Testing the use of biomarkers to trace organic carbon in a small rural catchment in the U.K

MELVIN, KATHRYN,RUTH

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Testing the use of biomarkers to trace organic carbon in a small rural catchment in the U.K

Kathryn Ruth Melvin

MRes thesis

Supervised by: *Professor Erin L. McClymont, Professor Louise J. Bracken and Professor Robert Hilton*

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Geography Department

Durham University

United Kingdom

Abstract

Testing the use of biomarkers to trace organic carbon in a small rural catchment in the U.K

The interaction between climate change and the carbon cycle on land is a pressing topic that is frequently discussed within both academia and government. Extensive research has been undertaken into organic carbon export in forested river systems, including estimating the organic carbon (OC) fluxes transported towards, and deposited in, the ocean. However, the origins of carbon transported by smaller, anthropogenically-modified river systems that are widespread in the UK are more poorly constrained. A novel approach to trace the source and pathway of OC is to use biomarkers – identifiable organic compounds that can be linked to the biological processes that formed them. This approach has been widely applied to reconstruct past environmental change and climate, but has recently been recognised as having promise to trace OC transport in rivers. In this thesis, the biomarker method was applied to a small river catchment to explore if this analysis could better constrain the origins, types and transfer of OC, furthering knowledge of the importance of catchment and fluvial process in a wider context. This thesis focuses on the River Esk in the North York Moors. The River Esk has been studied extensively because of the geology and the varied land use, from peatlands to agricultural and small forest areas, so that this catchment provides varied land uses and has the potential input of distinct OC sources which can be identified using the biomarker method. River sediments collected using a time-integrated sampling method were used to explore spatial patterns. Further work and the inclusion of more seasonal data would add even more information that is missing in this area of study. It was concluded that the use of biomarkers gave additional information when trying to understand river processes. All sample sites using biomarker analysis gave data consistent with what would be typically expected for the surroundings. An interesting difference was observed in two of the sample sites, where the biomarkers indicated an aged fossil signal. A human influence was confirmed as both sites were major sites in the iron industry in the 1800s.

This thesis titled "Testing the use of biomarkers to trace organic carbon in a small rural catchment in the U.K." produced by Kathryn Ruth Melvin and supervised by Professor Erin L. McClymont, Professor Louise J. Bracken and Professor Robert Hilton is submitted to Geography Department, Durham University, Lower Mountjoy, South Road, Durham, United Kingdom for the qualification of Masters of Research in 2022

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List of abbreviations

Abm: Area of the target biomarker on the chromatogram
ACL: Average chain length
ANC: Acid neutralising capacity
As: Area of the standard on the chromatogram
BGS: British geological survey
C: Commondale
CPI: Carbon preference index
C/N: Carbon and Nitrogen
CO_2: Carbon dioxide
DBK: Danby Beck
DBA: Danby A
DBB: Danby B
DCM: Dichloromethane
DOC: Dissolved organic carbon
FID: Flame ionisation detector
G: Grosmont
GC: Gas chromatography
GDSA: Glaisdale downstream A
GDSB: Glaisdale downstream B
GM: Glaisdale meander
H: hydrogen
L: Lealholm
Mbm: Mass of the biomarker that you want to be quantified
MeOH: Methanol
MS: Mass spectrometer
N: Nitrogen
NYM: North York Moor
NYMNPA: North York Moors National Park Authority
OC: organic carbon
OED: Odd/even distribution
POC: Particulate organic carbon
Pr/Ph: Pristane/Phytane
PTV: Programmable temperature vaporizer
TAR: Terrestrial over aquatic
TIC: Total inorganic carbon
TOC: Total organic carbon
W: Westerdale

Declaration

I declare that the material contained in this Master's thesis has not been previously submitted for a degree in this or any other institution

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1. Chapter 1: Introduction

1.1 The carbon cycle

Carbon is a crucial element in the Earth System because it dominates compounds that form the basis of all life, while its gaseous forms in the atmosphere (carbon dioxide and methane) control the Earth's surface energy balance and global climate (Figure 1.1; Killops and Killops, 2005).

The global carbon cycle includes both inorganic and organic forms and is a complex system containing many processes (Figure 1.1). The carbon reservoirs (stores) are where carbon can be held for a range of timescales, ranging from years (e.g., terrestrial vegetation) to millions of years (e.g., in bedrock, fossil fuels or on the ocean floor). Sedimentary rock is the largest of these reservoirs, accounting for 99.9% of carbon stores, mostly as carbonates. In the atmosphere, carbon exists as carbon dioxide (CO_2), which is the principal compound used in photosynthesis. At various points in time, the carbon flows between different stores either through natural processes or through human interference (Figure 1.1; Killops and Killops, 2005).

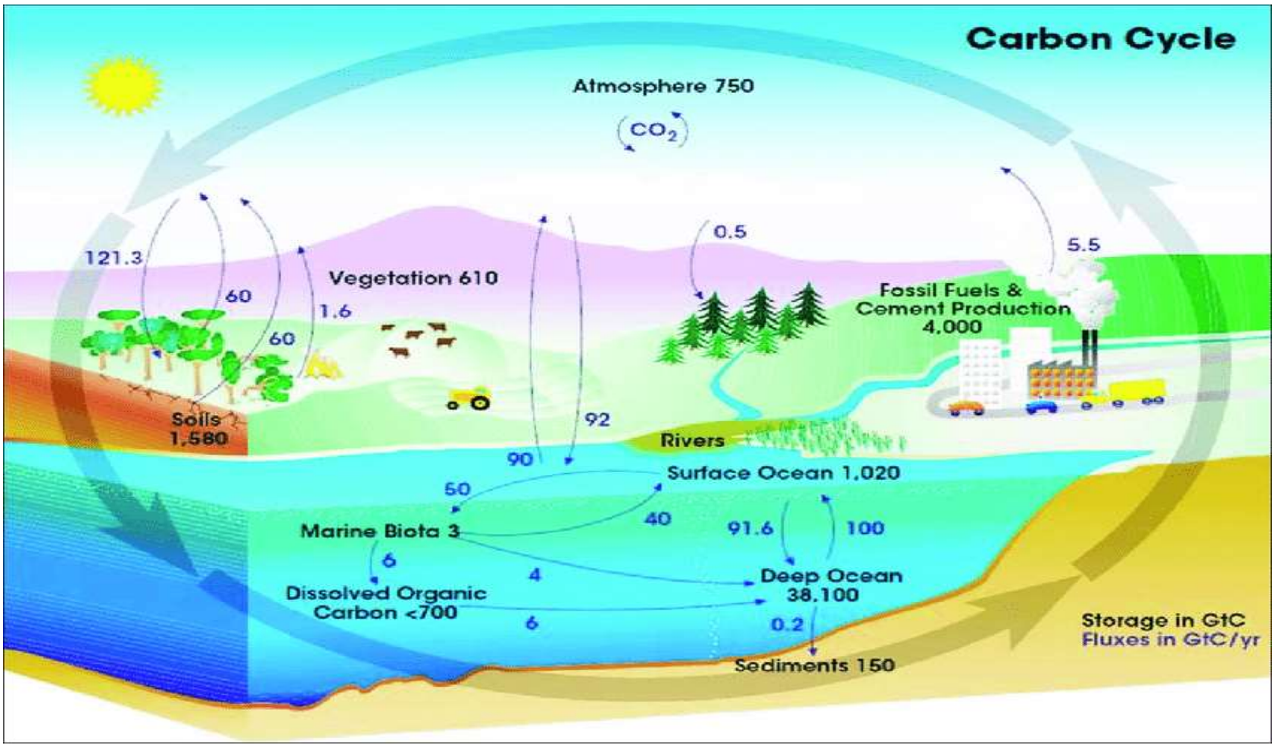


Figure 1.1: The global carbon cycle, indicating major pools and fluxes. Values in black next to the arrows indicate estimated carbon stores in our environment, whereas blue numbers by arrows indicate the transfers between those stores each year (United States Department of Agriculture, 2009).

It is important to understand the carbon cycle because the interactions between the stores and exchanges (fluxes) of carbon influence the atmospheric concentrations of CO_2. As a greenhouse gas, CO_2 concentrations control the energy balance at Earth's surface and thus play a role in global climate (Limpens *et al.,* 2008).

Carbon dioxide in the atmosphere continuously flows from and to other carbon stores. Fast transfers of carbon include leaf litter uptake then decay, releasing carbon back into the atmosphere on seasonal or annual timescales, whereas slower exchanges (e.g., million-year timescales) include the burial of organic carbon in the ocean and the formation of sedimentary rocks, some of which has then contributed to the formation of oil and gas reserves. Other flows of carbon may be stored then released through weathering, subduction or volcanism (Killops and Killops, 2005). As a result of these continuous carbon cycle transfers, it is difficult to measure carbon reservoirs, so values of carbon in each reservoir are mostly estimated (Figure 1.1).

Rivers play an important role in redistributing carbon at the Earth's surface, carrying organic matter from the land, through fluvial networks, to the coast and ocean. The global fluxes are ~0.5 PgC yr^{-1} (as POC and DOC, Regnier *et al*., 2013), which is an important natural transfer of carbon to the ocean. There is a need for more work to understand how these carbon fluxes in rivers impact global carbon cycling (Galy et al.,2015). For instance, understanding where the carbon in rivers come from is crucial to constraining the impact of the transfer: does it come from old soil/rock organic matter, from where it could be oxidised and leak CO_2 back to the atmosphere? or is it part of the more rapid cycling of CO_2 from atmosphere to vegetation? With further research on terrestrial carbon stores and river transport, improved estimates may be gained in this study.

1.2 Project Rationale

Few studies of carbon cycling have targeted river catchments where human activity has been quite minimal (Galy et al., 2015). Yet, large areas of the world, and the UK in particular, have a landscape that has been heavily modified and actively managed, particularly associated with agriculture. In addition, much work has focused on larger systems, while small rivers could be important for understanding the carbon cycle (Biddanda 2017; Staddon, 2004). In this study, a small river catchment in the North York Moors is studied, the River Esk, through one year of varying river flows. The North York Moors is an ideal site for this research as the river flows through different land uses, spanning peatlands, woodlands and agricultural. Previous research on the River Esk has investigated erosion, sediment transportation and water quality, but less is known about where the sediment originates and how carbon might be transferred through the catchment (Evans *et al.;* 2014; NYMNPA., 2001; Bracken and Oughton., 2013, NYMMP, 2012, Bracken and Warburton 2005; Bolland *et al.,*2010). The focus of this investigation is to consider the transport of organic carbon, by applying a new geochemical technique to existing samples. Using lipid biomarker analysis, this research will determine the source of the organic carbon in the suspended sediment being transported in the upper reaches of the River Esk.

1.3 Aims

The aim of this investigation is to determine the sources of organic carbon input into a small rural river in the UK, the River Esk.

1.4 Research questions and objectives

RQ1: Are biomarker proxies able to identify different sources of organic carbon supplied to rural rivers?

Objective 1.1: To analyse the lipid composition of particulate organic carbon using organic geochemistry (biomarker) analytical techniques.

Objective 1.2: To explore the geochemical data to identify likely sources of organic carbon.

RQ2: Do biomarker distributions shift downstream, through the catchment, and how does this reflect changing carbon inputs?

Objective 2.1: To assess whether spatial patterns in the geochemical data can be determined, using samples from multiple sites along the length of the river.

RQ3: Do the main inputs of carbon change with time?

Objective 3.1: To determine whether any seasonal changes in organic carbon input can be detected.

Objective 3.2: To compare results to other variables which might vary through time and affect river flow (e.g., rainfall).

1.5 Thesis Outline

To explore these questions, this thesis first reviews knowledge of organic carbon transport in river systems and how other research has shown its impact on the carbon cycle (Chapter 2). Then, I outline how biomarkers have been applied in other research, and which signals are useful for identifying sources (Chapter 2). In Chapter 3 I outline the research which has already been undertaken in the River Esk to provide context for this investigation. The methods used in this thesis (Chapter 4) and the results (Chapter 5) and findings (Chapters 6 and 7) are then presented.

Chapter 2: Literature Review

2.1 River transport of organic carbon

The primary focus of this research is to analyse terrestrial organic carbon in suspended sediments in river systems, in particular the River Esk. Inland rivers, lakes, streams, reservoirs, wetlands and estuaries cover less than 4% of the earth's surface, yet they act as major transit systems in the carbon cycle (Biddanda, 2017). It has been argued that freshwater systems can bury more carbon in sediment each year than the vast open ocean floor (Biddanda 2017), although this claim is debated (Xing *et al*., 2011; Goñi *et al.,* 2000; Hilton *et al.,*2008).

Within the water column there are various ways organic carbon (OC) is present, either as dissolved organic carbon (DOC <0.45 µm) and particulate organic carbon (POC >0.45µm-1000µm) (Dhillon and Inamdar, 2014; Hutchens Jr. *et al*., 2017; Hedges *et al*., 1997). POC can be present either in suspension within the water column and/or deposited on the river bed (Hilton *et al.,*2008*;* Hilton *et al.,*2015*;* Hilton *et al.,*2017). Both POC and DOC regulate aquatic metabolism and can also influence drinking water quality (Xing *et al*,. 2011; Goñi *et al.,* 2000).

As shown in Figure 1.1, aquatic plants utilise carbon dioxide during photosynthesis, generating OC, and transferring C from the atmosphere. The OC (POC and DOC) can be subject to various degradative processes including decay and remineralisation either *in situ* in the river or during transport (Killops and Killops, 2005; Hedges *et al*., 1997; Holland and Turekian, 2005; Maerz *et al.,* 2020; Jones *et al.,* 2020). Ultimately, respiration of OC then releases the C back to the atmosphere as CO_2 (Killops and Killops, 2005, Hedges *et al*., 1997, Holland and Turekian, 2005; Jones *et al.,* 2020).

In addition to aquatic OC, there are also inputs of OC from sediments or vegetation surrounding river systems. An extreme example is where tropical cyclones trigger storms which erode landscapes and drive high volumes of fluvial sediment to the ocean (Kao *et al*., 2014). In Taiwan, this OC is transported rapidly from land to ocean, where it can escape oxidation and degradation before reaching the ocean floor (Kao *et al.,* 2014). It has also been proposed that the origin of the carbon could potentially affect the atmospheric CO_2 sink related to river OC transport (Kao *et al.,* 2014). For example, soil and vegetation in the biosphere are estimated to contain 2000-2900 PgC at present, so that rapid transport to the ocean without oxidation means it continues to act as a sink from the atmosphere and forms one of the major carbon reservoirs (Hilton, 2017). In contrast, if rock derived carbon (fossil) is transported and buried in the ocean, it has little effect on the CO_2 sink because it was stored away from the atmosphere before transport (Bouchez *et al.,* 2010; Hilton *et al.,* 2015; Hilton *et al.,* 2017; Galy *et al.,*2015).

2.2 Peatlands as organic carbon stores

Peat is an organically rich biological sediment, which forms through the accumulation of compacted plant material in waterlogged swamp and bog environments (Holden, 2011). Peatlands have been recognised as a large carbon sink, as carbon fixed from the atmosphere by photosynthesis is stored in the peat layers for many thousands of years. Peatlands contain over one-third of the world's soil carbon (Holden, 2011), and may be a regulator of global warming via atmospheric CO_2 and a methane sink (Xiang and Freeman, 2008, Gorham, 1991).

Peatlands are characterised as bogs or fens, which have different environmental controls and characteristics. Bogs are wetlands covered by spongy peat deposits, acidic water, and low nutrients (Aertz *et al.,* 1999). Fens are nutrient-rich wetlands. The main water source for ombrotrophic bogs is from precipitation, unlike fens where the water source includes runoff and streams. Due to the low nutrients and acidic environment in bogs, *Sphagnum* mosses are a common type of vegetation (Aertz *et al*., 1999). Depending on the specific species of *Sphagnum* present, the environment of the bog at a specific point can be determined, as some species prefer certain water table depths (Blackford., 2000). In contrast to bogs, fens are more alkaline and have higher amounts of nutrients (Tahvanainen, 2004). The common vegetation associated in fen environments are sedges and heather (Aertz *et al.,* 1999).

Tracing inputs to the river from bogs or fens would provide useful information on OC sources in small rivers. Bogs and fens have been studied using both lipid biomarkers and macrofossils, which have shown that the main plant contributions to bogs and fens can be traced through time (Ronkainen *et al.,* 2014; Ronkainen *et al.,* 2013). Other studies have linked the importance of runoff from peatland areas to rivers and explored the impact of drying of peatlands during warmer climate (Evans *et al*, 1999; Holden and Burt, 2003; Lees, 2018). During seasonal climate changes and flash floods, the peat is vulnerable to erosion and is introduced into the river system, increasing the sediment load (Evans *et al*., 1999; Holden and Burt, 2003; Lees, 2018). However. the loss of peat is not always through weather conditions; peat research in Canada, USSR and America identified peat losses of 11.5×10^6 ha (3.3%) due to draining and about 4.4×10^6 ha (1.3%) due to mining for horticultural peat and fuel, amounting to 455 Pg of carbon loss from peat in these countries at a rate of 0.091 PgC yr^{-1} (Gorham, 1991).

To understand carbon sinks and sources, it is important to understand whether the carbon being released into the river system from peats will be readily oxidised as it is transported downstream, or if it is deposited and buried in the ocean. Research on six peatlands in Switzerland determined that peat draining as well as local/regional climate change and rainfall patterns affected the loss of the younger topsoil (Leifeld *et al.,* 2012). The same study determined that due to global warming-induced changes in the peat hydrology, the younger topsoil is likely to be lost, exposing and degrading older peat. In turn, the older degraded peat will oxidise, releasing stored carbon back into the atmosphere. However, Liefeld *et al.* (2012) did not consider the fate of the carbon which may be eroded and transported by fluvial systems, and whether this oxidation would continue. In Arctic River systems, however, rising temperatures and thawing of arctic soils have led to old, stored carbon being introduced into the carbon cycle, identified using biomarkers (e.g., lignin and phenols) and radiocarbon dating to trace higher plant and peat inputs, as well as ancient sedimentary rock. Identifying river inputs of peat from permafrost is important because permafrost stores half of the global soil organic carbon (Feng *et al*., 2013).

2.3 Soil organic carbon

Human activity has added additional processes into the carbon cycle. The industrial revolution of the 18th century caused a large perturbation to the carbon cycle and the balance of C fluxes to and from the atmosphere (Killops and Killops, 2005; Tomkins and Muller, 2019). After the mid-18th century, the carbon released from the geological reservoir occurred much quicker than ever before. The Intergovernmental panel on climate change (IPCC), states that human influences has warmed the climate, atmosphere, ocean and land at a rate that it is unprecedented in at least the last 2000 years. Since 2011, concentrations have continued to increase in the atmosphere, reaching annual averages of 410 parts per million (ppm) for carbon dioxide (CO2), 1866 parts per billion (ppb) for methane (CH_4), and 332 ppb for nitrous oxide (N2O) in 2019. Land and ocean have taken up a near-constant proportion (globally about 56% per year) of CO_2 emissions from human activities over the past six decades, with regional differences (IPCC, 2019).

Human influences including, deforestation and burning of some fossil fuels (tropical peat). It is stated that 8% of anthropogenic carbon dioxide emissions are from land-use change, and 3-9% is estimated to be from aged carbon, ranging from modern to >1,000 years old, which is mobilised into the river ecosystem by human disturbance (Butman *et al.,* 2014). With population growing rapidly the anthropogenic CO_2 inputs to the atmosphere from land-use change will most likely increase. Current trends of carbon transport from land to rivers suggest a 0.1 to 0.2 Pg increase every year as a result of deforestation and increasing agriculture as well as other factors due to human activity, these increase OC inputs (Butman *et al.,* 2014).

The stock of carbon in soil and organic matter (Figure 1.1) is calculated as 1600 gigatonnes, representing a major carbon store. Van Oost *et al*. (2007) highlighted that human activity has altered the carbon cycle, not just by the increased use of fossil fuels but a land use change, which is poorly investigated. Important processes linked to land use change are likely to include the fluxes between reduced carbon in soil and accelerated decomposition of soil organic carbon (SOC), which will either be re-buried or released to the atmosphere. Van Oost et al. (2007) found that soil erosion, especially from an agricultural setting, is overlooked and is an important process to include when looking at the global carbon budget and the contribution of CO2 to global warming. IPCC reported that land use contributes about one quarter of global greenhouse gas emissions from deforestation, CH_4 emmission from rice and ruminant livestock and N_2O emissions from fertilisers. However, there is no mention if this report includes small rural catchments in this study, which may increase the predicted global contribution (IPCC, 2019).

The largest loss was from the forest itself as a store, thus emphasising that this has the largest effect on the carbon pool for net land emissions. Hilton *et al*., (2015) observed that although carbon could be degraded in transport and contribute to the CO_2 in the atmosphere, erosion and re-burial of high latitude organic-rich soil contributed to an important geological CO_2 store (2.2 TgC yr^{-1} for the Mackenzie River, Canada). Schultz *et al.,* (2016) also found that land use change and the impact of CO_2 emissions from land cover changed in the last decade (~1.1% of the existing stock), caused by forest being changed to cropland.

2.4 Rocks as a source of river organic carbon

The weathering and erosion of bedrock is a widespread phenomenon, which contributes to the formation of soils, supply of dissolved solids to rivers, and also plays a role in the carbon cycle (Gaillardet et al., 1999 Chemical geology). Typically, it can be determined using analysis of anions and cations in river waters and sediments. Qu *et al*., (1993) researched anions and cations on major rivers in China and concluded that the rate of erosion increased with the wetter and hotter climate. They suggested that certain elements are more vulnerable to being leached in these conditions and that more erosion/weathering occurs when there is an increase in rain and temperature. In terms of the cycle of OC at Earth's surface, about 15,000,000 PgC are stored in rocks as fossil organic matter (Copard et al., 2007). In sedimentary rocks, it can be common that rocks contain ~0.5% OC, or fossil OC, for instance as found in the central range of Taiwan (Hilton *et al.,* 2015). For the River Esk catchment, there is a variety of bedrock types which could contain OC that may input to river sediments, and which will be important to trace (Chapter 3). A long history of organic geochemistry work for petroleum investigation and for reconstructing past environmental change has meant that there is a wide range of biomarker approaches which can be used to trace OC from bedrock sources (Killops and Killops, 2005; Gies *et al.,* 2020; Wiltshire *et al.,* 2021; Liu *et al.,* 2020).

2.5 Methods to trace organic carbon in rivers

2.5.1 Carbon and nitrogen content

The Carbon to Nitrogen ratio (C/N) of OC is a common analysis in environmental sciences, especially when distinguishing between marine and terrestrial plant input, as it reflects the fact that terrestrial plants have relatively more carbohydrates (with high C) than marine settings, where proteins (containing N) are important This is noticeable as the C/N ratio for marine sediments are less than 6, whereas land derived plants are at/below a value of 15 (Walsh *et al.,* 1981). The C/N technique can also be applied in the terrestrial setting to distinguish between aquatic plants and land plants. For example, in a study of the Godavari River, it was shown that soil and land plants display C/N ratios between 8-14, which was recorded with soil input during high rainfall seasons (Balakrishna *et al.,* 2005). For the rest of the seasons where rainfall is low, most of the C/N ratios were between 1-8, representing aquatic inputs as the main source (Balakrishna *et al.,* 2005).

One advantage of the C/N ratio is that it is relatively simple and sample analysis can be automated once the samples have been prepared, although processing can be difficult if the matrix is complex or moist and the sample is not homogenous (Beilke and Bockheim, 2013). A disadvantage is that samples which contain low carbon content, such as sand, can be difficult to combust and yield enough N for measurement. However, the use of a vanadium pentoxide in small quantities can increase the combustion by introducing more oxygen into the sample (Cargua *et al.,* 2017), although ensuring enough material for analysis remains difficult. Most samples for C/N analysis are prepared by acidification before combustion for total carbon analysis, by the DUMAS combustion method (Brodie, *et al.,* 2011). The principle of this approach is that the sample is acidified to remove the inorganic carbon before analysis, so that theoretically only the organic carbon part of the sample is analysed. However, there has been controversy regarding the efficiency of pre-treatment when gathering accurate results. It has been argued that the acid treatment is less sensitive and potentially inaccurate (Brodie, *et al.,* 2011) since biases may be introduced if the acid rinse method digest compounds other than carbonate. The impact is to over-estimate higher values of inorganic carbon content. Brodie *et al.,* (2011) recommends that the untreated method for C/N is most reliable and gives the least bias.

2.5.2 Biomarkers as tracers of carbon transport

Geochemical analysis of sediment can include examining OC biomarkers, which are individual organic molecules with a known biological source. Biomarkers have a wide range of structures: they can be aromatic (with ring structures), simple straight-chain molecules, or highly complex large molecules (e.g., lignin). They can remain preserved in the environment for millions of years before breaking down (Peters and Moldowan*,* 1993). Biomarkers are dominated by carbon and hydrogen and are present in living organisms (plants, animals, bacteria, archaea). After death, the biomarkers are then preserved in sediments, rocks and oils, and can indicate the source organism and/or the environment that the source organism thrived in when it was alive. The structure of biomarker compounds found in sediments provides information on the biomarker origin and history e.g., if it has been chemically transformed from it's original structure under certain conditions (Peters and Moldovan*,* 1993).

In terrestrial settings, biomarkers from plants give a fingerprint for determining what vegetation is present. Plant biomarkers including straight chain alkanes (*n*-alkanes) which are compounds that occur in freshwater, estuaries, marine sediments and soils (Regnery *et al.,* 2013). The *n*-alkanes are lipids from waxes found in terrestrial plants, as well as from the organic parts of aquatic algae, and can be identified by differences in chain lengths using gas chromatography-mass spectrometry (GC-MS, Chapter 3). These hydrocarbons are widespread biomarkers in terrestrial sediment and have been extensively researched to understand the main source organisms. Short chained, even numbered *n*-C_{12} to *n*-C_{22} *n*-alkanes are attributed to the presence of bacteria, whereas even numbered *n*-alkanes *n*-C_{15} to *n*-C_{22} are attributed to the presence of algae and photosynthetic bacteria (Gonzalez-Vila.,2003; Cranwell *et al.,* 1987). This distinction is important as the presence of high molecular weight odd-numbered alkanes *n*-C_{27}, *n*-C_{29} and *n*-C_{31} are associated with leaf waxes from higher plants (Eglinton and

Hamilton., 1967; Gonzalez-Vila., 2003, Ahad *et al*., 2011and Galy et al.,2015). After the death of the plants these *n*-alkanes may become incorporated into soils, and over million-year timescales they ultimately become part of the “petrogenic organic carbon” component of sedimentary rock (Ahad *et al*., 2011).

Biomarkers have been used to identify the sources of particulates and organic matter in lakes, rivers and oceans. They provide detail about carbon inputs to understand paleotemperature, phytoplankton community structure, vegetation history, dust provenance, nutrient cycling, ocean circulation and paleo-redox conditions (e.g., Das *et al.* 2008; Higginson 2009) as well as tracing vegetation and soil inputs to rivers (e.g., Feng *et al*., 2013). A common way to consider the relative contribution of different biomarkers is to generate ratios which relate to change in likely organic matter source. Here, the main ratios to be applied in this thesis are outlined.

2.5.2.1 Carbon preference index (CPI)

The Carbon preference index (CPI) is a way of representing the odd-over-even predominance in *n*-alkane chain lengths, focusing on specified carbon number range (Killops and Killops., 2005; Wang *et al.,* 2019; Howard *et al.,* 2017),(Equation 2.1). CPI values of <1 is associated with terrestrial and thermally immature rock, whereas values close to 1 or below are associated with fossil fuels. Catagenesis and metagenesis are stages in the carbon cycle where the OM is heated between 50-200 °C. Once the organic matter goes through this irreversible effect, changing the OM to thermally mature, there is a shift towards more even chains and a lower CPI (Killops and Killops., 2005, Ahad *et al.,* 2011).

Equation 2.1:

$$\mathrm{CPI} = \frac{\sum(\,n\text{-}C_{23} - \text{n-}C_{31})\ \text{odd} + \sum(\,n\text{-}C_{25} - n\text{-}\ C_{33})\ \textit{odd}}{2\sum(\,n\text{-}C_{24} - n\text{-}C_{32})\ \textit{even}}$$

(Allen and Douglas, 1977)

The CPI has been applied to sediments from the River Tyne, UK (Ahad *et al*., 2011) where the CPI was able to distinguish the main carbon source as terrestrial/recent plants (CPI value above 3). The River Tyne is located in the North East of England with dense industry: Ahad *et al.* (2011) indicated that the role of industry was likely reflected in the decrease of CPI moving downriver towards the industrial centre of Newcastle and Tyneside.

2.5.2.2 Average chain length (ACL)

Average chain length (ACL) is calculated as an average number of carbon atoms per molecule based on the abundance of the odd numbered *n*-alkanes and is designed to highlight difference sources (Ahad *et al.,* 2011) (Equation 2.2).

Equation 2.2:

$$ACL = \frac{(25*(n\text{-}C_{25})+27*(n\text{-}C_{27})+29*(n\text{-}C_{29})+31*(n\text{-}C_{31})+33*(n\text{-}C_{33}))}{(n\text{-}C_{25}+n\text{-}C_{27}+n\text{-}C_{29}+n\text{-}C_{31}+n\text{-}C_{33})}$$

(Poynter and Eglinton, 1990)

The ACL is applied as an indicator of the potential source of higher plant *n*-alkanes to an environment. For example, Sachse *et al.,* (2006) applied the ACL proxy to their investigation *Spagnum* moss and terrestrial leaf litter contributions to a lake sediment. They concluded that higher sphagnum inputs could be determined by lower ACL, since mosses are dominated by shorter chain lengths (~C_{23}), and proposed ACL as a suitable measurement tool to indicate climate change (Sachse *et al.,* 2006). Other authors have attempted to use ACL as a temperature indicator, because the leaf epicuticular composition of higher plants responds to temperature change, with increasing ACL (C_{27}-C_{33}) value during warmer periods (Yang et al. 2011). In warmer environments, land plants increase the amount of long chain compounds in their waxy coating as a protection from moisture loss. In cooler temperatures, shorter chain compounds are produced (and the ACL will decrease). Yang *et al.,* (2011) also proposed that the ACL detailed temperature variations in the source area, and this is supported in modern leaves of plant species which showed variation with seasons. However, the proposal of a temperature control on ACL remains debated, especially in environments in higher latitude such as peatlands where changing the dominant plant input (e.g. between sphagnum, sedges and/or heathers) can also impact the ACL (McClymont *et al.,* 2008).

Further challenges to the CPI and ACL proxies were identified by Bush and McInerney (2011) who studied trees, shrubs and mosses in the Chicago area, USA. The study investigated *n*-alkane distributions in mature leaves across 38 individual plants and from 24 species, comparing CPI and ACL. Bush and McInerney (2011) concluded that the CPI cannot be used as a quantitative indicator of *n*-alkane degradation in sediment, because gymnosperms (plants that do not flower or fruit, and conifers) have lower CPI than the angiosperms (plants that flower or fruit). Furthermore, there was no distinguishing difference in the ACL range value from summer and fall leaves which might be expected from a temperature/climate control. However, the study did conclude that sphagnum moss showed a low ACL and the group showing the lowest range of value for ACL were the aquatic plants.

2.5.2.3 Terrestrial to aquatic ratio (TAR)

The terrestrial to aquatic ratio (TAR) is applied to characterise the *n*-alkane signature in a sediment which is likely to have multiple inputs (equation 2.3). The *n*-alkanes which are associated to higher vascular plants (the longer chains) are divided by the shorter chain *n*-alkanes from aquatic plants:

Equation 2.3:

$$TAR= \frac{n\text{-}C_{27}+ n\text{-}C_{29}+ n\text{-}C_{31}}{n\text{-} C_{15}+ n\text{-}C_{17}+ n\text{-}C_{19}}$$

(Gonzales-Vila *et al.,* 2003)

The TAR has been applied especially to marine sediments to trace river, dust, or iceberg inputs of terrestrial organic carbon (Sanchez-Montes *et al*., 2020; Müller *et al*., 2018). Where high TAR is an indicator of high terrestrial inputs, the CPI can differentiate between the “fresh” or mature carbon origins (Sanchez-Montes *et al.,* 2020). TAR has been applied in lake settings, as an indicator to detail relative changes of land verses aquatic inputs, where TAR values above 5 were interpreted as “terrestrial” and below 5 as “aquatic” inputs (Routh *et al.,* 2006). TAR both above 5 (Routh *et al.,* 2006) and above 1 (Longbottom *et al*., 2017) has been interpreted as terrestrial input; the reasons for these differences might reflect the local differences in *n*-alkane production between the two end-members and/or transport pathways to the lake. These differences suggest that TAR might be best applied as an indication for relative changes in terrestrial/aquatic inputs to a site (Sanchez-Montes *et al.,* 2020).

2.5.2.4 P_{aq}

The P_{aq} ratio differentiates between terrestrial, emergent and floating/submerged species of plants (Equation 2.4).

Equation 2.4:

$$P_{aq} = (n\text{-}C_{23}+ n\text{-}C_{25})/(n\text{-}C_{25}+ n\text{-}C_{29}+ n\text{-}C_{31})$$

(Ficken *et al.,*2000)

Ficken *et al.,* (2000) applied P_{aq} to a lake in Africa, concluding that the ranges for the three inputs are: 0.01-0.23 (for terrestrial input), 0.07-0.61 (for emergent plants) and 0.48-0.94 (for submerged/floating plants). Similar ranges are also reported in other research (e.g. Mead *et* *al.,* 2005, Regnery *et al.,* 2013, Routh *et al.,* 2006 and Longbottom *et al.,* 2017). Unlike Ficken *et al.,* (2000), Yang *et al.,* (2011) who studied the Ximen Co Lake in the Tibetan Plateau, did not stipulate ranges for the distinction for the P_{aq} values, but instead used other ratios (Figure 2.1) which did shows similar trend ACL_{27-33} and P_{aq}. The inclusion of the additional ratios confirmed that there was a seasonal change in climate, and that ACL_{27-33} can be used as a temperature proxy, for this region. Yang *et al.,* (2011) concluded that the lake OC was a mixture of terrestrial and aquatic plants, and that in the past the input of algae, bacteria and the floating/submerged contributions were more distinctive than terrestrial when compared to the modern samples. P_{aq} has also been used to distinguish mosses on the range between 0.4 and1 (Ronkainen *et al.,* (2013), comparable values to those recorded by submerged and floating plants in a lake ecosystem.

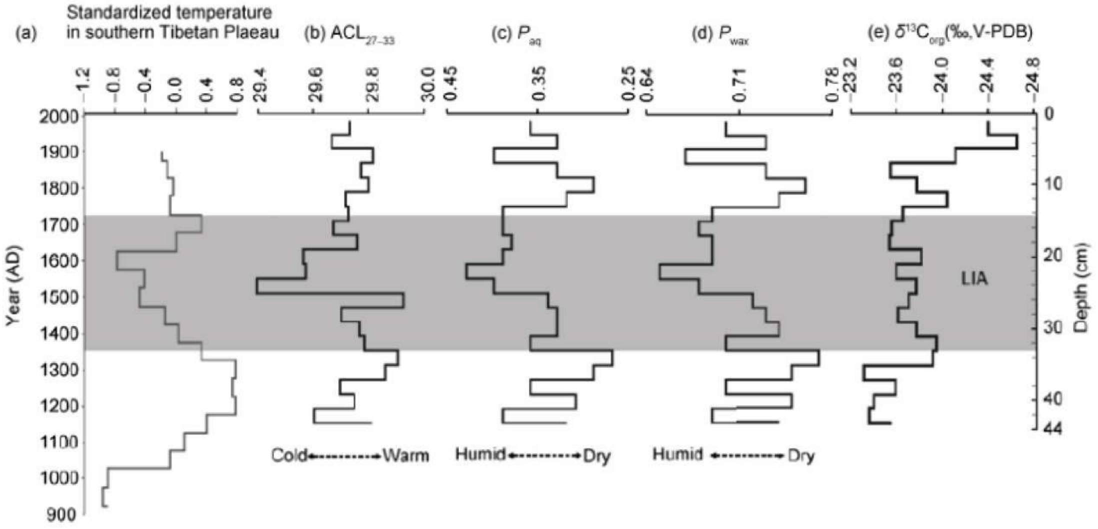


Figure 2.1: down-core profiles of $\delta^{13}C_{org}$, ACL_{27-33},P_{aq} and P_{wax} and comparison with the standardized temperature variation of the southern Tibetan Plateau. Source: Yang *et al.,* (2011).

2.5.2.5 Pristane/Phytane ratio

Isoprenoids have a five-carbon structure, the subunits of which are called isoprene. Typically, these are present in the form of pristane (C_{19}) and phytane (C_{20}), which originate from the phytol side chain of chlorophyll. Pristane occurs by oxidation and aerobic degradation of chlorophyll, whereas phytane occurs due to dehydration and reduction. Pristane and phytane might therefore give an indication of environmental conditions after deposition and are noted as the most common isoprenoids present in petroleum (Peters and Moldovan, 1993) (Equation 2.5).

Equation 2.5 :

$$Pr/Ph = Pristane/Phytane$$

(Ahad *et al.,* 2011)

If a Pristane/phytane (Pr/Ph) ratio is above 1, a terrestrial higher plant input is indicated, as well as a sample which is uncontaminated by petroleum sources, since the latter can have values up to 5. However, Pr/Ph below 1 is also proposed as an indicator of petrogenic contributions (Agrawal & Sharma,2018, Ahad *et al.,* 2011). In shale and coal environments, the Pr/Ph ratio has also been used to conclude the formation of coal in a swamp environment close to the sea (Korkmas and Gulbay, 2007).

2.5.2.6 Ratios for peatland contributions

The C_{23}/C_{25} ratio (Equation 2.6) has been suggested as a means of identifying sphagnum mosses, and below ground sedge roots in peatland environments.

Equation 2.6:

$$n\text{-}C_{23}/n\text{-}C_{25}$$

(Ronkainen *et al.,* 2013)

Peatland research in Finland identified chain lengths belonging to sphagnum mosses (C_{23}) and vascular plant species roots (C_{25}) (Ronkainen *et al.,* (2013), although this ratio has also been used to determine different species of sphagnum (Bingham et al. 2010). Ronkainen *et al.* (2013) also presented the C31/C27 ratio (Equation 2.7) as a way of distinguishing between the relative inputs of trees and grasses, which may be helpful alongside TAR or other ratios for overall higher plant contributions.

Equation 2.7:

$$n\text{-}C_{31}/n\text{-}C_{27}$$

(Ronkainen *et al.,* 2013)

2.5.3 Summary of biomarkers used in previous literature

Table 2.1 incorporates the findings of these studies and their differing interpretation of the possible sources of *n*-alkanes. It is notable that Bush and McInerney, (2013) and Nichols *et al.,* (2006) both agree that *Sphagnum* is represented by C_{23}-C_{25} and are both similar geographically (both USA). This interpretation is also supported by Ronkainen et al. (2013) in

Finland peats. One study instead defines sphagnum as C_{31} (Ahad *et al.,* 2011), but this is not repeated in other studies from the UK. Most studies depict algae starting with C_{15} *n*-alkane, apart from Regnery *et al*., (2013) whose study suggests algae from C_{17}. All terrestrial and higher plant inputs have proxies with the same range and this also similar for wood input and grasses. Table 2.2 summarises previous studies and the environmental interpretation of the ratios. It is noticeable that differences of ranges are used, with the largest differences for CPI, e.g., Wang *et al.,* (2015) suggests > 8 for vascular plants, Longbottom *et al.,* (2017) and Jeng (2006) both depict terrestrial >5 whereas Formolo et al., (2008) and Bush and Mclnerney (2013) determine anything above 1 as an indicator of terrestrial input. This is also seen in the TAR biomarker where Longbottom *et al.,* (2017) depicts >1 as terrestrial and Routh *et al.,* (2006) depicts > 5, this difference could be due to geographical context.

Table 2.1: Table showing previous research using biomarkers and their ranges of source identification.

Author	Algae	Floating/ submerge-ed	Sphagnum	Terrestrial (higher plant)	Wood	Grass-es	Location
Bush and Mclnerney, (2013)			C_{23} and C_{25}	C_{27},C_{29}	C_{27}, C_{29}	C_{31}	Chicago, USA
Yang *et al.,* (2011)	C_{15}-C_{19}	C_{21},C_{23},C_{25}		C_{27}-C_{33} Odd/even			Tibetan Plateau
Duan and Jinxian (2011)				C_{27} and C_{29}		C_{29} and C_{31}	China
Cranwell *et al.,* (1987)	C_{15}-C_{17}						
Nichols *et al.,*(2006)	C_{15}-C_{18}		C_{23} and C_{25}	Odd/even			Michigan USA
Ahad *et al.,* (2011)	C_{15}-C_{25} + CPI		C_{31}				Tyneside UK
Jeng W.L.,2006				Odd to even C_{25}-C_{35}			
Gonzalez-Vila *et al.,* (2003)	C_{15}, C_{17}, C_{21}			C_{27}-C_{31}			Guadiana River, Portugal
Ficken et al ., (2000)		C_{23}-C_{25}					Africa, Kenya
Regnery *et al.,* (2013)	C_{17}-C_{21}	C_{23}-C_{25}			C_{29} forest		

Wang *et al.,* (2015)	C_{15}			C_{27}, C_{29}, C_{31}			China

Table 2.2: Table showing various research using biomarkers and their ranges of source identification, ACL, CPI, Tar P_{aq}.

Author	ACL	CPI	TAR	P_{aq}	Location
Longbottom *et al.,* 2017		>5 terrestrial	>1 terrestrial	< 0.1 terrestrial 0.1-0.4 emergent 0.4-1 floating	Texas USA
Routh *et al.,* 2006			>5 terrestrial	< 0.1 terrestrial 0.1-0.4 emergent 0.4-1 floating	Sweden
Ronkainen *et al.,* (2013)				Mosses below ground 0.4-1	
Ahad *et al.,* (2011)	29.5 terrestrial vascular plants	>3 terrestrial plants ~1 fossil fuels Close to 1 fossils fuel			Tyneside UK
Jeng W.L.,2006	27.8 fossil fuel	5-10 land plants 1 petrogenic			Taiwan
Pancost and Boot., 2004		>4 terrestrial			
Formolo *et al*., (2008)		>1 terrestrial			USA
Bush and Mclnerney (2013)		>1 terrestrial and thermally immature source rock			Chicago, USA
Ficken *et al*., (2000)				< 0.01-0.23 terrestrial 0.07-0.61 emergent 0.48-0.94 floating	Africa, Kenya
Mead *et al.,* (2005)				0.01-0.23 terrestrial 0.13-0.51 emergent everglades 0.45-1.0 submerged fresh water	Florida
Regnery *et al.,* (2013)	Lower ACL and Higher P_{aq} value-submerged vegetation			Increase in P_{aq} and decrease of C/N submerged vegetation Low P_{aq} +C/N>15 indicate terrestrial input	
Wang *et al.,* (2015)	Increases with warmer/drier conditions	>8 vascular plants			

Table 2.3: Table showing various research using biomarkers and their ranges of source identification, Pr/Ph, Pr/n-C_{17}, Ph/n-C_{18}, C_{23}/C_{25} and C_{31}/c_{27}.

Author	Pr/Ph	Pr/n-C_{17}	Ph/n-C_{18}	C_{23}/C_{25}	C_{31}/c_{27}
Routh *et al.,* 2006		Lower bio-degration	Lower bio-degration		
Ronkainen *et al.,* (2013)				<3 below ground parts >3 above ground parts	
Ahad *et al.,* (2011)	<1 petroleum	>2 algae <1 weathered oil			
Hakimi and Al-Sufi (2018) (Yemen)		0.40-0.6 source rock with mixed organic matter	0.45-0.6 source rock with mixed organic matter		
Wang *et al.,* (2015)	<1 anoxic conditions > 1 oxic conditions				

2.6 Summary

This chapter identified a range of analytical methods used to address the research questions outlined in Chapter 1. Previous research investigating OC interpretations has mostly applied biomarker analysis to large river systems, lakes and Oceans. Chapter 2 has outlined the research in likely OC sources to river systems, and the potential for biomarker applications to trace these in small rivers. In the following Chapters, the River Esk is introduced (Chapter 3), and the methodology applied in this thesis is detailed (Chapter 4).

Chapter 3: The River Esk

3.1 Introduction

This chapter gives an overview of previous research undertaken within the study catchment. The River Esk was chosen as a study site because it has had extensive investigations on the erosion and transport of sediment in the context of whether this is affecting the ecology of the river including an endangered species (Bracken and Oughton., 2013). The River Esk also flows through different types of land use, from upland moor to agricultural land and small forested areas, each of which will provide different inputs of carbon to the river system and will allow testing of the biomarker approach.

3.2 Study Area

The North York Moors (NYM) National Park covers an area of 1436 km^2 and is approximately 400m above sea level at the source at Westerdale moor (EA, 2011). The River Esk flows east for 45km through small, low populated villages, open moorland and farmland, to meet the North Sea at Whitby (EA, 2011, NYMNPA, 2012). The UK has 70% of the world's wild heather moorlands and one of the locations where this is present is the NYM national park where the River Esk is situated (NYMNPA , 2012). The NYM includes 4,100 hectares of blanket peat and 46,000 hectares of peaty soil with an estimated 6 million tons of stored carbon (North York Moors National Park Management Plan (NYMNPA, 2012).

The landscape of the NYM is a result of 200 million years of rock formation as well as the action of rivers and ice-sheets. The last British ice-sheet covered the area ~20,000 years ago and, during its retreat and melt many steep valleys were carved which can be seen today in North Yorkshire (NYMNPA, 2012). Typical of the Jurassic Period, the rocks found here are sandstones, shales and limestone (NYMMP, 2012). NYMNPA (2012) state that a rise in temperatures during both the summer and winter periods, along with wetter conditions, has increased peat erosion since the beginning of the 20th century. Projects to reduce the moorland erosion include one delivered by Yorkshire Peat Partnership, whose aim is to restore affected areas by implementing woody debris dams, in turn reducing the amount of sediment being deposited into the river (NYMNPA 2012, Bracken and Oughton., 2013). This intervention aims to improve the water quality and lock more carbon in the peat instead of it being introduced into the river, retaining water on the peatlands. Walling *et al.* (2003) discussed these methods and determined that sediment load decreased when reservoirs were implemented into the major river system, which is similar to the implementation of dams for much smaller rivers. Implementing these projects in the North Yorkshire Moor (NYM) is proposed to provide financial efficiencies for the region including the local water company (by providing clean water for drinking more efficiently due to reduced contaminants and particulates) and reducing the potential of flooding in the typical high rainfall months (NYMNPA, 2012).

3.3 Geology

The geology of the area studied consists of shale and ironstone, Ravenscar sandstone, Oxford clays and Corallian Limestone from the Jurassic era (BGS, 2015) (Figure 3.1). Compared to other upland areas (Pennines) this is the one of the youngest and softest rock types in the UK (BGS, 2015). As shown in Figure 3.1, the Lias group is characterised by a well bedded marine mudstone, with silty mudstone, beds of limestone with thick units of sandstone, siltstone and ironstone. Limestone and sandstone mark the upper boundary, which is commonly eroded (BGS, 2015). The Ravenscar group is composed of fluvial and mudstone, siltstone and sandstone. Marine units of calcareous sandstone, mudstone, siltstone, limestone and ironstone are also found, along with additional thin seems of coal. The upper boundary is mainly sandstone, siltstone and mudstone (BGS, 2015).

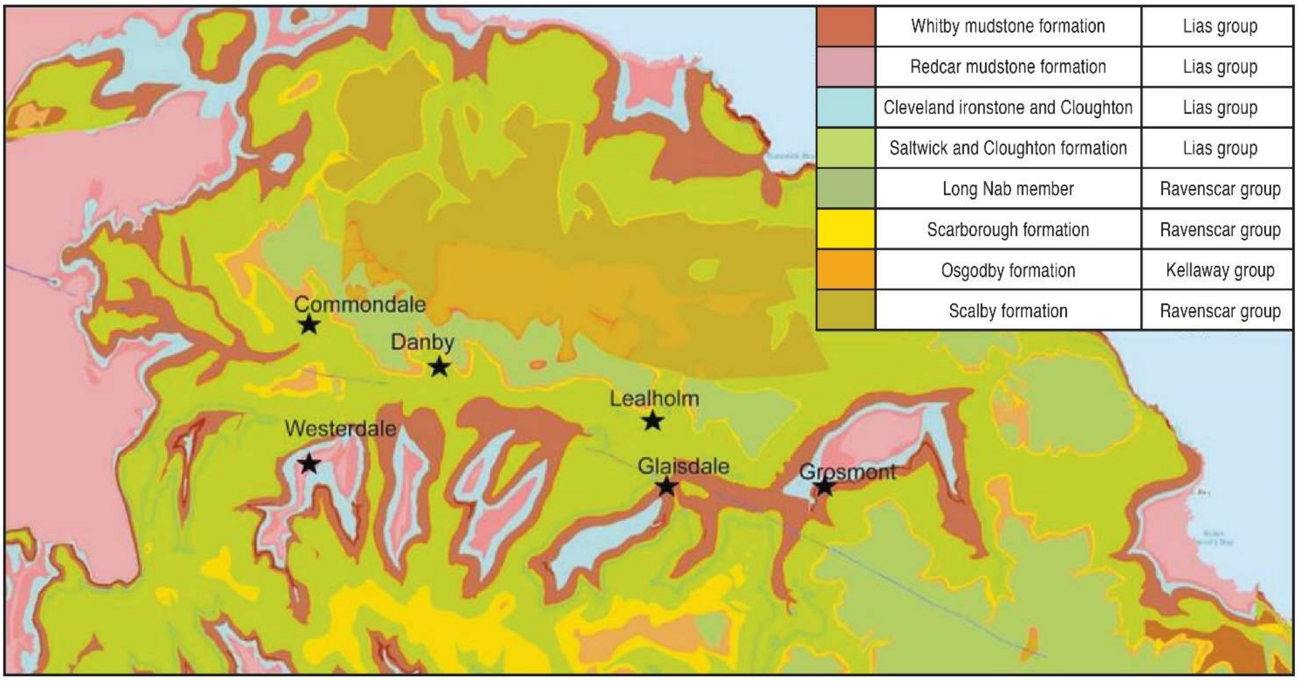


Figure 3.1: Map showing the main types of rocks for locations in this research, Ravenscar group (Middle Jurassic era) consisting of: Shale, sandstone, limestone, siltstone and mudstone. Lias group (Mesozoic) consisting of Shale, sandstone, siltstone and mudstone) and Kellaways formation (Jurassic era) consisting of: mudstone, siltstone and sandstone (BGS, 2021).

3.4 Land use and vegetation

The land use is relevant in this study as it could have an impact on both the types of vegetation contributing organic matter to the river, and to soil disturbance which would influence carbon input from sediments into the river system. The River Esk flows through a patchwork of moorland, mixed woodland and farmland before joining the sea. The most upstream site, Commondale, is mainly populated by shrubs, upland heather, sphagnum moss bracken and grasses. Westerdale contains similar plants to Commondale but additionally has a bog environment with peat greater than 0.5 m deep (Perks. 2013). Downstream, Danby is a mixture of moorland, woodland and farmland. Entering Lealholm there is woodland followed by a steep sided valley, which then changes into farmland downstream. Increased use of agricultural grassland and cereals occurs as you head downstream toward Whitby (Figure 3.2; Perks. 2013). Small settlements are located at all sites included in this study. The major economies in this area are agriculture and tourism (Bracken and Warburton 2005). There is no heavy industry near the river system, only a sewage treatment works at Danby (Norbury, 2015) with no reports on effects in organic carbon.

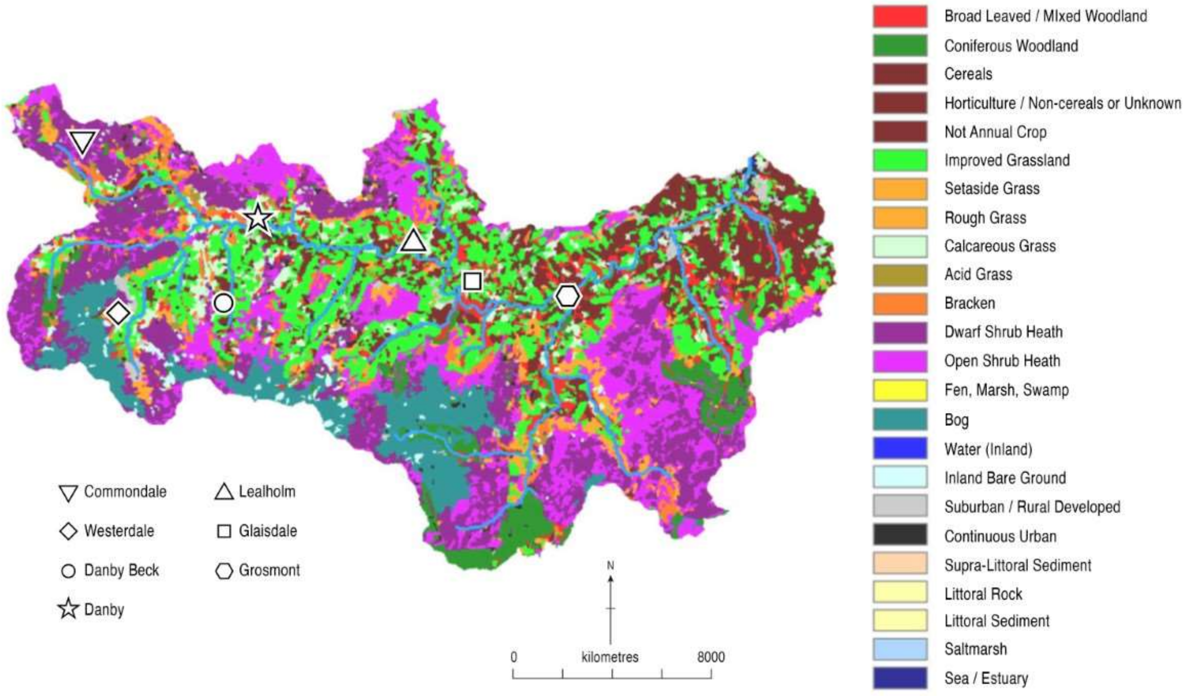


Figure 3.2: **Map** Dominant land-use in the River Esk catchment, from Perks, (2013) and adapted to show sites in this study

3.5 Previous studies of the River Esk and its catchment

3.5.1 Water quality

The quality of water in rivers, estuaries and catchments in the NYM National Park has been investigated previously (Evans *et al.,* 2014; NYMNPA., 2001; Bracken and Oughton., 2013), because of the importance of the rivers as the main source of freshwater to the public, industry and the ecosystem of plants and animals within and adjacent to the river. The River Esk has been targeted in particular because it is the only river in the North East of England that supports an ecology of declining species e.g. otter, water vole, kingfisher, dipper and freshwater pearl mussels (Evans *et al.,* 2014). The water quality is crucial to the survival of these endangered species and their natural habitats. In recent times, efforts have been made to try and improve the River Esk water quality, including restoration of the banks of the river (Evans *et al.,* 2014; NYMNPA., 2001; Bracken and Oughton., 2013).

Most rivers in the UK are monitored on a daily/weekly basis (GOV.UK, 2016). This allows environmental organisations to quickly identify if there are any sudden decreases in the quality of the river water that may result in the ecosystem being affected. In the River Esk, the Environmental Agency reports for Danby Beck and Glaisdale include hydrological regime, morphology of the river system and the biological qualities such as vertebrates and macrophytes. The Environment Agency reports outline chemical and physical properties such as dissolved oxygen, pH, temperature, ammonia, phosphate, lead, zinc, copper, nickel, cadmium, triclodon, nonylphenol, tributyltin and Di-(2-ethylhexyl)-phthalate and relating compounds. However, the methodology that is used to undertake analysis and the exact concentrations of key variables are not defined; instead, the Danby Beck and Glaisdale reports state that water quality is good/poor. The Environment Agency report, which is produced on an annual basis, also does not detail seasonal or monthly values, which would give a more detailed reflection of what is happening in the catchment. In addition to this, the Environment Agency reports do not outline which specific chemicals are investigated, as it compiles them as “specific pollutants” or “priority hazardous substances” (GOV.uk, 2016).

3.5.2 Sediment transport

Sediment transport is an important aspect in river systems (Newton and Gray, 1972; Perks, Warburton and Bracken, 2013) transporting elements such as nutrients. It is estimated that sediment transports 90% of elements such as phosphate, nickel, manganese, lead, iron and aluminium to the ocean (Walling and Fang 2003). Sediment in a fluvial system can be categorised into two main distinctive elements: bed load, which consist of particles 1mm in diameter, and suspended load, which normally consists of sand and silt below 0.1mm diameter (Hemond and Fechner, 2015., Rheinheimer and Yarnell., 2017). Bed load particles spend most of the time on the river bed, although in high flow they can move a short distance (Hemond and Fechner, 2015). In contrast, the suspended load consists of particles mobilised in the water column, which can also interact with particles on the bed. Both suspended sediment and bed load contains organic carbon.

Previous research estimated that the calculated yield of dry sediment was 12.8 m^3 km^{-2} yr^{-1}, this is not classed as high compared to larger water bodies (Lovell *et al*., 1973). However, Lovell *et al.,* (1973) did not collect sediment upstream of the reservoir to quantify the true amount of sediment transport and deposition in the river. Subsequently, Bolland *et al.* (2010) and Perks *et al.* (2013) measured the transport of fine sediment (<2mm) and bulk organic carbon, with particular focus on the transport of particles and the effects of contaminants. Perks *et al.,* (2013) used a “rocket sampler” (Philips *et al.,* 2000), which traps between 35% and 70% of fine sediment particles. Perks et al., (2013) determined that the use of this type of sampler gave the most accurate results compared to other sampling methods, however there were limitations with the sampler that on many occasions’ debris and leaf litter could block the sampler opening which gave some bias for the overall sediment load.

Understanding sediment transport in the River Esk may be important for the health of the ecology that are in and around the river system, pearl mussel population an example of this (Geist & Auerswald, 2007). Fresh water pearl mussels (*Margaritifera margaritifera*) have thrived in UK rivers for over 100 years (Geist & Auerswald, 2007; Bolland *et al.,*2010) yet their population has recently declined, and they are now considered to be endangered (Geist & Auerswald, 2007; Bolland *et al.,* 2010). Causes of the decline in freshwater pearl mussels include overexploitation (fishing), water pollution, flow modification (dam), destruction or degradation of habitat, invasion by exotic species (cray fish), as well as sediment deposition/ remobilization and catchment land use changes (e.g., agriculture and forestry), riverine habitat modifications (dredging), and a decline in host fish (Geist & Auerswald, 2007; Bolland *et al.,* 2010). It has been proposed that an increase in bank erosion (e.g., due to flooding, livestock crossing, change in land use) can cover the mussels to such an extent that they become suffocated (Geist & Auerswald, 2007).

Several projects have been introduced with the aim of conserving *Margaritifera margaritifera,* including the UK Biodiversity Action Plan (UK BAP) process, WREN Biodiversity Action Fund, a national Species Action Plan and the Esk Pearl Mussel and Salmon Recovery Project). Although Bolland *et al.,* (2010) have shown that nitrate limits in the water may have exceeded tolerable limits (Figure 3.3), the main initiatives have aimed at reducing the sediment in the river by installing river bank fences to reduce the amount of bank erosion, applying buffer strips to reduce the runoff from agriculture land, improving livestock crossings and vegetation management to the river banks to improve the water quality (Bracken and Oughton 2013).During a monitoring study from June 2007 to February 2009, the majority of samples demonstrated low concentrations of nitrate (Figure 3.3), however exceptions were found where nitrate concentrations exceeded the threshold deemed as damaging (e.g., January 2008, Figure 3.3). This is likely to be caused by the increase of sediment in the wetter months.

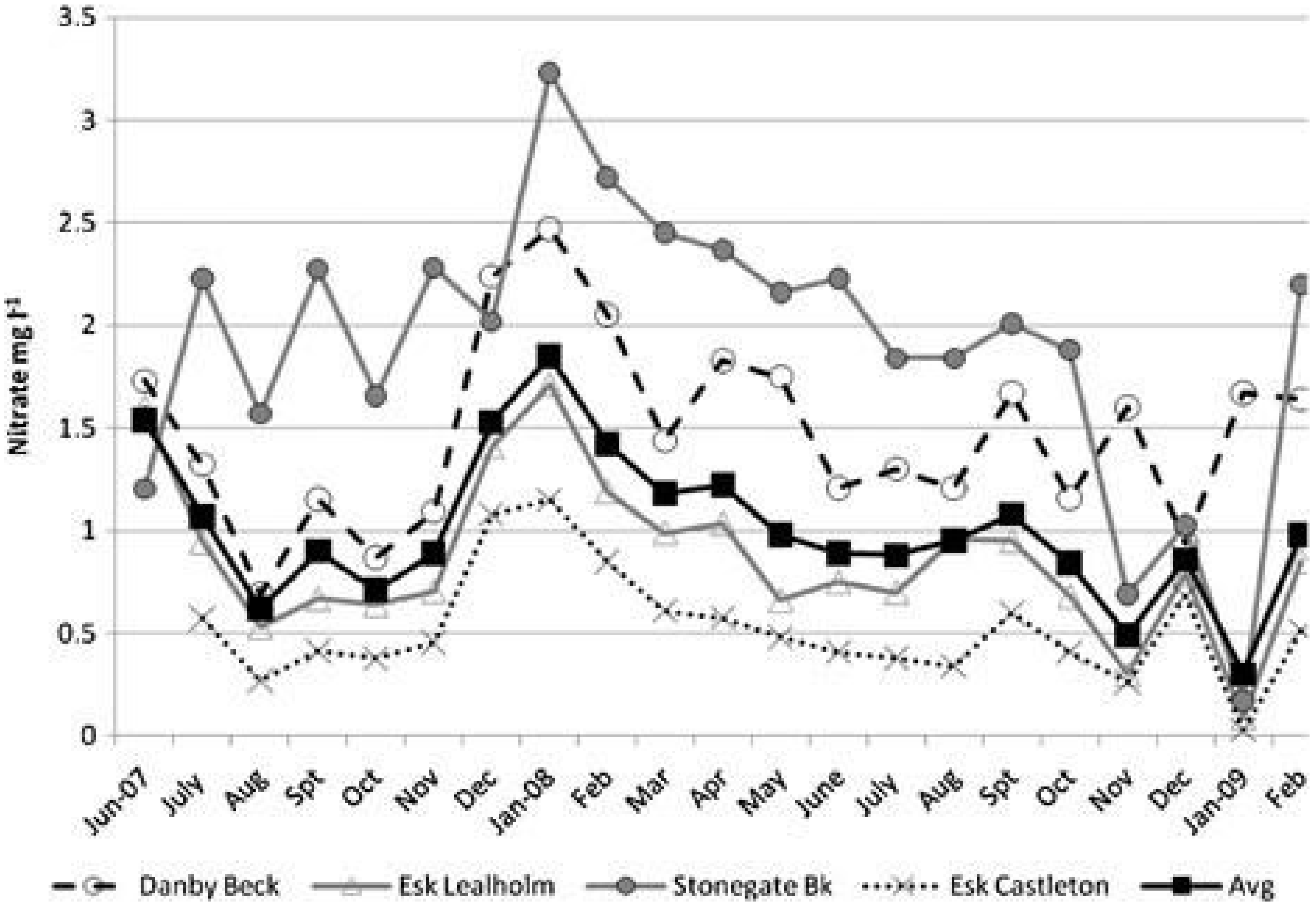


Figure 3.3: Nitrate concentrations in the River Esk from July 2007 to Febuary 2009 stating that the upper tolerable limits for *M. margariteifera* is 1mgL^{-1}(taken from Bolland *et al,* 2010).

Bolland *et al.,* (2010) studied the River Esk, whereas Geist & Auerswald's, (2007) study included various rivers around Europe. Bolland *et al.,* (2010) and Geist & Auerswald, (2007) concluded that the fine sediment was a factor for the decline of the pear mussels as well as water quality and that land management issues needed to be monitored over long periods of time. Both investigations (Bolland *et al.,* (2010) and Geist & Auerswald, (2007)) highlighted the importance of sediment transport and determining the source.

3.6 Sources of pollution

3.6.1 Industrial pollutants

The NYM catchment is in close proximity to industry and downwind from coal fired power stations, steel works and chemical plants (Evans *et al.,* 2014). Using pollen, diatom and isotope analysis, changes in acidity through the mid to early 20th century have been related to air contamination inputs from the nearby industries to the North York Moors (NYM) (Gray Heugh slack) and Danby Beck, a peat catchment that was formed 220 years ago; Battarbee *et al.,* 2014).

Another study in the River Esk (focusing on Danby), identified that the River Esk is located downwind from a power plant, and has been hypothesised to cause the river and soil to become more acidic (Evans *et al.,* 2014; Figure 3.4). In contrast, the River Esk catchment contains limestone which might buffer acid deposition. Prior research undertaken by NYMNPA had concluded that the watercourses were too acidic to support significant fish stock and that acidification had been and (will remain) a problem in this area.

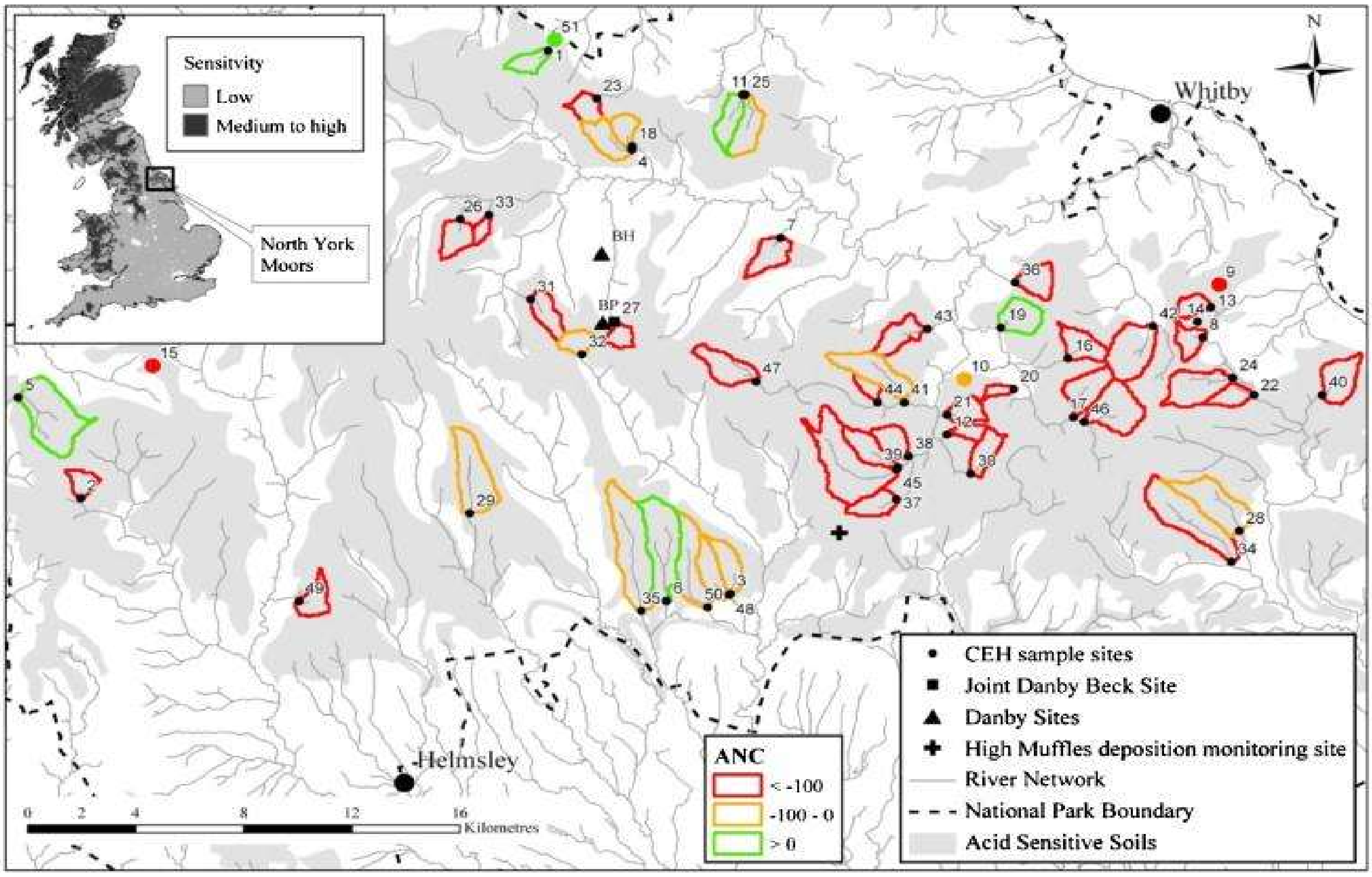


Figure 3.4: Acid sensitive soil areas (grey), Acid Neutralising Capacity (ANC) (red, yellow and green), Danby sites (triangles) (taken from Evans *et al.,* (2014)

Figure 3.4 highlights sites where acid neutralising capacity (ANC) is also very low, in locations where acid sensitive soil is predominantly present. Variable acid sensitivity is important because of the potential impacts on the erosion and introduction of old stored carbon back into the carbon cycle (see Section 1.1), especially given that most of the bedrock in this area consists of limestone and sandstone. Figure 3.5 details how the pH in the river at Danby Beck has evolved. The river water has becoming less acidic since 1995-1999 (pH ~3.5).

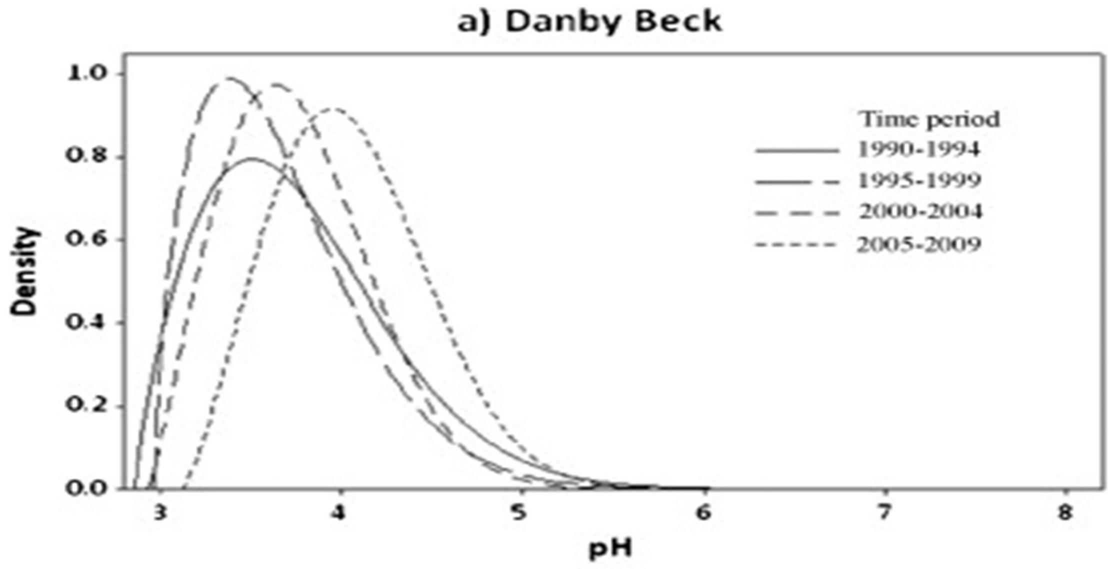


Figure 3.5: Change in acidity over a time scale of 1990-2009 (taken from Evans *et al.,* 2014).

3.7 Sampling Site Locations

The sediment samples analysed in this study were provided from the Perks (2013) study which was undertaken from 2007 to 2009. Samples were taken to cover a wide spatial area, to include most of the river and its tributaries. Figure 3.6 shows the locations of the sites along the River Esk, from Westerdale in the west, close to the source of the river, to Grosmont in the east, towards the mouth of the river.

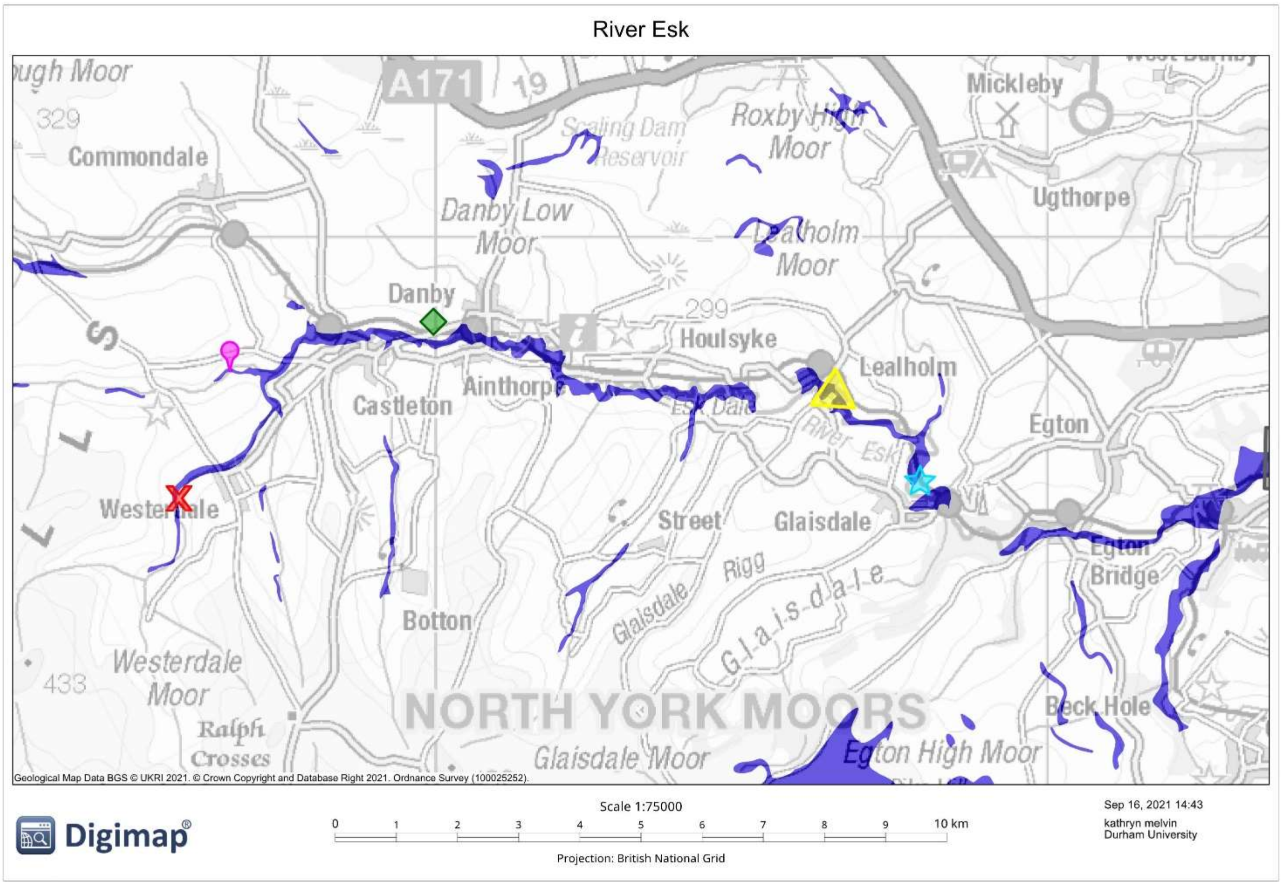


Figure 3.6: A map showing the site locations and flood potential along the River Esk in the North York Moors. Taken from the Edina Digi map on 15th March 2021 (Purple indicating flood potential, pink icon for the Commondale site, red cross for the Westerdale site, green diamond Danby, yellow triangle for Glaisdale, blue star for Lealholm and black square for Grosmont).

3.8 Climate for the NYM for the study period (June 2007 - February 2008).

The NYM area is characterised as a cold wet temperate climate, with temperatures ranging from -1 °C to 7 °C in the winter and from 11 °C to 22 °C in the summer months (NYMNPA., 2001). The timing of this study coincides with one of the coldest winters recorded in this region. The rainfall data at Danby for the year that the samples were collected is shown in Figure 3.6.

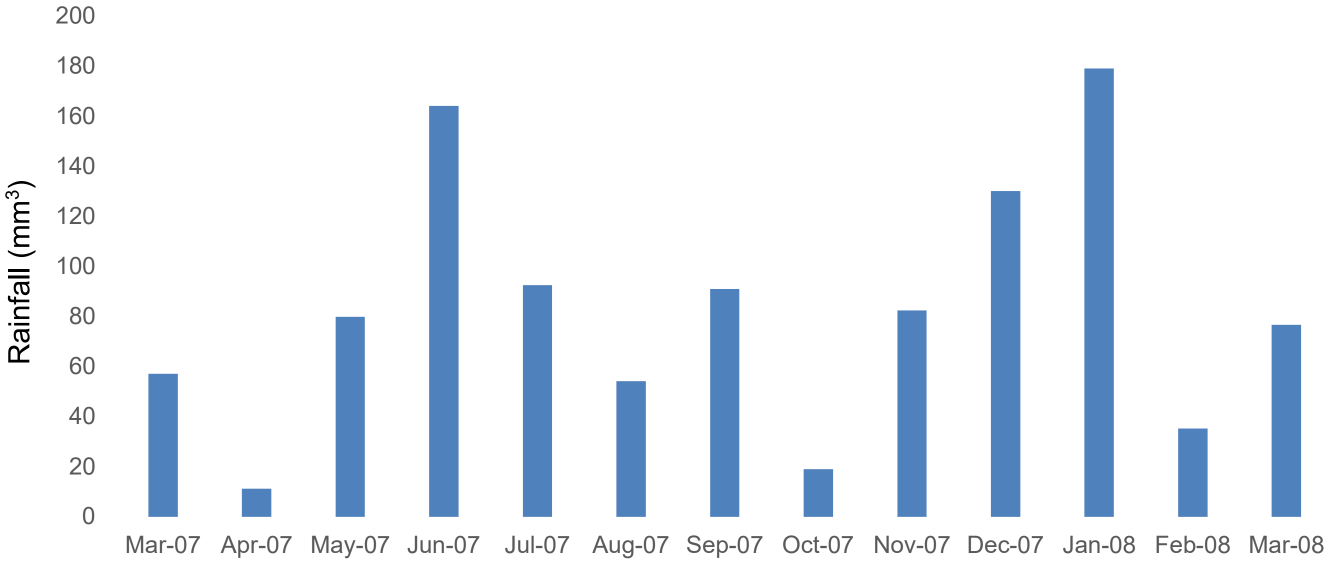


Figure 3.7: The gauged monthly rainfall (mm/month) for Danby over the 2007 to 2008 period, the highest amount recorded was in January in which some of the samples included in this research were collected.

The annual rainfall is relatively low (~11 - 179mm, Figure 3.7) for an upland environment when compared to other UK areas for example the Lake District where average rainfall is >2000 mm (Hammond, 2005). However, there was a flood event in June 2007 which is noticeable in the graph. Combining the low rainfall for the environment and the acidic soil in the region, a change rainfall or temperature would be expected to have significant effects on the diversity of the water chemistry and ecology of the river system. This could explain the decline in number of certain species (Pearl mussels) which inhabit the river, as they need neutral and pollution free environments for their survival (Evans *et al.,* 2014; NYMNPA., 2001).

3.9 Chapter Summary

In summary, existing literature highlights a number of drivers that may affect the river water quality, acidity of the river, sediment and suspended sediment transport in the river. Previous research on the River Esk (Evans *et al.,* 2014; NYMNPA., 2001; Bracken and Oughton, 2013; Perks et al., 2013; Bolland *et al,* 2010) suggests that any changes to these variables are important to understand due to their influence on the habitants in and around the river system. All studies highlight the importance to regularly monitor the river quality and sediment transport. However, no studies have examined the role played by changing sediment inputs and transport of organic carbon using biomarker tracers in small rural rivers in the UK. The following chapter details the methodology applied in this thesis to apply biomarker tracers of OC transport.

Chapter 4: Analytical Methodology

4.1 Introduction

This chapter outlines the preparation of equipment and samples that were analysed for this investigation. This includes the methods of lipid extraction from sediment, and its analysis by gas chromatography instruments. Carbon/nitrogen ratios, total organic carbon and biomarkers will be investigated in this project, as different approaches to characterising organic carbon in sediment samples. Over the course of the project 35 samples were analysed.

4.1.1 Sediment Collection

Perks (2013) used a rocket sampler to collect sediment load. Designed by Philips *et al,.* (2000) figure 4.1, this system has a recovery of fine sediment particles, of 35-70%, which Perks (2013) investigated. The low cost of the rocket sampler is also a benefit for sediment load measurement. The rocket sampler can identify sediment flow along the whole river, which will give a more accurate sediment load prediction. However, Perks (2013) identifies that if during a high flow event, the representative of sample is in question as the sampler will not sample accurately in flood events.

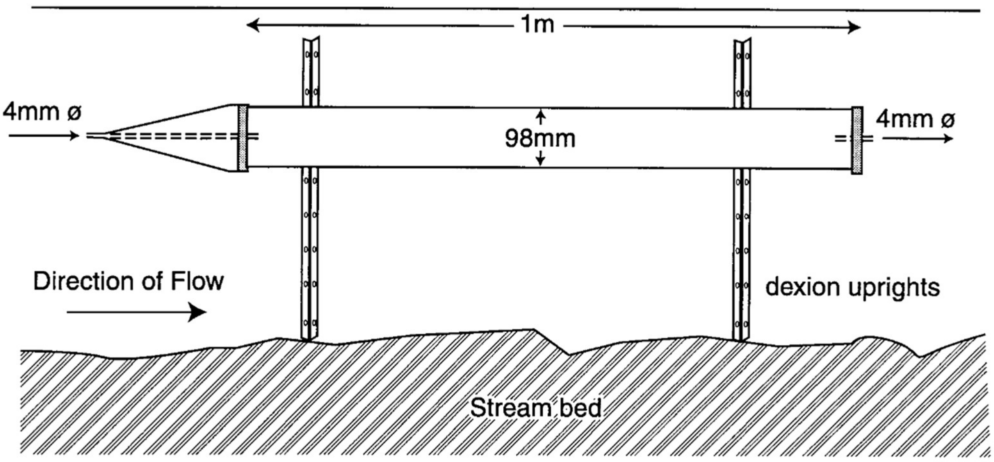


Figure 4.1: Cross-section of the suspended sediment sampler. Source Philips *et al.*,2000.

4.2 Preparation of materials

4.2.1 Glassware

The analysis for this research requires optimum cleanliness, to reduce carbon contamination. To achieve this, the glassware was thoroughly rinsed using tap water, again with deionised water and submerged in 1% Decon 90 for 24 hours. Once soaked, a further rinsing with tap water was followed by a final rinse with deionised water 18 Ω is undertaken. Glassware was then left to drain and air-dry. The glassware (except volumetric flask) was then covered in foil, and furnaced at 450°C for 4 hours, before being allowed to cool.

4.2.2 Consumables: solvents and reagents

All solvents were either from Fisher Scientific or Acros and are of pesticide trace grade (Table 4.1). Cotton wool was prepared in advance by washing with Dichloromethane (DCM): Methanol (MeOH) mix (at 3:1), then covered in aluminium foil and left in the fume hood to evaporate. It was then stored in a desiccator once completely dried. Silica gel (for column chromatography) was heated to 120 °C for 24 hours, and then stored in a desiccator.

Table 4.1: Solvents, supplier and grade used in this study

Supplier	Name	Grade
Acos	Dichloromethane (Methylene chloride)	Pesticide analysis
Fisher Scientific	Methanol	Pesticide analysis
Fisher Scientific	Hexane	Pesticide analysis
Fisher Scientific	decon 90	-
Sigma Aldrich	Silica	Analytical

4.2.3 Standards

Table 4.2 details the internal standards which were added to all samples and which fraction could be found following silica gel column chromatography (see Section 4.4). All standards were stored in a desiccator and prepared by weighing into a non-static boat on a 6-figure balance. The volumetric flask used was 10ml, and hexane was used to wash the standard into the volumetric flask before being topped up to the 10ml mark.

Table 4.2: Standards used in this investigation and the associated fraction the standard will be present in.

Name	Formula	Mass added to standard (mg)
Heptatriacontane	$C_{36}H_{74}$	3.9
5α cholestane	$C_{27}H_{48}$	4.6

4.3 Sample preparation

All samples were placed into the -80 °C freezer for a minimum of 12 hours. Once frozen, they were freeze-dried for 24 hours, to remove any water by the process of sublimation. To avoid contamination with any plastics or other samples, samples were ground with a hand-held agate pestle and mortar, rinsing with acetone in-between samples and storing the homogenous powder in glass containers. ~2-5g of sample were weighed into thermally-resistant teflon tubes for lipid extraction.

4.4 Total Lipid Extraction

The microwave-assisted lipid extraction method was used in this research because it uses reduced volumes of solvent and the overall extraction time is much shorter than the commonly used sonication method (Kornilova and Rosell-Mele, 2003). The solvent mixture DCM:MeOH (3:1) was used because this is found to efficiently absorb microwave energy and convert to heat (Kornilova and Rosell-Mele, 2003).

The microwave teflon vessels were rinsed three times using the DCM:MeOH mix, then covered with foil and left in a fume hood to dry before use. Between 2-5 g (to 4 decimal places) of ground sediment was weighed into the Teflon microwave vessels. A known aliquot of internal standard (Table 5) was added to each microwave vessel, including the blanks, as well as magnetic stirrers. 12 ml of DCM:MeOH (3:1) was added to each sample and the blanks.

Using the Mars 5 microwave, the vessels were heated to 70°C over two minutes, then the temperature was held (70°C) for five minutes, before cooling the samples. The samples (solvent and sediment) were then decanted from the Teflon vessels into pyrex test-tubes, centrifuged, and then the solvent (the supernatant) was decanted into a clean round bottom flask. The rotary evaporator was used to remove most of the solvent from the sample.

Using a clean pipette per sample, all liquid was removed from the flask and transferred into 3ml vials. DCM was used to rinse the round bottom flask, transferring into the 3ml vial with each rinse. Sample vials were then placed in the nitrogen blow down to remove the majority of the solvent.

The extracted lipids were then passed through packed silica columns to isolate the *n*-alkane fraction. A glass pipette was packed with partially deactivated silica (up to 5% w/w) and cleaned cotton wool. The lipids were dissolved in a small volume of DCM and loaded onto the column. The *n*-alkanes were then eluted using 4 column volumes of hexane, and taken to dryness with N_2 before analysis by gas chromatography.

4.5 Gas chromatography analyses

Gas chromatography (GC) is a technique in which the sample is passed through a capillary column (30 m used in this study) that is coated in a 'stationary phase' using the inert carrier gas helium. The separation of the compounds depends upon how the compound interacts with the stationary phase in the capillary column. Strong interactions with the column accounts for the compound being on the column for a longer length of time, compounds that have fewer interactions will come off the column earlier. These interactions and different speeds of elution through the column cause separation of the different compounds in a mixture, and compounds are identified using the 'retention time' (when the compound is eluted off the column). The gas chromatograph can have a flame ionisation detector (FID) or a mass spectrometer (MS) as the detector.

4.5.1 GC with Flame ionization detector (GC-FID)

The FID operates by having the sample gas from the end of the GC column being introduced into a hydrogen flame inside the FID detector, where any hydrocarbons in the sample will produce ions when they are burnt. In the FID, ions are detected using a metal collector which is biased with a high DC voltage. The current across this collector is proportional to the rate of ionisation, which in turn depends upon the concentration of hydrocarbons in the sample gas, producing a peak on the chromatogram identified by the retention time (Cambustion Limited., 2019). The GC-FID system allows for quantification of compounds, by referring to the known amount of internal standard added to each sample (Table 4.2 above and Section 4.1). However, the GC-FID is unable to confirm peak identification, which requires a GC coupled to a mass spectrometer.

The *n*-alkane fraction was analysed by different sets of gas chromatography (GC) configurations for compound quantification and identification. A Thermo Scientific Trace 1310 gas chromatograph was fitted with flame ionization detector (GC-FID) and a split-splitless injector. Compressed air is set as the air flow, helium (He) is set as the carrier flow, nitrogen (N) as a make-up flow and hydrogen (H) to aid ignition. The oven temperature was set at 70 °C for 2 min, then increased to 170 °C at 12 °C min^{-1}, then increased to 310 °C at 6.0 °C min^{-1}, then held at 310 °C for 35 min. *N*-alkanes were separated using a 60 m x 0.25 mm i.d Restek RXi-5ms column (0.25 μm 5% diphenyl-95% dimethyl polysiloxane coating). Compounds were quantified with reference to internal standards (5α-cholestane) and normalised by dividing the biomarker concentration by the TOC content for each sample (section 4.6).

4.5.2 GC coupled with Mass spectrometry (GC-MS)

Mass spectrometry is an analytical technique commonly used to identify unknown compounds within a sample. This is done by the sample being introduced in a gaseous state by electron ionisation, which is fragmented into ions that make up the compound or molecule. The ions are then separated in the mass spectrometer according to their mass to charge ratio, which can be characterized relative to the abundances. The molecular ion marks the complete compound passing through the mass spectrometer, shown as the highest value of m/z (followed by ions containing heavier isotopes) and gives the molecular mass of the compound to allow identification of e.g., the n-alkane chain length (Premierbiosoft.com, 2019).

Compound identification was confirmed using a Thermo Scientific Trace 1310 gas chromatography mass spectrometer (GC-MS), equipped with a programmable temperature vaporizer (PTV) injector. Helium was used as a carrier flow and the oven temperature program was set at 60 °C during 2 min and then after the 2 minutes raised to 12 °C min^{-1} until reaching 150 °C and then raised again to 310 °C with a rate of 6 °C min^{-1} and held for 25 min.

4.6 Calculating *n*-alkane masses

Once the samples have being analysed, the target peaks are identified and integrated. Equation 4.1 calculates the *n*-alkane concentrations in the River Esk sediments, μg g^{-1}.

Equation 4.1: $$MBm = \frac{\left(\frac{Ms}{As}\right)*ABM}{weight\ extracted}$$

Mbm = mass of the biomarker that you want to be quantified (mg).

As = Area of the standard on the chromatogram

Abm = Area of the target biomarker on the chromatogram

Ms = Mass of standard

Weight extracted = dry weight of sediment (g).

Chapter 5: Results

5.1 Introduction

Suspended sediment was collected as part of the research conducted by Perks (2013) between 2007 to 2009, from the specified sites along the River Esk, North York Moors (NYM). In this Chapter, the biomarker distributions are presented for each site, individually. The sampling strategy was to collect one sample per month where possible, but on some dates, sites were not accessible, for instance if high rainfall meant that the river levels were too high or sampler became blocked with leaf litter.

In addition to the limited accessibility of some of the sampling locations outlined above, for some samples taken there was not enough sediment to analyse, which restricted a full suite of sample comparisons for each site to be undertaken (Table 5.1). In this Chapter, the complete data recovered from each site are presented (C/N ratios and *n*-alkane distributions), starting from the most upstream site (Westerdale) and then moving downstream.

Table 5.1: Index for abbreviation of names of site

Site name	Abbreviated	Colours associated with site
Commondale	C	🟪
Westerdale	W	🟥
Danby Beck	DBK	🟧
Danby A	DDA	🟦
Danby B	DDB	🟩
Lealholm	L	🟪
Glaisdale meander	GM	⬜
Glaisdale downstream A	GDSA	🟦
Glaisdale downstream B	GDSB	🟨

Table 5.2: Suspended sediment sampling in the River Esk. “Y” and Blue. = sampled, “N.s.” = not sampled, “na.” = sampled but not enough sediment to analyse. Sampling was undertaken by Perks (2013).

	C	W	DBK	DA	DB	L	GM	GDA	GDB	G
June 2007	na	**Y**	na	na	**Y**	na	na	na	na	na
July 2007	na	na	na	**Y**	na	na	na	**Y**	na	na
Aug 2007	na	na	na	na	na	na	na	na	na	na
Sept 2007	na	na	na	na	na	na	na	na	na	na
Oct 2007	na	na	na	**Y**	**Y**	**Y**	na	**Y**	**Y**	na
Nov 2007	na	na	na	na	na.	na.	na	na	na	na
Dec 2007	**Y**	na	**Y**	**Y**	**Y**	**Y**	na	**Y**	**Y**	na
Jan 2008	**Y**	**Y**	na	**Y**	**Y**	**Y**	**Y**	**Y**	na	**Y**
Feb 2008	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**

5.2 Westerdale

Samples were processed from the Westerdale site on two occasions (January 2008 and February 2008), unfortunately for other months there was insufficient sample to analyse. The C/N ratio at Westerdale is 16.25 in January 2008 yet falls by a factor of 3 to 5.34 in February 2008 (Figure 5.1(a)). The dominant *n*-alkane chain lengths are C_{18}, C_{27}, C_{29}, C_{31} and C_{33} (Figure 5.1(b)). A decrease in the ACL proxy occurs between January and February 2008, driven by a decrease in C_{31} and an increase in C_{29} (Figure 5.2(a)). The CPI shows a similar trend (Figure 5.2(a). TAR indices increase from 11.10 to 22.22 between January and February 2008 (Figure 5.2(b)). The P_{aq} index falls from 0.35 to 0.26 (figure 5.2(b)). Figure 5.2(c) depicts Pr/Ph, Pr/nC_{17} and Ph/*n*-C_{18} being higher in February 2008 than January (Figure 5.2(d)). Figure 5.3(a) and (b) show higher values in C_{23}/C_{25} and *n*-C_{31}/*n*-C_{27} in January 2008 compared to February 2008.

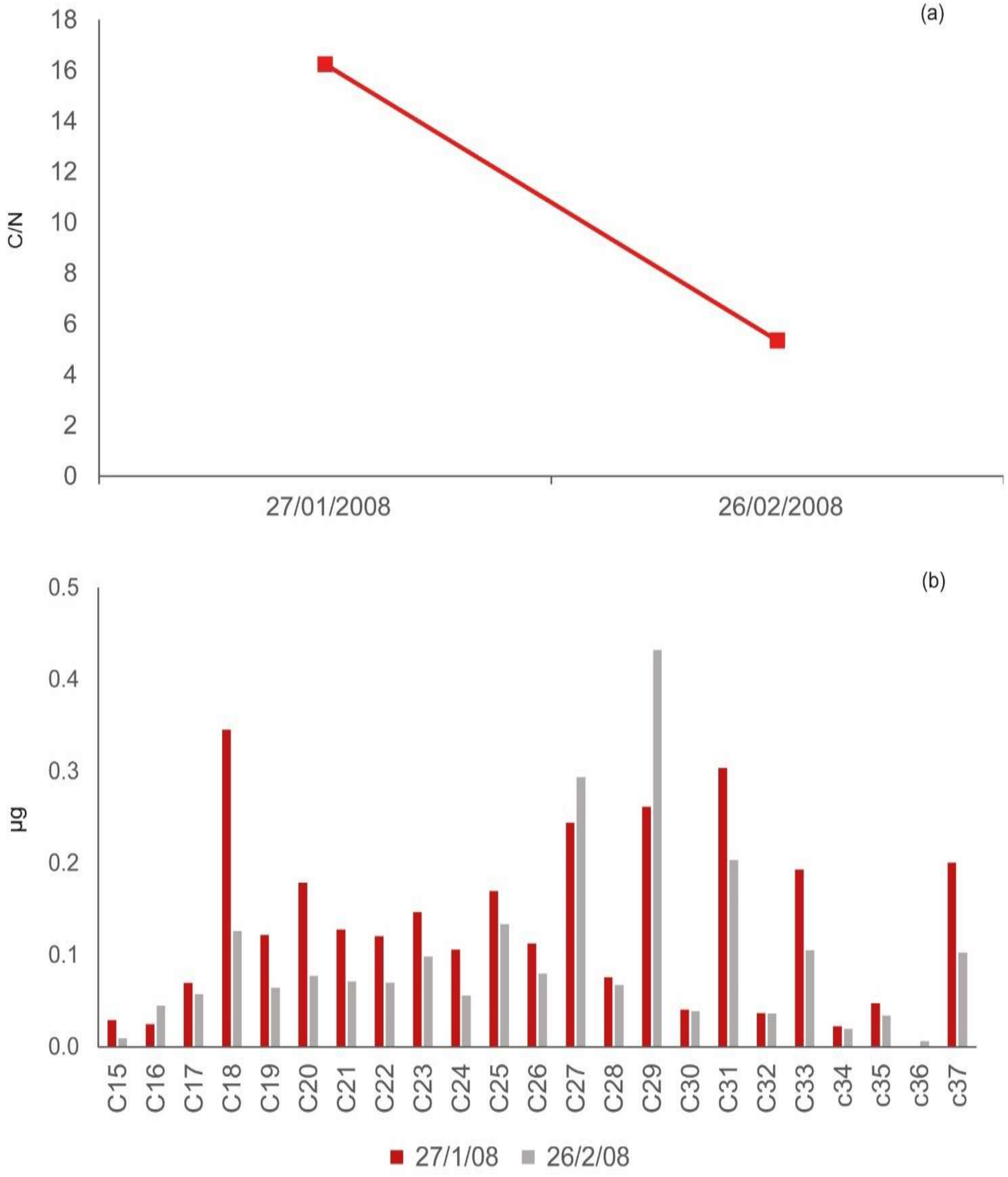


Figure 5.1: Westerdale elemental and biomarker data for January 2008 and February 2008 (a) C/N ratio. (b) *n*-alkane chain lengths

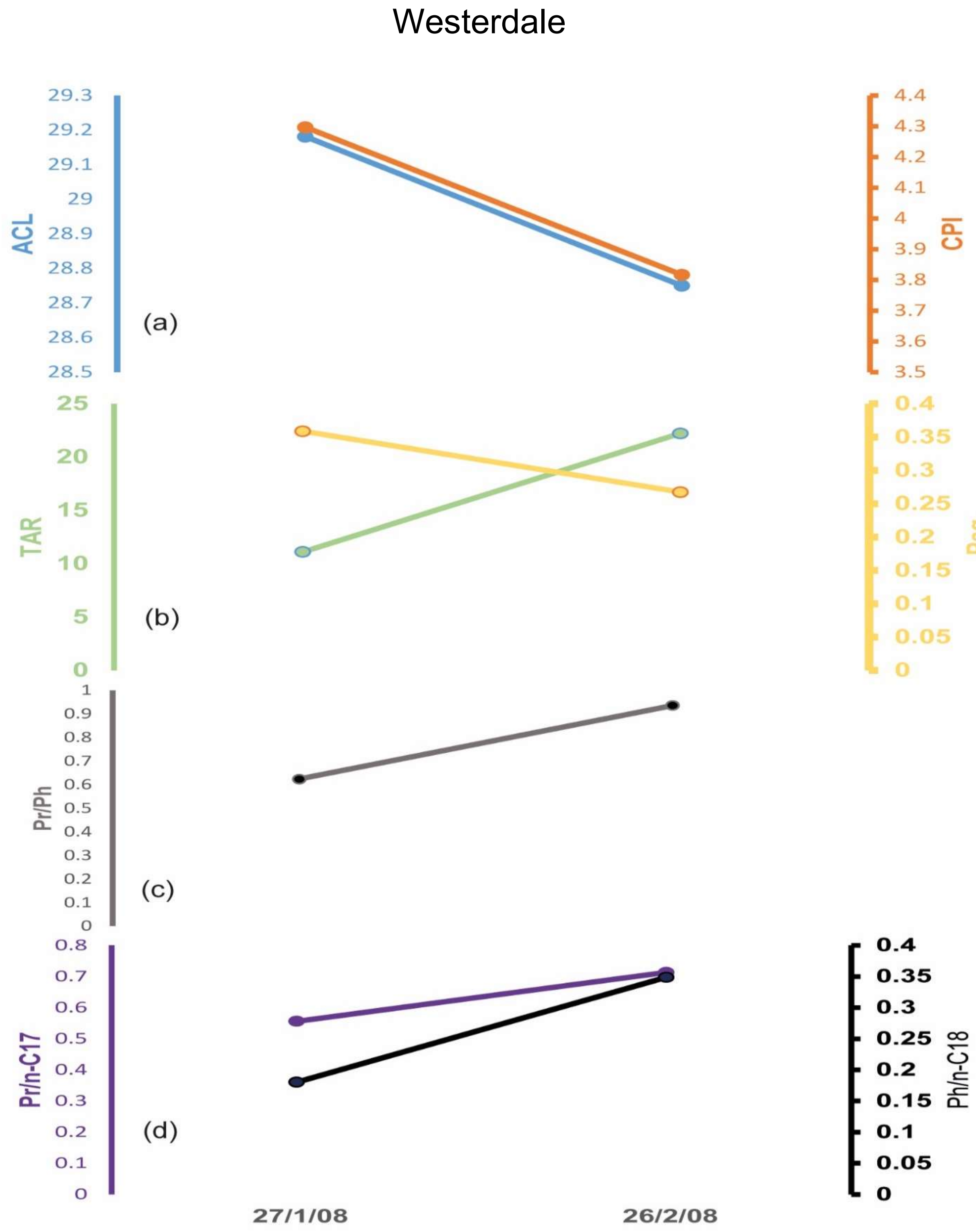


Figure 5.2: (a) Average chain length (ACL); Carbon preference index (CPI). (b) TAR index; P_{aq}. (c) Pr/Ph ratio. (d) Pr/n-C_{17} ratio and Ph/n-C_{18} for January to February 2008.

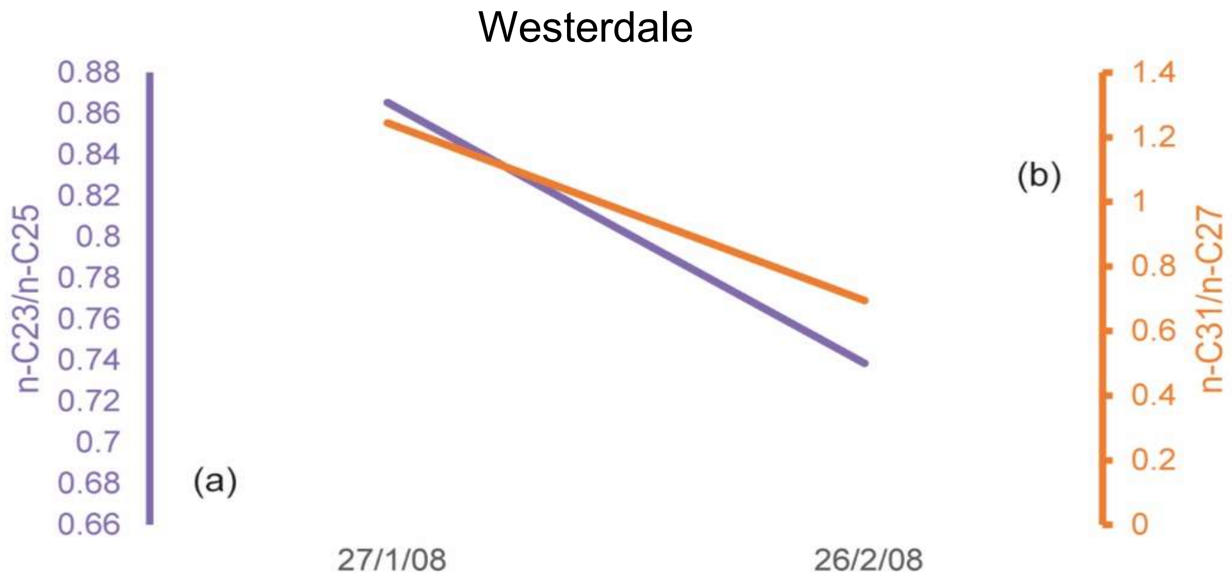


Figure 5.3: (a) *n*- C_{23}/C_{25} ratio for January and February 2008. (b) *n*-C_{31}/*n*-C_{27} for January and February 2008.

5.3 Commondale

Data was recovered from Commondale on three occasions (December 2007, January 2008 and February 2008). Unfortunately for other months there was insufficient sample to analyse. The C/N ratio at Commondale is relatively constant but increasing, varying from 14.72 in December 2007, 14.92 in January 2008, and 15.14 in February 2008 (Figure 5.4(a)). The dominant *n*-alkane chain lengths are C_{18}, C_{25}, C_{27}, C_{29}, C_{31} and C_{33} (Figure 5.4(b)). A gradual decrease in the ACL proxy also occurs from December to February 2008, driven by a decrease in C_{31} and an increase in C_{29} (Figure 5.5(a)). CPI increased from December 2007 to January 2008 and then decreases to the February 2008. TAR increases from 4.17 in December 2007 to 5.40 (January 2008) then 5.45 in February 2008 (figure 5.5(b)). The P_{aq} index rises from 0.26 to 0.31 in February 2008 (Figure 5.5(b)). Figure 5.5(c) depicts Pr/Ph for January 2008 0.95 result being slightly higher in value than December 2007 0.83, then the February drops in value to 0.57. In Pr/*n*-C_{17} December 2007 being highest value 0.81 then decreasing to 0.59 in January 2008, then raising again for February 2008 0.75 (Figure 5.5(d)). In Figure 5.5(d), Ph/*n*-C_{18} values gradually increase from the December 2007 to the February 2008. Figure 5.6(a) C_{23}/C_{25} shows an increase from the December 2007 to the January 2008 then a slight decrease to the February 2008 and *n*-C_{31}/*n*-C_{27} a gradual decrease from December 2007 to January 2008, then increases to February 2008.

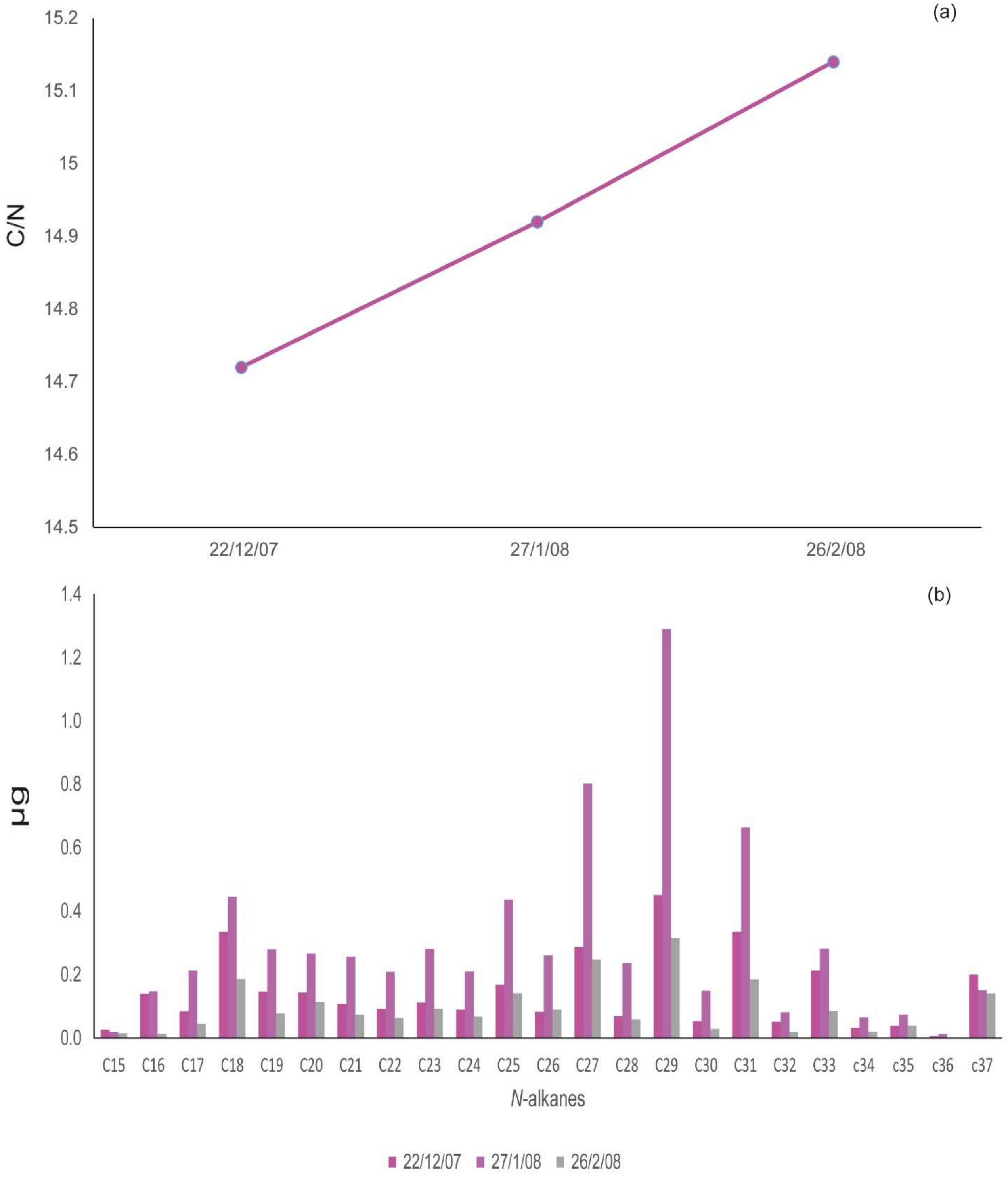


Figure 5.4: Commondale elemental and biomarker data for December 2007 to February 2008 (a) C/N ratio. (b) *n*-alkane chain lengths.

Commondale

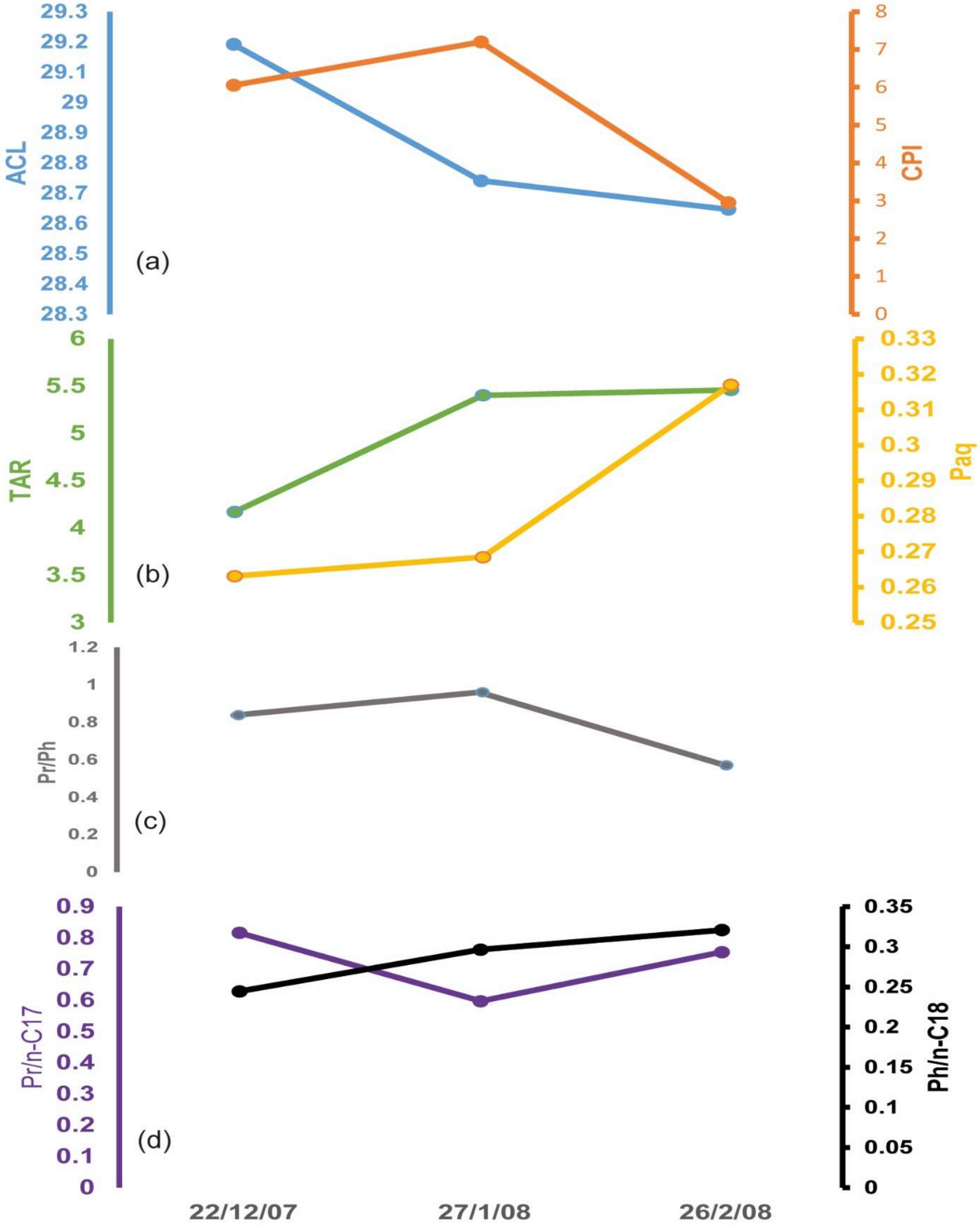


Figure 5.5: (a) Average chain length (ACL) and Carbon preference index (CPI). (b) TAR index and (P_{aq}). (c) Pr/Ph ratio. (d) Pr/n-C_{17} ratio and Ph/n-C_{18} ratio December 2007 to February 2008.

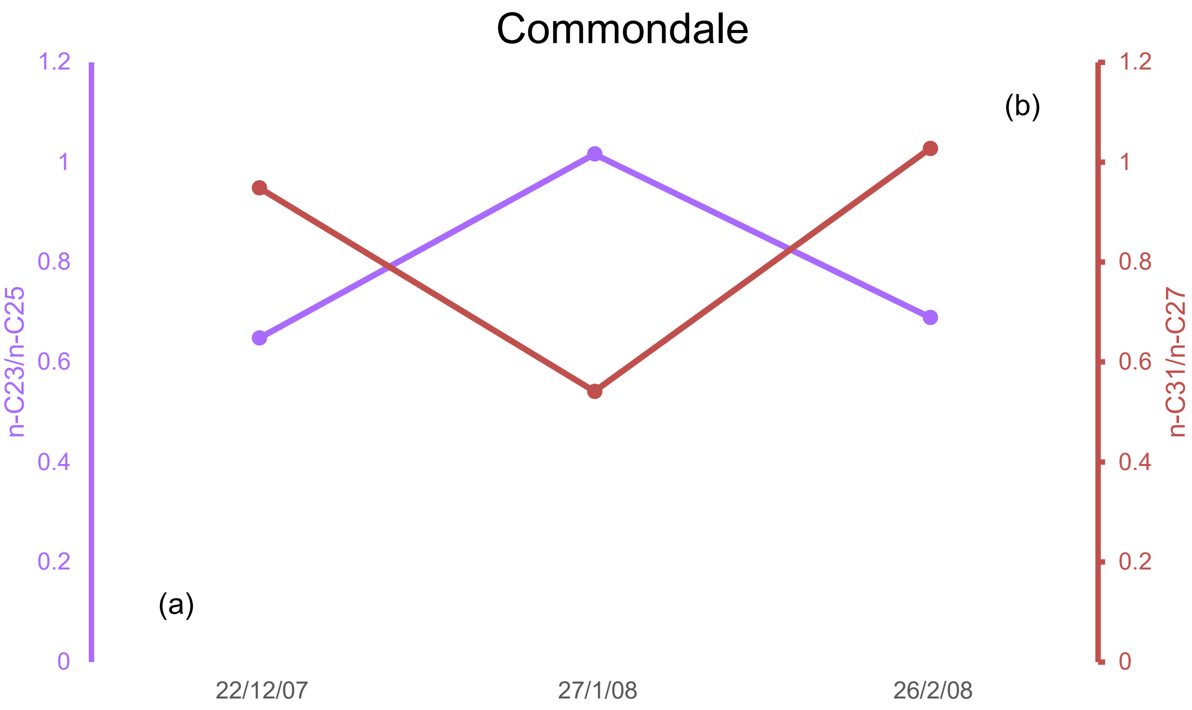


Figure 5.6: (a) *n*- C_{23}/C_{25} ratio shows December 2007 to February 2008. (b) *n*-C_{31}/*n*-C_{27} December 2007 to February 2008.

5.4 Danby Beck

Data was recovered from Danby Beck on two occasions (December 2007 and February 2008). The C/N ratio at Danby Beck is 4.23 in December 2007 and falls to 4.19 in February 2008 (Figure 5.7(a)). The dominant *n*-alkane chain lengths are C_{18}, C_{25}, C_{27}, C_{29}, C_{31} and C_{33} (Figure 5.7(b)). An increase in the ACL proxy also occurs between December 2007 and February 2008, driven by an increase in C_{31} and a decrease in C_{29} (Figure 5.8(a)). In the CPI and TAR indices increase also from 8.24(CPI), 5.45 (TAR) to 12.44 (CPI), 11.91 (TAR) between December 2007 and February 2008 (figure 5.8(a)+(b)). The P_{aq} index falls from 0.22 to 0.17 from December 2007 to February 2008 (figure 5.8(b)). Figure 5.8(c) depicts Pr/Ph for the February 2008 result being slightly higher in value than December 2007, the same shown in Ph/*n*-C_{18} (Figure 5.8(d)). In Figure 5.8(d), Pr/*n*-C_{17} values in February 2008 are lower than December 2007. Figure 5.9(a) and (b) higher value in the December 2007 for both C_{23}/C_{25} and *n*-C_{31}/*n*-C_{27} and lower value in the February 2008.

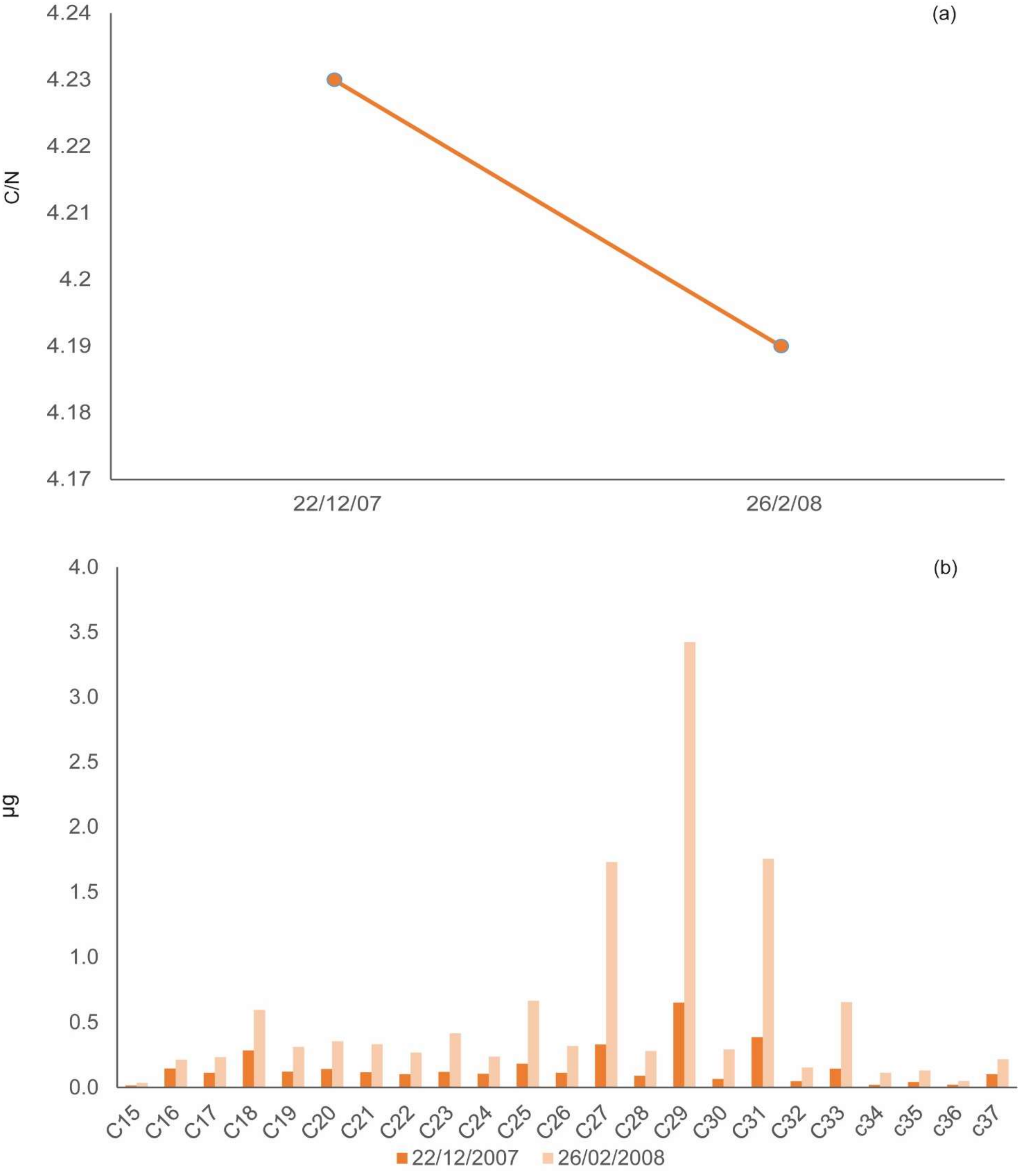


Figure 5.7: Danby Beck elemental and biomarker data for December 2007 and February 2008 (a) C/N ratio. (b) *n*-alkane chain lengths

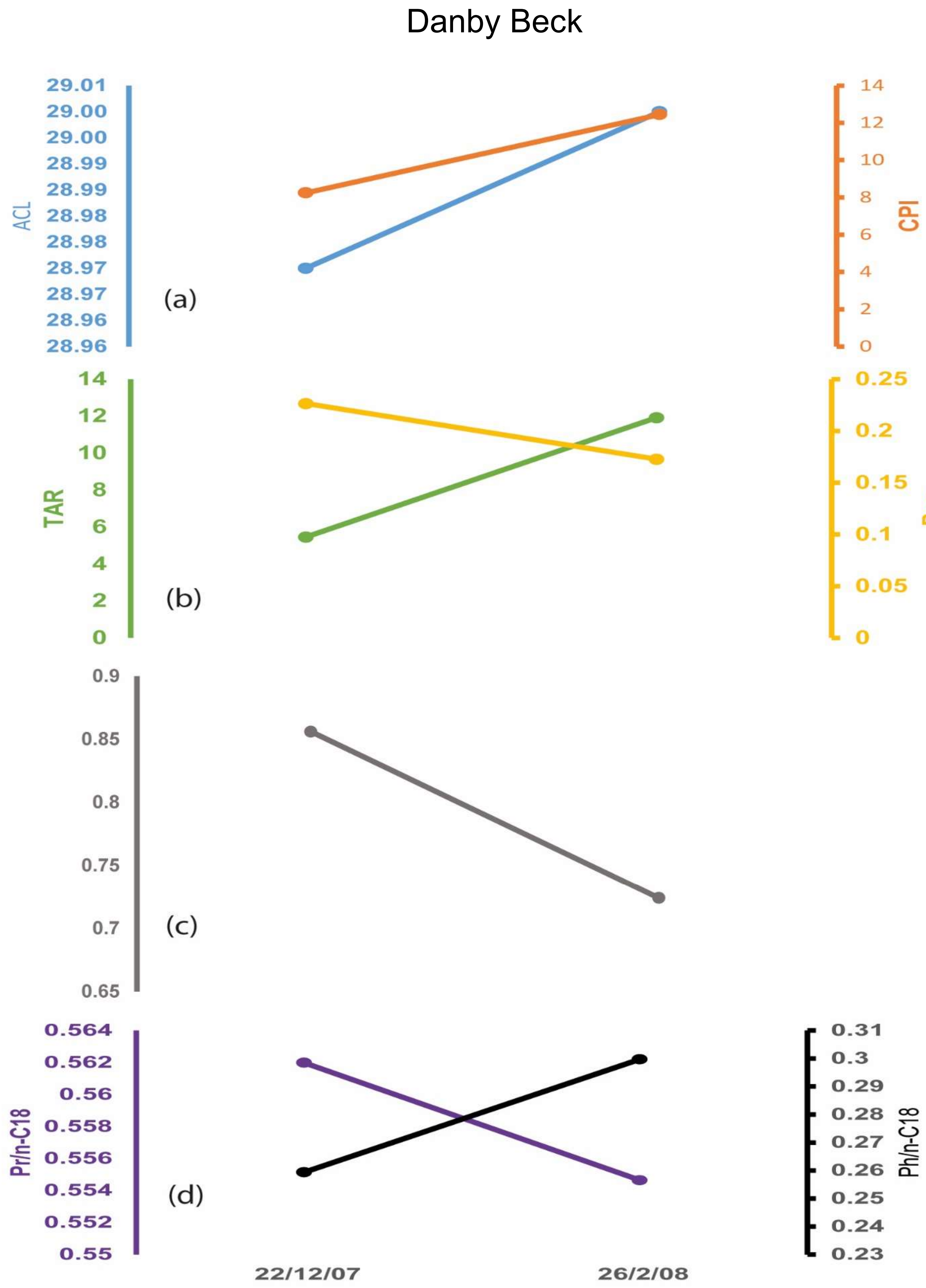


Figure 5.8: (a) Average chain length (ACL) and Carbon preference index (CPI). (b): TAR index and (*P$_{aq}$*). (c) Pr/Ph ratio. (d) Pr/*n*-C$_{17}$ ratio and Ph/*n*-C$_{18}$ ratio for December 2007 and February 2008.

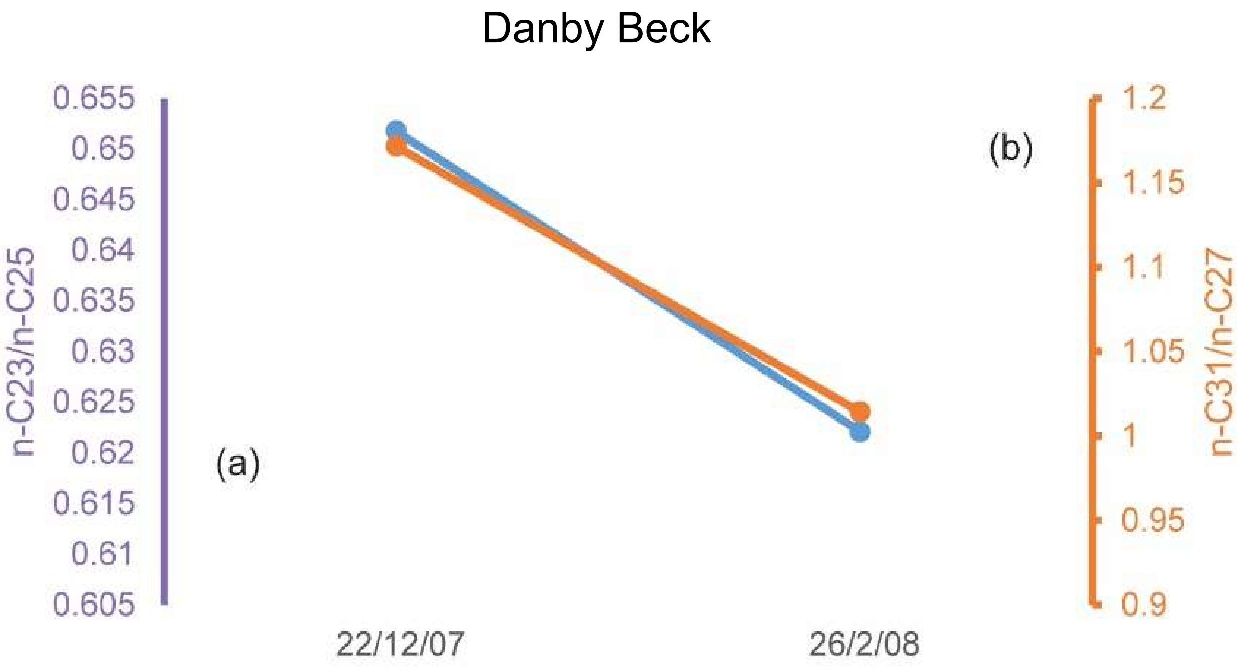


Figure 5.9: (a) *n*- C_{23}/C_{25} ratio for December 2007 and February 2008. (b) *n*-C_{31}/*n*-C_{27} for December 2007 and February 2008.

5.5 Danby A

Data was recovered from Danby A on five occasions (July 2007, October 2007, December 2007, January 2008 and February 2008), making it one of the sites with the most constraint on temporal variability in suspended sediment composition. Danby A and Danby B are located on either side of the river with A referring to the right-side near the bank downstream and B the left. The C/N ratio at Danby A is 24.64 in the July 2007, then falls by a factor of about 2 in the October 2007 and again to the December 2007, then in the January 2008 increases to 15.64, yet falls by a factor of 3 to 5.51 in February 2008 (5.10(a)). The dominant *n*-alkane chain lengths are C_{25}, C_{27}, C_{31} and C_{33} (5.10(b)). The CPI and P_{aq} proxies (Figure 5.11a+b) show a similar trend in the months of July through to December 2007, increasing from July 2007 to peak in the October 2007, then from October decreasing to December 2007. CPI continues to decrease through to the February 2008. P_{aq} increased slightly from the December to 0.31 in February 2008 (Figure 5.11(b)). ACL increases gradually peaking in the December 2007 then gradually decreased through to the February 2008. TAR decreased from July to October 2007, then gradually increased through to the January with slight difference through to the February

2008. Biomarker data for Pr/Ph, Pr/n-C_{17}, Ph/n-C_{18} and C_{23}/C_{25} shows no visual pattern from the July 2007 to February 2008. In figure 5.12(b) n-C_{31}/n-C_{27} most values are around 1 value apart from October 2007 where the value drops to 0.54.

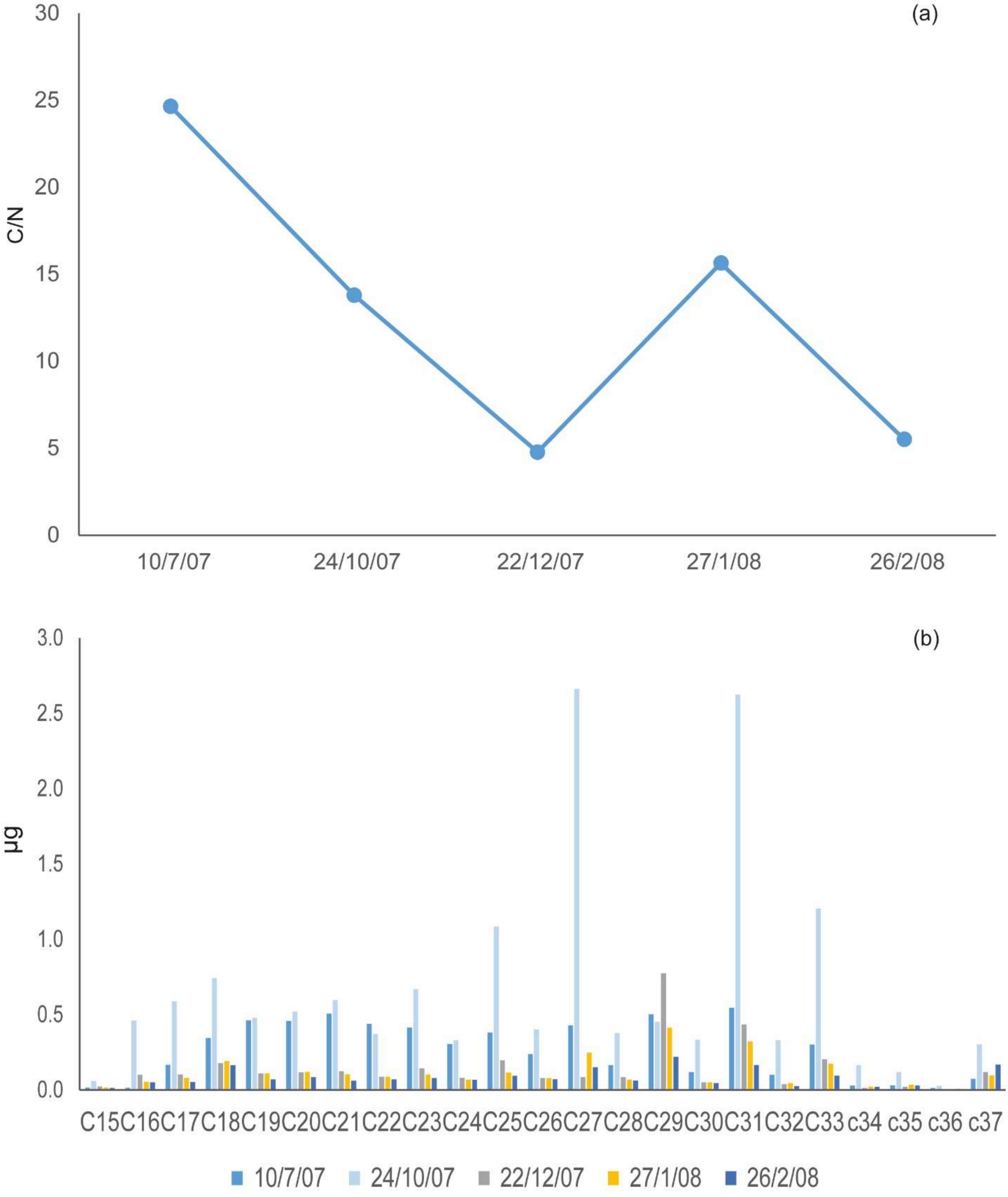


Figure 5.10: Danby A elemental and biomarker data for July 2007, October 2007 to February 2008 (a) C/N ratio. (b) *n*-alkane chain lengths.

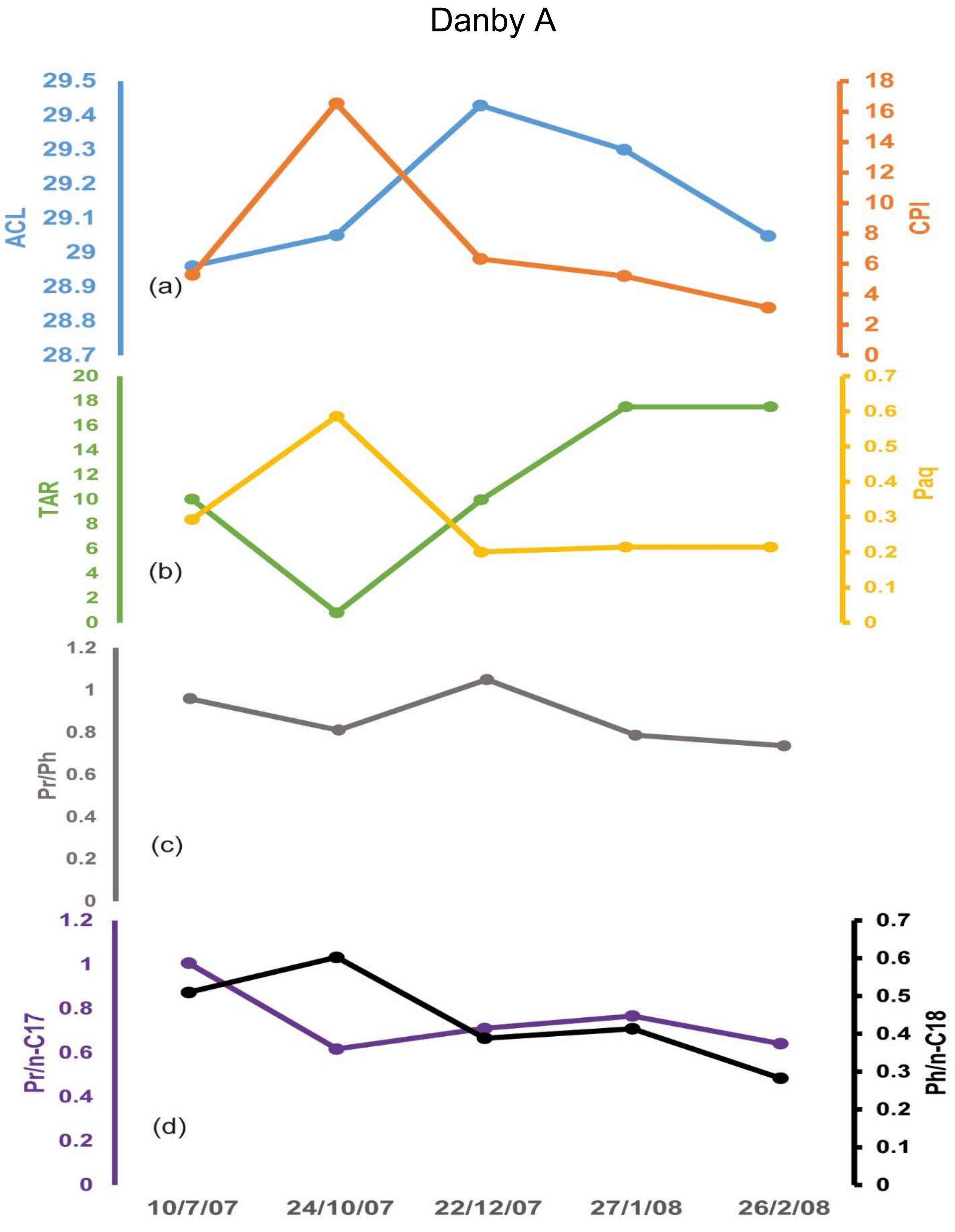


Figure 5.11: (a) Average chain length (ACL) and Carbon preference index (CPI). (b) TAR index and (P_{aq}) values. (c) Pr/Ph ratio. (d) Pr/n-C_{17} ratio and Ph/n-C_{18} ratio for July 2007, October 2007 to February 2008.

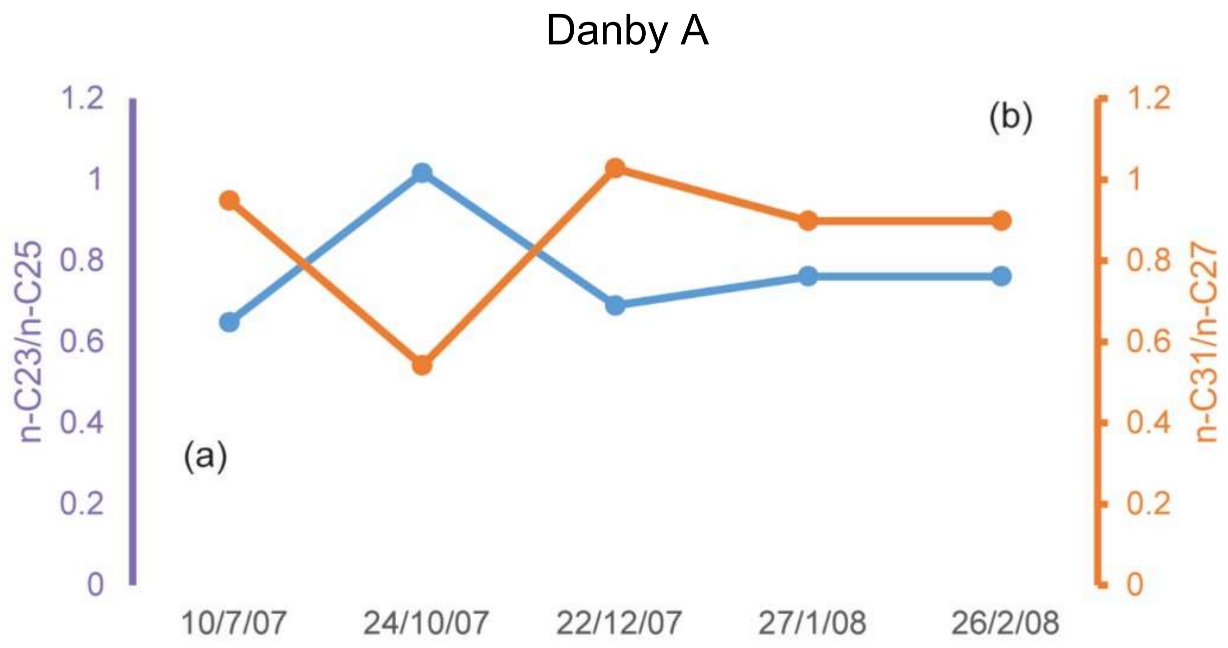


Figure 5.12: (a) *n*- C_{23}/C_{25} ratio shows July 2007, October 2007 to February 2008. (b) *n*-C_{31}/*n*-C_{27} showing July 2007, October 2007 to February 2008.

5.6 Danby B

Data was only recovered from Danby B on five occasions (June 2007, October 2007, December 2007, January 2008 and February 2008). Danby A and Danby B are located at the same cross-section of the river, sample B referring to the left-side near the bank downstream and A the right. The C/N ratio at Danby B is 13.96 in June 2007, yet falls to 4.39 in October 2007, and then rises to 14.11 in December 2007 and then the highest value in the January 2008 14.76. Then drops to 5.00 in the February 2008 (Figure 5.13(a)). The dominant *n*-alkane chain lengths are C_{25}, C_{27}, C_{29}, C_{31} and C_{33} (Figure 5.13(b)) the most abundant in the June 2007. ACL shows no visual trends, CPI shows a gradual decrease from July 2007 to February 2008. TAR shows the highest value in the July 2007 (17) compared to all other values which are all below 7. The P_{aq} index decreases from 0.22 to 0.20 July 2007 to October 2007 then gradually increases to its peak in February 2008 value 0.28 (figure 5.14(b)). Figure 5.14(c) Pr/Ph no visual pattern shown. Pr/*n*-C_{17} shows a gradual increase peaking in the December 2007, then decreasing from the December 2007 to February 2008. Ph/*n*-C_{18} gradual decrease from its highest value in July 2007 till January 2008 then rises again in the February 2008. C_{23}/C_{25} and *n*-C_{31}/*n*-C_{27} shows no visual pattern (Figure 5.15(a) and (b).

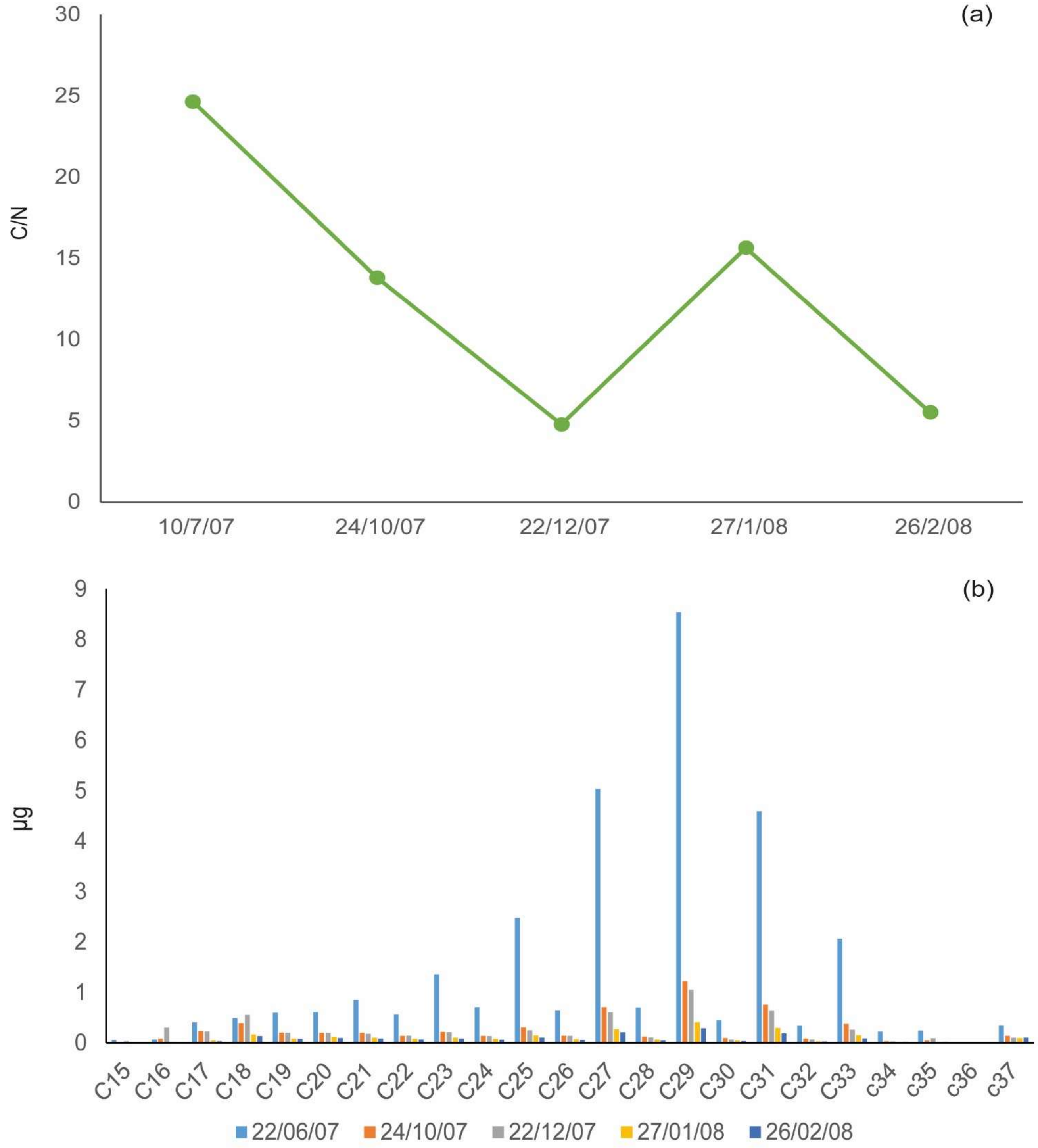


Figure 5.13: Danby B elemental and biomarker data for June 2007, October 2007 to February 2008 (a) C/N ratio. (b) *n*-alkane chain lengths.

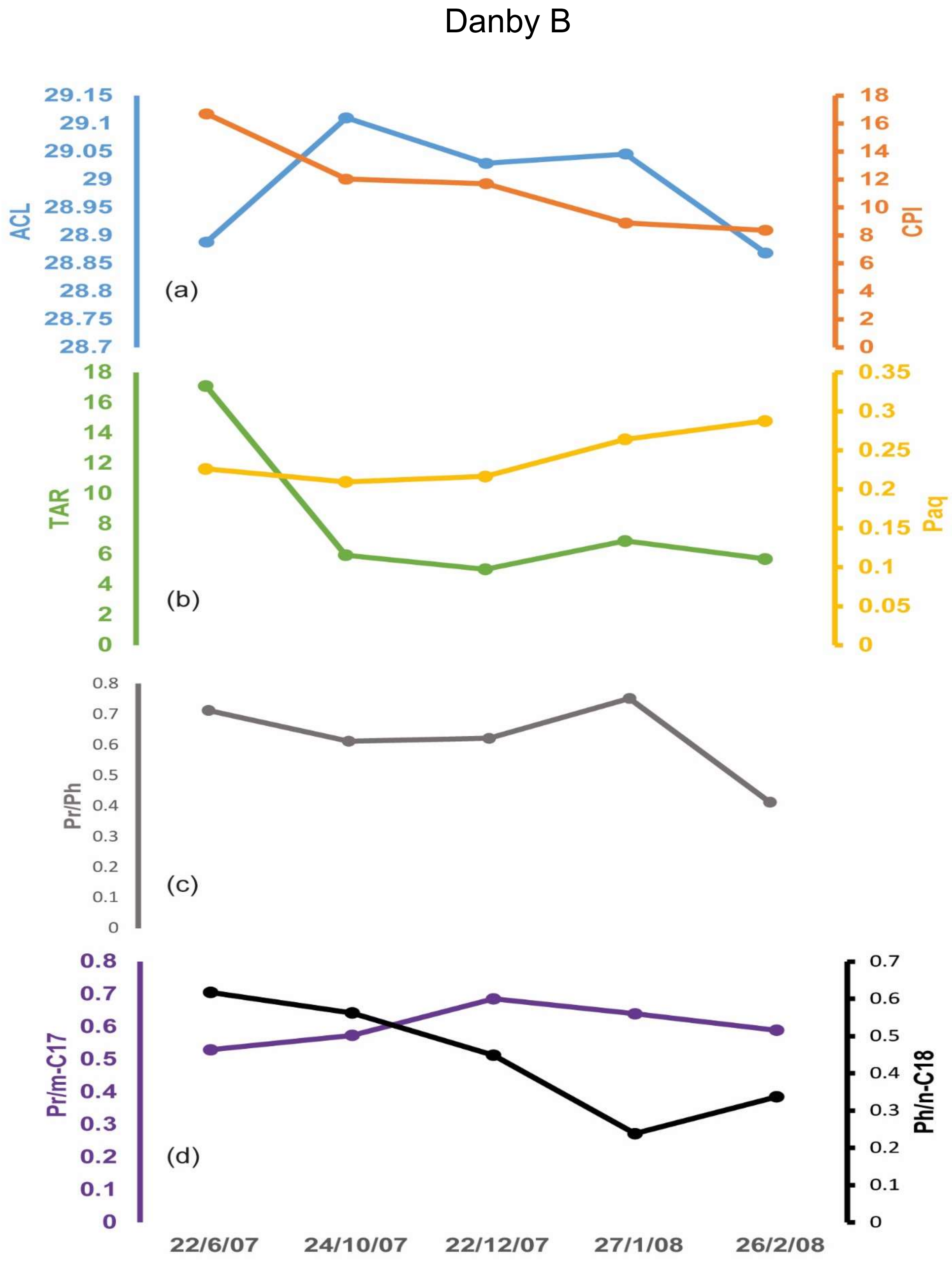


Figure 5.14: (a) Average chain length (ACL) and Carbon preference index (CPI). (b) TAR index and P_{aq}. (c) Pr/Ph ratio and (d) Pr/n-C_{17} ratio June 2007 and Ph/n-C_{18} ratio for June 2007, October 2007 to February 2008.

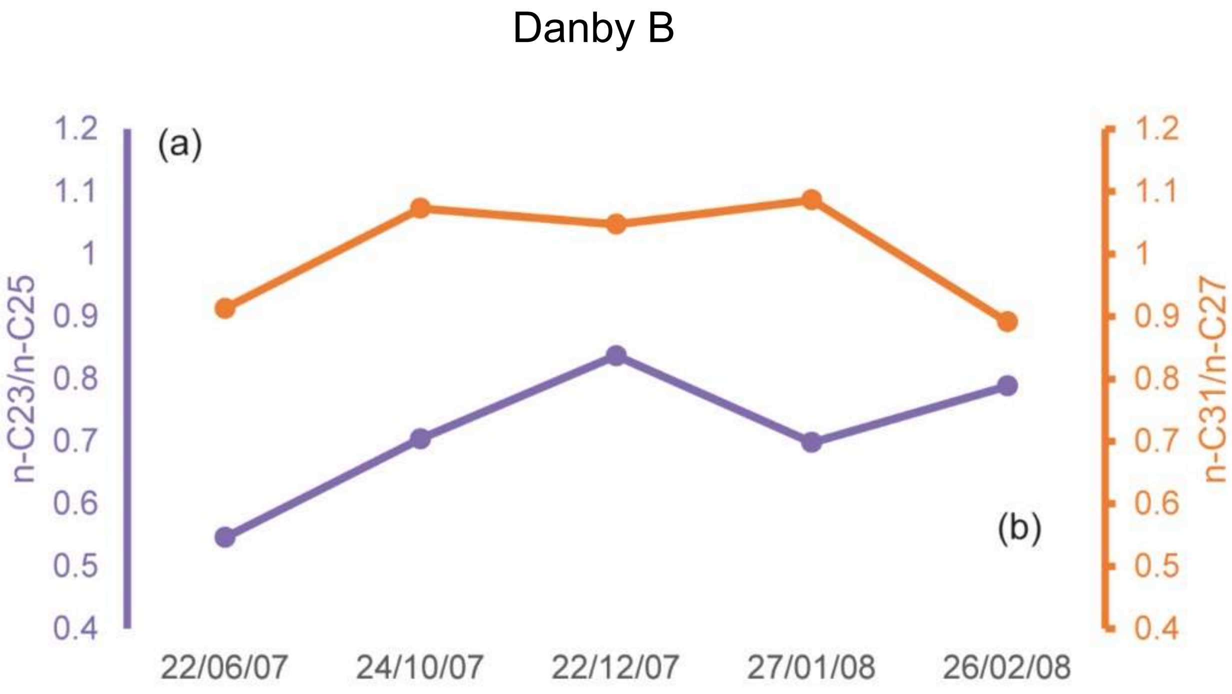


Figure 5.15: Danby B biomarker data (a) *n*- C_{23}/C_{25} ratio shows June 2007, October 2007 to February 2008. (b) *n*-C_{31}/*n*-C_{27} showing June 2007, October 2007 to February 2008.

5.7 Lealholm

Data was recovered from Lealholm on four occasions (October 2007, December 2007, January 2008 and February 2008). The C/N ratio at Lealholm is 4.13 in the October 2007 rising to 4.64 in the December 2007 then 4.74 in January 2008 yet falls slightly to 4.73 in February 2008 (Figure 5.16(a)). The dominant *n*-alkane chain lengths are C_{18}, C_{23}, C_{25}, C_{27}, C_{29}, C_{31} and C_{33} (Figure 5.16(b)). The ACL and CPI biomarkers show a decreasing pattern from October 2007 to December 2007 then increases to the January 2008 and then decreases again to the February 2008. In P_{aq} and TAR shows a gradual decrease in terrestrial input from October to December 2007 and increasing to January 2008 and in TAR February 2008. Figure 5.17(c) and Figure 5.17(d) depicts Pr/Ph and Pr/*n*-C_{17}, both have similar patterns and have distinctively high values in the February 2008. Ph/*n*-C_{18} values are very low with a decrease from December (3.9) to January 2008 (0.2), then increases to January 2008 and peaks in the February 2008. Figure 5.18(a) and (b) C_{23}/C_{25} and *n*-C_{31}/*n*-C_{27} both show no visual pattern.

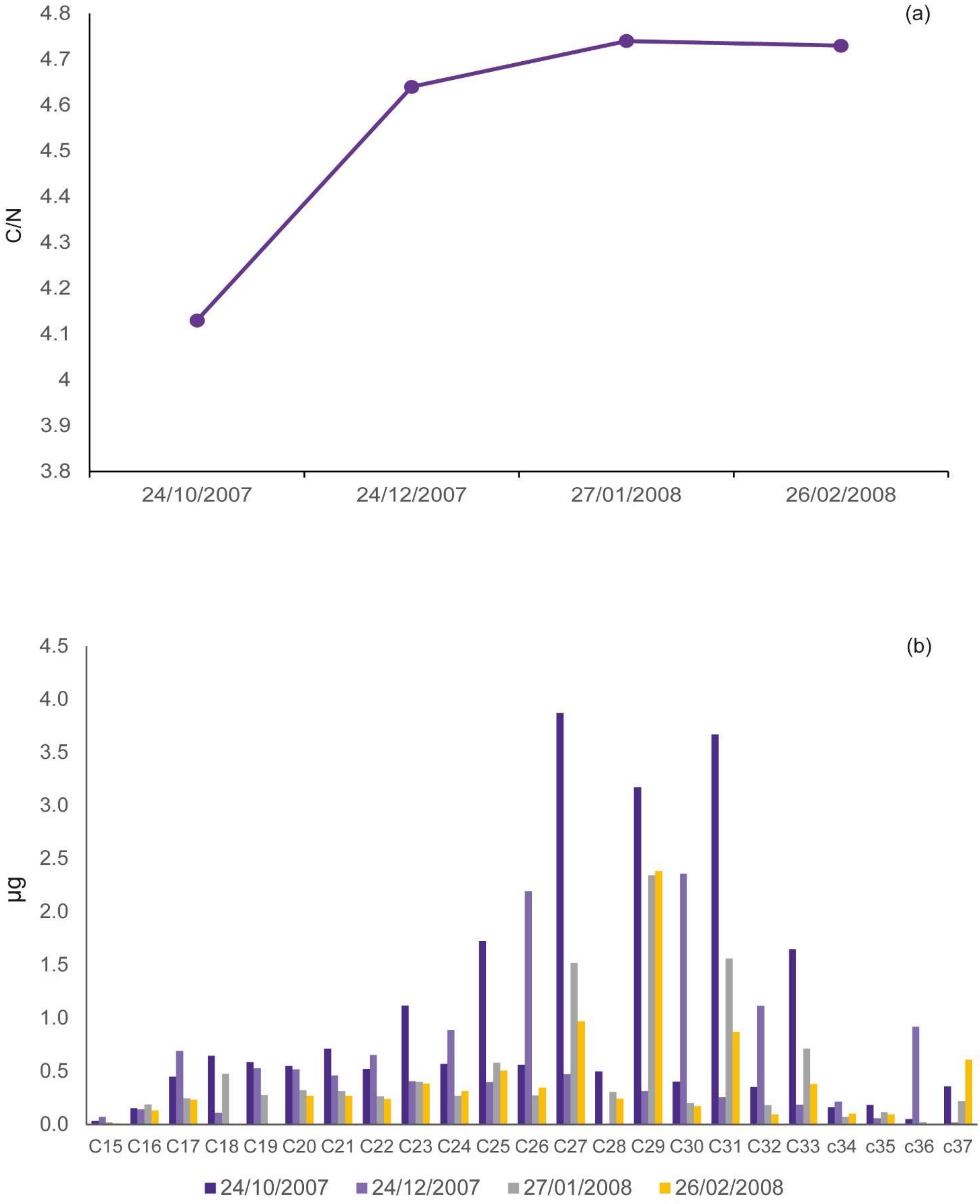


Figure 5.16:Lealholm elemental and biomarker data for October 2007 to February 2008 (a) C/N ratio. (b) *n*-alkane chain lengths

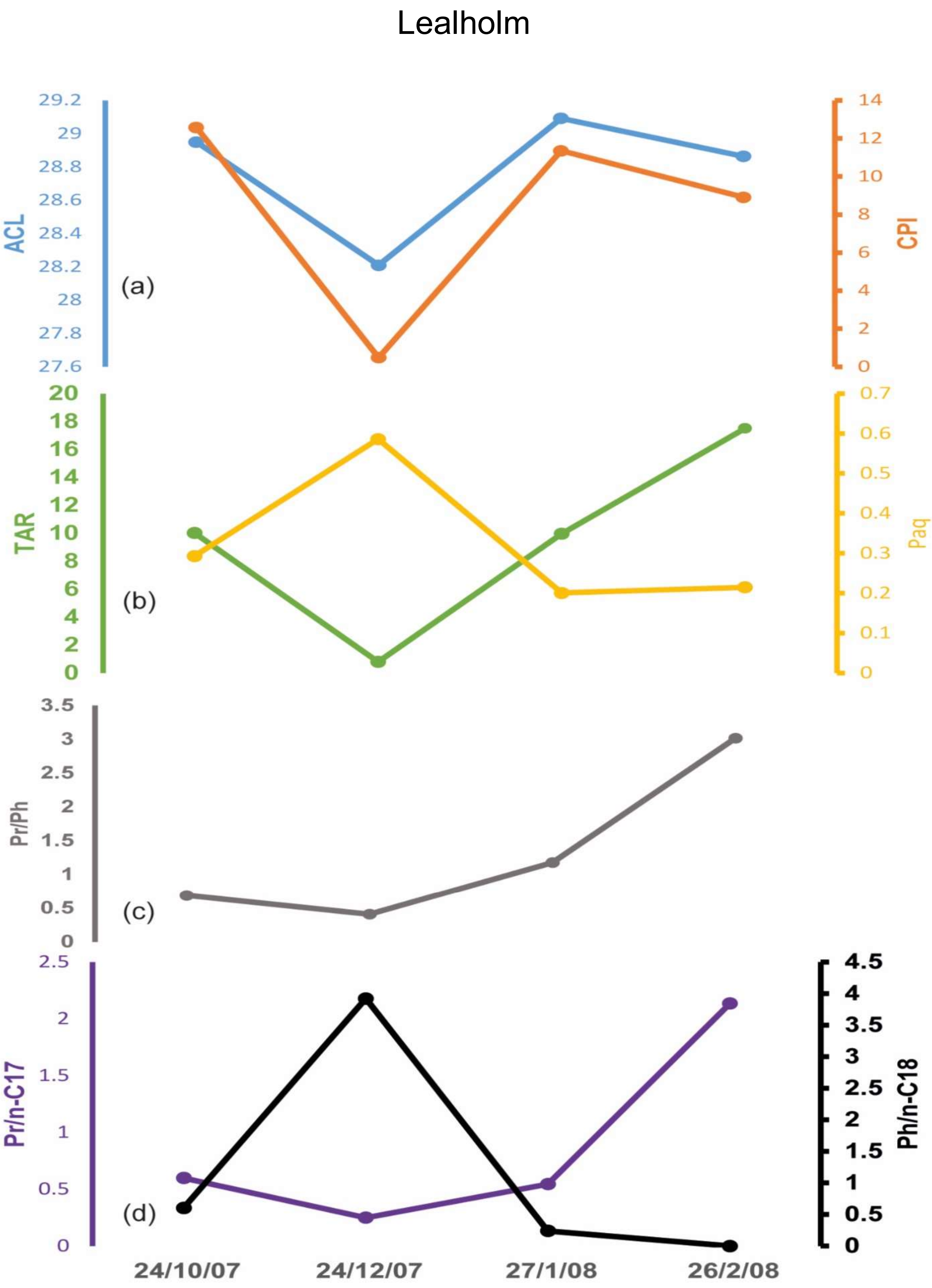


Figure 5.17: (a) Average chain length (ACL) and Carbon preference index (CPI). (b) TAR index and P_{aq}. (c) Pr/Ph ratio and (d) Pr/n-C_{17} ratio and Ph/n-C_{18} ratio October 2007 to February 2008.

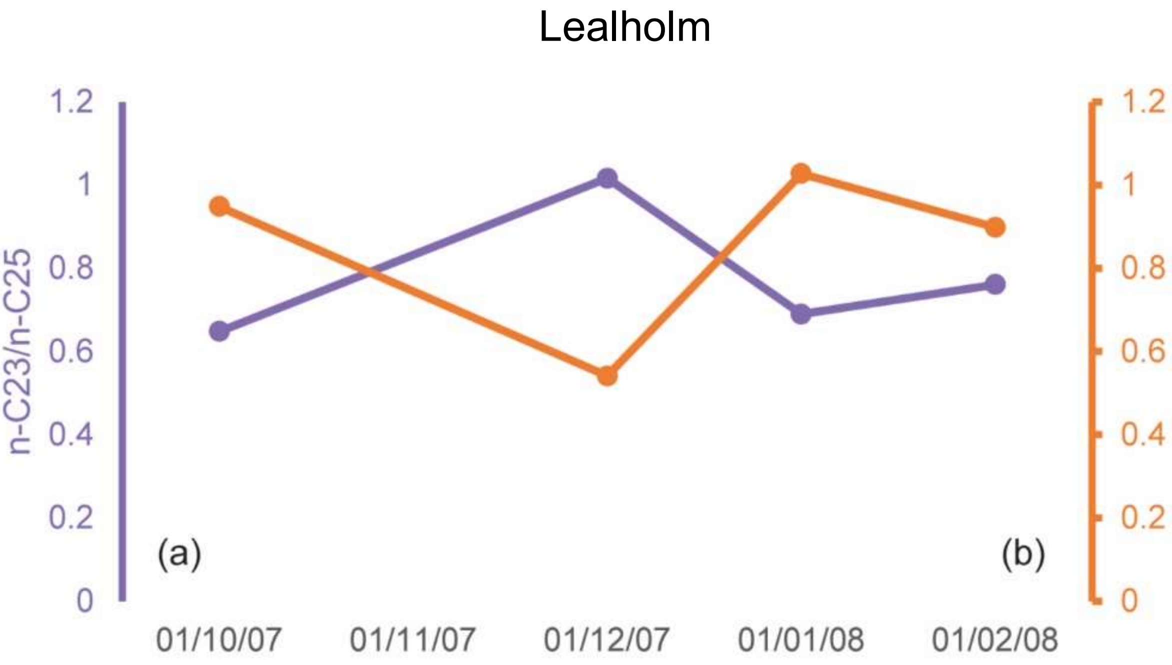


Figure 5.18: Lealholm biomarker data (a) *n*-C_{23}/C_{25} ratio October 2007 to February 2008. (b) *n*-C_{31}/*n*-C_{27} October 2007 to February 2008.

5.8 Glaisdale meander

Data was only recovered from Glaisdale Meander on two occasions (January 2008 and February 2008) as unfortunately for other months there was insufficient sample to analyse. The C/N ratio at Glaisdale meander is 5.18 in January 2008 yet falls to 4.85 in February 2008 (Figure 5.19(a)). The dominant *n*-alkane chain lengths are C_{18}, C_{25}, C_{27}, C_{29}, C_{31} and C_{33} (Figure 5.19(b)). A decrease in the ACL proxy also occurs between January and February 2008, driven by a decrease in C_{31} and an increase in C_{29} (Figure 5.20(a)). In CPI and TAR indices decrease from 9.75 (CPI), 10.40 (TAR) to 6.90 (CPI), 4.93 (TAR) between January and February 2008 (figure 5.20(a) and figure 5.21(b)). The P_{aq} index rises from 0.27 to 0.30 from January to February 2008 (figure 5.20(b)). Figure 5.20 (c) depicts Pr/Ph for the February 2008 result being higher value than January 2008, the same shown in Pr/*n*-C_{18} (Figure 5.20(d)). In Figure 5.20(d), Ph/*n*-C_{17} values in February 2008 are lower than January 2008. Figure 5.21(a) displays C_{23}/C_{25} January with higher values compared to February and *n*-C_{31}/*n*-C_{27}, Figure 5.21(b) shows February has larger value.

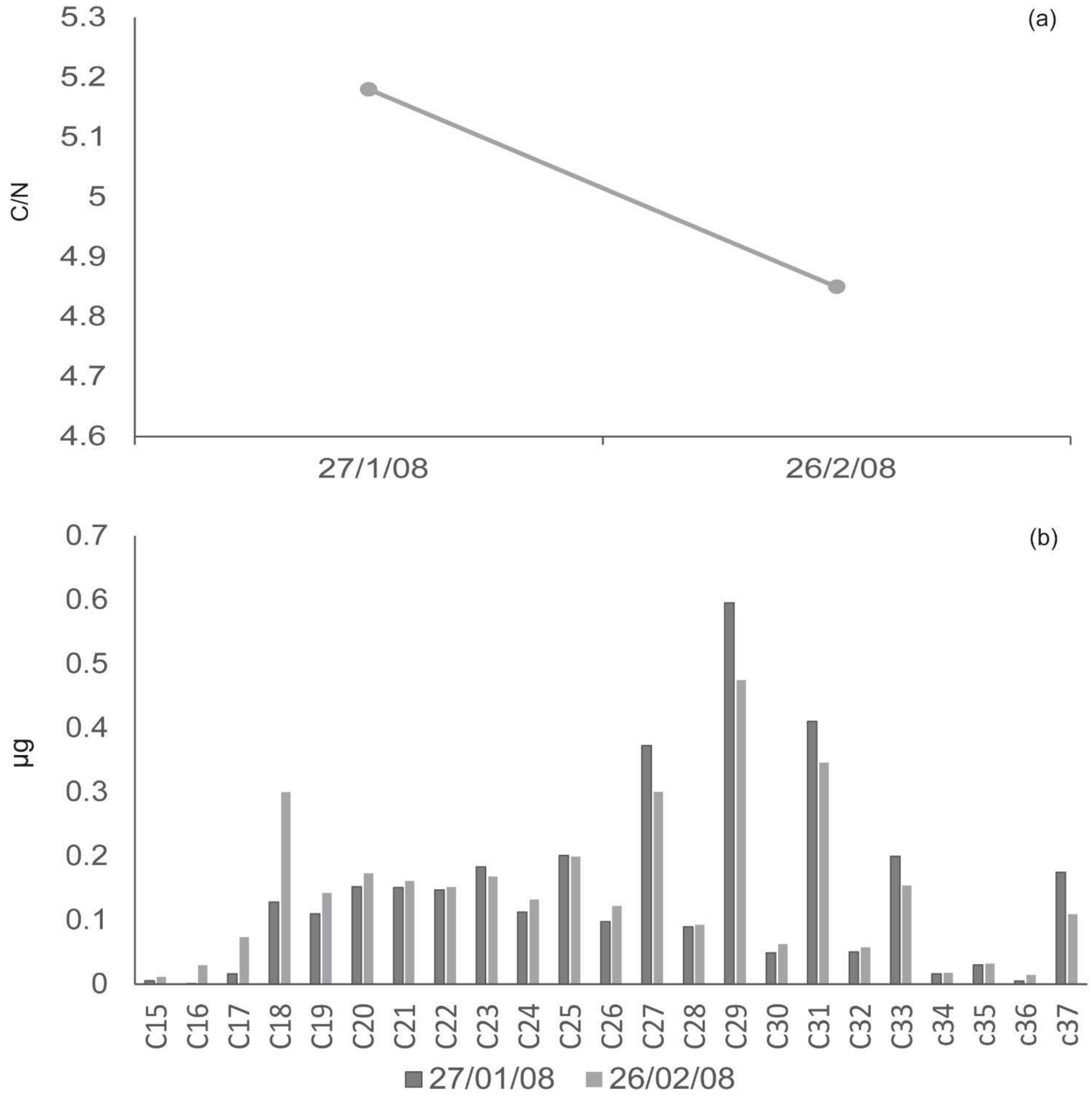


Figure 5.19: Glaisdale Meander elemental and biomarker data for January 2008 to February 2008 (a) C/N ratio. (b) *n*-alkane chain lengths.

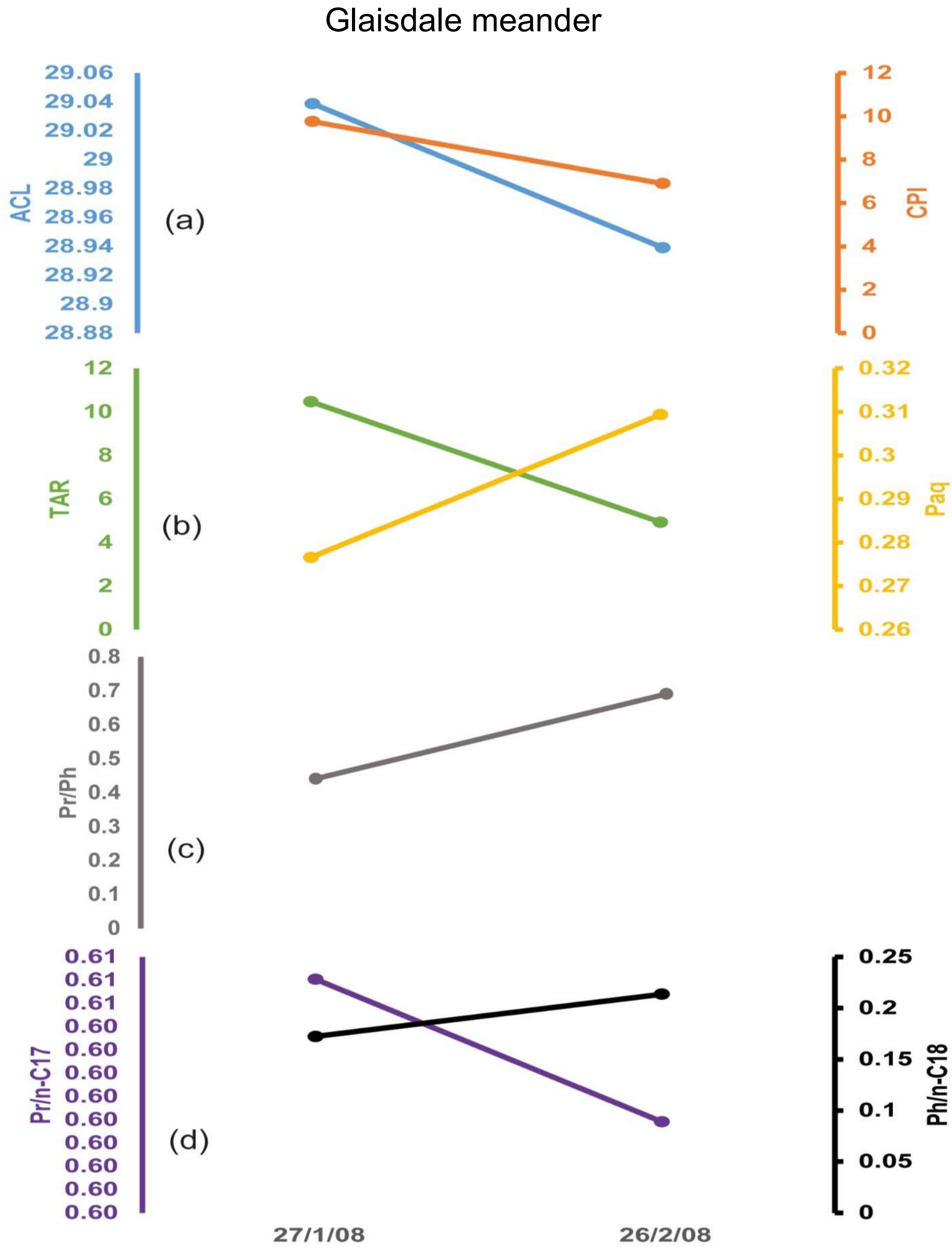


Figure 5.20: Glaisdale Meander biomarker data (a) Average chain length (ACL) and Carbon preference index (CPI). (b) TAR index and P_{aq}. (c) Pr/Ph ratio and (d) Pr/n-C_{17} ratio and Ph/n-C_{18} ratio January 2008 to February 2008.

Figure 5.21: Glaisdale Meander biomarker data (a) *n*-C_{23}/C_{25} ratio shows January 2008 to February 2008. (b) *n*-C_{31}/*n*-C_{27} January 2008 to February 2008.

5.9 Glaisdale downstream A

Data was recovered from Glaisdale downstream A on six occasions (July 2007, October 2007, 3rd December 2007, 23rd December, January 2008 and February 2008). The C/N ratio at Glaisdale downstream A is 6.61 in July 2007 yet decreases to 3.87 in October 2007 staying around this value for the rest of the months until February 2008 where there is an increase to 15.13 (Figure 5.22(a)). The dominant *n*-alkane chain lengths are C_{23}, C_{25}, C_{27}, C_{29}, C_{31} and C_{33} (Figure 5.22(b)). Figure 5.23(a) ACL shows January 2008 being the highest value. Figure 5.23(a) CPI shows the highest values in October 2007. Figure 5.23(b) shows the Tar index for most months being similar, however October is 3 times higher compared to the other months for Glaisdale downstream A. P_{aq} proxy (b) shows higher values in July 2007 and February 2008. Figure 5.23(c) Pr/Ph has its highest value in January 2008 and the lowest in October 2007. Figure 5.23(d) displays all values below 3 apart from July 2007 and February 2008 which are above 0.4. Figure 5.23(d) has its highest value in October 2007 which was above 1.0 whereas all others are below 1 and the lowest value in July 2007 below 0.5. Figure 5.24(a) C_{23}/C_{25} has its highest value in July 2007 and the lowest value in December 2007, with results for July 2007 rising above 1. All samples in Figure 5.24(b) n-C_{31}/n-C_{27} are 1 or below apart from January 2008 which has results above 1.5.

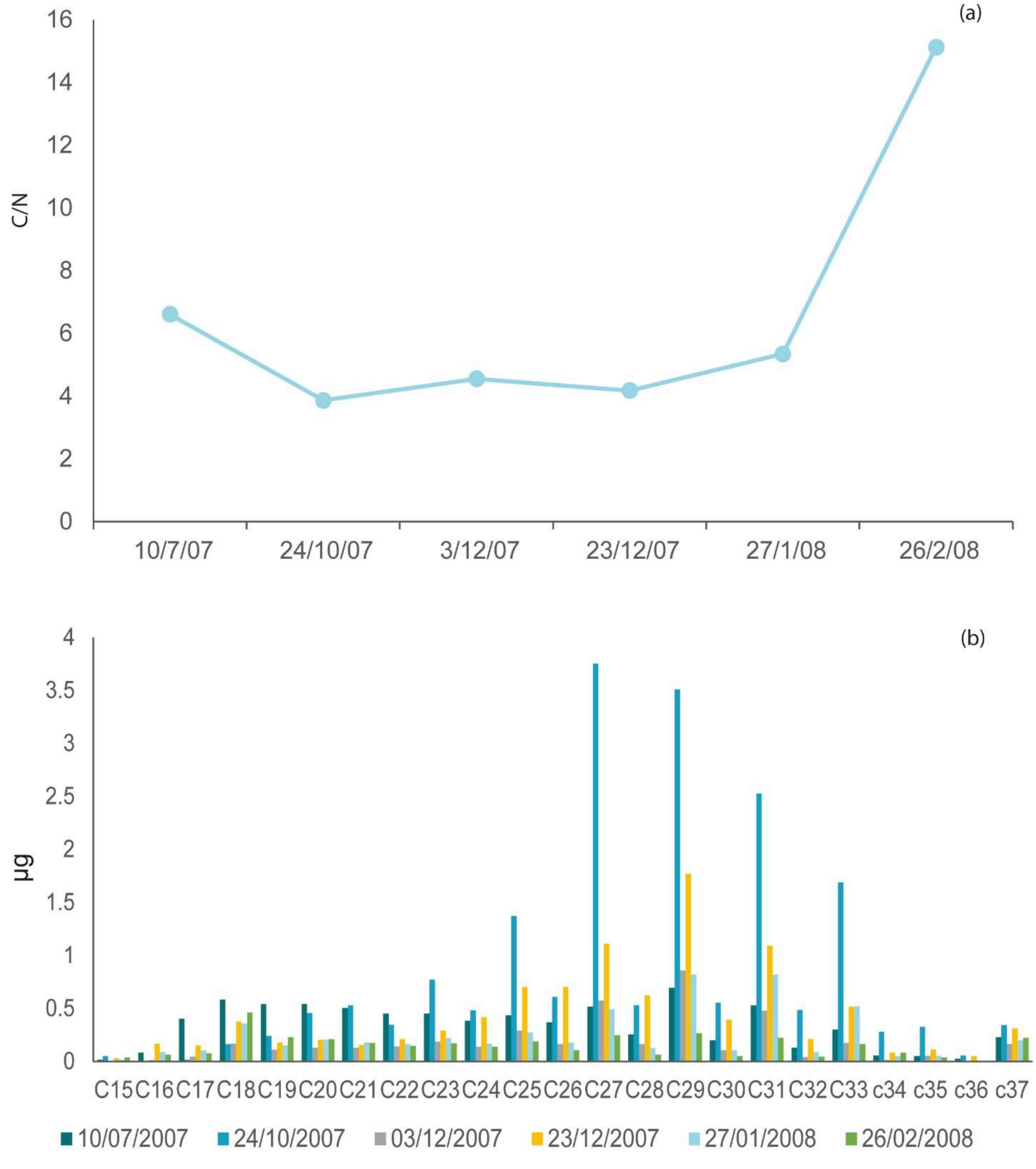


Figure 5.22: Glaisdale downstream A elemental and biomarker data for July 2007, October, December 2007 January 2008 and February 2008 (a): C/N ratio. (b): n-alkane chain lengths

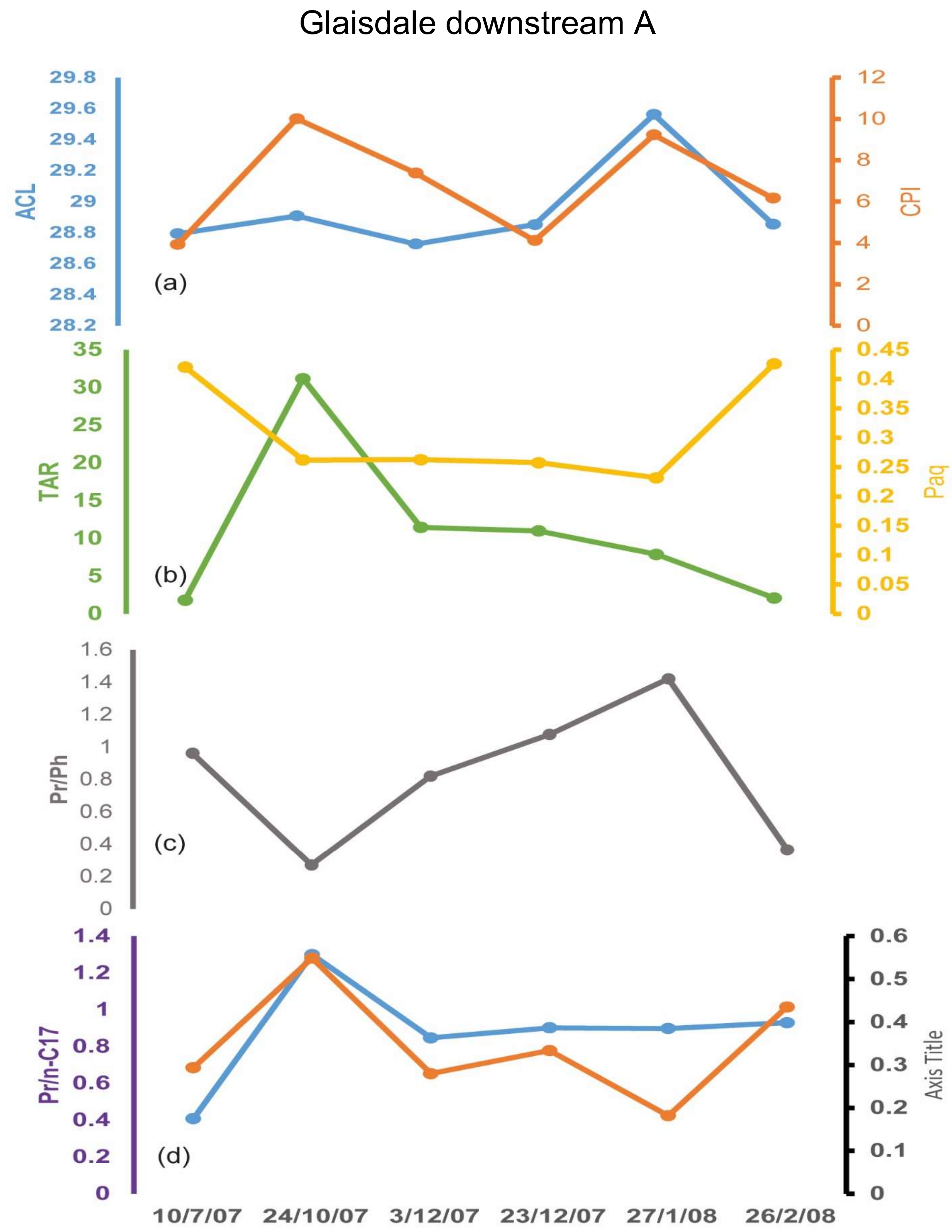


Figure 5.23: (a) Average chain length (ACL) and Carbon preference index (CPI), (b) TAR index and P_{aq} (c) Pr/Ph ratio July 2007, October 2007, early December, later date in December 2007 and February 2008. (d): Pr/n-C_{17} ratio and Ph/n-C_{18} for July 2007, October 2007, early December, later date in December 2007 and February 2008.

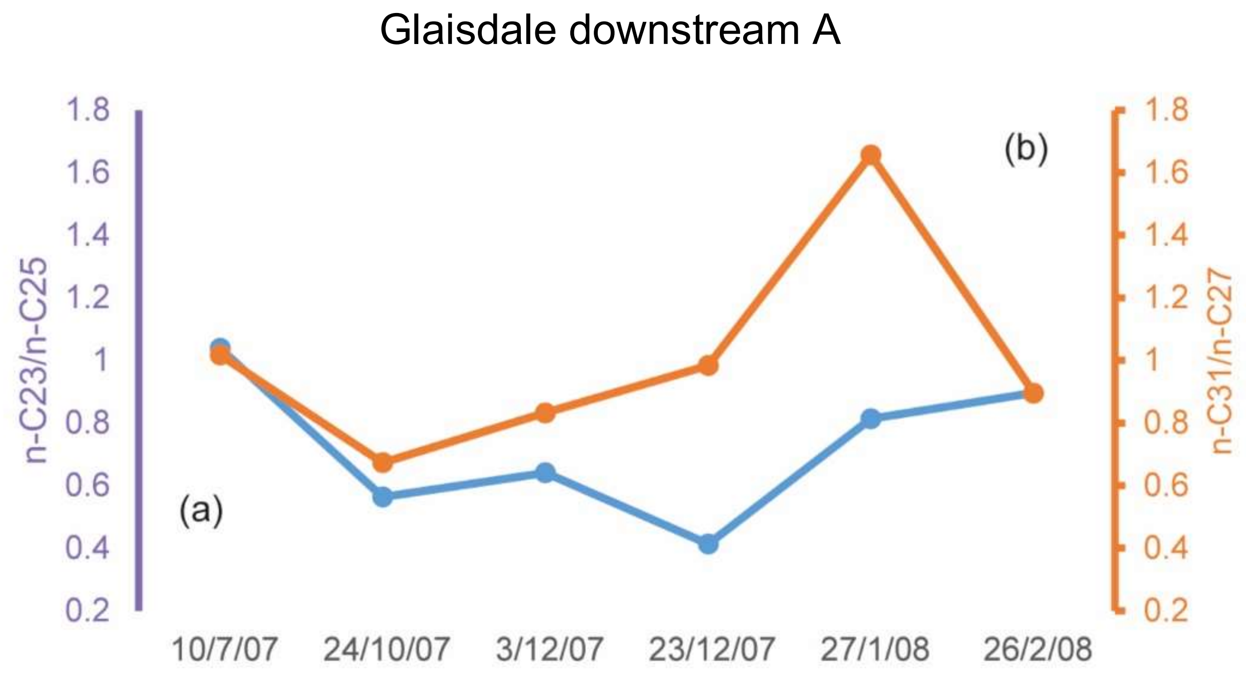
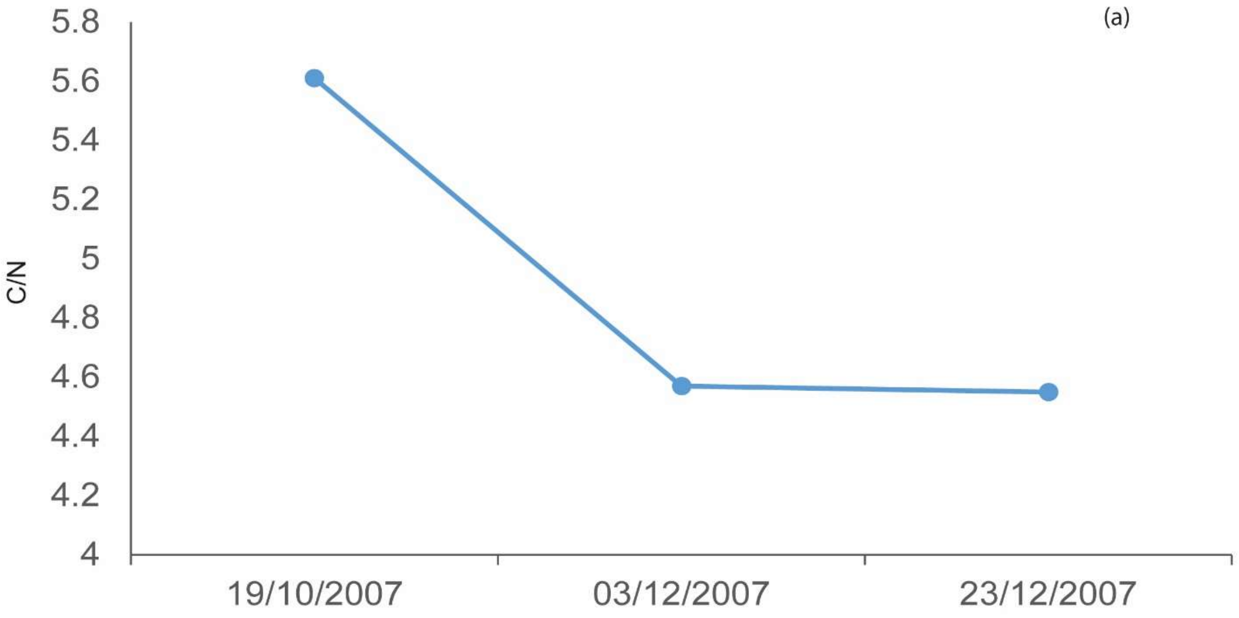


Figure 5.24: Glaisdale downstream A biomarker data (a) *n*- C_{23}/C_{25} ratio shows July 2007, October, December 2007 January 2008 and February 2008. (b) *n*-C_{31}/*n*-C_{27} July 2007, October, December 2007 January 2008 and February 2008.

5.10 Glaisdale downstream B

Data was recovered from Glaisdale downstream B on four occasions, and only three for C/N due to lack of sample (October 2007, 3rd December 2007, 23rd December 2007, January 2008 and February 2008), unfortunately for other months there was insufficient sample to analyse. The C/N ratio at Glaisdale downstream B is 5.61 in October 2007, then decreases slightly to 4.57 3rd December 2007, the decreases to 4.55 on the 23rd of December 2007, to little sample remaining to analyse C/N for February 2008 (Figure 5.25(a)). The dominant *n*-alkane chain lengths are C_{18}, C_{25}, C_{27}, C_{29}, C_{31} and C_{33} (Figure 5.25(b)), Figure 5.26(a) ACL shows February 2008 being the highest value. Figure 5.26(a) CPI shows the highest values is in the month of 23rd December 2007. Figure 5.26(b) shows the Tar index for later December 2007 is the highest by 3 times compared to the other months. P_{aq} proxy figure 5.26(b) shows higher values in October and December compared to the other two months. Figure 5.26(c) Pr/Ph highest value in October and gradually decreasing until 23rd December 2007, where it changes and starts increasing to February 2008. Figure 5.26(d) Pr/*n*-C_{17} shows all values significantly above 0.5. Figure 5.26(d) Ph/*n*-C_{18} displays its highest values in October 2007 with values reaching above 0.5 whereas all the rest are below the 0.5. Figure 5.27(a) C_{23}/C_{25} and 5.27(b) *n*-C_{31}/*n*-

C_{27} display similar trends, decreasing from the October 2007 to December 2008 then increasing to the February 2008.



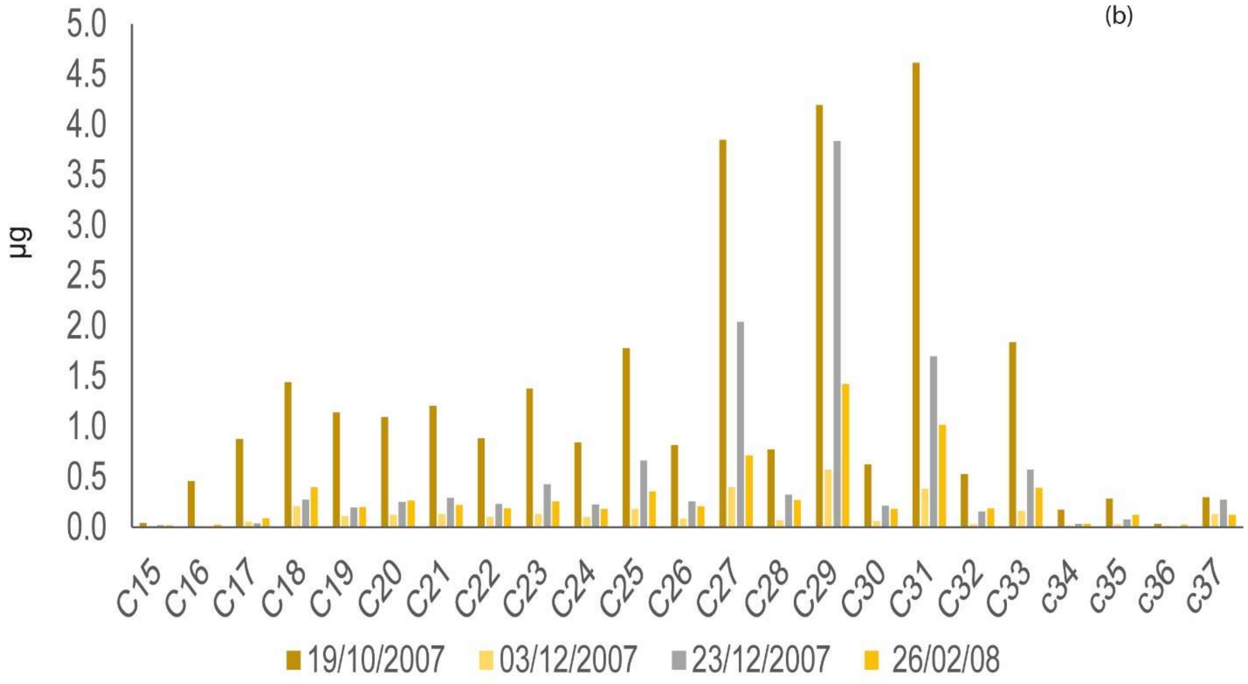


Figure 5.25: Glaisdale downstream B elemental and biomarker data for October 2007 to February 2008 (a) C/N ratio. (b) *n*-alkane chain lengths.

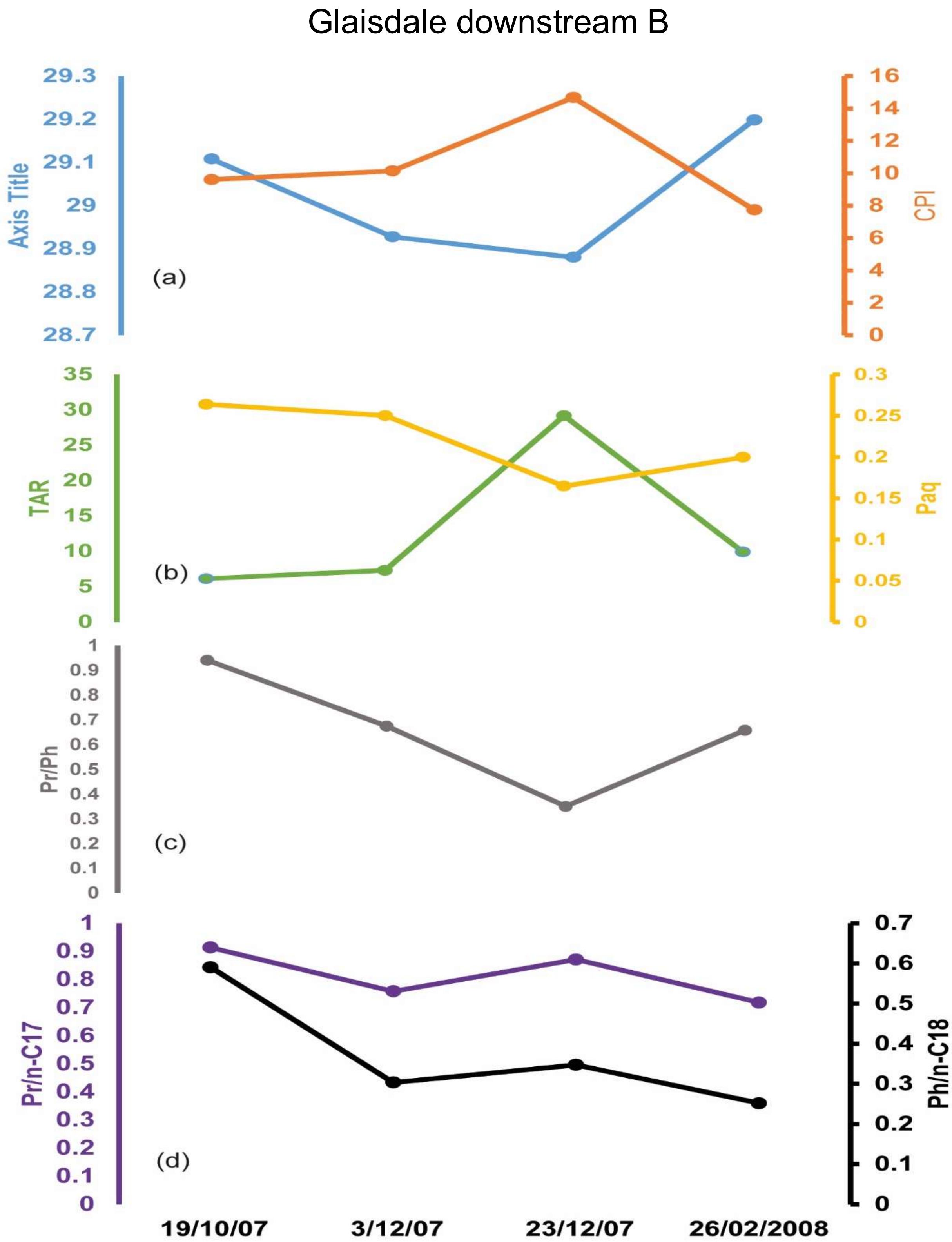


Figure 5.26: (a) Average chain length (ACL) and Carbon preference index (CPI) for October 2007 through to February 2008. (b): TAR index and P_{aq} showing a value in October 2007, earlier December 2008, later December 2007 and February 2008. (c) Pr/Ph ratio October 2007 December 2007 and February 2008. (d): Pr/n-C_{17} ratio and Ph/n-C_{18} October, December 2007 and February 2008.

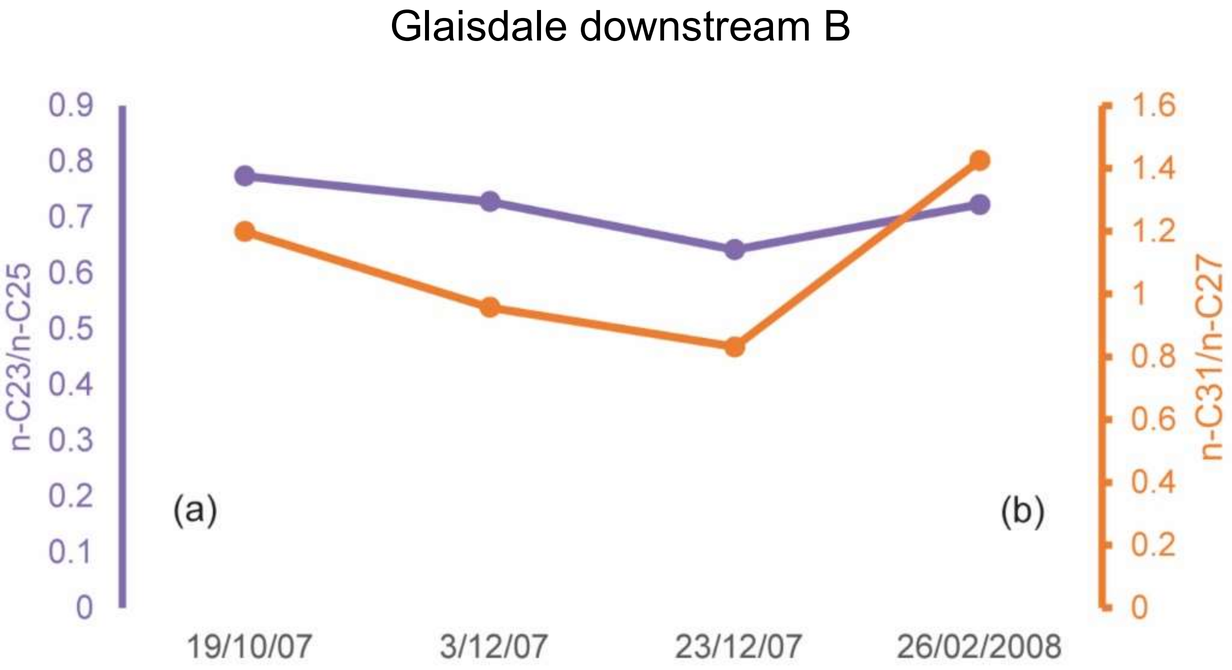


Figure 5.27: Glaisdale downstream B biomarker data (a) *n*-C_{23}/C_{25} ratio shows October 2007 December and February 2008. (b) *n*-C_{31}/*n*-C_{27} October 2007 December and February 2008.

5.11 Grosmont

Data was only recovered from Grosmont on two occasions (January 2008 and February 2008), unfortunately for other months there was insufficient sample to analyse. The C/N ratio at Grosmont is 5.16 in January 2008 yet decreases to 4.87 in February 2008 (Figure 5.28(a)). The dominant *n*-alkane chain lengths are C_{17}, C_{26}, C_{30} and C_{32} (Figure 5.28(b)), Figure 5.29 (a) ACL shows February 2008 being the highest value for the ACL at this site. Figure 5.29(b) CPI shows the highest values in January 2008, however there is no significant difference between the two months. Figure 5.29(b) TAR shows a higher value for February 2008 compared to January 2008 by 0.2. Figure 5.29(b) *Paq* where January is higher in value than February 2008. In figures 5.29(c) there is a slight decrease through to the February 2008. In figure 5.29(d) February has higher values compared to the January 2008. In figures 5.30(a) C_{23}/C_{25} and figure 5.30(b) *n*-C_{31}/*n*-C_{27} both show higher values in the month of February 2008 than the January 2008.

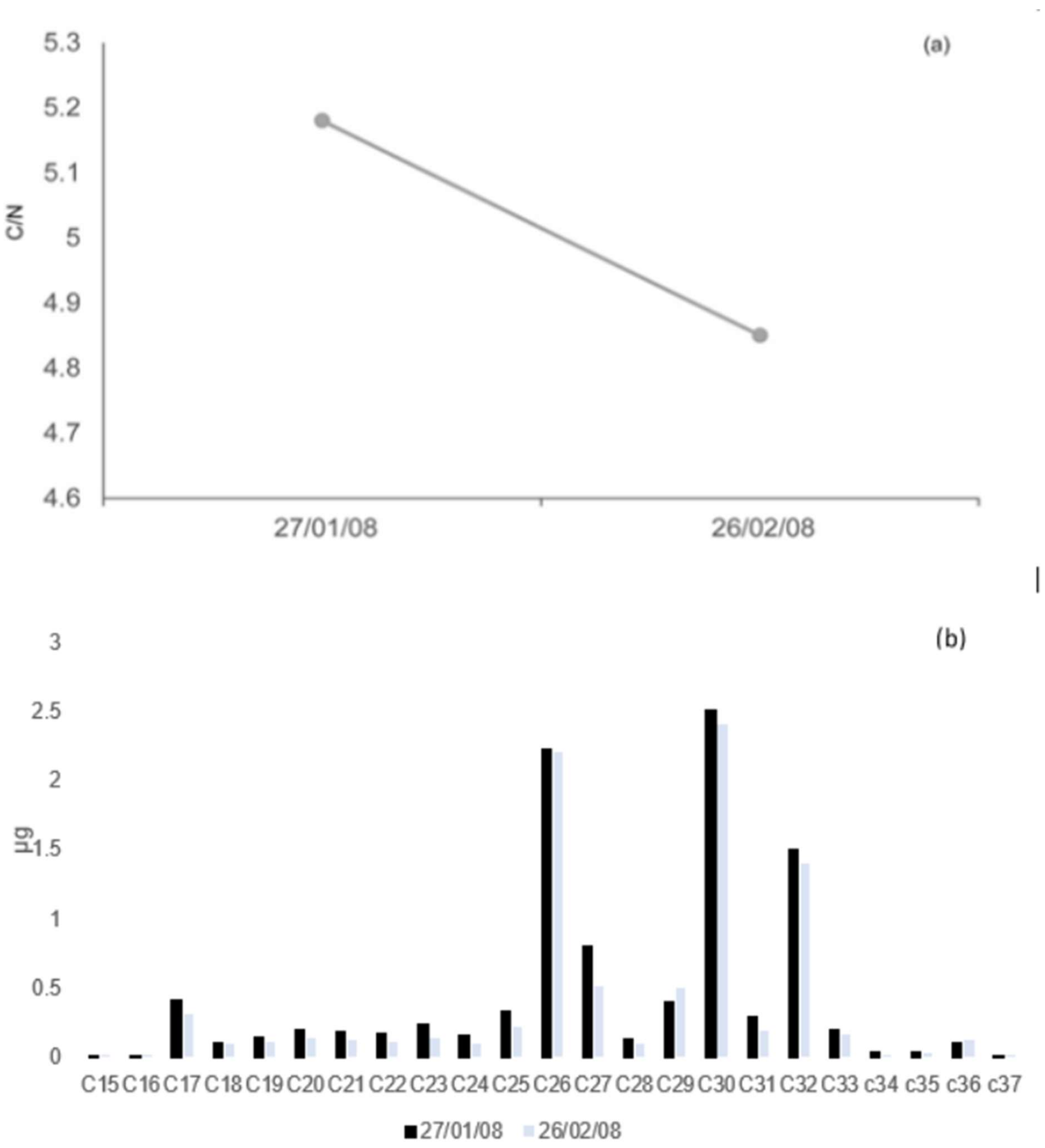


Figure 5.28: Grosmont elemental and biomarker data for January 2008 to February 2008 (a) C/N ratio. (b): *n*-alkane chain lengths.

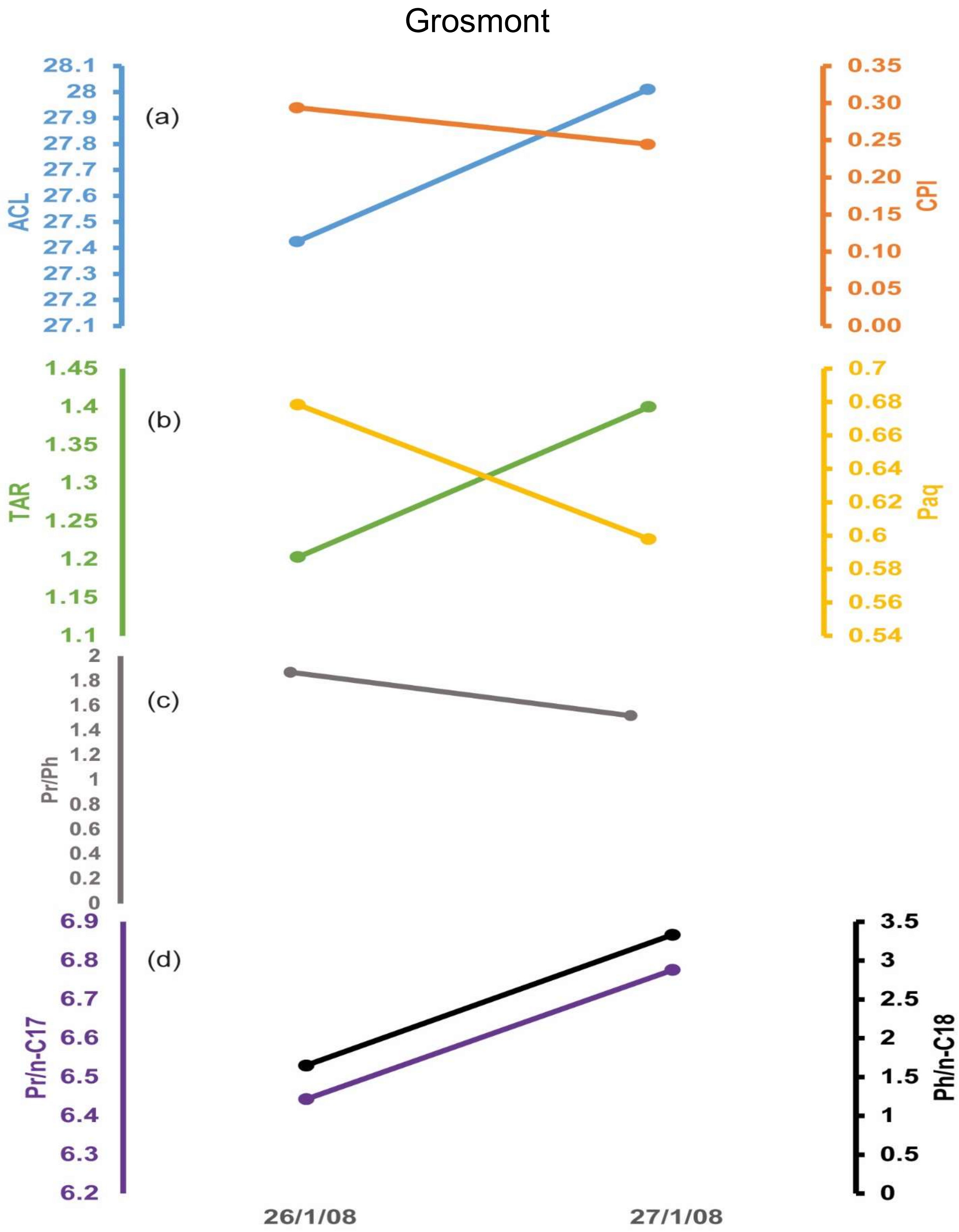


Figure 5.29: (a) Average chain length (ACL) and Carbon preference index (CPI) for January 2008 to February 2008. (b) TAR index and P_{aq} for January 2008 to February 2008. (c) Pr/Ph ratio January 2008 to February 2008. (d) Pr/n-C_{17} ratio and Ph/n-C_{18} ratio January 2008 to February 2008.

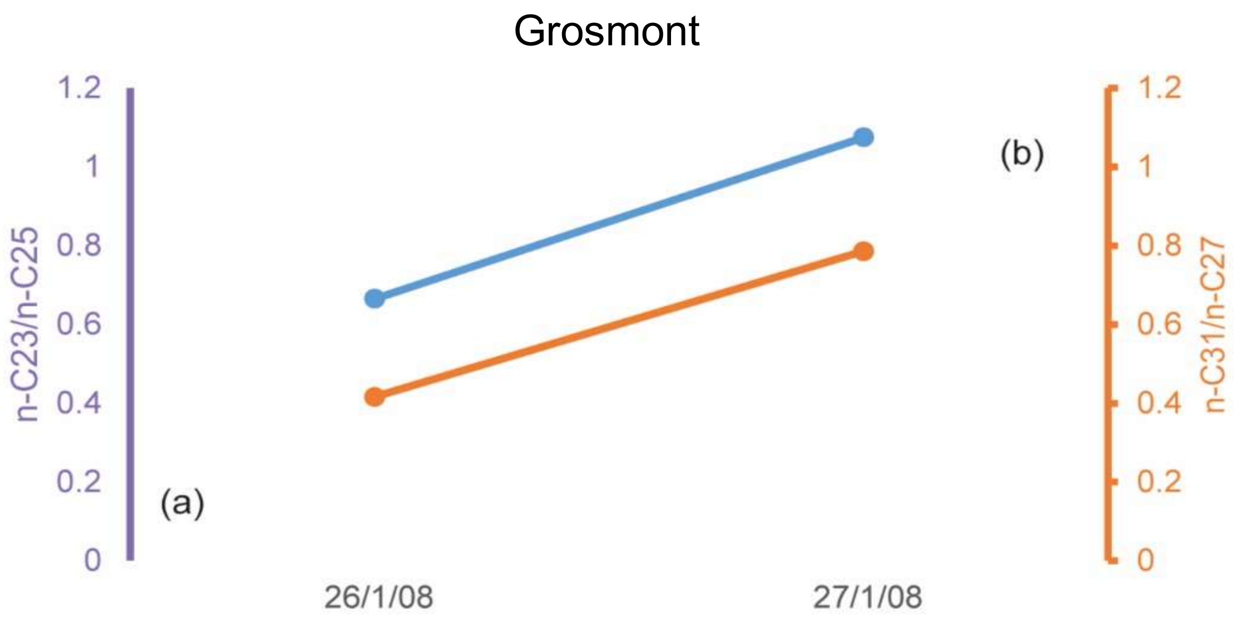


Figure 5.30: Grosmont biomarker data (a) *n*- C_{23}/C_{25} ratio shows January 2008 to February 2008. (b) *n*-C_{31}/*n*-C_{27} January 2008 to February 2008.

5.12 Results summary

Many samples were analysed along the River Esk, demonstrating biomarker analysis can be a useful method to add to our understanding and knowledge of river processes. Most samples presented *n*-alkanes with an odd over even distribution (excluding Grosmont) dominated by C_{27}, C_{29} and C_{31}. Most samples indicated a mixture of terrestrial and aquatic inputs. The ACL and CPI ratios showed the same trends through time, if one increased or decreased so did the other (Westerdale, Danby Beck, Lealholm, Glaisdale Meander and Glaisdale downstream A). TAR and P_{aq} also show, if one increased or decreased the other shows the same trend, however, each gives a slightly different indication of the dominant aquatic / terrestrial / emergent plant inputs, which is explored in more detail in Chapter 6. At Grosmont and Lealholm, these two sites show a signal of aged fossil carbon, (CPI below 1, both sites in Grosmont and at 24/12/2007 Lealholm). whereas all other sites do not display any signal for fossil carbon. There was also a noticeable difference in C/N ratios between Danby A and Danby B, where Danby A has high C/N and Danby B has low C/N, despite being sampled in close proximity, on opposing banks of a single cross-section of a river. In the following Chapter, the sources of OC and the processes affecting the different signals described here will be evaluated.

Chapter 6: Appling biomarkers to small rivers

6.1 Using biomarkers to understand OC in rivers

Previous biomarker research has focussed mainly on large river systems, lakes and marine environments (Routh *et al.,* 2006; Holland and Turekian, 2005; Ahad *et al.,* 2011, Schellekens *et al*., 2015), developing an understanding of biological process and changes that can be observed in the transport of organic matter in the environment. Biomarker techniques have not been applied to smaller rural rivers in the UK to characterise their carbon inputs. In this chapter, the results from the River Esk will be discussed with reference to the project research questions (Section 1.2), before concluding with the outcomes of the research.

6.2 Using biomarkers to identify different origins of carbon inputs into small rural rivers

The hydrocarbon fraction in the suspended sediments of the River Esk includes *n*-alkanes and isoprenoid alkanes (pristane and phytane), all of which are present at all sites (Figure 5.1). Shorter chain *n*-alkanes (C_{15}-C_{18}) show microorganism inputs, mainly from algae and bacteria (Nichols *et al.,* 2006). The C_{23}-C_{25} *n*-alkanes are mid-chain *n*-alkanes reported to be from sphagnum moss species (Nichols *et al.,* 2006, Ronkainen *et al*., (2013). However, all River Esk sites indicate a strong predominance of *n*-alkane peaks at C_{27}, C_{29} and C_{31}, and an odd/even distribution (OED) from the months June 2007, July 2007, October 2007, December 2007, January 2008 and February 2008. These patterns indicate that the dominant contribution of lipids to the River Esk is derived from higher vascular plants. For example, C_{27} and C_{29} are reported to be from trees (leaves and wood) and C_{31} and C_{33} are reported to be from grasses (Ahad *et al.,* 2011), all of which are present in the catchments. These higher plant biomarkers are likely to be introduced into the river by either erosion from the banks of the river and/or surrounding soils and vegetation, including leaves directly falling into the river. The presence of C_{23}-C_{25} *n*-alkanes is consistent with the upland peatland in this area, however the concentrations in the river sediment are small. In *Sphagnum imbricatum* samples from northern England, C_{23} and C_{25} *n*-alkane concentrations ranged from 15-40 $\mu g\ g^{-1}$ (McClymont et al., 2009), yet the highest value presented from all sites in the River Esk is 2.48 $\mu g\ g^{-1}$ (C_{25}, Danby B June 2007). The River Esk sediments therefore show a very low input of sphagnum markers, and no trends were shown with the C_{23}/C_{25} data set. However, caution is needed when using C_{23}-C_{25} *n*-alkanes to identify peat inputs, as Baas *et al.,* (2000) identified that not all sphagnum mosses are C_{23}-C_{25} dominated. Two of the sphagnum species analysed by Baas et al. (2000) were dominated by the C31 n-alkane: these are both S. fuscum and S.papillosum, are present in the North York Moors. As a result, some of the peat signal into the River Esk could be overlooked as terrestrial leaf litter if it came from one of these two sphagnum mosses. In turn, this might explain the lack of evidence for large peat inputs to the river which might be expected especially in the Commondale and Westerdale sites which lie closest to the upland bogs (Figure 3.4).

The C/N ratio alone is unable to determine where the sources of the terrestrial organic carbon contributing to the River Esk originate. However, the C/N ratios can determine algal inputs which typically ranges from ~4 to 10, and above 20 in vascular terrestrial plants (Meyers, 1997; Gonzales-Vila *et al*., 2003). The C/N ratios for the catchment as a whole (Figure 6.1) suggests aquatic input for the majority of the sites with C/N values <5. However in Figure 6.1, the sites show C/N ratio as a mix of aquatic and terrestrial sources for Westerdale (W)(January 08), Commondale (C) (all the months), Danby A (DBA) (October 07, and January 08), Danby B (DBB) (June 07, December 07 and January 08) and Glaisdale downstream A (GDSA) (February 08). In addition, an intermediate C/N ratio may reflect partially degraded plant debris eroded from soils. Across the dataset, the site DBA in July 2007 was an exception, with C/N >20 suggesting a dominantly fresh, terrestrial plant derived contribution, a clear indication of erosion especially after high rainfall, which will be discussed below for RQ3.

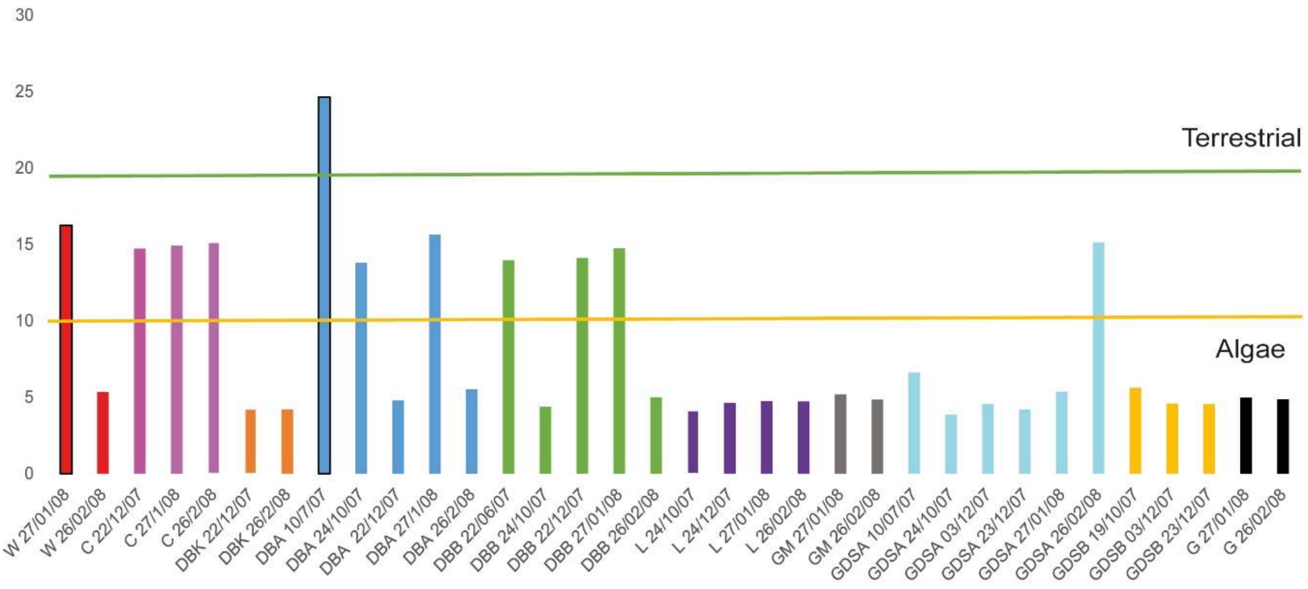


Figure 6.1: Carbon / nitrogen ratio, moving downstream and through time for all sample sites. C/N values above the green line indicate terrestrial sources and below the yellow line indicates algae inputs.

TAR and P_{aq} are two ratios used to describe terrestrial OC input and aquatic carbon input to sediments (Ficken *et al* ., 2000; Gonzales-Vila *et al.,* 2003; Sanchez-Montes *et al*., 2020; Müller *et al*., 2018; Mead *et al.,* 2005; Regnery *et al.,* 2013; Routh *et al.,* 2006) The P_{aq} ratio provides more detail than TAR, by distinguishing between floating and emergent aquatic plants, since the P_{aq} focuses only on mid chain length *n*-alkanes (down to C_{23}), whereas TAR looks at chain lengths as low as C_{15}. Some deviations of values are therefore to be expected, which is observed (Figure 6.2). There is a general relationship whereby low TAR values (high aquatic input) tend to align with high P_{aq} (high inputs from floating plants). There are some finer-scale differences in interpretation between the two ratios. For example, where TAR samples are categorised as terrestrial input, but P_{aq} presents as dominated by emergent plants, the combined signals suggest inputs of both emergent and terrestrial plants to the River Esk (excluding sites; Danby Beck, Glaisdale downstream B and Grosmont). It may also be that the P_{aq} range for emergent plants (e.g., Longbottom *et al.,* 2017; Routh *et al*., 2006; Ficken *et al*., 2000; Mead *et al*., 2005; Renery *et al*., 2013) differs between sites, perhaps reflecting different local conditions or vegetation types.

However, Peters *et al*., (2005) have also stated that TAR should be used with caution as it is sensitive to thermal maturation and biodegradation, which may also be detected using indicators such as CPI, since both are influenced by source inputs and maturity. Peters et al. (2005) also comment that if the CPI is ~1 then the fossil input could be from bedrock sources with a marine origin and/or more thermally mature sources. The TAR values for the two samples indicated in the CPI as fossil (Lealholm and Grosmont) may therefore also be from a thermally mature, marine rock (e.g., shale). A recommendation for further research is to target end member sampling in this catchment, to better understand the organic character of the local shales for the River Esk.

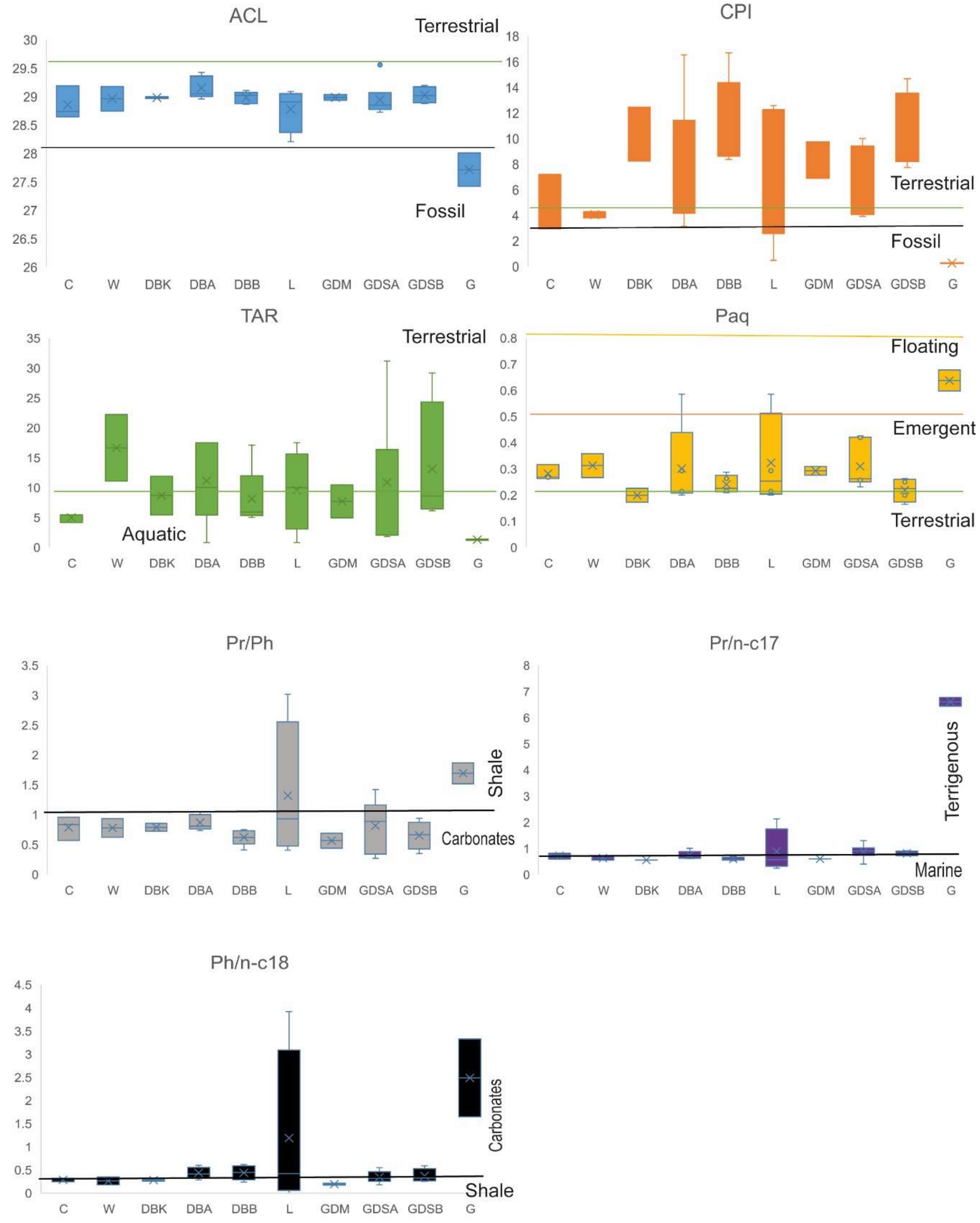
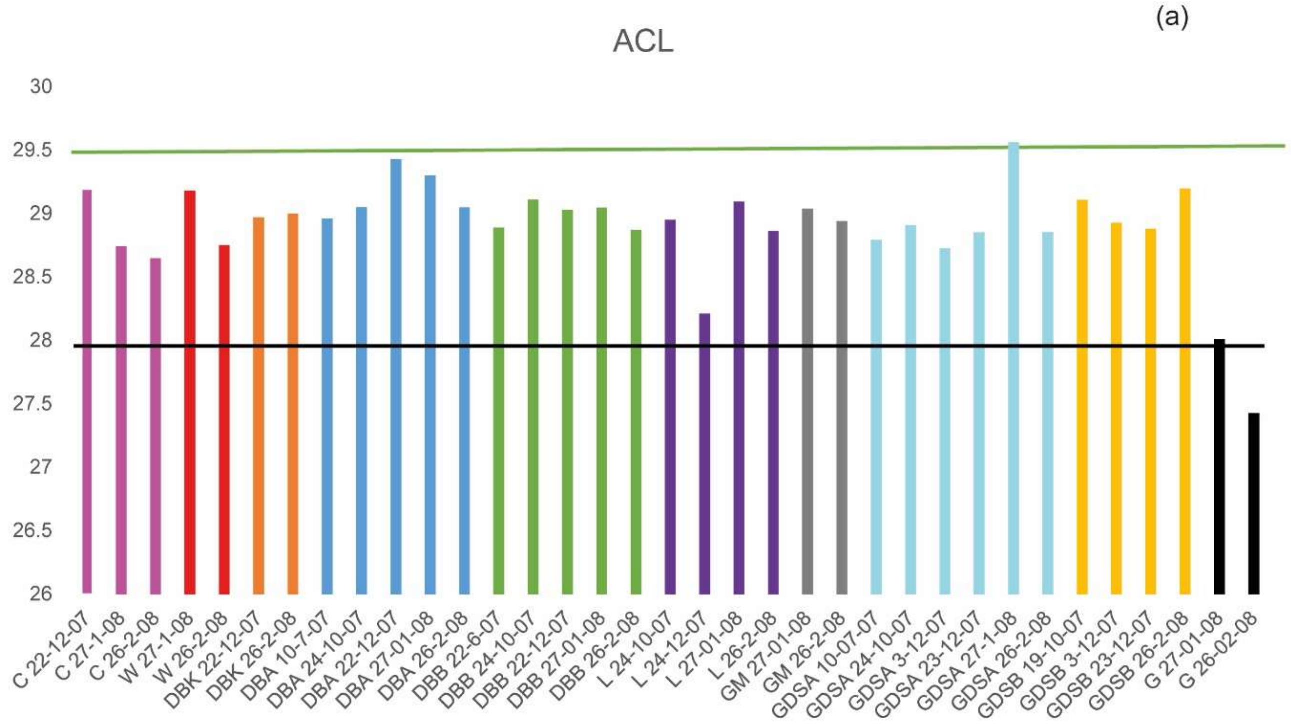


Figure 6.2: box plot, combining all values for each sampling site, ACL in blue, CPI orange, TAR green, P_{aq} yellow, Pr/Ph grey, Pr/n-C_{17} purple and Ph/n-C_{18} black. Green line depicting terrestrial input, orange line depicting emergent, yellow line depicting floating input black line depicting shale input.

To better understand the sources of the higher chain-length *n*-alkanes, their relative distributions were analysed using the ACL and CPI. The ACL and CPI may distinguish between terrestrial (fresher or relatively newly produced organic carbon) and fossil-derived carbon. It is notable that there is correlation between ACL and CPI (Figure 6.3), suggesting that the sources of long chain *n*-alkanes change with time and space. In marine samples or in larger river systems, these ratios have been used to identify terrestrial input (Figure 6.3b) although the thresholds between terrestrial and fossil inputs differ between studies (Jeng *et al*., 2006; Longbottom *et al.,* 2017; Ahad *et al*., 2011). Depending on the literature threshold, which is used, the contribution of terrestrial or fossil inputs to the River Esk is different (Figure 6.3b), although there is consistency in almost all sites having a dominantly terrestrial source, whereas Grosmont is unusual in showing a strong fossil signal ("G" data, Figure 6.3a, b), as well as one measurement from Lealholm ("L" 24-10-07). A limitation of Figure 6.3 is that the terrestrial/fossil thresholds used are not from the River Esk, but are published data from Texas (Longbottom et al., 2017) and Taiwan (Jeng *et al*., 2006). The data from Ahad *et al.,* (2011) is from the River Tyne, which more closely matches the climate regime in the River Esk and may support similar vegetation, noting that the underlying geology (and possibly the soils) are slightly different, however both sites have coal seams and limestone, however the Tyne is Permian geological period (Ahad *et al*., 2011). Figure 6.3b suggests that for most sites the River Esk sediments are dominated by terrestrial inputs, but that Lealhom and Grosmont have enhanced fossil inputs.



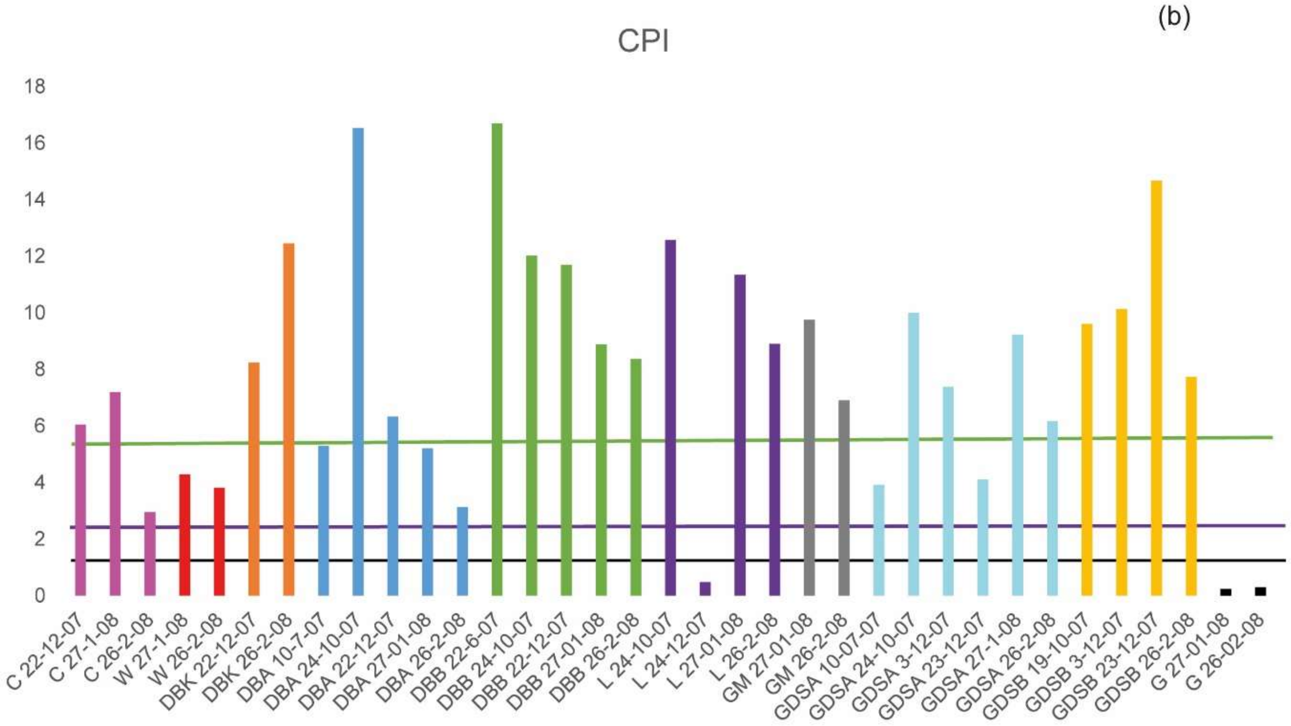


Figure 6.3: *N*-alkane proxies ACL (a) and CPI (b) values for the study sites. In both panels, values above the green line identify the terrestrial threshold, and below the black line identify the Fossil fuel threshold. In Figure 6.3b, values above the purple line identify the terrestrial range from Ahad *et al.*,(2011).

When plotting the samples collected from the River Esk the Ph/*n*-C_{18} against Ph/*n*-C_{17} data, the majority of the samples in the Ravenscar group reside in the oxidising and terrigenous organic matter environments, and the majority of the Lias group are in the mixed organic matter transitional environment, (Figure 6.4). The sample sites are divided into the underlying geological bedrock identified by British Geological Survey see figure 3.1 (BGS, 2015), highlighting the different bedrock contributions.

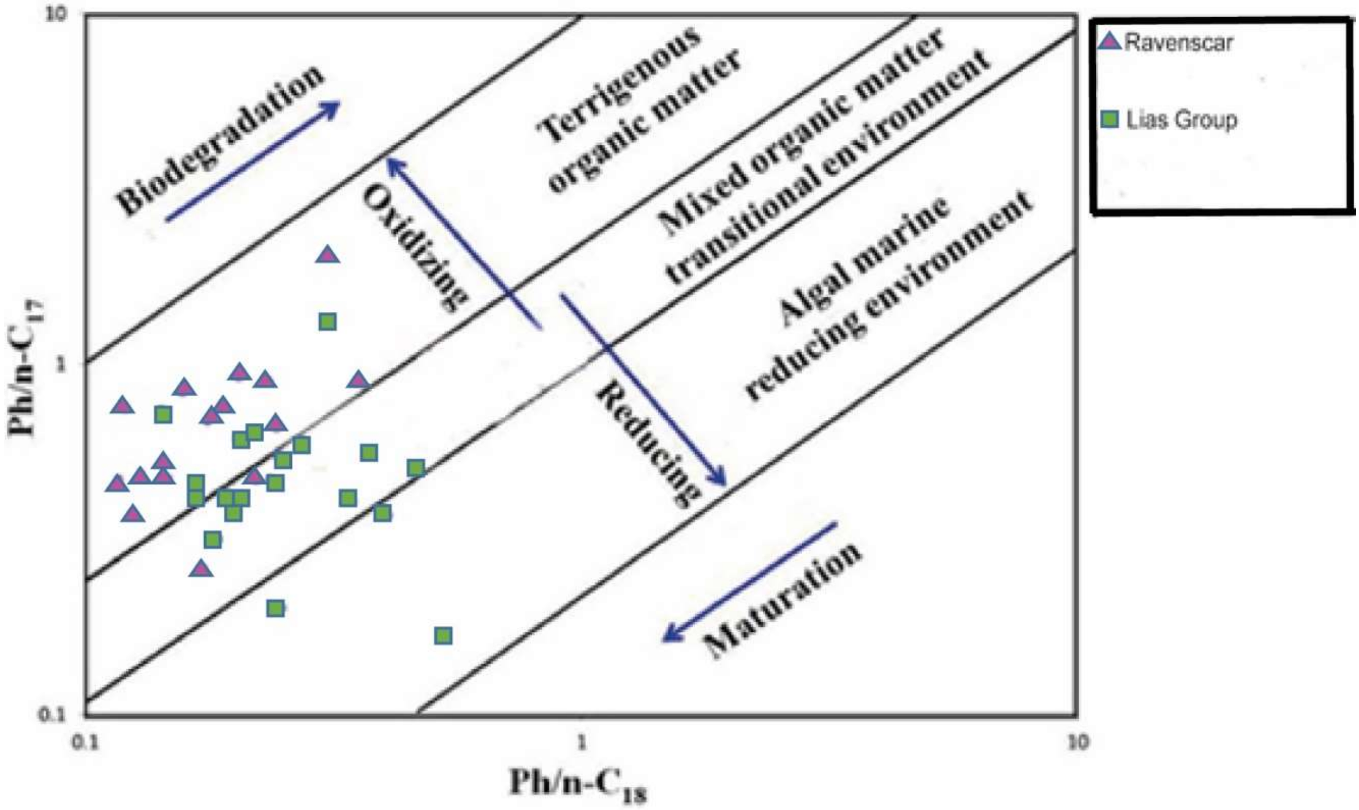


Figure 6.4: Graph taken from Hakimi *et al.,* (2018) and adapted to show data from this study. Pink triangles refer to the samples in the Ravenscar group and green squares from the Lias group.

The results from the River Esk also show that different inputs of organic carbon can be detected at a fine spatial scale by biomarker ratios and bulk sediment composition. Danby A and Danby B sites are on opposing sides of the river and have differences in biomarker ratios between December 2007 (high rainfall) and January 2008. There are consistently offsets between Danby A and Danby B (Figure 6.5): ACL and TAR at Danby A always exceed Danby B, whereas P_{aq} is always lower at Danby A. These differences suggest that one side of the river system is dominated by trees (Danby A), whereas the other side has more of a direct soil input (perhaps from agricultural land), and that Danby B's riverbank may be more unstable and susceptible to erosion (Figures 6.5). The P_{aq} values at Danby B indicate a greater presence of emergent plants than at Danby A.

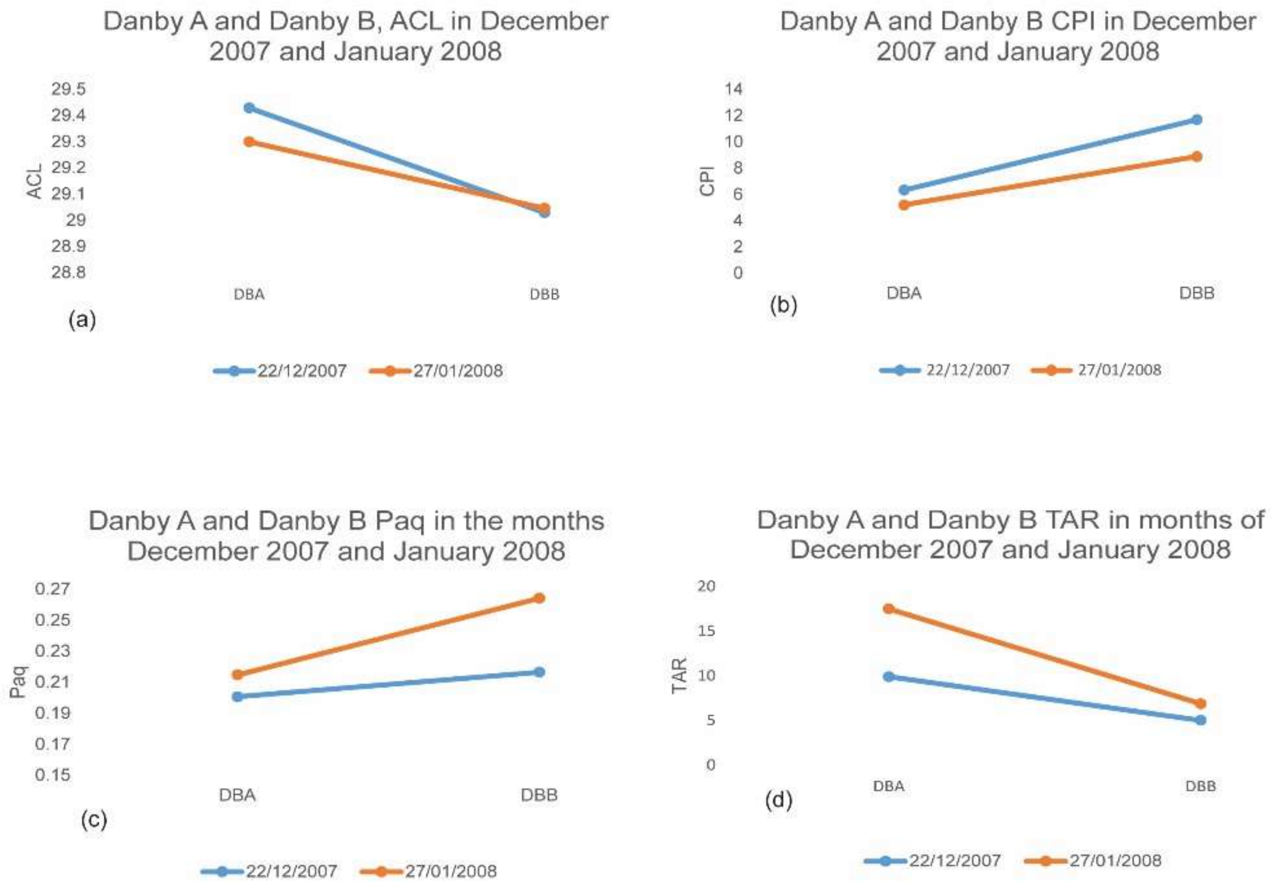


Figure 6.5: comparison between Danby A and Danby B in the wetter months December 2007 and January 2008 in the proxies; (a) ACL (b) CPI (c) P_{aq} and (d) TAR.

6.3 Using Biomarkers to record changing carbon inputs downstream, through the catchment.

To investigate the changes in biomarker distributions through the catchment, data were aggregated for each site into summary box and whisker plots (Figure 6.3). Overall, there are no clear trends to the biomarker proxies applied to the River Esk sediments moving downstream from Commondale to Grosmont. However, two sites show clear difference in organic matter source: Lealholm and Grosmont (Figure 6.3). The ACL and CPI ratios suggest that Grosmont's non-aquatic inputs are dominantly from a fossil source, although TAR and P_{aq} also highlight an aquatic floating plant input. With the available data, it is not possible to distinguish if the aquatic inputs are reflecting the properties of the fossil source, or if there is a mixture of input from modern aquatic and fossil sources.

The Pr/Ph ratios at Grosmont lie in the above 1 range. These values are consistent with published data from shales (Ahad *et al.,* 2011). In contrast, the Ph/n-C18 ratio ranges from 1 to 2.5 at Grosmont, which is consistent with published data from carbonates (Hakimi *et al.,* 2018; Killops and Killops, 2005). The catchment covers two main rock types: the Ravenscar group which, as mentioned earlier, consists of mudstone, siltstone, sandstone, limestone and ironstone, with thin seems of coal (BGS, 2015) and the Lias group which consists of limestone sandstone, siltstone and ironstone. Limestone and sandstone are located at the upper boundary (BGS, 2015). Therefore, both rock types are present in all sites in the River Esk catchment, however, indications of fossil inputs are only observed at Grosmont and Lealholm, their inputs could be explained after high rainfall causing increased erosion and transport to the river (figure 6.8). Another factor which should not be excluded is remobilisation of sediment from the bed load, which is always in the system but not always actively transported. Inputs of carbon from sedimentary rocks have been observed in very erosive settings elsewhere, for example mountain islands in Taiwan (Kao et al., 2014). In terms of the River Esk catchment, it is known that Grosmont and Lealholm were both sites of an old iron industry dating back from the 1800s, including mention of an exposed coal seam (Bewick, 1860). An explanation for the fossil signatures observed at these sites is that bedrock (likely coal) sources are more exposed, allowing un-weathered rock carbon to enter the modern river system. Grosmont is the furthest downstream site, so that one explanation is that the signal for shale has been carried downstream. However, between Lealholm and Grosmont, the sampling site Glaisdale Meander does not show high levels of Pr/Ph, suggesting that there is not an indication of the fossil carbon signal being transferred downstream; rather, remobilisation of sediments or very localised exposure of fossil OC at Grosmont seem more likely explanations.

6.4 Investigating inputs of carbon and the change over time.

Multiple factors complicated the ability of Perks (2013) to retrieve sufficient sediment samples through time, which included: high rainfall, debris blocking the sampler and low river levels (not enough sediment; Perks 2013). There are, however, three sample sites where summer, autumn and winter can be directly compared (Figure 6.6). It is notable that there is some slight difference mostly for the autumn. ACL indicates there is an increase of terrestrial input from the summer through the autumn to the winter (Figure 6.6). This pattern is consistent with more leaf litter being present on the valley floors, which could be incorporated into the river system, and is further confirmed in the *n*-C31/*n*-C27 where higher values are indicators of more grass than tree input. However, Danby B in the autumn has a higher grass input compared to the other two sites: this may reflect the woodland setting of Danby A, compared to the agricultural land found adjacent to Danby B. Other trends observed in Figure 6.6, Pr/Ph and Ph/*n*-C_{18} show that there is a carbonate input for these sites, Pr/*n*-C_{17} indicates a bedrock source with a marine signature however sources decrease in the autumn at Danby A, but increase at Danby B, which is not expected. As mentioned previously, Danby A is woodland and Danby B is agricultural, which explains the different inputs.

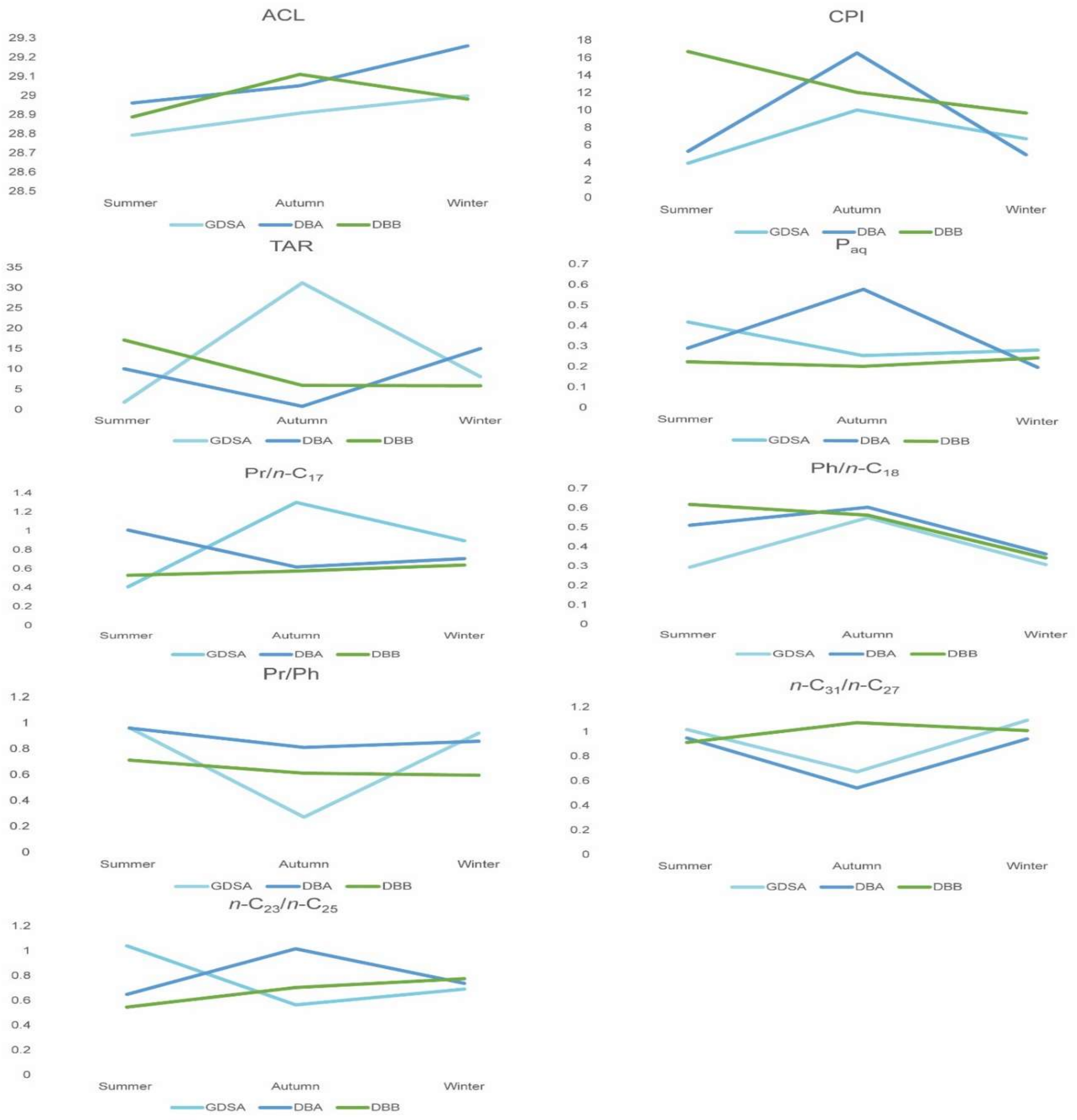


Figure 6.6: Biomarker Proxies, for the three sites that all have summer autumn and winter data set.

An initial assessment of the inclusion of the P_{aq} proxy for sphagnum moss concentrations proved inconclusive; the presence of the P_{aq} biomarkers were identified in all downstream samples which could indicate that there is an input from sphagnum moss. However, it would be expected that sphagnum moss concentrations are higher at the moorland and bog sites, but higher P_{aq} values are not observed. These results suggest that the signal further downstream could be reflecting dilution by other environmental inputs. Ronkainen *et al*., (2013) indicates that when looking for sphagnum moss and applying P_{aq} and C_{23}/C_{25} proxy to the data, if the data suggests emergent input, then the inclusion of the proxy C_{33}/C_{27} can further separate whether this could also be an indicator of sphagnum moss or emergent input. However, no trends were observed in this study, so no conclusions could be drawn from these ratios about a possible peatland input.

Figure 6.7(a) shows C/N values downstream in the month of December 2007, January 2008 and February 2008. It is clear in the month of December 2007 at the Commondale site, that the difference in values across sites might indicate a higher moorland input into the river at Commondale. The C/N value is vastly different compared to the other sites, but this unusual Commondale signal could be attributed to erosion due to very unstable river banks from the rainfall which occurred in December 2007. It is also notable in Figures 6.7(a) and 6.7(b) that the Lealholm site C/N values are predominantly lower which coincides with a change in land use between Danby and Lealholm, with the development of agricultural fields (cereal crops). In February 2008 Danby Beck, Danby A and Danby B, showed low C/N ratio <6 and high ACL >28.8, values which Renery *et al.,* (2013) attributed to submerged floating vegetation. The distinctive trends at these sites during February 2008 could be explained by the high rainfall washing the floating vegetation into the river and transporting it downstream (figure 6.8).

Carbon and Nitrogen, December 2007

January 2008

February 2008

Figure 6.7: (a) C/N values for December 2007. Sites are plotted moving from the catchment head (left) to downstream sites (right). The horizontal line indicates C/N value of 5. (b) C/N values for the month of January 2008. The sites are plotted moving from the uppermost catchment (left) to downstream sites (right). (c). C/N values for February 2008. The sites are plotted moving from the headward catchment (left) to downstream sites.

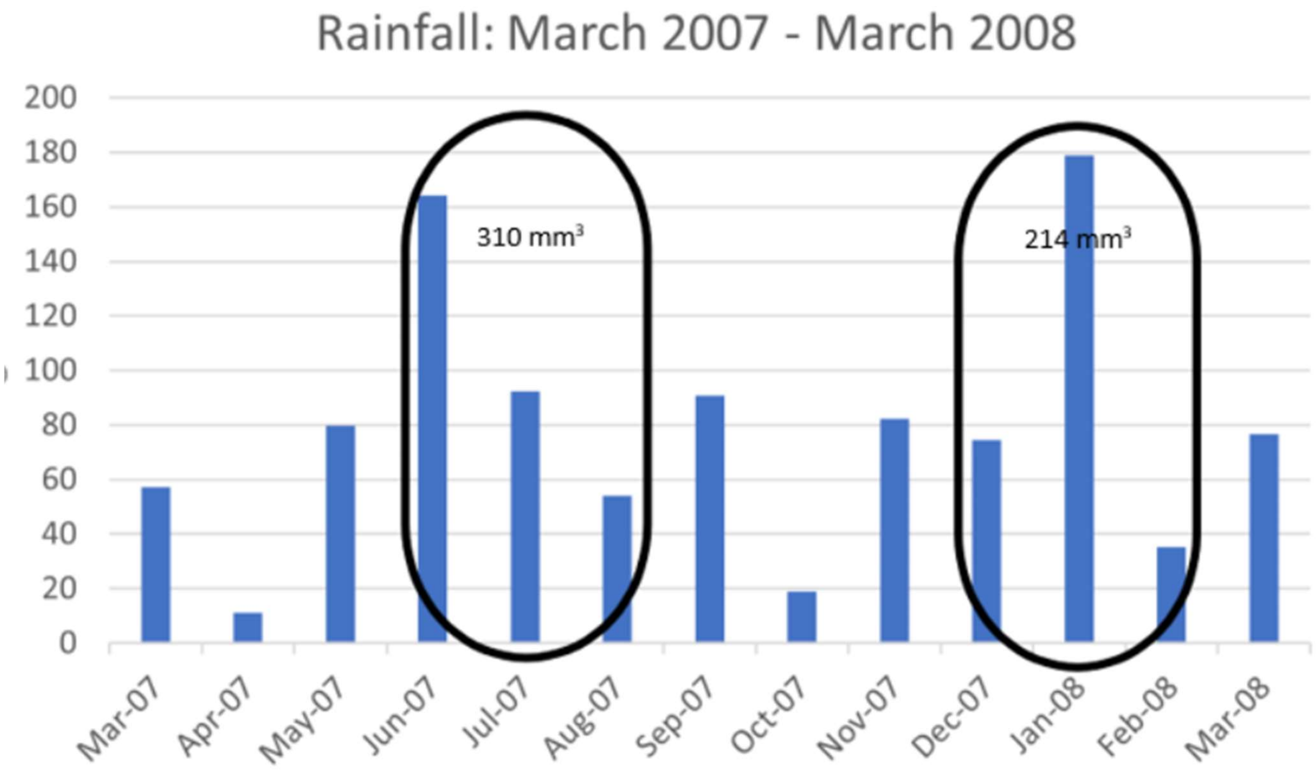


Figure 6.8: Rainfall for the Summer and Winter 2007/2008 highlighting the total for each period, (Met office, 2009).

Regnery *et al.,* (2013) concluded that combining ACL, CPI and P_{aq} could distinguish the distribution of vegetation over time, as well as to observe the impact of temperature on the vegetation signal. In their study, the lower ACL values decrease with decreasing temperatures, noting that the palaeoclimatic significance of this proxy requires further research. Findings in this study contradict what was observed in Regnery *et al.,* (2013): when applying their approach to the River Esk no visible trends were observed with the ACL ratio that could confirm the proxy being used as a climate indicator. The ACL temperature proxy may only be associated to a warmer climate or with different local vegetation, as this trend was not seen in the River Esk dataset.

Therefore, answering RQ3, there is some noticeable difference between the seasons. However, due to low numbers of sampling site samples, no clear distinctions can be made. Differences which were observed through the seasons did, however, show that during the period of this study there were similarities between summer and winter, which are interpreted here to be driven by the high volume of water reaching the catchment in both seasons. It would therefore be interesting for further work to generate a continuous time series to test whether, for instance, there is always typically high rainfall in both summer and winter months. Using the knowledge taken from this research project, for example knowing which sampling sites become problematic to retrieve samples in high rainfall, an alternative sampling protocol could be implemented so that there are no missing samples from the data set.

This research has identified that in the sites Grosmont and Lealholm, there is a fossil input from the coal in the area. This fossil carbon is not transported down stream (where it would potentially be reburied in the ocean), instead it remains *in situ*, where it could potentially be released back to the atmosphere as CO_2 or reburied in the river sediments (Galy & Eglinton, 2011). However, if the carbon is being released back into the atmosphere this project confirms the proposal that small rural rivers are overlooked when considering world carbon fluxes (Biddanda, 2017). UKCIP predict that in the future the North York Moors will be wetter in the winter months and warmer in the summer, therefore more carbon eroded into the river system with the potential of more aged carbon being released back into the atmosphere (Jenkins *et al.,* 2009). The importance of including small rivers in the global carbon budget, especially this study area as there is a peat store which could be at risk of releasing "old" carbon back into the carbon cycle like was previous mentioned that others found in their studies (Evans *et al*., 1999; Holden and Burt, 2003; Lees, 2018).

6.5 Limitations

There were a number of limitations in this study. The low sample resolution of this study highlights the need of further studies to improve the spatial and temporal biomarker characterisation in this area. Sample distributions were limited spatially and temporally, either by a restricted accessibility to collect sample due to high rainfall (Perks, 2013), or because samples were not abundant during collection. As a result, for some sites a full suite of samples and dates are not present. The collection of samples spanning a whole year, or the addition of samples to fill gaps in missing sampling dates, could have helped increase the coverage of samples. Samples with very little sediment could also have been combined over several days or sampling periods, to generate enough weight of sediment for the analyses in this study, recognising that this might lead to longer periods of time being represented. The inclusion of a whole year of all the samples may have shown more trends seasonally, especially if there were distinctive times of year that certain sources of sediment are introduced into the river system. Another option could be to change the sampling techniques either in high rainfall and low rainfall.

The interpretations presented here also rely on literature sources for identifying likely end member contributions to the catchment, which have shown some success (e.g., Figure 6.3) but may be better constrained by analysing existing soils, vegetation and bedrock in the River Esk itself. The analysis could also have considered broadening the biomarkers to be analysed, including sterols or fatty acids which are also known to have some specific vegetation and bedrock sources (Galy and Eglinton, 2011; Naafs *et al*., 2019; Tao et al., 2021). However, a detailed assessment of these indicators was beyond the scope of this thesis.

6.6 Future research

The interpretations presented here rely on literature sources for identifying likely end member contributions to the catchment, which have shown some success (e.g., Figure 6.3) but may be better constrained by analysing existing soils, vegetation and bedrock in the River Esk itself. The analysis could also have considered broadening the biomarkers to be analysed, including sterols or fatty acids which are also known to have some specific vegetation and bedrock sources (Galy and Eglinton, 2011; Naafs *et al*., 2019; Tao et al., 2021), or Branched glycerol dialkyl glycerol tetraethers (brGDGT) which are membrane lipids of soil bacteria, which have been used to trace soil OC from source in small rivers in the UK (Guo et al.,2020). However, a detailed assessment of these indicators was beyond the scope of this thesis.

Chapter 7: Conclusions

7.1 Conclusion

The aim of this investigation was to determine sources of organic carbon input into a small rural river in the UK. This study has identified sources of carbon input into the river system both spatially and temporally. A suite of biomarker ratios, alongside C/N ratios, were used to explore the OC sources to the River Esk. In answer to RQ1, this work confirms that that the use of multiple biomarker indices a good indicator of the origins of OC to a small UK river and can be used to differentiate between young and old carbon sources.

Different biomarkers were able to identify multiple sources of carbon input into the River Esk including higher plant, peatland plant, aquatic plant and fossil organic matter inputs (research question 1). The biomarker ratios applied here show that there is minimal variation in organic matter characteristics (and likely sources) moving downstream through the catchment. For most samples, the proxies indicate a mix of terrestrial and emergent plant inputs. However, data isolated two sites (Lealholm and Grosmont) which gave evidence for industrial activities (Bewick,1860) impacting the signals, with an input of fossil carbon from bedrock, which is attributed here to erosion of a shale source (Peters *et al.,* 2005) (research question 2).

There are no distinctive trends observed seasonally, but this likely reflects the limited data available for comparison work to be achieved. The only seasonal comparison (summer, autumn and winter) was in three samples which were collected at Danby A, Danby B and Glaisdale downstream A, but unfortunately not from the same month (Danby A 10th July 2007 and Danby B 22nd June 2007) thus limiting the comparison across the sites. The only comparison that can be drawn is that in the summer and winter months both had high rainfall where biomarker ratios showed similar trends. In autumn the data did not follow the same pattern as summer and winter. This cannot be confirmed as a distinctive trend with only three sample data sets (research question 3).

The inclusion of biomarkers does however demonstrate that they can identify sources of carbon to a small river; this additional information will be useful to help understand the river system process. This could be beneficial in many ways of developing our knowledge and understanding of fluvial process and may highlight areas of erosion that were not necessarily picked up in through other analyses, as observed with the identification of a fossil signal in the Lealholm and Grosmont sample sites.

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