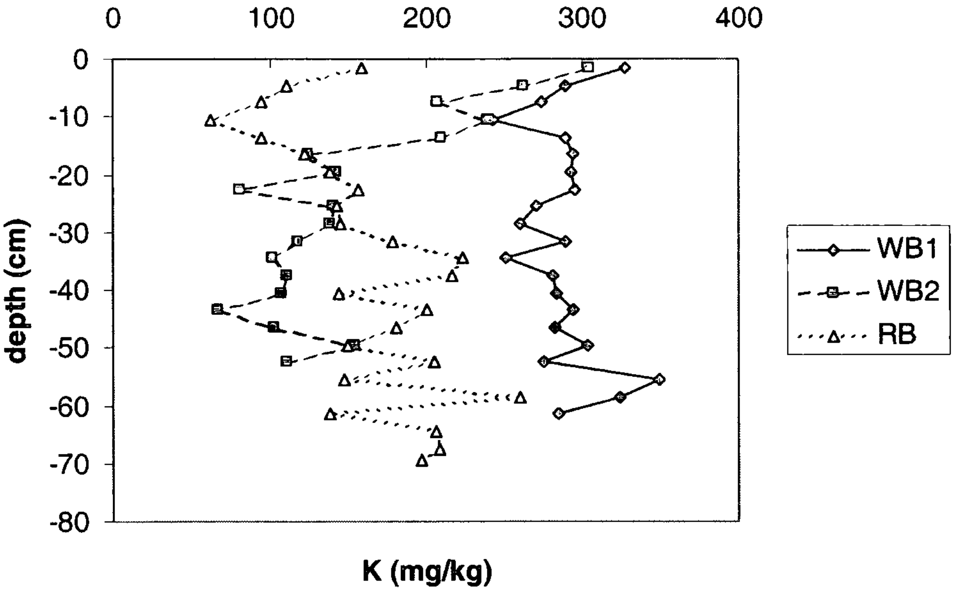


Figure 6.54. Stage 2 extractable K with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

6.7.4.8 Mg

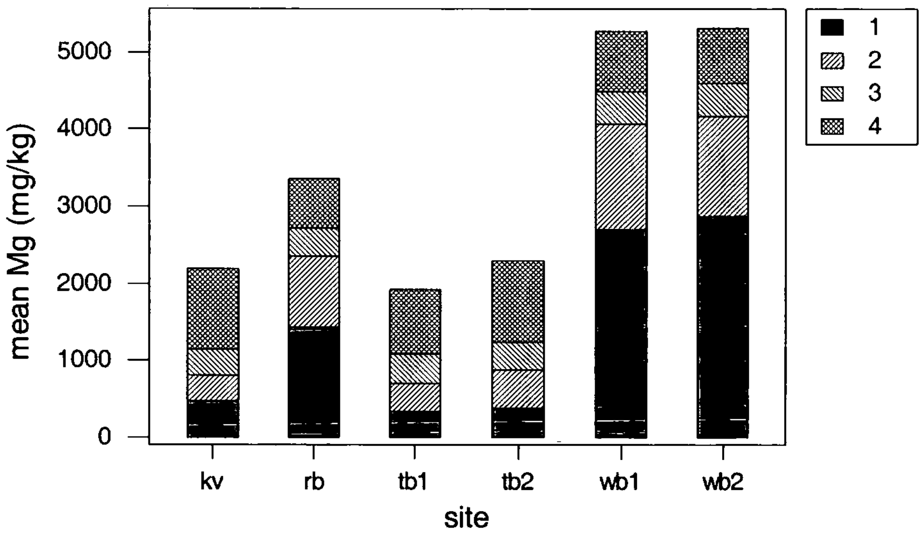


Figure 6.55. Mg concentration and speciation within the bottom sediments of the Tees and Wansbeck impoundments. Cores KV, TB1 and TB2 are from the Tees and cores RB, WB1 and WB2 are from the Wansbeck. Stages 1, 2, 3 and 4 of the sequential extraction scheme used represent exchangeable, carbonate bound, Fe and Mn bound and organic bound forms respectively.

Sediment	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Total**
Tees impoundment	387	403	459	969	2218
Wansbeck impoundment	2278	1175	406	712	4571
Organic stream sediment (Finland)					3800

Table 6.16. Average Mg concentrations in sediment (mg/kg) from the Tees and Wansbeck impoundments (stage 1 to 4 plus sum of stages of Tessier extraction scheme), and organic stream sediment (< 2 mm fraction, concentrated HNO_3 extraction; data from Lahermo et al. 1996).

As for K, available Mg concentrations are higher in the sediment of the Wansbeck than the Tees impoundment, with the main difference being in the concentrations between exchangeable and carbonate bound phases (table 6.16 and figure 6.55). The difference is assumed to be due to the difference in Mg content of the overlying water columns in the impoundments. Speciation of Mg is within all 4 phases modelled by the extraction procedure in sediments from both impoundments.

The profile for exchangeable Mg in the Tees sediment shows contrasting behaviour to that shown by K. Whereas K shows an increase with depth in the sediment Mg shows a strong decrease (figure 6.56). This may be due to ion exchange of K (which is generally at lower concentrations in the water body and has lower charge) by Mg (occurs at higher concentrations and has higher charge). The increase in Mg towards the sediment surface in cores from TB is approximately 27 mol/kg whilst the decrease in K is 14 mol/kg, implying that if this is an ion exchange effect then additional ions (Ca or Na) must be involved. Within the Wansbeck the profile for exchangeable Mg is constant with depth but with an increase due to the influence of seawater close to the sediment surface (figure 6.57). Carbonate bound Mg shows fluctuation but no trends with depth in the sediment in both impoundments (figures 6.58 and 6.59). Stage 3 extractable Mg is relatively constant with depth in the Tees but shows a greater concentration in the pre-impoundment sediment (figure 6.60), and shows a slight increase with depth in the Wansbeck sediment (figure 6.61). Stage 4 extractable Mg is also relatively constant with depth in the Tees but shows a lower concentration in pre-impoundment sediment (figure 6.62), and also shows a slight increase with depth in the Wansbeck sediment (figure 6.63).

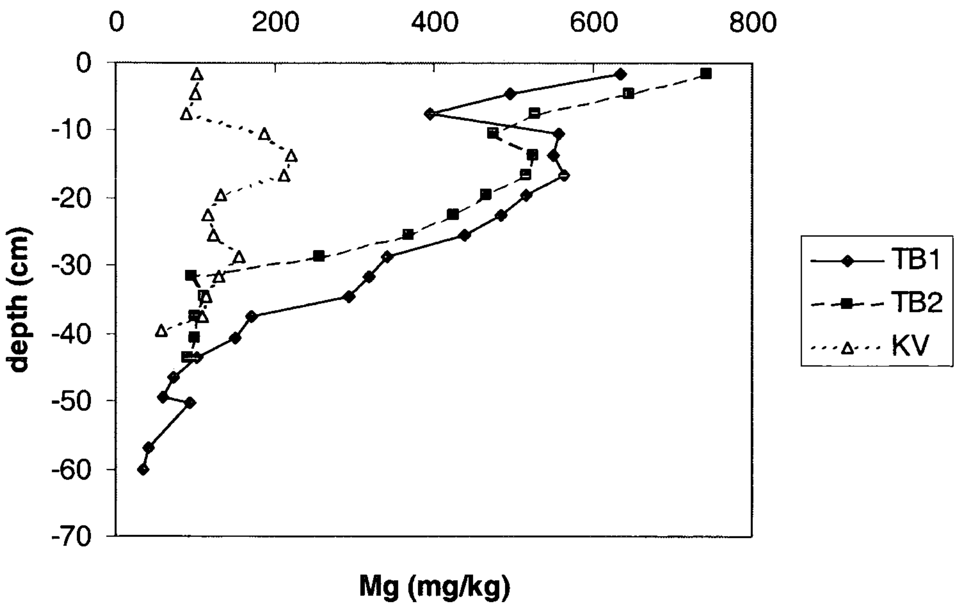


Figure 6.56. Stage 1 extractable Mg with depth in cores TB1, TB2 and KV from the Tees impoundment.

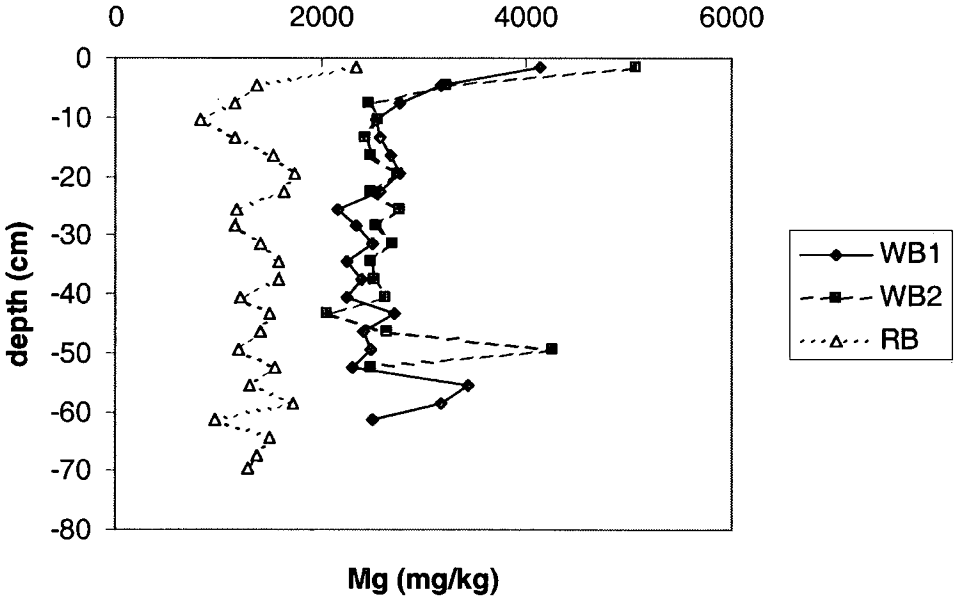


Figure 6.57. Stage 1 extractable Mg with depth in cores WB1, WB2 and RB from the Wansbeck impoundment (note different concentration scale to figure 6.56 above).

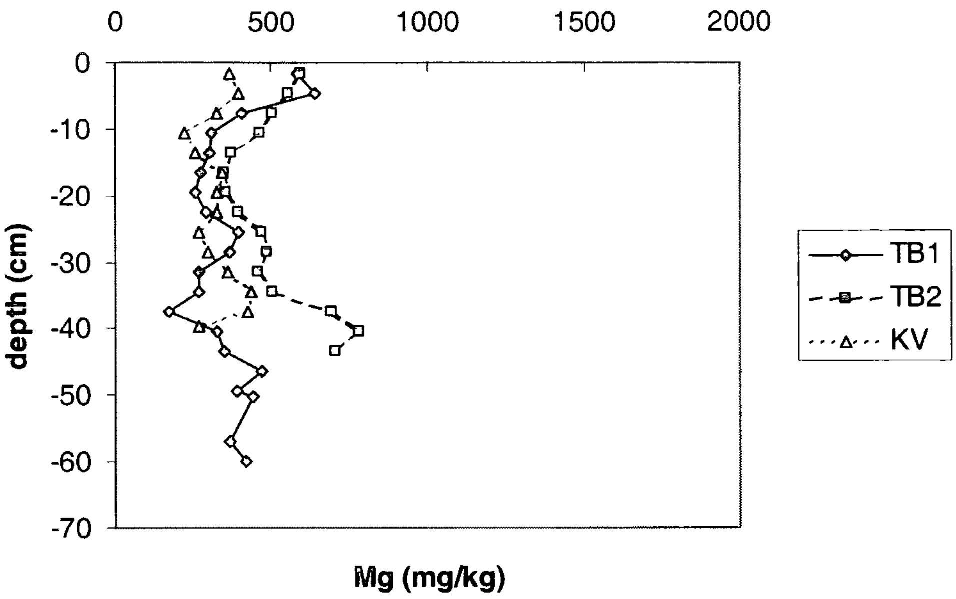


Figure 6.58. Stage 2 extractable Mg with depth in cores TB1, TB2 and KV from the Tees impoundment.

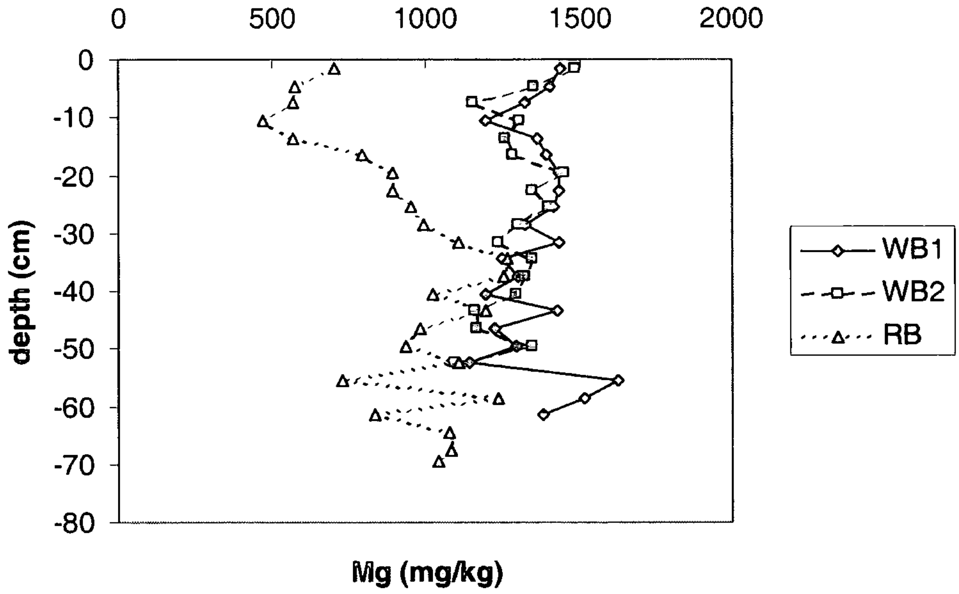


Figure 6.59. Stage 2 extractable Mg with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

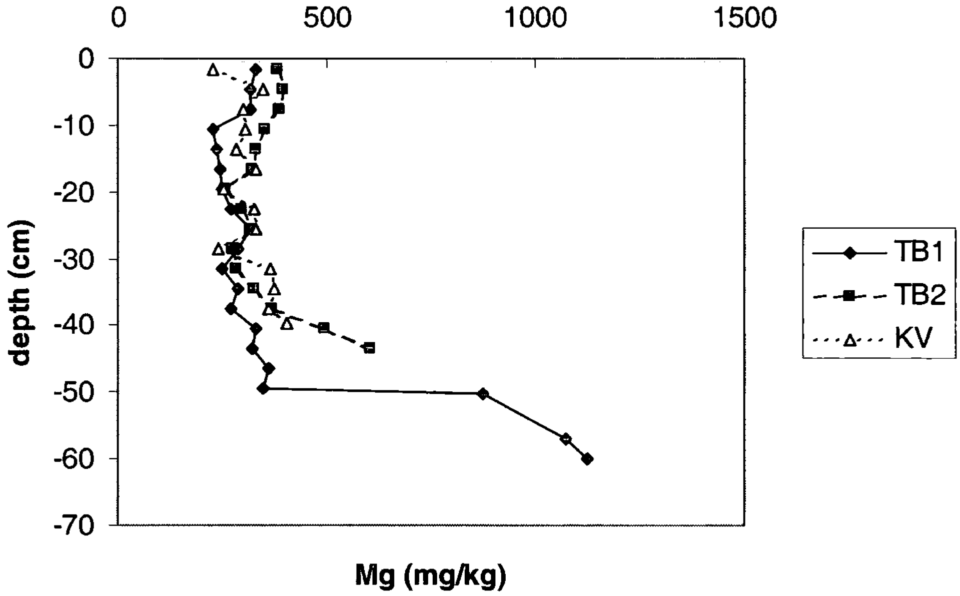


Figure 6.60. Stage 3 extractable Mg with depth in cores TB1, TB2 and KV from the Tees impoundment.

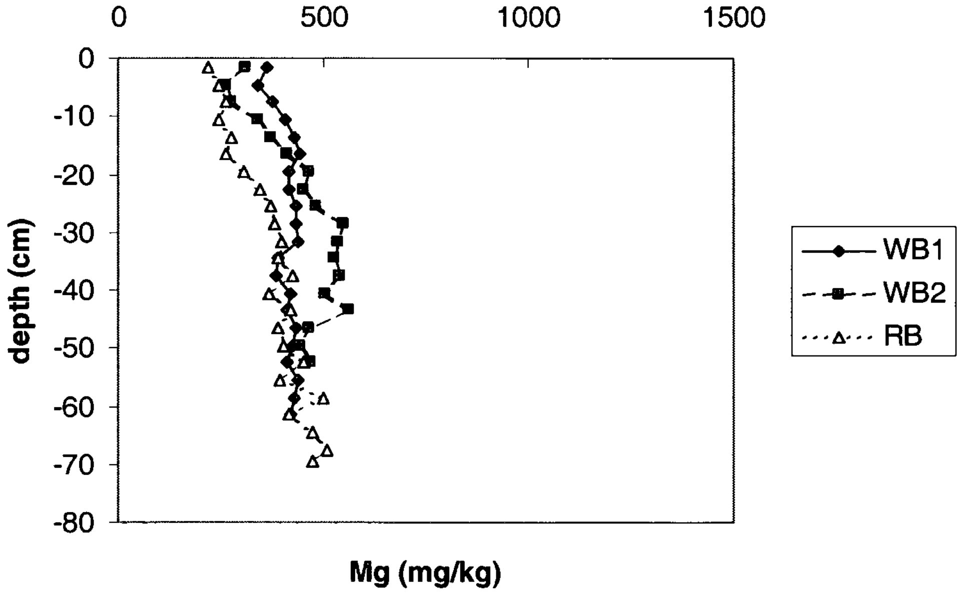


Figure 6.61. Stage 3 extractable Mg with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

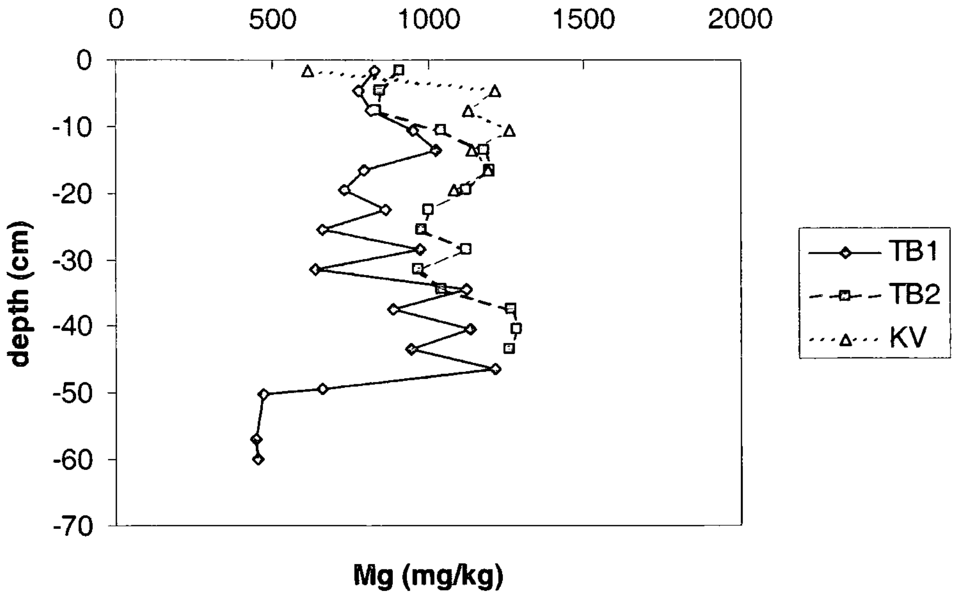


Figure 6.62. Stage 4 extractable Mg with depth in cores TB1, TB2 and KV from the Tees impoundment.

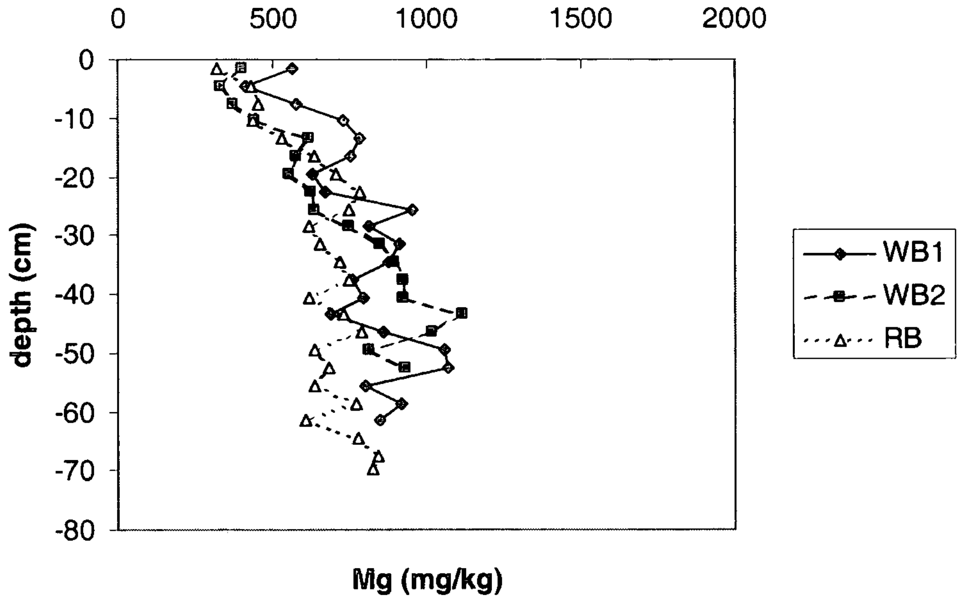


Figure 6.63. Stage 4 extractable Mg with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

6.7.4.9 Mn

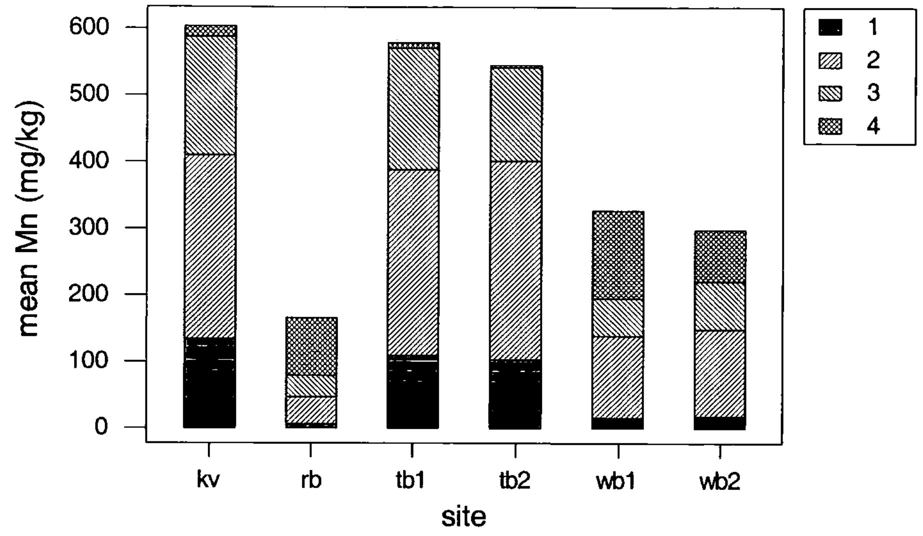


Figure 6.64. Mn concentration and speciation within the bottom sediments of the Tees and Wansbeck impoundments. Cores KV, TB1 and TB2 are from the Tees and cores RB, WB1 and WB2 are from the Wansbeck. Stages 1, 2, 3 and 4 of the sequential extraction scheme used represent exchangeable, carbonate bound, Fe and Mn bound and organic bound forms respectively.

Sediment	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Total**
Tees impoundment	115	284	168	10	577
Wansbeck impoundment	13	93	52	100	258
Organic stream sediment (Finland)					546
Humber estuary					1015

Table 6.17. Average Mn concentrations in sediment (mg/kg) from the Tees and Wansbeck impoundments (stage 1 to 4 plus sum of stages of Tessier extraction scheme), organic stream sediment (< 2 mm fraction, concentrated HNO_3 extraction; data from Lahermo et al. 1996), and Humber estuary (< 100 μm fraction, concentrated HNO_3 extraction; data from Bryan and Langston 1992).

Available Mn concentrations are higher in the sediment in the Tees than the Wansbeck impoundment (table 6.17). Mean Mn levels vary widely between UK estuaries, with concentrations in the Humber relatively high (mean Mn in the Tyne is 395 mg/kg for example; Bryan and Langston 1992).

The patterns of speciation for Mn differ between the impoundments (figure 6.64). Within the sediments of the Tees Mn is held exchangeably, bound with carbonates and bound in reducible form, with very little released in the oxidisable phase. Within the sediment of the Wansbeck Mn is held bound with carbonates, bound in reducible form and bound in the oxidisable phase, with very little held exchangeably.

Assuming that conditions are not significantly altered during sampling and pre-treatment, then the exchangeable Mn fraction represents the amount of (dissolved) Mn^{2+} in the sediment. Mn solubility is redox controlled, such that Mn^{2+} is released when Mn-oxides are used as secondary oxidants for the breakdown of organic matter as dissolved oxygen levels fall (see chapter 4). The profiles for exchangeable Mn thus represent the redox conditions within the sediment, with maxima approximating the depth at which maximum use of Mn as an electron acceptor is occurring. Within the Tees this is at approximately 15 cm at both sites sampled, and within the Wansbeck it is approximately 7 cm at the barrage site and almost at the surface at site RB (figures 6.65 and 6.66). The profiles are typical of organic rich anoxic nearshore sediments (Heggie et al., 1987; Upstill-Goddard et al., 1989). The depths of Mn maxima represent the relative anoxia in the sediments of the impoundments, with oxygen reaching greater depths in the sediment profile in the Tees, and anoxic conditions at the sediment-water column interface at site RB within the Wansbeck. The profiles for both carbonate and oxide bound Mn show a similar pattern to that of exchangeable Mn (figures 6.67, 6.68, 6.69 and 6.70), implying that either Mn is depleted at depth where Mn has already been released from the sediment or that on pre-treatment of the samples exposure of oxidising conditions caused precipitation of solid phases (particularly oxides) of Mn. Very little Mn is held in the oxidisable phase in the Tees (figure 6.71), but in the Wansbeck Mn in the oxidisable phase (assumed to be associated with organic material) shows an increase with depth (figure 6.72).

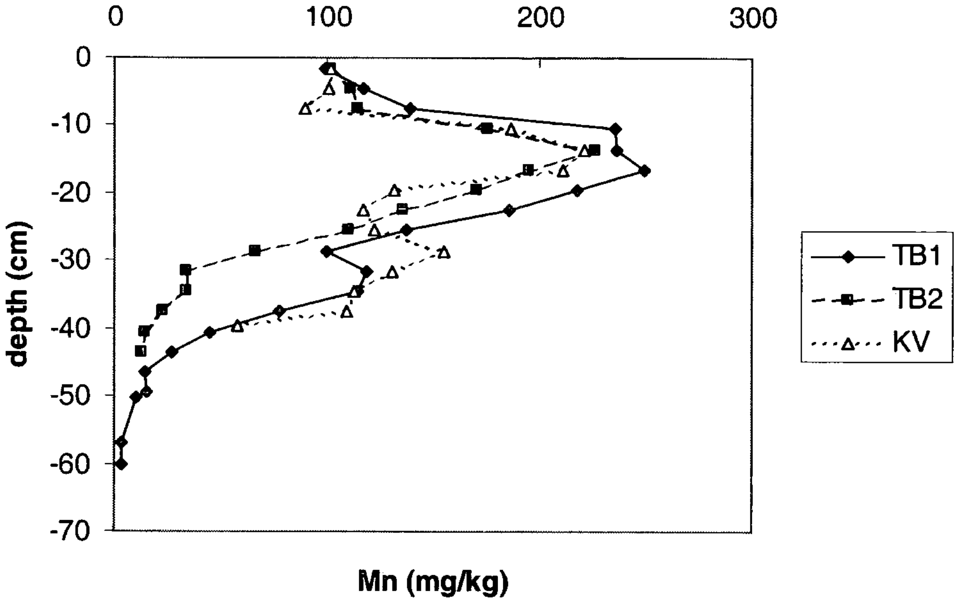


Figure 6.65. Stage 1 extractable Mn with depth in cores TB1, TB2 and KV from the Tees impoundment.

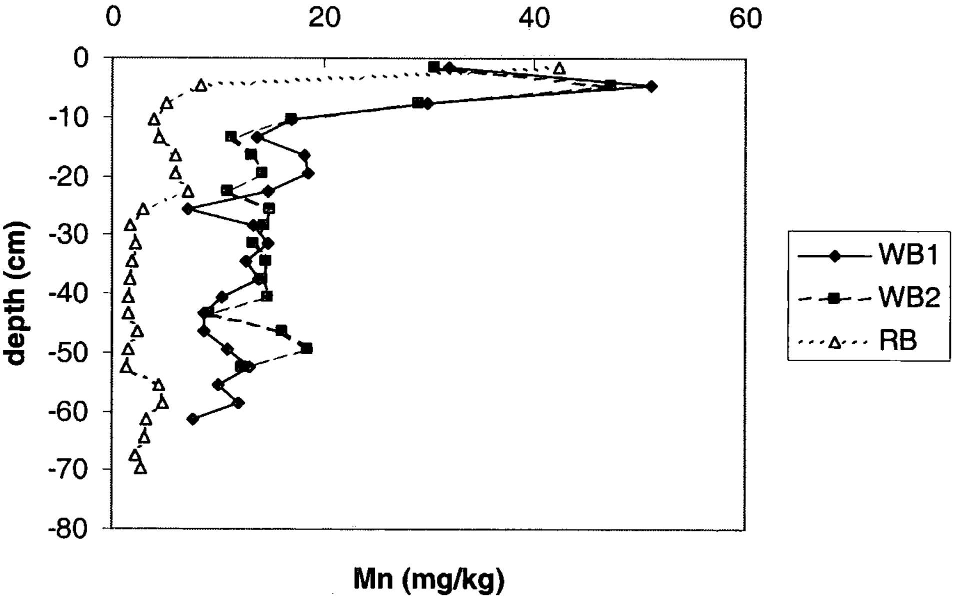


Figure 6.66. Stage 1 extractable Mn with depth in cores WB1, WB2 and RB from the Wansbeck impoundment (note different concentration scale to figure 6.65 above).

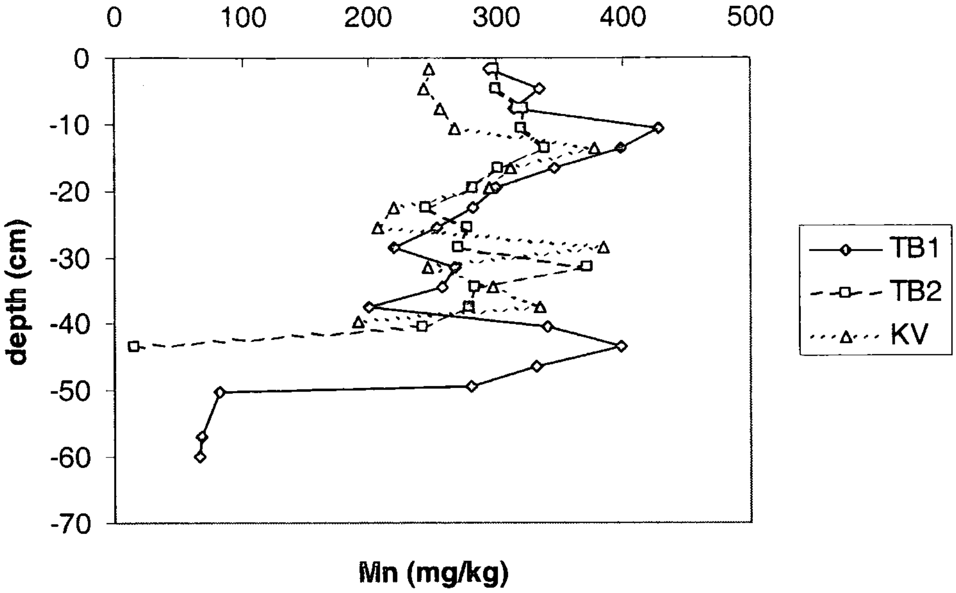


Figure 6.67. Stage 2 extractable Mn with depth in cores TB1, TB2 and KV from the Tees impoundment.

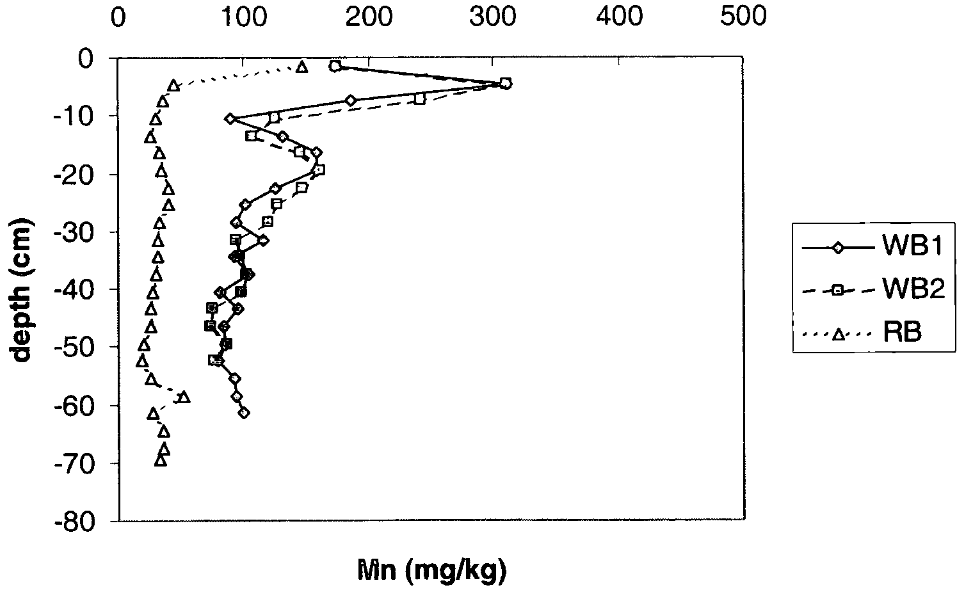


Figure 6.68. Stage 2 extractable Mn with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

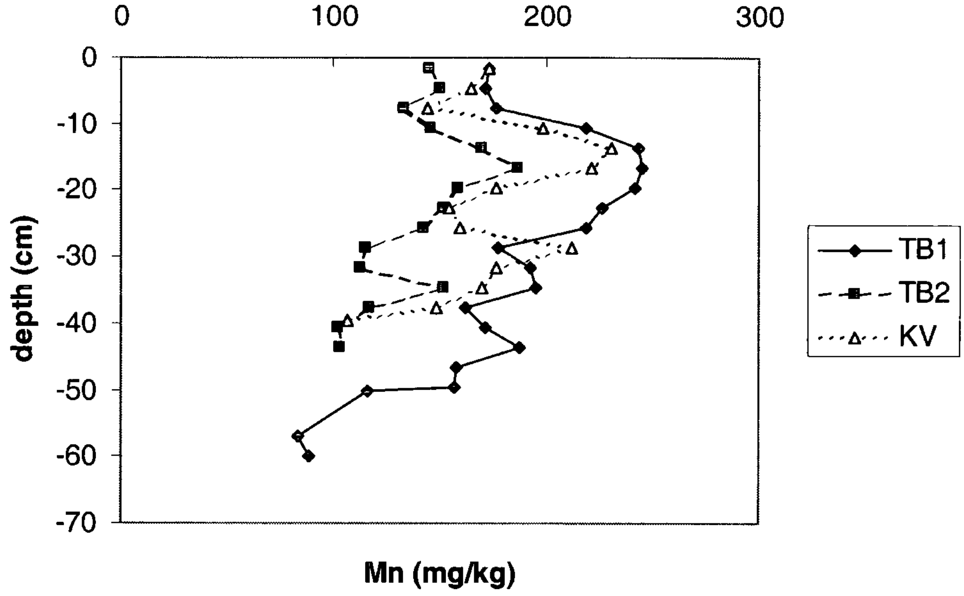


Figure 6.69. Stage 3 extractable Mn with depth in cores TB1, TB2 and KV from the Tees impoundment.

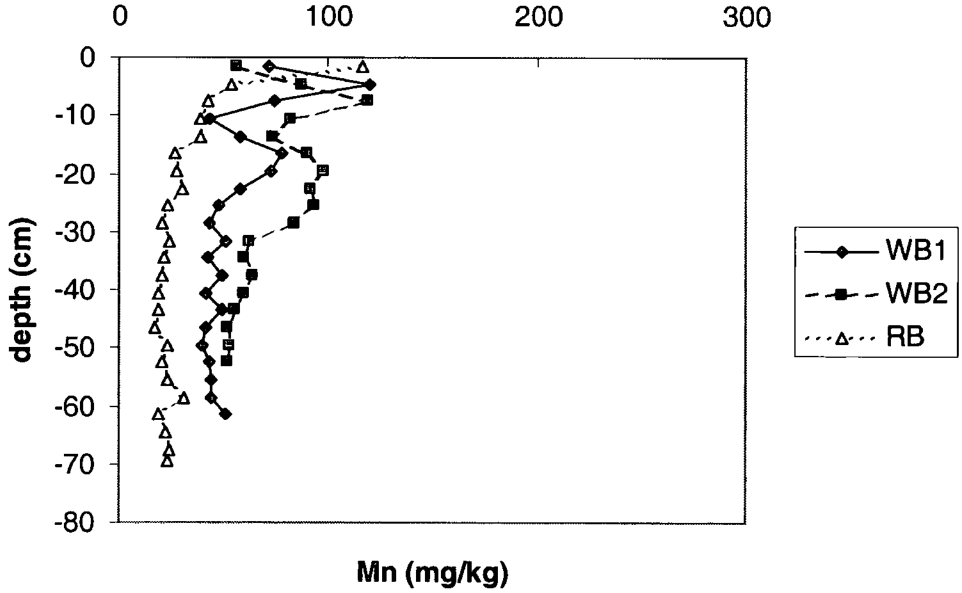


Figure 6.70. Stage 3 extractable Mn with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

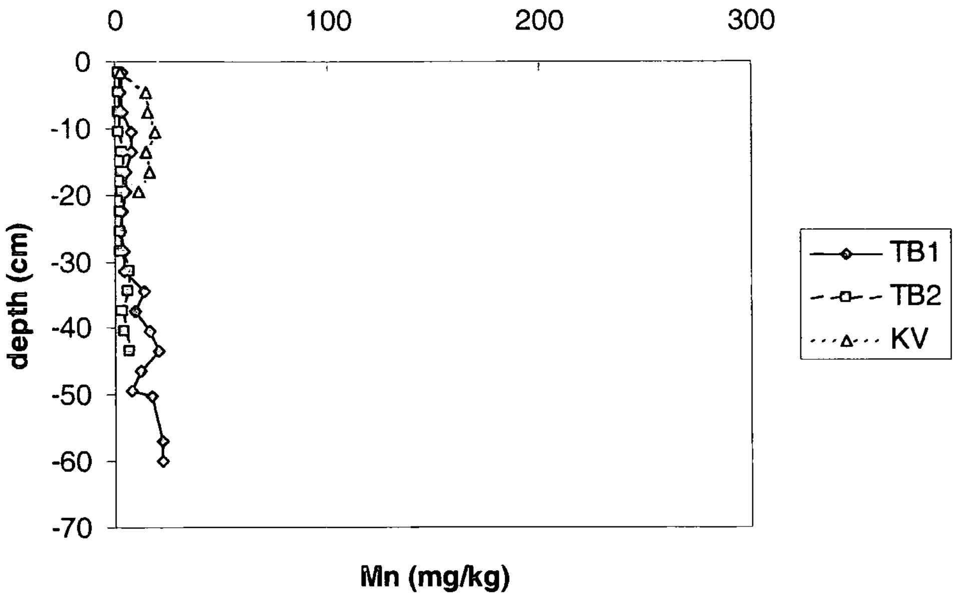


Figure 6.71. Stage 4 extractable Mn with depth in cores TB1, TB2 and KV from the Tees impoundment.

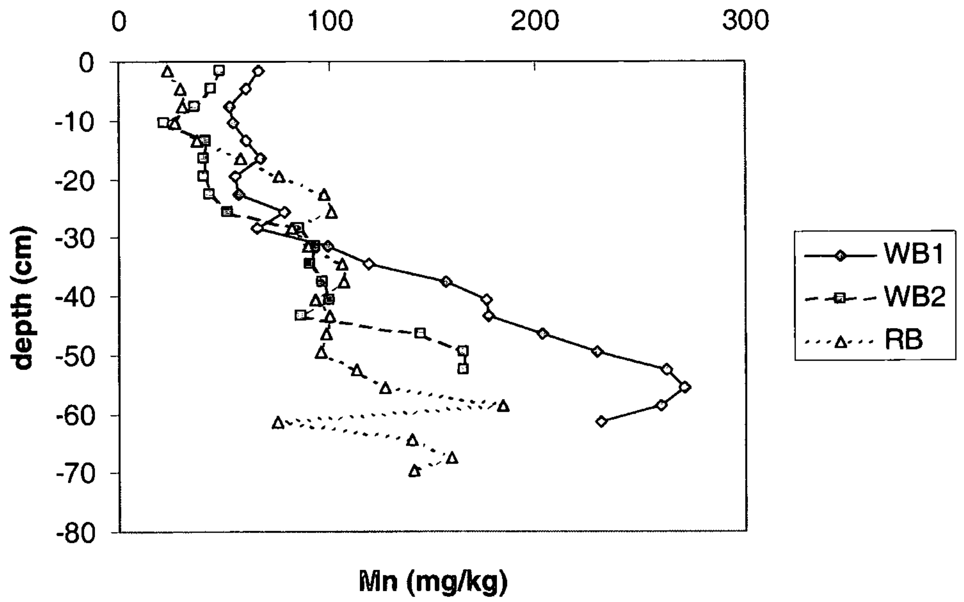


Figure 6.72. Stage 4 extractable Mn with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

6.7.4.10 Ni

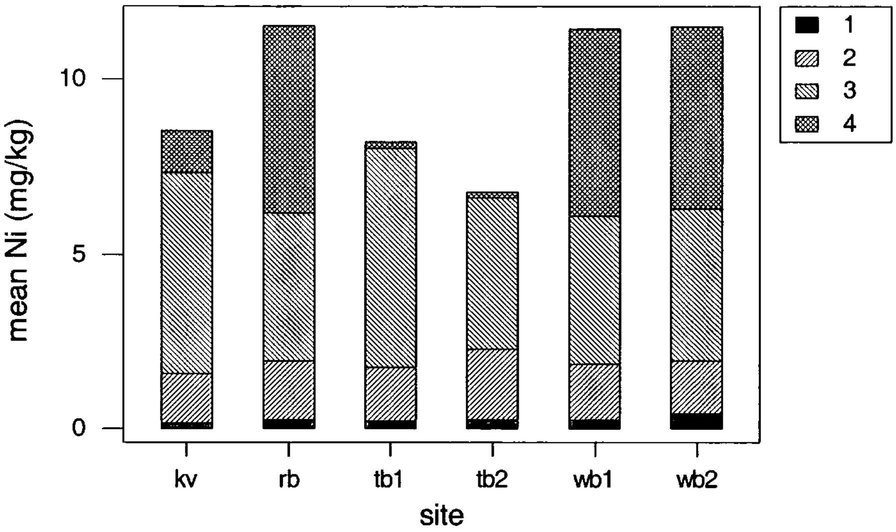


Figure 6.73. Ni concentration and speciation within the bottom sediments of the Tees and Wansbeck impoundments. Cores KV, TB1 and TB2 are from the Tees and cores RB, WB1 and WB2 are from the Wansbeck. Stages 1, 2, 3 and 4 of the sequential extraction scheme used represent exchangeable, carbonate bound, Fe and Mn bound and organic bound forms respectively.

Sediment	Stage 1	Stage 2	Stage 3	Stage 4	Total
Tees impoundment	0.22	1.65	5.54	0.46	7.87
Wansbeck impoundment	0.30	1.61	4.29	5.30	11.50
Organic stream sediment (Finland)					13.9
Tees estuary downstream of barrage					41
River Tees upstream of impoundment					36
Humber estuary					39

Table 6.18. Average Ni concentrations in sediment (mg/kg) from the Tees and Wansbeck impoundments (stage 1 to 4 plus sum of stages of Tessier extraction scheme), organic stream sediment (< 2 mm fraction, concentrated HNO_3 extraction; data from Lahermo et al. 1996), Tees estuary sediment from downstream of barrage

(total extraction; data from Jones and Turki 1997), River Tees sediment upstream of impoundment (< 63 μm fraction, total extraction; data from EA), and Humber estuary (< 100 μm fraction, concentrated HNO_3 extraction; data from Bryan and Langston 1992).

Available Ni concentrations are slightly higher in the Wansbeck than the Tees impoundment, mainly due to the fraction held in the oxidisable fraction (table 6.18 and figure 6.73). Concentrations are much lower than those reported for downstream of the barrage in the Tees estuary for total Ni, although approximately half the concentration of available (stage 1 to 4 of Tessier et al. (1979) extraction scheme) found downstream since the majority of Ni is held in residual (non-available) forms (Jones and Turki 1997).

Very little Ni is held exchangeably within the sediment of either impoundment, similar quantities of Ni are removed by extraction stages 2 and 3 in both impoundments, and stage 4 extractable Ni is only a significant fraction in the Wansbeck impoundment (figure 6.73).

The profile for carbonate bound Ni in the sediment of the Tees impoundment shows a similar pattern to that shown for Ca, with a peak in the sedimentation following impoundment, interpreted as due to high flow related high carbonate input (figure 6.74). The carbonate bound Ni profile in the Wansbeck is more constant with depth (figure 6.75). The profiles for stage 3 and stage 4 extractable Ni within the impoundments show the same pattern as that shown by Fe (and several other heavy metals), with the clearest trend being an increase in the stage 4 extractable portion with depth in the Wansbeck (figures 6.76, 6.77, 6.78 and 6.79).

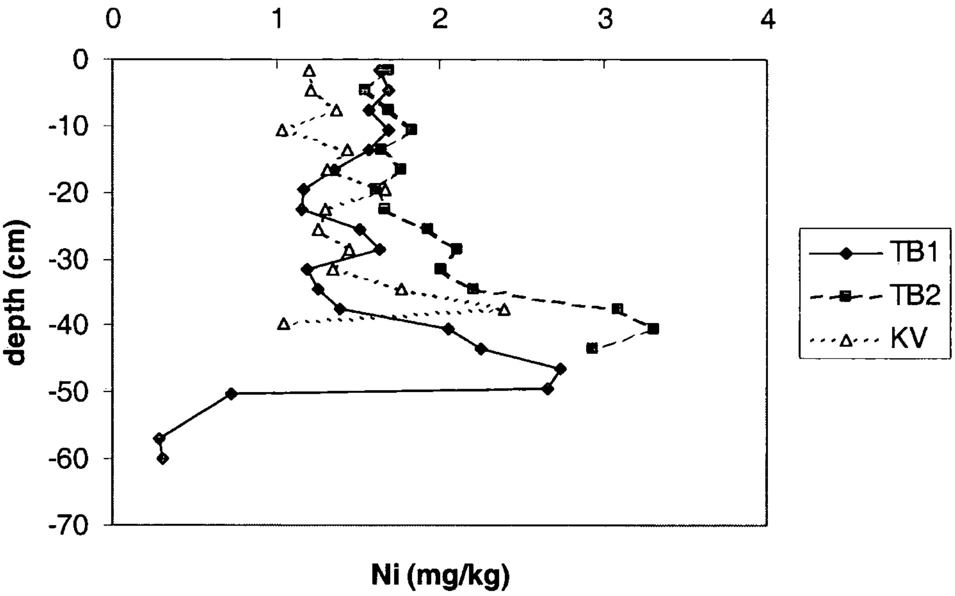


Figure 6.74. Stage 2 extractable Ni with depth in cores TB1, TB2 and KV from the Tees impoundment.

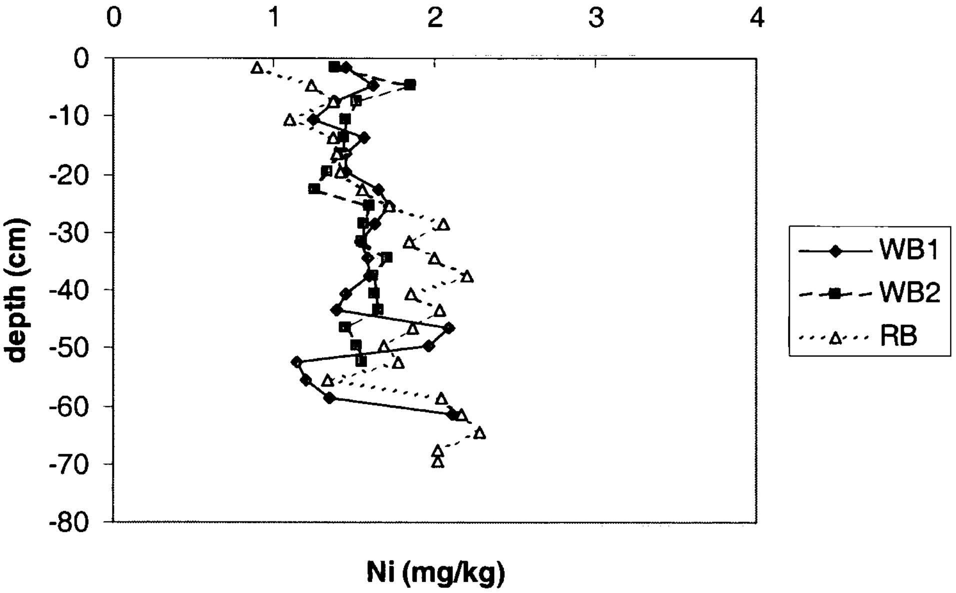


Figure 6.75. Stage 2 extractable Ni with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

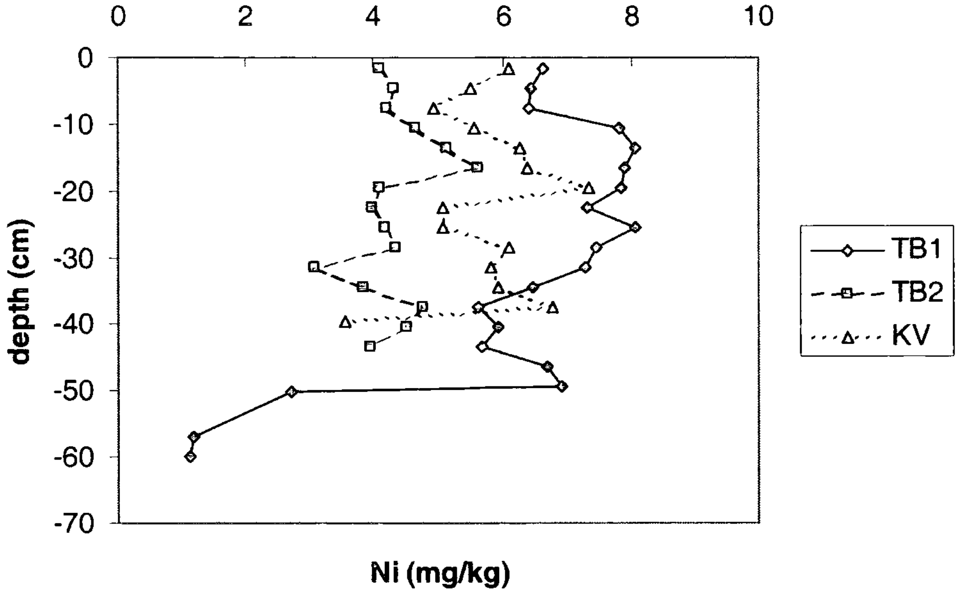


Figure 6.76. Stage 3 extractable Ni with depth in cores TB1, TB2 and KV from the Tees impoundment.

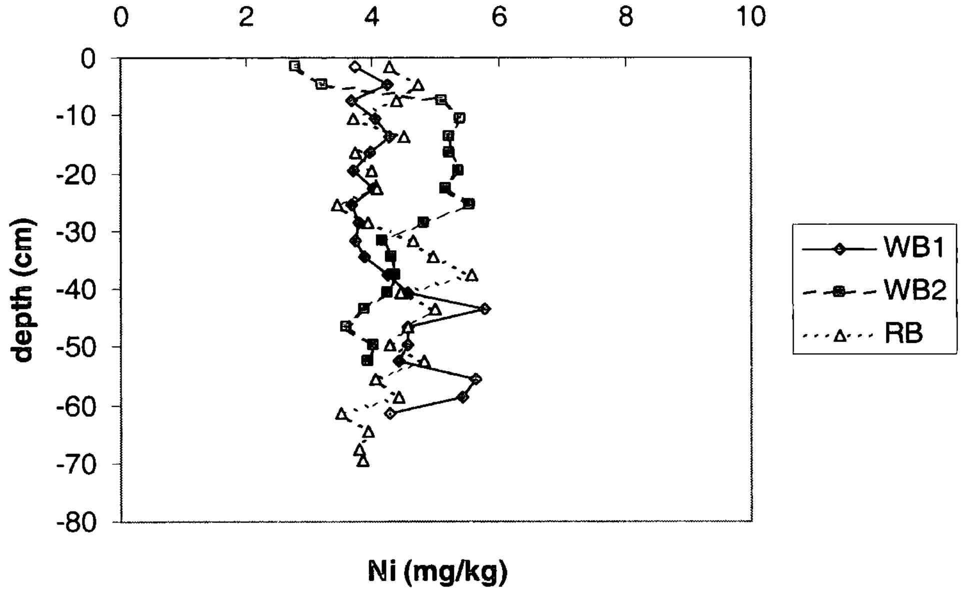


Figure 6.77. Stage 3 extractable Ni with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

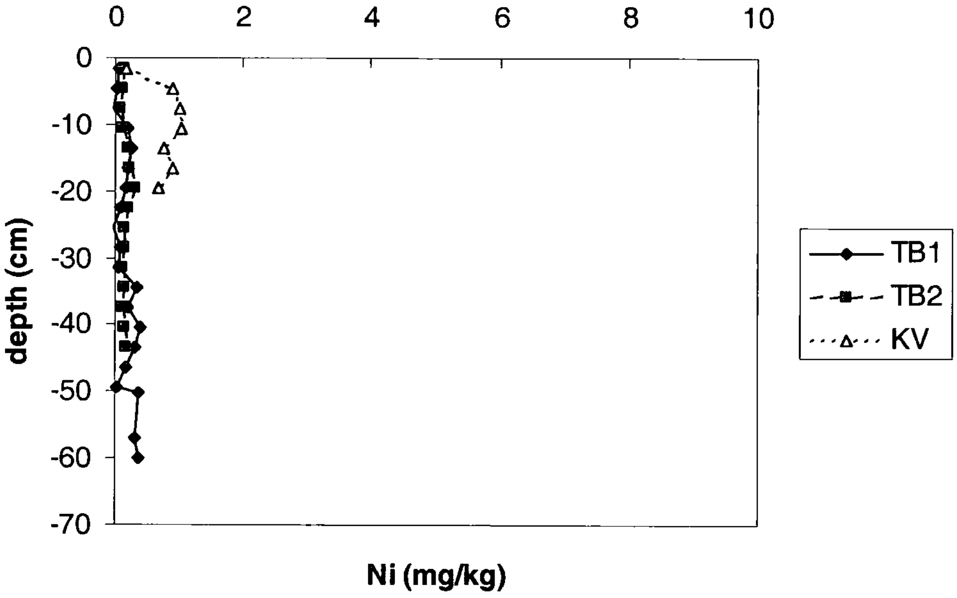


Figure 6.78. Stage 4 extractable Ni with depth in cores TB1, TB2 and KV from the Tees impoundment.

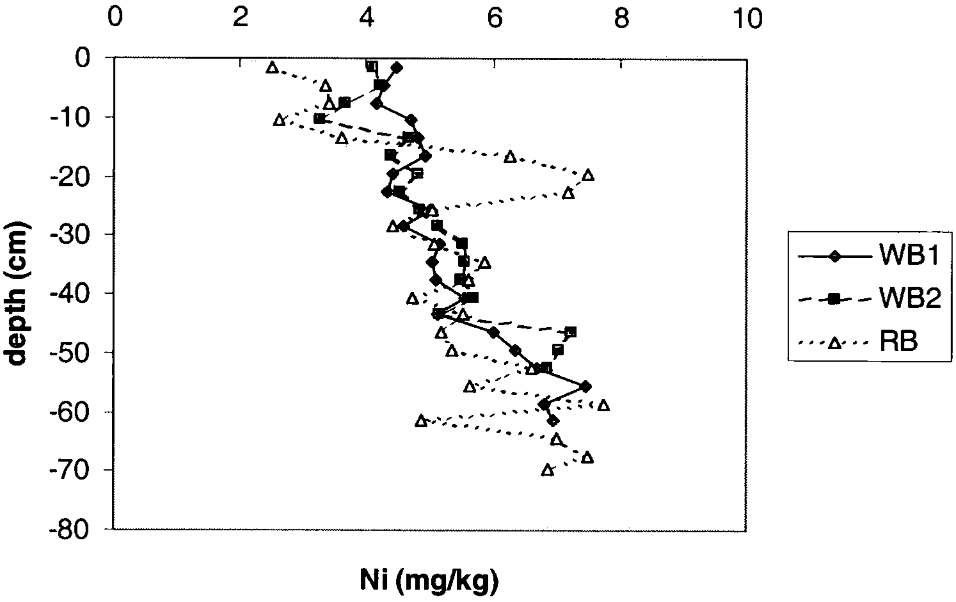


Figure 6.79. Stage 4 extractable Ni with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

6.7.4.11 P

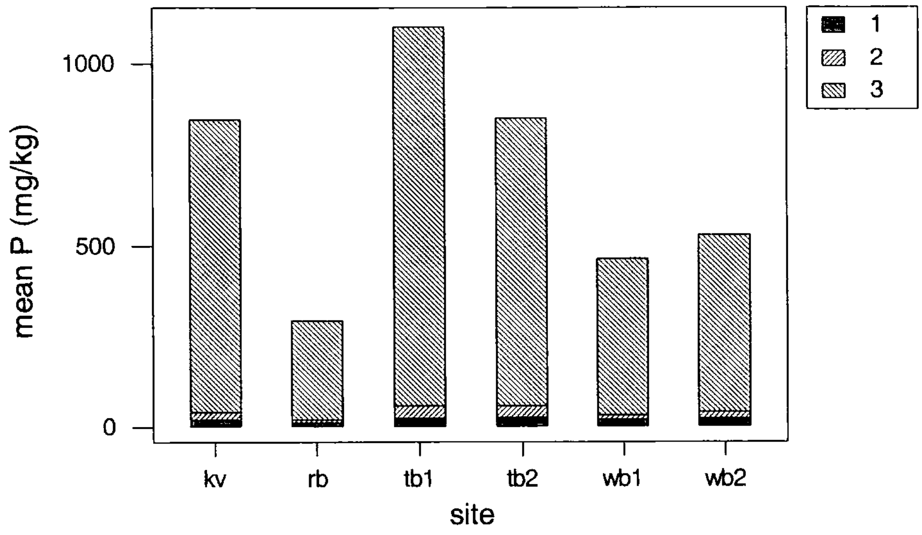


Figure 6.80. P concentration and speciation within the bottom sediments of the Tees and Wansbeck impoundments. Cores KV, TB1 and TB2 are from the Tees and cores RB, WB1 and WB2 are from the Wansbeck. Stages 1, 2, 3 and 4 of the sequential extraction scheme used represent exchangeable, carbonate bound, Fe and Mn bound and organic bound forms respectively. Note no data are available for stage 4 of the extraction procedure for P.

Sediment	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Total**
Tees impoundment	23	29	898	*	950
Wansbeck impoundment	17	12	389	*	418
Organic stream sediment (Finland)					870

Table 6.19. Average P concentrations in sediment (mg/kg) from the Tees and Wansbeck impoundments (stage 1 to 4 plus sum of stages of Tessier extraction scheme), and organic stream sediment (< 2 mm fraction, concentrated HNO_3 extraction; data from Lahermo et al. 1996). (* = data not available due to analytical problems).

P levels are higher in the sediment of the Tees than the Wansbeck impoundment (table 6.19), with mean concentration of P approaching 1 ‰ by mass in the sediments in this river.

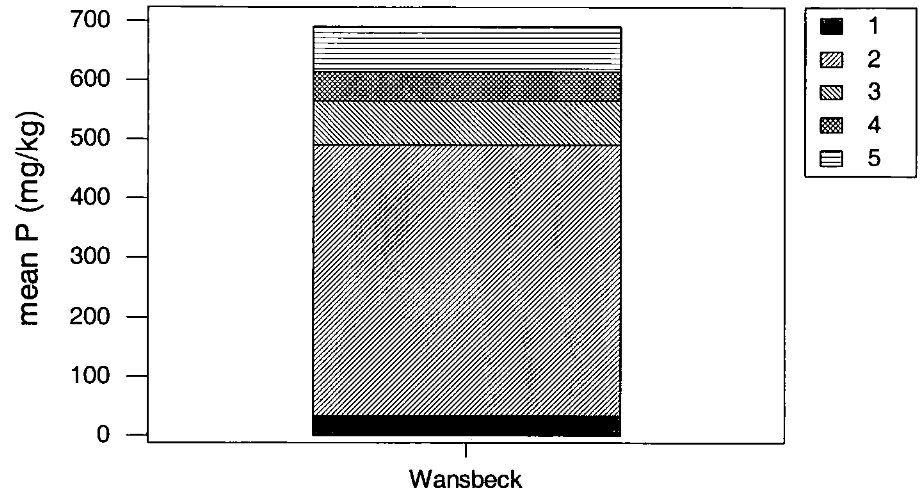


Figure 6.81. P concentration and speciation within the surficial sediments of the Wansbeck impoundment. Stages 1, 2, 3, 4 and 5 represent the exchangeable or loosely sorbed, Fe-bound, authigenic apatite plus carbonate bound plus biogenic apatite, detrital apatite plus other organic P and organic P phases of Ruttenberg's (1992) SEDEX sequential extraction procedure for P.

Little P is held exchangeably or stage 2 extractably in the sediments of either impoundment. The majority of P appears to be held in the stage 3 extractable phase (figure 6.80), although due to analytical problems unfortunately no results are available for the stage 4 extract for the Tessier et al. (1979) extraction experiments. Surficial sediments from the Wansbeck underwent sequential extraction using the SEDEX scheme of Ruttenberg (1992) (developed specifically for P) to ensure that results from the Tessier et al. (1979) procedure (which was developed for trace metals) accurately represented P speciation. The results (figure 6.81) confirm that the main species of P within the sediments is Fe-bound and that the main extraction procedure used adequately models P speciation, and in addition that a small amount of P is held in the oxidisable/organic phase. Davies (1997) reports that ferric-bound P is the major fraction in most lake sediments, accounting for over 50 % of the total mass of P.

Both stage 3 extractable Fe and P show an increase towards the sediment-water column interface from approximately 15 cm depth in core RB, which may imply that less reducing conditions at this point allow precipitation of Fe hydroxide and immobilisation of P (figure 6.82). The profiles for Fe and Mn oxide bound P within the sediments show relatively high variation with depth in both impoundments and approximately follow the profiles for stage 3 extractable Fe (figures 6.83 and 6.84). P concentrations are significantly lower in the pre-impoundment sediment of the Tees.

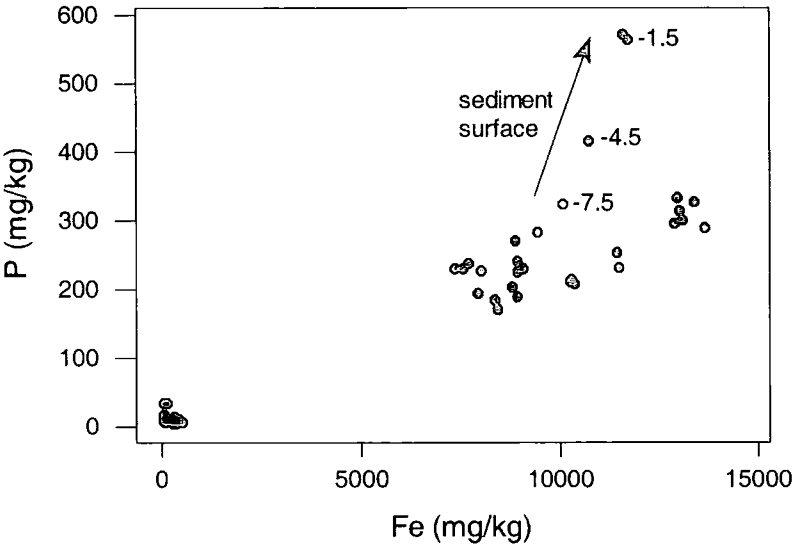


Figure 6.82. The relationship between P and Fe in sediment from site RB in the Wansbeck impoundment, showing enrichment of sediment in Fe-oxide and associated P at the surface of the sediments. Data labels show depth (cm) within sediment core.

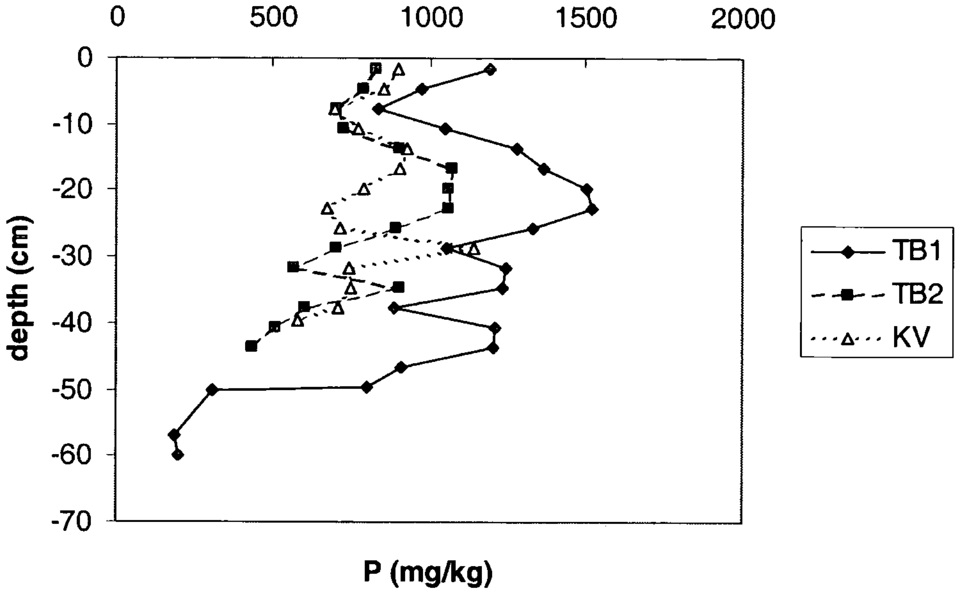


Figure 6.83. Stage 3 extractable P with depth in cores TB1, TB2 and KV from the Tees impoundment.

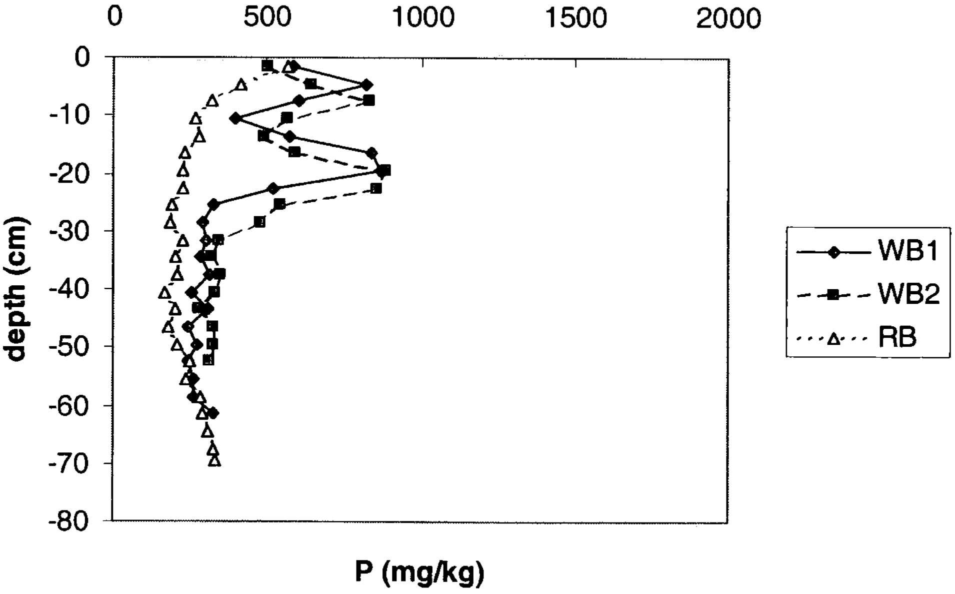


Figure 6.84. Stage 3 extractable P with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

6.7.4.12 Sc

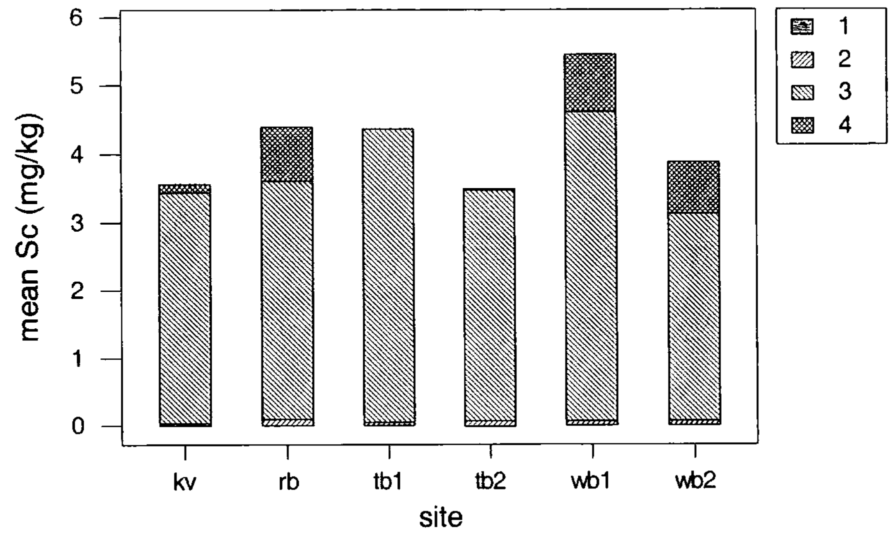


Figure 6.85. Sc concentration and speciation within the bottom sediments of the Tees and Wansbeck impoundments. Cores KV, TB1 and TB2 are from the Tees and cores RB, WB1 and WB2 are from the Wansbeck. Stages 1, 2, 3 and 4 of the sequential extraction scheme used represent exchangeable, carbonate bound, Fe and Mn bound and organic bound forms respectively.

Sediment	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Total**
Tees impoundment	0.00	0.05	3.78	0.03	3.86
Wansbeck impoundment	0.00	0.07	3.73	0.80	4.60
Organic stream sediment (Finland)					4.6

Table 6.20. Average Sc concentrations in sediment (mg/kg) from the Tees and Wansbeck impoundments (stage 1 to 4 plus sum of stages of Tessier extraction scheme), and organic stream sediment (< 2 mm fraction, concentrated HNO_3 extraction; data from Lahermo et al. 1996).

Unlike other transition metals Sc has a single oxidation state (Sc^{3+}) and shows similar behaviour in the environment to Al (Reimann and Caritat, 1998). Levels of available Sc are slightly higher in the sediment of the Wansbeck than the Tees impoundment, and comparable to the mean concentration in organic rich sediment (table 6.20 and figure 6.85).

The pattern of speciation for Sc is similar to that of Fe and Al, etc. Very little Sc is held exchangeably or carbonate bound, the stage 3 extractable phase is the dominant species for Sc in both impoundments, and a portion of Sc is held in the stage 4 extractable phase in the Wansbeck but not in the Tees.

The profiles for stage 3 and stage 4 extractable Sc are similar to those for Fe, with the distinctive patterns being a lower stage 3 extractable, but higher stage 4 extractable, content in the pre-impoundment sediment in the Tees, and a general increase in stage 4 extractable Sc with depth in the Wansbeck (figures 6.86, 6.87, 6.88 and 6.89).

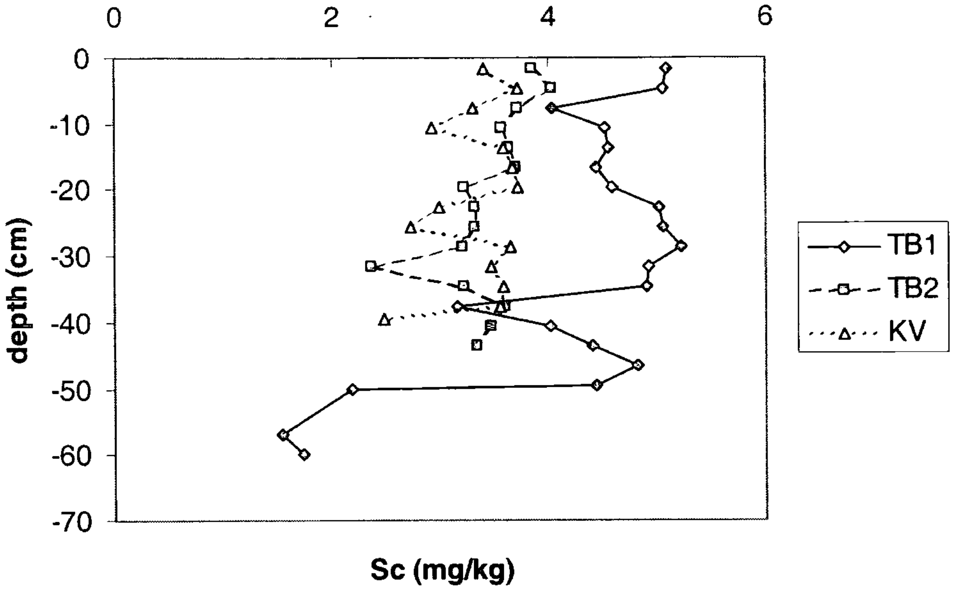


Figure 6.86. Stage 3 extractable Sc with depth in cores TB1, TB2 and KV from the Tees impoundment.

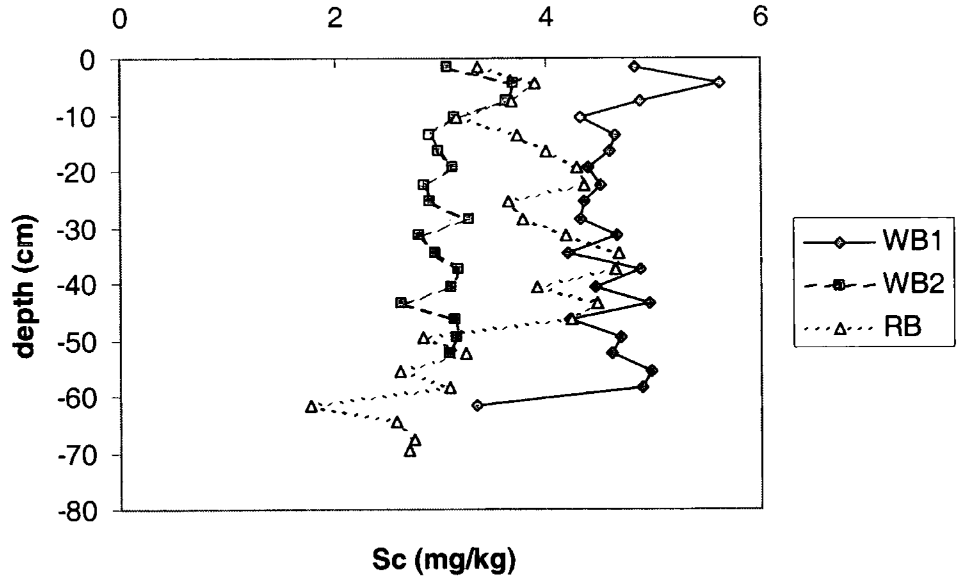


Figure 6.87 Stage 3 extractable Sc with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

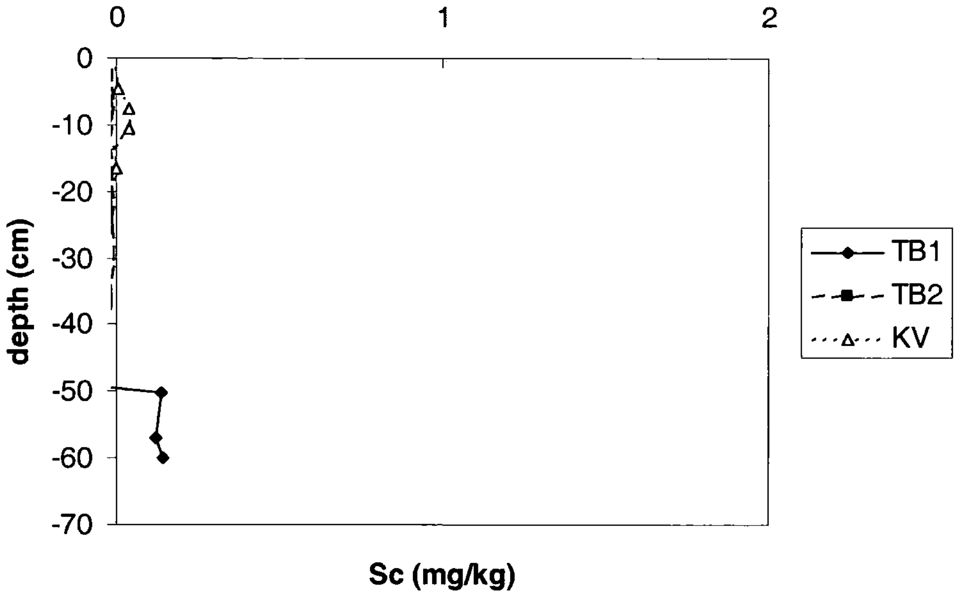


Figure 6.88. Stage 4 extractable Sc with depth in cores TB1, TB2 and KV from the Tees impoundment.

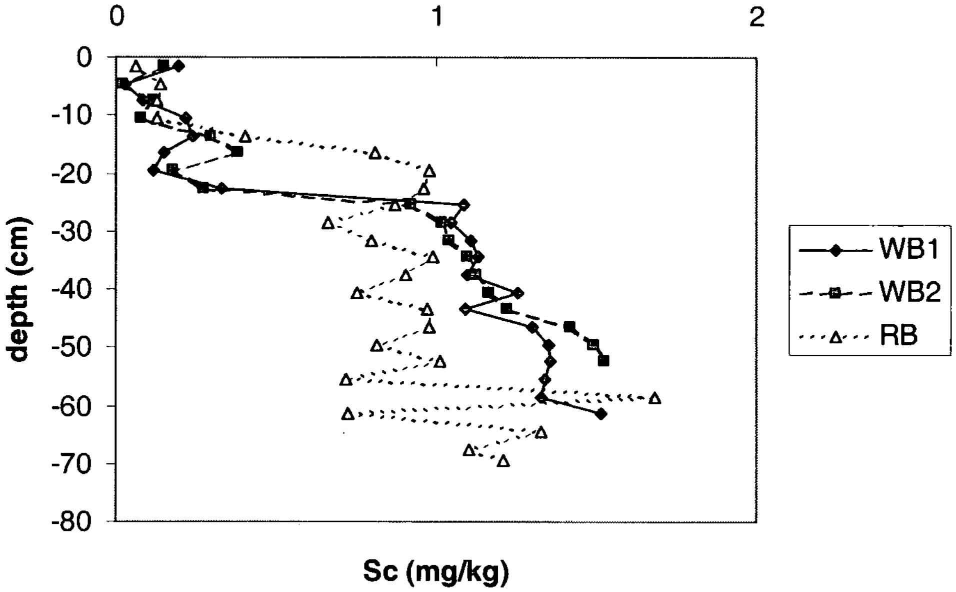


Figure 6.89. Stage 4 extractable Sc with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

6.7.4.13 Si

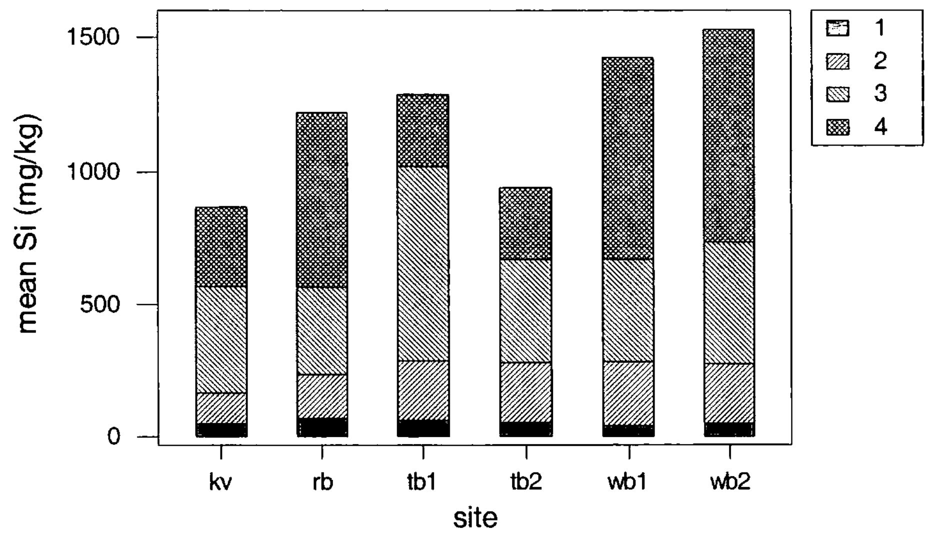


Figure 6.90. Si concentration and speciation within the bottom sediments of the Tees and Wansbeck impoundments. Cores KV, TB1 and TB2 are from the Tees and cores RB, WB1 and WB2 are from the Wansbeck. Stages 1, 2, 3 and 4 of the sequential extraction scheme used represent exchangeable, carbonate bound, Fe and Mn bound and organic bound forms respectively.

Sediment	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Total**
Tees impoundment	55	193	534	278	1060
Wansbeck impoundment	53	208	386	732	1379

Table 6.21. Average Si concentrations in sediment (mg/kg) from the Tees and Wansbeck impoundments (stage 1 to 4 plus sum of stages of Tessier extraction scheme).

Available Si concentrations are slightly higher in the sediments of the Wansbeck than the Tees impoundment (table 6.21 and figure 6.90). Only a small amount of Si is found exchangeably in the sediments of either impoundment. Significant quantities of Si are released during stage 2, 3 and 4 of the sequential extraction procedure.

The profiles for the carbonate bound phase show that Si is relatively constant to about 40 cm depth in the sediment in the Tees impoundment, but shows higher concentrations below this level (figure 6.91). This is interpreted as a combined grain-size and carbonate input effect, with higher levels in the coarser grained pre-impoundment sediment followed by high carbonate input to the overlying sediment due to high flow conditions during 1995. Within the Wansbeck stage 2 extractable Si (as with particle size) remains relatively constant with depth (figure 6.92). Stage 3 extractable Si is constant with depth in both impoundments but shows dramatically higher concentration in the pre-impoundment sediment encountered in the Tees, likely to be due to some dissolution of Si from marine quartz sand in these sediments (figures 6.93 and 6.94). The pattern is repeated for Si within the stage 4 extractions for both impoundments (figures 6.95 and 6.96), with Si closely following the organic matter concentration in the Wansbeck (figure 6.97) and therefore coal particles are suggested as the Si source in this phase.

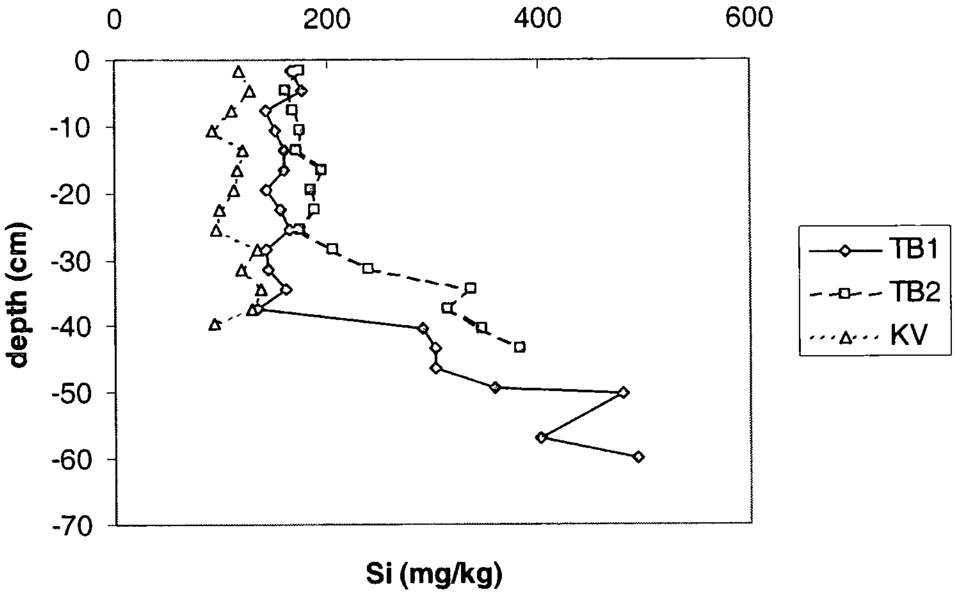


Figure 6.91. Stage 2 extractable Si with depth in cores TB1, TB2 and KV from the Tees impoundment.

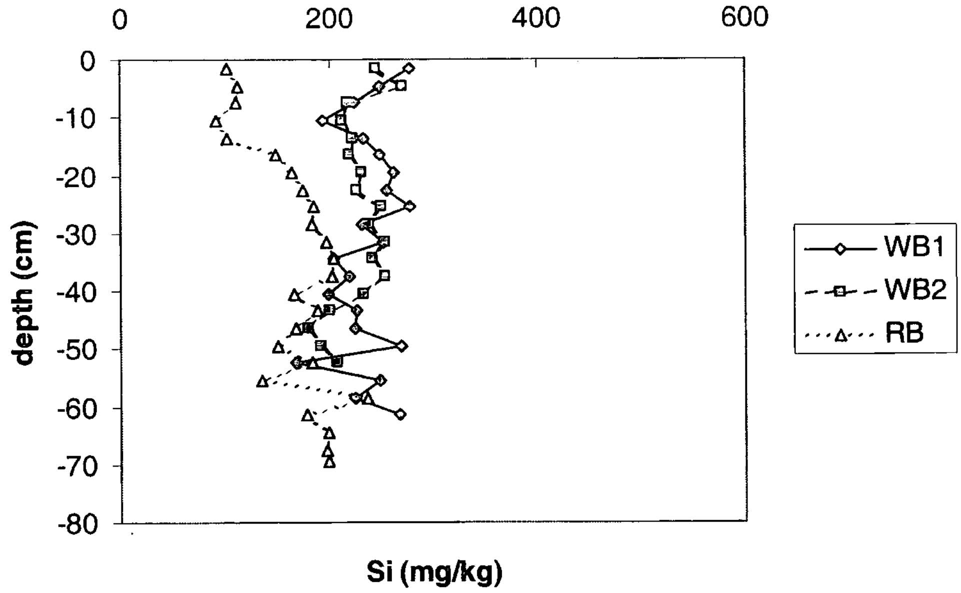


Figure 6.92. Stage 2 extractable Si with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

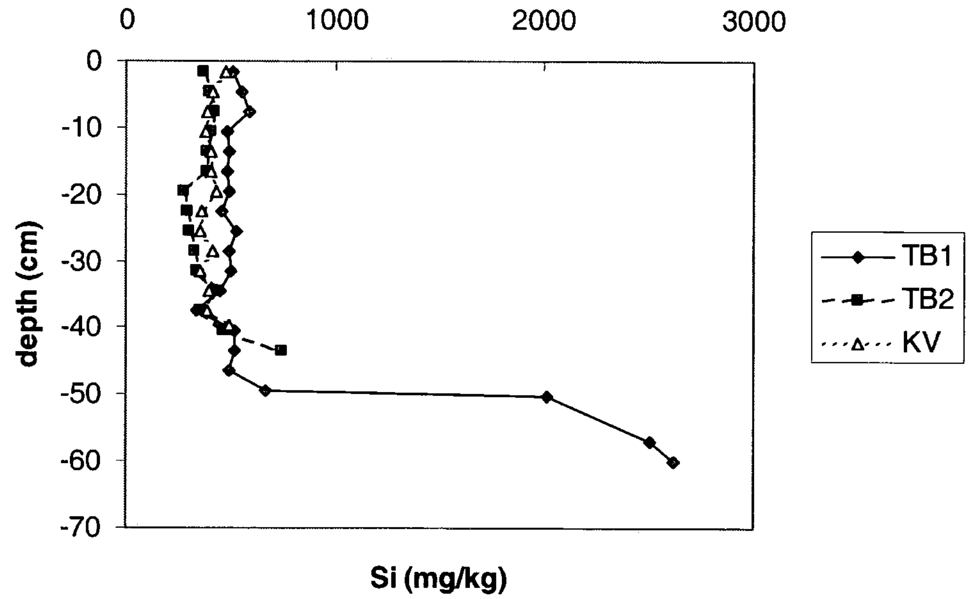


Figure 6.93. Stage 3 extractable Si with depth in cores TB1, TB2 and KV from the Tees impoundment.

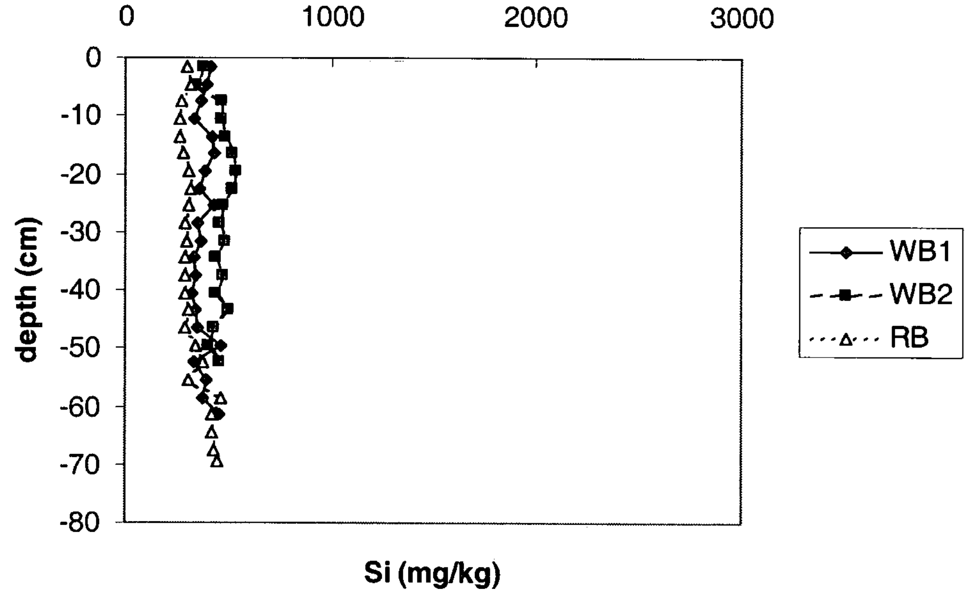


Figure 6.94. Stage 3 extractable Si with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

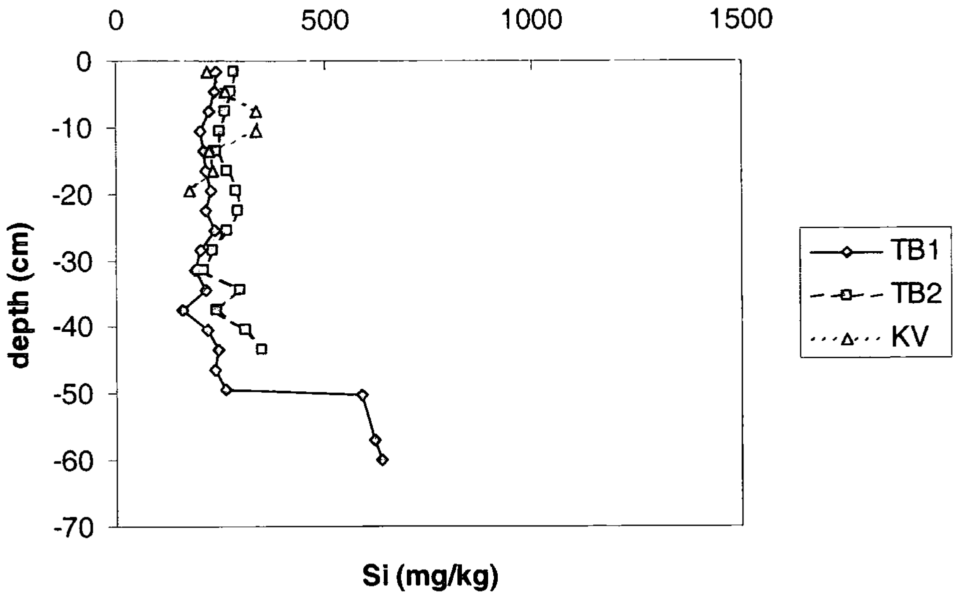


Figure 6.95. Stage 4 extractable Si with depth in cores TB1, TB2 and KV from the Tees impoundment.

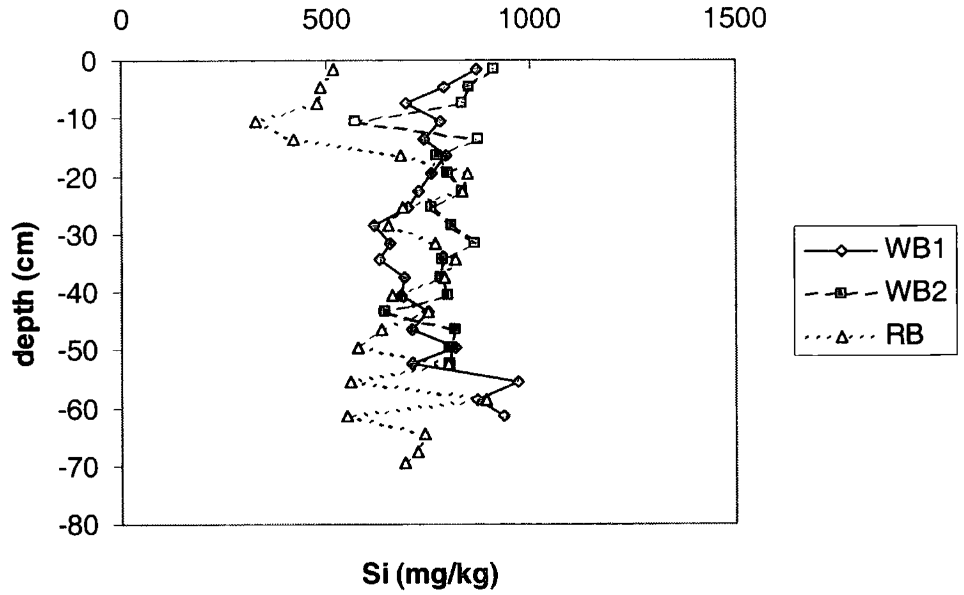


Figure 6.96. Stage 4 extractable Si with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

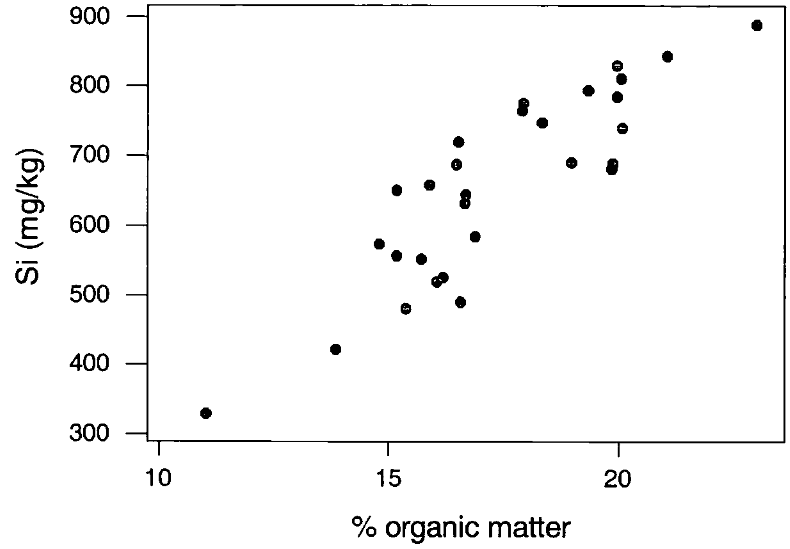


Figure 6.97. The relationship between Si in the stage 4 extraction and organic matter in sediment from site RB in the Wansbeck impoundment.

6.7.4.14 Ti

Sediment	Stage 1	Stage 2	Stage 3	Stage 4	Total
Tees impoundment	0.2	0.1	18.2	1.6	20.1
Wansbeck impoundment	0.4	0.1	12.6	1.3	14.4
Organic stream sediment (Finland)					1270

Table 6.22. Average Ti concentrations in sediment (mg/kg) from the Tees and Wansbeck impoundments (stage 1 to 4 plus sum of stages of Tessier extraction scheme), and organic stream sediment (< 2 mm fraction, concentrated HNO_3 extraction; data from Lahermo et al. 1996).

Potentially available Ti is in low concentrations in the sediments of the impoundments with the majority assumed to be contained within refractory (silicate) minerals. Ti is generally considered non-toxic. The majority of Ti is held in the stage 3 extractable phase, with small amounts extracted in stage 4, in the sediments of both impoundments (table 6.22 and figure 6.98).

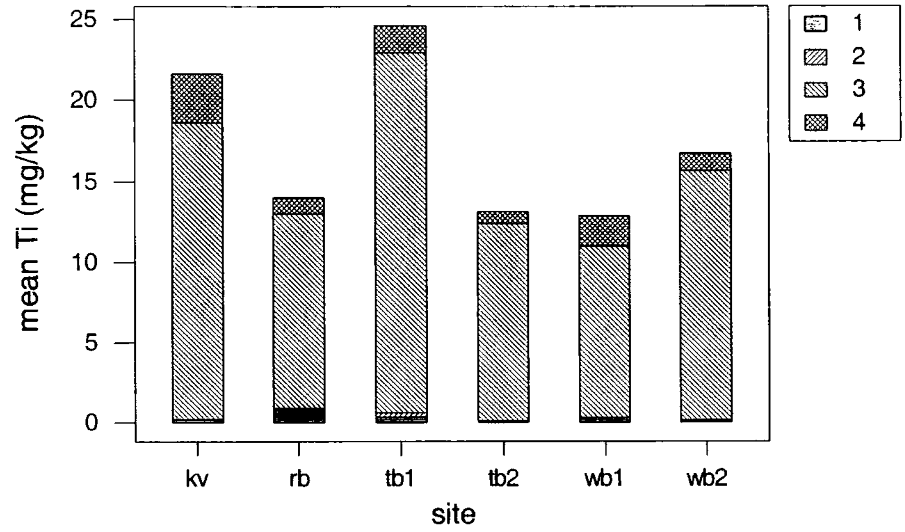


Figure 6.98. Ti concentration and speciation within the bottom sediments of the Tees and Wansbeck impoundments. Cores KV, TB1 and TB2 are from the Tees and cores RB, WB1 and WB2 are from the Wansbeck. Stages 1, 2, 3 and 4 of the sequential extraction scheme used represent exchangeable, carbonate bound, Fe and Mn bound and organic bound forms respectively.

The profiles for both stage 3 and stage 4 extractable Ti in the sediments of both impoundments show no clear trends with depth (figures 6.99, 6.100, 6.101 and 6.102). The only feature of note is that concentrations of Ti are higher in both stage 3 and 4 extractions in the pre-impoundment sediment of the Tees. This is likely to be due to industrial inputs to the estuary downstream of the position of the barrage from the Ti-oxide plant (Tioxide UK Ltd.) at Seal Sands. The peak in Ti (and Ni, etc.) levels at approximately 10 cm depth within the core from site KV is thought to be due to reduction of reagent volume during the vigorous reaction of stage 4 of the extraction procedure in these sediments (which, as mentioned, also led to boiling over and loss of sediment material from some samples in this core). The reason for the greater reactivity of the sediment from site KV could not be identified (the organic matter content is similar to other cores from the Tees).

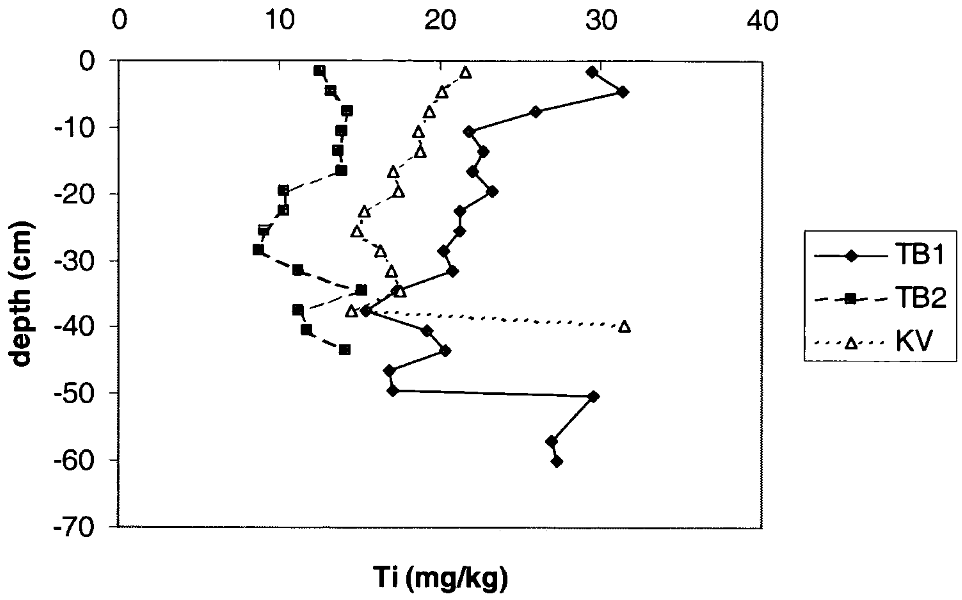


Figure 6.99. Stage 3 extractable Ti with depth in cores TB1, TB2 and KV from the Tees impoundment.

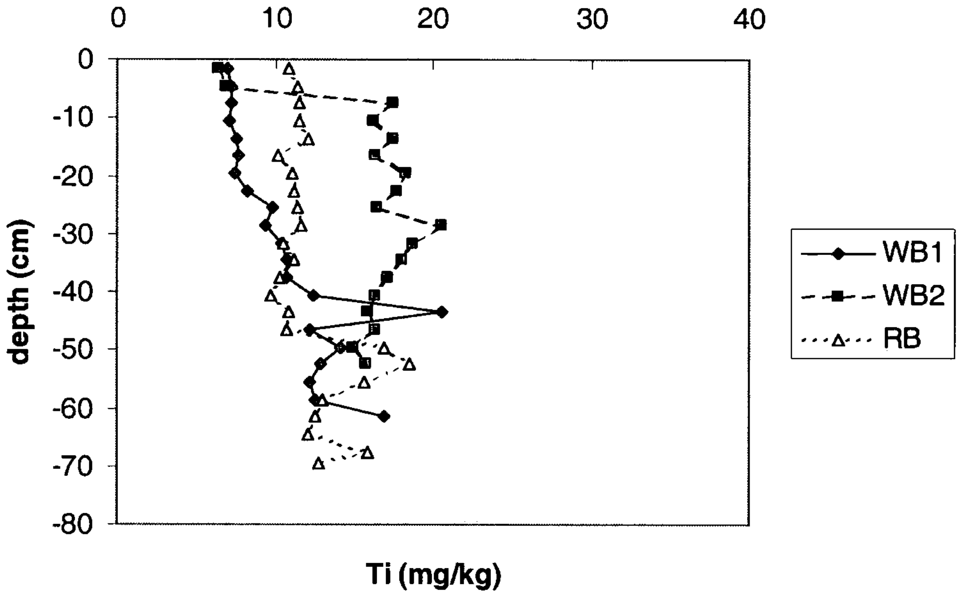


Figure 6.100. Stage 3 extractable Ti with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

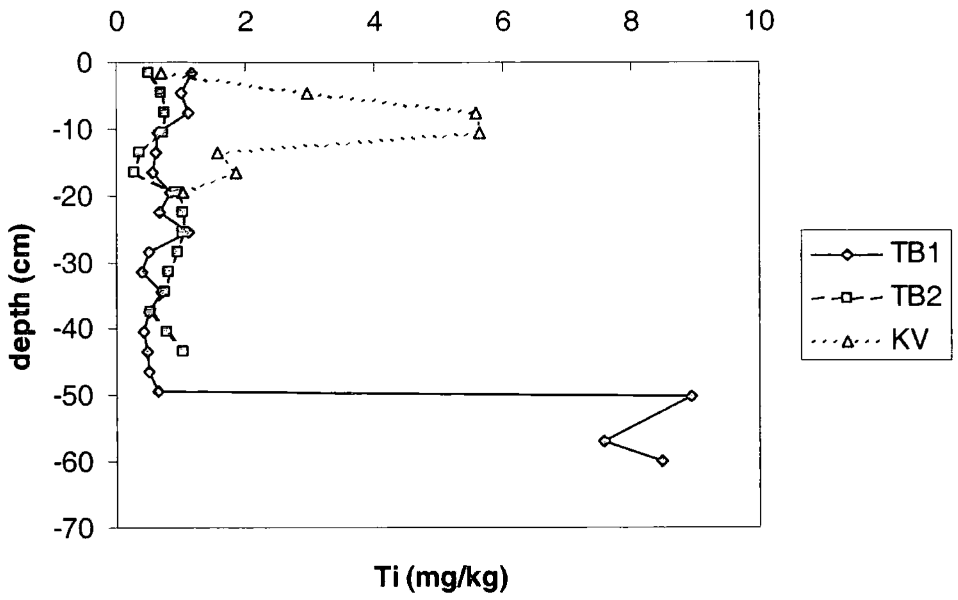


Figure 6.101. Stage 4 extractable Ti with depth in cores TB1, TB2 and KV from the Tees impoundment.

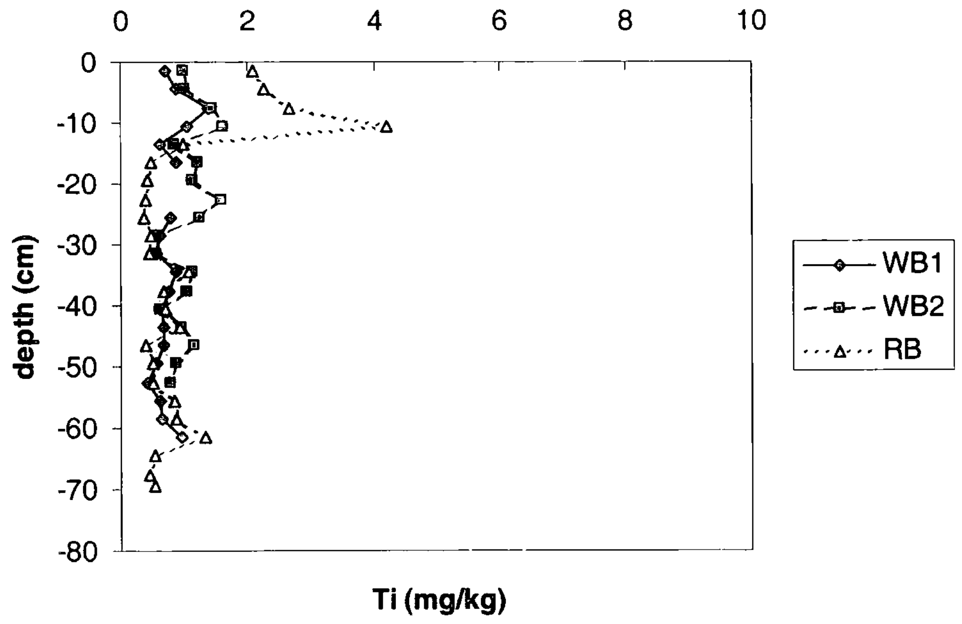


Figure 6.102. Stage 4 extractable Ti with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

6.7.4.15 Zn

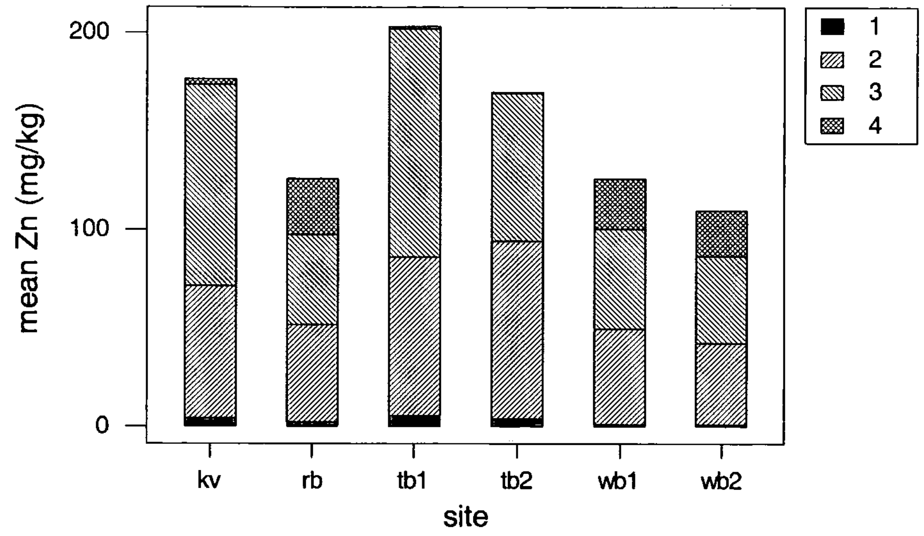


Figure 6.103. Zn concentration and speciation within the bottom sediments of the Tees and Wansbeck impoundments. Cores KV, TB1 and TB2 are from the Tees and cores RB, WB1 and WB2 are from the Wansbeck. Stages 1, 2, 3 and 4 of the sequential extraction scheme used represent exchangeable, carbonate bound, Fe and Mn bound and organic bound forms respectively.

Sediment	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Total**
Tees impoundment	4.4	80.0	99.5	1.0	184.9
Wansbeck impoundment	1.3	46.8	47.4	25.9	121.4
Organic stream sediment (Finland)					45.9
Tees estuary downstream of barrage					392
River Tees upstream of impoundment					518
Humber estuary					252

Table 6.23. Average Zn concentrations in sediment (mg/kg) from the Tees and Wansbeck impoundments (stage 1 to 4 plus sum of stages of Tessier extraction scheme), organic stream sediment (< 2 mm fraction, concentrated HNO_3 extraction; data from Lahermo et al. 1996), Tees estuary sediment from downstream of barrage

(total extraction; data from Jones and Turki 1997), River Tees sediment upstream of impoundment (< 63 μm fraction, total extraction; data from EA), and Humber estuary (< 100 μm fraction, concentrated HNO_3 extraction; data from Bryan and Langston 1992).

Zn concentrations are higher in the sediments of the Tees than the Wansbeck impoundment. Jones and Turki (1997) found that approximately 75 % of Zn held in the sediments of the Tees estuary downstream of the barrage is held in available forms (stages 1 to 4 of Tessier et al. (1979) extraction procedure). Zn is extracted almost equally in stages 2 (carbonate bound) and 3 (Fe oxide bound) of the extraction procedure from sediment from the Tees impoundment. For the Wansbeck sediment the amount of stage 2 and stage 3 extractable Zn is also similar, but additional Zn is held in the stage 4 (oxidisable) extraction phase (table 6.23 and figure 6.103).

Stage 2 extractable Zn within the Tees cores shows a similar pattern to that of Ca apart from an additional peak in concentrations in all cores between 10 and 20 cm depth (figure 6.104). It is likely that, as for Ca and K, the profile of stage 2 extractable Zn is strongly controlled by carbonate inputs to the sediment. For the Wansbeck, stage 2 extractable Zn shows a slight increase (as does Ca) with depth (figure 6.105). Both stage 2 and stage 3 extractable Zn increase in the sediment following impoundment of the Tees estuary, which fits with the higher reported values for sediment upstream of the impoundment compared with the estuary downstream, and is likely to be a dilution effect by coarse grained marine derived sediment. The profile for stage 3 extractable Zn is irregular in the Tees sediment, but as for stage 2 shows a clear peak at between 10 and 20 cm depth (figure 6.106). In the Wansbeck there is a steady decrease in stage 3 extractable Zn towards the sediment surface (figure 6.107). There is very little stage 4 extractable (sulphide and organic bound) Zn in the sediment of the Tees impoundment (figure 6.108), and an obvious increase with depth of this phase in the Wansbeck (figure 6.109).

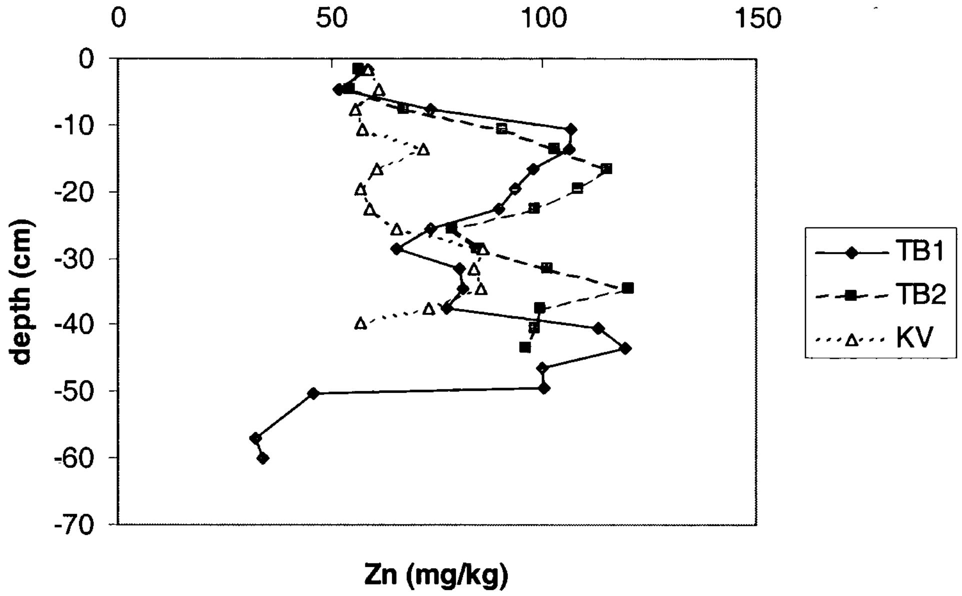


Figure 6.104. Stage 2 extractable Zn with depth in cores TB1, TB2 and KV from the Tees impoundment.

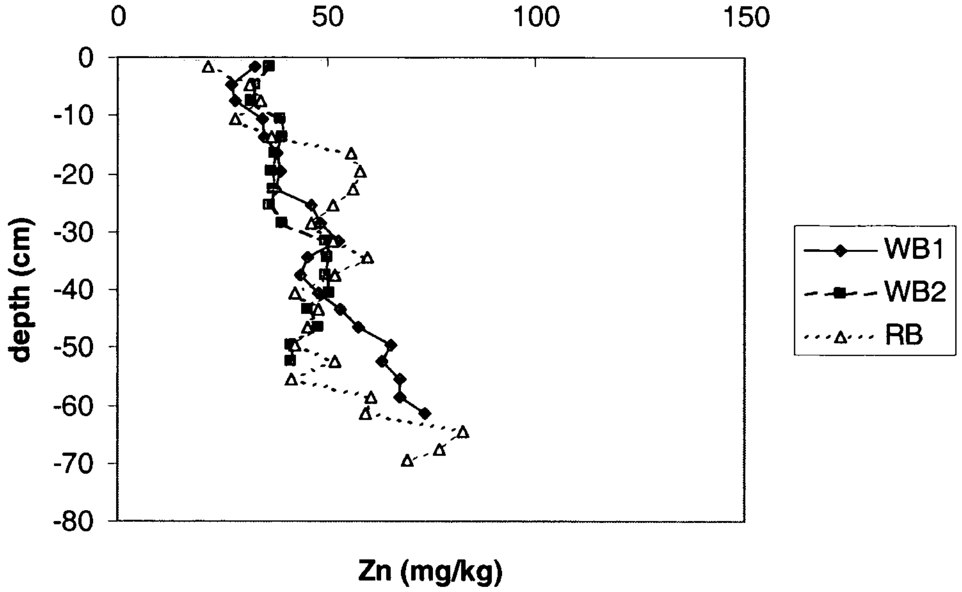


Figure 6.105. Stage 2 extractable Zn with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

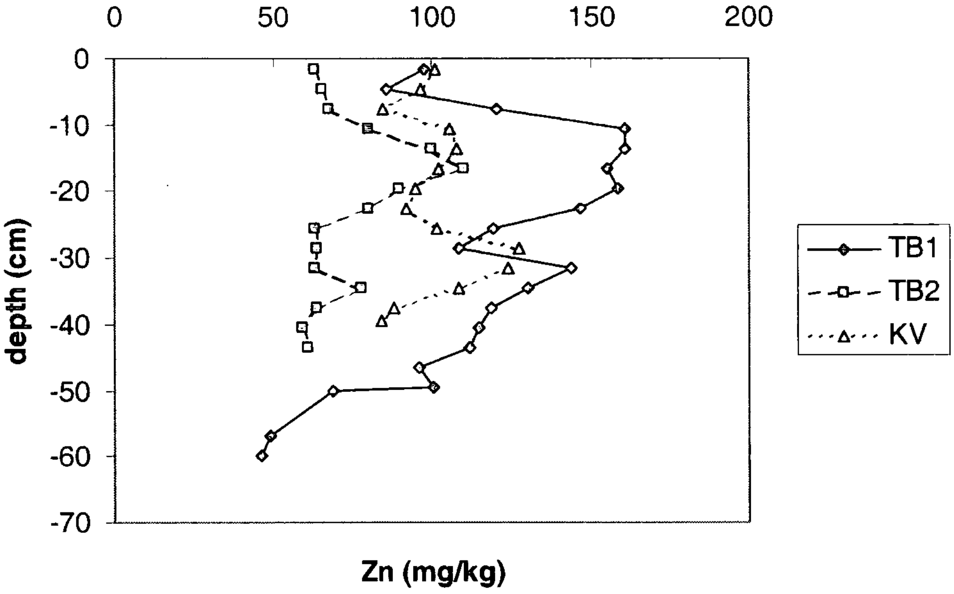


Figure 6.106. Stage 3 extractable Zn with depth in cores TB1, TB2 and KV from the Tees impoundment.

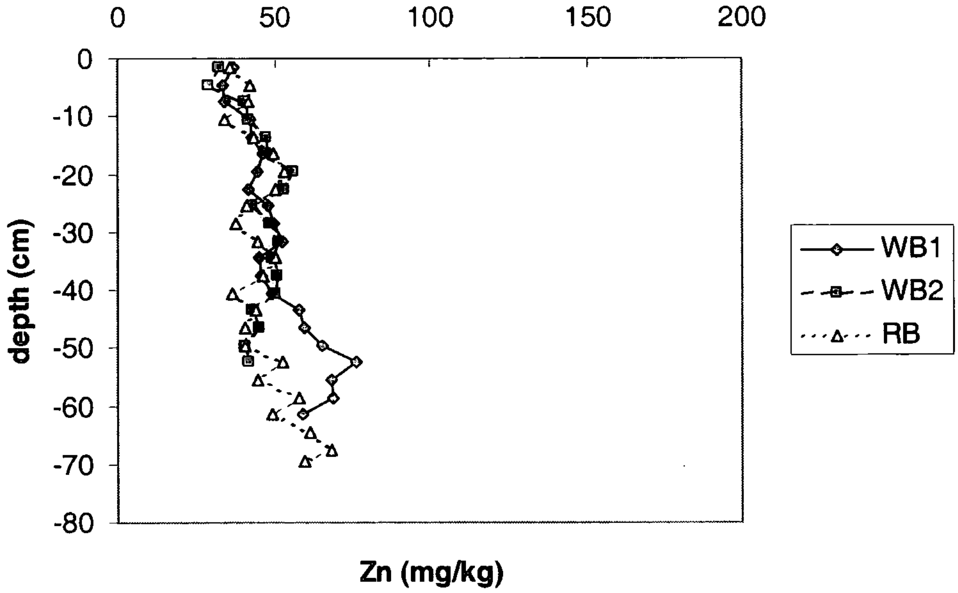


Figure 6.107. Stage 3 extractable Zn with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

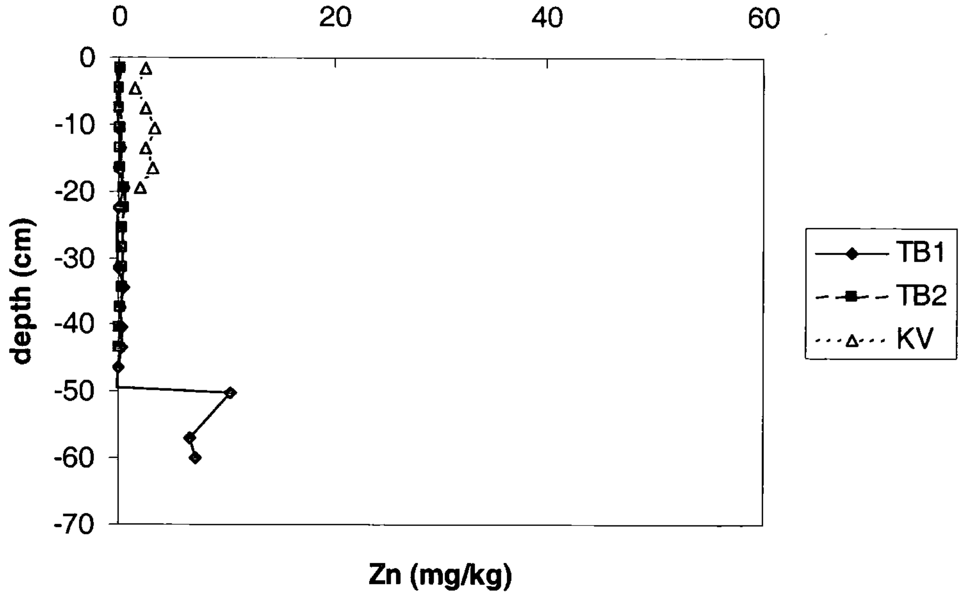


Figure 6.108. Stage 4 extractable Zn with depth in cores TB1, TB2 and KV from the Tees impoundment.

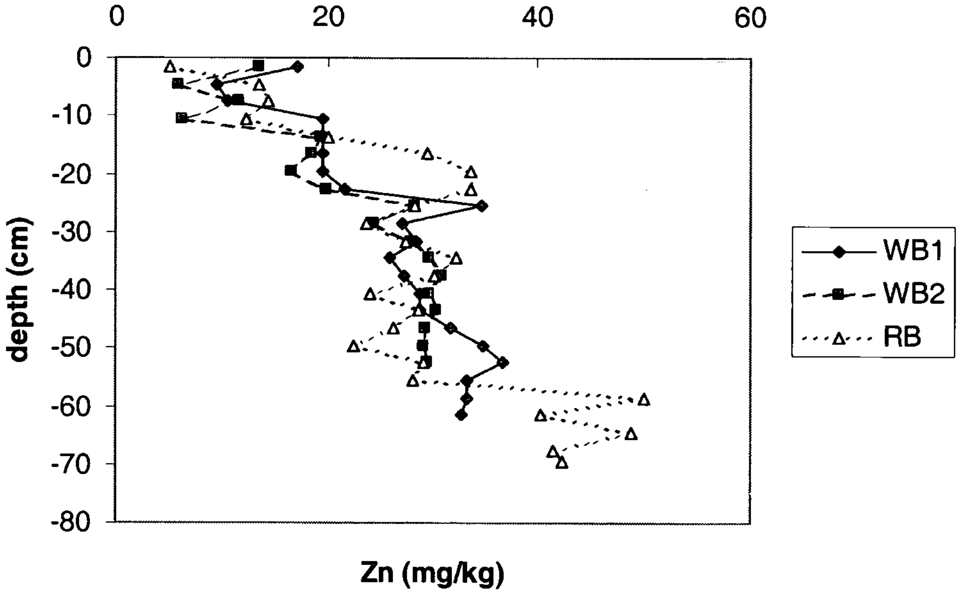


Figure 6.109. Stage 4 extractable Zn with depth in cores WB1, WB2 and RB from the Wansbeck impoundment.

6.8 Controls on sediment chemistry

Principal components analysis (PCA) (see appendix 1) was used to identify the controls on sediment chemistry in estuarine impoundments using data from the bed sediment cores taken from the Tees and Wansbeck impoundments. PCA was carried out using a correlation matrix (since parameters were measured on different scales) including the parameters of % organic matter content, % clay, silt and sand content, and concentrations of Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Sc, Si, Ti and Zn. As described above Sn and V were generally below the analytical LOD, sample was lost during stage 4 extraction of deep sample from core KV and analysis of P was problematic, and therefore these data were excluded from the PCA. The results in terms of eigenvalues and coefficients to the major principal components are summarised in tables 6.24 and 6.25 and figure 6.110.

Principal component	**Eigenvalue**	**Proportion of variance**	**Cumulative proportion of variance**
1	7.0425	0.391	0.391
2	3.0333	0.169	0.560
3	1.9872	0.110	0.670
4	1.7485	0.097	0.767
5	1.0722	0.060	0.827
6	0.9319	0.052	0.879

Table 6.24. Eigenvalues and proportions of variance for the first 6 principal components calculated for PCA of data from sediment cores from the Tees and Wansbeck impoundments.

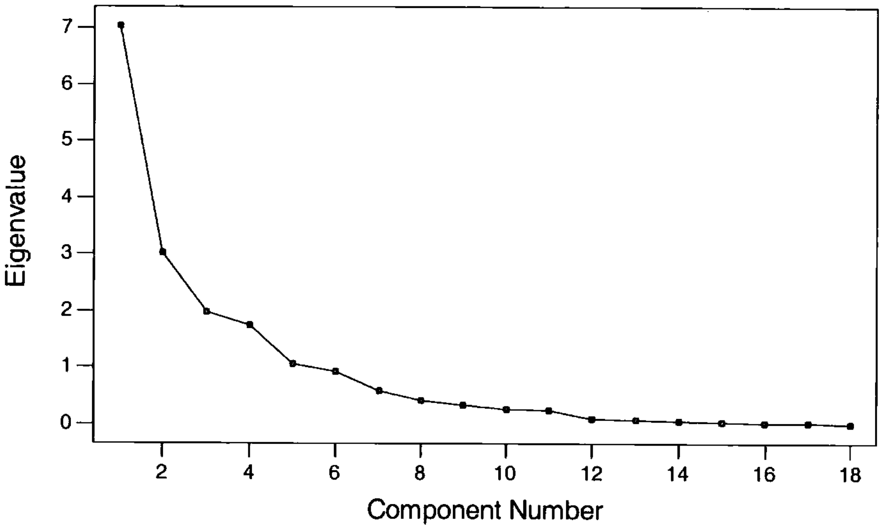


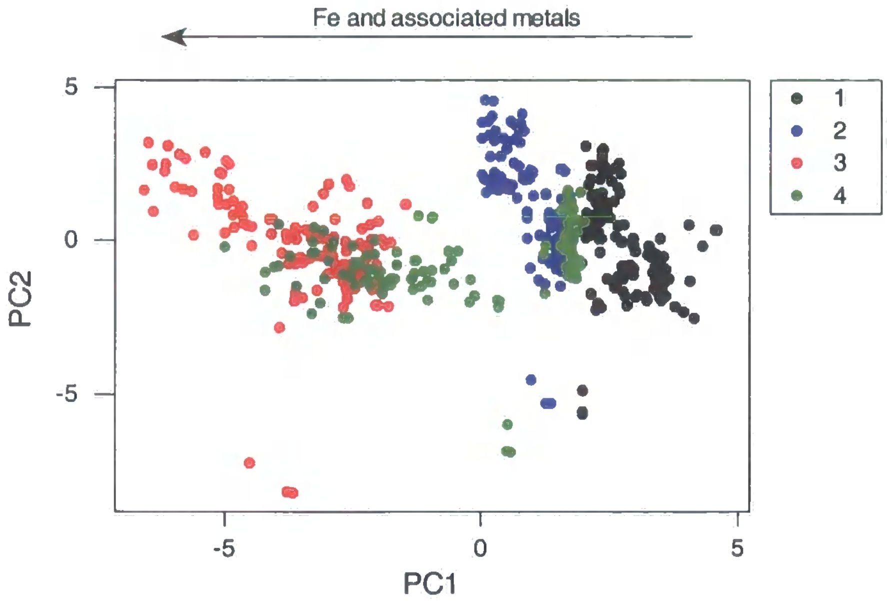
Figure 6.110. Scree plot of eigenvalues for principal components calculated for PCA of data from sediment cores from the Tees and Wansbeck impoundments.

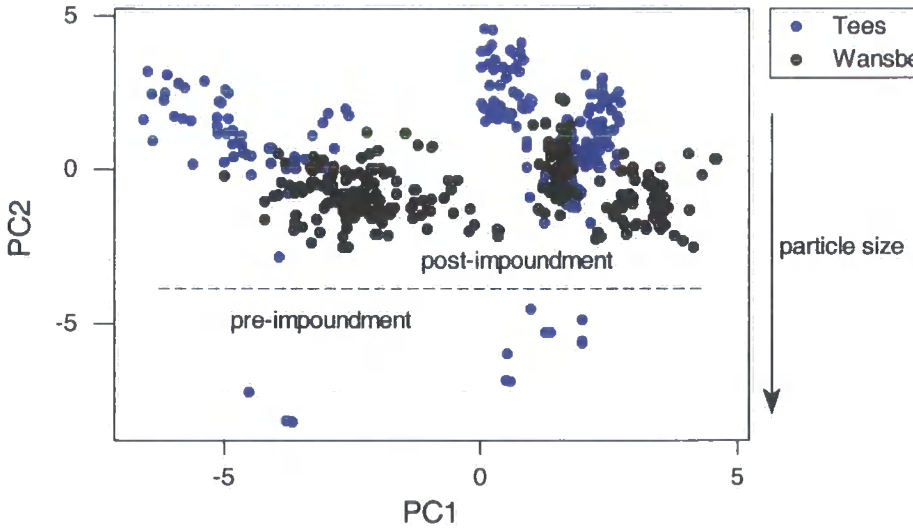
A large amount of variance in the dataset (39 %) is contained by the 1st principal component calculated (PC1) (table 6.24 and figure 6.110). Together the first 5 principal components contain 83 % of the variance in the dataset and eigenvalues fall below 1 from PC6 onwards. Only the principal components with eigenvalues > 1 are selected for discussion, and the coefficients for each of the parameters included in the analysis to each of these components are shown in table 6.25.

PC1 shows strong loadings (all in the same direction) for Al, Co, Cu, Fe, Ni, Sc, Si, Ti and Zn, with weaker correlations of the opposite sign for K and Mg. Particle size and organic matter content are not correlated with PC1. PC2 contrasts the levels of clay and silt in the sediment with that of sand, with elemental correlations being lower. PC3 has strong loadings of the same sign for organic matter, Mg and K. PC4 includes the majority of variables not included in the preceding components, with clay and Cr showing positive correlations and Ca and Mn showing negative correlations. PC5 shows the strongest correlation with Ti.

Variable	PC1	PC2	PC3	PC4	PC5
Al	-0.348	-0.084	-0.108	0.037	-0.089
Ca	0.183	0.192	0.132	-0.440	0.168
Co	-0.330	0.111	-0.051	-0.230	-0.078
Cr	-0.054	-0.166	0.317	0.440	-0.008
Cu	-0.263	-0.116	-0.187	-0.031	-0.329
Fe	-0.345	-0.021	-0.142	0.068	0.239
K	0.226	-0.087	-0.408	-0.007	0.308
Mg	0.213	-0.138	-0.412	-0.003	0.136
Mn	-0.109	0.345	0.185	-0.390	-0.071
Ni	-0.353	-0.003	-0.152	-0.090	-0.127
Sc	-0.316	-0.017	-0.133	0.086	0.345
Si	-0.253	-0.200	0.076	0.031	-0.359
Ti	-0.292	-0.047	0.002	0.166	0.507
Zn	-0.251	0.223	0.130	-0.282	0.301
% organic	0.003	0.092	-0.554	-0.120	-0.184
% clay	-0.008	0.405	0.108	0.340	0.055
% silt	0.002	0.482	-0.208	0.241	-0.135
% sand	0.001	-0.510	0.130	-0.299	0.089

Table 6.25. Coefficients for sediment parameters for the first 5 principal components calculated for PCA carried out using data from sediment cores from the Tees and Wansbeck impoundments.





Figures 6.111 and 6.112. Principal component scores for 1st and 2nd principal components for data from sediment cores from the Tees and Wansbeck impoundments. PC1 represents the speciation of Fe and associated metals within the sediment hence distinguishes between extraction stages (1 to 4 of Tessier et al (1979) sequential extraction procedure). PC2 represents the grain-size distribution in the sediments and hence distinguishes between the generally coarser grained Wansbeck and finer grained

Tees sediment, and between the pre and post-impoundment sedimentation within the Tees.

PC1 represents the association of a large number of the elements analysed with Fe. These metals show the same "speciation" as Fe, and as such plotting scores for PC1 distinguishes the stages of the sequential extraction procedure (figure 6.111). Stages 1 and 2, and stage 4 from the Tees, extract minor amounts of these metals (Al, Co, Cu, Fe, Ni, Sc, Ti and Zn) and show positive scores for PC1. Stage 3, and stage 4 from the Wansbeck, extractions contain the majority of the "available" portion of these metals and show negative scores for PC1. The relationships between Al and Sc and Fe, and Ni and Co are shown as examples of this association of elements within the sediments (figures 6.113, 6.114 and 6.115).

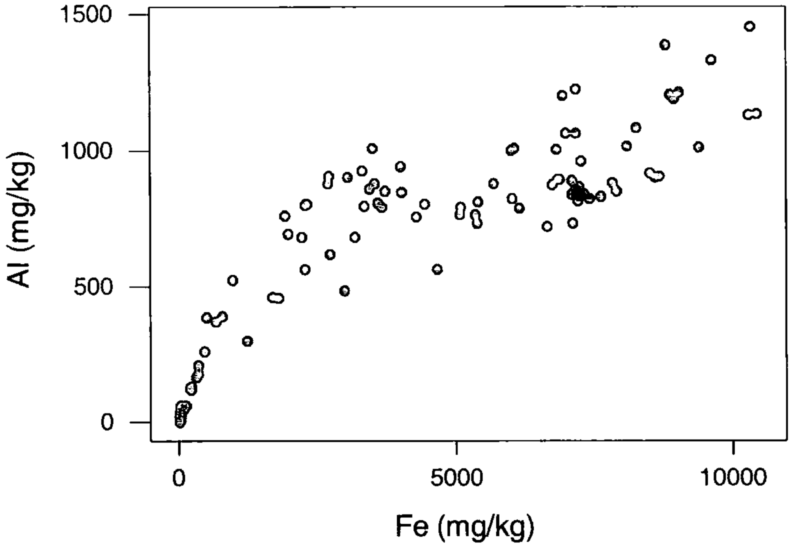


Figure 6.113. The relationship between Al and Fe within the stage 4 extraction (organic and sulphide bound fraction) in the sediments of the Tees and Wansbeck impoundments.

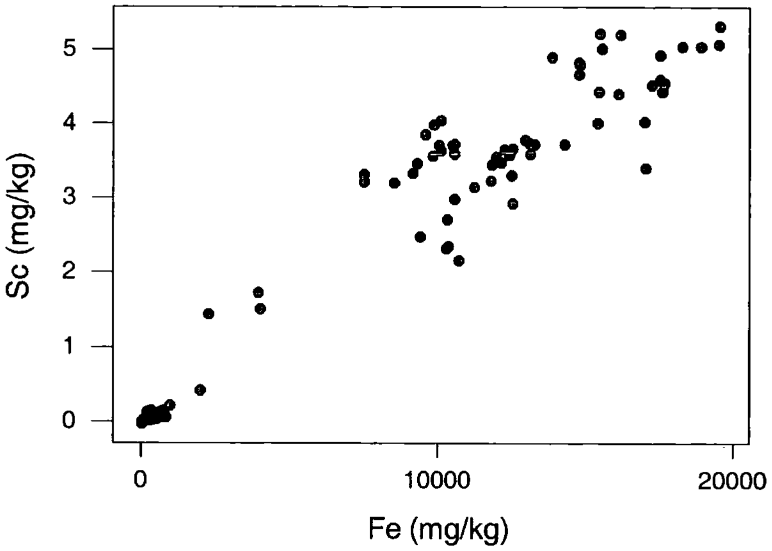


Figure 6.114. The relationship between Sc and Fe for all extraction stages within the sediment of the Tees impoundment.

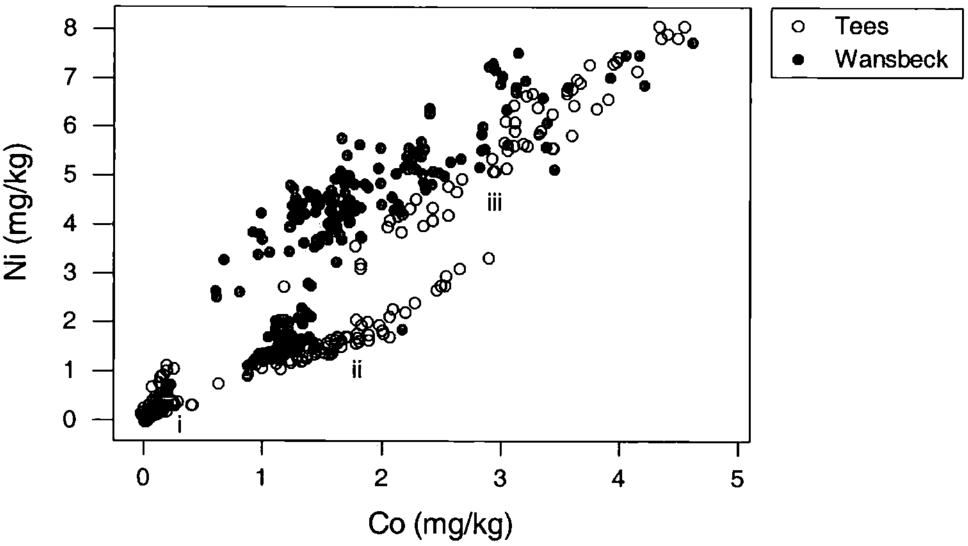


Figure 6.115. The relationship between Ni and Co for all extraction stages for the sediment from the Tees and Wansbeck impoundments. Group i is from extraction stage 1 from both impoundments and extraction stage 4 from the Tees, group ii is from

extraction stage 2 from both impoundments, and group iii is from extraction stage 3 from both impoundments and extraction stage 4 from the Wansbeck.

PC2 is related to particle size distribution, which surprisingly shows little relationship to elemental concentrations indicating that speciation effects (PC1) are larger than grain-size effects. Since particle size differences play a secondary role in controlling elemental concentrations all sediment sequential extraction data presented and discussed within this study is in a raw form, as opposed to grain-size normalised (see for example Loring and Rantala 1992). Since sediment within the Wansbeck impoundment is slightly coarser grained than that in the Tees, PC2 distinguishes between the two impoundments (figure 6.112). In addition scores for the sand-dominated pre-impoundment sediment from the Tees are much lower than those for the silt-dominated post-impoundment sedimentation.

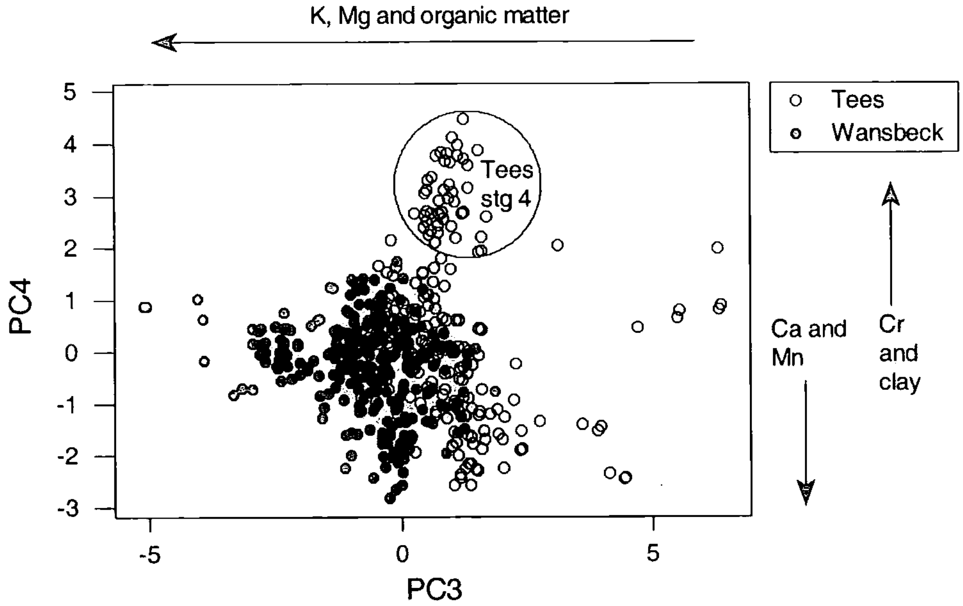


Figure 6.116. Principal component scores for 3rd and 4th principal components for data from sediment cores from the Tees and Wansbeck impoundments. PC3 relates to Mg and K (particularly within the exchangeable fraction) and organic matter, and groupings of scores for PC4 relate mainly to Cr concentration in stage 4 extractions from the Tees.

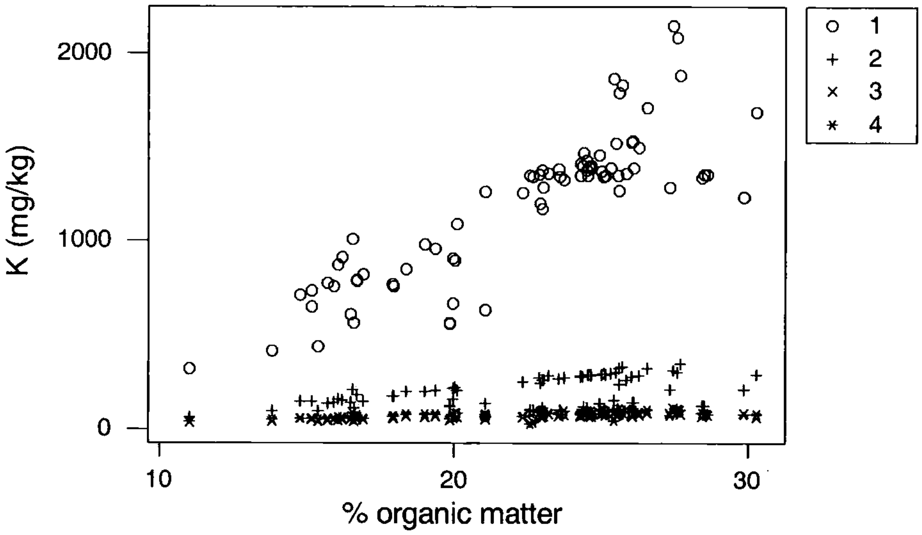


Figure 6.117. K vs. organic matter by speciation (stages 1 to 4 of Tessier et al. (1979) sequential extraction procedure) for bottom sediment from the Wansbeck impoundment, showing strong association of exchangeable K with organic material.

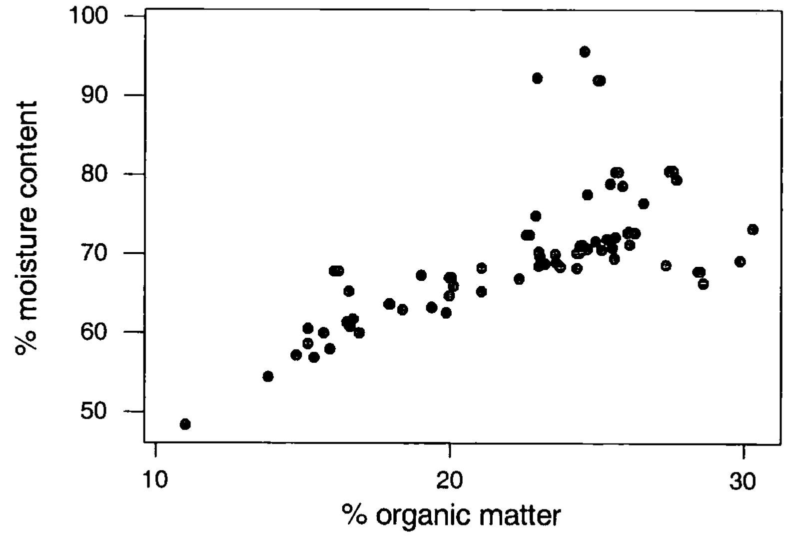


Figure 6.118. The relationship between moisture content and organic matter within sediment from the Wansbeck impoundment.

PC3 relates to the concentrations of Mg, K and organic matter within the sediment and, as with PC2, also generally distinguishes between the impoundments (however, since PCA forces components to be orthogonal the variables within PC2 are unlikely to be correlated with those in PC3). The Wansbeck is a partial tidal intrusion impoundment and periodically (including at the time of sediment coring) has seawater in contact with the sediment. Concentrations of Mg and K within the pore-water of the sediment are therefore higher than in the Tees, and much of this is associated with organic matter (also higher in the Wansbeck) so that scores on PC3 for the Wansbeck tend to be negative (figure 6.116). The relationships between K and organic matter, and between moisture content and organic matter within the sediment of the Wansbeck are shown in figures 6.117 and 6.118.

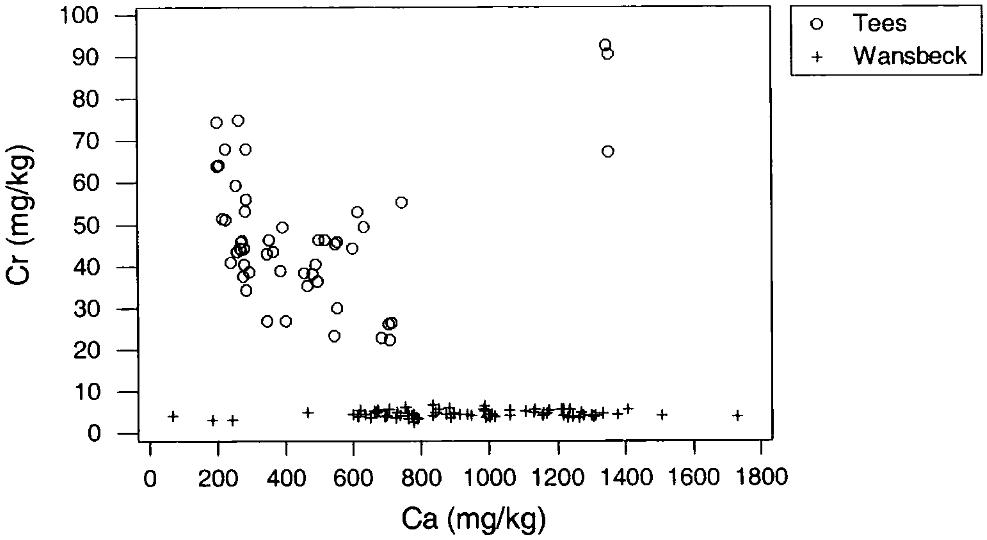


Figure 6.119. Cr vs. Ca within stage 4 extractions from sediment from the Tees and Wansbeck impoundments. The high Cr high Ca samples are from pre-impoundment sediment.

PC4 relates to the majority of elements which do not show covariance with Fe (PC1) or to organic matter (PC3), with the strongest loading for Cr which contrasts with the other elements studied in showing a far greater concentration in the stage 4 extractions for the Tees than the Wansbeck impoundment. As mentioned high Cr concentrations within the Tees are likely to be due to a chromium works in the upstream sections of this river. Within stage 4 extractions from the Tees Ca shows an approximate negative relationship to Cr (figure 6.119) and thus shows a similar coefficient (but of opposite sign) to Cr on PC4. Of note is that Mn shows greater correlation to PC4 than to PC1 (Fe and associated elements) implying that the behaviour of Mn differs from that of Fe. Briefly it can be stated that Mn/Fe shows a similar concentration in hydroxides and Mn concentration is therefore proportional to Fe concentration within stage 3 extractions, but that Mn shows greater relative concentrations within other species than do Fe or associated elements due to greater environmental mobility (figure 6.120).

PC5 explains approximately 6 % of the variance in the dataset and relates to variation in Ti levels between the extraction stages and cores, with this and subsequent components likely to be related to analytical and other errors to a large extent.

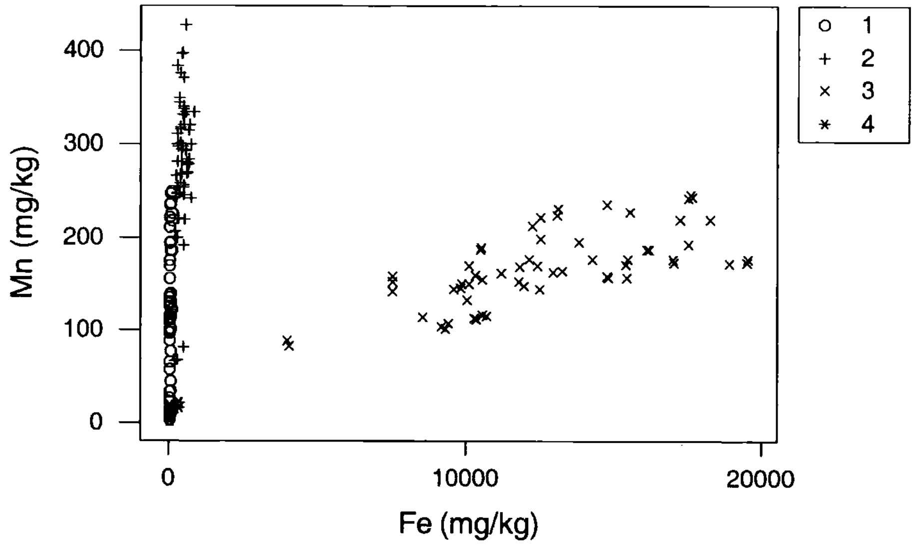


Figure 6.120. Mn vs. Fe by speciation (stages 1 to 4 of Tessier et al. (1979) sequential extraction procedure) for bottom sediment from the Tees impoundment, showing correlation between Mn and Fe within oxides (stage 3 extraction), but greater variation of Mn (due to greater environmental mobility) than Fe within other phases.

6.9 Summary and conclusions

Within this section the data collected from a total of 6 bottom sediment cores of approximately 50 cm length taken from the Tees and Wansbeck impoundments have been presented and discussed. Data from an additional core taken from an emergent sand-bar in the Wansbeck impoundment is discussed briefly. For each sub-sample taken at 3 cm intervals the parameters of particle size, organic matter, and the concentration and speciation of Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Sc, Si, Ti and Zn based on a modified sequential extraction procedure as developed by Tessier et al. (1979), have been determined. Elemental results are presented in terms of mean concentrations within each operationally defined "species" (exchangeable, carbonate bound, Fe and Mn oxide bound, and organic or sulphide bound) and profiles of concentration of each species with depth in each of the sediment cores. Comparison of the concentrations determined in this study is made where possible with data from comparable surveys (e.g. the Tees upstream and downstream of the impounded area and the Humber estuary). Similarities between the behaviours of groups of elements, and possible controlling mechanisms on the speciation, concentration and distribution of elements is suggested and are summarised below. PCA was carried out to aid identification of the controls on elemental behaviour.

6.9.1 PCA

The principal components having Eigenvalues > 1 are considered. The 1st principal component calculated accounts for 39 % of the variance in the dataset, with the first 4 components together including 77 % of the variance. Subsequent components are interpreted as relating to a large extent to random variation (error and local heterogeneity) in the data collected. The major principal components represent:

- PC1 = covariance between Fe and a suite of elements (Al, Co, Cu, Fe, Ni, Sc, Ti and Zn) particularly related to association with Fe hydroxide.
- PC2 = particle-size variation (significantly this is relatively independent of the major controls on elemental concentrations implying that grain-size normalisation (e.g. Loring and Rantalla, 1992) is inappropriate for this kind of speciation study).
- PC3 = pore-water component showing variation of exchangeable cations between impoundment types (freshwater and mixed seawater/freshwater), and relating to organic matter within each of these systems.

- PC4 = strongly related to anthropogenic Cr inputs to the sediments.

6.9.2 Geochemistry

	Species	Controls
Al	3 4	Held in sulphides and oxides of Fe with contrast between impoundments based on prevailing oxygen conditions in overlying water.
Ca	1 2 3 4	Ion exchange removes Ca from exchangeable phase. Variation in allochthonous (catchment) carbonate inputs. Some Ca associated with sulphides and oxides of Fe.
Co	2 3 4	Variation in allochthonous (catchment) carbonate inputs. Held in sulphides and oxides of Fe with contrast between impoundments based on prevailing oxygen conditions in overlying water.
Cr	3 4	Concentration controlled by industrial input of Cr. Speciation controlled by sulphides and oxides of Fe.
Cu	3 4	Held in sulphides and oxides of Fe with contrast between impoundments based on prevailing oxygen conditions in overlying water.
Fe	3 4	Held in sulphides and oxides with contrast between impoundments based on prevailing oxygen conditions in overlying water.
K	1 2	K content of overlying water plus organic/moisture content of sediments controls exchangeable phase. Variation in allochthonous (catchment) carbonate inputs.
Mg	1 2 3 4	Mg content of overlying water plus ion exchange (increasing Mg) for exchangeable phase. Variation in allochthonous (catchment) carbonate inputs. Some Mg associated with sulphides and oxides of Fe.
Mn	1 2 3 4	Redox controlled mobility/speciation, varies between impoundments based on prevailing oxygen conditions in overlying water.

Ni	2	Variation in allochthonous (catchment) carbonate inputs.
	3 4	Held in sulphides and oxides of Fe with contrast between impoundments based on prevailing oxygen conditions in overlying water.
P	3	Anthropogenic inputs of P, strongly associates with oxides of Fe in sediment.
Sc	3 4	Held in sulphides and oxides of Fe with contrast between impoundments based on prevailing oxygen conditions in overlying water.
Si	2	Variation in allochthonous (catchment) carbonate inputs.
	3 4	Grain-size effect relating to change from pre to post-impoundment sedimentation in the Tees. Associated with organic matter (coal) in the Wansbeck.
Ti	3 4	Held in sulphides and oxides of Fe with contrast between impoundments based on prevailing oxygen conditions in overlying water.
Zn	2	Variation in allochthonous (catchment) carbonate inputs.
	3 4	Held in sulphides and oxides of Fe with contrast between impoundments based on prevailing oxygen conditions in overlying water.

Table 6.26. Summary of the operationally defined species in which the elements analysed are held, and suggested controls on speciation and concentration, within the bottom sediment of the Tees and Wansbeck estuarine impoundments. Within the species column 1 to 4 represent the first 4 stages of the sequential extraction procedure (Tessier et al. 1979). The principal phases removed by each of these extractions are:

1 = Exchangeable
2 = Carbonates
3 = Fe and Mn oxides
4 = Organic matter and sulphides

Together with PCA, graphical presentation of the sediment geochemistry data has allowed several controls on patterns of speciation and concentration of elements within the bottom sediments of the Tees and Wansbeck impoundments:

1. Redox controls.
2. Input controls.
3. Overlying water composition and ion-exchange controls.
4. Particle-size controls.

6.9.2.1 Redox controls

A large number of the elements analysed (Al, Co, Cu, Ni, Sc, Ti and Zn) show similar behaviour due to association with Fe in the sediment. Insoluble Fe^{3+} hydroxides (and Mn^{4+} oxides) are the major species of Fe in oxic conditions in both the water column and bottom sediments of many water bodies, and due to high adsorptive capacities and low degrees of crystallinity are of major importance in adsorbing or occluding trace metals (Turner, 2000). These metals are potentially bioavailable to filter-feeding and burrowing organisms since acidic, reducing conditions are present within their digestive systems (Bryan and Langston, 1992; Langston and Spence, 1995). As described in chapter 4, under reducing conditions Fe hydroxides are reduced and release soluble Fe^{2+} ions (along with any associated heavy metals). With increased anoxia with depth in sediments the onset of sulphate reduction to sulphide (as an electron source in the decomposition of organic matter) rapidly converts remaining Fe hydroxides to insoluble Fe sulphides. Metals associated with Fe hydroxides also tend to undergo transfer to sulphides, although Huerta-Diaz and Morse (1992) found that Cr and Zn partition less strongly to sulphides than Co, Cu and Ni. Under sustained reducing conditions these metal sulphides represent a sink for metal pollutants, but may be resolubilised under a change in redox conditions (such as upon dredging or erosion of sediment).

Assuming that the change in speciation upon sampling and pre-treatment of sediment was minimal (descriptions of the effects of preservation on metal speciation are given in Kersten and Förstner (1987) and Rapin et al. (1986)), then the distributions of species for Fe and associated metals within and between the impoundments represent the distribution of redox conditions in the sediments. In reality a proportion of the sulphides are likely to be oxidized on drying of the sediment samples and so speciation is misrepresented (gel-probe sampling (chapter 7) overcomes the redox change problems of sample preparation during the study of elemental mobility by “in-situ” sampling). Nevertheless, comparison of these speciations suggests that sediment within the Tees impoundment is less reducing than that of the Wansbeck since far less sulphide bound fraction is seen for any of the metals given above. Within the Wansbeck sediment significant proportions of the metals are found within the "sulphide" extraction, and the sediment can be interpreted as being more reducing through a combination of greater organic matter content and a generally lower DO concentration in the overlying water column (see chapter 4). This interpretation is supported by visual and olfactory examination of the sediment cores, with those from the Wanbeck being black throughout their length apart from a small (2 mm) oxidised zone at the surface and a distinct smell of hydrogen sulphide, and those from the Tees paler in colour with less odour. It is also possible that part of this difference between the stage 4 extractables in Tees and the Wansbeck sediment is due to the presence of sulphides within coal particles in the Wansbeck, although there is no clear relationship between concentration of sulphide bound metals (which show a general increase with depth in the sediment) and organic matter content (which shows no trend with depth in the sediment). The trend of greater sulphide bound metals with increasing depth in the sediment of the Wansbeck is due to increasing stability of reducing conditions with depth, with diffusion into the overlying water column of Fe^{2+} periodically taking place from the surface of the sediment.

The water quality surveys showed that increased dissolved Fe and Mn concentrations due to release from sediment periodically occur in the Wansbeck impoundment, but that only elevated Mn was observed in the Tees due to the differences in the redox conditions in the water columns between the impoundments. Reduction of Mn^{4+} oxides to release soluble Mn^{2+} takes place under less reducing conditions than Fe. Within the sediments sampled the dissolved Mn maxima (i.e. the development of < approximately 50 % DO) were within the sediment at approximately 15 cm depth in the Tees, but at approximately 7 cm depth (at the WB site) and at the surface (site RB) in the Wansbeck, confirming that more reducing conditions are encountered both in the sediment and the water column of the Wansbeck impoundment. Metals associated with Mn in the sediment may also be released to the water column, although concentrations were generally found to be below the analytical LOD during the water quality surveys and no similar patterns could be observed in the sediment for trace metals. Since the concentrations of Fe are far greater than those for Mn, Fe speciation exerts a greater control on speciation and availability than does Mn in the sediments studied.

The distribution of P also appears to be controlled by Fe behaviour, with the Fe hydroxide phase being the major P fraction in the sediments. The redox controlled behaviour and sediment-water column exchanges of P and a range of metals is explored further in chapter 7 through the use of gel-probes.

6.9.2.2 Input controls

Whilst P speciation follows that of Fe, the actual amount of P within the sediments varies between impoundments (figure 6.121). Levels of both dissolved orthophosphate and total dissolved P are greater in the water of the Tees impoundment than the Wansbeck impoundment (mean phosphate = 0.225 and 0.109 mg/l P respectively), and the higher levels in the sediment represent these inputs through the overriding affinity of ferric hydroxide for P ions (Reynolds and Davies, 2001). Indeed the ratio of mean sedimentary P in the Tees/Wansbeck (2.3) is very similar to that for mean dissolved orthophosphate P in the Tees/Wansbeck (2.1).

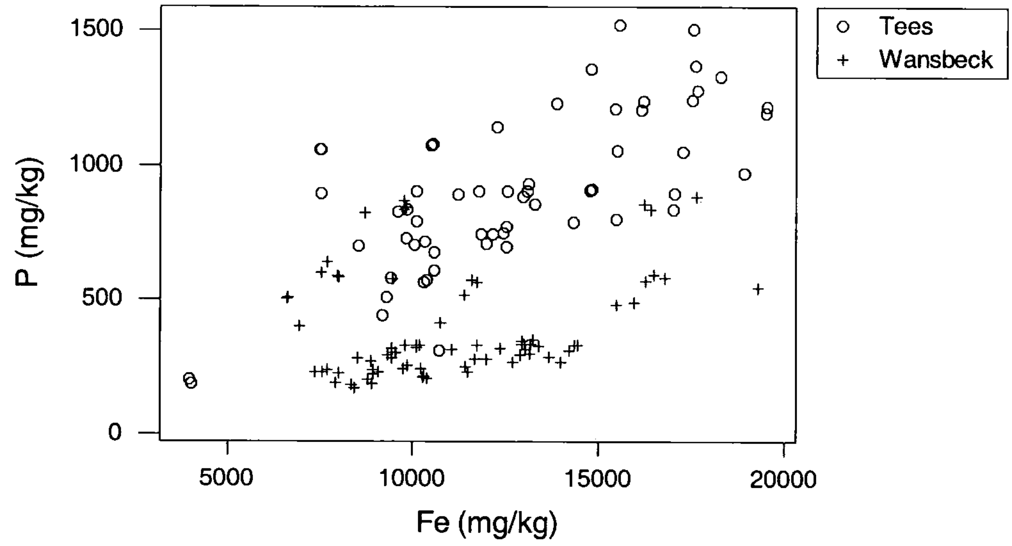


Figure 6.121. P vs. Fe within Fe hydroxide phase within sediments from the Tees and Wansbeck impoundments. Greater P in the sediments of the Tees reflects greater P inputs to the river.

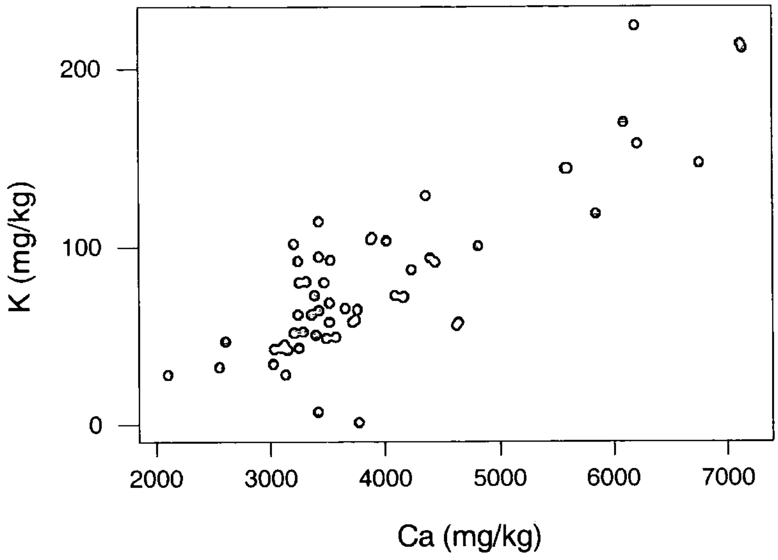


Figure 6.122. The relationship between K and Ca in the carbonate phase of sediments from the Tees impoundment.

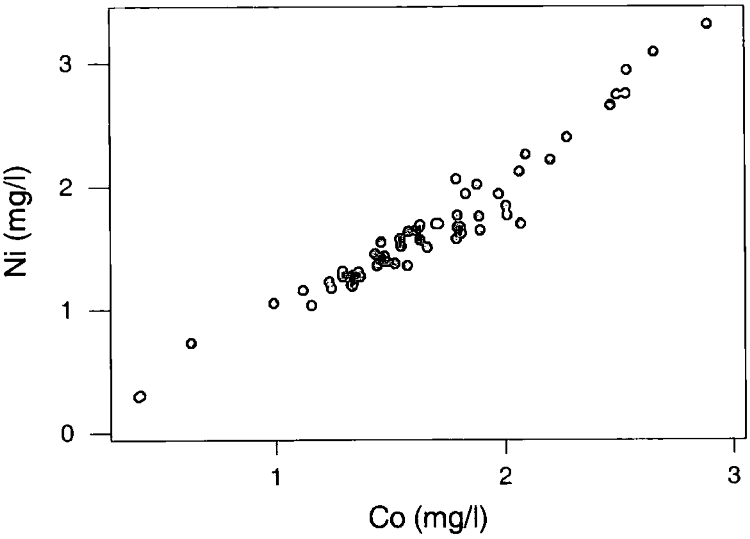


Figure 6.123. The relationship between Ni and Co in the carbonate phase of the Tees sediments.

Transport of carbonate material to the sediments of the impoundments is also significantly input controlled. The elements associated with the carbonate phase of the sediments (Ca, Co, K, Mg, Ni, Si and Zn; figures 6.122 and 6.123), and therefore the inputs of carbonates to the systems, have shown variation over time (with depth in the sediment cores). The input of allochthonous carbonates to the sediment from the geologies of the catchments is likely to increase with increasing river discharge, and the peak in stage 2 extractable (carbonate bound) Ca, etc. following impoundment of the Tees estuary is interpreted as due to the high flow conditions encountered in 1995.

Cr concentration in the sediments is also interpreted as significantly input controlled, and industrial discharges from a Cr works is suggested as causing the far higher levels within the sediments of the Tees than the Wansbeck. The pattern of speciation of Cr differs to other metals, with the largest fraction from the Tees sediment being extracted in stage 4 (oxidisable phase). Since generally little sulphide is encountered in the sediment samples Cr is therefore likely to be associating with organic material within the river. A similar association of Cr with organic matter was also found in the sediments of the Tees estuary downstream of the barrage (Jones and Turki, 1997).

6.9.2.3 Overlying water composition and ion-exchange controls

The group 1 and 2 elements analysed (K, Mg and Ca) show significant fractions in the exchangeable phase within the sediments of both the Tees and the Wansbeck, but the concentrations and distributions of these metals differs between the impoundments due to differences in the composition of the overlying water bodies and ion-exchange behaviour. Clay minerals, Fe and Mn hydroxides and humic acids are all well known to demonstrate adsorption of metals (Tessier et al., 1979), and changes in the ionic composition of overlying waters affects sorption and desorption processes. It is suggested that in the Wansbeck adsorption of major ions from seawater to particulate material takes place, giving higher exchangeable concentrations of Mg and K within the sediments of this impoundment than the Tees. Within the Wansbeck it is seen that the proportion of Mg and K within the exchangeable fraction of the sediment is closely related to organic matter. The profiles of Ca and K within the exchangeable fraction of the Tees sediment show the opposite trend to that for Mg, and it is suggested that this may be due to an ion-exchange by Mg (figure 6.124).

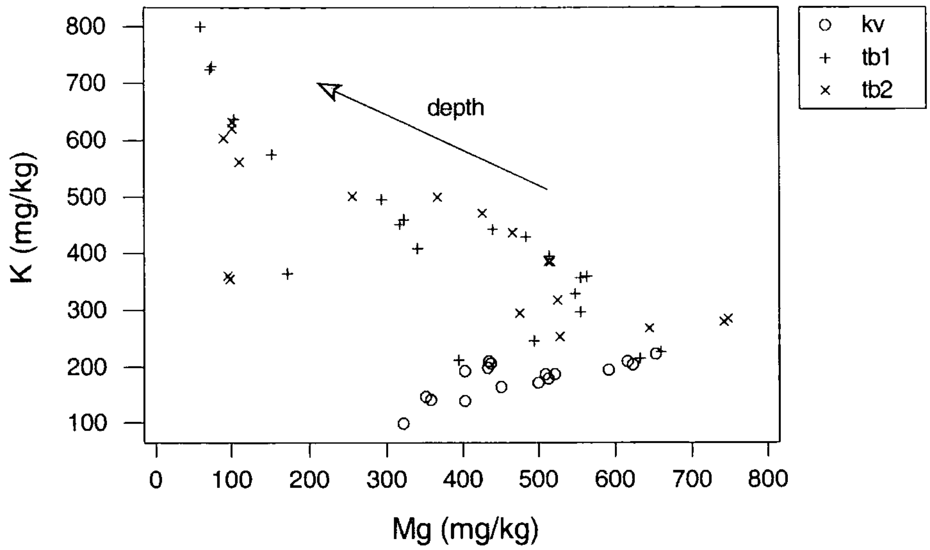


Figure 6.124. K vs. Mg in the exchangeable phase within the sediments of the Tees impoundment, showing possible replacement of K by Mg towards the sediment surface.

6.9.2.4 Particle-size controls

Generally it is found that particle size is not a major factor in controlling elemental concentrations, and particle-size distributions are relatively constant with depth in the sediments of the two impoundments. For these reasons it was felt unnecessary to apply grain-size corrections to the data such as are suggested where metal data from distinct sedimentary environments are to be compared (Loring and Rantalla, 1992).

The only large difference in particle-size distribution occurs in the sediment of the Tees where there is a distinct difference between sand dominated pre-impoundment sedimentation and silt dominated post-impoundment sedimentation. The majority of elements analysed show distinct concentrations through some or all of the speciations in which they occur across this boundary. It is impossible to tell to what extent these differences are due to a grain-size effect, and to what extent they are due to distinct concentrations within the water body and within the sediments deposited during the pre and post-impoundment periods. For Fe and associated metals concentrations tend to be lower in the pre-impoundment sediment for the Fe hydroxide bound fraction, but higher for the sulphide and organic bound fraction. Si concentrations are higher in pre-impoundment sediment for all species and a quartz sand source is suggested (a true grain-size effect). The contrasting behaviour for different elements and even different species to grain-size differences confirms that particle-size normalisation techniques (which typically assume a dilution effect by sand-sized material) are inappropriate for this kind of multi-elemental speciation study.

6.9.3 Sediment quality

Within the UK no Environmental Quality Standards (EQSs) for levels of pollutants in sediment in rivers, lakes and estuaries have been set. For 'List I' pollutants of the European Dangerous Substances Directive (1976, 76/464/EEC) the official position of the EA is that levels should remain at 'standstill', i.e. no increase from current levels is permissible. Unofficially sediment quality guidelines produced by the Canadian Council of Ministers of the Environment (CCME, 1999 and 2001) are used as an aid in assessing levels of contamination within freshwater sediments. These consist of lower Interim Freshwater Sediment Quality Guidelines (ISQGs) and higher Probable Effects Levels (PELs) at which adverse biological effects become likely, derived according to CCME (1995). Table 6.27 compares the mean levels of potentially toxic metals found in the sediments of the Tees and Wansbeck impoundments (as the sum of means for stages 1 to 4 of the extraction procedure) with the CCME guideline values and the Maximum Permissible Concentrations (MPC) of the Dutch National Institute of Public Health and the Environment (RIVM, 1997):

Metal	ISQG	PEL	MPC	Tees	Wansbeck
Co	-	-	10	4.9	5.3
Cr	37.3	90.0	1620	71.6	9.5
Cu	35.7	197	37	13.0	28.7
Ni	-	-	9.4	7.7	11.5
Sn	-	-	22000	-	-
V	-	-	14	-	-
Zn	123	315	480	185	121

Table 6.27. A comparison of mean metal levels in the sediments of the Tees and Wansbeck impoundments with Canadian (ISQG and PEL) and Dutch (MPC) sediment EQSs. Concentrations are in mg/kg dry weight, and for EQSs refer to total extractions and for the Tees and Wansbeck to the sum of partial extractions (excluding the residual/silicate bound phase).

The concentrations given in table 6.27 for the Tees and Wansbeck refer to the potentially environmentally available fraction within the sediment, and thus are likely to underestimate the total concentrations within the sediments. Jones and Turki (1997) found that the residual (not environmentally available) fraction was significant in the sediments in the Tees estuary downstream of the barrage for a range of heavy metals, particularly Co and Ni for which the largest fractions are in this phase.

The sediments of the two impoundments are generally relatively high in metals, due to a combination of anthropogenic inputs to the water bodies and the fine grained and organic rich nature of the sediment. Whilst Co levels are reported as below the Dutch standards, it is likely that total values are close to or in excess of the MPC since the majority of Co is found to be associated with the residual phase (Jones and Turki, 1997). By the same argument, Ni is likely to be significantly above the MPC in the sediments of both impoundments. Zn is well below the Dutch standard within both impoundments, but exceeds the more stringent Canadian ISQG standard in the Tees sediment. CCME (2001) give 32 % adverse biological effects in the Zn range between the ISQG and PEL concentrations. Comparison of Cu concentrations suggest that the sediments in both impoundments are unpolluted with this metal. Sediment in the Wansbeck is unpolluted with respect to Cr but the Tees, on which Cr industry is based, shows levels approaching the PEL standard. CCME (2001) suggest an incidence of adverse biological effects of approximately 19 % within this range of Cr concentrations, although actual environmental impact is likely to depend on the oxidation state (Cr^{3+} is considered relatively harmless whereas Cr^{6+} is highly toxic with some compounds carcinogenic).

An important reason for studying the speciation of metals within the sediment of the estuarine impoundments was to assess the likely impact of dredging on water quality. It has been shown that impoundments are infilling with sediment. Within the Tees an approximate rate of sediment infill of 7 cm/annum is seen. In the Wansbeck sedimentation has caused extensive areas of shallow (< 50 cm depth) water in which debris (mainly parts of trees) carried by high flows can become stuck, interfering with leisure activities (rowing and jet-skiing) on the impoundment. Dredging is a possible solution to this sediment infilling, but may have negative water quality impacts relating to resuspension of polluted sediment (Peterson et al., 1997). The largest remobilisation of metals on dredging occurs where heavy metals are held within sulphides in anoxic sediments (and have low solubility and bioavailability; Bryan and Langston, 1992). These sulphides may be oxidised on suspension in the oxic overlying water column and release metals in dissolved (toxic) forms. Dredging is therefore likely to cause greater water quality problems in the Wansbeck impoundment in which a large proportion of the metals are seen to be associated with sulphides. In the Tees the change in redox conditions from sediment to water column is interpreted as lower, and the impacts of dredging are therefore likely to be less. An additional problem (not considered here) created by dredging activities is the safe disposal of large quantities of (often contaminated) dredged material.

Whilst this study has allowed an approximate assessment of levels of a selection of metal pollutants in the sediments of the Tees and Wansbeck impounded estuaries and identified likely contamination, further work is suggested to determine the extent and impact of the problems. In particular it is recommended that total extractions of sediments are carried out to allow comparison with guideline values, and that a broader range of heavy metals is analysed (e.g. by ICP-MS) to include the EU 'List I' metals Hg and Cd. In addition sampling and the assessment of metal concentrations in biota is recommended to identify the relationship between potentially bioavailable concentrations in sediment and bioaccumulation (see e.g. Landrum and Robbins, 1990). Guisti (2001) has shown significant correlation between levels of Cu, Zn and Pb in sediments contaminated by colliery spoil and brown algae for a section of coastline immediately north of the Tees estuary. Detailed study may try to establish the link between specific "species" (i.e. exchangeable, associated with Fe and Mn oxides, etc.) in which metals are held and the impact on organisms. At present this link between biological and chemical studies is little explored.

6.9.4 Sediment fingerprinting

One of the aims of the sediment analyses within the impoundments was to assess the pattern of metal distributions and speciations with a view to developing studies to fingerprint sediment sources to the impoundments. Sediment fingerprinting essentially characterises or 'fingerprints' a variety of potential sediment sources to a system using a range of physical and chemical characteristics, and comparison with the equivalent information within the suspended sediment allows the relative importance of the sources to be determined (Oldfield et al., 1979; Peart and Walling, 1986; Walling and

Woodward, 1992). Sediment fingerprinting studies generally assess the contribution of sediment sources to the suspended sediment within a system. Within this study the physical and chemical characteristics showing the maximum amount of variance in the sediment cores are determined, with the aim of assessing the potential for using bed sediment as the downstream end member of a multivariate mixing model. As described above, variance in the multivariate dataset collected relates to several groups of factors. These include covariance in Fe and associated elements, particle size variations, variations relating to ionic composition of the overlying water column, and a range of external inputs (of which Cr variation is the most significant).

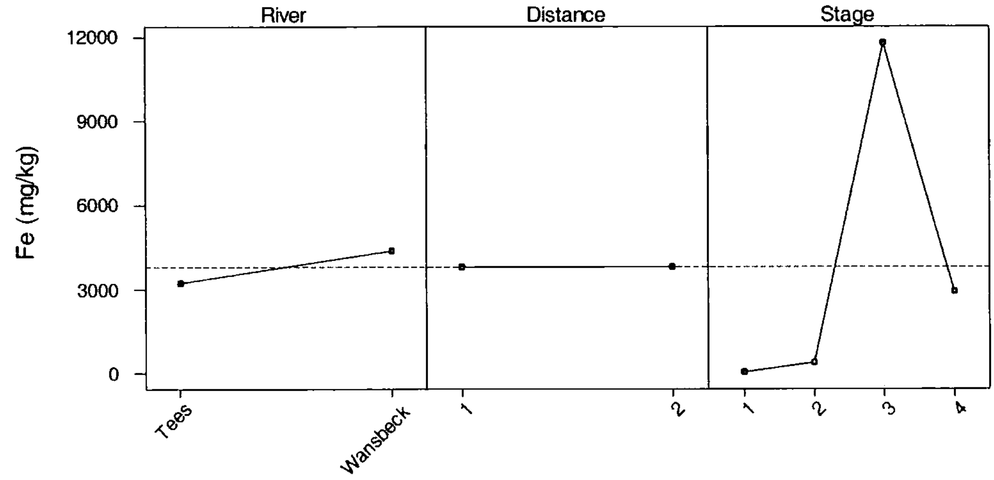


Figure 6.125. Main effects plot for GLM of the factors of river, distance and extraction stage on Fe in the sediment of the impoundments (LS means for factor levels).

The majority of variation in Fe and associated metals is related to their speciation (figure 6.125), with the majority of these metals associated with Fe and Mn oxides and organic material and sulphides. These phases have been shown to be subject to redox controlled mobilisation within the sediments (including potential exchanges across the sediment-water interface), and because of this are likely not to represent the patterns of metals within source sediment. In addition group 1 and 2 metals are shown to show variation within the exchangeable fractions dependent on the ionic strength and composition of the overlying water column (i.e. concentration of these metals changes on contact with seawater in impoundments). Use of metals within sediment fingerprinting studies for bed sediment is therefore suggested to concentrate on the residual mineral phase of sediment since this has no potential for alteration following sediment deposition.

The particle size of suspended material is likely to vary with distance downstream in a river system with changes in flow velocities. The impoundments are generally stable environments in which a reduction of flow velocities relative to the rivers entering them allows deposition of fine particulate material. Particle size distributions in the bed sediments of the impoundments will bear little relationship to those in the sediment sources, and can therefore not be used in fingerprinting.

Cr shows large amounts of variation both between and within the two impoundments, and is interpreted as relating to anthropogenic inputs to the systems. Within the Tees it was seen that there is a significant difference between the sediment deposited pre-impoundment and that deposited post-impoundment through all extraction stages. Elements showing distinct concentrations in sediment entering the impoundments from the seaward and the landward directions has the potential to be used to assess the relative contribution of these fractions to the bed sediment in partial tidal exclusion systems. The carbonate bound phase was also interpreted as showing variation based on sediment source, with changing sediment source during prolonged high flow periods suggested. Of the parameters studied within this work elements associated with this phase show the greatest potential for discriminating between catchment sediment sources to the bed sediments of the impoundments.

Chapter 7

Sediment Pore Water Sampling

7.1 Introduction

In situ sampling of pore waters within the sediment of estuarine impoundments was carried out, together with speciation experiments (chapter 6), to:

1. assess the biogeochemical processes occurring in the systems, and,
2. estimate exchanges between sediment and water-columns.

The diffusive equilibration in thin film (DET) technique (a.k.a. gel probes) (e.g. Davison W and Zhang H 1994; Zhang H et al. 1995; Krom et al. 1994; Davison W et al. 1994) was used to sample pore waters from sediment cores taken from two impounded estuaries from within the SIMBA project (see section 7.3 for further details of analytical techniques).

7.2 Survey design

7.2.1 Estuaries studied

To allow comparison with the results collected during both water quality surveys (chapters 3 and 4) and sequential extraction experiments (chapter 6), the Tees and Wansbeck impounded estuaries were chosen for pore water sampling. This choice allowed comparison of pore waters in a total tidal exclusion (freshwater) impoundment (the Tees) with a partial tidal exclusion (mixed freshwater and seawater) impoundment (the Wansbeck).

7.2.2 Sampling sites and dates

For consistency the same sites at which cores were taken for the sequential extraction sediment sampling were chosen for sediment pore water sampling. These were immediately upstream of the barrages in both impoundments, and further upstream at site KV in the Tees (table 7.1). Unfortunately, due to equipment constraints, only 5 cores could be examined, and site RB from the Wansbeck (NZ 2775 8585) was excluded from the sediment pore water sampling experiments.

Coring was carried out on 26th October 2001 for sites in the Wansbeck impoundment. On this date the water body of the Wansbeck impoundment was predominantly freshwater. For the Tees impoundment, coring for pore water sampling was carried out on the 16th November 2001.

River	Site name	Site abbreviation	Number cores taken	Grid reference
Tees	Opposite Kvaerner Building	KV	1	NZ 4570 1905
Tees	Tees Barrage	TB	2	NZ 4616 1905
Wansbeck	Wansbeck Barrage	WB	2	NZ 2935 8536

Table 7.1. Sediment pore water sampling sites.

7.2.3 Replicates

As with the sediment quality surveys (chapter 6) replicate pore water sampling was carried out using replicate cores taken from within 1 m of each other at sites TB and WB to allow assessment of local variation in conditions (table 7.1).

7.3 Sampling procedure

7.3.1 Sediment coring

The five cores used for *in situ* pore water sampling were collected from the project RV using a Mackereth corer in the same manner as described in chapter 6. Undisturbed cores of approximately 50 cm length and which included at least 10 cm of the overlying water column were selected. Comparison of deployment made by divers and that in cores of 7 cm diameter indicates that the structure of surface 1 cm of sediment may be lost when DET probes are used in cores (Davison et al. 1994).

Cores were transported in the dark with the minimum of disturbance, and were chilled to 4°C within 1 hour of sampling. The gel probes were deployed in the sediment cores after a settling period of approximately 2 hours.

7.3.2 Gel probe description

The gel probes used in the pore water sampling experiments were prepared by DGT Research Ltd., Lancaster (email: h.zhang@lancaster.ac.uk). These consist of a polyacrylamide sheet of gel of approximately 1 mm thickness and 96 % water content prepared according to Krom et al. (1994), housed in a Perspex casing giving a 15 cm by

1.8 cm window of gel along one side of the probe (figure 7.1). The polyacrylamide gel surface is covered by a 0.45 μm (pore size) cellulose nitrate membrane filter to avoid damage to the gel during insertion and authigenic deposition of oxyhydroxides on the gel during deployment (Davison et al. 2000). The probe casings have a sharpened end to aid in insertion.

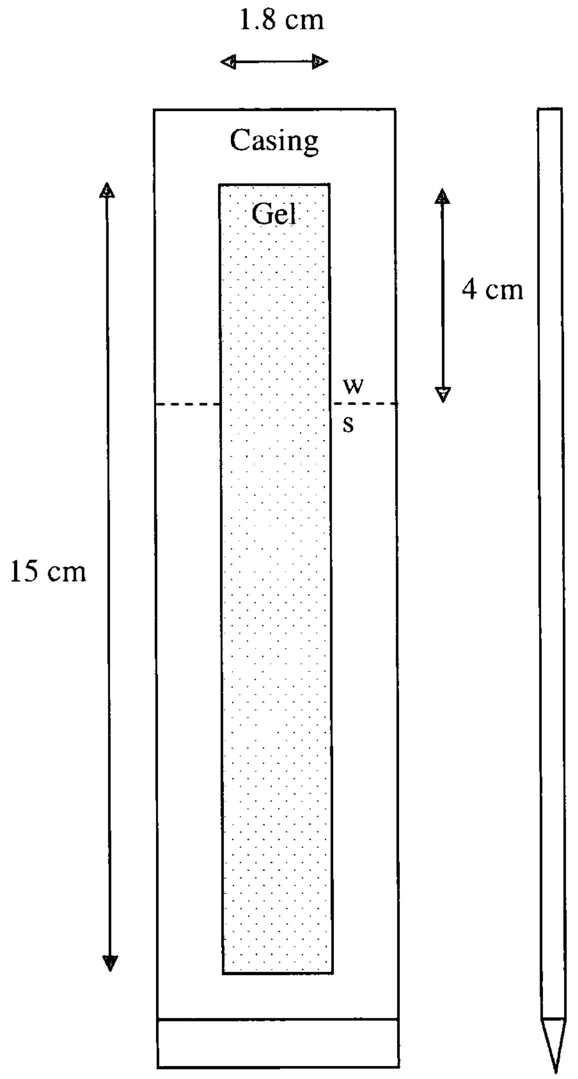


Figure 7.1. Diagram and dimensions of the DET gel probes used. s-w marks the level of the sediment-water column interface during deployment of the probe.

7.3.3 Gel probe deployment and front equilibration

Probes were marked with a fine line at either 4 or 5 cm (exactly) below the top of the gel window and deoxygenated prior to deployment in the sediment cores. Probe deoxygenation was carried out by bubbling oxygen free nitrogen through 18 MΩ.cm water containing the probes for 24 hours immediately preceding deployment. Clean gloves were worn at all times when handling probes to minimise the possibility of contamination.

Probes were inserted gently and slowly by hand into the sediment, until the marks at 4 or 5 cm below the top of the gel window were in line with the sediment-water interface. Care was taken to keep the probes as vertical as possible during deployment. One probe was inserted to each sediment core collected.

Probes were left in the sediment cores for a period of 72 hours to ensure complete equilibration with the pore waters and overlying water column. Mortimer et al. (1998) determined that anions in marine and estuarine pore waters require up to 48 hours for complete front equilibration, and that Ca and alkalinity require up to 8 hours. The sediment cores were stored in the dark at 4°C during this equilibration period to minimise alterations from the in situ conditions (particularly in terms of redox conditions).

7.3.4 Gel probe retrieval and slicing

On retrieval following front equilibration with pore waters in the sediment there is a relaxation of concentration differences within the gel probes due to diffusional equilibration (Harper et al. 1997), and gels must be rapidly sliced or chemically fixed to avoid loss of fine scale (< 2 mm) features in the profiles. Within this project the former option was chosen, and the whole process of probe removal, slicing and placement in specimen containers was carried out in under 10 minutes for each probe.

After 72 hours of front equilibration probes were removed from the sediment cores and rinsed briefly with a minimum of deionised water, and adhering sediment wiped away with a tissue. A cut was made across the gel at the sediment-water interface mark and around the edge of the gel window using a Teflon coated razor blade, and the gel and covering membrane were removed and placed on an acid washed Perspex cutting board using plastic tweezers. The filter membrane was then removed, and the gel sliced into 1 cm sections and placed into 5 ml polystyrene specimen containers. This process was carried out within a laminar flow hood to avoid the possibility of contamination of the gels by airborne particulates. The weights of the slices were determined to allow calculation of the original gel concentrations following back equilibration and analysis.

7.3.5 Back equilibration of gel slices

Analysis by ICP-MS required the elements contained within the gels to be in solution (gels can also be dried for analysis by PIXE or ICP-laser ablation techniques (Fones et al. 1998), and so gel slices were back equilibrated into 4 ml of 3.5 % HNO_3. Gel slices were left for at least 1 week to back equilibrate prior to analysis.

7.3.6 Elemental analysis

The elution solutions obtained from back equilibration of the gel probe slices were analysed using ICP-MS.

Principle:

Inductively coupled plasma was first successfully used as an ion source for a mass spectrometer in 1981 at the University of Surrey (Gray 1986a). It can be used on a wide variety of samples (waters, or solids after suitable digestion) (Montaser and Golightly 1992, Date and Gray 1989), and allows rapid analysis of most elements in the periodic table over wide concentration ranges down to levels of 10 ng/l (Houk and Thompson 1988). The ICP provides essentially the same function in MS as in OES/AES analysis (Jarvis et al. 1992), i.e. to evaporate and dissociate samples into free atoms and ions, and to excite the free atoms and ions into higher energy states. Ions are extracted from the plasma due to a decrease in pressure into the mass spectrometer. Mass spectrometers operate under high vacuum, and the pressure differential between the plasma (at atmospheric pressure) and spectrometer is maintained by two conical nickel apertures (sampling cone and skimmer) which allow ions to pass into the spectrometer but deflect away the majority of uncharged particles (Jarvis 1997).

After passing through the skimmer, ions are focused to a beam by a set of electrostatic lenses before passing in to the mass analyser. Mass spectrometry works by distinguishing particles on the basis of their mass-to-charge ratio (m/z). The most common form of mass analyser used in ICP-MS is a quadrapole mass filter (Jarvis 1997). A quadrapole consists of four parallel stainless steel or molybdenum rods across which a potential is applied in such a way to only allow particles of one m/z ratio to pass through to the (electron-multiplier) detector, with lighter or heavier particles being deflected into the rods and neutralised. By sweeping the combination of potentials, the detector will scan across the m/z ratios. The responses of several scans are normally combined, and the composite peaks produced are processed by computer to give elemental concentrations in the sample analysed.

Method:

A Perkin Elmer Sciex Elan 6000 ICP- Mass Spectrometer was used for all ICP-MS work (Perkin Elmer 1996). Signal processing was carried out using Elan NT software (Perkin Elmer 1996). Samples were run either manually or using a Perkin Elmer AS90 autosampler.

A semi-quantitative "TotalQuant" methodology was used. This provides a good (±10%) estimate of the concentration of 65 elements across the total mass range (excluding halogens and lighter elements which cannot normally be effectively measured on ICP-MS, and those that showed significant interferences) in each sample. It has the advantages of rapid analysis and no requirement of prior knowledge of sample.

Response factors for the machine were determined by the running of a 10ppb external standard containing a suite of elements from across the mass range (Mg, Cu, Cd, Pb, Sc, Rh, Tl, Ce, Tb, Ba, Ge, P and Si.

To account for any possible suppression and/or drift in machine sensitivity 20µl of 1mg/l indium (In) was added per 10ml of sample as an internal standard (spike). It was assumed that the response across the whole mass range was the same as that for the internal standard.

Quality control included periodically analysing the standard solution as an unknown sample during sample runs as a check on accuracy. LOD values determined in this study are generally low, the majority of elements detectable to below 10ng/l (table 7.2):

LOD<10ng/l	LOD<100ng/l	LOD>0.1μg/l (value in μg/l in brackets)
Si, Sc, V, Co, Ga, Ge, Se,	Mn	Mg (3.347)
Rb, Y, Zr, Nb, Mo, Ru, Rh,	Ni	Al (0.110)
Pd, Ag, Cd, Sn, Sb, Te, I,	Cu	P (0.402)
Cs, La, Ce, Pr, Nd, Sm, Eu,	Zn	K (13.328)
Gd, Tb, Dy, Ho, Er, Tm,	As	Ca (23.375)
Yb, Lu, Hf, Ta, W, Re, Os		Ti (0.112)
,Ir, Pt, Au, Hg, Tl, Pb, Bi,		Cr (0.132)
Th, U		Fe (8.921)
		Sr (0.129)
		Ba (0.108)

Table 7.2. Analytical LOD values for the ICP-MS pore water analyses.

LOD values tend to be higher for lighter elements where interferences from polyatomic ions are significant (e.g. P has a mass number (m/z) of 31 which is equal to the polyatomic species of $^{15}N^{16}O$ and $^{14}N^{16}O^{1}H$). High Cl concentrations in samples form argon chlorides and oxides which interfere significantly in the determination of V, Se and As, however as only freshwater samples were analysed it is assumed that this was not a problem.

The operating software used assumed normal isotopic ratios existed in all samples, and corrected for isobaric interferences (isotopes of a different elements having the same m/z as the element being determined) on this basis.

The flush time between samples was set at 90 seconds and was assumed to be sufficient to avoid any memory effects in the equipment. Suppression of signal and machine sensitivity drift were minimal during all sample runs.

7.3.7 Method development experiments and LODs

Method limits of detection were determined by carrying out the slicing and back equilibration procedures on a blank DET gel probe. 3s LODs in μg/l for each element analysed are given in table 7.3. The majority of elements measured in the pore waters of the sediment are above the LODs for the procedure.

Element	LOD	Element	LOD	Element	LOD	Element	LOD
Mg	166	**Zn**	574	**Sn**	0.955	**Tm**	0.000
Al	58	**Ga**	0.07	**Sb**	0.115	**Yb**	0.000
Si	0.00	**Ge**	0.05	**Te**	0.000	**Lu**	0.000
P	7.08	**As**	0.02	**I**	0.000	**Hf**	0.000
S	na	**Se**	0.00	**Cs**	0.000	**Ta**	0.032
Cl	na	**Rb**	0.54	**Ba**	90	**W**	0.000
K	609	**Sr**	2.97	**La**	0.021	**Re**	0.033
Ca	436	**Y**	0.00	**Ce**	0.016	**Os**	0.074
Sc	0.02	**Zr**	0.09	**Pr**	0.016	**Ir**	0.000
Ti	2.76	**Nb**	0.02	**Nd**	0.016	**Pt**	0.000
V	0.14	**Mo**	0.17	**Sm**	0.000	**Au**	0.000
Cr	4.26	**Ru**	0.00	**Eu**	0.016	**Hg**	0.000
Mn	6.59	**Rh**	0.00	**Gd**	0.016	**Tl**	0.000
Fe	250	**Pd**	0.00	**Tb**	0.000	**Pb**	0.205
Co	0.47	**Ag**	0.10	**Dy**	0.000	**Bi**	0.028
Ni	11.6	**Cd**	0.03	**Ho**	0.000	**Th**	0.000
Cu	5.11	**In**	spike	**Er**	0.000	**U**	0.035

Table 7.3. Process LODs (3s) in µg/l (ppb) for the DET gel probe pore water analysis technique. na = not measured for technical reasons. In was added to all samples as an internal standard (spike) during ICP-MS.

Several workers have shown that gels equilibrated in the laboratory with solutions of known analyte concentrations contain the same concentration as in the solution (Krom et al. 1994; Davison et al. 1994; Mortimer et al. 1998; Zhang et al. 1999). In this study an experiment was carried out to test the recovery of various elements from gels. A series of 5 gel slices were left to forward equilibrate in standard solutions containing 200 mg/l Ca, 20 µg/l Cu and 20 µg/l Pb (to test through a large mass range of metals) for 72 hours, before being back equilibrated and analysed using the procedures outlined above. The mean recovery factors for these experiments were:

- Ca = 89.4 ± 1.2 %,
- Cu = 96.5 ± 4.9 %, and
- Pb = 93.4 ± 3.5 %.

The reported values for concentrations of analytes are therefore likely to represent well, but slightly underestimate, true pore water values across the whole mass range measured.

7.4 Results and discussion

Results are presented for the sediment pore water sampling carried out using DET gel probes as described above. Comparison of the pore water behaviour between types of impoundments is carried out by comparing results from cores collected from sites WB and TB (immediately upstream of the Wansbeck and Tees barrages respectively). Data from site KV in the Tees impoundment are not discussed in detail.

Whilst the ICP-MS analysis allowed the collection of data for 65 elements within pore waters, discussion concentrates on those elements which were also examined during study of the sediment quality (chapter 6), and on elements included in both 'List I' and 'List II' of the European Dangerous Substances Directive (1976, 76/464/EEC). These elements are Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Ni, P, Pb, Sc, Si, Sn, Ti, V and Zn. Cd and Hg are within 'List 1' and have Environmental Quality Standards (EQSs) assigned by the EU, and As, Cr, Cu, Fe, Ni, Pb, Sn, V and Zn (and B which cannot be measured by ICP-MS) are within 'List 2' and setting of appropriate EQSs is left to individual Member States (table 7.4).

List	Element	Annual average (µg/l)
I	Cd	2.5
	Hg	0.3
II	As	25
	Cr	15
	Cu	5
	Fe	1000
	Ni	30
	Pb	25
	Sn (as tributlytin/triphenyltin)	0.002/0.008
	V	100
	Zn	40

Table 7.4. Saline EQSs for elements included in the EU Dangerous Substances Directive. Values refer to dissolved forms except for V and organotin compounds which are for total.

Cd was undetectable in almost all gel slices and Ni, Sn and Zn concentrations were generally below the LOD for the method and these results are not presented. In addition gel probe WB1 was interpreted as contaminated with Al, and there were analytical problems measuring Cr in gel probe TB2, and therefore these data are also not presented. Please note that whilst data within the chapters on water and sediment quality is generally given in ppm (mg/l or mg/kg), data for pore waters is presented in units of µg/l (ppb). A summary of the mean levels found within pore water and water immediately overlying the sediment is given in table 7.5.

Element	**Mean World Streamwater**	**Mean level in Wansbeck water**	**Mean level in Wansbeck pore water**	**Mean level in Tees water**	**Mean level in Tees pore water**
Al	300	30	71	107	283
As	4	5 (√)	32 (×)	0.5 (√)	3.9 (√)
Ca	18000	67000	226000	62000	150000
Co	0.2	1.7	3.5	2.0	5.0
Cr	0.7	17 (×)	26 (×)	13 (√)	15 (×)
Cu	3.0	76 (×)	33 (×)	63 (×)	9 (×)
Fe	40	2500 (×)	29100 (×)	2940 (×)	72700 (×)
Hg	0.05	0.00 (√)	0.06 (√)	0.00 (√)	0.00 (√)
K	2300	34000	208000	7600	15000
Mg	4100	66000	612000	17000	51000
Mn	4.0	2200	5900	2100	10700
P	20	340	10560	408	10950
Pb	3.0	21 (√)	3.5 (√)	21 (√)	4.4 (√)
Sc	0.004	0.7	4.4	0.0	0.0
Si	6000	2300	7500	3600	10600
Ti	3.0	8	54	4	41
V	0.9	6 (√)	29 (√)	0 (√)	1 (√)

Table 7.5. Summary of elemental concentrations (µg/l) within pore water and water overlying sediment from the Tees and Wansbeck estuarine impoundments and estimated World mean streamwater concentration (data from Koljonen, 1992). Comparison with UK Environmental Quality Standards for water quality (not specific to pore waters): × = level exceeds EQS; √ = level does not excede EQS.

7.4.1 Al

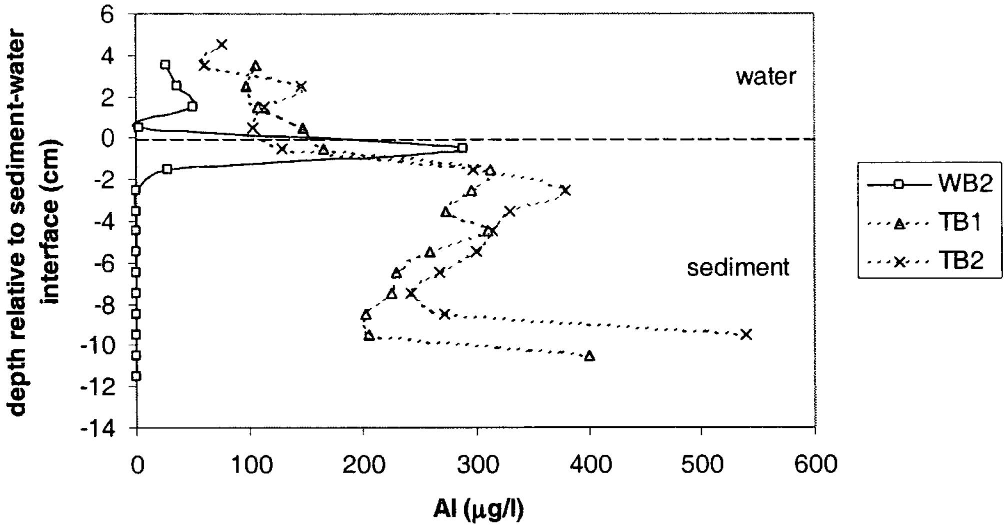


Figure 7.2. Pore water profiles for Al in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

The profiles for Al within pore water and overlying water (figure 7.2) show distinct differences between the two impoundments studied. Within the Wansbeck the levels in pore waters through most of the length sampled are practically zero, with a peak in Al levels very close to the sediment-water interface (SWI). Within the Tees sediment levels are greater than 200 μg/l through the depth of sediment studied, with both cores showing a peak in levels at approximately 2 cm depth in the sediments with a subsequent decrease to a depth of 10 cm, at which point Al levels increase dramatically. Levels in the overlying waters of both impoundments are low, and diffusive gradients exist between the sediments and water.

The profiles for Al closely follow those for Fe and Mn (Pearson correlation for Al to Fe = 0.585, P = 0.000; figure 7.3), and the amount of Al within the pore waters is associated with the amount of Fe and Mn oxide reduction and dissolution. As described below, the maximum reduction of Fe hydroxide takes place just below the SWI in the Wansbeck sediments but at a depth greater than that sampled by the DET gel probes (> 12 cm) in the Tees. It is likely that Al shows sorption to the surface of Fe hydroxides since the maximum in Al in the dissolved phase precedes that of Fe (in terms of depth/reducing state in the sediments).

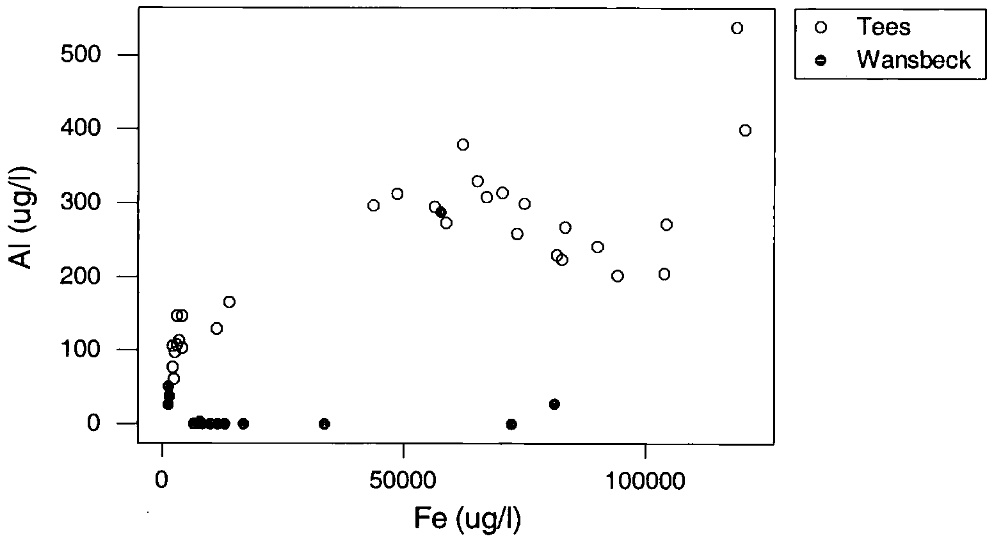


Figure 7.3. The relationship between Al and Fe within the pore waters of the Tees and Wansbeck impoundments.

7.4.2 As

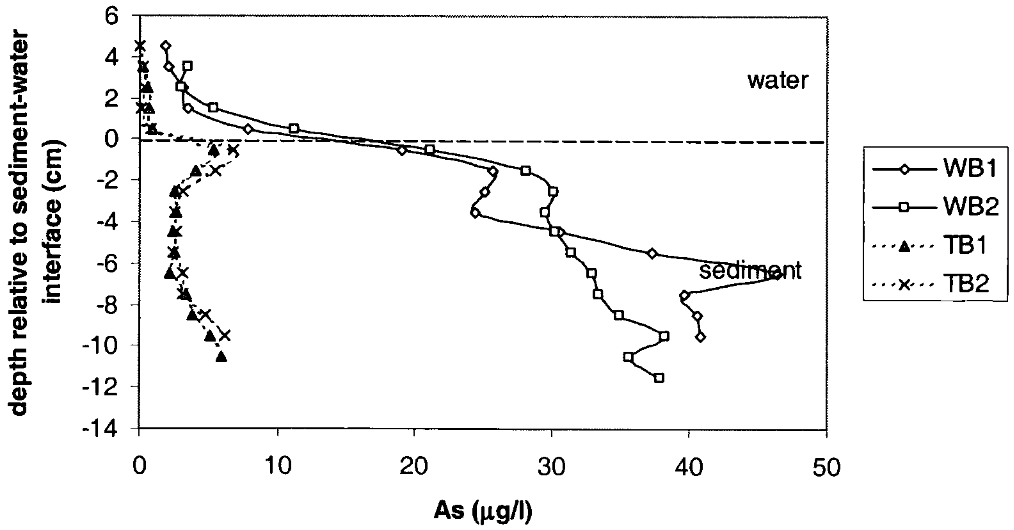


Figure 7.4. Pore water profiles for As in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

As is below the EQS in the waters of both impoundments and in the sediment pore water of the Tees impoundment, but the mean level in the sediment pore water of the Wansbeck exceeds the EQS (table 7.5). High concentrations of pollutants in sediment pore waters may have an impact on benthic biota in the impoundments (As^{3+} is particularly toxic and teratogenic). As shows a distinct peak immediately below the SWI in the Tees with an apparent diffusion from (anoxic) sediment at depth up to this point. Within the Wansbeck there is some localised variation in As levels which may relate to heterogeneity in As concentration in the particulate material. The general trend is of a diffusion upwards in the sediment. As input to the Wansbeck sediment is probably associated with coal mining in the area. In both impoundments a diffusion gradient for As exists between the levels in pore water and the lower levels in the overlying water across the SWI.

Association of As with Fe in the solid phase of sediments has been observed (DeVitre et al., 1991), and Davison et al. (1997) suggest simultaneous (and localised) remobilisation of these metals, but no evidence for a Fe association is seen in this project (Pearson correlation = -0.204, P = 0.115). Within the cores studied As appears to be released from anoxic sediments even at depths at which Fe is assumed to be immobilised as sulphides (see section 7.4.7 below), and decomposition of organic material at depth is proposed as the source of As to the pore water.

7.4.3 Ca

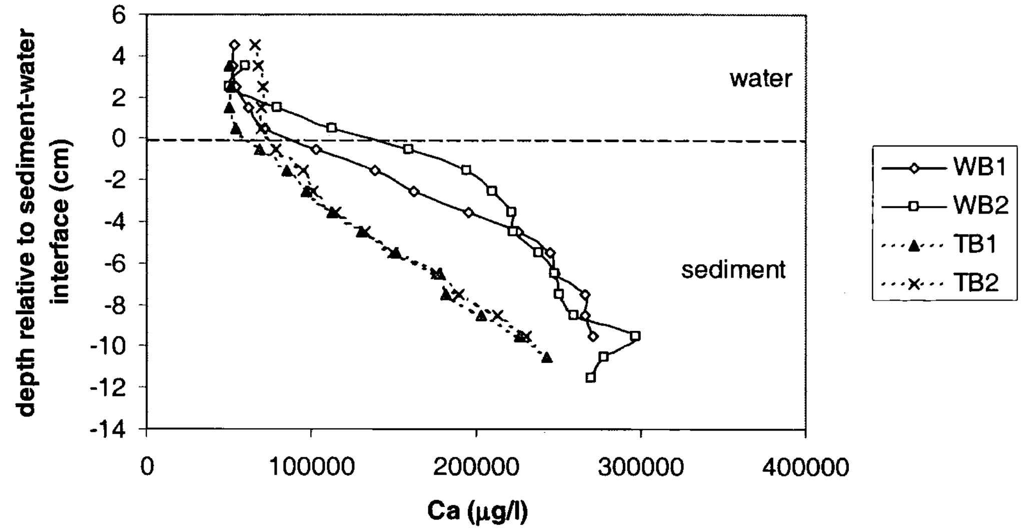


Figure 7.5. Pore water profiles for Ca in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

Ca shows similar diffusion controlled profiles for both the Tees and the Wansbeck sediments, with concentrations higher at depth than within the overlying water. Note that coring on the Wansbeck was carried out during a period following high river flow and therefore the water overlying the sediments was fresh. This is in contrast with the coring for sequential extraction experiments (chapter 6) during which sediments in the Wansbeck were overlain by saline water. The Tees impoundment is designed to totally exclude tidal waters and is almost exclusively freshwater. The source of Ca within the pore waters of the Tees sediment could either be from carbonate dissolution or from seawater. The World mean seawater Ca concentration is approximately 412000 μg/l (Reimann and Caritat, 1998). That the relationship between K or Mg and Ca (Pearson correlation = 0.793 and 0.815 respectively; P = 0.000) is lower than that between K and Mg (Pearson correlation = 0.996; P = 0.000), and that the ratio of Mg/Ca differs to that in seawater (Mg/Ca in pore water = 1.79; Mg/Ca in world mean seawater (Lide, 1996) = 3.13) suggests that some carbonate dissolution is taking place. The gradient of Ca (and K and Mg) with depth in the Wansbeck pore waters changes at approximately 5 cm depth. The same change in gradient (but in the opposite direction since sampling was during a period in which the overlying water was saline) is observed in the exchangeable fraction of the sediment cores (figure 7.5), and represents the depth to which short term changes in overlying water composition with tidal input and freshwater flow (fresh vs. seawater) impact on these ions in the sediments.

7.4.4 Co

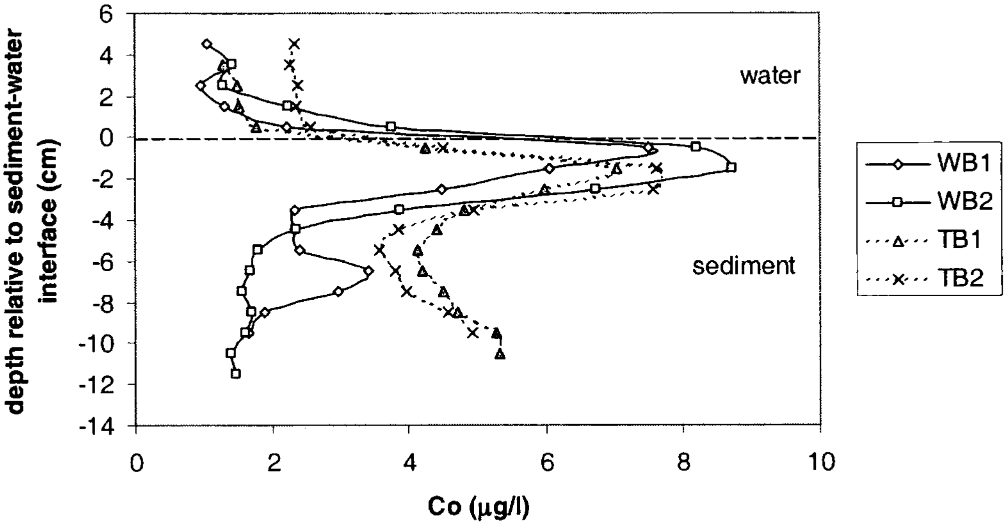


Figure 7.6. Pore water profiles for Co in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

Co shows low concentrations in the water column with peaks in concentration just below the SWI in both impoundments, with lower levels in pore waters deeper within the sediments. The peak in Co is slightly closer to the SWI in the Wansbeck than the Tees sediment (figure 7.6).

In chapter 6 it was shown that Co is held in the solid phase of sediments in association with carbonate, oxides of Fe and Mn and in sulphides or organic matter. The pattern within pore waters is similar to that for Mn and Fe (Pearson correlation = 0.707 and 0.712 (P = 0.000) respectively; figure 7.7) and Co is interpreted as redox controlled, undergoing release to pore waters with reduction of Fe and Mn hydroxides.

Release of Co is seen to precede Mn and Fe release in the reduction sequence (with depth) in the sediment, implying that Co may be associated with hydroxide particle surfaces and therefore be disproportionately released at the onset of hydroxide reduction.

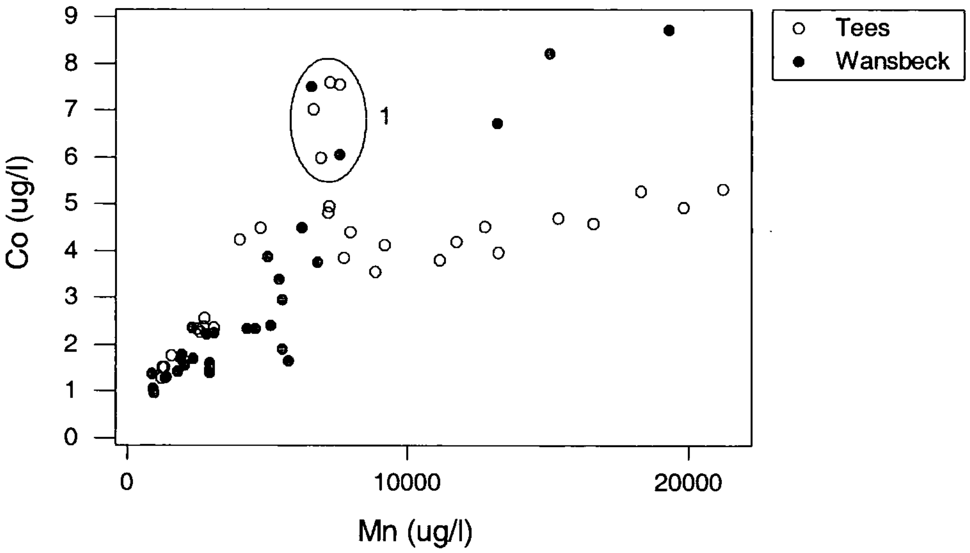


Figure 7.7. Co vs. Mn within the pore waters of the Tees and Wansbeck impoundments, showing release of Co preceding Mn release (1) in the reduction sequence.

7.4.5 Cr

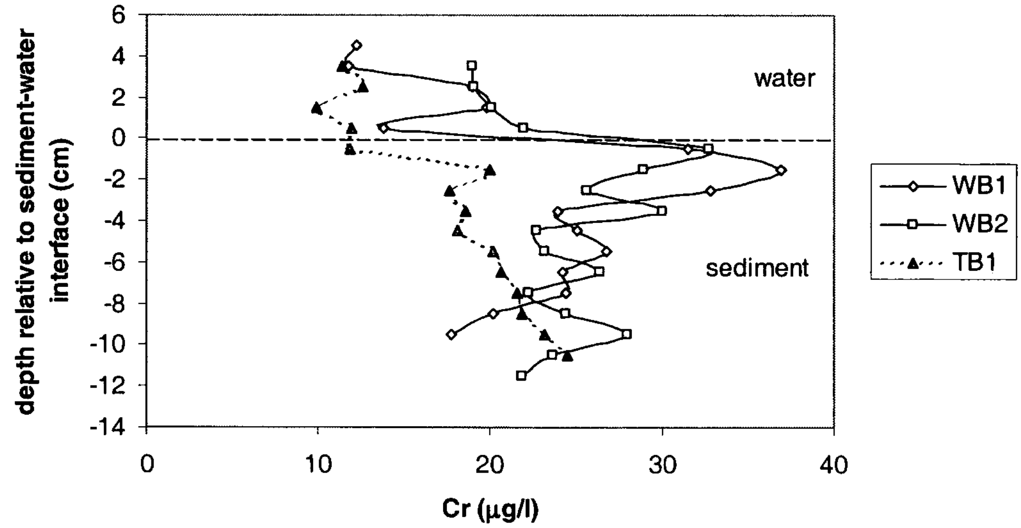


Figure 7.8. Pore water profiles for Cr in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

The LOD for Cr is relatively high (4.26 μg/l) and much of the scatter within the dataset is due to analytical error. Equally, Cr analysis failed for several gel slices from the TB2 probe and these data are therefore not presented. Nevertheless a redox controlled behaviour is suggested by the similarity with Fe profiles in the two systems (figure 7.8), with a peak in Cr release at approximately 2 cm below the SWI in the Wansbeck and a gradual increase in Cr release with depth in the Tees sediment. The correlation between Fe and Cr in the pore waters is 0.502 (P = 0.000; figure 7.9).

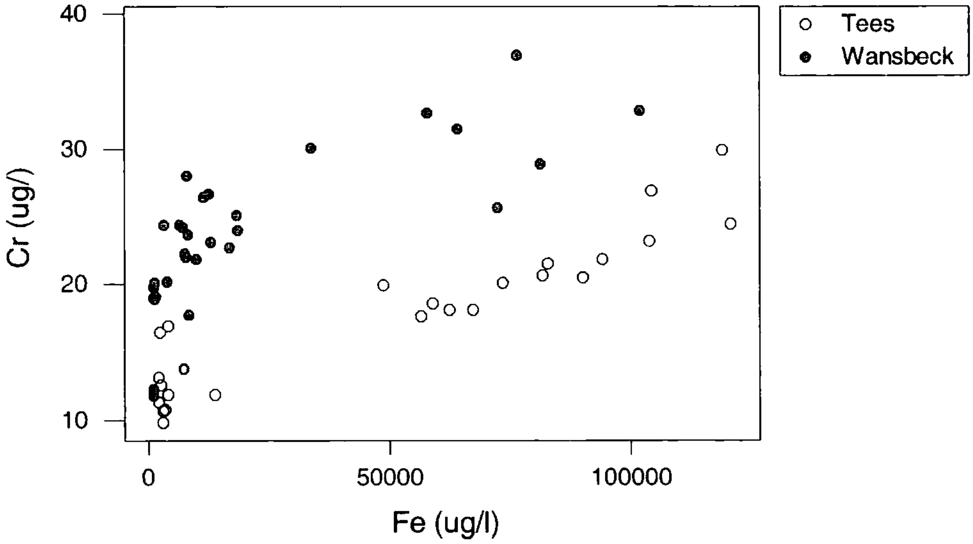


Figure 7.9. Cr vs. Fe within the pore waters of the Tees and Wansbeck impoundments.

Whilst overall levels within the solid phase are shown to be greater within the sediment of the Tees than the Wansbeck impoundment (relating to industrial input from an upstream Cr works), under the current conditions encountered in the sediments this difference does not appear to be represented in the dissolved forms.

7.4.6 Cu

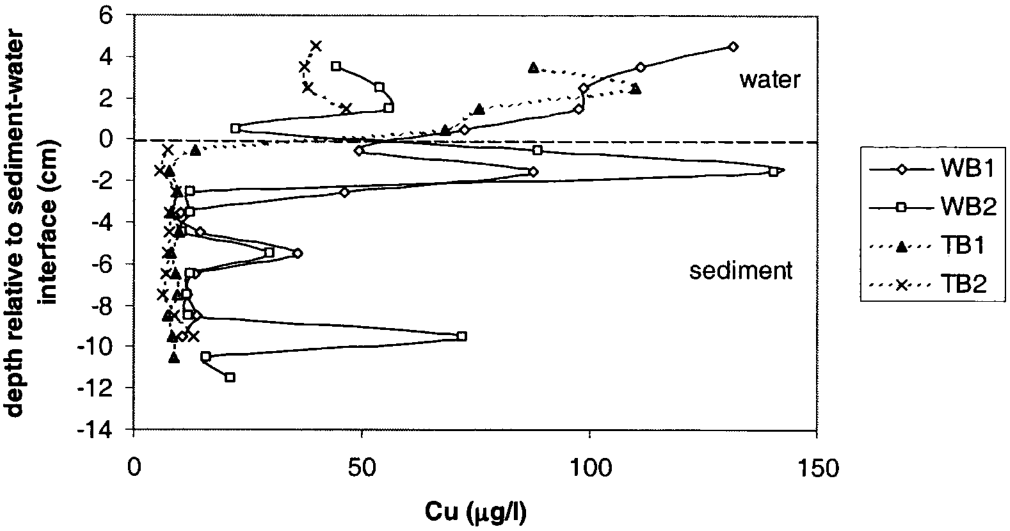


Figure 7.10. Pore water profiles for Cu in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

Cu concentrations are on average higher in the overlying water than in the sediment pore waters within both impoundments, and exceeds the EQS in both the water and pore water of both the Tees and Wansbeck. These dissolved Cu levels are higher in the Wansbeck than the Tees reflecting the pattern within the solid phase of the sediments (chapter 6). Although it was seen that Cu is largely associated with Fe and Mn oxides through sequential extraction experiments, Cu does not closely follow the pattern in pore water shown by Fe and for example Co. Within the Tees sediment pore water Cu is relatively constant with depth, but in the Wansbeck there exist distinct horizons showing peaks in Cu (figure 7.10).

These peaks may relate to variable inputs of Cu to the sediments, although no effective comparison could be made with the sediment extractions due to the different scale of sampling (sediment cores were sampled at 3 cm intervals compared with 1 cm slices for pore water sampling). The strongest relationship of Cu with the elements discussed is with Pb (Pearson correlation = 0.749, P = 0.000) suggesting a similar source for these two metals.

7.4.7 Fe

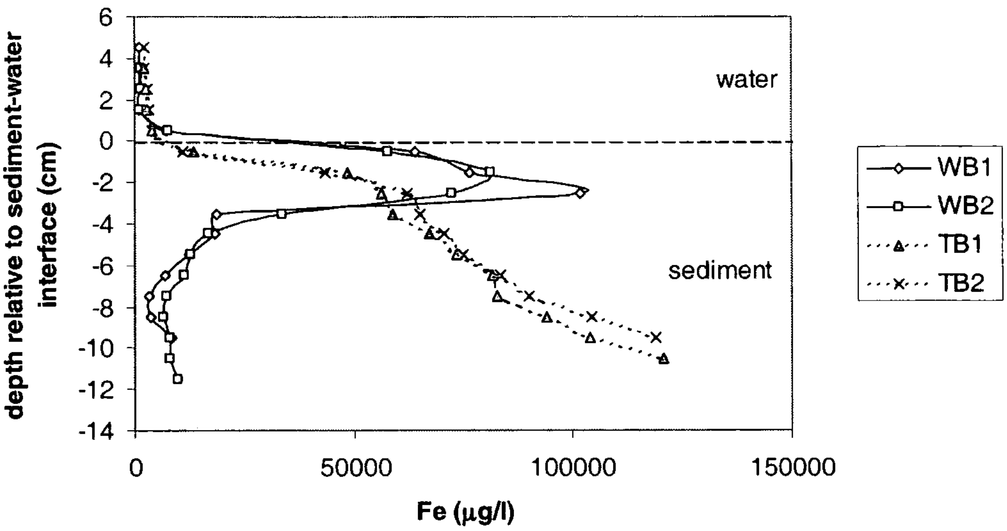


Figure 7.11. Pore water profiles for Fe in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

Levels of Fe in the overlying water and pore waters of both impoundments studied are greater than the recommended EQS. Although the EQS is exceeded within the overlying water of the sediment cores during the DET equilibrations, this does not necessarily translate to the situation in the impoundments in which a much larger volume of water is available to dilute any Fe release from sediment. Water quality surveying showed mean values of 167 and 168 µg/l – well below the EQS of 1000 µg/l - in the Tees and Wansbeck respectively.

The distribution of Fe reflects the redox profile within the sediments. The sequence of redox reactions in surface sediments follows the order of use of:

oxygen → nitrate → Mn(IV) → Fe(III) → sulphate

as thermodynamically favourable electron acceptors for the breakdown of organic material (Stumm and Morgan, 1996; Santschi et al., 1990). Within the overlying water of both impoundments some oxygen is present and the majority of Fe is in the insoluble state Fe(III) and hence concentrations sampled by the DET gel probes were low (figure

7.11). With progression into the sediment the above sequence of reductions takes place, with the depth at which each occurs dependent on the relative concentration of each electron acceptor and the amount of organic material present. Within the sediments of the Wansbeck, which are organic rich and have a periodically anoxic overlying water column (see chapter 4), oxygen and nitrate are rapidly depleted and Fe(III) hydroxides are reduced to release dissolved Fe^{2+} ions at a depth of 2 to 3 cm in the sediment. Below this depth redox potentials fall further and the presence of sulphide from the reduction of sulphate forms insoluble FeS, and the level of dissolved Fe in the pore waters is low. This pattern is typical of that of anoxic nearshore sediments (e.g. Aller, 1980; Elderfield et al., 1981; Heggie et al., 1987). Within the Tees the sediments are less reducing and the maximum release of Fe^{2+} is not encountered in the depth of sediment sampled (i.e. it is assumed to be at > 12 cm depth in the sediment). Sequential extraction experiments (chapter 6) showed that the sediments of the Tees contain very little sulphide within the circa 50 cm cores taken, supporting the conclusion that conditions are less reducing. The reason for this is likely to be higher DO levels in the overlying water column (normally close to saturation) than in the Wansbeck, with lower organic matter content of the sediments possibly also important (although this could relate to better preservation of organic material in the sediments of the Wansbeck rather than differences in organic inputs).

7.4.8 Hg

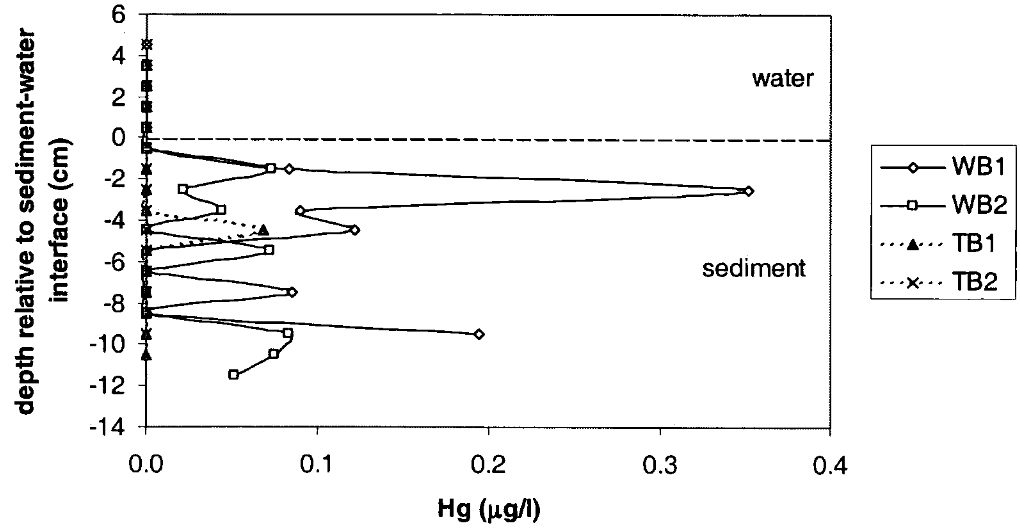


Figure 7.12. Pore water profiles for Hg in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

Hg levels are virtually zero in both the sediment pore waters and water column of the Tees impoundment. Within the Wansbeck levels are almost zero within the water column but show significant levels in the pore water. These concentrations are generally below the EQS.

Hg behaviour has been shown to be strongly related to sulphides in pore waters and sediments (Benoit et al., 1998; Dryssen and Wedborg, 1991), with the presence of free sulphide increasing the solubility of Hg(II). The presence of Hg within the pore waters of the Wansbeck conforms to the idea that within these sediments sulphate reduction to sulphides is taking place. The distribution of Hg shows a large amount of variation within this free sulphide zone, and patterns cannot be correlated between the two cores sampled implying that Hg dissolution occurs in very localised zones. Microniches of heavy metal remobilisation have been noted by Davison et al. (1997), Harper et al. (1999) and Zhang et al. (2002).

7.4.9 K and Mg

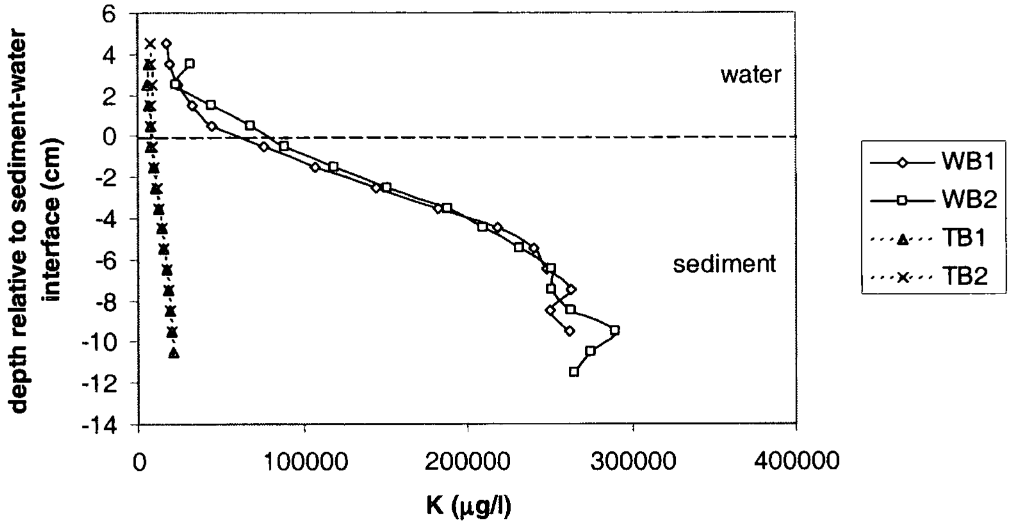


Figure 7.13. Pore water profiles for K in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

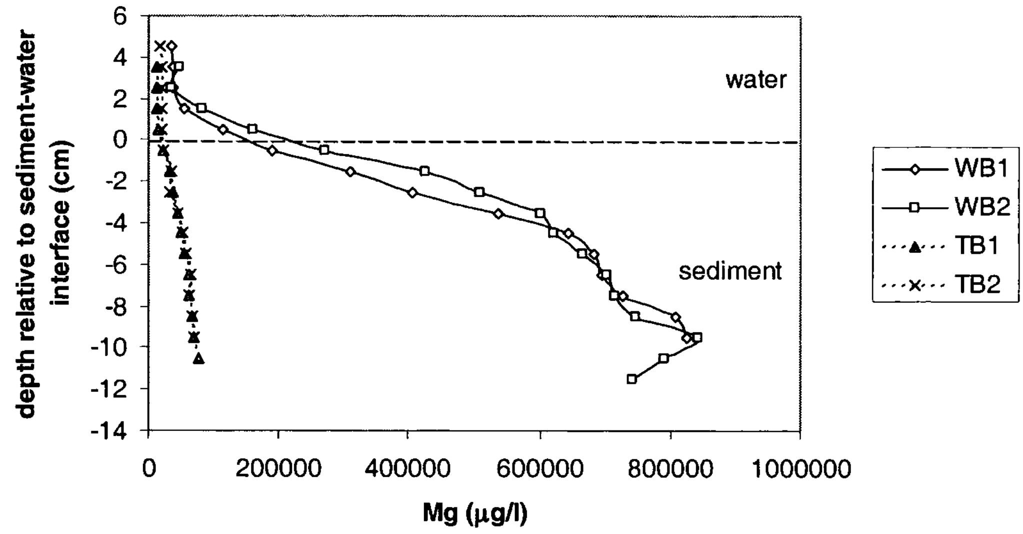


Figure 7.14. Pore water profiles for Mg in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

K and Mg are strongly correlated in the pore waters of the impoundments (Pearson correlation = 0.996). Both K and Mg, as for Ca, show diffusive behaviour in pore water related to the salinity of the overlying water column. Whilst the diffusion profile is likely to remain relatively constant over time in the Tees impoundment, in the Wansbeck the salinity of the overlying water varies dependent on the tidal state and river discharge and the direction of diffusion will vary. The ratio of Mg to K in the pore waters of the impoundments is 2.96 compared with a ratio of 3.23 in seawater. In chapter 6 some replacement of K by Mg on ion exchange sites in the sediment was suggested, and it is possible that the reduction of this ratio relative to seawater relates to this exchange.

7.4.10 Mn

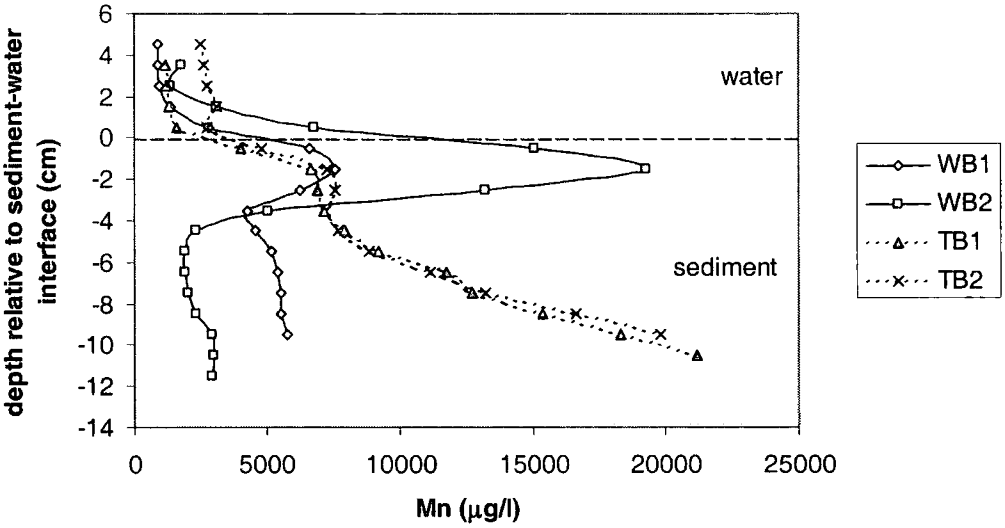


Figure 7.15. Pore water profiles for Mn in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

Mn shows similar redox controlled behaviour to Fe in sediments, although its reduction and release to pore waters slightly precedes that of Fe in the series of reductions which takes place during organic decomposition. The profile for Mn at the SWI in the two impoundments (figure 7.15) is very similar to that for Fe (figure 7.11), and the two elements show strong correlation (Pearson correlation = 0.887; figure 7.16). The maximum release of Mn^{2+} ions to the pore water within the Wansbeck sediment takes place at a slightly shallower depth than the Fe^{2+} release (between 1 and 2 cm compared with between 2 and 3 cm), conforming with the expected sequence of reductions. As for Fe, the maximum release of Mn^{2+} to the pore water of the Tees is interpreted as occurring at greater depth in the sediment than was sampled.

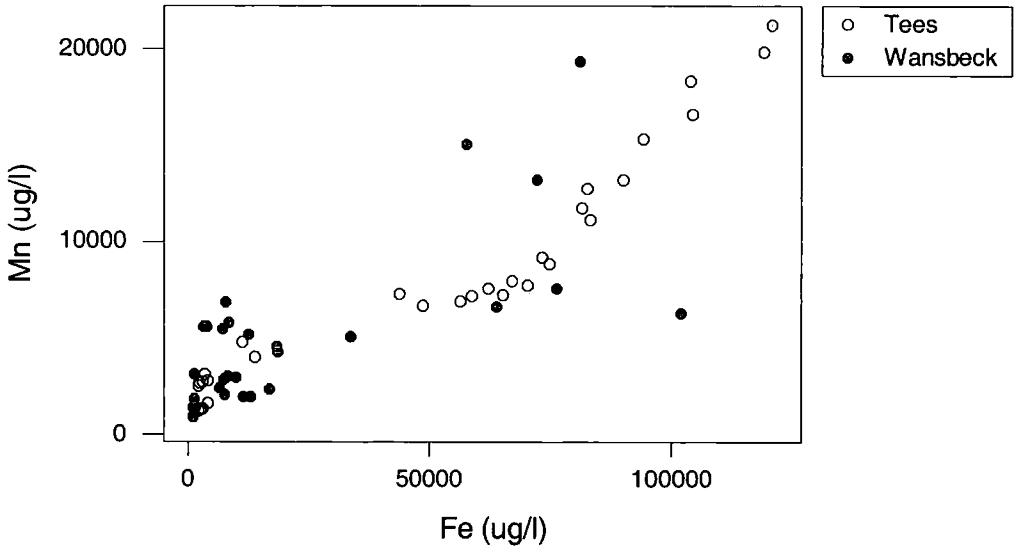


Figure 7.16. The relationship between Mn and Fe in the pore waters of the sediments of the Tees and Wansbeck impoundments.

7.4.11 P

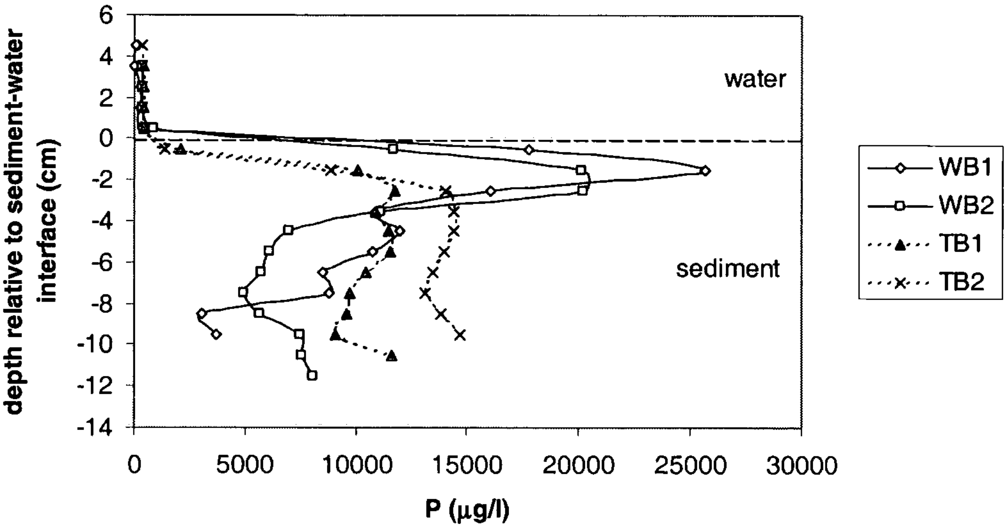


Figure 7.17. Pore water profiles for P in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

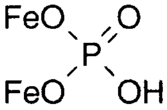


Figure 7.18. P association with Fe hydroxides in oxic sediments (from Golterman et al., 1983).

Sequential extraction experiments (chapter 6) showed P to be strongly associated with Fe in the sediments of both impoundments, and the affinity of P with Fe and Mn oxides is well reported (e.g. Davies, 1997; Jensen et al., 1992; figure 7.18). The distribution of P in the pore waters and overlying waters of the sediments of the Tees and Wansbeck impoundments are quite closely related to the patterns of behaviour of Fe and Mn (figure 7.19). P release to pore waters is proportional to Fe release from hydroxides at the onset of reduction but is lower than Fe as reduction progresses, especially in the Tees sediments, implying that P may be associated with the surface of oxide particles.

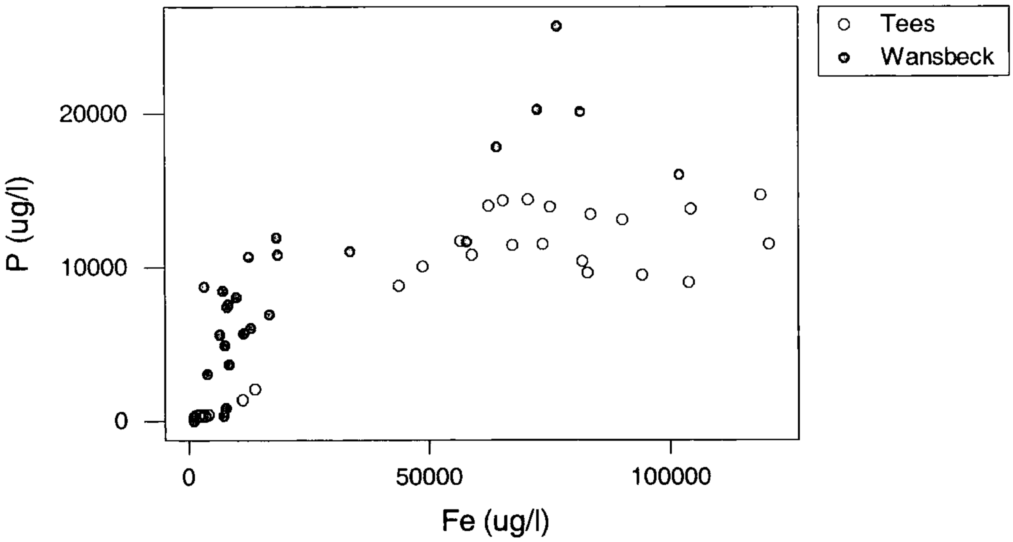


Figure 7.19. P vs. Fe in the pore waters of sediments of the Tees and Wansbeck impoundments.

7.4.12 Pb

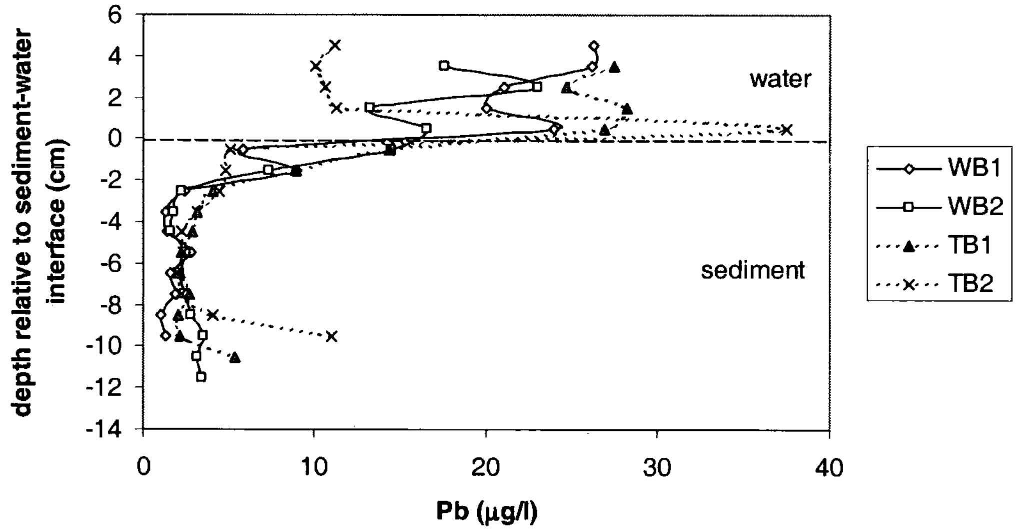


Figure 7.20. Pore water profiles for Pb in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

Mean Pb concentrations are lower than the EQS in the sediment pore waters but approach the EQS (25 µg/l) in the overlying waters of both impoundments (figure 7.20). The pattern for Pb distribution shows no relationship to the Fe and Mn profiles, indicating that within these sediments Pb is not scavenged by oxides. That concentrations are much higher in the overlying water column than the pore waters of the sediments implies that Pb is in stable dissolved forms (perhaps associated with organic colloids) in the water columns and does not partition into the solid phase. As for Cu the profiles for Pb suggest that the direction of diffusion is from the water column to the sediment pore water.

7.4.13 Sc

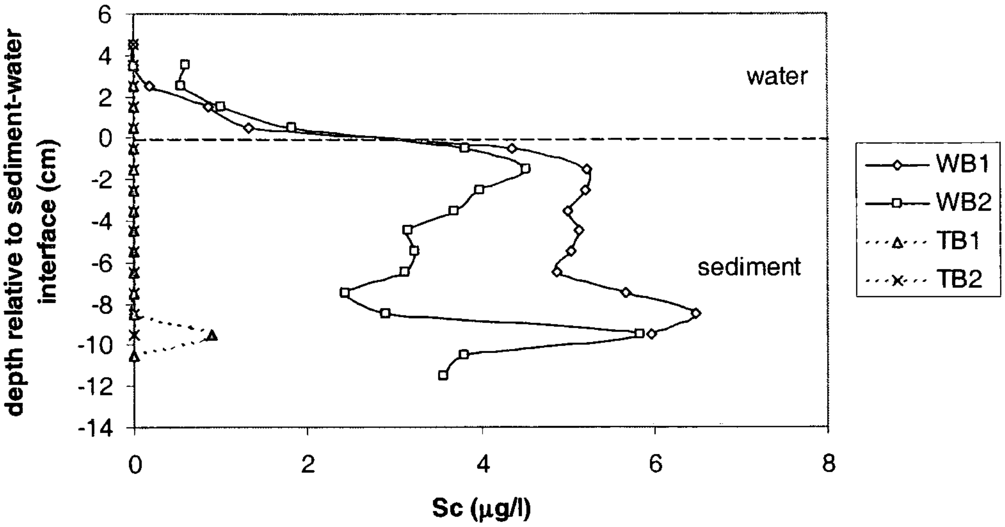


Figure 7.21. Pore water profiles for Sc in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

Overall Sc concentrations within the solid phase were shown to be similar for the sediments of the two impoundments, with Sc speciation following that of Fe (chapter 6). Within the solid phase of the Tees sediments Sc is associated with Fe and Mn oxides and within the Wansbeck with both Fe and Mn oxides and sulphides/organic matter. Sc concentrations within both the pore water and overlying water of the Tees sediment are effectively zero. In the Wansbeck Sc concentrations in pore water are higher than those in overlying water, with a diffusion gradient across the SWI.

Sc and As (and V) show good correlation within the pore waters (Pearson correlation = 0.929; P = 0.000; figure 7.22), but show no relationship to the behaviour of Fe (Pearson correlation = -0.162; P = 0.213). As for As, release on decomposition of organic matter is the likely source of Sc within the Wansbeck impoundment. The pattern of Sc concentration in the pore waters fits with the finding that a fraction of the Sc in the solid phase is associated with organic matter/sulphide within the Wansbeck but not in the Tees.

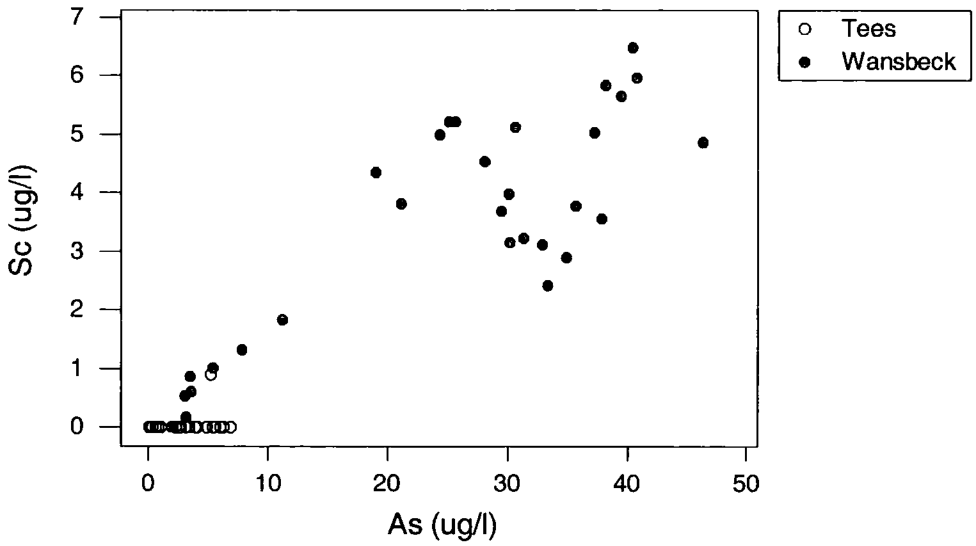


Figure 7.22. The relationship between Sc and As in the pore water of sediments of the Tees and Wansbeck impoundments.

7.4.14 Si

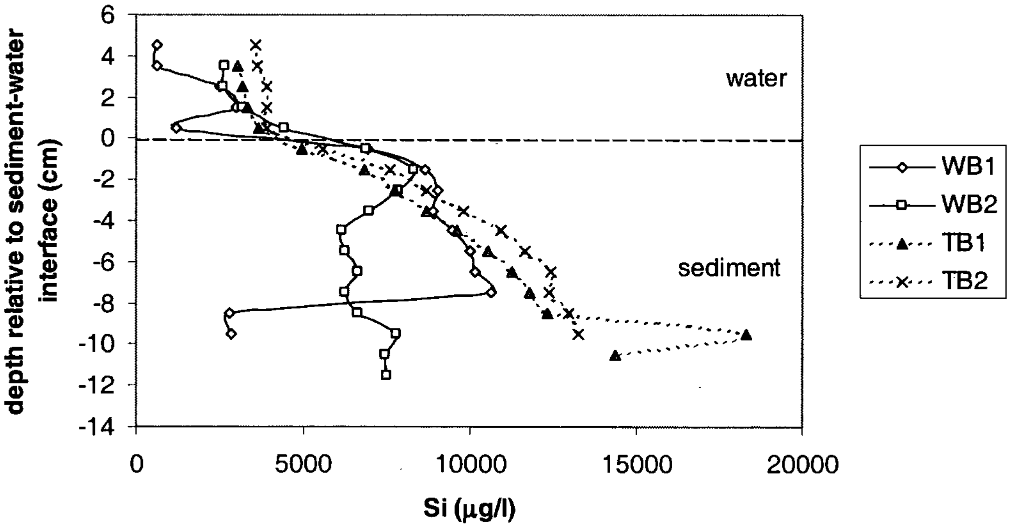


Figure 7.23. Pore water profiles for Si in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

Within the Tees Si dissolution from the solid phase to the pore waters is interpreted as relatively constant with depth, with concentrations in pore water being controlled by diffusion to the overlying water column (figure 7.23). The profile within the Wansbeck is less regular, with localised variation in dissolved Si levels with depth. This variation may relate to differences in particle size, although no PSD analysis was carried out at the same resolution as DET pore water sampling and this cannot be tested.

Si concentration within the pore water shows relatively strong correlation with Fe (Pearson correlation = 0.814, P = 0.000; figure 7.24), and may be controlled by dissolution of (authigenic) Fe-Al silicates (formed by reaction of Si from diatoms with Fe hydroxides; Wetzel, 1983).

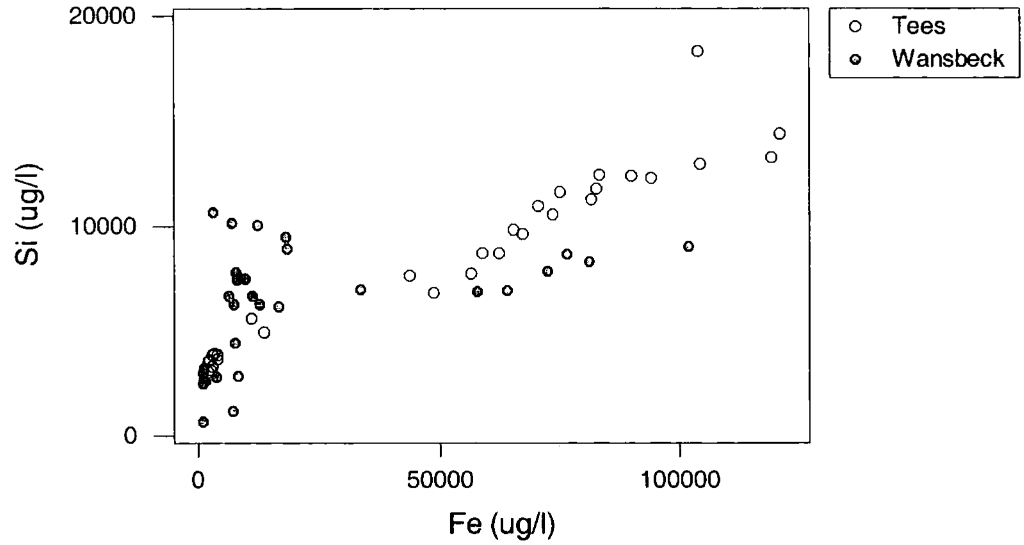


Figure 7.24. The relationship between Si and Fe in the pore water of sediments of the Tees and Wansbeck impoundments.

7.4.15 Ti

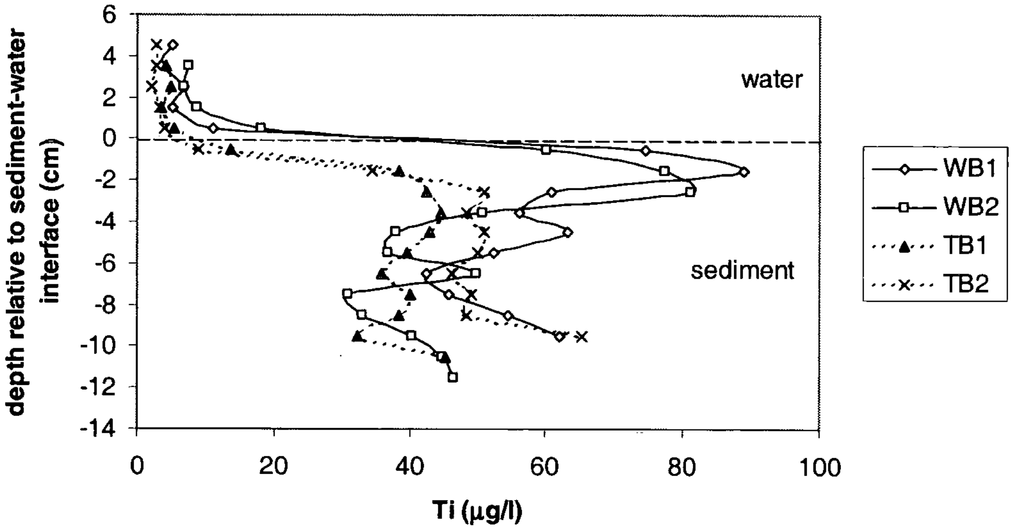


Figure 7.25. Pore water profiles for Ti in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

Ti concentrations are low in the overlying waters of both impoundments and significantly higher in the pore waters of the sediments, with a diffusion gradient across the SWI (figure 7.25).

Ti is significantly correlated with Fe (Pearson correlation = 0.607, P = 0.000; figure 7.26) and, as for Al, Co, Cr and P, release to pore waters is related to the dissolution by reduction of Fe hydroxides in the sediment. Whilst levels in the solid phase of the sediment are higher in the Tees than the Wansbeck (chapter 6), there is no clear reflection of this in the relative concentrations in the pore water between the two impoundments.

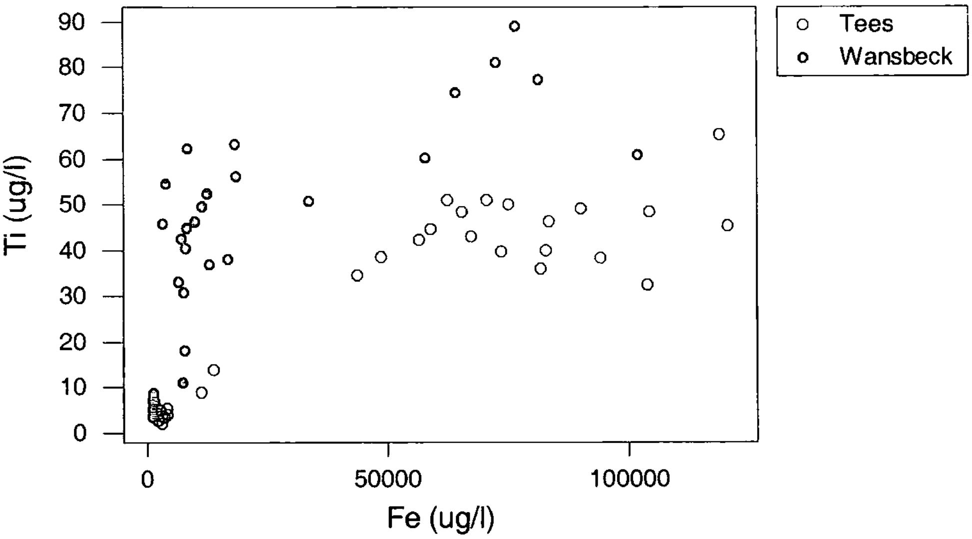


Figure 7.26. The relationship between Ti and Fe in the pore water of sediments of the Tees and Wansbeck impoundments.

7.4.16 V

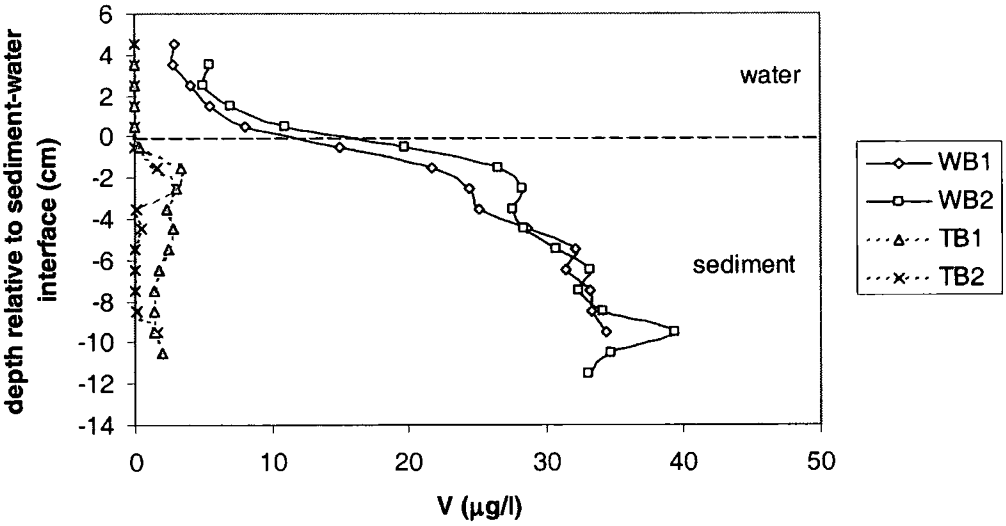


Figure 7.27. Pore water profiles for V in sediment in the Tees (TB) and Wansbeck (WB) impoundments.

V concentrations within both the pore waters and water columns of both impoundments are well below the EQS (table 7.5). Concentrations in both impoundments are lower within the overlying waters than in the pore waters and diffusion gradients exist across the SWI. V concentrations are higher in the pore waters of the Wansbeck than in the Tees.

V shows no significant correlation at 99 % probability level with Fe within the systems (Pearson correlation = -0.255, P = 0.047), but is strongly correlated with As (Pearson correlation = 0.983, P = 0.000; figure 7.28). As for As and Sc, V release to pore waters is likely to be associated with organic matter/sulphides in the sediment, with the difference between the Tees and the Wansbeck due to the difference in the quantities of metals held within this phase within the sediment.

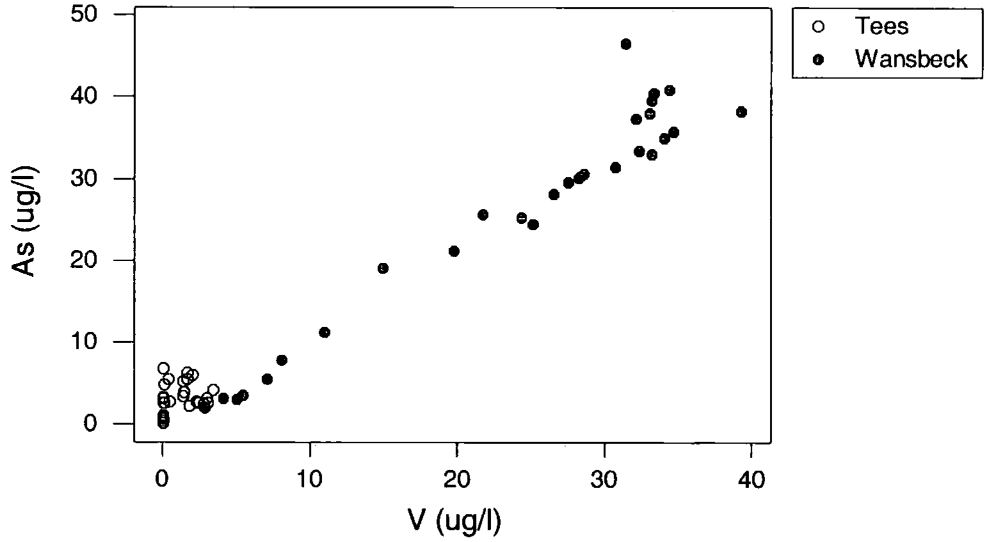


Figure 7.28. The relationship between As and V in the pore water of sediments of the Tees and Wansbeck impoundments.

7.5 Summary and conclusions

7.5.1 Biogeochemistry/diagenetic controls

DET gel probe sampling has allowed detailed profiles of elemental concentrations about the SWI (to approximately 12 cm depth in the sediment and 3 cm of the overlying water column) to be plotted. The results suggest that a variety of physical, chemical and biochemical processes are important in controlling the distribution and concentration of elements within the pore waters of the sediments. These controls and the elements associated with them are outlined in table 7.6.

Element	**Distribution**	**Control**
Fe, Mn, Al, Co, Cr, P, Si and Ti	Lower in overlying water than in pore water. Maximum at 2-3 cm below SWI in Wansbeck. Maximum deeper in Tees.	Associated with sequence of Fe reduction processes (particularly release of Fe^{2+} ions on reduction of Fe^{3+} hydroxide).
Ca, K and Mg	Lower in overlying water than in pore water. Approximate linear increase with depth in sediment.	Diffusion relating to salinity of overlying water column (no biological mediation).
As, Hg, Sc and V	Lower in overlying water than in pore water. Concentrations low in pore waters in Tees but increase with depth in Wansbeck. Irregular profile for Hg in Wansbeck.	Related to organic matter/sulphides within sediment.
Cu and Pb	Greater in overlying water than in pore water.	Dissolved inputs greater than sediment bound inputs.

Table 7.6. Summary of suggested controls on distributions of elements in pore waters in the Tees and Wansbeck estuarine impoundments.

7.5.1.1 Fe, Mn, Al, Co, Cr, P, Si and Ti

Fe, Mn, Al, Co, Cr, P, Si and Ti are associated with Fe hydroxides in the solid phase of the sediment, and show pore water profiles relating to the reduction of these oxides to release free ions. In the Wansbeck the overlying water column is periodically anoxic and the sediment is organic rich, and so oxygen is rapidly depleted on progression into the sediment column. The onset of use of Fe and Mn oxides as electron acceptors in the breakdown of organic matter is marked by peaks in the concentrations of the above elements. With greater depth in the sediment of the Wansbeck (4 cm below the SWI and deeper) organic matter decomposition is by sulphate reduction, and the presence of free sulphide allows precipitation of FeS together with the above metals to varying degrees. In the Tees less reducing conditions are encountered in the sediment due to greater oxygen content in the water column and lower organic content in the sediment. In the Tees sediment the maximum release of free ions by reduction of Fe and Mn oxides is deeper than the depth sampled (12 cm), and no sulphate reduction is encountered.

7.5.1.2 Ca, K and Mg

Ca, K and Mg show diffusion from the sediment to the water column in both impoundments. In the Wansbeck the direction of diffusion of these ions will reverse during periods in which the overlying water column is saline, whereas in the (freshwater) Tees the diffusion is permanently unidirectional. The source of saline water at depth in the sediment in the Tees is either from the pre-impoundment sediment (deposited under saline conditions) or from current saline intrusion beneath the barrage. Whilst K and Mg are directly proportional in the pore waters and in the same ratio as in seawater, Ca shows a lower correlation and dissolution of carbonates is suggested as providing an additional source for this ion.

7.5.1.3 As, Hg, Sc and V

As, Hg, Sc and V show poor correlation with Fe in the pore waters and show maximum concentrations at the depth at which sulphides are present (i.e. concentrations are low in the overlying water and upper sediment in the Wansbeck and throughout the depth sampled in the Tees). These elements are associated with sulphate reduction to sulphides in the sediment, or release from organic material in the presence of sulphides. It is possible that these metals are present in stable dissolved forms as organometal compounds. The methylisation of As and Hg have been studied in detail (Andreae, 1986; Mason et al., 1993) due to the toxicological properties of these organometals. It is likely that methane production occurs at depth in the Wansbeck sediment as the next stage in the sequence of redox processes following sulphate reduction. The distribution of Hg in the pore waters of the Wansbeck is very irregular suggesting that sulphate reduction and mobilisation of this metal occurs in localised zones within the sediment.

7.5.1.4 Cu and Pb

Cu and Pb show greater concentrations in the overlying water column than in the sediment pore water implying that, unlike the other elements studied, these metals are present in stable dissolved forms and do not partition into the sediment. Cu is strongly chelated by organic matter in natural waters, particularly in biologically productive systems (such as the impoundments), giving stable dissolved forms, and Pb is mainly present as dissolved Pb^{2+} at pH > 7 (Stumm and Morgan, 1996). Sediments (suspended or bed) do not therefore act as sinks for these metals in the impoundments.

7.5.2 Fluxes across the SWI

In addition to helping to understand diagenetic processes taking place within the sediments, DET gel probe sampling was carried out to allow estimation of the exchanges taking place across the SWI. The movement of dissolved materials from the sediment pore water to the water column may be simply modelled as a diffusion (ignoring the effects of hydrostatic pressure gradients and sediment and water mixing at the SWI by bioturbation and water turbulence) according to Fick's first law (Gill et al., 1999):

$$F = -\left(\frac{\varphi D_w}{\theta^2}\right)\frac{\delta C}{\delta x}$$

where F is the diffusive flux of a solute with concentration C at depth x, θ is the tortuosity (dimensionless), φ is the sediment porosity, and D_w is the diffusion coefficient of the solute of interest in water without the presence of a sediment matrix. Tortuosity is generally related to porosity according to:

$$\theta = 1 - \ln\left(\varphi^2\right)$$

The diffusion coefficients for most aqueous species, including organics, are similar differing by, at most, a factor of two from the self-diffusion coefficient of water which is 2.4 x 10^{-5} cm^2/s at 25°C (www.ufaventures.com). Diffusion coefficients in porous media that are less than 10^{-5} cm^2/s result from mechanisms or conditions other than the inherent mobility differences between the species themselves. These mechanisms include path length differences due to water content differences and retardation due to sorption and transient chemical effects.

The fluxes of a selection of ions (PO_4^{3-}, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, CrO_4^{2-} and CH_3HgCl^0) across the SWI interface were estimated using the above expression of Fickian diffusion and diffusion coefficients for the charged ions calculated according to Boudreau (1997), assuming a temperature of 15°C, atmospheric pressure and salinity of 0.5 ‰ (table 7.7).

Ion	**Diffusion coefficient ($cm^2/s \times 10^{-5}$) in freshwater (0.5 ‰ salinity)**
PO_4^{3-}	0.48
Ca^{2+}	0.63
Mg^{2+}	0.56
Fe^{2+}	0.56
Mn^{2+}	0.55
CrO_4^{2-}	1.1
CH_3HgCl^0	1.3

Table 7.7. Diffusion coefficients used for calculation of diffusive fluxes across the SWI.

Note that PO_4^{3-} was chosen as the major phosphate species present and the effects of the presence of H_2PO^{4-} and HPO_4^{2-} (which have greater diffusion coefficients) were ignored. The estimate for phosphate flux is therefore at the lower boundary. CH_3HgCl^0 was chosen as the species of Hg present since the majority of dissolved Hg in natural waters has been shown to exist in colloidal forms, with the diffusion coefficient given in Gill et al. (1999) being used. Based on the moisture content determinations from the sediment coring a value of porosity of 70 % was used. The concentration gradients across the SWI were taken from the pore water profiles sampled by the DET gel probes. The results are summarised in tables 7.8 and 7.9.

Ion	Flux in Wansbeck ($\mu g/m^2/day$)	Flux in Tees ($\mu g/m^2/day$)	Flux in Tamar ($\mu g/m^2/day$)
$P\text{-}PO_4^{3-}$	1420	570	1360
Ca^{2+}	29500	23000	
Mg^{2+}	118000	4900	
Fe^{2+}	37800	23000	5030
Mn^{2+}	4240	2400	4200
$Cr\text{-}CrO_4^{2-}$	27.8	12.1	

Table 7.8. Diffusive fluxes for a selection of ions across the SWI at sites WB and TB in the Wansbeck and Tees impoundments respectively (data from this project) and mean fluxes in the Tamar Estuary (data from Upstill-Goddard et al., 1989).

Ion	Flux in Wansbeck ($\mu g/m^2/day$)	Flux in Tees ($\mu g/m^2/day$)	Flux in Lavaca Bay ($\mu g/m^2/day$)
$Hg\text{-}CH_3HgCl^0$	0.138	0.000	0.139

Table 7.9. Diffusive fluxes for Hg of across the SWI at sites WB and TB in the Wansbeck and Tees impoundments respectively (data from this project) and mean flux in Lavaca Bay, Texas (data from Gill et al., 1999).

Under higher salinities, such as are periodically encountered in the Wansbeck, diffusion coefficients (and hence fluxes) are reduced. For example in the Wansbeck under 15 ‰ salinity the flux of Mn is 4240 $\mu g/m^2/day$ compared to 4400 $\mu g/m^2/day$ under freshwater. For phosphate the respective values are 1420 and 1480 $\mu g/m^2/day$ P.

The fluxes across the SWI determined through DET gel probe pore water sampling in the Tees and Wansbeck impoundments are similar to data reported for un-impounded estuarine and nearshore environments (e.g. Upstill-Goddard et al., 1989; Rowe et al., 1975; Klump and Martens, 1981; Gill et al., 1999). Mean data are presented above for studies carried out in spring 1983 on the Tamar Estuary, UK (largely unpolluted organic rich sediments) and in spring 1996 in Lavaca Bay, Texas (an estuary historically impacted by Hg discharges). The calculation of flux of Hg within the Wansbeck assumed that all of the Hg present was in monomethyl form and is therefore likely to overestimate Hg-CH_3HgCl^0 flux. Gill et al. (1999) found that monomethyl Hg represented on average 35 % of total Hg present in the sediments of Lavaca Bay. Assuming a similar ratio in sediments in the Wansbeck gives a flux of Hg-CH_3HgCl^0 of approximately 0.048 μg/m^2/day, i.e. significantly lower than that reported in the historically contaminated sediments of Lavaca Bay.

7.5.2.1 Relative contribution of sediment P to the impounded water bodies

In chapter 3 it was suggested that the major controls on P concentrations in the impoundments are catchment related, and that internal cycling of P from sediment is small relative to these external inputs. The size of the contribution of P to the water body by release from the sediment may be approximately quantified using the estimates of fluxes reported above.

The surface areas of the sediment showing P release in the two impoundments were estimated as the surface areas of the impoundments underlain by predominantly silt and clay sized bed material (and therefore showing anoxia within the sediment column). Within the Wansbeck impoundment this area was taken as the area of the length of river between the barrage (NZ 2935 8536) and Stakeford Bridge (NZ 2715 8595) and within the Tees impoundment the area of the length of river between the barrage (NZ 4616 1905) and the railway bridge (NZ 4469 1800). The estimated surface areas are 0.38 $km^2$for the Wansbeck and 0.28 km^2 for the Tees. No account of the morphology of the beds was taken and a flat bed was assumed for both impoundments. These surface areas of the sediments in the impoundments are therefore likely to be slight underestimates.

Knowing the flux per surface area of sediment and the surface area of the sediment the mass of P released per unit of time may be calculated:

Wansbeck = 540 g/day
Tees = 160 g/day

Assuming steady state conditions, the impact of these mean inputs of P on the concentration of P in the water column may be estimated on the basis of mean discharges of the two rivers. The mean discharges (taken as the mean discharges at the nearest upstream gauging stations: see chapter 2) over the periods of this study were 3.4 m^3/s in the Wansbeck and 10.5 m^3/s in the Tees. Since DET sampling was carried out under a period of non-overtopping on the Wansbeck the effect of tidal input of water may be ignored. The mean increases in P concentration in the water of the two impoundments are therefore:

Wansbeck = 0.00184 mg/l
Tees = 0.00018 mg/l

Mean P concentrations measured in the water of the impoundments during the sampling periods were 0.27 and 0.80 mg/l for the Wansbeck and the Tees respectively (median concentrations were 0.24 and 0.76 mg/l). The overall impact of release of P from sediment to the water columns on phosphate concentrations in the impounded water is therefore negligible (< 1 % in each system).

7.5.2.2 Relative contribution of sediment Mn to the impounded water bodies

Whereas it has been shown that the major controls on P concentration in the water bodies are external to the impounded areas, a large proportion of dissolved Mn is sourced internal to the impounded areas and release of Mn from sediment under conditions of low DO is suggested. Using the same methodology as used above for P, the mean increases in Mn concentration in the water column due to diffusion across the SWI may be estimated:

Wansbeck = 0.00548 mg/l
Tees = 0.00074 mg/l

During the period studied the median Mn concentrations measured in the water of the two impoundments were 0.043 and 0.012 mg/l for the Wansbeck and Tees respectively. The flux calculations based on the DET pore water sampling therefore confirm that release from sediment under low DO conditions is a significant source of Mn (and associated metals) to the water body (approximately 13 and 6 % of the average values). As mentioned these approximations are based on the assumption of steady state flow conditions (i.e. output = input plus complete mixing of the water body). As is described in chapter 4, in reality the impounded water bodies are often stratified such that the riverine input progresses along the surface of the impoundment and undergoes no interaction with the bed sediments. The residence time of deeper water is therefore much longer than it would be in a non-stratified water body, and given steady diffusion from the sediments, concentrations of Mn at depth continue to rise for as long as the water bodies remain unmixed.

An approximate estimation of the effect of the release of Mn on a stratified water body may be carried out. Assuming a mean thickness of a stratified layer at depth of 1 m receiving constant Mn input from the sediments according to the diffusive fluxes given above, the rates of increase in Mn concentration at depth will be:

Wansbeck = 0.00424 mg/l/day
Tees = 0.00240 mg/l/day

Water quality surveying (chapter 2) revealed a maximum rate of Mn increase in the water column in the Wansbeck impoundment (at site CP) of 0.131 mg/l/day, i.e. it would appear that DET estimations of fluxes may seriously underestimate true fluxes for Mn. As described in chapter 2, rapid Mn release from sediment occurs with the onset of conditions of below 50 % DO, and it is likely that the low diffusion observed in the gel probes is due to DO saturations in the water column above the sediment cores being above this level. Sampling under a range of DO conditions should therefore be key to any future work examining diffusive fluxes of redox controlled elements across the SWI.

Chapter 8

Sterol Biomarkers in Estuarine Impoundments

8.1 Introduction

Measurement of sterols in the sediments of estuarine impoundments was carried out in order to:

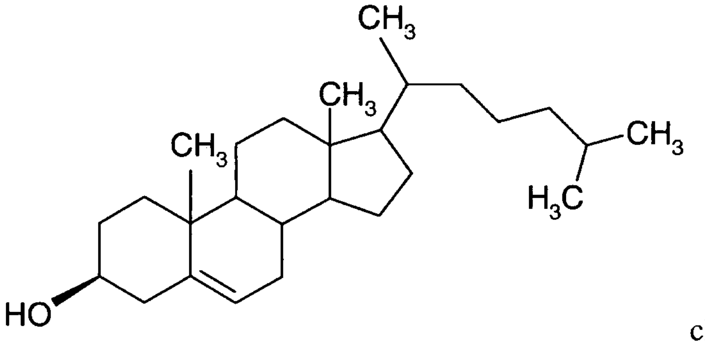
- Assess the potential use of sterol biomarkers in identification of sewage inputs to estuarine impoundments.
- Make a preliminary estimate of the nature and quantity of sewage inputs to the sediments of the impoundments studied.

Sterol compounds are powerful tracers of organic matter in aquatic systems due to their good preservation in recent sediments and specificity of biosynthesis (Saliot et al., 1991). When faecal matter is introduced to a water body, the sterol compounds strongly partition to particulate material and, once deposited into sediments, show little degradation (Bartlett, 1987; Leeming et al., 1996). The source specificity of faecal sterols is due to differences in both the diets, and biosynthesis and bacterial biohydrogenation of sterols in the gut, between different warm-blooded animals. The ratios of these sterols may therefore be used to determine the sources of organic material, and the absolute value of coprostanol (the major faecal sterol present in human waste (Brown and Wade, 1984)) may be used to assess relative amounts of sewage input.

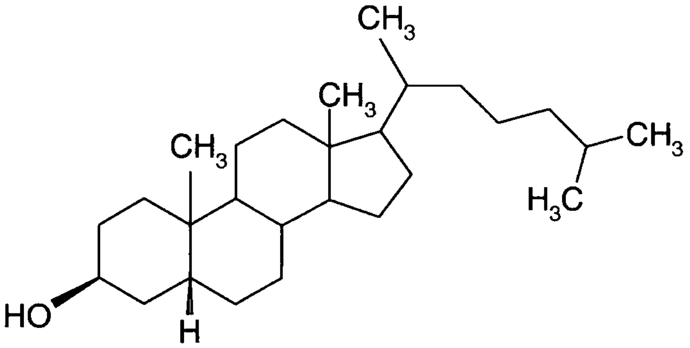
Preliminary identification of sewage inputs to the impoundments in this study was carried out by determination of the concentrations of cholesterol (cholest-5-en-3β-ol), and the primary products of biohydrogenation of cholesterol in the guts of warm-blooded animals and in the environment (coprostanol (5β-cholestan-3β-ol), epicoprostanol (5β-cholestan-3α-ol), and cholestanol (5α-cholestan-3β-ol)) (e.g. LeBlanc et al., 1992; Mudge and Norris, 1996; Patton and Reeves, 1999; Elhmmali et al., 2000). The systematic names and structures of these sterols are given in table 8.1 and figure 8.1 respectively.

Trivial name	Systematic name
Cholesterol	cholest-5-en-3β-ol
Coprostanol	5β-cholestan-3β-ol
Cholestanol	5α-cholestan-3β-ol
Epicoprostanol	5β-cholestan-3α-ol

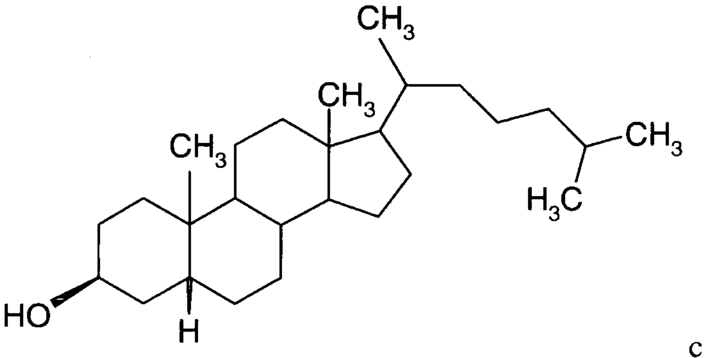
Table 8.1. Trivial and systematic names for the sterol compounds measured in this study.



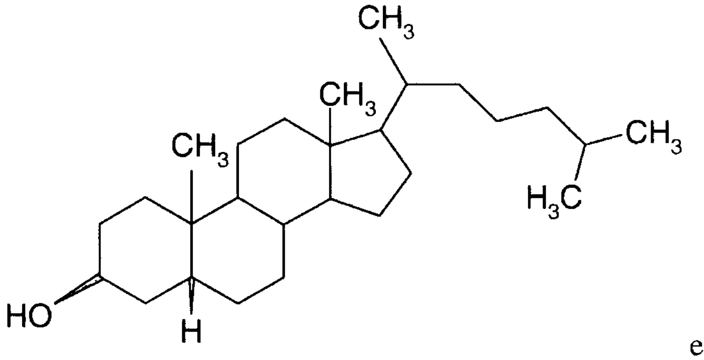
cholesterol



coprostanol



cholestanol



epicoprostanol

Figure 8.1. The structures of the sterol compounds measured in this study.

8.2 Survey design

8.2.1 Estuaries studied

Sterol concentrations were measured in the sediments from the Tees and Wansbeck impounded estuaries, with the aim of determining whether sewage is a major organic input to these systems.

8.2.2 Sampling sites and dates

For convenience sterol analysis was carried out on sub-samples of sediment from cores taken during the sediment quality surveys as described in chapter 3. The scope of this project allowed sterol analysis to be carried out on one sediment core each from the Tees and Wansbeck impoundments, taken immediately upstream of the respective barrages (table 8.2). Replicate cores were not sampled.

River	Site name	Site abbreviation	Grid reference
Tees	Tees Barrage	TB	NZ 4616 1905
Wansbeck	Wansbeck Barrage	WB	NZ 2935 8536

Table 8.2. Sampling sites for cores taken for sterol analysis.

The cores taken were sub-sampled as 3 cm thick portions at 15 cm intervals (giving a total of 5 depths sampled in the Wansbeck and 4 depths in the Tees) and replicate analyses of these sub-samples was carried out. The depths in the sediments relative to the SWI sampled were therefore -0-3, -15-18, -30-33, -45-48 and –60-63 cm within the Wansbeck and -0-3, -15-18, -30-33, and -45-48 cm within the Tees. All depths sampled represent post-impoundment sedimentation. Sampling was carried out on the 23/07/01 for the Wansbeck and 24/07/01 for the Tees.

8.3 Methodologies

8.3.1 Sediment sampling

Sediment cores were collected using a Mackereth corer, frozen, and sub-sampled at 15 cm intervals using stainless steel equipment as described in chapter 6. These sub-samples were wrapped in fired aluminium foil and stored frozen for a maximum of one month before thawing and sterol extraction.

8.3.2 Sterol extraction

Analytical grade reagents were used in all the laboratory work described, and all appropriate care was taken to avoid organic contamination. Equipment was acid and Decon 90® (non-ionic surfactant) washed (soaked overnight in 1% HNO_3, followed by overnight in 5% Decon 90® and rinsed in de-ionised water), and fired overnight at 500°C. Sterol extraction from the sediment samples was carried out using the procedure of Mudge and Norris (1997):

1. Known wet weight circa 30 g of samples refluxed for 4 h in 50 ml of boiling 6 % w/v potassium hydroxide in methanol.
2. Samples centrifuged in glass centrifuge tubes.
3. Supernatant decanted to separating funnels and shaken with 5 ml of organic free water.
4. Free non-polar lipids extracted into hexane (three 25 ml hexane washes) from the supernatant by liquid/liquid extraction.
5. Samples concentrated by rotary evaporation to circa 2 ml.
6. Any remaining water removed from samples by pipetting through cleaned anhydrous sodium sulphate.
7. 5 μg 5α-cholestane added as an internal standard.
8. Samples evaporated to dryness under oxygen free nitrogen and stored at -20°C for a maximum of 2 weeks prior to analysis.
9. Samples derivatised by the addition of 100 μl of bis-(trimethylsilyl) trifluoroacetamide (BSTFA) and heating to 60°C for one hour.
10. Samples evaporated to dryness under oxygen free nitrogen and redissolved in 1 ml of hexane for injection to the GC column.

Analysis for sterols was carried out within 24 h of derivatisation of samples.

8.3.3 Sterol analysis

Principle:

Sterols were analysed by flame ionisation gas chromatography (GC-FID). In gas chromatography a mobile phase (a carrier gas) and a stationary phase (nowadays usually a capillary column coating) are used to separate individual organic compounds. The column is held in a temperature controlled oven with one end connected to a temperature controlled injector block and the other to some form of detector. On injection to the column samples are vaporised and transported through the column by the carrier gas, with the rate of movement (and hence the time of appearance at the detector) dependent on the partitioning between the mobile and stationary phases of the individual compounds. Using the appropriate temperature program, column (in terms of stationary phase material, length and diameter) and carrier gas flow gives retention times in the column unique to each of the analytes of interest.

A variety of detectors are used in gas chromatography, including electrolytic conductivity detectors, electron capture detectors, photo ionisation detectors, flame ionisation detectors and mass spectrometers. The most widely used detector is the flame ionisation detector due to its high sensitivity to a large range of organic carbon-containing compounds and general analytical ease of use and robustness to impurities (APHA, 1998). A flame ionisation detector consists of a small hydrogen flame across which a voltage is applied at the end of the GC column. As organic compounds enter the flame, electrically charged intermediates are formed which transport a current across the flame. The size of the current produced is proportional to the mass of compound entering the detector and therefore, by use of standards for the analytes of interest, quantification may be carried out.

Method:

Sterol analysis was carried out using a Fisons GC 8065 GC-FID using splitless injection with a hot needle technique. To give maximum repeatability, injections were made using a Fisons AS 800 autosampler. The carrier gas was helium with a column flow rate of 3 ml/min. A conditioned non-polar (5 % phenyl polysiloxane) capillary column (Phenomenex® Zebron ZB-5) of 30 m length, 0.32 mm internal diameter and 0.25 µm film thickness was used for all sterol analyses. The temperature program started at 60°C (held for 1 minute) followed by a ramp of 20°C/min up to 200°C, then at 6°C/min to a maximum of 310°C (isothermal for 23 minutes). Data handling was carried out using Chromeleon Dionex software.

Retention times of the sterols were determined using standards, and quantification was determined by comparison with the peak area of the internal standard (5α-cholestane) for each analysis. Sterol concentrations are expressed in μg/g by dry weight of sediment as the mean of the replicate extractions for each sample. The conversion from wet weights to dry weights was made on the basis of % moisture contents determined during the sediment quality surveys (chapter 3).

8.4 Results and discussion

Results are presented for the sampling of sterols (lipid biomarkers) from the sediments of the Tees and Wansbeck impoundments. Physical properties and metal speciations for these sediments are described in chapter 6. The mean concentrations of sterols found in μg/g dry weight of sediment are presented in table 8.3. As mentioned in chapter 6, the sediments from these locations are silt dominated and with only minor variation in particle size distribution with depth in the sediment column, and therefore no particle size corrections are applied to the data.

	Tees	**Wansbeck**
Coprostanol	1.650	0.699
Epicoprostanol	0.289	0.156
Cholesterol	0.912	0.882
Cholestanol	0.612	0.427

Table 8.3. Mean concentrations in μg/g dry weight of sediment of the lipid biomarkers sampled in the Tees and Wansbeck impoundments.

Levels of coprostanol (the major faecal sterol present in human waste) are comparable to concentrations reported at other locations (table 8.4). Brown and Wade (1984) give the coprostanol concentration in raw sewage as being approximately 160 μg/g. Levels in the Tees and Wansbeck sediments are significantly lower than this, indicating dilution or loss of sterols from the systems. Based on the relative coprostanol levels in the impoundments and in raw sewage it may be roughly estimated that approximately 1 % of the sediment in the Tees is from sewage sources compared with <0.5 % in the Wansbeck.

Location	**Concentration (μg/g)**	**Reference**
Antarctica	<0.001-1.282	Green and Nichols (1995)
Hong Kong	0.34-5.09	Chan et al. (1998)
Venice Lagoon, Italy	0.04-4.41	Fattore et al. (1996)
Coasts of Florida, USA	<1	Sherblom et al. (1997)
Firth of Clyde, Scotland	152.2	Kelly (1995)
Firth of Tay, Scotland	0.603-1.534	Patton and Reeves (1999)

Table 8.4. Recently reported levels of the lipid biomarker coprostanol in near-shore and estuarine sediments.

8.4.1 Ratios and sources of sterols

Ratios between the lipid biomarkers may be used to determine provenance of the sterols (Patton and Reeves, 1999). The ratio of coprostanol/cholesterol may be used to distinguish between mainly biogenic (autochthonous) sources or mainly sewage sources for the sterols (raw sewage being the primary source of coprostanol and zooplankton being a major source of cholesterol (Mudge and Norris, 1997)). It is suggested that ratios <1 indicate biogenic sources and ratios >1 indicate sewage sources (Nichols et al., 1996). The ratio of coprostanol/epicoprostanol may be used to identify the primary faecal source as human as opposed to sources such as agricultural slurry or marine mammals (LeBlanc et al., 1992), by contrasting the dominant excreted metabolite of cholesterol (coprostanol) from the human gut with that of the majority of herbivores (epicoprostanol) (Leeming et al., 1996). A ratio of >1.5 indicates a human faecal source (Fattore et al., 1996). Finally the ratio of cholesterol/(cholesterol + cholestanol) may be used as a check that the concentrations of sterols have not undergone any significant changes over time due to diagenetic effects (i.e. as an indicator of sterol preservation). A constant ratio indicates that there are no significant changes in diagenetic alteration with either time or location. In summary:

- Coprostanol/cholesterol: <1 = biogenic source; >1 = sewage source.
- Coprostanol/epicoprostanol: >1.5 = human faecal source.

- Cholesterol/(cholesterol + cholestanol): constant ratio = no change in diagenesis.

The mean values for these ratios in sediments of the Tees impoundment (table 8.5 and figures 8.2 and 8.3) indicate that sewage is the dominant major source of sterols within the Tees and that this sewage is strongly dominated by human sources, with little change in the nature of the inputs of sterols with depth in the sediment. As stated in chapter 3, the depth of sediment sampled represents the sedimentation over the 7 years since the Tees estuary was impounded, and therefore the sterol signature indicates that there has been little change in the nature of discharges of sewage to the river over this period.

Depth (cm)	**Coprostanol/ cholesterol**	**Coprostanol/ epicoprostanol**	**Cholesterol/ (cholesterol+cholestanol)**
0-3	1.67	6.41	0.71
15-18	1.81	4.83	0.57
30-33	2.18	6.25	0.56
45-48	1.53	4.89	0.48

Table 8.5. Sterol ratios with depth in the sediment of the Tees impoundment.

Depth (cm)	**Coprostanol/ cholesterol**	**Coprostanol/ epicoprostanol**	**Cholesterol/ (cholesterol+cholestanol)**
0-3	0.60	9.42	0.80
15-18	1.01	3.83	0.59
30-33	0.88	1.93	0.58
45-48	0.93	3.41	0.59
60-63	0.96	3.29	0.57

Table 8.6. Sterol ratios with depth in the sediment of the Wansbeck impoundment.

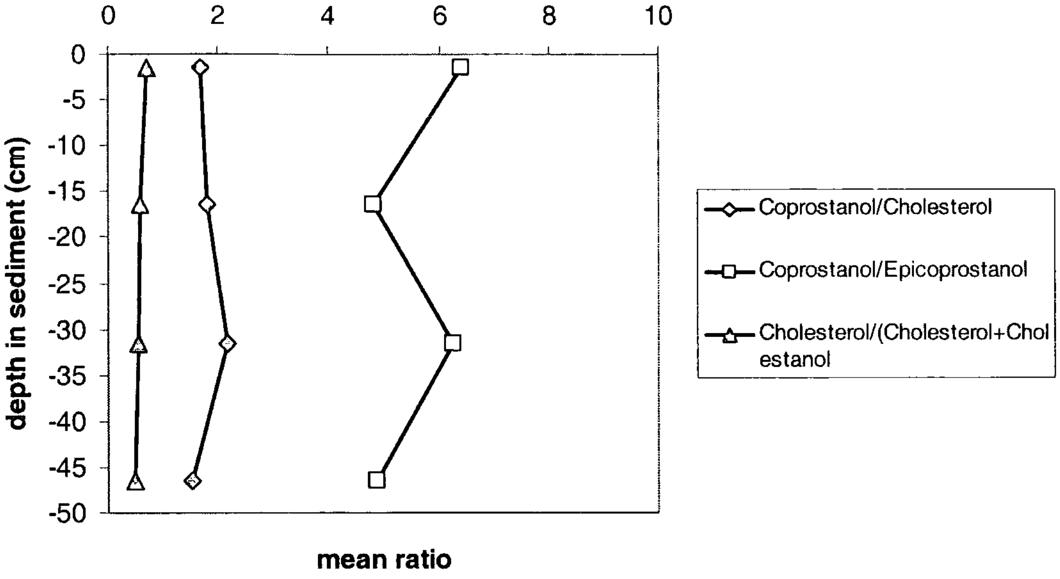


Figure 8.2. Sterol ratios with depth in the sediment of the Tees impoundment.

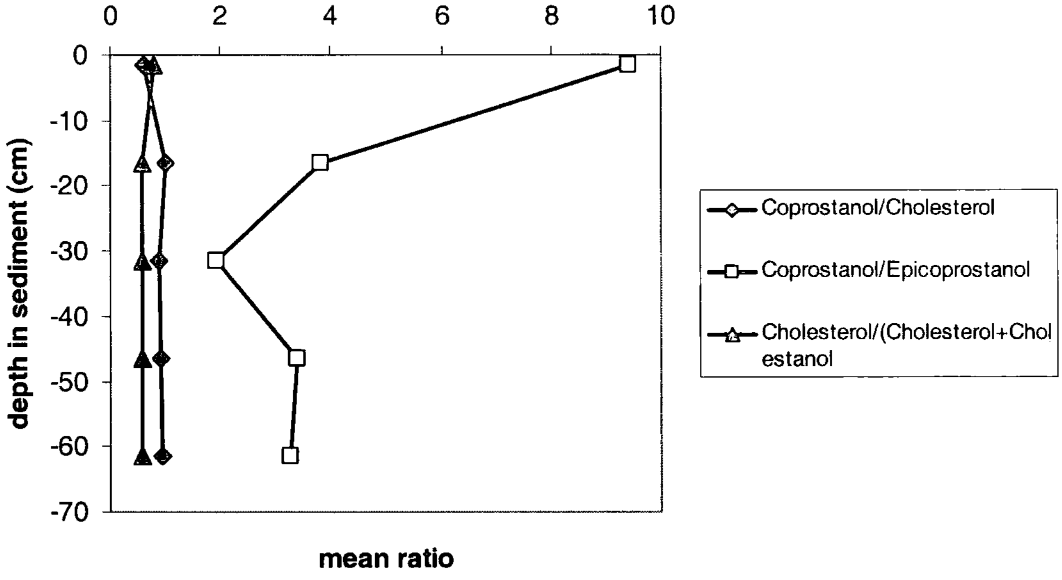


Figure 8.3. Sterol ratios with depth in the sediment of the Wansbeck impoundment.

The ratios in the sediments of the Wansbeck indicate that the sterols are of a combined biogenic (autochthonous) and sewage source, with the coprostanol/cholesterol ratio at <1 through much of the depth of sediment sampled. The coprostanol/epicoprostanol ratio indicates however that the fraction of the sterols that are sewage sourced is dominated by human faecal sources throughout the sediment depth sampled. As mentioned in chapter 3, in contrast to the Tees, no pre-impoundment sedimentation was sampled during the Wansbeck coring, and hence the sedimentation rates and the periods represented by the sediment cores sampled is not constrained. The coprostanol/epicoprostanol ratio does appear to indicate however that the ratio of human/agricultural faecal input has shown greater variation over time than that in the river Tees.

5α-cholestanol is the thermodynamically most stable microbial product from the reductive hydrogenation of cholesterol in the environment and is therefore produced during diagenesis (Patton and Reeves, 1999). Within the sediments of both impoundments the cholesterol/(cholesterol + cholestanol) ratio is relatively constant with depth in the impoundment indicating that little diagenetic alteration of the sterol signatures has taken place, and that hence the concentrations measured in the sediment reflect the relative concentrations in the inputs to the rivers. The minor decrease in this ratio with depth in the sediments of both impoundments fits with the corresponding presence of increasingly reducing conditions. That this decrease is more rapid in the Wansbeck may reflect the more rapid progression in the reductive series with depth in this system.

8.4.2 Coprostanol concentrations and faecal inputs over time

The absolute values of coprostanol give an approximate indication of the relative changes in human faecal input to the systems over time at a sampling site. However, without any calibration to known volumes of sewage input, coprostanol levels in the sediment cannot be used to determine actual amounts of faecal contamination to the water bodies. In addition, comparison of relative amounts of sewage input assumes that sedimentation conditions (for example sedimentation rates and particle size distributions) and sterol preservation have remained constant over the period of sediment deposition sampled. Whilst the cholesterol/(cholesterol + cholestanol) has been used to show that sterol preservation is relatively constant with depth in the sediment cores taken from the Tees and the Wansbeck, it has been suggested (chapter 3) that rates of sediment deposition in the impoundments have varied over time dependent on river discharges, and hence the sterol signature is likely to have shown variation in dilution over the periods studied.

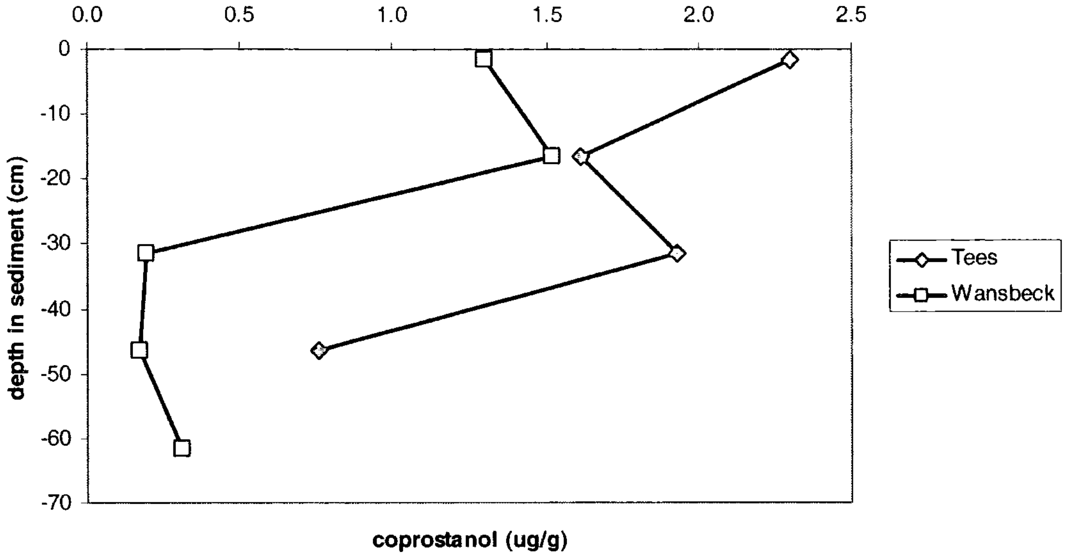


Figure 8.4. Coprostanol concentrations with depth in the sediment of the Tees and the Wansbeck impoundments.

The results for coprostanol concentrations (figure 8.4) do however suggest that inputs of human sewage organic material to the sediment show significant variation over time. This may relate to variation in inputs from CSOs to the rivers, or alternatively to variation in dilution of constant inputs with changes in flow and hence sediment transport. When discussing the impacts of sewage in the water of the impoundments (chapter 4) it was seen that phosphate, for example, shows strong negative correlation with flow in the rivers, and therefore CSO inputs (which only operate under high flow conditions) are likely to be insignificant relative to constant rates of input and their dilution effects.

8.5 Summary and conclusions

The salient points of this chapter are that:

1. Sewage inputs can be identified using lipid biomarkers in the sediments of both the Tees and Wansbeck impoundments with approximately 1 % of sediment in the Tees and <0.5 % of sediment in the Wansbeck being suggested as sewage sourced.

2. Sterol ratios show that faecal inputs to both the Tees and the Wansbeck are dominantly human.
3. Sterol signatures show good preservation in the sediments of both the Tees and the Wansbeck.
4. Coprostanol concentrations in the sediments of both the Tees and the Wansbeck have varied over time, but it cannot be determined whether this is due to variation in sewage inputs of variation in rates of sedimentation.

The preliminary work described in this chapter has shown that measurement of lipid biomarkers may be used effectively to determine the presence or absence, and the importance relative to other organic sources, of human sewage inputs to the sediments of estuarine impoundments. It is, however, clear that significant further work would need to be carried out to assess actual amounts of sewage inputs to water columns of the systems, and that faecal sterol identification in the sediments is not a particularly useful tool for this purpose.

Chapter 9

Conclusions

9.1 Review of research objectives

The aim of this research has been to progress the knowledge and understanding of water quality in the specific environment of estuarine impoundments. The main objectives of the research may be summarised:

1. **Assess** the current state of water and sediment quality in estuarine impoundments.
2. **Measure** the importance of the factors of season, barrage design and impounding on estuarine water quality.
3. **Understand** the processes controlling water quality that are affected by impoundment (particularly in terms of sediment-water interactions), and thus enable prediction of poor water quality events and the long-term sustainability of managed barrages.

9.2 Major findings

9.2.1 Current water quality

Within the estuarine impoundments studied water quality generally shows few problems in terms of the water quality parameters measured during most periods and at most locations within the water bodies. However, the water quality surveys carried out within this research have highlighted water quality issues in a number of areas. As described in detail, the most dramatic water quality problems relate to the depletion of DO, and associated reduction of pH and increases in ammonia and Mn (and associated metals), in stratified water bodies. DO concentrations of below the UK SWQOs for salmonid species (5 mg/l) and cyprinid and migratory species (3 mg/l) of fishery are periodically encountered at depth within the impoundments, particularly during the summer periods. The second water quality issue identified in this research, although one which has been conclusively shown to be sourced external to the impoundments, is of nutrient enrichment of the water bodies and the potential for eutrophic effects. Phosphate levels are greater than the OECD threshold level for lake eutrophy in all the systems studied, particularly within the rivers Tees and Wansbeck. Algal (cyanobacterial) blooms are periodically present during the growing season in the

Wansbeck impoundment, and algal problems are reported for the Tawe and Tees. In general (with the exception of the Tees in summer) phosphate is found to be the nutrient limiting primary production within the water bodies. Phosphate is shown to be dominantly derived from point sources in the rivers entering the three impoundments studied, and therefore management of these inputs is suggested as key in controlling eutrophication.

9.2.2 Seasonal variation in water quality

Analysis of the seasonal variation in water quality has been carried out for both an example of a total tidal exclusion impoundment (Tees) and an example of a partial tidal exclusion impoundment (Wansbeck). For the Tees it was shown that differences between summer and winter in water quality are mainly related to variation in river flow or temperature. Flow is important in terms of either dilution effects (major metals, alkalinity and phosphate), export effects (BOD, Si and Fe), or in relation to the homogeneity of the water body (stratification of the water body only occurring under low flow conditions). Temperature is important in terms of its influence on the rates of the biological processes of respiration and primary production. High rates of microbial respiration during the summer lead to reduced DO and pH, and increased ammonia and Mn and associated metals. It is shown in the Wansbeck that whilst lowest water quality is encountered during summer, low water quality conditions (particularly in terms of DO) are encountered throughout the majority of the year, with only winter freshwater discharges generally being sufficient to break down stratification of the water body and avoid poor water quality at depth. The same processes leading to low water quality are identified in both impoundments, but the degree and response to the seasonal effects are seen to differ. It is recommended that determination of the likely periods of low water quality be carried out on a case by case basis for individual impoundments.

9.2.3 Barrage design and water quality

There are significant differences in water quality between the Tees, Tawe and Wansbeck impoundments. These differences are a combination of differences between the rivers entering the impounded areas (external effects) and differences in processes occurring within the impounded areas (internal effects). External effects are independent of the construction of a barrage, whereas the internal variation may be affected by impoundment. For example, mean DO saturation varies by approximately 30 % between impoundments, with approximately half of this variation due to processes occurring within the impounded areas and the other half due to differences between rivers entering the impoundments. The worst water quality (in terms of DO and related parameters) is encountered in the Wansbeck impoundment due to strong (saline) density stratification existing for sustained periods (regularly 8 days or more) and isolating portions of the water column from sources of reoxygenation. Stratification exists for shorter periods in the Tees and Tawe impoundments due to a lack of saline water and a greater rate of tidal overtopping respectively, and hence the water quality impacts of the presence of a barrage are lower.

9.2.4 The effects of impounding on water quality

Impounding of estuaries is likely to have a negative impact on water quality. Decreases in tidal intrusion upon construction of a barrage lead to:

- changes in the relative amount and distribution of freshwater and seawater in the estuary,
- increased stratification leading to isolation of portions of the water column; and,
- decreased tidal currents and mobilisation of bottom sediments.

Nutrient levels (N and P) are generally higher in freshwater than seawater in the estuaries studied, and therefore increases in the relative proportion of freshwater cause an increase in the potential for eutrophication in impoundments. Increased residence times and decreased turbidities will also increase the likelihood of algal blooms. Reduced tidal influence leads to increased stratification of the water column and an increase in the periods of low water quality at depth described above. Finally, barrage construction causes a decrease in tidal scour and a marked increase in sedimentation in estuaries.

9.2.5 Sediment quality

Mean sediment quality within the Tees and the Wansbeck impoundments in terms of potentially toxic metals has been assessed. The sediments of the two impoundments are generally relatively high in metals due to a combination of anthropogenic inputs to the water bodies and the fine grained and organic-rich nature of the sediment. Concentrations of Co and Ni are above guideline values in the sediments of both impoundments. Both impoundments are unpolluted by Cu. The Tees sediment is polluted with Zn and Cr, with mean concentrations between the Canadian ISQG and PEL guidelines, although the oxidation state (and hence toxicity) of the Cr was not determined. Dredging is a possible solution to the sediment infilling observed in the impoundments. The largest remobilisation of metals on dredging occurs where heavy metals are held within sulphides in anoxic sediment, and hence water quality impacts on dredging are likely to be greater in the Wansbeck impoundment than the Tees.

9.2.6 Sediment geochemistry

Four controls on patterns of speciation and concentration of elements within the bottom sediments of the Tees and Wansbeck estuaries were identified. A large number of elements show behaviour controlled by the redox behaviour of Fe, with changes in their speciation from hydroxide to sulphide-bound forms with increased anoxia (depth) in the sediment column. The lower concentrations of sulphide-bound elements in the Tees reflect the less reducing conditions within these sediments. The Fe hydroxide phase is the major P fraction in the sediments, and although this has the potential for release to the water column under reducing conditions, data from the water quality surveys and pore water sampling show that sedimentary release is not a significant source of P in the water bodies. Secondly, the concentrations of several elements vary with changes in inputs to the sediments spatially and temporally. P concentrations in the sediments of the Tees and Wansbeck reflect differences in the P concentrations of the overlying water columns of these impoundments. Carbonate material and associated elements have shown significant variation in inputs over time due to variations in erosion of the geologies of the catchments. The large difference in Cr levels in the sediments between the two impoundments reflects the anthropogenic input of Cr to the River Tees. Thirdly, group 1 and 2 elements show significant fractions in the exchangeable phase of the sediments, with concentrations greater in the sediments of the Wansbeck due to the periodic presence of saline water within the impoundment. Finally, grain size effects on elemental concentrations in the sediments are seen to be minor compared to the factors described above, with the exception of Si (from quartz sand); the particle-size normalisation techniques usually employed in sediment quality surveys are inappropriate for multi-elemental speciation studies.

9.2.7 Pore water quality

The pore waters from sediments within the Tees and Wansbeck impoundments are below the UK EQSs for Hg, Pb and V. Levels of Cr, Cu and Fe, however, exceed the EQSs in both the sediment pore waters and in the water immediately overlying the sediment water interface (SWI) in both impoundments. As is in excess of the EQS within the pore water, although not in the overlying water column, of the Wansbeck impoundment. The dissolved form of these elements means that they are highly bioavailable to benthic organisms.

9.2.8 Biogeochemical processes at the sediment-water interface

Fe, Mn, Al, Co, Cr, P, Si and Ti are associated with Fe hydroxides in the solid phase of the sediment, and show pore water profiles relating to the reduction of these oxides to release free ions. The onset of oxide reduction and maximum pore water concentrations of these elements occurs at 2-3 cm below the SWI in the Wansbeck and at >12 cm below the SWI in the Tees, with the more rapid progression to reducing conditions being encountered in the Wansbeck sediments due to lower mean DO concentrations in the overlying water column and higher organic content of the sediments. Ca, K and Mg show simple diffusion profiles in the sediment pore waters dependent on the relative ionic strengths of the waters above and below the SWI. The direction of this diffusion periodically changes in the Wansbeck with tidal overtopping cycles. As, Hg, Sc and V are stable in dissolved forms at depths at which sulphides are present, possibly as organometal compounds (e.g. methylised As or Hg). Cu and Pb do not partition into sediments since they occur in stable dissolved forms in the water column overlying the SWI (chelated to organic matter and as a free ion for Cu and Pb respectively).

9.2.9 Fluxes across the sediment-water interface

Based on DET sampling results, fluxes for a selection of ions across the SWI were calculated based on Fick's law. Fluxes of P from the sediment contribute less than 1 % to the total dissolved P concentration in the water columns of the impoundments. Calculations of the proportion of Mn contributed to the water column through release from sediment are larger, but cannot account for the maximum concentrations observed during water quality sampling since pore water sampling was carried out under conditions of higher DO.

9.2.10 Sewage inputs to the impoundments

Sewage inputs can be identified in the sediments of the Tees and Wansbeck impoundments, and approximately 1 % of the sediment in the Tees and <0.5 % of the sediment in the Wansbeck is sewage sourced. Sterol ratios show that the faecal inputs to both the Tees and the Wansbeck are dominantly human. Whilst sterol concentrations may be used to assess the contribution of sewage to sedimentary material, they are unable to quantify volumes of sewage input to the water bodies.

9.3 Implications

The SIMBA (sustainability in managed barrages) project group, of which this research into water quality forms part, was set up to consider the long-term sustainability of impounded estuaries. Various aspects of the results from this study shed light on the future for impoundments in water quality terms.

The impoundments studied are infilling with sediment. Significantly, sedimentation rate and sediment quality have remained relatively constant over time since barrage construction. None of the current measures taken to avoid sediment build-up (flushing the impoundments by opening the lock gates (Wansbeck) or rapidly lowering the barrage crest (Tees)) are effective. Interactions between the sediment and the water column are generally small, and focussed in the top few centimetres (e.g. < 5 cm in the Wansbeck) of the sediment. No difference is seen in the rate of deoxygenation of water columns with different post-impoundment sediment thicknesses either within or between impoundments. The impact of sediment infilling of the impoundments is therefore not likely to cause large changes in water quality over time once barrages are constructed and initial sediment infill has taken place.

Sediment infill may be an issue for a variety of reasons. Firstly, all of the permanently operational estuarine barrages in the UK (i.e. excluding flood protection systems) are constructed to create amenity impoundments. Sediment infilling eventually leads to a loss in amenity value. The oldest UK estuarine impoundment (the Wansbeck; impounded in 1975) is less than 50 cm deep over large parts of the impoundment, and sediment build-up, and particularly the trapping of large tree branches carried under flood conditions, cause significant problems in the use of the impoundment for water sports. The Tees impoundment (impounded in 1995) had a greater initial water depth on impoundment and hence has a greater lifespan before sediment infill interferes with amenity use. The current depth of the impoundment next to the barrage is 7.3 m and a sedimentation rate of approximately 7 cm/annum has occurred since barrage construction, suggesting a lifespan for the Tees of close to 100 years. Secondly, sediment infill may necessitate dredging to be carried out as a remediation measure. The sediments have high metal concentrations, and are contaminated with Co and Ni (plus Cr and Zn in the Tees). Where these metals are held in sulphide bound forms (e.g. in the sediments of the Wansbeck) significant and potentially toxic concentrations will be released to the water column on dredging. Finally, sedimentation may change to topography of the bed of an impoundment over time. Pre-impoundment, freshwater flow through the estuary at low tide is along a thalweg which acts to drain upstream sections of the estuary of saline water. On impoundment, sediment build-up at the point at which the estuary widens from riverine to estuarine morphology means that the thalweg is infilled and upstream sections may show greater depth than downstream sections of the impoundment. The effect of this, as is seen clearly in the Wansbeck and Tawe, is that saline water may pond at depth in sections of the impoundment leading to the poor water quality conditions (low DO, high ammonia, etc.) described above.

The presence of sections of low water quality at depth may necessitate remediation measures (currently installed in the Tawe and proposed for the Wansbeck). Such remediation devices may include aerators, designed to reoxygenate low DO water, or mixing devices such as propellers or boom-skirts, designed to remove saline water at depth (Lamping, 2003). This research shows that the problems addressed by the remediation measures installed in the Tawe are common to all estuarine impoundments (including, although to a lesser extent, total tidal exclusion (freshwater) systems), with low water quality at depth encountered over the majority of the year. The cost of installation and running these likely remediation systems should therefore be included in any estuarine barrage proposals.

Importantly, this research shows that a large part of the water quality functioning of estuarine impoundments is dependent on processes occurring on the catchment scale. This is particularly the case for nutrients and the problems of eutrophication observed, with phosphate being point (urban wastewater inputs) sourced, and nitrate being point sourced in the Tees and the Tawe but predominantly diffuse (agriculturally) sourced in the Wansbeck. A very small proportion of nutrients are sourced from recycling from the sediments within the impounded areas. The implication of this for management of water quality in estuarine impoundments in the long-term is that reduction in eutrophication in the impoundments may only be carried out by reducing the inputs of nutrients to the rivers entering the impoundments.

The application of the knowledge gained in this research for the future construction of estuarine barrages needs final consideration in this thesis. Whilst it has been shown that barrage construction has negative impacts on water quality, these effects are not pervasive and the majority of the water within the impoundments is of good quality (according to UK EA criteria). Indeed, average water quality in the upstream (impounded) section of the Tees has increased following construction of a barrage due to the exclusion of poor quality tidal waters. The construction of barrages must also be considered in a broader environmental and social context, of which water quality is only a part. The essence of estuarine barrage construction is to improve quality of life for communities living and working in the regions of the estuaries. In this sense the developments and facilities provided in association with impoundment may be considered to outweigh the small decreases in water quality. Barrage construction may be hence a good thing. In terms of the type of barrage to build, this research conclusively shows that fewer water quality problems are encountered in total exclusion impoundments. Within these designs, to maintain maximum water quality, facilities should be included to allow removal of any saline water that might enter the impoundment (through groundwater flow or through locks), and to destratify and/or aerate the water column should stratification occur. Nutrient and other pollutant rich wastewater inputs to the impounded area should, if possible, be either terminated or diverted to enter estuaries downstream of the barrages. Detailed measurement of sediment loads carried by the rivers and modelling of sediment deposition are essential to determine the likely lifespan of a proposed barrage scheme. If dredging is to be considered an option, the concentration (and likely speciation once incorporated in bed sediments) of contaminants carried in the sediment load must be determined.

9.4 Suggestions for further work

During this project several areas of study have been identified as worthy of further work. These relate to both topics considered at the outset of this research and excluded due to time limitations and to issues raised as the research progressed. The areas can be summarised as:

1. Water quality surveying of organic pollutants, microbiological pollutants and bio-indicator species.
2. Further sediment studies including laboratory based modelling of the impacts of dredging, pore water sampling under a greater range of environmental conditions, and sediment quality and speciation surveys of the Tawe impoundment.

3. Time series water quality surveys over a number of years following impoundment, or from pre to post-impoundment conditions following construction of a new impoundment.
4. Catchment based studies focussing on sourcing inputs to the rivers entering estuarine impoundments.

At the outset of the project it was decided that the water quality surveys would concentrate on physical and chemical water quality parameters, and the discussion of water quality in this research refers to these aspects. More general comment on water quality could be made by the inclusion of organic compounds (pesticides, PCBs, etc.), microbiology (total coliforms, faecal coliforms and faecal Streptococci), and indicator species (macroinvertebrates and algae). In particular, sampling of bacteria would allow assessment of sewage inputs to the water bodies (whereas the sterol analysis carried out in this study only allows assessment of inputs to the sediment). In addition, the eutrophication of impoundments (whilst visually observed and noted in terms of effects on DO in this study) and the relationships to nutrient status of the water bodies should be explored through measurement of chlorophyll *a*.

The impacts of dredging on water quality are estimated in this research through determinations of the concentrations and speciations of metals within the bed sediments of the impoundments. Laboratory-based studies on the release of metals to the water column on re-suspension of sediments would allow better judgement of the impacts of dredging as a potential remediation process. Within the pore water sampling chapter discrepancies between the impact of exchanges across the sediment-water interface (SWI) on concentrations in the water column and the actual concentrations measured in the water column during water quality surveys were noted. It was suggested that this was due to sampling being limited to one set of environmental conditions, and that sampling over a greater range of conditions (salinities and levels of DO) would reveal large variation in exchanges across the SWI, and validate the DET gel-probe technique. It is also suggested that the sediment work carried out (sediment quality, speciation and pore water studies) be transferred to the Tawe impoundment. The industrial heritage of the Tawe (Cu, Fe, Sn and Zn smelting) means that these sediments are highly contaminated (Shackley, 1986; Dyrynda, 1994), and studies would allow assessment of the impacts of this on water quality.

Much of the assessment of the impacts of barrage construction in this research is made on the basis of the processes occurring within the impoundments and comparison of similar impounded and un-impounded estuaries. The models could be validated by the long term study of an impounded estuary over a number of years, preferably including a period preceding barrage construction. Obviously this approach showed limitations for PhD research!

One of the major findings of this research is that water quality in estuarine impoundments shows strong control by processes occurring external to the impounded areas. The water quality surveys carried out in this research have allowed tentative suggestion of the sources of these riverine inputs to the impoundments, generally based on relationships to river flow. Further research into the behaviour of these catchment scale inputs is strongly recommended and is considered key in allowing the long-term management of water quality in estuarine impoundments.

9.5 Concluding remarks

Impoundments (estuarine or otherwise) are a contentious issue. Ideas concerning the environmental costs and economic and social benefits of barrage construction are often in conflict. It is hoped that the research presented in this thesis goes some way towards aiding in objective decision making in the planning and management of impounded estuaries.

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Appendix 1

Statistical Methods Used

A brief outline of the statistical methods used in data analysis within this research follows. More detailed description of the methods may be found in standard statistical texts (e.g. Anderson, 1984; Howard, 1991).

A1.1 One-way tests

A1.1.1 ANOVA

One-way analysis of variance (ANOVA) tests the hypothesis that the means of several populations are equal. It requires a response variable (e.g. water quality parameter) measured for different levels of a factor (e.g. estuary). The null hypothesis is that no difference exists between the means of factor levels. ANOVA compares the variance within factors with the variance between factors. Estimates of variance are calculated as mean squares (MS; i.e. the sum of squared differences from the mean divided by the degrees of freedom). If the null hypothesis is correct then these two variances will be equal. If the null hypothesis is incorrect then the between factor variance will be greater than the mean of the within factor variance. To test whether it is significantly greater, a one-tailed F-test is used, and the result compared with critical values of F at the chosen significance level (generally $P = 0.05$, i.e. 95 % confidence). General assumptions of ANOVA calculations are that variance is homogenous (i.e. each factor has the same variance), data is normally distributed (although, as discussed in chapter 2, ANOVA is fairly robust against departures from normality), and that observations are independent of one another.

A1.1.2 Kruskal-Wallis

Kruskal-Wallis analysis is a non-parametric or distribution-free equivalent of one-way ANOVA, and does not rely on assumptions of normality in the dataset used. Kruskal-Wallis analysis uses ranking of data and compares the medians as opposed to the means of factor levels. In chapter 2, Kruskal-Wallis tests were applied as a check that departure from normality of the water quality data did not invalidate the results from parametric (ANOVA) tests. The advantage of parametric tests over equivalent distribution-free tests is that they have greater power (see section A1.3 below).

A1.2 General linear model

A1.2.1 Multivariate ANOVA

General linear model (GLM) ANOVA uses a least-squares (LS) multiple-regression framework to carry out comparisons of the means of multiple factors (e.g. estuary, distance and depth). A design matrix is formed from the factors (and covariates) in the model and response variables are regressed on the columns of the design matrix. The significance of both a selection of main effects (e.g. estuary, distance and depth) and interactions between these main effects (e.g. estuary*distance) may be tested. As with one-way ANOVA, the null hypothesis that the means from several populations are equal is tested using F-tests based on the MS for each factor. Tables of results for GLM ANOVA within this thesis show values of F and P for each factor used (table A1.1).

Source	**F**	**P**	**σ^2**	**Size of Effect (ω^2)**
Season	188.75	0.000	532.0	0.41
Distance	16.82	0.000	224.2	0.17
Depth	13.49	0.000	70.8	0.05
Season*distance	16.10	0.000	213.9	0.17
Season*depth	15.05	0.000	79.6	0.06
Depth*distance	2.10	0.025	31.3	0.02
Season*distance*depth	2.20	0.019	33.9	0.03
Error			102.0	0.08

Table A1.1. Example of a table of results for GLM ANOVA (results for DO % with season within the Tees).

Size of effects may be calculated as the variances accounted for by each of the factors or interactions included in the model (σ^2), with these variances as a proportion of the total variance of the dataset being the size of effect (ω^2).

A1.2.2 Main effects plots

The LS means calculated for factor levels in GLM ANOVA may be plotted as main effects plots to give a visual indication of the difference in response of the variable of interest between factor levels and comparison of the size of effects between factors (e.g. figure 3.1). The overall mean for the factor is shown as a horizontal dashed line.

A1.2.3 Interactions plots

In addition, interaction plots may be plotted (e.g. figure 3.3) as a visual indication of whether a change in factor level (e.g. season) gives the same response within two or more other factors (e.g. estuary). If the lines on the interaction plot are parallel then there is no interaction. The greater the lines depart from being parallel, the greater the interaction.

A1.2.4 Tukey method of multiple comparisons

Whilst multivariate ANOVA can determine whether or not significant differences exist between factor levels, it does not assess whether all of the factor levels show significant differences between them. The Tukey method compares all possible pairs of level means for the specified factors. Within this research Tukey pairwise comparisons were carried out where the main factor of interest (season or estuary) had greater than two factor levels. For example within chapter 2, for comparisons of the summer and winter seasons for the Tees Tukey comparisons were not necessary, whereas for comparison of spring, summer, autumn and winter for the Wansbeck the significance of the difference between each pair of seasons was tested (e.g. table 3.23). Where adjusted P values are greater than the chosen significance level (generally 0.05 within this work), then no difference between the pair of factor levels is assumed.

A1.3 Power analysis

Power analysis was performed retrospectively for the one-way ANOVA analyses carried out in chapter 2 as a check on the validity of the experimental design. Power is the probability of detecting a significant difference where one exists (Howell 1997).

In statistical testing, the validity of a null hypothesis (H_0) (which states that no significant difference exists) is tested. When carrying out an experiment to test a null hypothesis two types of error may occur. A type I error (probability = α) occurs when the H_0 is true but is rejected. The probability α represents the significance (P) for the test. The second possibility is that the H_0 is accepted when it is in fact false. This is defined as a type II error (probability = β). Power is the probability of not making a type II error ($P = 1 - \beta$).

Used retrospectively power shows whether the experimental design used was good enough to be able to detect any statistically significant results. The power of an experimental design is influenced by four factors:

- The significance of a test: high significances give high powers.
- The variability in the data: higher variability gives low powers.
- The size of the significant difference between treatment (e.g. river): the larger the difference the higher the power.
- The sample size: larger sample sizes give higher powers.

Parameter	Minimum sample size	Power
River flow	125	1.0000
Temperature	125	1.0000
DO	84	0.4910
pH	125	0.9988
Conductivity	125	1.0000
Alkalinity	125	0.9925
Secchi depth	51	1.0000
TSS	125	1.0000
Nitrate	125	1.0000
Ammonia	125	0.9998
Phosphate	125	1.0000
Silica	125	1.0000
Major Elements (Na, K, Mg, Ca, S)	125	1.0000
Fe	125	0.9970
Mn	125	0.7854

Table A1.2. One-way ANOVA Powers at $\alpha = 0.05$ (95% level), Number of Levels = 4 (Tees, Tawe, Blyth and Wansbeck).

A check on the power of the experimental design used in the water quality surveys was carried out. The lowest powers will occur for the smallest sample size. It is therefore only necessary to carry out power analysis for the smallest sample size used in the test. For the one-way ANOVA to test for between river differences (chapter 2) the smallest sample size was that of the Blyth, in which 125 samples were taken for the majority of parameters. This sample size decreases for DO due to a fault in the meter used in the water quality surveys meaning that these parameters were not measured on 3 of the days of sampling. The sample size for Secchi depth is also smaller since it was only taken once at each site for each sample date.

The results shown in table A1.2 indicate that the experimental design was powerful enough to pick up any statistically significant differences in the majority of water quality variables measured between rivers. Only 2 variables do not meet the 99 % probability level (i.e. had less than a 99 % likelihood of detecting differences between the rivers). For Mn this is mainly due to the large amount of variability in the dataset relative to the size of the differences between rivers. For DO it is due to the reduced minimum sample size due to missing data due to problems with the DO meter, in addition to large within treatment (river) variance within the dataset. Using the next smallest sample size (that for the Tees: 197 samples) increases the power to the greater level of 0.8795.

A1.4 Principal components analysis

Principal components analysis (PCA) is a multivariate statistical technique developed to reduce complexity in a dataset by transforming a large number of variables into a smaller set of new variables (principal components) which contain most of the information held in the original data matrix. As such PCA can be used to either determine the covariance structure of a dataset and/or to create a smaller number of independent variables for subsequent analysis. In this research PCA is used to determine the covariance structure of the water quality dataset and hence identify possible controlling factors of water quality.

Mathematically, principal components are normalised linear combinations (eigenvectors) of the variables based on matrix diagonalisation. The components produced are orthogonal (uncorrelated) to one another and are organised in order of decreasing variance, i.e. the 1st principal component (PC1) explains most of the variance in the dataset and has the maximum eigenvalue, with successive components having decreasing variances. The maximum number of components calculated is equal to the number of variables included in the analysis, but usually only the first few components are considered since they normally explain the majority of the variance in the dataset (subsequent components are often strongly influenced by analytical errors). A convention is to only examine the principal components with eigenvalues > 1. Scree plots of the eigenvalues may be used to graphically represent the relative amounts of variance explained by each of the principal components.

Within environmental multivariate datasets, variables are often measured using different scales (e.g. for the water quality dataset parameters are measured in mg/l, µS/cm, % saturation, etc.), and so PCA is carried out using a correlation matrix. For data measured in the same units a covariance matrix may be used.

The coefficients of the variables to the principal components are used to determine groupings of variables, and to calculate scores for each of the rows (water samples) in the dataset. These principal component scores can be plotted on scatterplots using the principal components of interest as axes, and often show groupings of data based on underlying controlling processes, although care must be taken not to subjectively over-interpret results (further numerical analysis such as regression should be carried out). Detailed discussion of the principles, use and advantages and disadvantages of PCA are included in Jobson (1992), Howard (1991) and Wilson and Wilson (1999).