UNIVERSITY OF SOUTHAMPTON

FACULTY OF SOCIAL, HUMAN AND MATHEMATICAL SCIENCES

Geography and Environment

Volume 1 of 1

Palaeoenvironmental reconstruction of Poole Harbour water quality and the implications for estuary management

by

Laura Helen Crossley

Thesis for the degree of Doctor of Philosophy

July 2018

UNIVERSITY OF SOUTHAMPTON

ABSTRACT

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Eutrophication and sedimentation affect estuaries globally as catchments are developed by humans and sea levels rise. Estuaries are complex open systems with lag times between environmental cause and effect that may be longer than is identifiable using available instrumental data series which span fewer than 50 years. Managers are often faced with short term datasets and modelling studies to develop strategies to govern these systems which potentially do not capture the long term complex processes of the system. Longer term datasets which monitor environmental change may improve understanding of estuary biogeochemistry and ecosystem responses.

This thesis uses palaeoenvironmental techniques to reconstruct the last ca. 150 years of nutrient and ecological development of Poole Harbour, southern England. There is established concern regarding eutrophication due to a range of human activities. Managers are challenged with setting limits to macronutrient supply that will not adversely affect the estuarine ecosystem, though unambiguous data supporting the process of eutrophication has yet to be presented.

Results showed that agricultural practices post WWII increased sediment and nutrient delivery to the estuary, consequently increasing sediment accumulation rates and promoting algal growth. Pigment and geochemical evidence indicates eutrophication of the estuary post ca. 2000 AD. A water quality indicator proxy was developed which demonstrated a lag time of ca. 20-30 years between catchment drivers and water quality decline. The importance of lag times and step-change behaviour within the Poole Harbour system are stressed as being critical in the formulation of future management interventions.

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Academic Thesis: Declaration Of Authorship

I, Laura Helen Crossley, declare that this thesis and the work presented in it are my own and has been generated by me as the result of my own original research.

PALAEOENVIRONMENTAL RECONSTRUCTION OF POOLE HARBOUR WATER QUALITY AND THE IMPLICATIONS FOR ESTUARY MANAGEMENT

I confirm that:

1. This work was done wholly or mainly while in candidature for a research degree at this University;
2. Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;
3. Where I have consulted the published work of others, this is always clearly attributed;
4. Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work;
5. I have acknowledged all main sources of help;
6. Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself;
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   Crossley, L.H., Langdon, P., Sear. D., Dearing, J. & Croudace, I. (In Review) Long term development of the Poole Harbour ecosystem: a case study from Holes Bay. In: Humphreys, J. & Clark, R. (eds) Marine Protected Areas: Evidence, Policy and Management. Elsevier.

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Acknowledgements

First, I would sincerely like to thank my supervisory team Prof Peter Langdon, Prof David Sear and Prof John Dearing. Thank you for your continued support, encouragement and advice throughout this process, it really has been appreciated. And I'm sorry I repeatedly picked days with gale force winds to be out in the boat on Poole Harbour!

Thank you to Wessex Water and Geography and Environment at the University of Southampton for their funding of this research. I would like to thank the following organisations who have helped with this project in the form of sharing information, advice and field work permissions; Wessex Water, National Trust, Dorset Wildlife Trust, Natural England, Borough of Poole, Poole Harbour Commissioners, RSPB, Poole Harbour Study Group and Poole Harbour Delivery Group. Thank you also to Andy House with helping gather information.

I would like to thank Peter Morgan, Hayley Goodes and Dr Tom Bishop for your technical support. Thank you for your assistance in the lab and field, I'm sorry I made you move the big boat so many times! I would also like to thank the assistance of Dr Rob Collier and Dr Jon Hassall for their assistance in the field. Thank you to Charlotte Clarke, Dr Catherine Langdon and Prof Rob Scaife for your assistance in the lab, you certainly provided entertainment while counting all those SCPs and diatoms. And Cath, thank you for teaching me there is so much enjoyment in what people have for lunch! I would like to thank Prof Melanie Leng, Prof Suzanne McGowan, Prof Ian Croudace, Dr Nigel Cameron and Dr Suzanne Maclachlan for your expertise and advice. Thank you to Mark Dover, Kate Rawlings and Luke Brown for helping me with my GIS and map skills. Dr Thierry Fonville, I would like to express my sincere thanks for your time and patience helping me with my diatoms, needless to say if you hadn't, they wouldn't have been counted.

To the friends I've made while doing this PhD, thank you! Nay, I'm very glad we became friends during the short time we knew each other in Southampton, luckily our respective relocations have meant we can continue enjoying our favourite pastimes together again. Ben, thank you for the Tivoli experience and memories. Elaine, thank you for our coffee, cake and chats on a Thursday. Charlotte, Roseanna and Ali, thank you so much for being the noisy office next door, you really helped with the productivity and you were always there for a chat. To David and Jon, you were my first friends in Southampton, thank you for all the entertainment and fun times we had together, even though I know you'll never play Articulate with me again. Harry and Kate, thank you for being my 'office buddies', you are great friends who are always encouraging and supportive, I feel lucky to have had you cheering me on to the end.

Kerry, James, Harvey and Amelie. I was so lucky to have you in Southampton when I didn't know anyone, I mean who else would have given me a few shots (and the rest) of limoncello the night before my interview?! You made moving to Southampton so much easier and I can't say what enjoyment I've had with you all. Thank you for always being around the corner, for providing me with a southern home when I needed it and for so many great memories.

Mum and Dad. Thank you for always being there, whether I needed to laugh or cry. Even though I moved to the bottom of the country, I have always felt your love, encouragement and support and I could not have gotten here without you. Thank you for all your help over the years that meant I could get to this stage.

Finally, to Rob. You have spent countless hours proof reading, talked things through with me when I was stressing and calmed me down during the tears and tantrums; you made sure I got to this stage. Thank you for always being there and always offering to help, I mean you went barefoot into Poole Harbour to get a core for me! I was so lucky to have met you during our time in Southampton doing our PhDs and we'll always have our love of SCPs! I just want to say thank you for your unconditional love and support.

For Mum and Dad

"You're braver than you believe, and stronger than you seem, and smarter than you think"

-A.A. Milne

"If we knew what it was we were doing, it would not be called research, would it?"

-Albert Einstein

Definitions and Abbreviations

δ	delta (where comparing ratio of isotopes in a sample to a standard)
^{12}C	Carbon-12 (radioisotope)
^{13}C	Carbon-13 (radioisotope)
^{14}N	Nitrogen-14 (radioisotope)
^{15}N	Nitrogen-15 (radioisotope)
^{137}Cs	Caesium-137 (radioisotope)
^{210}Pb	Lead-210 (radioisotope)
^{226}Ra	Radium-226 (radioisotope)
^{238}U	Uranium-238 (radioisotope)
^{60}Co	Cobalt-60 (radioisotope)
AD	Anno Domini
*a*DNA	ancient DNA
AMS	Accelerater mass spectrometry
Br	Bromine
BROC	Broccoli (isotope standard)
C	Carbon
C/N	Carbon/Nitrogen ratio
Ca	Calcium
Ca.	Circa
CA	Correspondence Analysis
CAP	Common Agricultural Policy
CF:CS	Constant Flux: Constant Sedimentation
Cl	Chlorine
CO_2	Carbon dioxide
CONISS	Constrained Incremental Sums of Squares
Cu	Copper
DAIN	Dissolved available inorganic nitrogen
DCA	Detrended Correspondence Analysis
DIN	Dissolved inorganic nitrogen
DOC	Dissolved organic carbon
DWI	Drinking Water Inspectorate
EWS	Early warning signals
H_2O_2	Hydrogen peroxide
HCl	Hydrogen chloride

HCO_3^-	Bicarbonate
HF	Hydrogen fluoride
HNO_3	Nitric acid
HPLC	High-performance liquid chromatography
ITRAX	High resolution XRF core scanner
LOI	Loss on ignition
MoD	Ministry of Defence
MS	Magnetic susceptibility
N	Nitrogen
OM	Organic matter
Pb	Lead
PCA	Principal Components Analysis
PHCI	Poole Harbour Catchment Initiative
POC	Particulate organic carbon
r	Correlation coefficient
r^2	Coefficient of determination of a linear regression
RACER	Rivers and Coastal Environments Research
Rb	Rubidium
RSJOS	Regional safe and just operating space
SAR	Sediment accumulation rate
SCP	Spheroidal carbonaceous particle
S.D.	Standard deviation
S.E.	Standard error
Si	Silicon
SJOS	Safe and just operating space
SoR	Start of record
SOS	Safe operating space
SSSI	Sites of special scientific interest
STW	Sewage treatment work
Ti	Titanium
UVR	Ultraviolet radiation
WFD	Water Framework Directive
XRF	X-ray fluorescence
Zr	Zirconium

Chapter 1 Introduction

1.1 Project rational

1.1.1 Estuarine palaeoenvironmental reconstructions

Estuaries are important transitional environments where the freshwater from rivers meet the saline water of the ocean (Cooper, 1999; Leussen & Dronkers, 1988; Ross, 1995). There have been increased socio-economic pressures on the Earth's system, including estuaries, in recent decades (post 1950) (Steffen et al., 2015a). Estuaries are under pressure from sea level rise, increased human populations and intensification of farming and industry (Mimura, 2013; Cooper, 1999; Jickells et al., 2000; Korpinen et al., 2012). Many estuarine environments worldwide are exhibiting declines in biodiversity and showing signs of eutrophication as they receive an increased abundance of nutrients, mainly nitrogen and phosphorus, typically from anthropogenic sources, such as Sewage Treatment Works (STW) effluent and industrial discharges (Cooper, 1999; Sullivan, 1999). It is estimated that approximately 60% of the world's population live within coastal margins, not including the industries which are situated within these areas (Alongi, 1998). If estuaries are altered to unfavourable states, e.g. through eutrophication, the ecosystem services these environments provide to residents and businesses, e.g. water filtration and biodiversity, may be detrimentally impacted. It is therefore important that estuaries are managed appropriately to ensure these services can be supplied and possibly enhanced over the coming decades. A thorough understanding is needed of how relationships between drivers, e.g. catchment changes, and response, e.g. estuary water quality and biodiversity, have changed over time to estimate how the estuarine system will change in the future and allow targets to be set for catchment managers. To determine background conditions, e.g. pre-impact states, knowledge of the system's past is required. Many ecological systems respond to change over decadal-centennial timescales (Taffs et al., 2017a), hence using contemporary monitored data, which can typically span to 50 years at best, may not reveal the full range of ecosystem responses to fast and slow drivers. Therefore, understanding the interaction of estuarine processes and assessing their trajectories of change require long term data to analyse how catchment drivers cause water quality responses, e.g. eutrophication and algal blooms. While methods to gather long term data sets, e.g. palaeoenvironmental reconstructions, have been readily applied to lake systems, estuarine environments have been relatively understudied as archives of long-term (ca. 150-200 years) environmental change (Taffs et al., 2017a).

1.1.2 Safe Operating Space framework

Understanding the context of changing (eco)system response to more variable and greater magnitude drivers requires a framework in which to assess key processes. At a planetary scale Rockström et al., (2009a, 2009b) proposed the 'planetary boundaries' framework to address such thinking. The theory identifies a 'safe operating space' (SOS), a boundary within which a system may remain stable, for nine global processes, e.g. climate change and ocean acidification. Each process has a threshold that once surpassed can have disastrous, i.e. not easily reversible, consequences because of the non-linear and abrupt environmental changes that will occur within the system (Rockström et al., 2009b). For example, increased manufacture and application of fertilisers accumulates in the land systems, pollutes aquatic environments and adds to the concentration of gases in the atmosphere e.g. the greenhouse gas nitrous oxide increasing radiative forcing (Rockström et al., 2009a). The framework was proposed on a global scale, however it has been applied to regional scales, notably by Dearing et al., (2014) who developed a 'regional safe and just operating space' (RSJOS) conceptual framework and applied it for two rural Chinese areas using palaeoecological reconstruction techniques in lake systems. This thesis intends to apply the SOS theory, for the first time, to a local scale of an estuarine environment in the U.K., Poole Harbour.

1.1.3 The scope and focus of this study

Poole Harbour has been selected as the study site for this research at the request of the funding partner Wessex Water.

Poole Harbour, southern England, is an estuary with a history of eutrophication (Langston et al., 2003). The two main rivers which are a source of nutrients to the estuary, the River Frome and River Piddle, drain the farming landscapes of this groundwater fed catchment. Changing farming practices post WWII and an increasing population putting pressures on STWs have increased the nutrient loading to the estuary. The increase in nutrient loading has consequently led to the eutrophic state of the harbour and increased algal blooms in various locations, including the Wareham Channel where the River Frome and Piddle enter the estuary (Acornley et al., 2008). Holes Bay, to the north of the harbour, is an area of increased nutrient loading as a result of Poole STW effluent draining directly into the bay. Holes Bay has therefore suffered from increasing algal blooms (Langston et al., 2003). Tackling issues which affect the Poole Harbour catchment, such as nature conservation, landscape and water quality, are important to many individuals, organisations and stakeholders within the Dorset area (PHCI, 2014).

Using Poole Harbour as a case study, this research will adopt the local SOS framework of Dearing et al. (2014) to understand recent historic changes in Poole Harbour water quality and determine to what extent catchment drivers have caused a decline in water quality into a potentially dangerous state. This approach will be used to provide guidance for catchment managers to reduce nutrient loading in order to improve water quality within Poole Harbour, i.e. that which meets regulatory standards, e.g. Water Framework Directive (WFD) and Drinking Water Inspectorate (DWI) standards.

1.2 Aims and objectives

Relatively high nitrate levels within the waters of the Poole Harbour system are a cause of the harbour and catchment failing many directives and standards, e.g. Water Framework Directive, Drinking Water Incorporate and SSSI standards. The Catchment Plan put in place by the Poole Harbour Catchment Initiative (PHCI) (2014) has been successful in setting targets to improve the surface and groundwaters of the Poole Harbour catchment and has had some success with trialled activities to improve water quality, e.g. the Win Catchment sediment delivery reduction measures (PHCI, 2014). Current approaches to Poole Harbour and catchment management depends on the general standards of water quality, but there is debate over the sources of water quality changes and thus the actions required to reduce them. Understanding the past and how the system has changed recognises the complexity of the system with regards to catchment drivers and water quality responses which can be used to help set system specific targets. This thesis proposes that a SOS approach will be an improved method for catchment managers (Wessex Water) to implement better water conditions and help them remain within regulatory standards.

Understanding complex ecological systems requires datasets of sufficient temporal range, e.g. multi-decadal to centennial scale (Dearing et al., 2014), in order to track the nature of the interactions between different components of the system; in particular to identify when and why thresholds (a change in the system) and/or tipping points (transition to a new system state) in ecosystem components have been crossed. Contemporary measurements of nutrients and sediment data are normally too short (<50 years, commonly <30 years) to address these questions. Datasets of greater duration are therefore required to study contemporary ecosystems in the context of long-term variability, and to address concerns about the proximity of the ecosystem to potential critical thresholds. Fortunately, sediment records from estuary deposits provide valuable archives with which to reconstruct many key ecosystem variables over multi-decadal and centennial timescales, e.g. nutrients, sediment loads and ecological responses. Sediment cores and their analyses are required to determine the longer term (~150 year) nutrient and ecological history of Poole Harbour and its catchment.

The aim of this thesis is:

- To establish the safe operating space (SOS) for Poole Harbour water quality, determine if good water quality can be restored and what implications this poses for the management of the Poole Harbour catchment.

These aims will be met by the following objectives:

- To reconstruct Poole Harbour's historic water quality and assess the drivers of change using palaeoenvironmental reconstruction techniques.
- To determine when and where tipping points in water quality occurred and establish the driver/response interactions of them.
- To determine how the system responds to catchment drivers, i.e. in bifold, step change or linear manner (Scheffer et al., 2001; Scheffer & Carpenter, 2003).

1.3 Thesis structure

This thesis comprises of eight chapters. Chapter 1 has outlined the project rational and aims for this research. Chapter 2 provides a review of the literature surrounding the theory of the SOS framework and its application in this study, an overview of Poole Harbour, the study site, and the importance for this research followed by the use of palaeoenvironmental reconstructions within estuarine environments. Chapter 3 details the fieldwork and study sites alongside the laboratory and analytical methodology. Chapter 4 provides the chronology of the cores used in this research. Chapter 5 establishes the sediment accumulation rates of the four cores and the reasons behind their change over time. Chapter 6 presents and explains the changes in the ca. 150 year nutrient and ecological record of Poole Harbour. Chapter 7 draws together the analysis of Chapters 5 and 6 to investigate the acceptable water quality for Poole Harbour and the feasibility to restore it. Chapter 8 summarises this research and presents conclusions drawn from this thesis and addresses potential future work.

Chapter 2 Literature Review

2.1 Introduction

Eutrophication within aquatic environments can lead to algal blooms and anoxic events, resulting in both ecological and economic loss (Carpenter, 2005). Estuaries are where freshwater and saltwater habitats converge; they are associated with high human population densities and their semi-enclosed nature means that they are highly sensitive to nutrient, sediment and toxin loads promoting algal growth (Evans & Scavia, 2013). Estuarine environments not only provide ecological benefits, with some of the highest biodiversity and ecological production compared to other aquatic environments (Bianchi, 2007), but they are also of economic value, e.g. tourism and oyster hatcheries (Jones & Pinn, 2006). Such environments are under increasing pressures from anthropogenic changes within their catchments, e.g. increasing populations and agriculture, increasing nutrient enrichment of the systems. Poole Harbour is no exception to this as it has suffered a history of algal blooms and associated eutrophication since the 1960s (Langston et al., 2003). River monitoring records within the River Frome have indicated these changes are a response of macronutrient drivers to increased anthropogenic loading, namely nitrogen (PHCI, 2014). However, to better understand the system interactions with the catchment and responses, long term time series data are required, such as algal community and geochemical changes within the estuarine waters. To obtain such data, palaeoenvironmental reconstruction techniques can be used to establish the nutrient and ecological history of the system. From these records, system responses to multiple and interacting drivers, e.g. catchment changes, can be established to determine if the system exhibits any state changes, e.g. tipping points, or responds in other ways, e.g. in a linear manner. Collating these alongside the time series data for each of the variables of the system, e.g. agricultural, population and algal community changes, will allow a safe operating space (SOS) to be developed for Poole Harbour.

The following literature review will be split into four sections. The first will outline the SOS framework and why it is useful in the context of Poole Harbour. The second will briefly introduce the importance of estuaries and why they are becoming increasingly under pressure and at risk for ecological destabilisation. The case study area itself, Poole Harbour, will be addressed in the third section where understanding will be given to the problems it faces and why. How a SOS will be established using palaeoenvironmental data is discussed in the fourth section.

2.2 Safe Operating Spaces framework

The planetary boundaries framework was proposed by Rockström et al., (2009a, 2009b). It defines nine planetary biophysical boundaries within which lies the safe operating space (SOS) for humanity, i.e. the space where biophysical subsystems or processes can be sustainably exploited to avoid destabilising the Earth system (Rockström et al., 2009a; Figure 2.1). Though the framework can be valuable to decision makers for determing desirable courses for societal development (Steffen et al., 2015b) it is not without its critiques, e.g. Running (2008). Each of the nine boundaries are considered soley, consideration is not given to the interactions and processes between the different variables. Not all of the Earth system's processes are identified within the framework, and those that are cannot necessarily be easily measured on a global scale. The analysis of such global biospheric limits is therefore subject to many assumptions and uncertainties (Running, 2008). It is worth noting there are significant differences between regions with regards to their contribution to the global total for each biophysical system. In the case of phosphorus, some regions across the globe are P-saturated, resulting in eutrophic waters, and others are P-deficient where P becomes a limiting factor to agriculture (Carpenter & Bennett, 2011; MacDonald et al., 2011; Figure 2.2). Hence, the value given for a global planetary boundary parameter negates much regional-scale variability. Such variablility therefore undermines the usefullness of the tool for policy makers as legislation is made on national, regional and local scales, seldom on a global scale.

Despite the critiques outlined above, the concept may be useful at sclaes where the interactions can be more easily measured, e.g. at a regional scale. The use of a smaller scale SOS can be used to determine a region's contribution to a global planetary boundary, e.g. the loss of carbon sinks such as the Greenland ice sheet pushing the climate system to a global threshold (Steffen et al., 2015b).

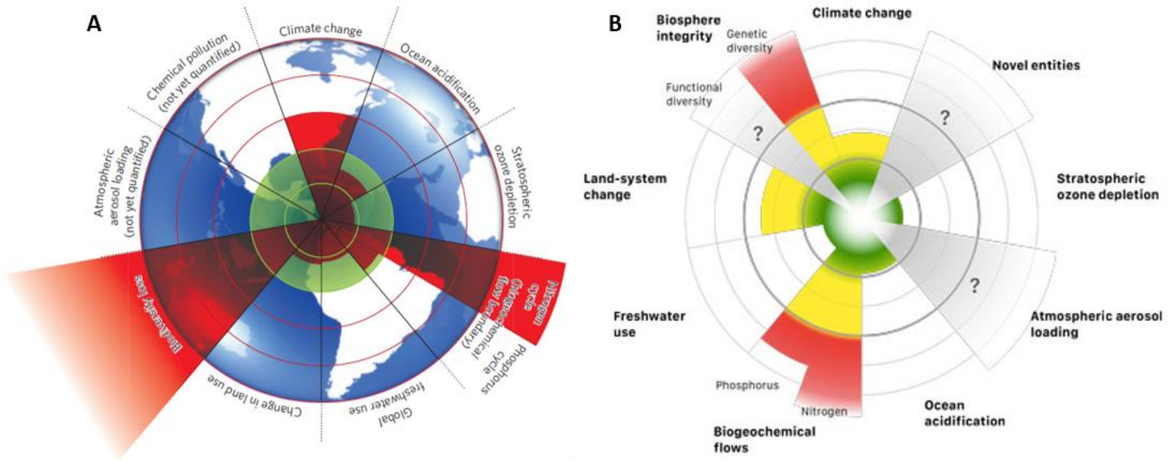


Figure 2.1: A: The nine planetary boundary systems as defined by Rockstrom, et al., (2009a); green shading highlights the safe operating space whilst the red areas illustrate the current position for each variable. B: Current status for seven of nine planetary boundaries; red illustrates beyond the zone of uncertainty at high risk, yellow in the zone of uncertainty with increased risk and green in the safe area, grey areas have not yet been quantified (Steffen et al., 2015b). Comparison between the two diagrams illustrates that phosphorus is now at high risk globally out of the safe zone and change in land use is now at increasing risk.

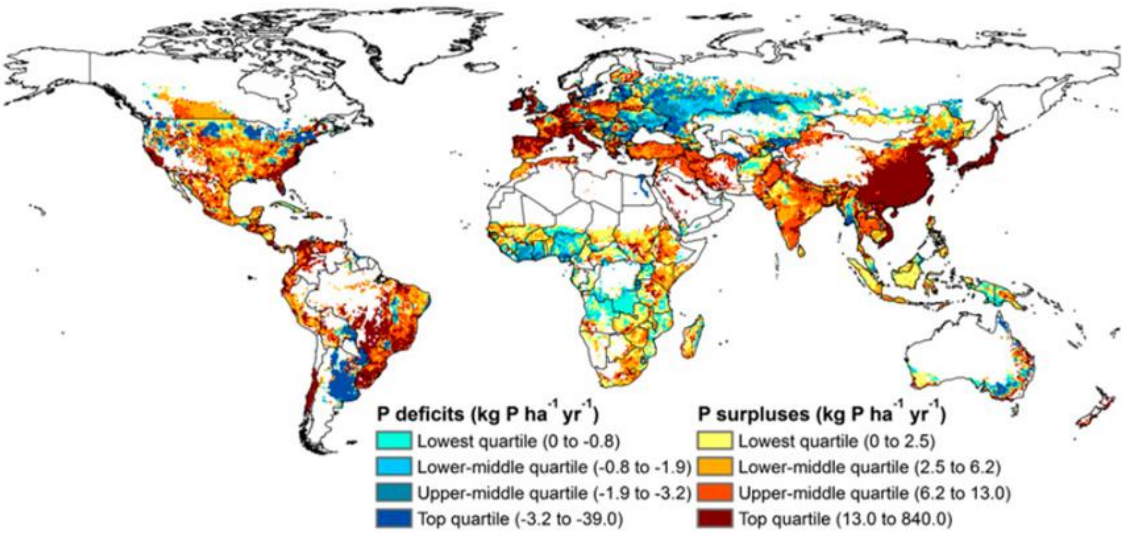


Figure 2.2: Agronomic phosphorus imbalances for the year 2000 with surpluses and deficits classified according to global quartiles; 0-25th, 25-50th, 50-75th and 75-100th percentiles (MacDonald et al., 2011).

A SOS can help manage a system with regards to maintaining or reversing unwanted states, e.g. reversing eutrophic waters, by setting parameters of drivers to keep within the SOS. To facilitate this, understanding how a system responds to drivers is essential to determine what parameters to set the drivers of the system at. There are three types of system: linear, step change and bifold (Figure 2.3).

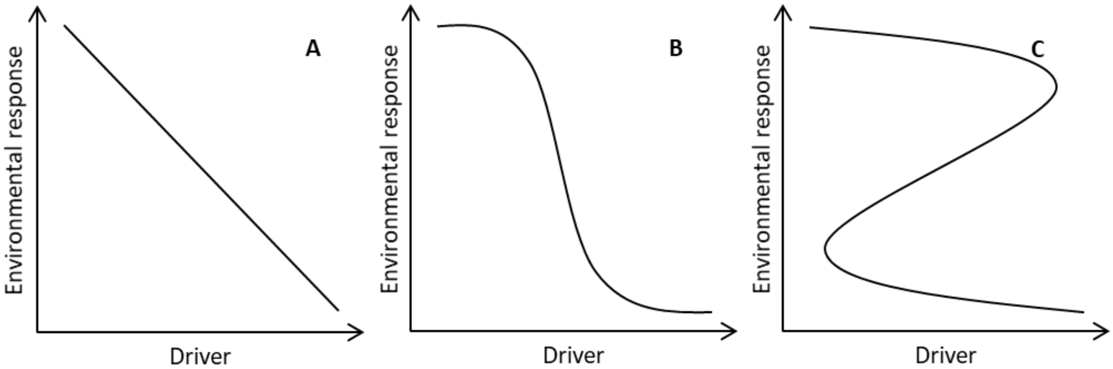


Figure 2.3: Three types of system responses to environmental drivers; A: linear, B: step change and C: bifold (Scheffer & Carpenter, 2003).

A linear relationship (Figure 2.3A) is simple in the fact that a change in a driver, e.g. increasing nitrogen loads, has a direct impact on the response, e.g. decreasing water quality (Scheffer et al., 2001). Thus, a reverse in the direction of the driver, e.g. decreasing nitrogen loads, should result in a reversal in the response variable, e.g. increase in water quality.

A step change (Figure 2.3B) is a system whereby a change in the driver, e.g. increasing nitrogen loads, can maintain a response, e.g. good water quality, until a threshold or tipping point is reached and results in the collapse of the response, e.g. poorer water quality (Scheffer & Carpenter, 2003). A threshold is a change in a system which, for example, may alter its processes, whilst a tipping point is a critical threshold which once surpassed alters the state or development of the system (Lenton et al., 2008) where after the system drivers need to be considerably reduced or changed for the system state to change back (Scheffer et al., 2001). Before the collapse and after can be classed as steady states as a range of forcings can maintain constant environmental conditions (Scheffer & Carpenter, 2003). This type of system, like the linear, should be able to be reversed by reversing the driver, e.g. decreasing nitrogen loads. However, unlike in linear systems, this process will take longer as there will be a lag time between a change in the driver and response, e.g. increase in water quality, as each stable state can be maintained over a range of driver conditions.

A bifold system (Figure 2.3C) is one with two steady states (Scheffer et al., 2001; Scheffer & Carpenter, 2003). While a driver, e.g. nitrogen loads, increases, the system can maintain its state, e.g. good water quality, until a critical threshold, or tipping point, is reached. Once this critical threshold is met, the system 'folds' in on itself to settle at a new state, e.g. poorer water quality. These systems are hard to return to the first steady state, e.g. good water quality, once a threshold is crossed. It is not enough to restore forcings, e.g. nutrient loading, to their level prior to the first collapse, and instead forcings need to be reduced to much below those levels prior to the initial collapse (Scheffer et al., 2001). In some cases, it may be impossible to reverse a system to its previous state, e.g. where phosphorus recycling in a lake is so large, no feasible reduction to phosphorus inputs can return the lake to a non-eutrophic state (Carpenter et al., 1999).

Since the introduction of the planetary boundaries concept, it has been developed to incorporate social objectives which led to the development of the 'Oxfam doughnut' (Raworth, 2012; Figure 2.4). A 'social foundation' (boundary 1) encompasses the centre of the 'doughnut' below which lies human deprivations, e.g. hunger and poverty (Raworth, 2012). The outer ring, the 'environmental ceiling' (boundary 2), is a representation of the environmental limits, past which critical transitions or tipping points may be surpassed and cause destabilisation of the Earth's system, e.g. global warming (Raworth, 2012). Between these two boundaries lies the 'safe and just operating space for humanity' (SJOS) where development is underpinned by the sustainable use of natural resources; this space is where both human and planetary well-being can be, arguably, assured (Raworth, 2012). The SJOS concept is more applicable at smaller scales, i.e. national and regional, where policy makers can use the framework to ensure development does not contribute to surpassing a global critical threshold. An example of this use of a SJOS is to investigate the increase in use of fertilisers to increase agricultural yields and ensure sufficient food supply, but at an environmental cost of nutrient loading to rivers causing eutrophication of water bodies and thus depletion of fish supply (Zhang et al., 2015).

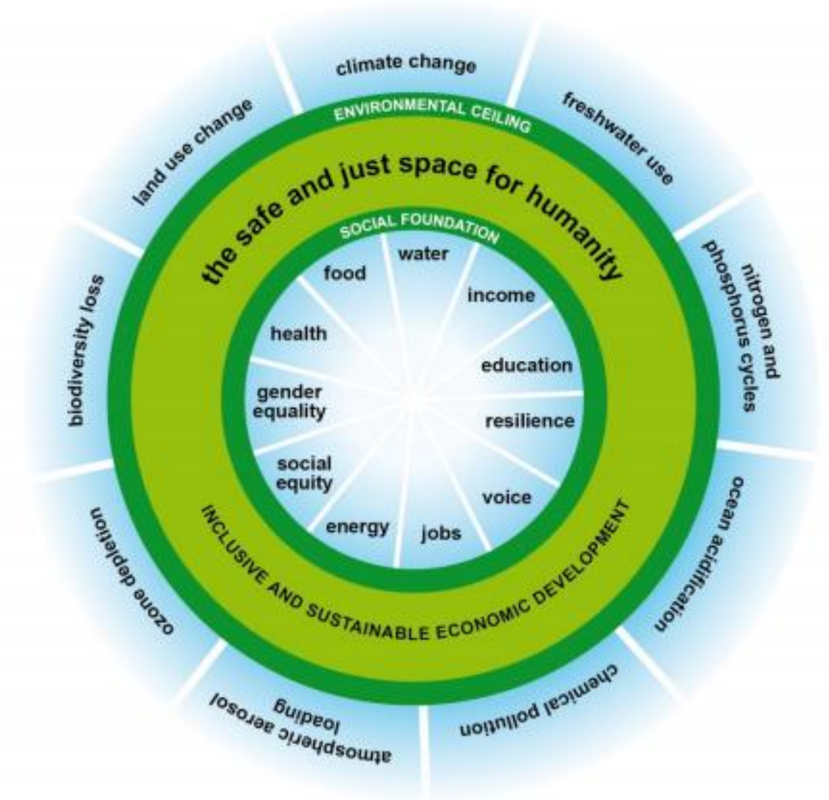


Figure 2.4: The safe and just space illustration including the nine planetary boundaries and eleven social dimensions to develop the 'Oxfam doughnut' (Raworth, 2012).

Humanity strongly influences environmental processes from global to local scales; as such, critical transitions or tipping points can occur at any scale (Folke et al., 2004; Scheffer et al., 2001). These thresholds are the critical values which once surpassed can have disasterous cosequences (Rockström et al., 2009a). The SOS framework has already been applied to a smaller scale e.g. the first national scale 'barometer' created for sustainable development in South Africa by Cole et al., (2014). The 'barometer' highlighted the environmental risks, e.g. freshwater use and biodiversity loss, and unacceptable social deprivations, e.g. safety and income, to prompt public debate surrounding development and show that similar 'barometers' could be developed for other countries (Cole et al., 2014). The barometer was further developed on a smaller scale for all the South African provinces to highlight the variation in key indicators of environmental stress and social deprivation across South Africa (Cole et al., 2017). Dearing et al., (2014) demonstrated the use of the SOS framework for sustainable management on a regional scale for two rural Chinese areas (Figure 2.5). Such work has shown that this framework can evaluate the relative state of the environmental viability and social wellbeing within an area, whether at a national or regional scale, and can be used to evaluate relationships between social and environmental variables (Cole et al., 2014; Dearing et al., 2014; Cole et al., 2017). Social-ecological systems are complex and if they reach a threshold, or tipping point, systems can exhibit rapid changes with negative consequences for both the environment and the people using them (Rockström et al., 2009b). Understanding of the complex behaviour within social-ecological systems is vital where policy makers seek to make changes to a system to combat a problem, e.g. eutrophication. As discussed, changes at the smallest scale can contribute to a wider and larger environmental and/or social issue. This research proposes a novel approach to UK estuary management by examining the social-environmental relationships at a local catchment scale in order to develop a SOS that can be used by policy makers.

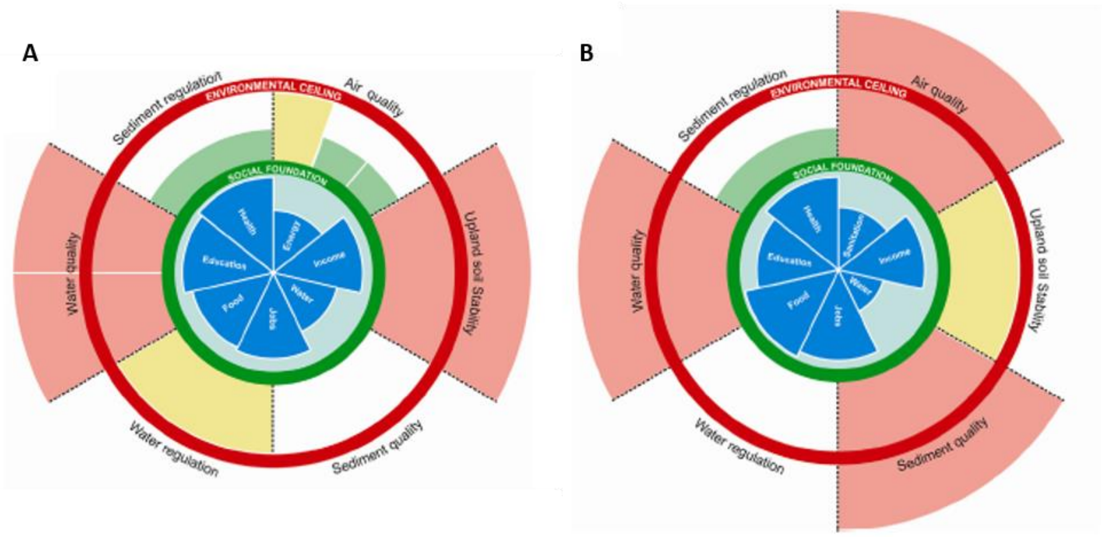


Figure 2.5: The safe and just operating spaces for a) Erhai lake-catchment system, Yunnan Province and b) Shucheng County, Anhui Province (Dearing et al., 2014).Blue sectors show how each region currently meets the expected social standards for an acceptable social foundation, the green circle; the red circle, the environmental ceiling, defines the approximate sustainable and unsustainable boundary; the green, yellow and red segments represent the safe, cautious and dangerous levels respectively; and the doughnut between the green and red circle is the RSOJS (Dearing et al., 2014).

Humans obtain many benefits from ecosystems and depend on them for their existence; these are known as ecosystem services (Nicholson et al., 2009). A SOS is an area within which humans can use ecosystem services at no detrimental effect to the environment and ecosystem. Exceedance of the SOS would lead to unsustainable exploitation of the environmental resources. It is important to understand where the point of no return lies, i.e. a tipping point, beyond which the SOS is exceeded. Once a tipping point has been reached, a 'regime shift', or sudden shift in the ecosystem, can occur (Figure 2.3B and C), e.g. the Caribbean coral reefs sudden dramatic shift to being overgrown by algae as a consequence of the removal of herbivorous organisms via intensive fishing and pathogens (Scheffer & Carpenter, 2003). It is worth noting that the boundary of a SOS sits prior to the tipping point in order to provide a buffer area or area of uncertainty (Rockström et al., 2009a; Steffen et al., 2015b). Once such a tipping point has been identified, some studies argue that early warning signals (EWS) that occur prior to a regime shift may be possible to observe (Scheffer et al., 2012). When one fully understands the system drivers and responses, the identification of EWS can possibly be used to prevent future critical transitions if such behaviours are detected and acted upon in time. It is important to understand that EWS do not always precede a catastrophic shift, they likely indicate that 'something' is going to happen, but the change will not necessarily be critical and just a shift in the system (Kéfi et al., 2013). These false positives cast doubt on the efficacy of EWS as an applied tool of ecosystem management.

This research project aims to use palaeoenvironmental archives to explore the trajectory of a range of biophysical aspects of the Poole Harbour system and to test whether they currently operate in a safe space by examining historical changes of the state of the estuarine environment (Dearing et al., 2014; Figure 2.6). For example, sediment regulation in Figure 2.6, exhibits an envelope of variability, i.e. the values increase and decrease over time within an upper and lower limit. If at any point in time the sediment regulation was measured, it could give the impression it was too high or too low. However, understanding this variability is the baseline for this biophysical variable means it would not falsely be categorised as a cautious or dangerous state as this is the normal safe state behaviour for sediment regulation. Within this research, focus will be given to identifying the relationships between catchment drivers and water quality response in Poole Harbour in the hope that understanding the behaviour of these relationships can allow a safe water quality space to be identified which could be used to potentially aid future management decisions.

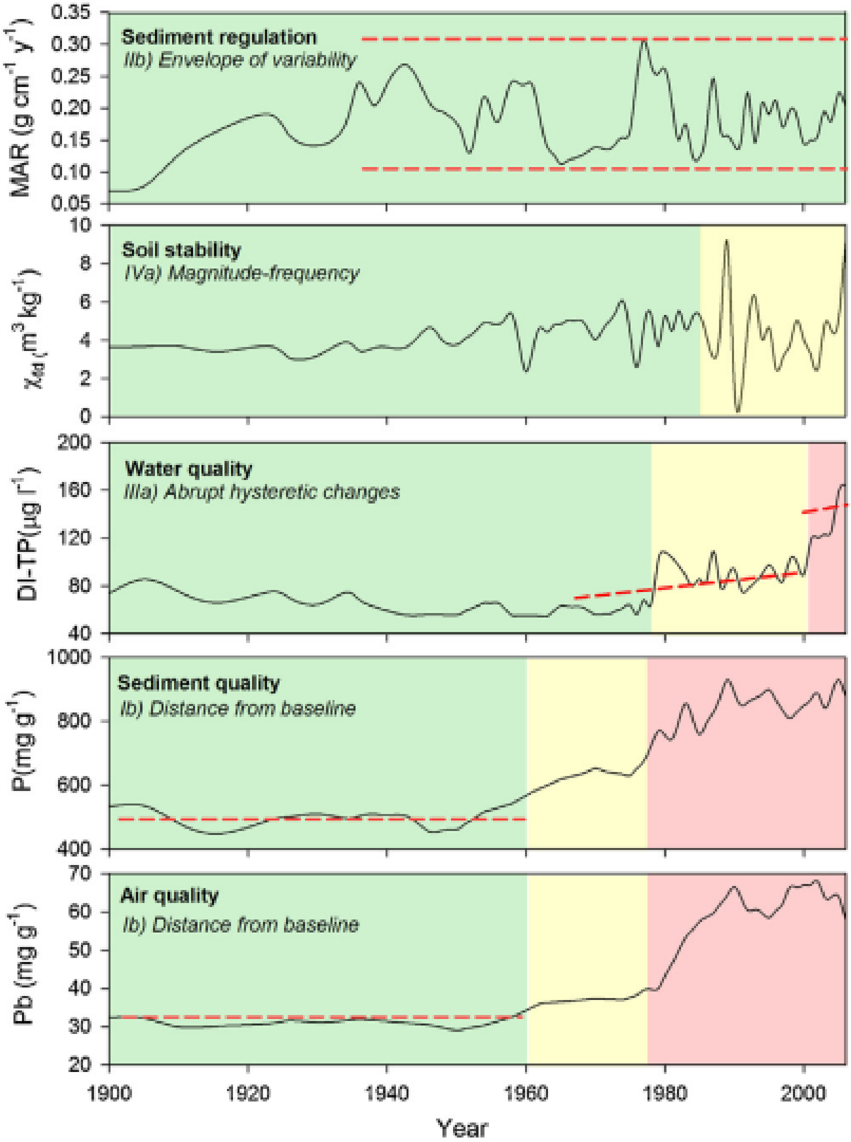


Figure 2.6: Time series data 1900-2010 for the ecological boundaries in Shucheng County, Anhui Province illustrating time series data for sediment regulation, soil stability, water quality, sediment quality and air quality (Dearing et al., 2014). Red dashed lines indicate the basis for using different types of dynamical behaviour (italicised within diagram) to define safe, cautious and dangerous status for each ecosystem service (green, yellow and red respectively).

By understanding the catchment driver interactions and water quality responses of the Poole Harbour system, estimates can be given to how drivers of the system, e.g. catchment changes, cause a response in water quality, e.g. eutrophication. This understanding is essential to provide any parameters to drivers of the system, e.g. nitrogen loads, which can maintain or reverse system changes such as eutrophication within Poole Harbour. By investigating the system catchment-estuary relationships, a Poole Harbour water quality SOS can be established to aid catchment manager decisions, e.g. with regards to nutrient loadings in an effort to reduce eutrophication.

2.3 The importance of estuaries and the need for appropriate management

The coastal zone is the area in which rivers enter the ocean (Ross, 1995). Around 2.8 billion tons of dissolved material is carried to the oceans via rivers each year worldwide, containing both nutrients needed for the survival of organisms alongside harmful pollutants, e.g. from industrial and municipal waste (Ross, 1995). Estuaries are a complex part of the ocean acting as biological, chemical, physical and geological transition areas (Ross, 1995). Interactions between physics and biogeochemistry in estuaries occur at various spatial scales (Geyer et al., 2000), making their study somewhat complex as no two estuaries are the same. Various physical variables contribute to the control of the biogeochemical cycles including estuarine circulation, river and groundwater discharge, tidal flooding, resuspension of sediments and the exchange flow with adjacent marsh systems (Bianchi, 2007; Leonard & Luther, 1995).

Estuaries are open systems in that they receive and exchange fluxes, e.g. pollutants and nutrients, with their catchment and the ocean they are connected to. In this way, estuaries are dynamic ecosystems with some of the highest biotic biodiversity and production, compared to other aquatic and terrestrial environments, in the world (Bianchi, 2007). They are highly important areas for a wide range of biota with many marine organisms beginning their lives in the estuary or marshes, or spending a major portion of their lives in the estuarine environment (Ross, 1995). As with Poole Harbour, estuaries typically provide a habitat for commercial species of fish and shellfish (Jones & Pinn, 2006) and also provide shelter and food resources for commercial shelf species who spend their juvenile stages of life in the estuarine marshes (Bianchi, 2007). For example, the discharge from the rivers Mississippi and Atchafalaya are linked with the high production of fish and shellfish in the northern Gulf of Mexico with commercial fishing in the region bringing in 769 million kg of seafood/$575 million per year, data taken from 1997 (Chesney & Baltz, 2001).

Human activity compounds the complexity of ‘natural’ estuarine processes (Ross, 1995). Over half of the world’s population live within coastal margins, not including the industries which are situated within these areas (Alongi, 1998;

Reker et al., 2006). Demographic changes in human population have had a detrimental effect on estuary biogeochemical cycling (Bianchi, 2007). Such effects include dredging and filling of estuaries changing intertidal habitats, overexploitation of commercial fish and shellfish, increased organic and inorganic contaminants and nutrient loading of rivers and thus estuaries (Hobbie, 2000 cited in Bianchi 2007). Nutrient enrichment from both point, but more so non-point sources, e.g. urban and agricultural runoff, is one of the greater concerns for eutrophication in coastal waters (Howarth et al., 2002); a concern which Poole Harbour managers acknowledge (Jones & Pinn, 2006; Langston et al., 2003). An example of such a problem elsewhere is shown in Figure 2.7 which highlights forty four estuaries along the coastline of the U.S. which have been declared as having nutrient enrichment problems (Bricker et al., 1999).

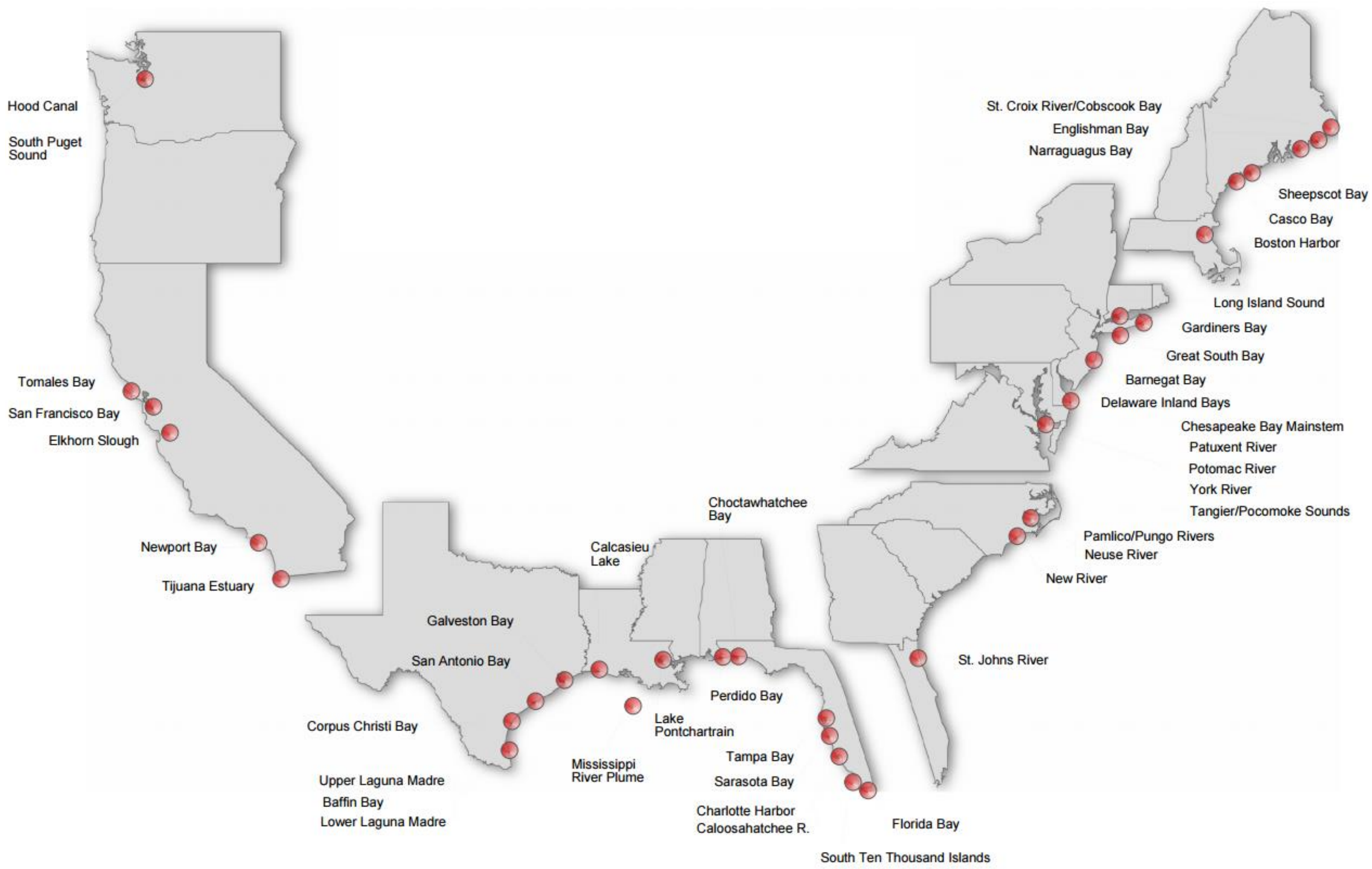


Figure 2.7: Estuaries along the U.S. coastline exhibiting varying eutrophic symptoms, e.g. algal blooms, high chlorophyll a, low dissolved oxygen (Bricker et al., 1999).

Estuaries are important on various scales for their environmental and economic contributions to society. The complex interactions of these biophysical and social systems pose difficulties when studying their responses to a changing world. The increase in human population across the globe, coupled with a changing climate, forces more pressure on these complex systems. Unlike other aquatic systems, the open nature of estuaries can make them more resilient to anthropogenic pressures as the riverine and oceanic waters can flush the estuary system. On the other hand, the open nature of the system can make estuaries more susceptible to external drivers of change as any forcing within the estuary itself, the catchment or the sea, or a combination of all, can drive biological, chemical and/or ecological changes. Poole Harbour is such an estuary whose catchment has been subject to an increasing population and increased nutrient loading levels, likely a result of increased fertiliser use common across the UK since the 1940s (Robinson & Sutherland, 2002; Figure 2.8). As will be discussed, this increase in land use pressure has resulted in shifts in nutrient loading from the rivers which drain the catchment to the estuary, with a biological consequence of algal blooms and the associated eutrophication within the water body of Poole Harbour.

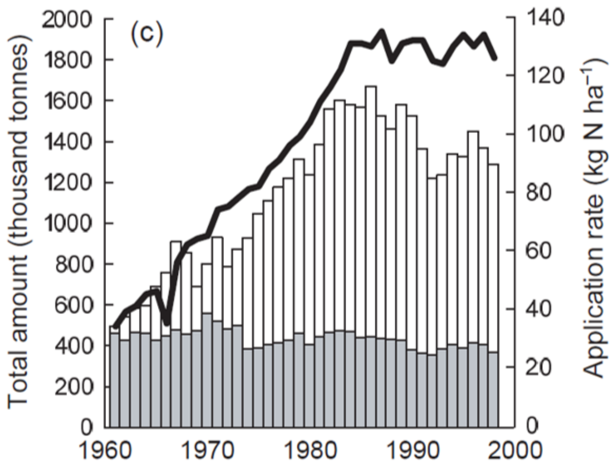


Figure 2.8: The total amount of fertiliser applied in Britain; bars and left axis: nitrogen (open bars), phosphate (filled bars); line and right axis: average application rates of nitrogen to all crops (Robinson & Sutherland, 2002).

2.4 Poole Harbour

Poole Harbour is located in the county of Dorset and has a drainage area covering approximately 820km^2, this accounts for ~31% of the county (PHCI, 2014). It has a mainly chalk geology with some older clays and greensand in the north west and younger tertiary clays, gravel and sand overlaying the chalk in the lower catchment; thus Poole Harbour is dominantly groundwater fed (PHCI, 2014). Wareham is situated to the west of the harbour, through which flows the River Piddle to the north and the River Frome to the south of the town (PHCI, 2014).

Poole Harbour is an area of significant ecological importance with reports of algal blooms since the late 1960s and estuarine waters which have been subject to extensive nutrient fluxes (Langston et al., 2003). The estuary extends from Wareham to Bournemouth for approximately 10km (Langston et al., 2003) and is one of the largest and shallowest natural harbours in the world at approximately 38km^2 with an average depth of 48cm (PHCI, 2014). It is fed by two major rivers, the Frome and Piddle, two smaller rivers, the Sherford and Corfe and also a number of small streams that drain tributary catchments (RACER, 2004). The rivers Frome and Piddle drain the chalk agricultural lands of Dorset and enter the harbour from the West (Gray, 1985). The two main rivers are likely the main nutrient sources into the harbour (Gray, 1985) combined with Poole STW effluent which flows directly into Holes Bay in the north (Figure 2.9 and Figure 2.10).

The following sub-sections provide further detail on specific aspects of the Poole Harbour system, these being: defining whether Poole Harbour is an estuary or lagoon, the tidal pattern, sea level rise and details of the Poole Harbour catchment, before discussing why Poole Harbour requires a SOS and where the knowledge gaps are.

It is worth noting throughout this section of the literature review that Rivers and Coastal Environments Research, RACER (2004) and Poole Harbour Catchment Initiative, PHCI, Catchment Plan (2014) will be heavily used as sources of information on Poole Harbour. RACER (2004) is an online source created using peer reviewed literature on behalf of the Standing Conference on Problems Associated with the Coastline. PHCI's Catchment Plan is a synthesises of information from many partnering groups of the PHCI, e.g. Wessex Water, Natural England and the Environment Agency, to provide a concise report of Poole Harbour, the problems it faces and details of trialled and existing activities to reduce the undesirable effects on the estuary.

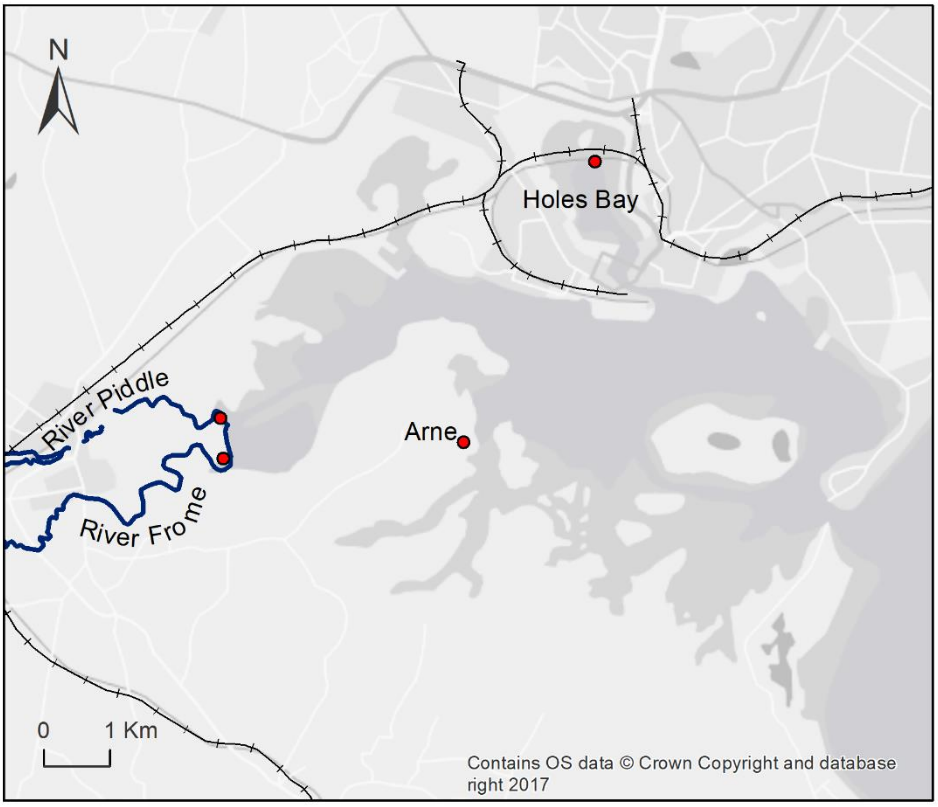


Figure 2.9: Poole Harbour with areas of interest within this study highlighted: the Rivers Frome and Piddle which drain the agricultural land of the catchment, Holes Bay which has a railway line running through it, is surrounded by the industrial area of the catchment and where Poole Sewage Treatment Works effluent drains directly into and Arne which has been selected as the control site. Note red markers identify the position of sediment cores retrieved and used in this study.

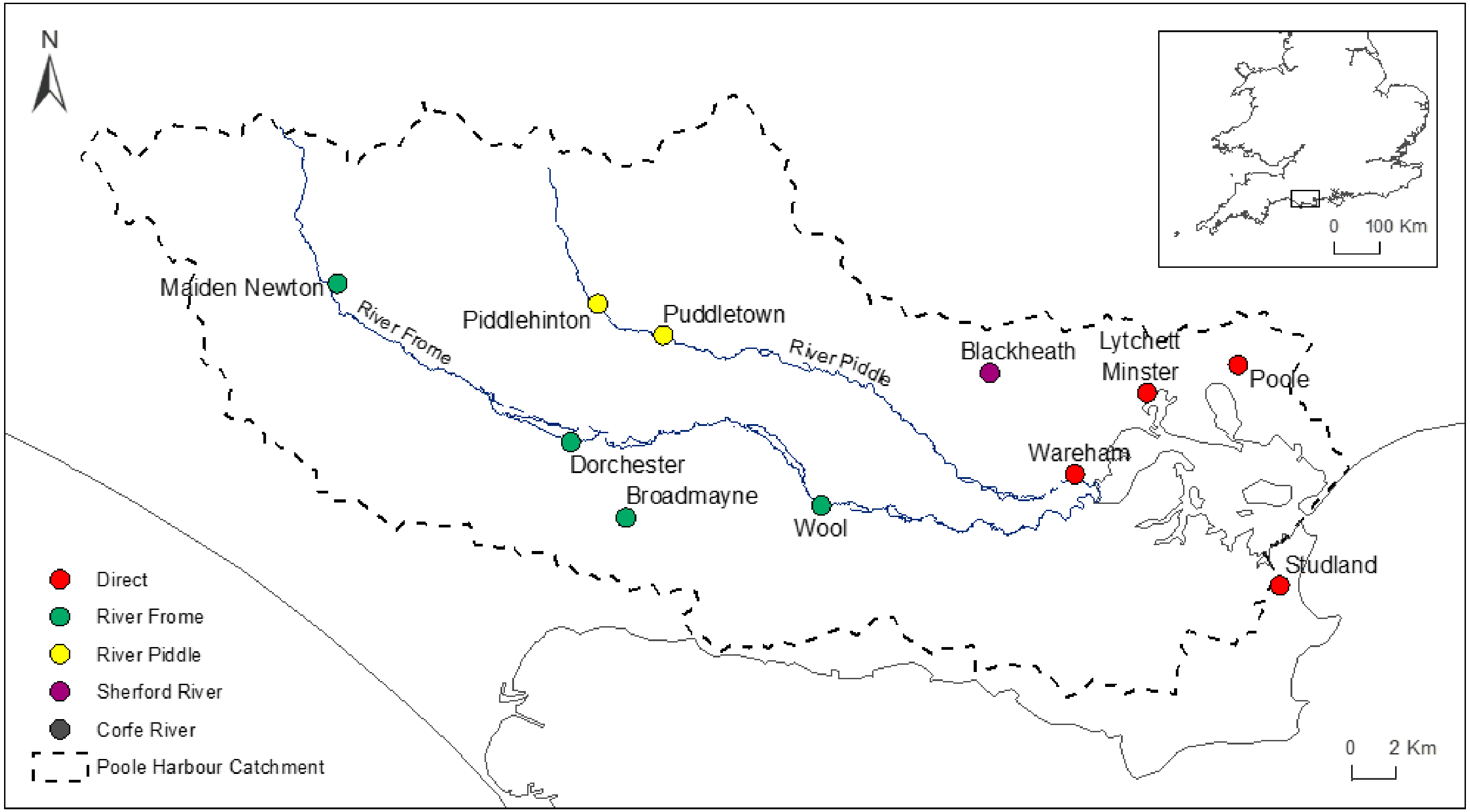


Figure 2.10: Sewage Treatment Work locations within the Poole Harbour catchment detailing how their effluent reaches the aquatic system, note Poole Sewage Treatment Works flows directly into Holes Bay which is investigated within this study.

2.4.1 Estuary or lagoon

There is debate regarding the classification of Poole Harbour, as to whether it is an estuary or lagoon. An estuary has three definitive characteristics which distinguishes it from all other bodies of water (Biggs & Cronin, 1981). Two of these characteristics are geomorphic in that 1) the water body must be coastal and semi-enclosed and 2) it must have free connection to the open sea (Biggs & Cronin, 1981). The third characteristic is a chemical classification in that the dilution of seawater by the freshwater must create a salinity gradient (Biggs & Cronin, 1981) which supports the argument of free connection.

Poole Harbour is a result of Holocene post-glacial sea level rise which submerged the river system of the lower Poole Basin (Gray, 1985; RACER, 2004; Humphreys & May, 2005). It's original entrance, 6000 years BP, was approximately 3.5km in width but has since been narrowed to approximately 350m (RACER, 2004). This has been a result of spit growth forming the Sandbanks and South Haven Peninsulas (RACER, 2004) which allows the Harbour to reside semi-enclosed on the south coast of Britain and to be classified as a spit-eclosed type estuary (Dyer, 1977; Environment Agency & DEFRA, 2013).

As aforementioned, Poole Harbour has several freshwater contributors to the estuary but its narrow entrance restricts the flushing of the primary basin (Langston et al., 2003). However the ability to freely exchange with the open sea is a cruicial characteristic of an estuary and is one that seperates it from a lagoon (Perillo, 1995). Poole Harbour's narrow entrance could be restricting this transfer between the riverine inputs and the sea. Tidal flow and salinity can determine whether the waters of Poole Harbour are freely able to exchange with the open sea (Humphreys, 2005). A lagoon is semi-isolated from the open sea and therefore retains an abundance of the water during low tide of the adjacent sea (McLusky & Elliot, 2004). This facilitates a stable salinity gradient from high at the seaward end of the estuary and lowers further towards the river inputs (Humphreys, 2005). Within an estuary the salinity gradient fluctuates with the ebb and flow of the tide due to the free connection between the estuary and the sea (Humphreys, 2005). Therefore a fluctuation of the salinity should be recorded on a semi-diurnal basis, in accordance with the tide (Humphreys, 2005) and Poole Harbour's character defining double high tide. Figure 2.11 demonstrates that the salinity varies in accordance with the tidal cycle as far up as the Wareham Channel.

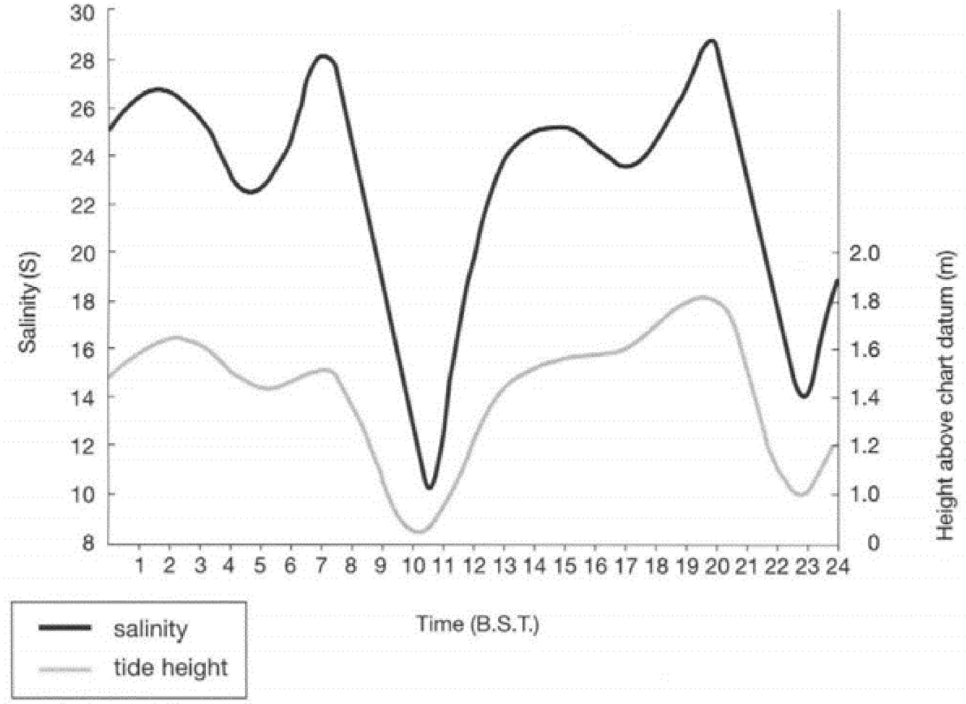


Figure 2.11: A 24 hour record of surface salinity of the Wareham Channel with relation to the predicted tidal level at Poole Bridge (Humphreys, 2005). Salinity units: dissolved inorganic matter expressed as grams per kilogram of water (g kg-1).

In summary, Poole Harbour is a coastal, semi-enclosed body of water which demonstrates a salinity gradient from river to sea indicating a free connection with the open sea and therefore can be classified as an estuary and not a lagoon.

2.4.2 Tidal Pattern

Figure 2.12 illustrates the tidal cycles at Poole Bridge. The harbour is subject to a small tidal range of 1.8 m during spring tides and 0.6 m at neaps (Humphreys & May, 2005). Often the water is above the mean tide level for 16 hours of the day which means the harbour is subject to a double high water (Humphreys & May, 2005). This has a particular impact on the ecology of the area due to the limited availability of mudflats for the wader populations but also increases the opportunity for filter feeding invertebrates to feed (Humphreys, 2005).

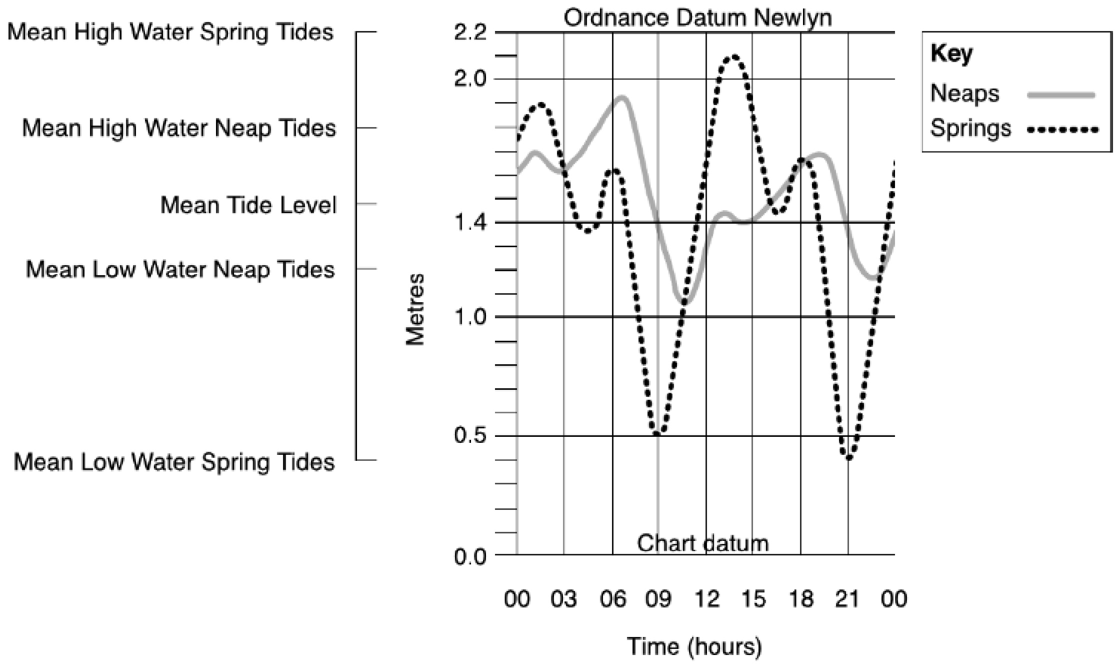


Figure 2.12: Typical spring and neap tidal curves at Poole Bridge (Humphreys, 2005). Spring tides occur at full and new moons and neap tides occur ca. 7.4 days after a spring tide.

2.4.3 Sea Level Rise

Sea level rise may have an effect on estuarine processes with greater flushing potential from the larger coastal body. Flushing could result in increased sediment erosion and an associated increase in pollutant and nutrient release, but may also reduce nutrient concentration if sea level rise is greater than increased nutrient release. However, sea level rise effects occur over longer time scale, e.g. historically centenial, than that of catchment behaviour changes, e.g. increased fertiliser applications which are associated with more decadal scales.

Long et al., (1999) discuss the increase in sea level rise in Poole Harbour which was expanded upon by Edwards and Horton’s (2000) foraminiferal transfer function. They concluded, with limited sediment core dates, that the rise in mean tide level during the last couple of centuries is considerably above the average for the last 3500 years (Edwards & Horton, 2000). Edwards (2001) used this to determine the mean tide level for Poole Harbour in conjunction with accelerater mass spectrometry (AMS) radiocarbon dated material using multiple cores collected from marshes within Poole Harbour (Figure 2.13).

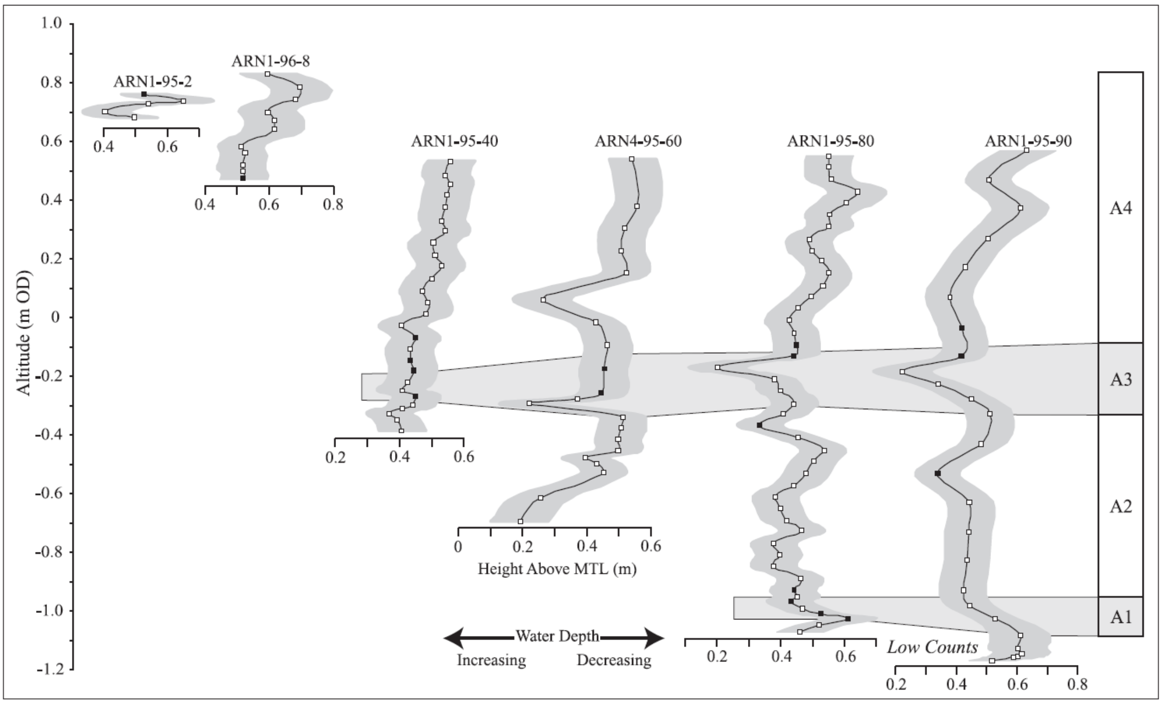


Figure 2.13: Reconstructed water level changes for Arne using foraminiferal transfer function, plotted relative to mean tide level (Edwards, 2001). Four changes of sedimentation and water level changes indicated: A1: 4700-2400 BP rising RSL; A2: 2400-1200 BP stable to falling RSL; A3: 1200-900 BP brief rise in RSL; and A4: 400/200 BP – present recent increase in rate of RSL rise (Edwards, 2001).

2.4.4 Poole Harbour Catchment

As discussed, Poole Harbour is majority nutrient fed by the Rivers Frome and Piddle which have a combined catchment of >770km^2 (Humphreys & May, 2005). These rivers discharge into Poole Harbour in close proximity to each other and provide good scientific parallel in terms of its flow regime, geology and geomorphological characteristics (Adams et al., 2003). Another primary nutrient source for Poole Harbour is the Poole STW which releases effluent directly into Holes Bay in the north of the harbour (Langston et al., 2003; Figure 2.10).

The River Frome has a catchment of 439km^2 of which 46% is chalk allowing it to be claimed as the westernmost major chalk stream in England (Casey & Newton, 1973). It is sourced at Evershot and is joined by its tributaries, River Hooke, River Cerne, Sydling Water, South Winterbourne, Tadnol Brook and the River Win, before it reaches its shared estuary with the River Piddle in Poole Harbour (Casey & Newton, 1973).

The River Piddle, like the River Frome, is also situated within a chalk catchment but its size is relatively smaller in comparison with a length of 40km (Strevens, 1999). It's source is situated near Alton Pancras and the Devil's Brook and the Bere Stream are the River Piddle's two primary tributaries before it flows to meet the River Frome in their common estuary (Walling & Amos, 1999; Strevens, 1999). 43.5% of the 197M l/day which is abstracted from the catchment, originates from the groundwater which reflects the importance of the area's chalk aquifer (Strevens, 1999).

Land cover within the catchment has remained predominantly agricultural at approximately 615km^2 equating to approximately 75% of the area (Grabowski & Gurnell, 2016; PHCI, 2014; Figure 2.14A). The major changes in the catchment with regards to land use is the shift to more cereal crop cultivation during and post- World War II (WWII) (Grabowski & Gurnell, 2016; Figure 2.14B). Livestock numbers have also substantially changed with dominance of sheep in the early 1900s to an increase in cattle towards the latter end of the century (Grabowski & Gurnell, 2016; Figure 2.14C). On a smaller scale, the River Frome catchment has seen little change over the past 70 years and agriculture has consistently covered nearly 90% of its catchment with a shift to more arable than pasture agricultural land use in 2000 and 2007 (Grabowski & Gurnell, 2016; Figure 2.15).

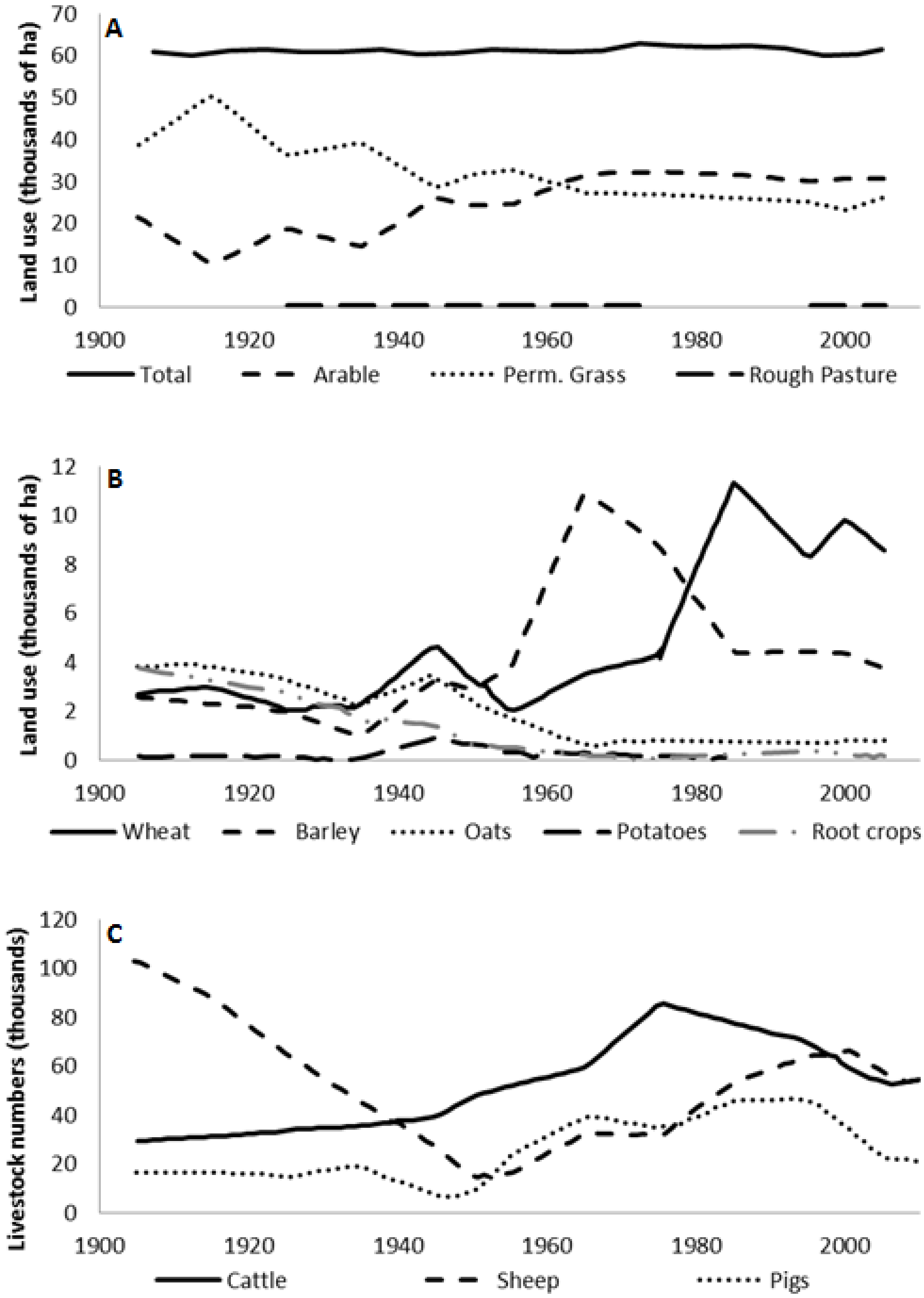


Figure 2.14: Agricultural land use for the Poole Harbour catchment by A: area of land use types; B: area of land under different crop types; and C: livestock numbers. Adapted from Grabowski and Gurnell (2016) assuming equal distribution of land use throughout Dorset.

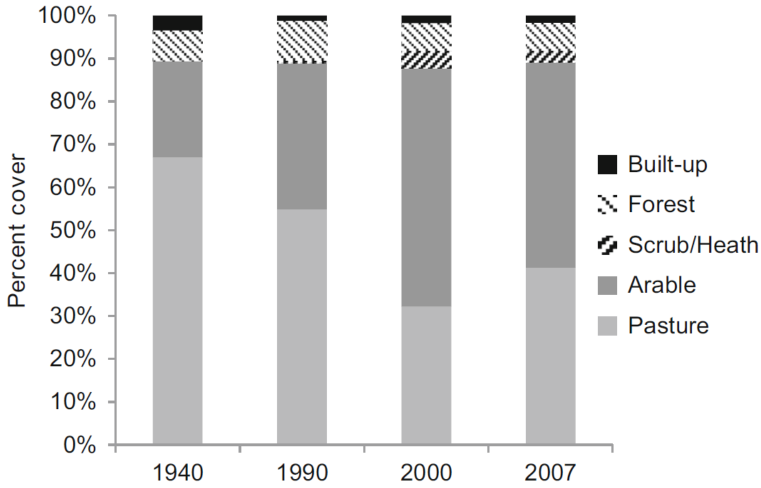


Figure 2.15: Land cover of the River Frome catchment (Grabowski & Gurnell, 2016).

While the vast majority of the land within the Poole Harbour catchment is agriculture, agriculture itself only accounts for 5% of Dorset's economy (PHCI, 2014). The leading industry within the Poole Harbour catchment is tourism with greater numbers of visitors seen in the summer months (PHCI, 2014). The population of the catchment has continued to increase and is predicted to increase by 25000 by 2035 (PHCI, 2014; Figure 2.16). Along with the tourism contribution, the population increase is predicted to increase sewage waste discharges by 13% in Dorchester and 80% in Wareham (PHCI, 2014).

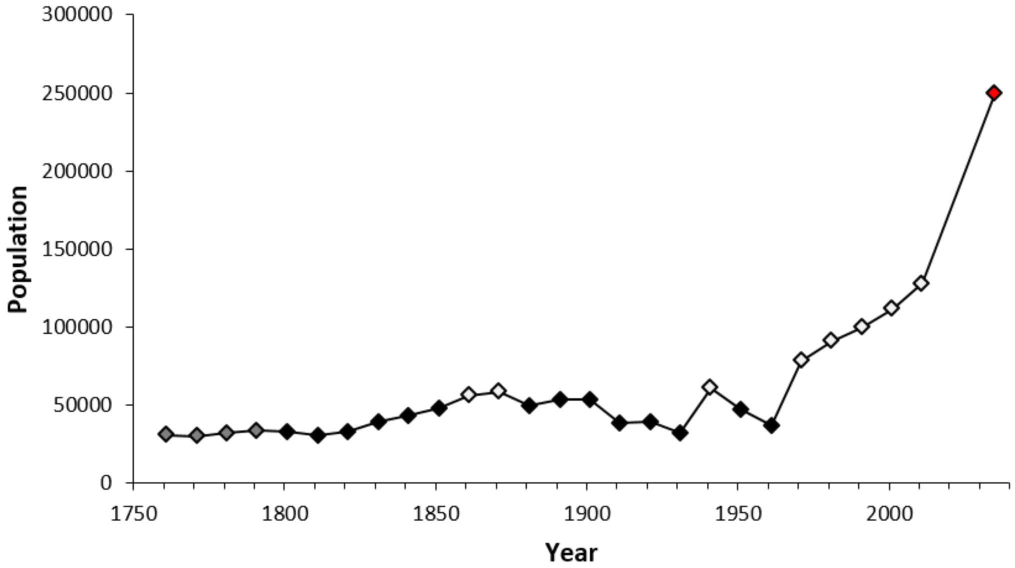


Figure 2.16: Population of the Poole Harbour catchment showing an increase in population towards present. Where parish level data (black symbols) was not available, 31% of the county level data (white symbols) for Dorset was used (Southall & University of Portsmouth, 2017) and 31% of Wrigley's (2007) Dorset county data was used for 1761-1791 (grey symbols). PHCI (2014) 2035 prediction as red symbol.

2.4.5 Why does Poole Harbour need a SOS?

In June 2013 the government officially nationally adopted the Catchment Based Approach which encourages catchment stakeholders to work together to deliver improvements to the rivers and groundwaters in the catchment (PHCI, 2014). The aim of the Catchment Plan is for stakeholders to work collaboratively to meet the needs of local people, businesses, wildlife and European legislation and to protect the groundwater, rivers and Poole Harbour in general for those who live in, work in and enjoy the catchment (PHCI, 2014). The Frome and Piddle Catchment Initiative, now known as the Poole Harbour Catchment Initiative Catchment Plan, was one of 25 national pilots to trial a Catchment Based Approach (PHCI, 2014). It uses scientific approaches to develop potential solutions to improve and protect the Poole Harbour catchment to benefit all the catchment stakeholders (PHCI, 2014). The Poole Harbour Catchment Initiative (2014) was implemented to ensure that the status of the Poole Harbour system conforms to a range of domestic and international directives (Table 2.1), given:

- the Water Framework Directive (WFD) standards failed to be met by some groundwaters and rivers (Figure 2.17);

- some groundwater sources are at risk of failing the Drinking Water Inspectorate (DWI) standards;
- the River Frome SSSI currently fails the SSSI condition assessments proposed by Natural England; Poole Harbour currently fails to meet the requirements of a Special Protection Area for internationally valuable birdlife and the WFD transitional water (estuary) designation;
- in recent years there has been huge variability in salmon stocks and;
- climate change is likely to result in more extreme flow events and so measures are required to provide flood mitigation (PHCI, 2014).

Table 2.1: Examples of directive standards and their corresponding statuses for Poole Harbour.

Directive	Aspect	Standard	Poole Harbour status	Reference
Nitrates Directive	Nitrate	<50mg l^{-1}	Polluted Water (Eutrophic)	European Commission (2010) PHCI (2014)
Water Framework Directive	Dissolved inorganic nitrogen (DIN)	Good: <0.25mg l^{-1} for salinity 30-34.5‰ <0.42mg l^{-1} for salinity <30‰	Moderate – Environment Agency consider an exceedance of 'good' status threshold should be subject to further assessment (Figure 2.17)	Cascade Consulting and Wessex Water (2012) PHCI (2014)
Water Framework Directive	Chemicals e.g. tributyl-tin compound (hull paint)	<0.2 ng l^{-1}	Failing	PHCI (2014) Alasonati et al., (2016)
Drinking Water Inspectorate	Nitrate Nitrite	<50 $mgNO_3l^{-1}$ (11.3 mg N l^{-1}) <0.5 $mgNO_3l^{-1}$ (at consumer taps)	Groundwater sources risk of failing	Drinking Water Inspectorate (2010) PHCI (2014)

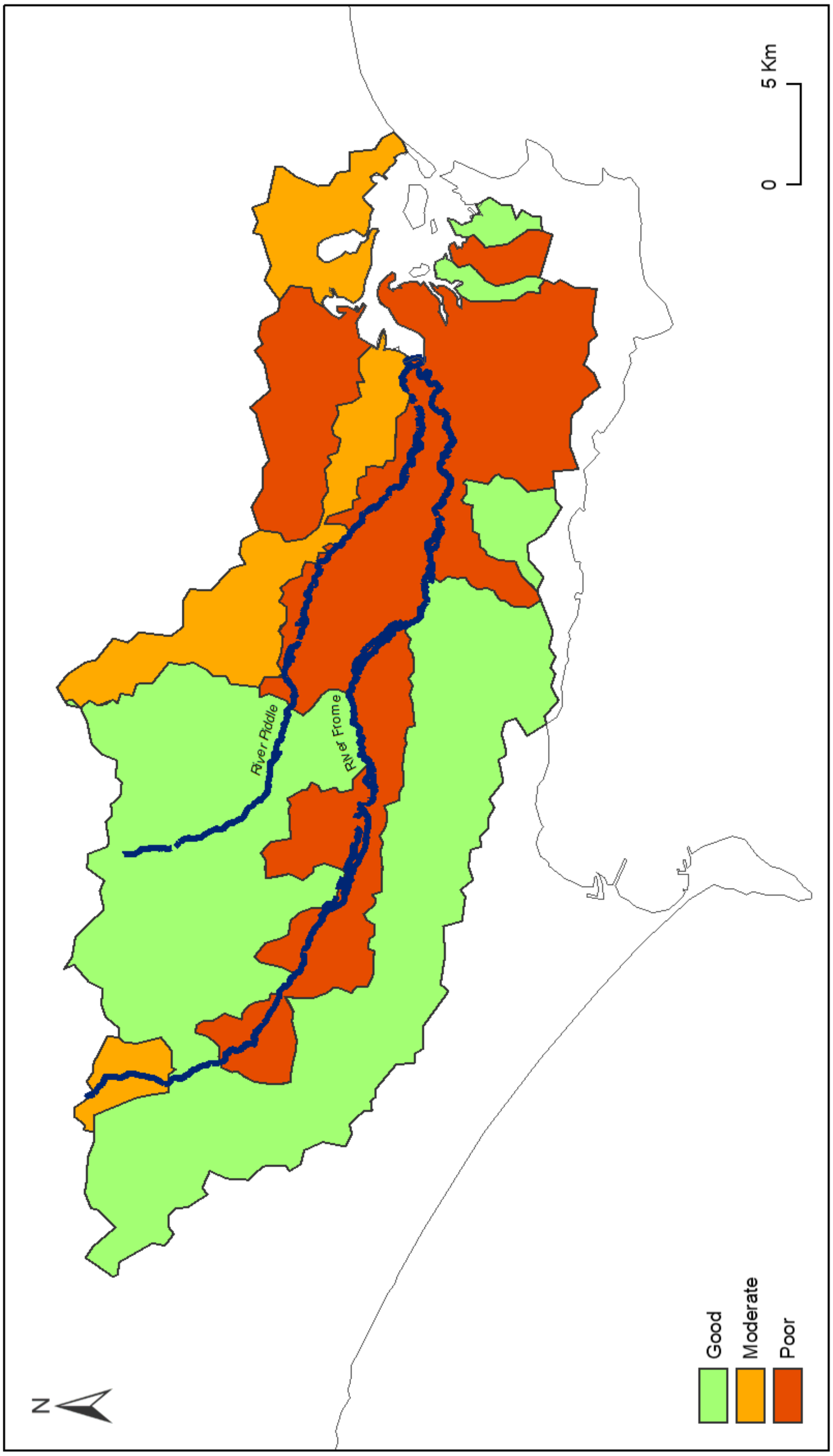


Figure 2.17: The Water Framework Directive status of Poole Harbour surface waterbodies (PHCI, 2014).

Nutrient loading of the system has not only caused the catchment to fail directive standards but as a consequence has caused undesirable algal blooms and eutrophication (Langston et al., 2003). Eutrophication is a product of nutrient over enrichment within an aquatic system which leads to algal blooms and anoxic events, causing not only ecological losses but also economic, e.g. costs associated with water purification, losses of fish and recreational amenities (Carpenter, 2005). Poole Harbour has a history of algal blooms and eutrophication as detailed in Table 2.2; hence this research aims to identify historical relationships between nutrient and ecological dynamics.

It is worth noting that the majority of algal bloom records from Poole Harbour are mainly focused on Holes Bay (Table 2.2). This is not to say that algal blooms have not been present in other areas of the harbour, e.g. the Wareham channel, but focus has primarily been given to Holes Bay in published records. Using palaeoenvironmental archives collected within this study, spatial and temporal records of algal changes can be established to determine if algal blooms are mainly prominent in Holes Bay or are detected elsewhere within the estuary.

Table 2.2: Summary of the history of algal blooms within Poole Harbour (Langston et al., 2003).

Date	Algal growth and eutrophication status
Late 1960s	Growth of green algae in Holes Bay was identified when cooling water intake screens of a power station were blocked and complaints of a smell of rotting seaweed were made. Investigations established that the growth of *Enteromorpha* and *Ulva* had been stimulated by high levels of ammonia and nitrate.
1980	Aerial photographs and follow up surveys identified in addition to those in Holes Bay and Blue Lagoon, substantial growths of macroalgae in the Southeast of the Harbour, south of Brownsea Island.
1980’s	Eutrophication was noted to be less of an issue as a result of the removal of multiple causes. During the 1970s Poole power station went onto intermittent production and finally closed down in the early 1980s. Intertidal areas of Sterte Bay within Holes Bay where algal growth and anoxic sediments were particularly evident were infilled for a road building development.
1995-1997	Intertidal areas of Holes Bay have significant increase of macroalgae cover which was linked to shellfish mortalities.
1997-2000	Chemical and biological data was collected and indicated the Harbour, in particular Holes Bay, was eutrophic or at risk of becoming eutrophic.
1998	Aerial photography indicates Poole Harbour still has an eutrophication problem due to excessive nutrient inputs with macroalgae blooms on intertidal mudflats (greater coverage in summer months (Jones & Pinn, 2006)) and dense growth in Blue Lagoon, Holes Bay, Lytchett Bay, Keysworth Point and Ower and Brands Bay.

Poole Harbour’s algal mat and eutrophic history has been summarised by Langston et al., (2003) and Jones & Pinn (2006) further investigated the effects macroalgal mats have on benthic biodiversity within Holes Bay. Observations were carried out over a six month spring/summer period but there was a lack of a control area to compare changes to, to directly link biodiversity changes to mat development (Jones & Pinn, 2006). However, the faunal community would be expected to exhibit its greatest species diversity and abundance at the time of year the study occurred thus it is assumed the observed community changes are associated with the algal mat development (Jones & Pinn, 2006).

An initial increase in infaunal diversity and abundance was found as the mat developed but this rapidly declined as the mat became more dense (Jones & Pinn, 2006). Macroalgal blooms cause changes to benthic communities as a result of complex interactions of factors such as reduced current velocity leading to siltation (Hull, 1987; Raffaelli et al., 1998), reduced oxygen exchange (Norkko, 1998), anoxia and production of toxic hydrogen sulphide (Bolam et al., 2000). Carbon and nitrogen levels within sediments covered with algal mats have been found to be three times higher compared to unvegetated areas (Pihl et al., 1999). While the macroalgal mat biomass increases, proportions of the mat can no longer be photosynthetically active due to the blocking of light penetration, resulting in a net carbon release (Peckol & Rivers, 1996). This can lead to a continuous input of organic matter and release of nutrients to the system as the rate of decomposition can be high (Pihl et al., 1999). Such states can thus provide nutrients for future algal development where water exchange is limited and produce a feedback mechanism as the macroalgal blooms can be self-regenerating (Norkko & Bonsdorff, 1996a; Pihl et al., 1999). Such a feedback is likely where water turnover is limited, like Holes Bay, and active management is required to reduce anthropogenic sources of nutrients (Jones & Pinn, 2006).

As the work of Jones & Pinn (2006) has indicated, patchy macroalgal mats can benefit the benthic community but the development of larger, extensive mats are likely to result in impoverished benthic assemblage with altered species composition (Norkko & Bonsdorff, 1996b). Such changes cause alterations higher up the trophic web reducing the diversity and abundance of larger organisms that feed on the benthos (Deegan et al., 2002). The eutrophic state as a result of algal mat formation reduces the system's capacity to transfer carbon to higher trophic levels, promoting microbial feedback loops as the carbon is no longer transferred to larger consumers (Baird et al., 2004) . It is therefore important the source and causes of macroalgal blooms are understood to allow a chance to reduce and ultimately reverse the unwanted eutrophic effects (Jones & Pinn, 2006).

The Poole Harbour Catchment Plan identified five key issues which need to be managed to stabilise and potentially reverse the effects on water quality and the biophysical responses to anthropogenic activities: nitrogen, phosphorus, sediment, channel and habitat alterations and water quantity (PHCI, 2014). By addressing these key issues, it is hoped the agreed outcomes and targets of the catchment plan will be met including:

- surface waters within the catchment meet WFD good ecological status by 2027;
- the River Frome and the Bere Stream SSSI reach favourable condition by 2020;

- the catchment groundwater bodies and Poole Harbour reach good status and favourable condition as soon as possible and;
- no drinking water supply will be at risk of failing the DWI standards (PHCI, 2014).

The following sections, nitrogen (2.4.5.1), phosphorus (2.4.5.2), sediment (2.4.5.3), channel and habitat alterations (2.4.5.4) and water quantity (2.4.5.5)2.4.5, outline the problems and targets for each of the five key issues identified and the actions that have been taken thus far to address the problems.

2.4.5.1 Nitrogen

Nitrogen is required for protein synthesis during plant growth while phosphorus is required for DNA, RNA and energy transfer (Conley et al., 2009). These nutrients are essential for agricultural activity (Wang et al., 2016), the principle land use within Poole Harbour's catchment. As Poole Harbour is a groundwater fed system, a lag between leached nitrate applied to soils to discharge into the freshwater systems can be expected of up to multiple decades (Wang et al., 2016). There has been a general increasing trend in mineral fertiliser use since the 1940s as a result of the intensification of agriculture, but since the 1980s this trend has reversed and there is now a decline in artificial fertiliser applications (Smith et al., 2010; Figure 2.18). These macronutrients are key limiting nutrients for aquatic plant growth (Conley et al., 2009). Understanding their sources, recycling and regulation within the Poole Harbour catchment is therefore key to understanding patterns of estuarine eutrophication.

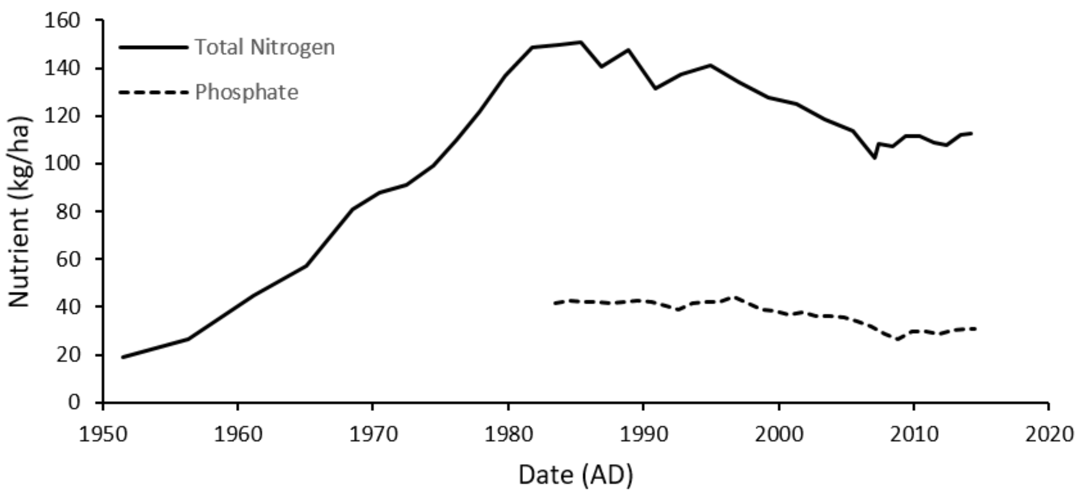


Figure 2.18: Fertiliser use in Great Britain 1950 – 2015 (Smith et al., 2010; DEFRA, 2016).

Within the Poole Harbour catchment, a rise in nitrate concentrations has been related to changes in land use, fertiliser applications and increase in STW effluent entering the aquatic system (Casey et al., 1993). Estimated contributions from sources of nitrogen to Poole Harbour are given in Table 2.3, with agriculture (fertiliser and manure) and STW effluent being the greatest contributors. Rivers contribute the largest nitrate proportion to Poole Harbour with 73% of nitrates derived from surface waters, 19% from the English Channel and 8% from direct charges (PHCI, 2014). Between 2006 and 2011, the dissolved available inorganic nitrogen (DAIN) loads contribution from the Rivers Frome and Piddle varied in response to rainfall with loads from the Frome twice that of the Piddle, reflecting the larger catchment size (Cascade Consulting & Wessex Water, 2012). Not only are the loads from the River Frome of greater quantity but they have also increased from an average annual load of 606 tonnes between 1966-1975 to 1080 tonnes for 2006-2010 (Cascade Consulting & Wessex Water, 2012). As stated by the Catchment Plan, the River Frome, one of Poole Harbour's main nutrient sources, currently has an average nitrate concentration level of 6.5 mg/l, an increase on the historical level of 2 mg/l in 1965 (Figure 2.19). Regression analysis on the monitored data indicates there is a continuous significant increase in nitrate concentration within the freshwater system since the start of monitoring at East Stoke (Figure 2.19). This indicates that while there may have been a decrease in fertiliser application in recent decades, this effect has not been detected within the water course itself, a likely result of the lag time expected from a groundwater dominant system. Catchment managers believe the increase of nitrogen quantities in the River Frome is the cause of the observed changes in ecology detected in Poole Harbour, e.g. increased algal mat coverage (PHCI, 2014). This assumption is likely because of an assumed observed linear relationship between increased nitrogen and increased algal presence from monitored records since the 1960s however this theory will be tested within this research.

Table 2.3: Estimated percentage contribution of nitrogen sources to Poole Harbour (PHCI, 2014).

Source	**Contribution (%)**
Fertiliser from tillage	51.3
Manure from livestock	25.1
Sewage Treatment Works	14.6
Atmospheric deposition	4.7
Fertiliser from grassland	3.6
Unsewered development	0.7

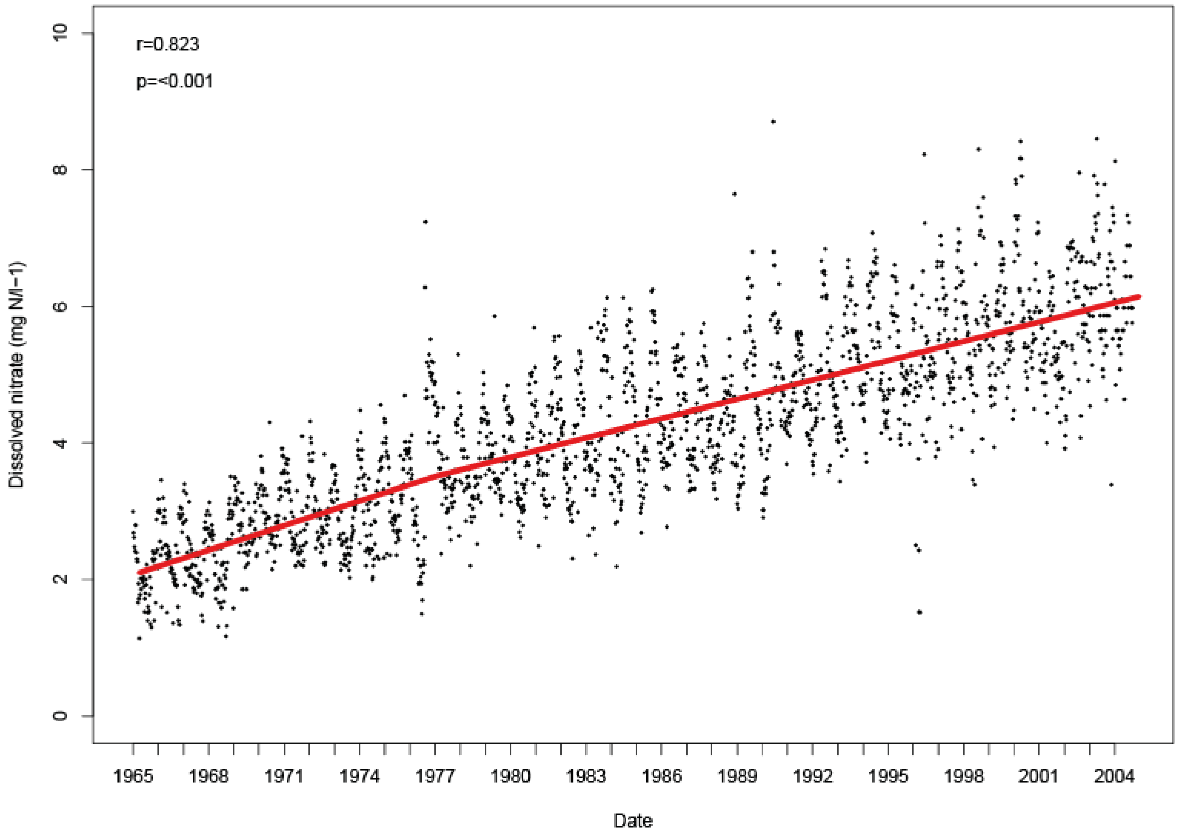


Figure 2.19: East Stoke River Frome monitoring station nitrate concentrations for 1965-2014 (PHCI, 2014). Red line illustrates subsequent segmented regression analysis which detected no significant change in a continuous significant positive trend in nitrate concentration with time.

Not only have the increased concentrations of nitrogen been associated with the algal blooms and eutrophication of the harbour but the public water supply sources have been threatened. Raw water from boreholes at Eagle Lodge, the groundwater source supplying the Dorchester area, failed DWI nitrate standards several times between 1999 and 2001. A nitrate removal plant was planned for the site in 2004 but due to construction and running costs, Wessex Water investigated a catchment management approach (PHCI, 2014); the success of which is discussed further in this section. Raw water concentrations were calculated to contribute up to a third of the DAIN influent to Poole Harbour by the Cascade Report (2012) with the River Frome contributing 53% and the River Piddle 31%.

The chalk groundwater dominance of the Poole Harbour catchment results in a lag time of up to 30 years, or more, for the nitrogen within fertilisers to reach the aquatic system as well as via direct run-off (PHCI, 2014). Therefore, the effects of the increased application of fertiliser to the land may not be detected in the system response, e.g. ecological changes, for some time after application. The DAIN concentrations have increased since the 1960s, with groundwater DAIN concentrations between 5.5-10mg N/l within the chalk geology of the catchment (Cascade Consulting & Wessex Water, 2012; PHCI, 2014). Although the rate of the increase may reduce as a response to reduced agricultural nutrient application, the trends in nitrogen loading into the harbour are expected to increase as a consequence of farming practices from 30 years ago (Cascade Consulting & Wessex Water, 2012; PHCI, 2014). This contribution is expected to stabilise around 2300 tonnes N/yr with a peak between 2020 and 2030 (PHCI, 2014). The predicted population increase previously mentioned is also expected to contribute an additional 21 tonnes N/yr via the STW (PHCI, 2014). The Cascade Consulting report on behalf of Wessex Water (2012) estimated that non-sewered properties within the Poole Harbour catchment contribute 15 tonnes N/year as groundwater and surface water DAIN loads. Tighter consents have been implemented at Poole STW and this has resulted in a decrease in direct DAIN releases into Poole Harbour, however DAIN loads are increasing at Dorchester STW (2006-2010) (Cascade Consulting & Wessex Water, 2012). For the period 2006-2010, total STW loads for the River Frome were 99-151 tonnes and 9-14 tonnes for the River Piddle (Cascade Consulting & Wessex Water, 2012). STWs accounted for 13% of the overall 2009 DAIN load with direct STW discharges from Poole, Wareham, Lytchett Minster, Studlands and Holton Heath accounting for 4.3% of the total load to Poole Harbour (Cascade Consulting & Wessex Water, 2012). However, 89% of the River Frome and 98% of the River Piddle DAIN loads were determined to originate from non-STW sources (Cascade Consulting & Wessex Water, 2012).

To delay the expectant increased nitrogen concentration, targets have been set so that by 2035: all new residential and commercial developments should not result in a net increase in nitrogen and; diffuse agricultural sources have the greatest nitrate reductions within the catchment with a target of 1730 tonnes N/yr (PHCI, 2014), though this level seems a somewhat arbitrary threshold and requires testing.

Some reduction of nitrogen within the catchment has already taken place with nitrogen removal at Poole STW and a reduction in groundwater sources where the Wessex Water catchment management team have engaged with farmers to minimise nutrient inputs on a voluntary basis (PHCI, 2014). However, this only accounts for a relatively small area of the catchment of Poole Harbour (PHCI, 2014).

As previously mentioned, at Eagle Lodge a catchment management approach was implemented. This commenced in 2005, with the aim that nitrate inputs in the catchment did not result in peaks above the nitrate standard under high groundwater situations (PHCI, 2014). Communication with farmers and farm records were used to suggest changes in farming practices, for example including improved nutrient and manure management, fertiliser spreader calibrations and the use of winter cover crops (PHCI, 2014). Since 2006, there have been some nitrate peaks during the wetter winters, but now these peaks are well below the 11.3 mg N l^{-1} drinking water standard limit (PHCI, 2014).

2.4.5.2 Phosphorus

As well as the discussed source of phosphorus from agricultural practices, phosphorus can also enter water courses from municipal and industrial waste (Conley et al., 2009), e.g. STW effluent. Future phosphorous effluent concentrations leaving the STW are not expected to change despite the projected increase in catchment population, primarily on account of the effectiveness of the current waste treatment practices, however the volume of such effluent may increase and hence phosphorus supply would still increase. Such an assumption does not account for any increase in the number of dwellings which are not directly connected to the STW.

Sources of phosphorus within the Poole Harbour catchment can be characterised as diffuse and point sources (PHCI, 2014). Diffuse sources include agricultural land from manure, fertilisers, soil and sediment and also septic tanks; these sources can be an input via run-off or through leaching (PHCI, 2014). They are estimated to account for 64%, 15 tonnes per year, of the total phosphorus load into the River Frome and account for approximately 77% of the total phosphorus reaching the River Piddle (PHCI, 2014). The point sources of phosphorus are primarily from STWs, including human and trade waste combined with detergents (PHCI, 2014). The point sources are estimated to account for approximately 36%, 8 tonnes per year, of the total phosphorus load to the River Frome and 23% to the River Piddle (PHCI, 2014). The estimated percentage contributions of total phosphorus to the Rivers Frome and Piddle are detailed in Table 2.4.

Table 2.4: Estimated total phosphorus contributions to the River Frome and River Piddle (PHCI, 2014).

Source	**Contribution (%)**	
	River Frome	**River Piddle**
Manure	28	24
Soil	22	20
Fertiliser	19	20
Sewage Treatment Works	19	28
Urban	6	3
Particulate	5	4
Direct	1	1

During the low flows of the summer, the STWs effluent contributes to a higher proportion of the total phosphorous in the flow, enhancing the aquatic plant growing season (March to September) (PHCI, 2014). Within these low flow periods, intermittent high phosphorus concentrations could possibly be accounted for by several fish farms located on the tributaries of the River Frome; in themselves they do not contribute considerable amounts of phosphorous but during low flow events they contribute a higher proportion of the supply (PHCI, 2014). It is estimated that there are more than 3500 unsewered properties within the catchment and their septic tanks may either discharge into the ground or directly into the river (PHCI, 2014). Those directed into the ground have phosphorous which is bound up within the chalk, those which discharge directly into the watercourse are estimated to contribute a low quantity to the total phosphorous in the river but during the low flows contribute a higher proportion (PHCI, 2014).

In the River Frome, ortho-phosphate concentrations peaked in the mid-late 1990s but have decreased over the last ca. 30 years (Figure 2.20). The concentrations are not consistently at sufficiently low concentration to meet favourable condition standards, particularly during summer growth seasons when phosphorus inputs account for a higher proportion of the flow, and periods of wet weather when there is increased run off and thus nutrient loading from the catchment. Even with lower phosphorus levels within the River Frome, excessive algal growth still occurs during high summer temperatures when combined with low velocities, i.e. when phosphorus accounts for a greater proportion of the water volume (PHCI, 2014). Ultimately, the increase in algal growth reduces the oxygen concentrations within the water, negatively affecting plant growth and river and estuarine ecology (PHCI, 2014). The WFD classed the diatoms of the River Frome and the River Piddle as poor and macrophytes as moderate (PHCI, 2014).

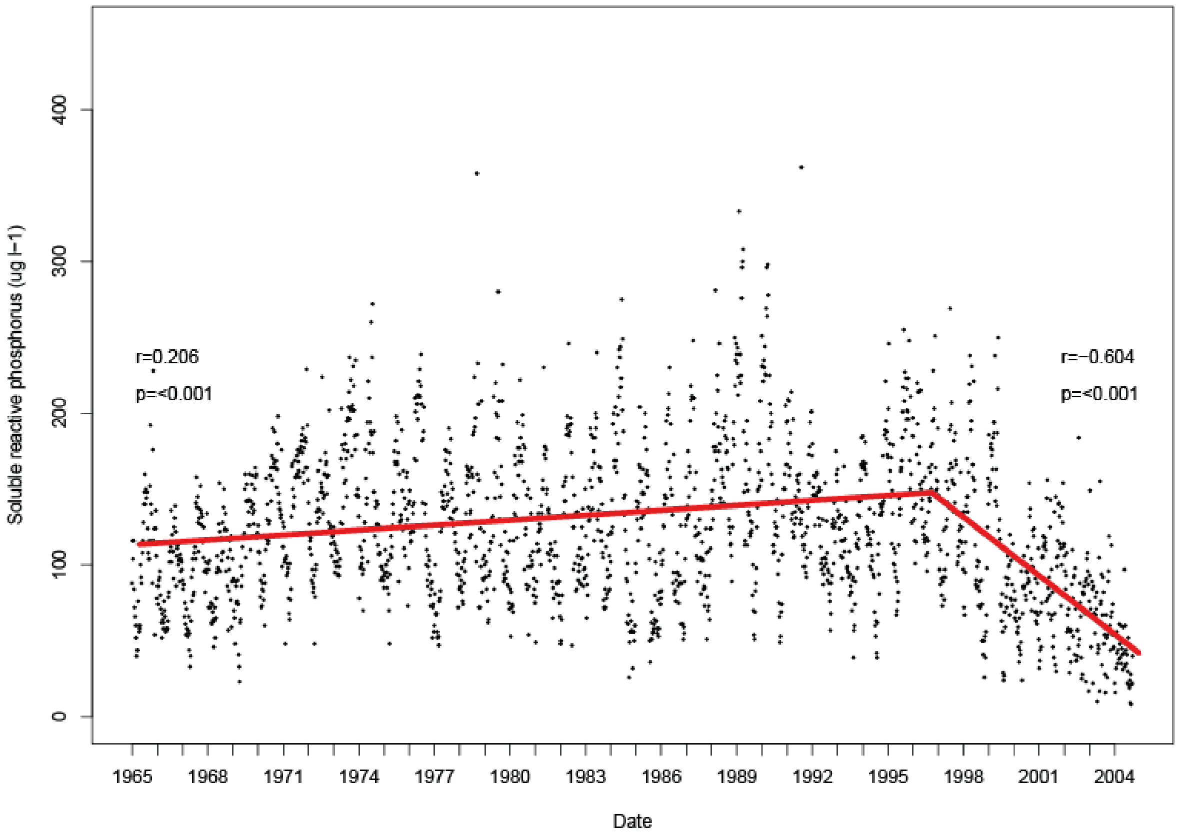


Figure 2.20: East Stoke monitoring station ortho-phosphate concentration for 1965-2014 (PHCI, 2014). Red line illustrates subsequent segmented regression analysis indicating a significant but small increase in concentration to 1996 and then a significant and more rapid decrease in concentration to present.

The Poole Harbour Catchment Initiative Catchment Plan (2014) states that the River Frome SSSI, between Dorchester and Wareham, and the Bere Stream SSSI will meet the SSSI targets by 2020; that is that ortho-phosphate concentrations are no greater than 50 ug/l P as the growing season average and no greater than 50 ug/l P as an annual average. All rivers within the catchment must also reach WFD Good Status for the ortho-phosphate concentrations by 2021, or the latest of 2027 (PHCI, 2014).

It is worth noting Casey & Newton (1973) and Casey (1975) determined that nitrogen contribution to the River Frome was a consequence of Dorchester STW and that the majority of this was from fertiliser, whilst some of the phosphorus contribution was from fertiliser use, 70% originated from STW effluent. Thus, the decline of ortho-phosphate concentrations recorded within recent decades has been associated with the phosphorus removal at Dorchester and Wool STWs using chemical treatment (iron dosing), alongside changes in manure management practices and decline in phosphorous fertilisers (PHCI, 2014). A change to the treatments at STWs to successfully remove more phosphorus reduces the concentrations in the effluent. However to do this for a prolonged period at an environmentally beneficial standard is expensive with not only the start-up costs but also the continuing running, transport of chemicals and removal of sludge, all resulting in a high carbon footprint (PHCI, 2014).

Sustainable phosphorus removal would be beneficial to both the ecosystem and the wider environment if reduced carbon footprints can be maintained, an example of which is the phosphorus removal trial at Somerton STW using reedbeds in 2010 (PHCI, 2014). Within reedbeds, phosphorus can bind to the material of the reedbed or be taken up by plants, thus removing it from the discharge waters (Arias et al., 2001). The trial consisted of using reedbeds of different media, with steel slag, a by-product of the steel industry, as the most promising, resulting in less than 2 mg/l of orthophosphate in the final effluent within the summer months (PHCI, 2014). The reedbed media would require replacing every four to five years and options are being explored to find a use of the exhausted media (PHCI, 2014). Though the reedbeds do require a relatively large area, the results suggest they are a relatively cheap and sustainable option for phosphorus removal at a small scale (PHCI, 2014).

From the data provided, it is apparent that while nitrogen is increasing in concentration within the water course, phosphorus is decreasing and there has been no noted change in the algal blooms or eutrophic state of Poole Harbour. It is therefore assumed the regulatory macronutrient in Poole Harbour is nitrogen. While phosphorus is usually the driving macronutrient for eutrophication in freshwater systems, within estuarine environments, eutrophication is primarily controlled by nitrogen (National Research Council, 2000; Conley et al., 2009).

Primary production by phytoplankton is a function of the relative availability of nitrogen and phosphorus within the aquatic environment, the preferential storage, recycling or loss of one of the macronutrients in the ecosystem and the amount of biological fixation (National Research Council, 2000). Phytoplankton approximately requires a nitrogen: phosphorus ratio of 16:1 moles, the Redfield ratio (National Research Council, 2000; Redfield, 1958). While lakes receive nutrient inputs from upstream terrestrial ecosystems and the atmosphere, estuaries receive nutrients from not only these sources but also from the connected ocean water masses (National Research Council, 2000). Estuaries are more likely to be nitrogen limited compared to lakes as they receive lower ratios of nitrogen: phosphorus than the Redfield ratio from the ocean waters, due to denitrification of the continental shelves, and from catchment land, especially those that are agricultural as there is a greater proportion of phosphorus to nitrogen (National Research Council, 2000). In summer months phosphorus can be rapidly recycled from within the water column and sediments (Conley et al., 2009). This is more likely to occur in coastal waters where it is more saline whereas in freshwaters it is not biologically available because it is absorbed by clay and other particles (Conley et al., 2009; Blomqvist et al., 2004). Therefore reducing phosphorus in the freshwater system may reduce algal blooms and eutrophic states directly but further down the water course in the estuary, where more nitrogen can be transported, reducing phosphorus may exacerbate eutrophication problems (Conley et al., 2009).

Reducing phosphorus loadings from wastewater treatment and banning phosphorus based detergents reduced algal blooms in the freshwater portions of the Neuse River estuary, North Carolina, USA, but it increased eutrophication downstream in the estuary where phosphorus was more rapidly recycled (Paerl et al., 2004). However, within the River Frome a reduction in phosphorus concentrations has not produced the same results. While phosphorus has decreased in concentration, there have still been accounts for algal blooms within the water course. This could be explained via seasonality; as discussed, during the summer months the phosphorus concentrations are higher and thus more readily available for phytoplankton, but algal bloom data for this area has only been provided qualitatively and thus further relationships cannot be explored at this time. Further investigation, in accordance with theory, may show less prominent algal blooms and eutrophic waters in close proximity to the River Frome and Piddle estuary but in other areas of the harbour where there is a greater salinity, greater algal blooms and eutrophication are likely to be detected.

2.4.5.3 Sediment

Sediment has been defined by the Poole Harbour Catchment Initiative as “any substance that does not readily dissolve in water” (PHCI, 2014 p. 24). It is a consequence of erosion within the channel and soil and organic run-off from the catchment’s land (PHCI, 2014). It is an important variable to consider when discussing nutrient and ecological systems as it can become trapped by plants and debris and also settles out at low velocities (PHCI, 2014). Sediment can affect biota through: physical smothering when it settles out of suspension; fish and invertebrate damage (e.g. gill damage) whilst suspended; reduction of light penetration through the water body; oxygen depletion with the increased breakdown of organic silt by microorganisms and; fine sediments can carry pollutants such as harmful chemicals and phosphorous leading to algal blooms in the waters (PHCI, 2014). Estuarine waters receive contaminants, such as nutrients and pollutants, via local anthropogenic activities, e.g. industry and tourism, and also those from riverine inputs (Eggleton & Thomas, 2004), the River Frome and Piddle. Contaminants can affine to solid-phase fractions of the sediment which can be stored within floodplains for hundreds or in some cases thousands of years (Eggleton & Thomas, 2004; Dennis et al., 2009). However, floodplains are not necessarily permanent stores for sediments and thus contaminants and the reworking of such floodplains, e.g. by erosion, can release the sediment and the associated contaminants back into the water course (Eggleton & Thomas, 2004; Dennis et al., 2009) alongside those that have been directly washed in and not accreted. This remobilisation can cause future environmental problems with historical contaminants, once trapped within the accumulated sediment, able to become a part of the system once again (Dennis et al., 2009) and interact to cause algal blooms, for example. Such sediment-contaminant relations have been widely studied on metal contaminated sediments (e.g. from mining activity (Eggleton & Thomas, 2004; Dennis et al., 2009; Macklin et al., 2006)) but macronutrients such as nitrogen and phosphorus can also adhere to sediment particles (Nicklow et al., 2013; Petersen et al., 2013). It is therefore important to understand the sources, transport, accumulation and process of sediment from the Poole Harbour catchment into its estuarine waters.

Sediment contribution and storage within Poole Harbour has been studied by Hubbard & Stebbings (1968) and Collins & Walling (2007a) for example, and the subject has been somewhat summarised by RACER (2004) in a synthesised Sediment Transport Study collating research papers and reports on the area.

A somewhat limited study was carried out by Hubbard & Stebbings (1968) to estimate the suspended sediment contribution from the River Frome into Poole Harbour. On 23rd January 1967, Hubbard & Stebbings (1968) collected four liters of water from the River Frome at Wareham Quay which they filtered, dried and weighed. From this, and using an estimated flow of the River Frome, they were able to estimate the suspended sediment as 36 tons, or 36700kg, per day (Hubbard & Stebbings, 1968). This was then multipled to provide an estimate for the annual discharge from the River Frome into Poole Harbour estuary (RACER, 2004). The four liters used by Hubbard & Stebbings (1968) cannot be a reflection of a whole river watercourse or for any time period of the year or as an annual representative. The study should have considered multiple collections, at various points along the watercourse, at multiple times of the year, months or even days. It is important that when studying and analysising a large complex system, as many factors and variables are considered and no assumptions and judgements are made on one single and/or limited analysis. With the aid of the documentary evidence supplied by Raybould (2005) on the *Spartina*-assisted mudflat expansion, Hubbard & Stebbings (1968) calculated that over the past 100 years, the amount discharged from the River Frome only quantified to about 1/25th - 1/30th of the total sediment accretion within the harbour (RACER, 2004). However, even though this quantity provides an estimate for the discharge rates, it must be regarded as an estimate as it may not be representative not only due to the timing and anticedent conditions under which the sample was collected (RACER, 2004), but also to the extensive limits in which the first calculations were made.

Collins & Walling (2007a) carried out a similar study whereby they determined the fine-grained sediment storage on the bed of the Frome and Piddle using the sediment remobilisation technique. This investigation was carried out over the period commencing Febuary 2003 and concluding July 2004 (Collins & Walling, 2007a). Their results revealed the total fine sediment stored on the channel bed of the Frome ranged between 5 t km^{-1} and 17 t km^{-1} with a mean of 7 t km^{-1} and the Piddle varied between 5 t km^{-1} and 14 t km^{-1} with a mean of 9 t km^{-1} (Collins & Walling, 2007a). These results are somewhat an improvement on the previous assessments as sampling has been carried out over a period of over a year, however the concluded ranges that have been presented are of a large varience of 12 t km^{-1} and 11 t km^{-1} for the Rivers Frome and Piddle respectively. It should also be noted that the results obtained by Collins & Walling, (2007a) are based on one individual year, it does not take into account the variation which may occur year to year. Therefore the analysis on a multidecadal timescale should provide better assessment of the sediment transport and accretion than an estimation based on one collection of a water sample or a study of only one individual year.

The poor flushing characteristics of the harbour due to the tidal regime, means the area becomes a sediment trap for the suspended load from the rivers and also a trap for the pollutants (Gray, 1985). Therefore changes within the river catchments that influence sediment dynamics, e.g. catchment erosion, will likely be detected within the estuary itself as the sediment is potentially transported downstream. As previously mentioned, annual sediment yields would be useful to determine how sediment dynamics have changed within the catchment to allow comparisons to be made to other variables to establish if there is any relationship between catchment changes and biological responses.

The shoreline of Poole Harbour is characterised by long sections of extensive mudflats, particularly on either side of the Upper Wareham Channel where there is reduced tidal and wave energy (RACER, 2004). The river suspended load of clay and fine silt particles has proved to have provided much of the material for the mudflat construction (RACER, 2004). The colonisation by the saltmarsh vegetation, in particular *Spartina anglica*, of the mudflats has been regarded as a considerable factor regarding the increasing rates of accretion and consolidation of sediment up until the mid-twentieth century (RACER, 2004).

Figure 2.21 and Figure 2.22 illustrate where the tidal currents flow and the contributions of different type of sediment are sourced and enter the estuary. Figure 2.22 may indicate the type of sediment transport into Poole Harbour but it does not provide any quantitative data on the volumes of such sediment input. However, these diagrams can be used to indicate potential locations for retrieving sediment cores from which time series data can be collected, the use of palaeoenvironmental time series data will be further discussed in Section 02.5. For example, the River Frome is illustrated to be a main source of fluvial sediment (Figure 2.22) and also an area with limited tidal influence in comparison with other areas of the harbour (Figure 2.21). Therefore, within this area of the estuary, cores should be representative of a continuous input of sources from the river and should be chronologically intact and subject to limited recycling from estuarine movement processes which is essential for obtaining good time series data from sediment cores.

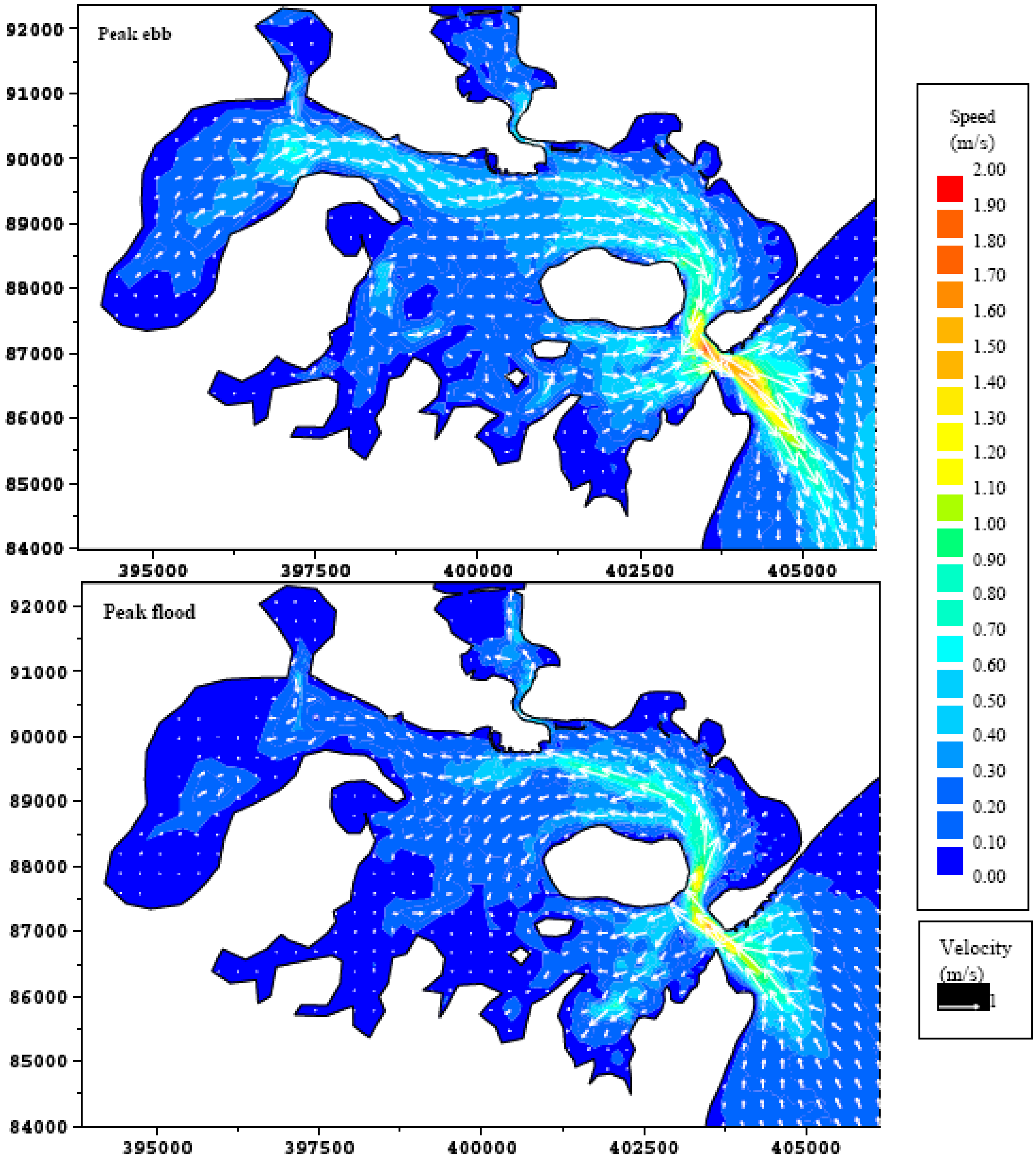


Figure 2.21: Poole Harbour predicted tidal currents (Poole Harbour Commissioners, 2012). Reduced tidal activity is noted in the mutual estuary of the Rivers Frome and Piddle, north of Holes Bay and some areas of the Arne peninsula, thus likely be good locations to retrieve sediment cores from.

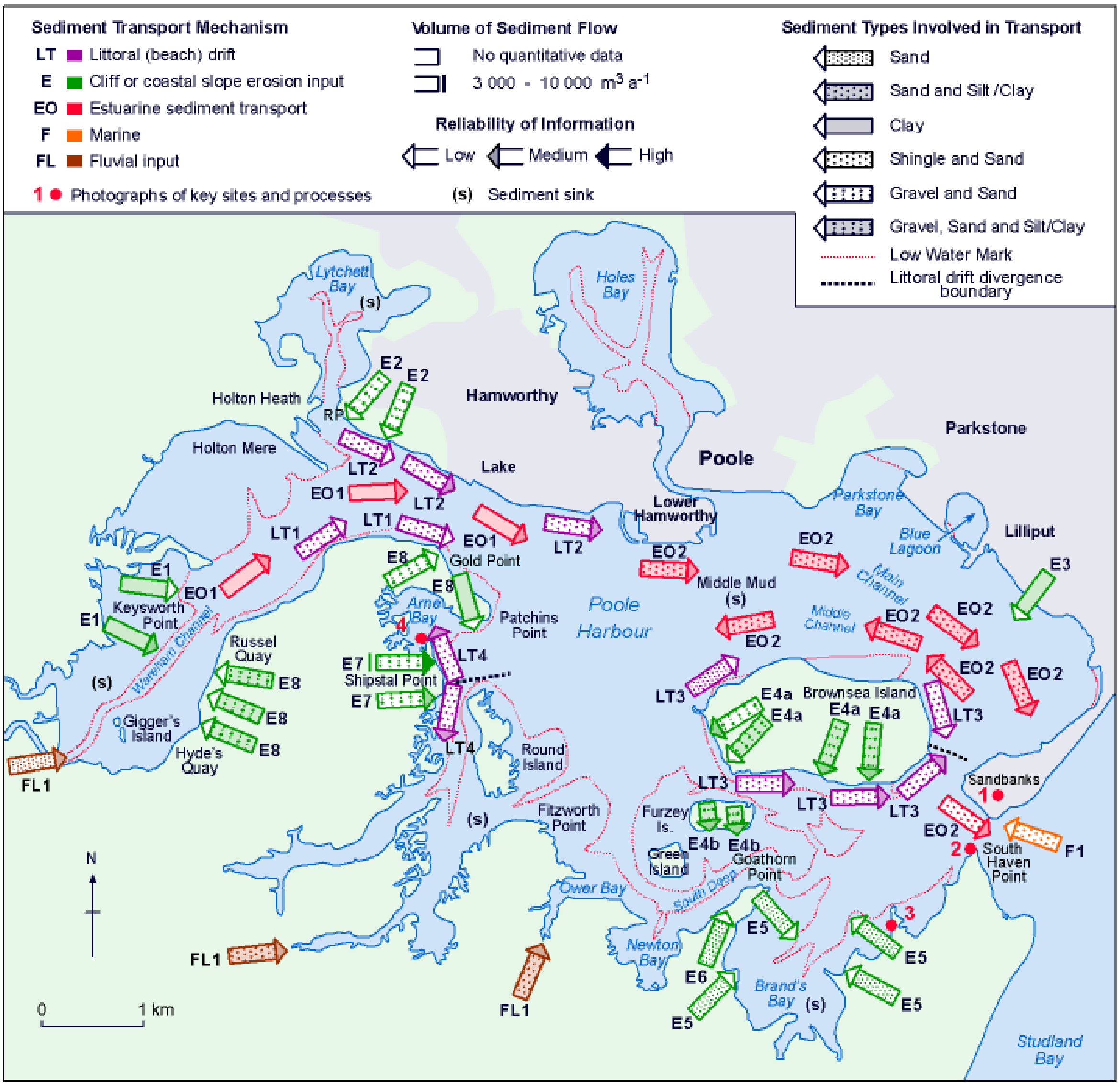


Figure 2.22: Sediment sources and type within Poole Harbour (Poole Harbour Commissioners, 2012). The Rivers Frome and Piddle estuary is deemed to be supplied predominantly by fluvial material, thus sediment cores recovered here likely represent fluvial contribution to the harbour from the agricultural catchment. Holes Bay has been illustrated as receiving no sediment transport from within the estuary and thus a sediment core from this location will likely represent the contributions from the industrial catchment of Holes Bay. The Arne peninsula receives multiple sources of sediment and thus would make a good control site.

Mudflat vegetation should be considered when investigating sedimentary deposits. Vegetation can act as a sediment trap and increase the accretion of sediment within the vegetated area, thus reduce sediment delivery to the estuarine waters, and the decline of vegetation can result in reduced sediment accretion in the vegetated areas and even release sediment back into the estuarine waters where an increase in sediment may be detected. Within Poole Harbour the colonisation and subsequent decline of *Spartina anglica* has been collaborated with sediment accumulation rates (SARs) as investigated by Long et al., (1999) and Marshall et al., (2007). The history of *Spartina* is described in Table 2.5, its first establishment and complete colonisation dates throughout Poole Harbour are illustrated in Figure 2.23 and the estimated loss and spread throughout the rest of the harbour are detailed in Table 2.6.

Table 2.5: Summarised vegetation history of *Spartina anglica* on Poole Harbour mudflats.

Date	**Vegetation status**
Prior late 1890s	Eel grass (*Zostera*) and algae primarily colonised mudflats (RACER, 2004).
Ca. 1895	*Spartina* originates from either violent storm which brings *Spartina* fragments from eroded marshes via tidal currents to Poole Harbour, or, seeds introduced to the harbour from visiting cargo ship (Hubbard, 1965). Fragments or seeds entangle within the *Zostera* and algae to allow the establishment of *Spartina* (Hubbard, 1965).
1899	First discovery of *Spartina* (Hubbard, 1965).
Mid 1920s	Maximum extent of *Spartina* reached ~800ha (RACER, 2004).
Late 1920s	Start of *Spartina* decline (RACER, 2004).
Early 1930s	Widespread decline (RACER, 2004).
1924-1980	300 ha lost and recession still continuing (RACER, 2004).

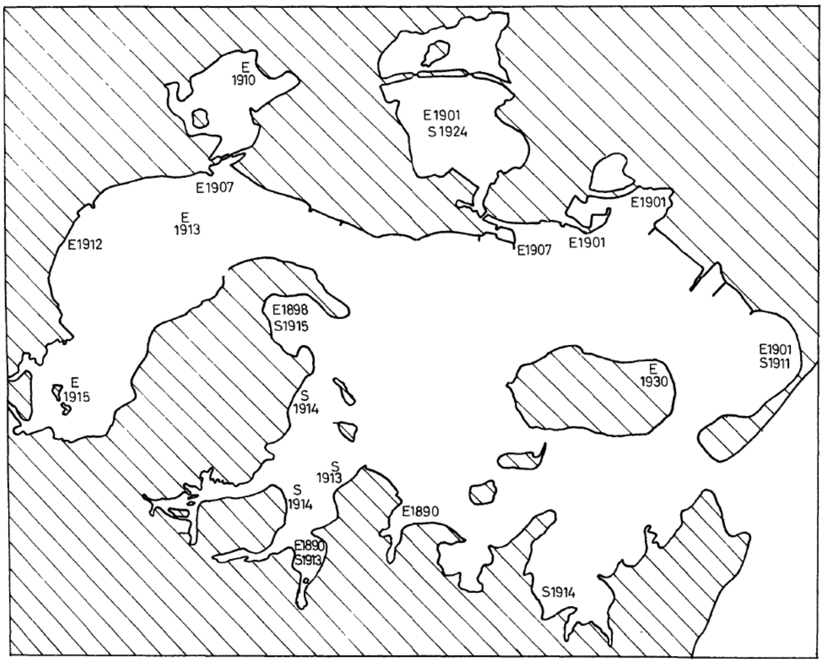


Figure 2.23: Approximate dates for the first establishment (E) and complete colonisation (S) of Spartina in various parts of Poole Harbour (Hubbard, 1965).

Table 2.6: Estimated loss or spread of *Spartina* between 1924 and 1952 within Poole Harbour (Hubbard, 1965).

Location	**Loss/gain (ha)**
Brands Bay	+4.9
Whitley Lake	+2.8
Furzey and Green Island	-31.4
Southern Shore (East)	-27.6
Parkstone Bay	-34.9
Adjacent to Brownsea Island	-52.3
Long and Round Island and Grip Heath	-14.0
Southern Shore (West)	+21.1
Arne Bay	+10.4
Holton-Rockley	+2.1
Holton Mere (Keysworth)	+17.4
Giggers' Island and Swineham	+11.5
Holes Bay	-87.3
Lytchett Bay	-0.3
Brownsea Island	+5.4
Total	-172.2

Mudflats which are consolidated by *Spartina* act as a temporary store for large quantities of silt and clay (RACER, 2004). Other wetland species, such as *Halimione portulacoides, Purcinetha maritima, Phragmites australis* and *Elsrmus prchanthus*, are also a likely contributing factor to the mudflat development as they successfully invaded areas which were vacated by the *Spartina* since the early 1960s (Gray, 1985; RACER, 2004). The sediment trapped within the vegetation prevents the release of associated pollutants and nutrients into the aquatic system which may interfere with the biophysical system. Conversely, the subsequent release of sediment from vegetation decline could result in such release and biophysical consequences.

Determining long-term SARs are useful to investigate changes within estuarine dynamics. Studies carried out in the Poole Harbour area can provide guidance of

SARs to enable cores of correct depth to be collected (Figure 2.24). Cundy (1994) and Cundy and Croudace (1996) determined net SARs for cores collected from Wytch Farm salt marsh and intertidal mudflats using radionuclide dating of ^{210}Pb, ^{137}Cs and ^{60}Co. Long et al., (1999) investigated the SARs of the Arne peninsula using pollen data, *Pinus* and *Spartina anglica*, as chronological markers. The work of Long et al., (1999) was further developed by Marshall et al., (2007) who integrated the use of 'bomb spike' calibration and conventional calibration of AMS ^{14}C dating to determine chronology and SARs within the same location. All of the published records mentioned above used sediment cores but those of Cundy (1994) and Cundy and Croudace (1996) were of a shorter length and could therefore only represent a shorter time period of the area's history.

Figure 2.25 illustrates these published SAR records for the Arne Peninsula. As expected, there is variation in the Long et al., (1999) and Marshall et al., (2007) SAR records as chronological markers have allowed for SARs to be calculated between multiple dates, not just an averaged SAR as calculated by Cundy (1994) and Cundy and Croudace (1996). The SARs of Marshall et al., (2007) shows more variation than that of Long et al., (1999) because more chronological markers have been used to date the sediment core and thus more dates to calculate SARs between. Where all cores provide SARs for the same date range, i.e. post ca. late 1800s, Long et al., (1999) and Cundy (1994) and Cundy and Croudace (1996) ^{210}Pb SARs are of the most similar. Cundy (1994) and Cundy and Croudace (1996) ^{137}Cs and ^{60}Co SARs are of the greatest value and Marshall et al., (2007) provides the lowest value until ca. 1960 when the SAR increases within the range of the other published SARs. Differences in SARs between the published data are likely a result of the different locations the cores were retrieved from and associated spatial variability in estuarine processes and the different methodologies used to obtain chronologies. The published SARs of Poole Harbour will be further explored in Section 5.3.1.

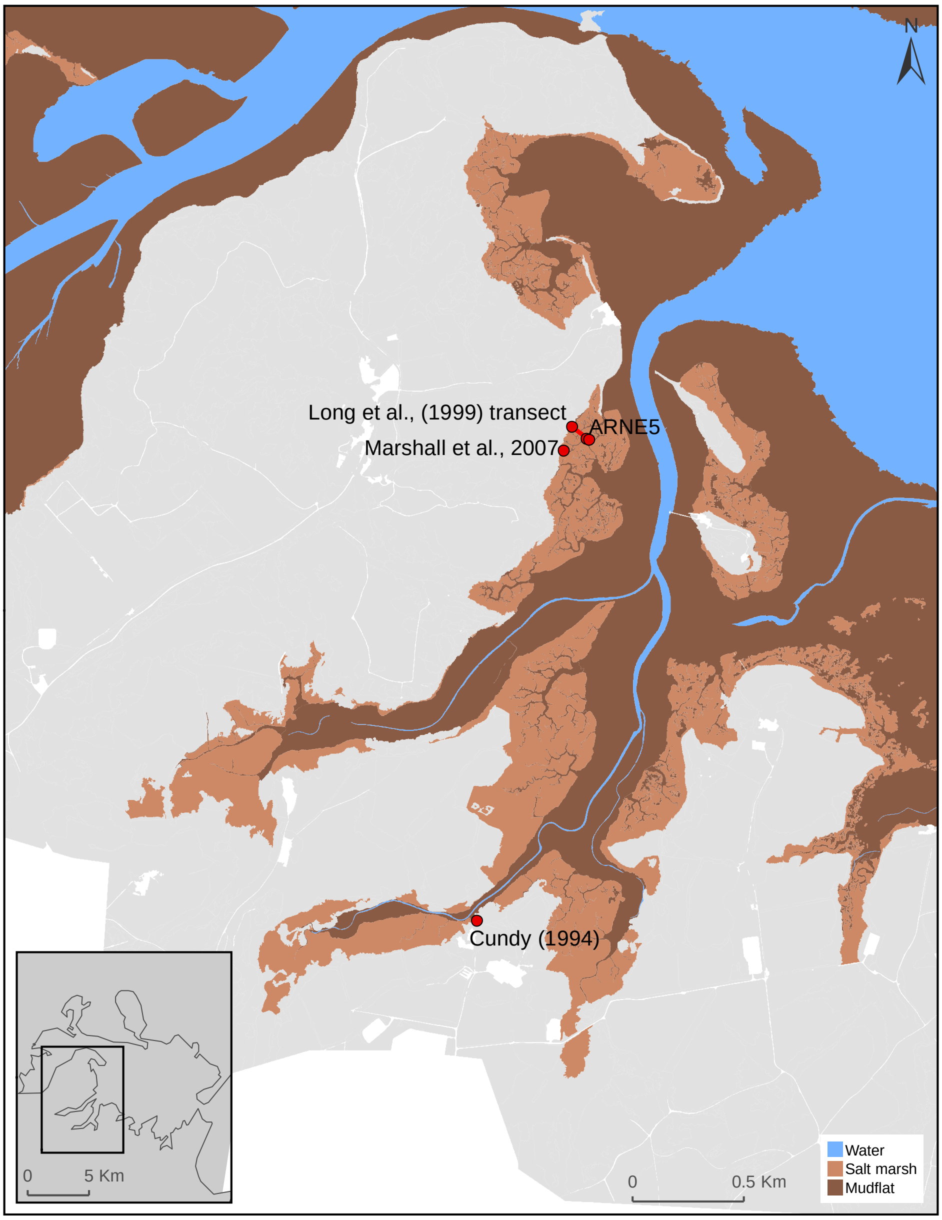


Figure 2.24: Location of published sediment accumulation rate studies within the Arne peninsula of Poole Harbour and ARNE5 (control site core).

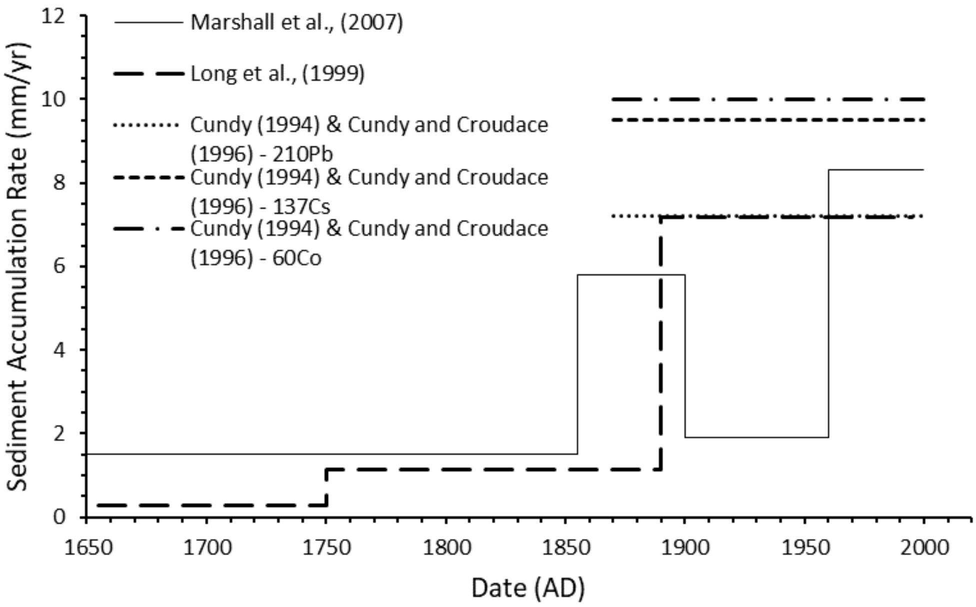


Figure 2.25: Published sediment accumulation rates from the Arne Peninsula.

In the Poole Harbour catchment, fine sediment has been identified as a key issue due to the effects it can have on biota through physical smothering, damage to organisms, e.g. gill damage of fish, reduction in light penetration for macrophytes communities, the transport of associated chemicals and nutrients and oxygen depletion due to increased breakdown of organic silt by micro-organisms (PHCI, 2014). The River Frome SSSI has failed to meet the favourable condition for suspended solids and siltation and is also cited as a reason for the Bere Stream SSSI failure (PHCI, 2014). The poor trout and salmon numbers have also been suggested to be a relation with the siltation of gravel (PHCI, 2014). The Catchment Plan aims to achieve a sustained reduction of sediment within the rivers of the catchment (PHCI, 2014).

Existing catchment activities aim to reduce sediment delivery to the rivers, with some measures also reducing associated nitrogen and phosphorus loading (PHCI, 2014). An example of such activity is that by the Ministry of Defence who installed settlement ponds on heathland tank ranges to reduce run off, sediment delivery and macronutrient loading to the River Frome tributaries (PHCI, 2014). This was successful but localised, however installation of such ponds elsewhere in the catchment could also have a similar beneficial effect on the water course (PHCI, 2014). Catchment Sensitive Farming practices have also had some success at reducing sediment from catchment diffuse sources by incorporating mitigation measures such as soil and manure management plans, establishment of buffer strips and changes in cultivation practices for example (PHCI, 2014).

The Win catchment, a tributary of the River Frome, underwent mitigation measures to reduce sediment delivery to the river in 2007 (PHCI, 2014). The steep land in the upper catchment is home to intensive arable and dairy farms (PHCI, 2014). Mitigation activities included minimum tillage, buffer strips and contour ploughing and has resulted in the reduction of sediment input from cultivated top soils of 80% to 4%, from pasture top-soils 11% to 5% and from roads 8% to 1% (PHCI, 2014). However, the original 1% contribution from the channel banks now represents 90% sediment delivery, but an overall 60% reduction of sediment on the river bed was recorded (PHCI, 2014). Reduction in suspended sediment within the River Frome has been detected by the East Stoke River Monitoring Station, where the weekly moving average is visually lower towards present than the period spanning 1999-2003, a possible indicator that catchment management to reduce sediment delivery is working (Figure 2.26). However, a proportion of the data is missing, as can be seen in Figure 2.26, thus a significant change in sediment delivery is somewhat uncertain.

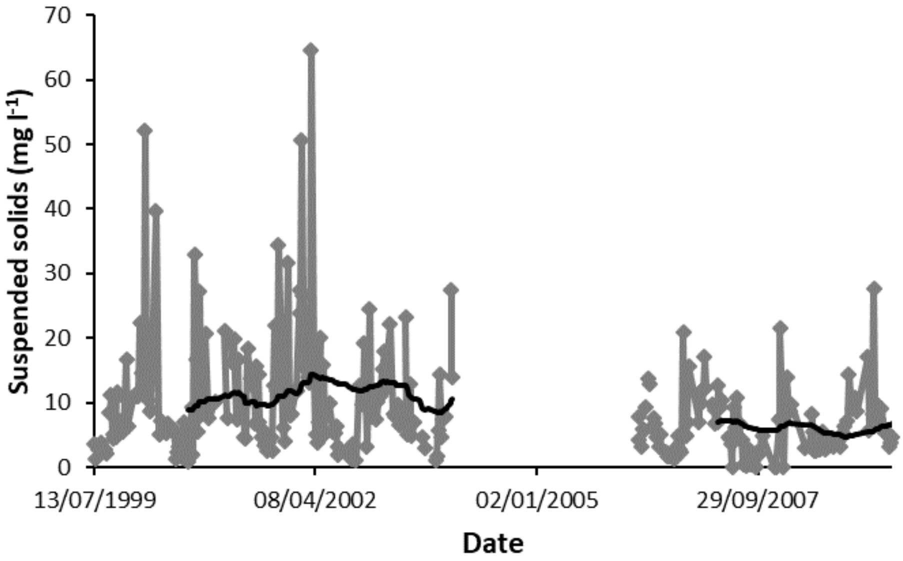


Figure 2.26: Suspended sediment concentration from the East Stoke River Monitoring Station (PHCI, 2014). Black line illustrates weekly moving average.

There has been successful attempts to reduce sediment delivery in the Poole Harbour catchment and this will not only likely benefit the ecosystem in the way it effects the biota, but will in turn reduce nutrient and pollutant loading which is associated with their transport with the catchment sediment. The mitigation strategies currently in place are only effective locally but show promise that catchment management can be used to aid sediment delivery reduction and water quality improvements of a system.

2.4.5.4 Channel and habitat alterations

River channel restoration, such as channel widening and straightening, has resulted in the loss of connectivity with the floodplain and the creation of additional channels has reduced the flow within the main channel (PHCI, 2014), increasing the concentration of sediment and pollutants within the river. Wetlands have been drained to improve land productivity, such as arable production, and bankside deforestation has reduced the shading of the water and therefore higher summer water temperatures have been observed (PHCI, 2014). These alterations can encourage increased algal production and could be a contributory factor for the WFD poor status for diatoms within the Lower Frome and Piddle (PHCI, 2014) and also likely results in increased soil erosion of the land during high precipitation events. The Catchment Plan states that improvements need to be made to the river channels in order to achieve good ecological status for all surface waters within the catchment under the WFD by 2027 and meet favourable condition for channel morphology and wetland habitat on the River Frome SSSI by 2020 (PHCI, 2014).

Existing activities to reduce sediment delivery from the catchment to the rivers, for example, include the River Frome Rehabilitation Plan which aims to improve the river's ability to function more naturally, alongside afforestation and wetland habitat creation of more than 15 hectares (PHCI, 2014). There are also many other mitigation strategies and activities outlined within the Catchment Plan illustrating how catchment management is critical if channel and habitat alteration targets are to be met (PHCI, 2014).

2.4.5.5 Water quantity

Water volume within the rivers can have significant impacts on river ecology and concerns grow higher with the uncertainties climate change will pose on water courses. Low flows can result in relatively higher concentrations of nutrients and pollutants already in the water but if there is extreme reduced precipitation, surface run off is also reduced along with the associated nutrients, limiting nutrient availability within the water bodies and thus limiting productivity (PHCI, 2014). High flow, and increased run off, results in greater sediment and macronutrient transport to the river from the catchment and thus providing greater nutrient availability downstream (PHCI, 2014). Vegetation plays a prominent role in limiting surface runoff but the location of good precipitation interceptors, such as woodland, is also significant (PHCI, 2014). Vegetation can intercept precipitation, reducing immediate surface runoff, washing sediment, nutrients and pollutants straight into the water course, therefore woodlands surrounding agricultural land could be effective at reducing surface runoff containing high concentrations of nutrients.

Poole Harbour is used by the fishery industries, e.g. shellfish and molluscs (Drake & Bennett, 2006). Such organisms can improve water quality as they have the capability to remove soluable pollutants from the water column. Boyden (1975) carried out a geochemical investigation on an oyster hatchery within Poole Harbour, taking samples from various locations within the harbour. It was found there were higher levels of trace metals in the shellfish and algae, namely *Ulva lactua*, collected from several sites from within the harbour than compared to the associated collected sediment samples (Boyden, 1975). Cundy & Croudace (1995a) stated the residence times of trace elements suspended in the water column are dependant on the interactions between such elements and the biota and suspended particles. Thus, it may be expected with increased molluscs and/or algae there are fewer soluable pollutants within the sediment records of that time.

By 2020 abstractions and discharges should mean that during average or above average flows there is no more than a 15% deviation from the natural flow; during below average flows there is more than 10% deviation and; at low flows more than 5-10% deviation along channels of the River Frome and Bere Stream (PHCI, 2014). Existing activity such as the Environment Agency Catchment Abstraction Management Strategies have been developed to balance the in river ecology with abstraction demands during low flow periods (PHCI, 2014). High flows are associated with flooding risks and therefore the Catchment Flood Management Plan has been implemented for the Poole Harbour catchment (PHCI, 2014).

2.4.5.6 Key issues summary

The data and literature so far presented indicate nitrogen is most likely the macronutrient driver for the reported post 1960s algal bloom increase and resulting eutrophic state within Poole Harbour. However, the rate of increase in algal blooms remains uncertain and requires refinement. While there has been a reduction in fertiliser application to agricultural land in recent decades, the benefit of this in terms of water quality and habitat integrity will likely take more time to be recorded within Poole Harbour due to the lag time effect of the groundwater dominant nature of the catchment.

Nitrate reduction activities have been trialled with some success; however, the advancement in such activities is not comparable to that of phosphorus and sediment reductions where reductions of ca. 73% and 38% respectively have locally been observed within the River Frome. Implementation of such efforts on a larger scale throughout the catchment could prove even more beneficial to the water body. Channel and habitat alterations and water quantity, though important variables and issues to consider, are not likely directly the cause of the algae and eutrophic changes mentioned. Their alterations may exaggerate the problem by increasing run off in response to rainfall and increasing nutrient and pollutant concentrations, but nitrogen and phosphorus are the direct nutrient sources of the problem and sediment delivery to the rivers also bring with it the associated pollutants and nutrients which attach to the material particles. Therefore, this study will bring to attention the influence of nitrates, phosphates and sediment loads have on the biological responses.

2.4.6 Poole Harbour – the conceptual model

Having collated literature detailing the nature of Poole Harbour and its catchment, including its problems, causes and management targets, a conceptual model has been created to illustrate the relationships that determine Poole Harbour's water quality (Figure 2.27). The model illustrates that changes to the water quality are indirectly driven by factors related to changes in population, e.g. increase in population results in an increased demand on STWs and an increase in effluent entering the estuarine system, thus increasing the nutrient loading to the water body. Whilst water quality itself regulates algal productivity, a shift in the water quality, e.g. increase in nutrients, results in an increase in algal production, leading to algal blooms and eutrophication. This in turn decreases the water quality with restricted oxygen levels in restricted flushing areas within the water body, reducing biodiversity and promoting more algal growth. This cycle can continue in a feedback loop, continually worsening the water quality, until it is broken by a change in the system.

The natural next step from this conceptual model would be to develop a systems dynamic model within which empirical data could be used to test the sensitivities of the system. However, this was beyond the scope of this thesis due to the time required to collect the empirical data, the palaeoenvironmental records. Developing a systems dynamics model provides a logical progression to the work presented here, to further aid catchment management understanding of the catchment-estuary relationships, and thus how best to manage water quality within the estuary.

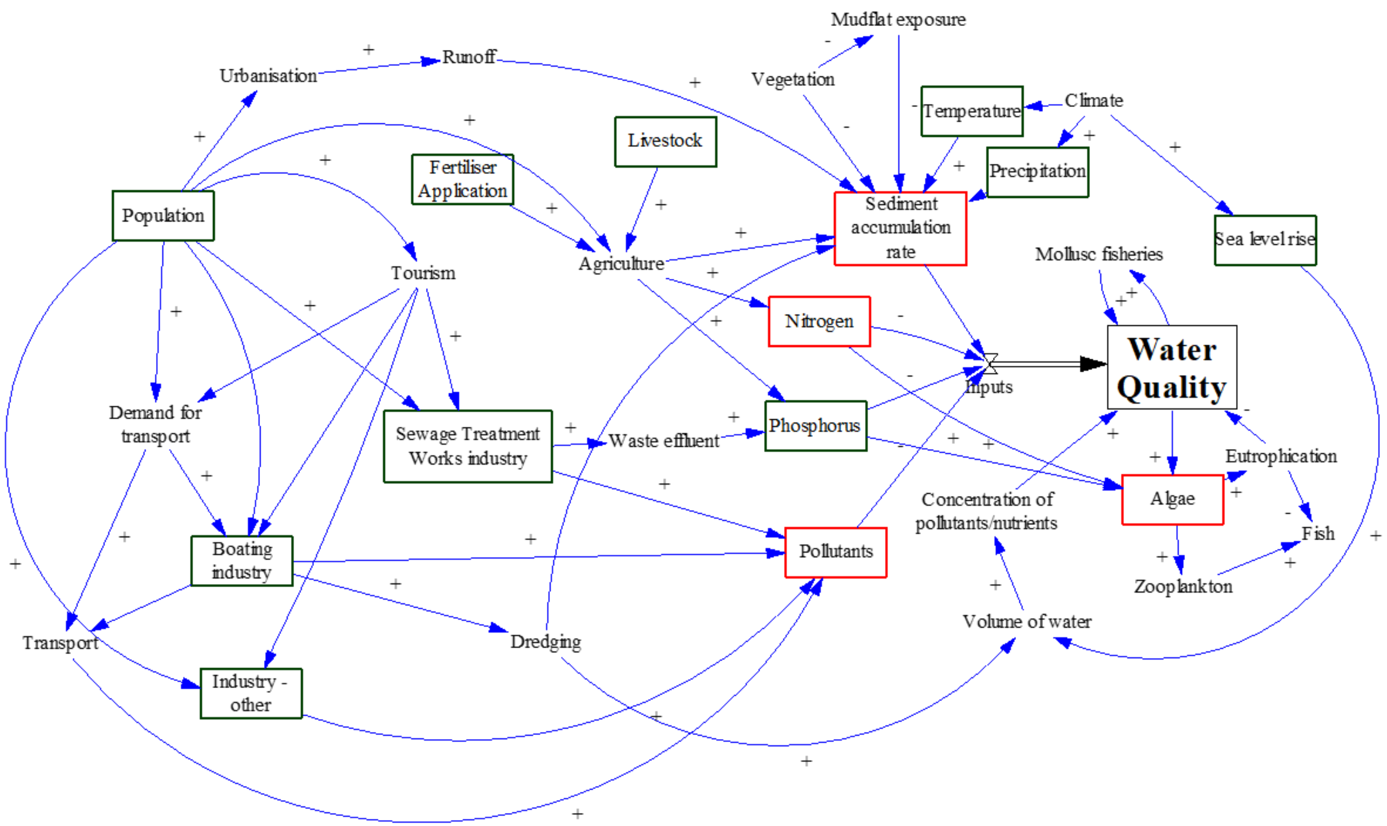


Figure 2.27: Conceptual model illustrating the contributions to Poole Harbour's water quality. Variables in boxes represent those where data can be collected and used within this research, green boxes represent secondary data and red boxes represent data that will be collected. Positive and negative signs have been assigned illustrating the increase/positive effect or decrease/negative effect respectively on the following process. Note: sediment accumulation rate has not been assigned an effect sign as it does not have a direct effect on water quality.

2.4.7 Knowledge gaps in Poole Harbour

From the literature synthesised within this review it has been identified that Poole Harbour suffers from macroalgal mats and eutrophic waters. River quality monitored data indicates the ecological changes detected within Poole Harbour are nitrogen driven as this macronutrient is still increasing while phosphorus has decreased over the past 20 years. However, within estuaries limited phosphorus does not necessarily mean there is limited algal production as phosphorus can be easily recycled from the sediments where the salinity is higher than in freshwater systems where this may more likely be a limiting factor.

The literature review surrounding previous investigations in Poole Harbour have highlighted the limited availability of long term data sets. While SARs have been established for the Arne Peninsula, no similar work has been carried out in other areas of the harbour. Therefore, it is not possible to state whether changes in SARs detected in Arne are representative of the whole harbour or represent local changes to the Arne area. It is important to understand the sediment source, transport and accretion behaviours of the system as sediment can carry nutrients with it and thus if stored quickly restrict its use within the system but if released can be a potential nutrient source in the future, e.g. from increase tidal activity from increasing sea level.

Even though some work has already been carried out on nutrient and ecological dynamics in Poole Harbour, this has been limited to particular areas of the estuary, undertaken over relatively recent time scales and not considered holistically. While nitrogen and phosphorus concentrations have been collected from the East Stoke River Monitoring Station along the River Frome, these records only span to 1965. As previously stated, ecological responses to drivers, e.g. catchment changes, occur over multi-decadal to centennial timescales, thus longer records than ca. 50 years are required to understand how both nutrient and ecological dynamics have developed in Poole Harbour. There is also no equivalent monitoring at any other location within Poole Harbour or its catchment, so knowledge is limited as to if changes within the River Frome are representative of the whole harbour. While some studies and reports of ecology, e.g. algal mats/blooms, have been published, there is no continuous long term record of ecological or algal bloom changes within Poole Harbour. Thus, to determine the relationship between drivers, e.g. catchment changes, and ecological response, e.g. algal blooms, long-term, i.e. multi-decadal to centennial, records of Poole Harbour ecology is required.

It is likely that if management actions do not control the anthropogenic sources of nutrients which enter the system, a feedback loop will ensue whereby the development of algal mats will provide a nutrient source for future algal mats as increased organic matter and nutrients are stored in the sediments. An indication of such times of high algal mat production is likely to be detected within the carbon levels of the sediment.

Reversing eutrophic status in water bodies is complex and challenging, thus determining the type of system, e.g. linear, step-change or bifold, assists with examining how Poole Harbour water quality will potentially respond to changes in drivers, e.g. catchment changes. A SOS can be used to provide an indication of levels of drivers, e.g. nitrogen concentrations, which can be used by catchment managers to maintain good water quality or reverse poor water quality, which can be used to aid policy implementation. Good water quality for the purpose of this research is defined as that which can maintain a stable ecosystem, i.e. one that is not eutrophic, and meets regulatory standards (as outlined in Table 2.1). As discussed, it has been assumed nitrogen is the driver of algal blooms within Poole Harbour. However, to be able to determine this, the ecological and nutrient history of the harbour and catchment need to be established to identify where in the nutrient record an adverse ecological response occurred. To do this, long term records are required to establish previous system behaviour. Estuaries are complex, and the relatively large groundwater contribution to Poole Harbour's catchment implies there are likely lag times between environmental cause and effect that may be longer than is identifiable using available data series which span fewer than 50 years (Dearing et al., 2015). To alleviate this problem, the use of palaeoenvironmental reconstruction techniques can extend the nutrient and ecological monitoring records to establish pre-impact baselines, the use of palaeoenvironmental data is further explained in Section 02.5. The use of such data can determine how the system has deviated from its 'natural' behaviours and ultimately identify whether thresholds or tipping points have been passed.

2.5 Techniques to establish a Safe Operating Space

It has been established within this literature review that the SOS approach can be used at smaller scales than its original global proposal. Such examples include national (Cole et al., 2014) and regional applications (Dearing et al., 2014; Cole et al., 2017). As stated, this research will aim to establish a SOS at the local catchment scale for Poole Harbour estuary to address the socio-economic challenges associated with its management. It is worthwhile therefore to discuss how such an application of a local scale SOS can be achieved.

Long-term monitoring data, e.g. decadal to centennial, is required in order to understand the past behaviours of a system before restraints on its future behaviour can be imposed. While the work of Cole et al., (2014) presented a methodology which could be adapted by others, South Africa was chosen for its wealth of data; an essential factor that may be lacking in other countries or regions. Dearing et al., (2014) overcame this lack of contemporary data by using not only monitored and historical records but also palaeoecological data as a proxy for environmental variables (Table 2.7). Using such methods, the ecological boundaries, social standards, environmental ceiling and social foundation were defined (Dearing et al., 2014; Figure 2.5).

Table 2.7: Palaeoenvironmental proxies which can be used to investigate ecosystem services (Dearing et al., 2012).

Ecosystem service	**Process/state**	**Proxy record**
Nutrient cycling	Weathering	Geochemistry Stable isotopes Diatoms
	Bigeochemical fluxes	Geochemistry
Photosynthesis	Aquatic	Carbon isotopes
Primary production	Aquatic productivity	Fossil pigments
Water purification and waste treatment	Nutrient fluxes/eutrophication	Diatoms Organic carbon Nitrogen and carbon isotopes

Dearing et al., (2014) used palaeoenvironmental data reconstructed from lake sediments. Such techniques can be applied to estuarine environments, but care must be applied to ensure chronologically intact cores are retrieved due to enhanced sediment disturbance from tidal processes. Chesapeake Bay, on the eastern coast of the U.S.A. is an estuary, like Poole Harbour, where anthropogenic activities within the catchment, e.g. land use change and increased population (Figure 2.28), have driven nutrient enrichment, algal blooms and eutrophication of the estuarine waters (D'Elia et al., 2003). Government attempts to solve the problem did not succeed, e.g. STW upgrades, as the reduction of phosphorus did not address the fact that the eutrophication of the estuarine waters are nitrogen driven (D'Elia et al., 2003). The still present algal blooms prompted scientific investigation including palaeoenvironmental reconstructions e.g. Cooper & Brush (1991) and Cooper (1995). The trending decline in diatom diversity and geochemical indicators correlated with the predominant changes in land use within the catchment and an increasing population (Cooper, 1995). The use of palaeoenvironmental data provided evidence to support a nitrogen removal strategy (D'Elia et al., 2003). The success of the strategy is yet to be determined, but further deterioration of the estuarine waters has reduced (D'Elia et al., 2003).

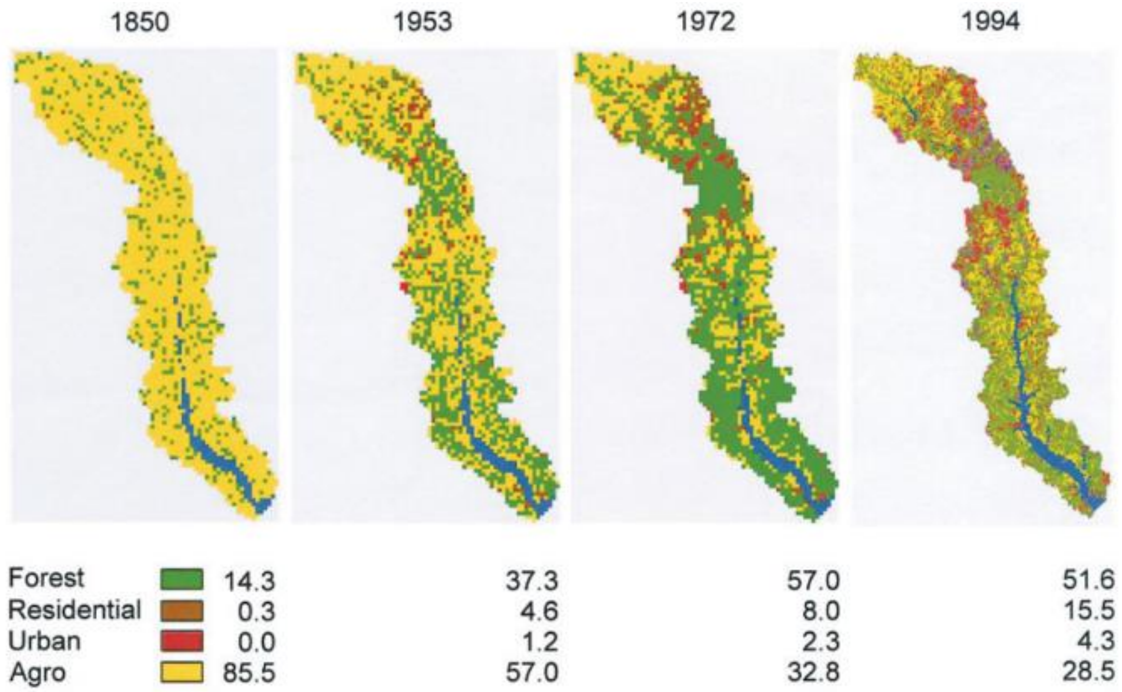


Figure 2.28: Land use maps for the Patuxent River catchment for 1850, 1953, 1972 and 1994 (D'Elia et al., 2003). Indication of an increase in urbanisation, a reflection of an increasing population and thus increasing source of nutrients from STW and ease of nutrients reaching the water course from increased surface run off.

2.5.1 Identifying tipping points using palaeoenvironmental data

The traditional conceptual framework for ecosystem services studies comprises of three components: human activities, ecosystem dynamics and biogeophysical drivers and/or responders, illustrated in Figure 2.29 (Redman et al., 2004). There is no defined methodology for analysing the relationships between both the social and biogeophysical records that are required to investigate social-ecological systems (Dearing et al., 2015) however Redman et al., (2004) proposed a three stage process to examine the three components of the framework. The framework, proposed here to be applied to Poole Harbour, is as follows:

1. Background information can be collected on population and agricultural data to look at land use change behaviours;
2. Palaeoenvironmental data can be used to identify changes within the ecological history of the catchment alongside changes in nutrient sources and inputs; and
3. System relationships can be established to understand how drivers, such as nutrients, control a system and how the response variables, such as ecology, change in nature as a result.

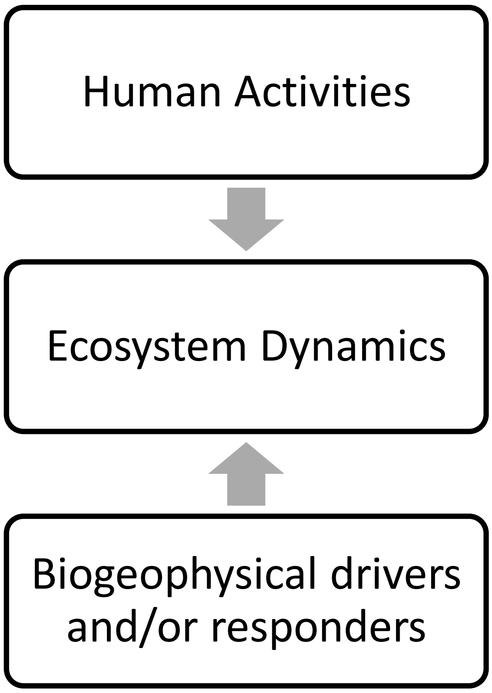


Figure 2.29: Traditional conceptual ecosystem studies framework. Adapted from (Redman et al., 2004).

It is important to understand how palaeoenvironmental data can be used in establishing system relationships and thus a SOS (Dearing et al., 2015). To identify the SOS of a system, the behaviour of each component trajectory (Figure 2.30) must be established to determine whether a threshold or tipping point can be identified (Wang et al., 2012). Complex social-ecological systems, such as estuaries, are subject to multiple drivers of change which likely result in abrupt, non-linear changes in ecosystem state. It is therefore important to improve the understanding of these systems to identify if and when a threshold or tipping point has been crossed and if the system has reached a critical state.

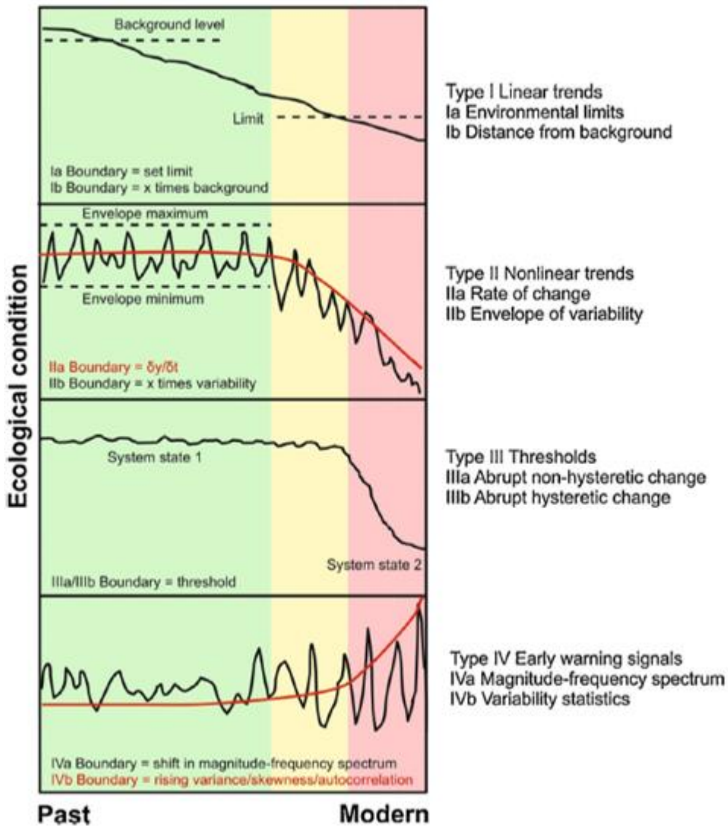


Figure 2.30: Classification of possible system behaviours as approaching the ecological boundary with colour coded segments to highlight the green 'safe', yellow 'cautious' and red ' dangerous' states of the services or processes which illustrate the theory and data easily to be used by policy makers, for example (Dearing et al., 2014).

Time series data collected by Dearing et al., (2014) for the Shucheng County, Anhui Province, China was used in the establishment of the RSJOS (Figure 2.6). In Figure 2.30, the red dashed lines within the diagram show the basis from which the different types of dynamical behaviour can be detected: sediment regulation data illustrates increased variability towards present; within the water quality there is an abrupt change from the baseline data; and within the sediment quality and air quality data there are dramatic deviances from the baseline (Dearing et al., 2014). Wang et al. (2012) found that the rising variance in the ecological proxy diatoms was likely a representation of multiple external drivers, e.g. catchment and land use change, causing an internal threshold in the lake system to be crossed, inducing flickering which was recorded in the lake's states of eutrophication and algal blooms (Wang et al., 2012).

Palaeoenvironmental proxies outlined in Table 2.7 can be used to study ecosystem service dynamics within Poole Harbour and its catchment. Such methods can be used to measure key drivers and responders before instrumental records commence. For Poole Harbour, instrumental records date back over 50 years, but it is assumed nitrate concentrations were lower in the past due to the groundwater nature of the catchment. However, to confirm this, data is needed that extends further back than historical and monitoring sources provide. By applying palaeoenvironmental analyses to sediment cores collected from within Poole Harbour, decadal to centennial scale records can be established to reconstruct the nutrient, ecological, sediment stability and delivery and water quality history of the estuary. From these, pre-impact baselines, trajectories, thresholds and/or tipping points can potentially be identified. Robustly characterising the system dynamics can allow a water quality SOS to be defined for the Poole Harbour catchment which can direct policy makers in how to reverse eutrophic status and/or maintain good water quality.

2.5.2 How to establish a Safe Operating Space for Poole Harbour

A SOS for Poole Harbour is one in which the water quality of the estuary meets regulatory standards and maintains a stable ecosystem with regards to not being eutrophic.

To define this area of 'good water quality', palaeoenvironmental data will be collected from various locations within Poole Harbour to gather a ca. 150 year holistic record with regards to nutrient and ecological dynamics. Looking at the trajectories of change within the proxy records can allow a baseline, i.e. pre-impact, to be established. This baseline likely represents the 'good water quality' for Poole Harbour as it will be associated with water quality that has not yet been altered extensively by anthropogenic activities, e.g. intensification of agriculture.

The palaeoenvironmental record can be used to explore the relationships between drivers, e.g. catchment changes, and response, e.g. algal community shifts or blooms. By looking at the nature of these relationships, it can be determined if Poole Harbour is a linear, step-change or bifold system. Understanding the type of system can allow estimates to be provided for levels of drivers, e.g. nitrogen, which will potentially reverse eutrophic status and maintain the ‘good water quality’.

2.6 Conclusions

From the literature reviewed within this chapter, it is apparent Poole Harbour is considered to be suffering from poor water quality conditions, namely as a consequence of nitrogen levels. Fertiliser and STW effluent have been identified as the main sources of increased nutrient delivery to the estuary. This has meant the harbour and the catchment are failing regulatory standards, e.g. WFD, DWI and SSSI standards. The Catchment Plan set out by the Poole Harbour Catchment Initiative (2014) have set targets to improve both surface and groundwaters, primarily nitrates, so that Poole Harbour and the catchment can meet regulatory standards, e.g. good ecological WFD status and favourable SSSI conditions and no drinking water source will be at risk of failing the DWI standards. It is evident a catchment approach to achieving these targets is best, with some existing activities within the catchment proving beneficial, and it is proposed a Safe Operating Space approach will be both favourable and sustainable.

Chapter 3 Methods

3.1 Introduction

This chapter discusses the methods used throughout this research to obtain the results presented in subsequent chapters. The first section details the location from which cores were collected and the method for their recovery. The second section explains the rationale for the dating methods used to establish chronologies. The subsequent sections provide a rationale for each of the proxies used in the palaeoenvironmental reconstructions of Poole Harbour. The following section outlines the sources of the secondary data used within this research. The penultimate section details the statistical methods used to identify transitions in water quality trajectories. The final section provides a summary of the analyses undertaken on the datasets collected and their sampling resolution.

3.2 Site selection and coring strategy

3.2.1 Site selection

The case study for this project is the estuary Poole Harbour, southern England. As such, sites selected for investigation were within the boundary of Poole Harbour's waters which were intended to represent the main nutrient and sediment sources in to the estuary and also one site was selected to act as a control.

In order to carry out palaeoenvironmental reconstructions on sediment sequences, the sediment profiles must be chronologically intact (Glew et al., 2001); therefore sites which were thought to have limited disturbance were chosen for sampling. This was determined using the predicted tidal currents as presented in Figure 2.21, to choose sites with limited tidal flow to minimise associated sediment disturbance. Sites were also chosen in areas where sediments were only covered during high tide to reduce sediment disturbance from tidal flow. Chronologically intact cores which display a steady sediment accumulation rate (SAR) have been collected from Poole Harbour as detailed in the work of Cundy (1994), Long et al., (1999) and Marshall et al., (2007). These published records were obtained from cores which were retrieved from mudflat and salt marsh areas of the Arne peninsula. Therefore, all sites for this study were characterised by either mudflats or salt marshes (Figure 3.1) where sediment accumulates around the marsh plants, thus suggesting good constant sediment accumulation (Cundy & Croudace, 1996). The areas selected require tides to reach 1.6-1.9 m above mean tide chart datum, this on average occurs at least once on 364-265 days per year respectively, calculated using 2016 data (Poole Harbour Commissioners, 2016). The dredging protocol for Poole Harbour was also referred to in order to avoid sites where sediment had either been dredged or within a dredging disposal area (Poole Harbour Commissioners, 2012).

Figure 3.1: Core locations in Poole Harbour.

As previously stated, the main nutrient sources into Poole Harbour are the River Frome and River Piddle draining the agricultural landscape of the catchment and Holes Bay where the STW effluent from Poole STW flows directly into and also contaminants from industrial activity within the catchment. For this reason, sites were selected where these nutrient sources flow into Poole Harbour. Two cores were recovered from within the River Frome (FRM4) and River Piddle (PID1) shared estuary, proximal to their respective rivers. A third core was recovered within Holes Bay (HB1) close to the effluent and industrial inlet. A fourth site was chosen as a control site. The control was chosen according to minimal tidal movement criteria where the predicted tidal flows suggest a supply of mixed waters from around Poole Harbour (Figure 2.21), thus receiving a mixed nutrient supply. The control site, Arne (ARNE5), was therefore presumed to reflect overall changes within Poole Harbour. The four coring locations are shown in Figure 3.1. Full details regarding core recovery date, location and depth can be found in Table 3.1.

Table 3.1: Core recovery summary.

	FRM4	**PID1**	**HB1**	**ARNE5**
Date of core recovery	7th July 2015	7th June 2016	30th October 2015	4th July 2016
GPS location	N 50°41.330'' W 02°04.695''	N 50°41.660'' W 02°04.731''	N 50°43'45.0" W 01°59'55.8"	N 50°41'27.9" W 02°01'36.9"
Depth of sediment core below sediment/ water interface	130cm	170cm	124cm	275cm

3.2.2 Site descriptions

Poole Harbour and its catchment have been detailed within the literature review of this thesis; this section details the individual core site locations.

3.2.2.1 River Frome and River Piddle estuary

As previously discussed, the River Frome and the River Piddle drain the agricultural landscape of Poole Harbour's catchment. FRM4 was recovered from where the River Frome enters the estuary and close to the reedbeds as possible to obtain a sediment profile in an area of constant sediment accumulation and least disturbance. Likewise, PID1 was recovered from where the River Piddle enters the estuary and close to the reedbeds.

Flow data obtained from the East Stoke River Monitoring Station along the River Frome only covers 1965 to present (2009) (Figure 3.2). Throughout this record there is no significant change in mean annual flow. River Frome flow data is though significantly correlated with 1) the nearest precipitation record at Hurn, ca. 20km to the east of the mouth of the Frome (Figure 3.3 and Figure 3.4) and 2) the long-term precipitation record from Southampton, ca. 55km to the east of the mouth of the Frome (Figure 3.5 and Figure 3.6). That neither of these precipitation records are from within the Frome catchment does though suggest that regional precipitation records may be used as a proxy for changes in flow within the River Frome. Neither of these precipitation records display a significant change over their covered time period thus it can be assumed there is no significant change in river flow to the estuary over the period 1855-2000. The long-term temperature record shows an increasing trend in temperature (Figure 3.7).

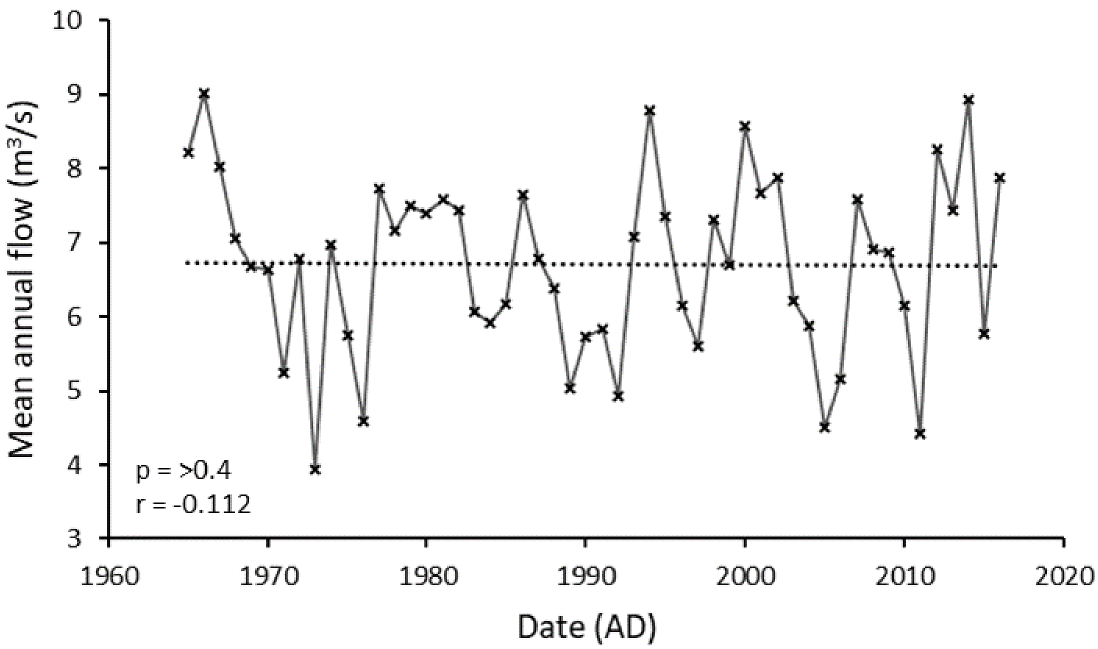


Figure 3.2: Mean annual river flow data for the River Frome taken from the East Stoke River Monitoring Station (CEH, 2017).

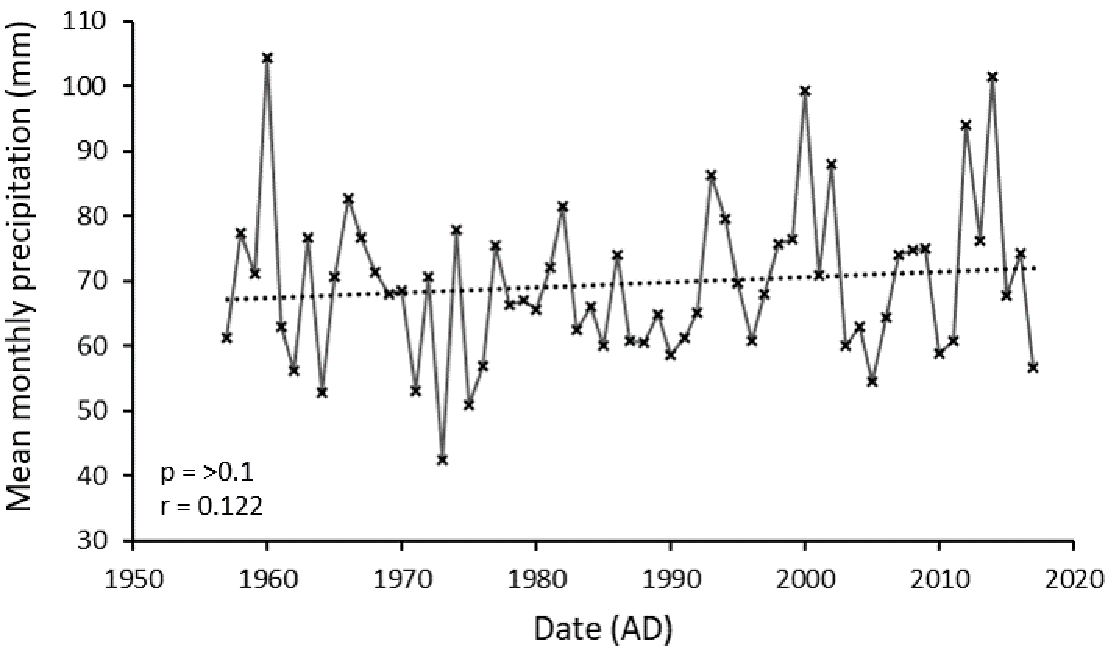


Figure 3.3: Mean annual precipitation for Hurn, the local meteorological station to Poole Harbour (Met Office, 2017).

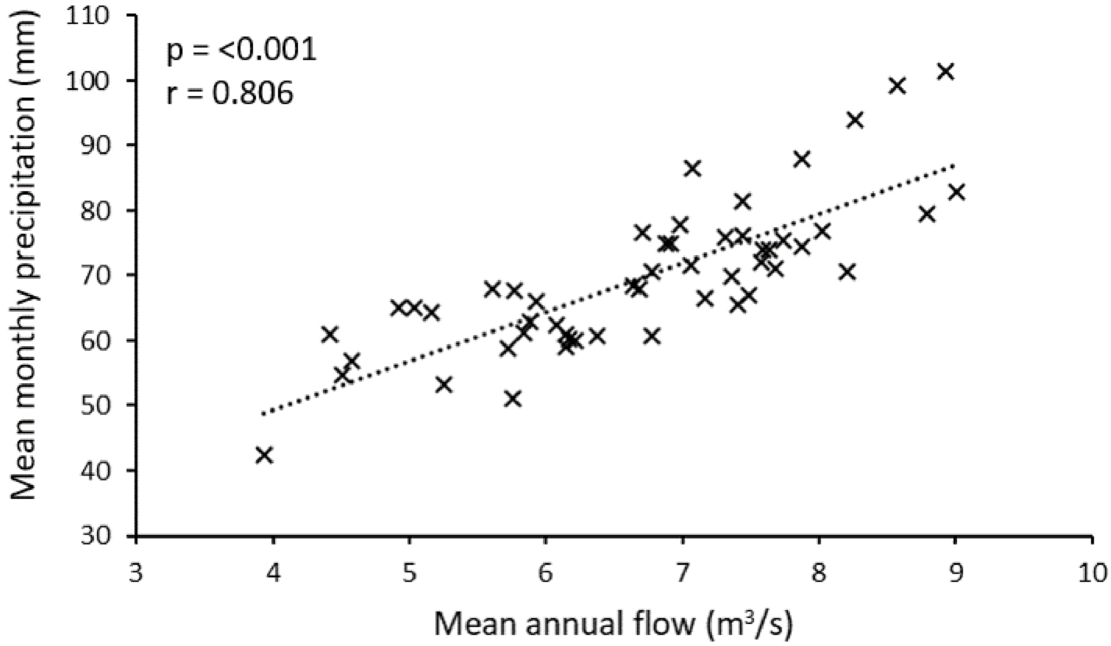


Figure 3.4: Positive correlation between mean annual flow of the River Frome and mean annual precipitation.

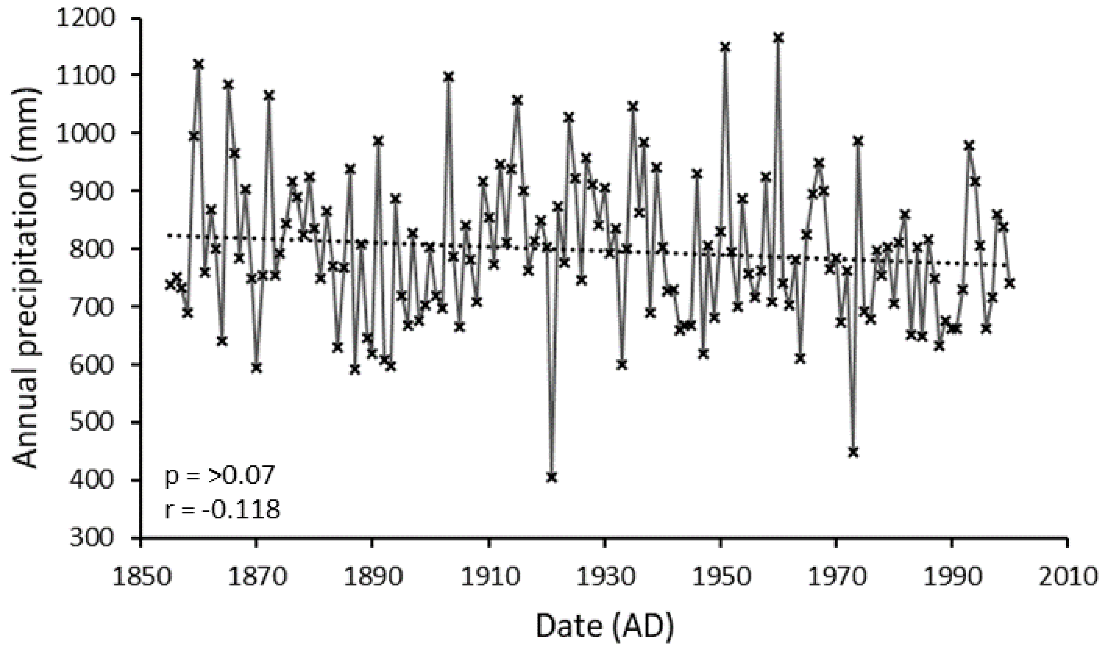


Figure 3.5: Long-term annual precipitation from Southampton (Met Office, 2018).

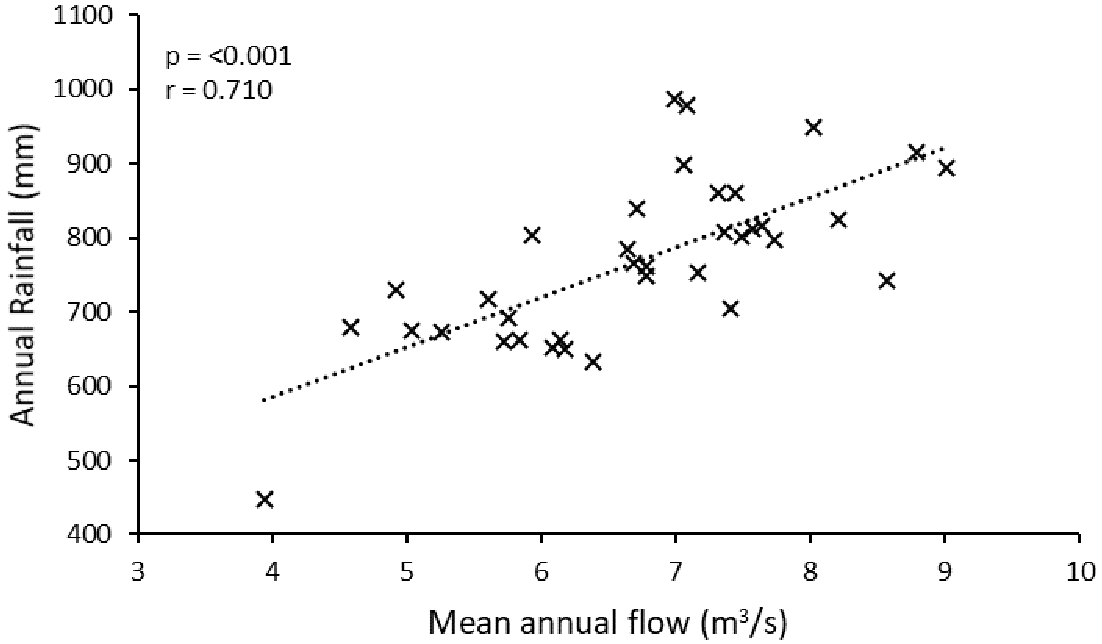


Figure 3.6: Positive correlation between mean annual flow of the River Frome and long-term annual precipitation of Southampton.

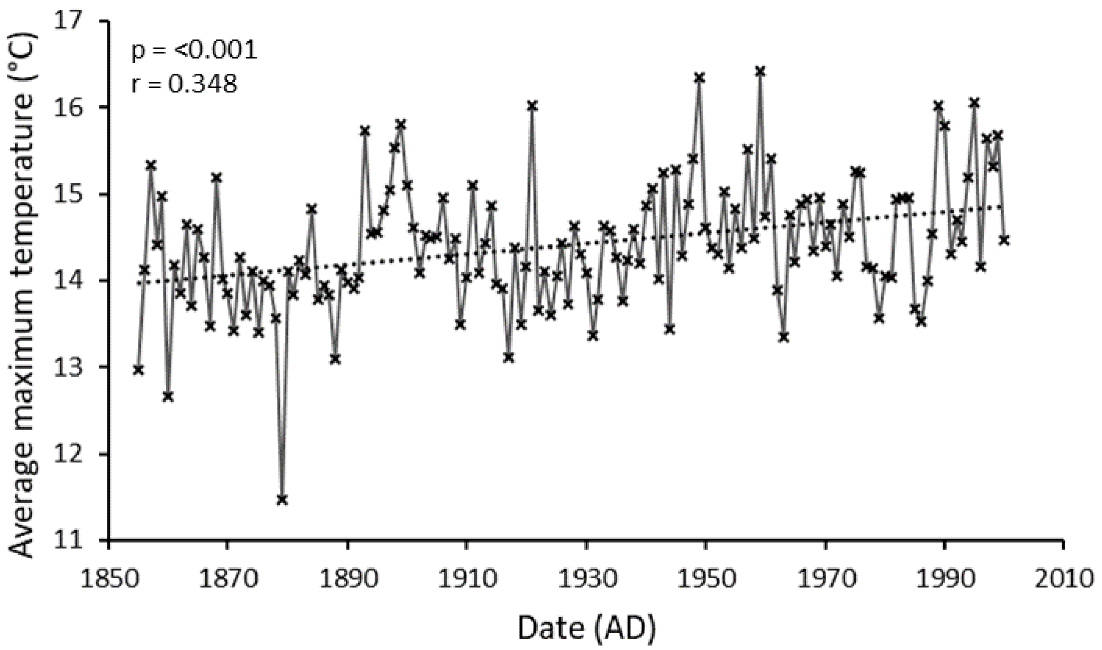


Figure 3.7: Average maximum long-term temperature from Southampton (Met Office, 2018).

3.2.2.2 Holes Bay

Sewage treatment effluent from Poole STW flows directly into Holes Bay alongside the industrial wastewaters of the catchment. There is a narrow entrance (ca. 100m) between Holes Bay and the rest of Poole Harbour, likely reducing mixing between the two water bodies. A railway line constructed in 1893 runs through Holes Bay to the north. This infrastructure restricts flow between the north and south portions of Holes Bay except two openings beneath the railway line to either side of the central saltmarsh. HB1 was taken on the east side of the saltmarsh, south of the railway line, in line of the flow of the STW effluent which enters to the north of the railway line.

The catchment of Holes Bay is primarily urban and industrial, with the water itself also being resident to boating industry. The Poole STW effluent drains directly into the bay. The STW has been in existence since 1922, with gradual development and expansion as population demands required (Jones, D. (Wessex Water) pers. comm. 2017). The effluent which drains into Holes Bay is likely one of the main nutrient supplies to the harbour.

3.2.2.3 Arne

Arne was selected as the control site. As discussed (Section 2.4.5.3) there have been other studies carried out within the Arne peninsula of Poole Harbour using sediment cores. Thus, it could be assumed chronologically intact sediment cores could be collected from this area. ARNE5 was recovered from along the transect used by Long et al., (1999) and within close (<100m) of the location used by Marshall et al., (2007) (Figure 2.24).

Atomic Energy Establishment (AEE) Winfrith, now decommissioned, discharged its waste via pipelines into the sea adjacent to Poole Harbour (Miller, 2009). This meant that the contaminants within the waste had the potential to be transported into Poole Harbour via tidal currents as illustrated by Figure 3.8. Nuclear activity produces ^{137}Cs which can be used to date sediments, the use of which will be further discussed in Section 3.3.3.1. It is important to identify historic major changes in the discharges from Winfrith to aid the understanding of the ^{137}Cs record which can be translated into a chronology of the sediments. Peak discharges from Winfrith occurred in 1975 and 1980/81 and it closed in September 1990 from which point on only small discharges occurred (Cundy, 1994).

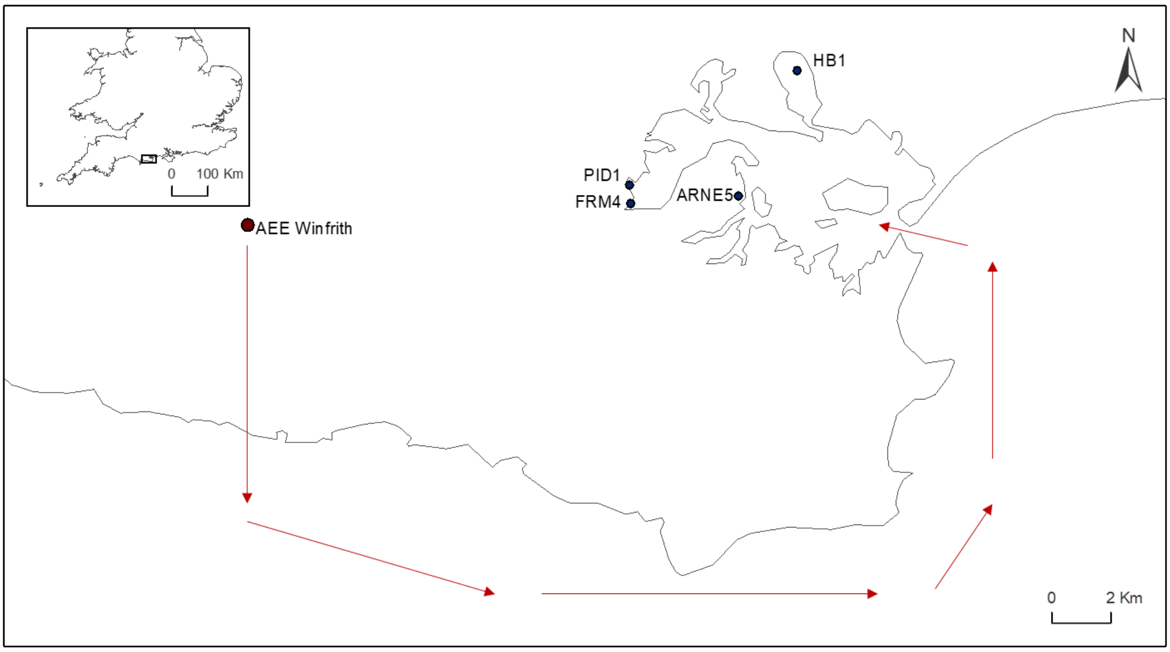


Figure 3.8: Schematic illustration demonstrating the transport of contaminated waste from AEE Winfrith into Poole Harbour.

Arne is the closest site to the harbour entrance, thus closest to the sea. It is likely ARNE5 will not only detect changes within the harbour but also marine influences, including those from the Winfrith discharges. Other core locations which have greater potential to mix with the sea water will also likely record the Winfrith discharge record, i.e. FRM4 and PID1.

3.2.3 Core recovery and storage

The River Frome, River Piddle and Holes Bay sites were sampled at extreme high tides to ensure sufficient water coverage of the coring location for core recovery. A rib boat was used to access the coring location and anchored in place. For access at Arne, coring was carried out at extreme low tide as it was possible to walk out to this site from the shore.

At all sites a Russian-type 50cm long corer was used (Glew et al., 2001). For cores taken from below water, FRM4, PID1 and HB1, cores were taken from over the side of the boat, at 10cm overlaps until the sediment became impassable. A depth gauge was used to calculate the position to take the core below water depth between each drive of the core to mediate changes in waters depth due to tidal regimes. The ARNE5 core was taken at 5cm overlaps and drives were taken from alternate bore holes until the sediment became impassable to ensure a full sediment sequence was retrieved. Cores were transferred into PVC guttering and covered with cling film. Cores were then stored refrigerated until analysed (Glew et al., 2001). At water covered sites, FRM4, PID1 and HB1, a UWITEC gravity corer, with a barrel length of 120cm, was used to capture the sediment-water interface (UWITEC, 2018). Cores were kept intact and kept in refrigerated storage until extrusion. The core was sampled at 1cm resolution and was used as supplementary material for ^{137}Cs and ^{210}Pb dating which is further explained in Section 3.3.3.

Cores remained in cold storage and in darkness where possible for pigment preservation until magnetic susceptibility (MS) and micro-XRF analysis could be carried out. Once such measurements were completed, the intact core was subsampled at 1cm resolution for LOI analysis. The remaining core material was subsampled at 1cm resolution. Approximately 1 teaspoon of material at each increment was frozen and kept in darkness where possible for pigment analysis. The remaining material at each increment was freeze dried for use for other proxies. In the case of FRM4 and HB1 time constraints meant U channels were taken from the cores post MS measurements to allow further analysis to be carried out whilst waiting for micro-XRF analysis.

The following sections outline the theory and method for each analysis and data used within this study. It is important to establish chronologies for sediment cores to ensure they are non-disturbed and to allow dates to be given to events that may be found within the collected data. For this purpose, spheroidal carbonaceous particles (SCPs), Caesium-137 (^{137}Cs) and Lead-210 (^{210}Pb) were used. There is a history of industrial activity within the catchment of Poole Harbour, for this reason the geochemistry of the sediment cores were established to determine industrial effects on the estuarine waters, this was established using X-ray fluorescence. To understand the nutrient and ecological dynamics within the estuary, productivity and its source is required, for this reason loss-on-ignition (LOI), C/N ratios and stable isotopes (δ^{13}C and δ^{15}N) were analysed. To understand what algal changes have occurred, the analysis of pigments and diatoms were used to establish algal community changes over the last ca. 150 years. Data to understand the potential drivers of these changes were collected from secondary data, e.g. population, agriculture and sea level.

3.3 Dating methods

3.3.1 Introduction

Palaeoenvironmental methods can be applied to sediment cores obtained from estuarine systems. However, estuarine systems are highly active and thus sediment mobility and transport can cause substantial spatial variation in sediment accumulation. Thus, establishing the chronology of cores collected from estuarine environments is essential before palaeoenvironmental reconstructions techniques commence. This section details the methods used for establishing the chronology of the sediment cores used in this research, spheroidal carbonaceous particles (SCPs), Caesium-137 (^{137}Cs) and Lead-210 (^{210}Pb).

3.3.2 Spheroidal carbonaceous particles

3.3.2.1 Introduction

Spheroidal carbonaceous particles (SCPs) are a product of incomplete combustion of fossil fuels, primarily coal, and can provide a record of historic atmospheric pollution according to their accumulation profile in sediments (Rose et al., 1995; Rose, 2008). SCPs are easily extractable from any environmental medium due to their robust nature given the strong mineral acids used in preparation (Rose, 2008). SCPs are morphologically distinct and are not produced naturally over the industrial time period they are used to indicate (Rose, 2008). Therefore, SCPs are unambiguous indicators of fossil fuel use in industrial processes (Rose, 2008).

The start of the SCP record in sediment cores is attributed to the increase in fossil fuel burning during the industrial revolution, and their increased abundance post WWII occurs due to the rapid expansion of the power generation industry (Rose et al., 1995). A peak in SCPs within a sediment profile is a marker for 1970±5 years for South and Central England, as SCP production decreased following this horizon as a result of legislation to reduce particle emissions into the atmosphere, e.g. the Clean Air Act 1968 and the Control of Pollution Act 1974, hence their deposition in sediments is reduced (Rose & Appleby, 2005; Rose et al., 1995). The peaks and declines in SCP concentrations within sediment cores can be correlated with documentary sources to provide not only a measure of atmospheric pollution but also the chronology of sediments across the mid- to late-nineteenth and twentieth centuries (Rose et al., 1995). An idealised SCP concentration profile highlighting the three dateable features is presented in Figure 3.9.

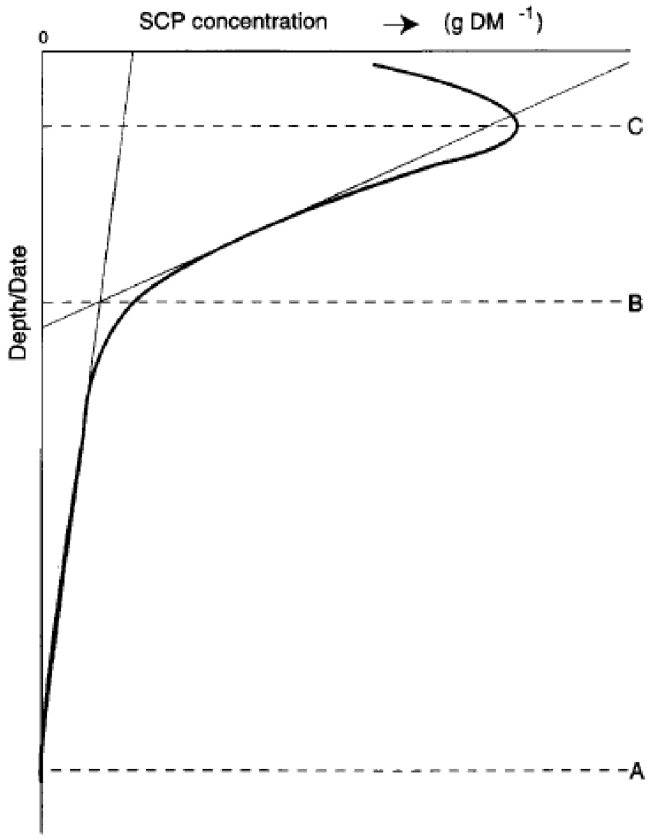


Figure 3.9: Schematic diagram demonstrating an ideal SCP concentration profile (Rose et al., 1995). The three dateable features are indicated by A: start of the record, B: rapid increase in SCP concentration and C: the peak SCP concentration.

Two methods have been proposed for the dating of sediment profiles, the 3-point method which utilises the three dateable markers as indicated in Figure 3.9 (Rose et al., 1995) and the 10% cumulative concentration method (Rose & Appleby, 2005).

The 10% cumulative concentration method assigns dates to each 10% increase in cumulative SCP concentration, commencing from the start of record (SoR) (1850±25), the first zero count occurrence, to the peak concentration (1970±5) (Rose & Appleby, 2005). There is considerable variation within the UK with regards to industrial activity and thus the production and deposition of SCPs within sediment profiles. SCP concentration curve profiles obtained throughout the UK were analysed and with the use of radiometric dating (^{210}Pb, ^{137}Cs and ^{241}Am), regional dates were established for each of the cumulative 10% increases in concentrations within the SCP profile curves (Rose & Appleby, 2005). The associated dates for each 10% cumulative concentration for South and Central England, within which Poole Harbour is located, are detailed in Table 3.2. The use of these dates can be assigned to undated sediment cores to provide a chronology for the last ca. 165 years.

Table 3.2: South and Central England dates for each 10% of the SCP cumulative percentage profile and their associated confidence limits. (Rose & Appleby, 2005).

Cumulative %	**Age (year ± error)**
Start of Record – 0%	1850±25
10%	1890±25
20%	1910±20
30%	1920±20
40%	1940±15
50%	1955±15
60%	1960±10
70%	1962±6
80%	1965±5
90%	1966±6
SCP peak -100%	1970±5

3.3.2.2 Methodology

SCPs have been readily applied to lake and peat sedimentary systems however their use is relatively novel in estuarine environments but previous application in Poole Harbour was carried out by Marshall et al., (2007). The method used here follows Rose (1990, 1994) with slight modifications (Goodes, H. pers. comm. 2015). Initial samples were recovered at 4cm increments and once the SoR and peak concentrations were determined, samples were also recovered at 2cm increments either side of these horizons to refine the location of these key markers. 0.10-0.15g of freeze dried sediment was accurately weighed into a 15ml polypropylene tube. 3ml of concentrated HNO_3 was added and left overnight in a fume cupboard. A further 3ml of concentrated HNO_3 was added and the tubes placed in a hot bath at 80-90°C for 2 hours. Samples were then centrifuged at

3000rpm for 3 minutes, decanted and then the residue was rinsed, centrifuged and decanted twice. 5ml 40% HF was added to each tube and placed in a hot bath at 80-90°C for 2 hours. The samples were then centrifuged, decanted and then the residue rinsed, centrifuged and decanted three times. The protocol here was then adapted by the addition of a Lycopodium tablet to the rinsed sample as it was a more time-effective method than the standard protocol. 10% HCl was added until the Lycopodium tablet dissolved, topped to 10ml with deionised water, vortexed, centrifuged, decanted and rinsed, centrifuged and decanted again. The Lycopodium facilitated the calculation of SCP concentrations given a known quantity of Lycopodium were added to each sample. The use of Lycopodium in SCP samples has occurred in the analysis of salt marsh deposits within Poole Harbour (Marshall et al., 2007) and also within other mediums, e.g. peat deposits, and returned successful results (Hendon & Charman, 2004; Parry et al., 2013). Finally, the residue at the bottom of the test tube was pipetted into a glass vial. A small proportion of the residue was evaporated onto a microscope slide and coverslip added with the aid of Aquatex. Each slide was counted at x400 to 500 or 250 Lycopodium depending on the Lycopodium batch number used during laboratory preparations.

Once counts were completed, SCP concentrations were calculated for each depth using Equation 3.1 and Equation 3.2, where A is Lycopodium concentration (particles per g), B is number of lycopodium particles added to each sample, C is the dry weight of each sample (g), D is the SCP concentration, E is raw SCP count of each sample and F is the raw count of Lycopodium of each sample.

$$A = \frac{B}{C} \qquad \text{Equation 3.1}$$

$$D = \frac{A \: x \: E}{F} \qquad \text{Equation 3.2}$$

Dates were assigned to the SoR, rapid increase in concentration and peak SCP concentration as demonstrated in Figure 3.9. Cumulative SCP concentrations were also calculated and dates were assigned at 10% increments (Table 3.2) to create age-depth relationships. Both the 3-point and 10% cumulative concentration methods were applied to the sediment cores. Results from these methods were compared to other chronological techniques (radionuclide dating) before concluding to use the 3-point method within this research.

3.3.3 Radionuclide dating

3.3.3.1 Caesium-137

It is good practice to validate SCP age-depth models of sediment records using an independent date marker, in the case of this study Caesium-137 (^{137}Cs) and Lead-210 (^{210}Pb) (Section 3.3.3.2) was used (Appleby, 2001; Marshall et al., 2007; Parry et al., 2013; Le Roux & Marshall, 2011).

^{137}Cs is a product which is created and released into the atmosphere, thus incorporated into sediments, during nuclear activity. The three ^{137}Cs age markers that are commonly used to date sediments are 1) the start of atmospheric testing in 1953, 2) the 1963 nuclear weapons peak, and 3) the 1986 Chernobyl reactor incident fallout (Marshall et al., 2007). However, in Poole Harbour it is not as simple as assigning the three age markers; consideration must be given to the ^{137}Cs discharged from the Atomic Energy Establishment at Winfrith as discussed in Section 3.2.2.3 (Cundy & Croudace, 1996; Marshall et al., 2007; Figure 3.8). Notable dates from discharge activity from Winfrith which may be detected in sediments are 1975 and 1980/81 and its closure in September 1990 peaks (Cundy & Croudace, 1995a, 1996). These changes in discharge may hinder detection of atmospheric nuclear testing/accident peaks (Cundy & Croudace, 1995a, 1996), but equally may aid sediment aging through local interpretation of ^{137}Cs activity. Therefore, the analysis of ^{137}Cs should be given some caution when applying results to age-depth models within Poole Harbour, especially sites of well-mixed areas, e.g. Arne.

3.3.3.2 Radionuclide Lead-210

The use of ^{210}Pb has been a widely applied method for the dating of coastal and estuarine environments, e.g. Marshall et al., (2007), Cundy et al., (2002) and Cundy and Croudace (1996). Radioactive ^{210}Pb is an isotope that is produced during the decay series of Uranium-238 (^{238}U) (Appleby, 2001). The heavy metal isotope diffuses into the atmosphere where it becomes attached to natural aerosols. Over time, the ^{210}Pb returns to earth via atmospheric processes, e.g. rainfall (Appleby, 2001). The ^{210}Pb that falls onto the water of coastal and estuarine areas is then deposited in the surface sediments at the bottom of the water column (Appleby, 2001).

^{210}Pb has a half-life of 22.3 years and thus can be used to date sediments over the last 130-150 years (Appleby, 2001). The application of ^{210}Pb dating becomes problematical as the concentration of ^{210}Pb at the sediment-water interface is a function of ^{210}Pb supplied to the sediment via atmospheric and terrestrial inputs as well as being produced in situ through the decay of naturally occurring Radium-226 (^{226}Ra). To resolve this issue, models have been developed that calculate sediment age using the ^{210}Pb activity data. Within this research the 'simple' Constant Flux: Constant Sedimentation (CF:CS) model has been applied (Krishnaswamy et al., 1971). The CF:CS model is applicable when the $^{210}Pb_{excess}$ shows a uniform exponential decline with depth, indicating that there have been no prolonged or large-scale variations in sediment accumulation rate over time. This model provides an average accumulation rate based on the straight-line fit of a of $\ln^{210}Pb_{excess}$ vs. depth graph.

3.3.3.3 Methodology

Freeze dried sediment samples from the Russian cores were weighed into plastic vials and their weight and height to which they reached within the vials were recorded. Samples were analysed at 2cm resolution until the point of no more detection occurred. Samples were analysed in the GAU-Radioanalytical Laboratories at the National Oceanography Centre, University of Southampton using high resolution gamma spectroscopy.

It became apparent that some sample sizes were too small for radionuclide analysis, particularly ^{210}Pb, thus material extracted from the UWITEC cores was used to provide a complete radionuclide record. No UWITEC core was taken for ARNE5, thus ARNE5 was not subjected to ^{210}Pb analysis.

PID1 and HB1 partial ^{137}Cs profiles from the Russian cores were matched against the UWITEC cores to allow depths to be assigned to the UWITEC cores taking into consideration sediment compaction during extrusion. The UWITEC and Russian core measurements were then combined to provide a full radionuclide profile for the cores. For FRM4, only UWITEC core measurements were used because the Russian core exhibited no features to match against.

The dated features from the ^{137}Cs profiles were compared to the estimated date for that depth according to the simple (CF:CS) ^{210}Pb model. This comparison was performed to corroborate the reliability of ^{137}Cs dating as the start of the ^{137}Cs profile, i.e. the start of atmospheric testing, would not necessarily be detected in some of the samples due to their small sample size. Good agreement was found between the ^{137}Cs estimated dates and that date estimated by the simple (CF:CS) ^{210}Pb models.

3.4 Sedimentological methods

3.4.1 Magnetic susceptibility

3.4.1.1 Introduction

Magnetic susceptibility measures the magnetisability of a material (Dearing, 1994). The magnetic behaviour of a material is measured when it is placed within a magnetic field; different materials and substances affect the magnetic field in different ways (Dearing, 1999). The measurement of magnetic susceptibility can provide information on the minerals present within sediments and identify processes of the formation or transport of the material (Dearing, 1999).

3.4.1.2 Methodology

Low frequency magnetic susceptibility of whole cores was measured at 1cm contiguous resolution using a Bartington MS2K high resolution surface scanning sensor. Background readings of ambient magnetism were taken prior to and at the conclusion of core measurements to correct the sample measurements (Dearing, 1994). Scanning of the cores was repeated to account for anomalous readings and a mean average of the repeated scans was used as the final measurements.

3.4.2 Loss-on-ignition

3.4.2.1 Introduction

Loss on ignition (LOI) can be used to determine the organic and carbonate content of sediments (Dean, 1974; Heiri et al., 2001). A sample of material is heated in a furnace at 500-550˚c, at which point the organic matter is oxidised (Dean, 1974). A second reaction occurs at 900-1000˚C where the carbon dioxide is evolved from the carbonate (Heiri et al., 2001). The weighing of the sample before and after burning provides the weight loss during these reactions which closely correlates to the sediment sample's organic matter and carbonate content (Heiri et al., 2001). LOI can be used as a predictor for organic carbon and thus an indicator of productivity within the system with an increase in productivity resulting with an increase in organic matter being incorporated into the sediment (Craft et al., 1991).

3.4.2.2 Methodology

Application of LOI on samples followed that of Lamb (2004) at 1cm contiguous resolution on all cores. Wet subsampled material was weighed in a crucible of known weight and dried in a convection oven overnight at 105˚C, once cooled they were reweighed to find the dry sediment weight. Ignition of the samples then occurred at 550˚C (LOI_{550}) for 2 hours to estimate organic content and then 950˚C (LOI_{950}) for 4 hours to estimate carbonate content in a furnace with measurements of weight taken after each burn.

3.5 Geochemical methods

3.5.1 Scanning X-ray fluorescence

3.5.1.1 Introduction

The use of X-ray fluorescence (XRF) as a geochemical proxy within palaeoenvironmental investigations is an important analytical tool (Schillereff et al., 2015; Croudace et al., 2006). XRF allows an elemental estimation to be derived of the composition of sediments (Weltje & Tjallingii, 2008). XRF instrumentation has now progressed to XRF core scanners which can provide on-line analysis of soft sediment cores and are therefore becoming more commonly used to support interpretations made from palaeoenvironmental records (Weltje & Tjallingii, 2008).

Analysis of cores using core scanning technology, such as ITRAX, allows whole sediment cores to be analysed quicker and at a higher resolution of a millimetre or even sub-millimetre (Kelloway et al., 2014). Analysis at such a high resolution can allow insights at finer temporal resolution than that of conventional bulk XRF, namely decadal, annual or even sub-annual time scale (Rothwell & Croudace, 2015).

ITRAX analysis has been readily applied to marine and lacustrine environments alongside estuarine deposits, e.g. polluted Severn estuary sediment records (Croudace et al., 2006). Some geochemical investigations have taken place in Poole Harbour, e.g. Boyden (1975), but as of yet, no geochemical analysis has been carried out on sediment core profiles from within the estuary, this study shall be the first. Examples of elements and ratios of elements obtained from ITRAX analysis on the sediment cores collected from the four study sites within Poole Harbour and their associated environmental proxies are outlined in Table 3.3.

Table 3.3: Element and element ratios that can be obtained from core scanning analysis, ITRAX, and their environmental indicators (Croudace et al., 2006; Schillereff et al., 2015; Wilhelm et al., 2012, 2013; Thomson et al., 2006; Ytreberg et al., 2010; Jones & Bolam, 2007).

Element/ratio	Environmental indication
Si	Terrigenous or productivity indicator.
Ca	Erosion from the catchment which is majority chalk.
Pb	Industrial activity indicator.
Br Cl	Sea water indicators.
Zr/Rb	Grain size proxy, increased ratio indicates increase in grain size.
Cu	Element in antifouling paint used on the hull of ships.

3.5.1.2 Methodology

Whole cores, or U channels in the case of FRM4 and HB1, were analysed using an Itrax core scanner at the National Oceanography Centre, University of Southampton. Cores were prepared for scanning by ensuring sediment surfaces were as flat as possible. Optical and radiographic images were taken of all the cores prior to the XRF scanning. All cores were scanned at a resolution of 200μm. Detection of an element depends on the excitation efficiency from the X-ray tube and the energy of the characteristic X-rays. As the atomic number of an element gets heavier, this effect decreases and the absorption losses become less significant. Si is an element which has a moderately weak X-ray energy and therefore is absorbed easily. 30kV is able to excite all the main elements, including Si (Jarvis et al., 2015). Where excitation efficiency is poor or X-rays are absorbed readily, then increasing the count time can help, therefore a count time of 30 seconds was used (Jarvis et al., 2015). Full details of the analytical parameters are detailed in Table 3.4. Elemental profiles were then averaged every 0.5cm to allow dates to be assigned to the data.

Table 3.4: Parameter settings for Itrax XRF analysis. *Note FRM4 was ran at 50mA due to a technical mistake. To allow comparisons between cores to be made a section of FRM4 was ran at 30mA and 50mA to check the same trends in the elemental profile was detected.

Parameter	**Setting**
Tube	Mo
Voltage	30 KV
Current	30 mA*
Exposure time	30 seconds
Step size	200μm

3.5.2 C/N ratios and stable isotopes

3.5.2.1 C/N ratios and $\delta^{13}C$

Estuaries are highly productive habitats and receive their sediment from a multitude of sources. The saltmarshes and mudflats reflect this variance in fluvial and marine driven minerogenic sediment and particulate organic matter (Lamb et al., 2006). The analysis of stable isotopes from sediment core records can be used to evaluate environmental change through changing uses of carbon/nitrogen, for example, within the estuary. The development of this analytical tool in estuarine environments is somewhat limited relative to the established use of isotopes in marine and lacustrine settings (Leng & Lewis, 2017).

Organic matter within the sediments of estuaries are derived either via autochthonous (internal productivity, e.g. plants growing on sediment surface) or allochthonous (external to the water body, e.g. catchment) processes (Leng & Lewis, 2017). Allochthonous sources of organic matter also includes marine particulate organic carbon (POC), mainly from phytoplankton, but also riverine derived terrestrial and fluvial material (Leng & Lewis, 2017). Saltmarsh sediments tend to be dominated by autochthonous vascular plant material where infrequent tidal inundation allows vegetation cover to become established, these sediments are likely high in organic matter (Leng & Lewis, 2017). Tidal flat areas tend to dominated by allochthonous organic matter as frequent tidal inundation inhibits vascular plant vegetation growth (Leng & Lewis, 2017).

Organic matter from different sources within an estuarine system have different C/N and $\delta^{13}C$ compositions, thus in theory the analysis of bulk organic C/N and $\delta^{13}C$ should reflect the sources of organic matter (Leng & Lewis, 2017). The use of $\delta^{13}C$ has been used to determine the source of organic matter within the sediments of saltmarsh studies, e.g. Haines (1976), Ember et al., (1987) and Chmura and Aharon (1995). Carbon sources can be determined by evaluating a sample's weight ratio of organic carbon to total nitrogen (C/N) alongside $\delta^{13}C$ (Lamb et al., 2006; Figure 3.10). Within estuaries of limited flushing, e.g. Poole Harbour due to its narrow entrance relative to other estuaries, autochthonous sources of carbon tend to dominate the system (Leng & Lewis, 2017).

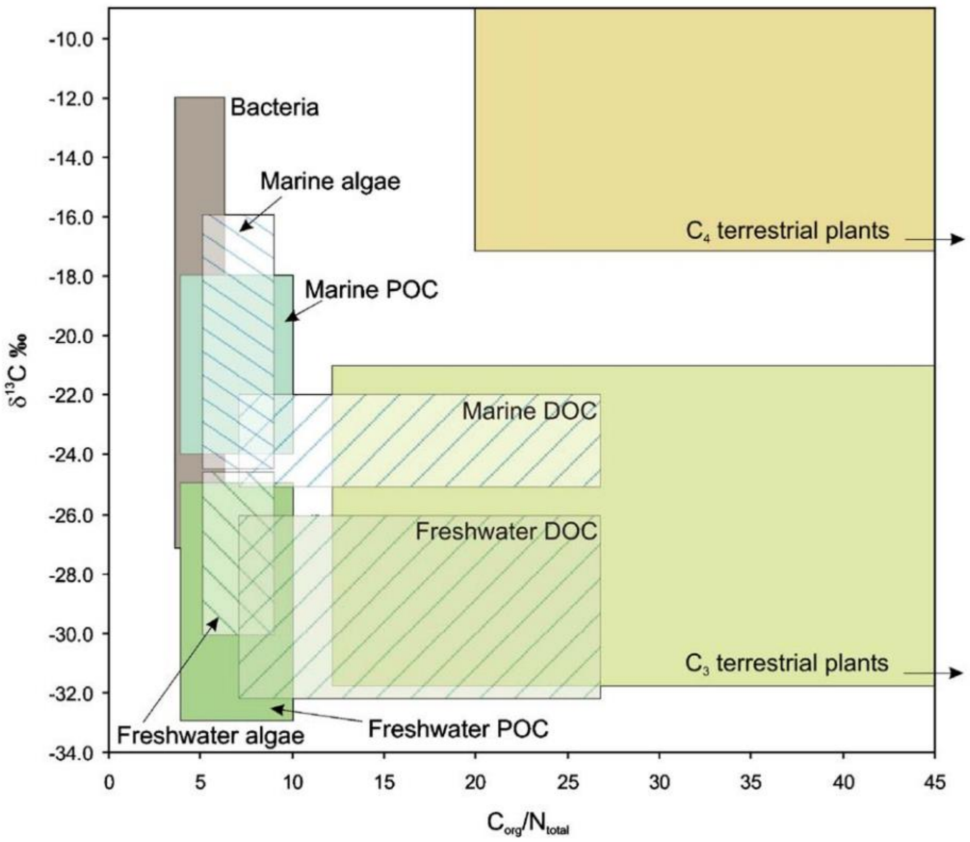


Figure 3.10: $\delta^{13}C$ and C/N typical ranges for organic inputs to coastal environments (Lamb et al., 2006).

Terrestrial plants preferentially take up ^{12}C from atmospheric CO_2, consequently producing organic matter that is ^{13}C depleted compared to the atmosphere; there are different types of terrestrial plants with their specific $\delta^{13}C$ values shown in Figure 3.10 (Leng & Lewis, 2017). Terrestrial plants grow in estuarine environments but such plant material also enters the system via riverine sources (Leng & Lewis, 2017). Plant species that have adapted to tolerate saline conditions, e.g. some saltmarsh species, are commonly of the type C4 (Leng &

Lewis, 2017). Terrestrial plants are predominantly composed of cellulose and lignin which are relatively nitrogen poor thus resulting in high C/N values (>10) (Leng & Lewis, 2017; Prahl et al., 1980).

Aquatic plants and phytoplankton can utilise bicarbonate (HCO_3^-) and dissolved CO_2 (Benedict et al., 1980). In comparison to HCO_3^-, dissolved CO_2 has lower $\delta^{13}C$ values (Leng & Lewis, 2017). Aquatic plants and phytoplankton preferentially take up dissolved CO_2, switching to HCO_3^- following the exhaustion of the CO_2 source (Lamb et al., 2006). The CO_2 to HCO_3^- ratio is a function of pH, hence alkaline marine waters are enriched with HCO_3^- relative to more acidic freshwater (Lamb et al., 2006). The predominance of marine plants using HCO_3^- in estuaries therefore means their remains have higher $\delta^{13}C$ values relative to freshwater remains (Lamb et al., 2006). In C3 dominated environments, freshwater algae tend to have lower $\delta^{13}C$ values (-26 to -30‰) in comparison to marine algae (-16 to -23‰) but in C4 dominated environments, algae tend to have relatively high $\delta^{13}C$ values (≥-16‰) as they can also utilise dissolved organic carbon from the decomposition and oxidation of C4 plants (Leng & Lewis, 2017).

Algae and bacteria have C/N ratios which are <10 because nitrogen preferentially occurs in nucleic acids and proteins which are abundant in aquatic plants (Leng & Lewis, 2017). Bacterial activity can introduce nitrogen to the sediment resulting in decreased C/N ratios (Leng & Lewis, 2017). However, aquatic plants and bacteria become a less significant component of bulk organic C/N and $\delta^{13}C$ because they contain high levels of labile compounds and decompose more rapidly than vascular plants (Leng & Lewis, 2017).

Within coastal environments particulate organic carbon (POC) encompasses suspended organic matter such as phytoplankton, e.g. diatoms and green algae, and is mixed with terrestrial natural, e.g. plant detritus, and anthropogenic, e.g. sewage, organic matter (Lamb et al., 2006). The value of $\delta^{13}C_{POC}$ tends to increase closer to the mouth of the estuary as a consequence of the different contributions from the marine and freshwater $\delta^{13}C_{POC}$ sources (Leng & Lewis, 2017). Marine POC has higher $\delta^{13}C$ values (-21 to -18‰) compared to freshwater $\delta^{13}C$ values because fluvial POC is formed of contributions from mainly freshwater phytoplankton ($\delta^{13}C_{POC}$ values -30 to -25‰) and particulate terrestrial organic matter ($\delta^{13}C_{POC}$ values -33 to -25‰), thus meaning fluvial POC $\delta^{13}C$ values are relatively very low (Leng & Lewis, 2017). The large phytoplankton component of POC results in low C/N (ca. 5-7) and diatoms, a particular type of phytoplankton, have particularly low C/N values (ca. 5) (Leng & Lewis, 2017). The use of diatoms within this study will further be explored in Section 3.6.2.

Dissolved organic carbon (DOC) is primarily comprised from the decomposition of phytoplankton within marine environments and from a mix of terrigenous organic matter and phytoplankton in the fluvial environment (Rashid, 1985). Within estuarine environments, $\delta^{13}C_{DOC}$ values have been shown to highly reflect the source of the DOC, whether it be marine or freshwater (Leng & Lewis, 2017).

In general, during algal productivity, lighter ^{12}C is preferentially used. During periods of increased productivity, e.g. eutrophication, ^{12}C becomes diminished and the algae are forced to utilise the heavier ^{13}C isotope (Torres et al., 2012). This results in organic matter with higher $\delta^{13}C$ values during high productivity. However, the reverse relationship can be found, i.e. decrease in $\delta^{13}C$ values during high productivity, when the aquatic system has been over enriched by nutrients, negating the need for carbon fractionation, thus lower $\delta^{13}C$ values can be found during high productivity periods (Torres et al., 2012).

An alternative to nutrient enrichment driving lower $\delta^{13}C$ values in sediment cores is provided by the Suess effect. The effect has been detected in some published records since the industrial revolution, in that during fossil fuel formation, carbon is fractionated through photosynthesis, producing fossil fuel rich in ^{12}C and lower in ^{13}C (Bacastow et al., 1996). Therefore, during fossil fuel combustion, more ^{12}C is released and reduces the ^{13}C in the carbon pool (Bacastow et al., 1996; Surge et al., 2003; Sonnerup et al., 2000). Thus, lower $\delta^{13}C$ values recorded in post industrial revolution sediment must be considered in light of the Suess effect, i.e. lower $\delta^{13}C$ values may not solely be attributable to nutrient dynamics.

When using C/N ratios and $\delta^{13}C$ values to derive organic matter source, the decomposition of the organic matter should be considered (Leng & Lewis, 2017). Decomposition can have a potential effect as the values of $\delta^{13}C$ change due to the loss of labile compounds in vascular plants (Lamb et al., 2006) and C/N ratios differ as a result of the loss of organic carbon in sediments and an increase in inorganic nitrogen to organic nitrogen (Sampei & Matsumoto, 2001). It is therefore directional changes in C/N and $\delta^{13}C$ which become important in detecting past changes rather than changes in absolute values (Leng & Lewis, 2017). Such relative changes are commonly retained in Holocene sediments, thus the use of C/N and $\delta^{13}C$ in the most dynamic estuaries can still be employed (Leng & Lewis, 2017).

3.5.2.2 δ ^{15}N

As already discussed in Chapter 2 (Section 2.4.5.2) nitrogen is the main macronutrient controller on eutrophication in estuarine systems with an increase in nitrogen loading leading to an increase in estuarine algal blooms. Biologically available nitrogen is either endogenous (internally) or exogenous (externally) sourced to the estuary (Paerl, 1997). Within estuarine environments, nitrogen supplied via exogenous sources heavily dominate the system including anthropogenically driven sources, e.g. fertilisers and wastewaters (Paerl, 1997). Nitrogen stable isotopes can be used as indicators of nutrient source and delivery (Cole et al., 2004).

During algal production, ^{14}N is preferentially taken up rather than ^{15}N, with the exception of cyanobacteria (blue-green algae) which does not discriminate between the two nitrogen isotopes (Talbot, 2001). This organic production rich in ^{14}N consequently results in a ^{15}N enriched dissolved inorganic nitrogen (DIN) reservoir (Talbot, 2001). During eutrophication where there is an increase in algal production, there is intensified utilisation of the ^{15}N enriched DIN reservoir (Talbot, 2001). When this organic nitrogen is transferred to the sediments as productivity and burial of phytoplankton increases, e.g. as a result of increased nutrients from fertilisers and wastewaters, the organic matter of the sediment will be enriched with δ ^{15}N (Talbot, 2001).

The study of δ ^{15}N can be used as tracers of nitrogen sources (Peterson & Fry, 1987). Within groundwaters, nitrogen in wastewater, including that from animal waste, tends to drive δ ^{15}N values higher, typically between +10 and +20‰ (Torres et al., 2012; McClelland & Valiela, 1998; Kreiter et al., 1978; Cole et al., 2004), whereas δ ^{15}N from natural soils and atmospheric deposition are between +2 and +8‰ (McClelland & Valiela, 1998; Kreiter et al., 1978; Cole et al., 2004) and from fertilisers δ ^{15}N values range between –8 to 6.2‰ with the abundance within -3 to +2‰ (Kreiter et al., 1978).

The analysis of C/N ratios, δ ^{13}C and δ ^{15}N stable isotopes from sediment organic matter throughout sediment core records can indicate periods of increased algal production. In general, aquatic systems will show an increase in δ ^{13}C values and δ ^{15}N values during phases of increased algal production (Torres et al., 2012). However, during nutrient enrichment δ ^{13}C values may remain low or decline due to little fractionation of carbon (Torres et al., 2012). To determine the cause of δ ^{13}C value changes, δ ^{13}C should be analysed against δ ^{15}N and other proxies to determine if changes in $\delta^{13}C$ are due to productivity or other causes, e.g. terrestrial in wash. Not only can these stable isotopes inform about periods of increased algal blooms, they can also indicate the sources of the nutrients used for the production.

3.5.2.3 Methodology

Samples for stable isotope analysis were carried out at 2cm resolution on all cores commencing from 1cm rather than 0cm in comparison to other proxies due to limited material available.

Isotope analysis was conducted at the Stable Isotope Facility at the British Geological Survey. Carbon isotope samples were decarbonated in 5% HCl prior to their analysis to remove inorganic carbon. Nitrogen isotope analysis was carried out on a separate aliquot and ran with no pre-treatment. $\delta^{13}C$ analyses were performed by combustion in a Costech ECS4010 Elemental Analyser (EA) on-line to a VG TripleTrap (plus secondary cryogenic trap) and Optima dual-inlet mass spectrometer, with $\delta^{13}C$ values calculated to the VPDB scale using a within-run laboratory standard (BROC2) calibrated against NBS-19 and NBS-22. Measured results were deemed reliable given 1) standards measured during analyses demonstrated low analytical error (Figure 3.11) and 2) replicate analysis of well-mixed samples indicated a precision of $\pm$ <0.1‰ (1 SD). %C and %N analyses were run at the same time and calibrated against an Acetanilide standard. $\delta^{15}N$ analyses were performed by combustion in a Thermo Finnigan Flash EA (1112 series) on-line to a Delta Plus XL mass spectrometer. $\delta^{15}N$ was calculated to the $\delta^{15}N$ value of air using the BROC2 standard as a within-run laboratory standard calibrated against UGS40 and UGS41. Measured results were deemed reliable given 1) standards measured during analyses demonstrated low analytical error (Figure 3.12) and 2) replicate analysis of well mixed samples indicated a precision of $\pm$<0.2‰ (1 SD).

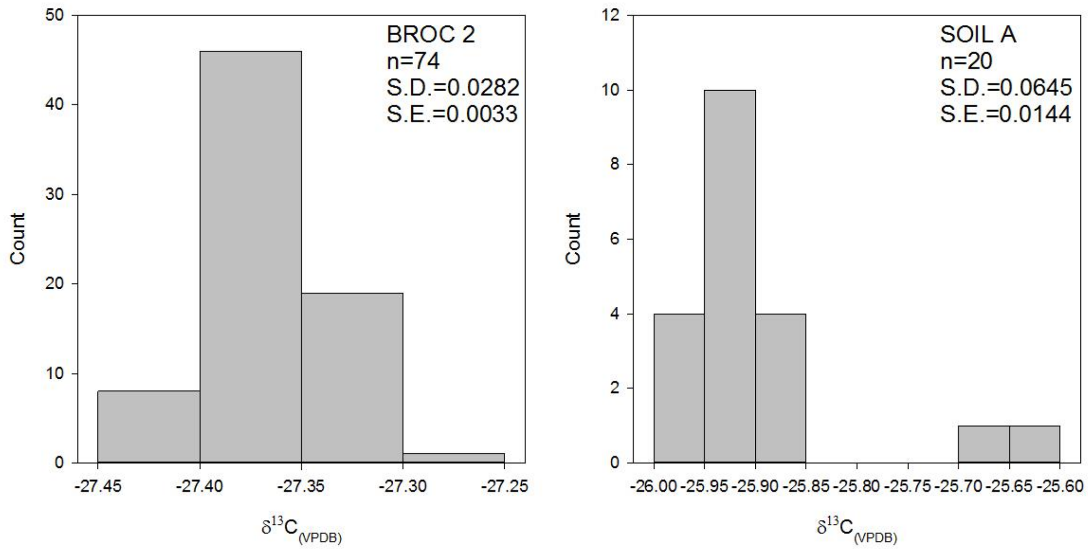


Figure 3.11: $\delta^{13}C$ measurements of internal laboratory standards BROC 2 and SOIL A with statistics indicating low analytical error.

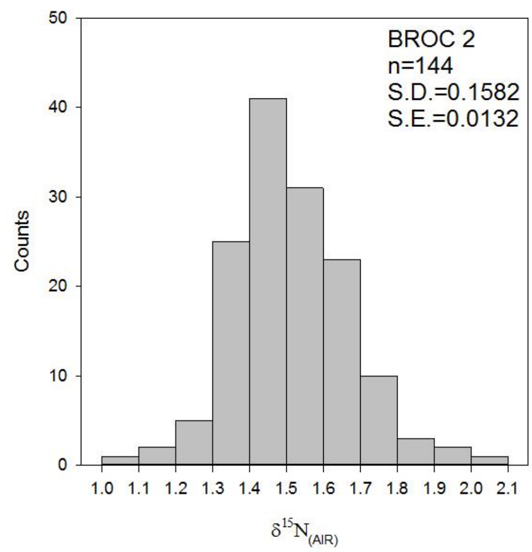


Figure 3.12: $\delta^{15}N$ measurements of internal laboratory standard BROC 2 with statistics indicating low analytical error.

3.6 Palaeoecological methods

3.6.1 Pigments

3.6.1.1 Introduction

Pigments are biochemical fossils produced by algae, phototrophic bacteria and aquatic plants (McGowan, 2007, 2013). While some photosynthetic organisms leave limited morphological remains in sediment due to their soft bodied nature, pigments can provide an indicator of previously present organisms (McGowan, 2007, 2013). Pigments can provide an indication of taxonomy and thus can provide information about algal community changes which may be used to quantify past primary production in aquatic systems (McGowan, 2007, 2013). The pigments found in this study are summarised in Table 3.5 alongside their affinities.

Pigment preservation favours aquatic environments where they are rapidly buried to remove them from light, heat and oxygen which can degrade them (McGowan, 2007, 2013). They are well preserved in shallow lakes where sinking depths are low and thus the pigments can be promptly incorporated into the sediment (McGowan, 2007, 2013). Relative to lacustrine environments, marine environments are characterised by deeper water columns, tidal exposure and lower rates of productivity which result in reduced rates of pigment burial and compromised preservation (McGowan, 2007, 2013). Despite such issues, pigments have been shown to be effective environmental indicators in coastal, including estuarine, environments where multi-proxy approaches are used, e.g. Schüller and Savage (2011) and Schüller et al., (2015), including in prior investigations of eutrophication, e.g. Bianchi et al., (2000), Bianchi et al., (2002), Clarke et al., (2006), Ellegaard et al., (2006), Reuss et al., (2005) and Vahtera et al., (2007) (McGowan, 2007, 2013).

Table 3.5: Pigments found in the sediments of Poole Harbour.

Pigment	**Affinity** (McGowan, 2007, 2013)
Chlorophyll *a*	All photosynthetic algae, higher plants
Chlorophyll *b*	Green algae, euglenophytes, higher plants
Pheophytin *a*	Chlorophyll *a* derivative
Pheophytin *b*	Chlorophyll *b* derivative
Phaeophorbide *a*	Grazing, senescent diatoms
Lutein/Zeaxanthin	Green algae, euglenophytes, higher plants, cyanobacteria
β-Carotene	Most algae and plants
Alloxanthin	Cryptophytes
Diatoxanthin	Diatoms, dinoflagellates, chrysophytes
Canthaxanthin	Colonial cyanobacteria, herbivore tissues

3.6.1.2 Methodology

For each core, pigment analysis was carried out at 1cm resolution down to the last depth that could be dated (1850) and then at 8cm resolution thereafter to, and including, the bottom depth of the core. For the samples which were analysed for pigments within each core refer to Table 3.6.

Table 3.6: Sampling resolution for pigment analysis.

	FRM4	**PID1**	**HB1**	**ARNE5**
1cm (number of samples)	0-50cm (51)	0-46cm (47)	0-70cm (71)	0-68cm (69)
8cm (number of samples)	58-129 (10)	54-169 (16)	78-123 (7)	76-274 (26)
Total number of samples analysed	61	63	78	95

Material which had been subsampled from the original core was kept frozen and in the dark to reduce pigment degradation (Reuss & Conley, 2005). Pigments were freeze dried in the dark prior to analysis in as a close timeframe as possible, the freeze dried samples were kept frozen in the dark until time of analysis

(Reuss & Conley, 2005). Analysis of pigments was carried out following the method of McGowan (2007, 2013):

- At all times the sediment and pigment solutions were limited to exposure of light and heat throughout the analysis.
- Pigments were extracted from the sediment material:
  - Freeze dried sample was weighed into a labelled glass vial and 5ml of acetone based extraction solution was added. The vials were placed in a dark freezer overnight for the sediments to soak.
  - After the sediments had soaked, the resulting pigment solution was filtered from the sediment material using a syringe and 0.22μm lock-on filter into a clean labelled glass vial. The sediment was washed three times using approximately 5ml of HPLC grade acetone and passed through the filter into the glass vial containing pigment solution to ensure all the pigments were removed from the material.
  - The glass vials containing the pigments in solution were dried under nitrogen gas. Once completely dry, lids were placed as quick as possible on the vials to capture the nitrogen gas while they remained in a dark freezer until ready for using high-performance liquid chromatography (HPLC) analysis.
- HPLC was used to separate the pigments in the mixture:
  - Injection solution of a known volume was used to remove the dried pigment from the glass vial and was transferred to an autosampler vial of known location on the HPLC autosampler tray.
  - The autosampler tray was then placed into the HPLC machine for analysis.
  - A green standard was used as the first and last sample to compare resulting chromatograms to identify pigments present.
- Pigments were identified:
  - Pigments are identified using a combination of retention times and spectral characteristics when passed through a spectrophotometer. The position and retention time of a pigment on a chromatogram can be used to identify the pigments present, e.g. Figure 3.13.
  - The chromatogram for each sample was analysed, from which the pigments present were identified by comparison to known commercial pigment standards detected under the same separation conditions, e.g. Figure 3.14.

- Identified pigments were quantified:
    - The areas under the identified pigment peaks on the chromatogram were noted to allow conversion to pigment concentration. This is expressed as nanomoles to correct for the differences in molecular weights and is calculated with respect to the organic content of the sediment sample.

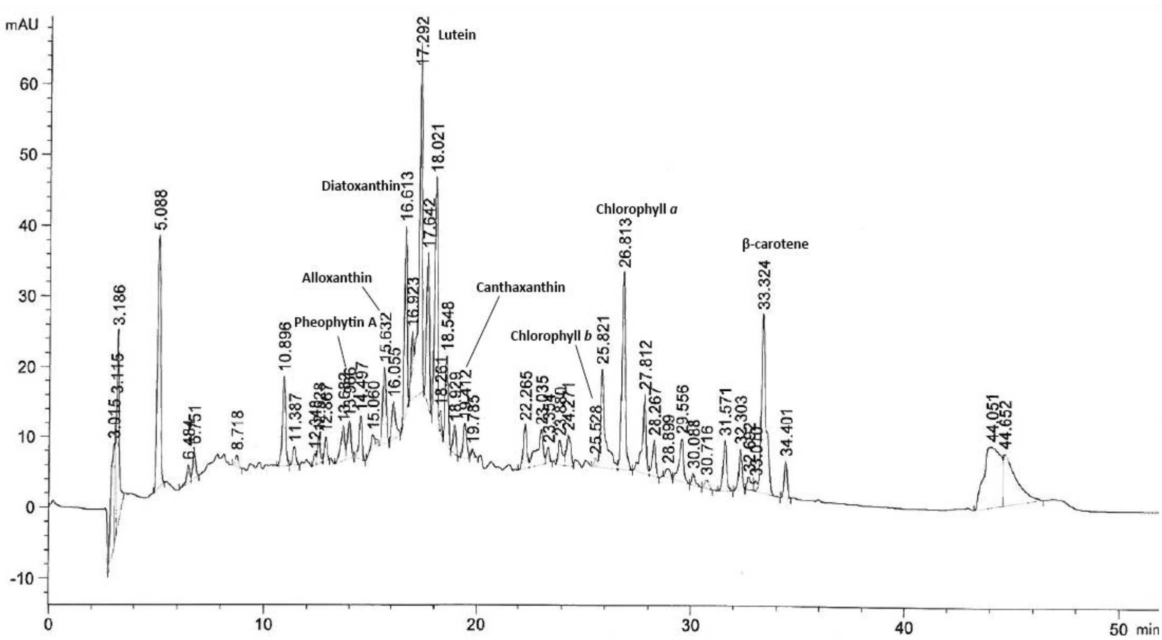


Figure 3.13: Example chromatogram showing a range of pigments, main pigments detected within this study labelled.

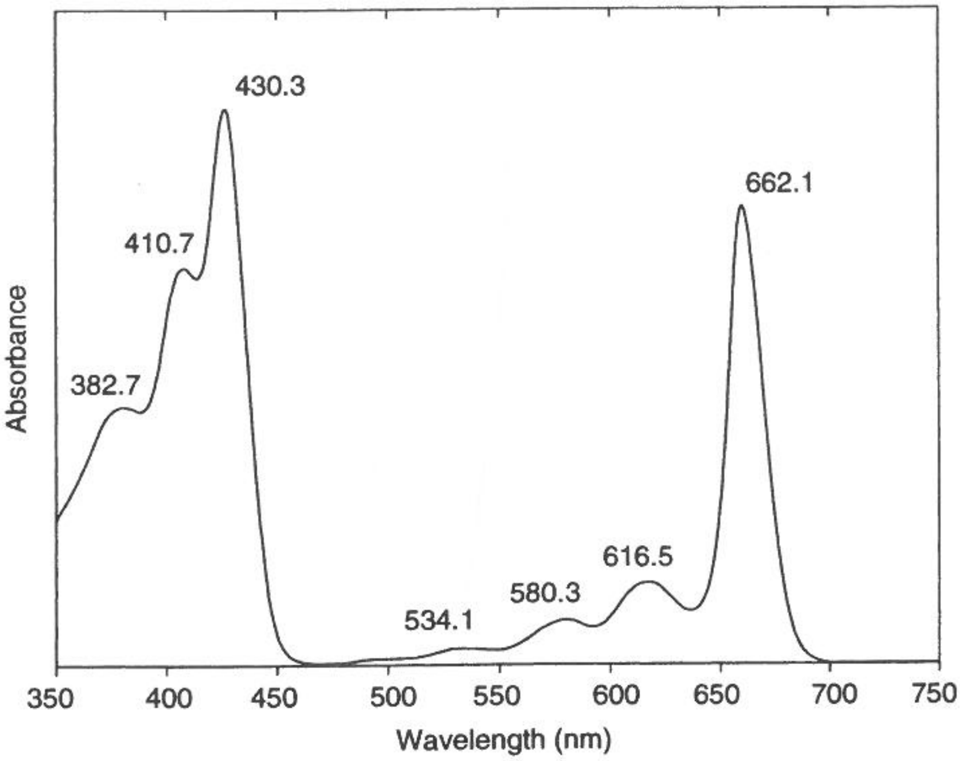


Figure 3.14: Standard spectrum of Chlorophyll *a* (Jeffrey et al., 1997).

The ultraviolet radiation (UVR) index was calculated from the pigment abundance to evaluate light/UVR exposure using Equation 3.3 (Leavitt et al., 1997). Light exposure can degrade pigment preservation but it can also indicate times of clear water (high UVR index) or eutrophic conditions where an increase in algae reduces the penetration of light to lower in the water column (low UVR index) (Leavitt et al., 1997).

$$UVR\ index = \frac{UVR\ pigment}{Alloxanthin + Diatoxanthin + Lutein/Zeaxanthin} x100 \qquad \text{Equation 3.3}$$

3.6.2 Diatoms

3.6.2.1 Introduction

Diatoms are small (5-200μm), unicellular, eukaryotic, photosynthetic algae and are important members of the planktonic food chain (Round et al., 1990; Jones, 2007; Jeffrey & Vesk, 1996). Diatoms can be split into three main types: Cenrtrics (round diatoms) and pennates (elongated diatoms) of which there are two types, raphid and araphid (with or without a raphe respectively) (Jones, 2007; Figure 3.15). They comprise of two values, made of silica, which fit together in a box-like structure (Jones, 2007). The application of diatom analysis is based on the observation of uniquely sculptured valves (Jones, 2007). There may be more than 200000 species of diatoms, each with their own unique valve sculpturing, making them the most species rich group of algae (Jones, 2007). The preservation of diatoms within sediments is attributed to their high silica content and their unique valves make them taxonomically diagnostic (Stoermer & Smol, 1999; Lowe & Walker, 2015).

Diatoms are found in almost all waters, the exception is the hottest and most hypersaline environments (Jones, 2007). Each species has its own habitat and ecological tolerances, e.g. pH and nutrient availability, which determines what species are present in the aquatic environment. Planktonic diatoms are common in open waters and are influenced by two main controls: 1) the availability of silicate and 2) the tendency for the diatoms to sink as they are equally or more dense than water (Jones, 2007; Taffs et al., 2017b). Planktonic diatoms may exhibit a long cylindrical shape or long chains as this can slow their sinking from the photic zone which is often turbulent due to currents, winds and convection (Jones, 2007). Benthic diatoms are diverse as they can live either on or in the sediments or attached to the substratum, e.g. rocks, sand grains and plants (Jones, 2007). Aerophilic diatoms grow as subaerial forms, e.g. on damp rocks, terrestrial soils or leaves of plants in damp environments (Jones, 2007). While habitat is a control on diatom flora, they are also controlled by physical e.g. temperature, turbulence and light, chemical e.g. pH, nutrients and salinity, and biological e.g. grazing and parasitism controls (Jones, 2007). Diatoms exhibit specific habitat and ecological preferences and respond promptly to environmental changes given their rapid reproduction cycle (Taffs et al., 2017b). The study of changes in diatom species abundance through sedimentary records can therefore provide a proxy of changes within the environment over time.

While the use of diatoms is not a common technique within estuarine sciences, they are good palaeo-indicators of environmental changes caused by human activities within such aquatic environments (Taffs et al., 2017b). There are challenges associated with diatom studies within estuaries compared to those in lacustrine environments, e.g. increased sediment disturbance from tidal currents and lack of analogue sites for transfer function analysis (Taffs et al., 2017b). However, the study of diatoms in coastal habitats, including estuaries, has provided reliable quantitative and qualitative reconstructions of environmental change, including how estuarine ecosystems and diatoms have responded to past nutrient changes which may act as analogues to their future response, e.g. Andrén et al., (1999), Andrén et al., (2000), Savage et al., (2010), Weckström (2006), Ellegaard et al., (2006), Clarke et al., (2006) and Lundholm et al., (2010) (Taffs et al., 2017b).

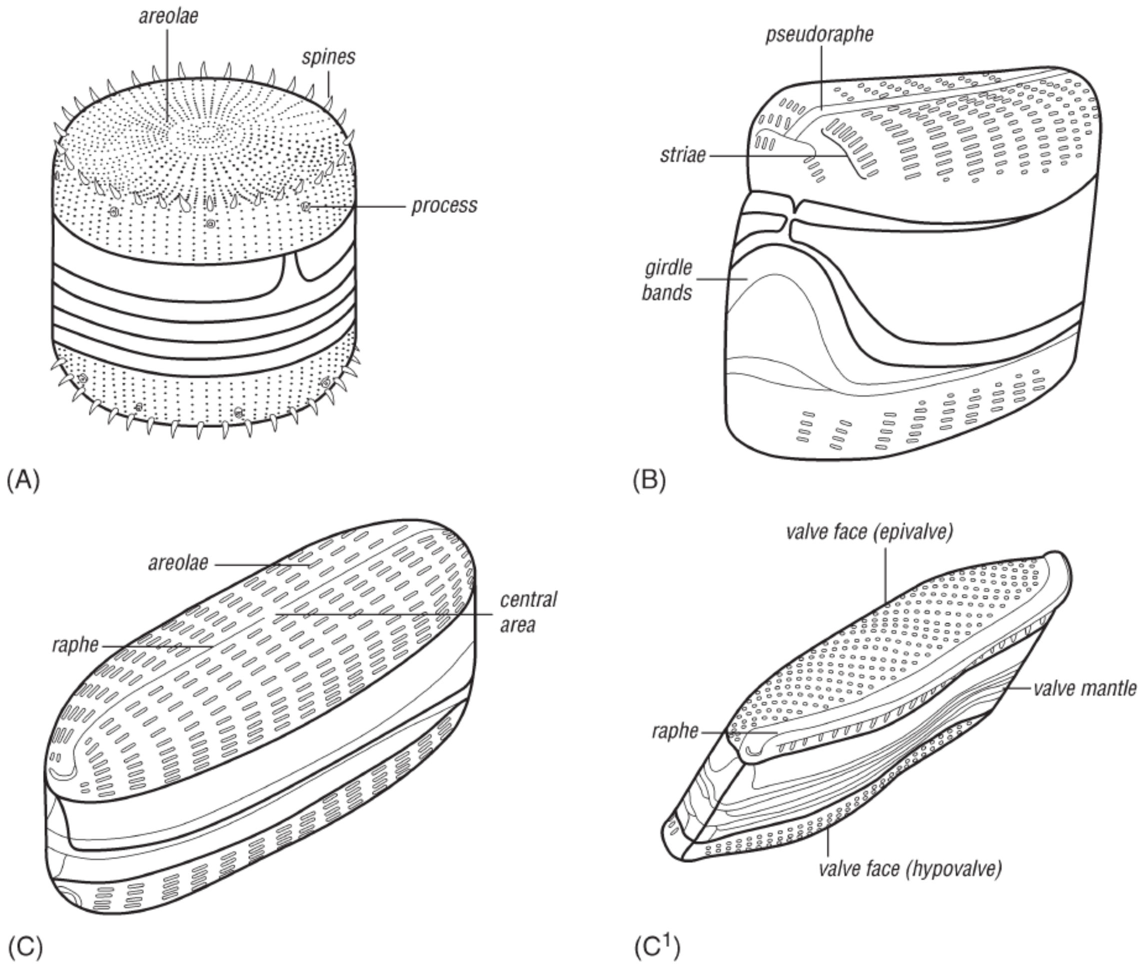


Figure 3.15: Schematic diagram of the three main classes of diatoms: A) centric, B) araphid pennate, C) centric raphid pennate (raphe running along the central axis of the valve), C[1]) eccentric raphid pennate (raphe running along one margin) (Jones, 2007).

3.6.2.2 Methodology

FRM4 and ARNE5 underwent diatom analysis. This allowed comparison between the control site and the main nutrient source draining the agricultural landscape of the catchment. Analysis was carried out at a higher resolution towards the top of the core to better understand recent changes with resolution decreasing further down the core in an attempt to determine previous conditions. For FRM4 samples were recovered at 4cm non-contiguous increments from 0-16cm, at 8cm non-contiguous increments from 24-48cm and at 32cm non-contiguous increments from 64 to 96cm. For ARNE5 samples were recovered at 4cm non-contiguous increments from 0-16cm, at 8cm non-contiguous increments from 24-72cm and at 32cm non-contiguous increments from 104-264cm.

Preparation of the diatom samples followed the method of Battarbee et al., (1986) with slight modifications (Goodes, H. pers. comm. 2016; Fonville, T. pers. comm. 2017). Approximately 0.1g of freeze dried sediment was weighed into a 50ml centrifuge tube. A few drops of 10% HCl were added to each sample to remove any carbonates if present in the sample. Samples were then topped with distilled water, centrifuged, decanted and then rinsed, centrifuged and decanted again. Samples were then digested in approximately 5ml concentrated H_2O_2, this took approximately two hours. Once reaction ceased, a few more drops of H_2O_2 was added to check the reaction had completed. A few drops of 10% HCl was then added to cease reaction and the samples were topped with distilled water, centrifuged and decanted. The samples were rinsed, centrifuged and decanted four times until the supernatant appeared clean. Deionised water was added to each tube, the volume noted, and 0.5ml of each sample was transferred to a new 15ml polypropylene tube, these were topped with deionised water until the solution became transparent. 0.5ml of the diluted material was evaporated on a coverslip and mounted onto a microscope slide with the use of Naphrax.

At least 250 diatom valves were counted for each sample analysed at x1000 magnification using a Nikon Eclipse 80i microscope. Identification of the diatom frustules followed that of Krammer and Lange-Bertalot (1991a, 1991b, 1997, 1999) and Hartley (1996).

Diatom counts presented within the main body of this thesis account for taxa which occurred >3%. Full diatom taxa counts are presented in Appendix C.

3.6.3 Statistical methods for analysing palaeoecological data

Palaeoenvironmental studies often result in large, multivariate data sets from which trends in taxa communities over time need to be determined (Shi, 1993). Data is usually sampled at numerous points in space and time. The changes in taxa community assemblages over time can be qualitatively observed in ecological stratigraphic diagrams. However, multivariate statistical methods, such as ordination techniques and cluster analysis, can be applied to provide a quantitative representation of environmental change. These methods will be used to explain how taxa, i.e. diatoms and pigments, change over time.

Ordinations techniques determine the direction of variations within the data by arranging the data points according to their relationship to a number of variables. The data points are arranged according to their position of axis one and two, as these axes represent the variables which hold the most control over the data point distribution (Shi, 1993). Data points which are of the most similarity are plotted closely together on a biplot as they exhibit similar Axis one and two values.

Detrended Correspondence Analysis (DCA) is an ordination technique which is commonly applied to palaeoenvironmental data. A DCA was selected for this study because it overcomes the arch effect detected when using a Correspondence Analysis (CA) and thus is preferential to utilise to CA when analysing data via ordination techniques (Shi, 1993). The arch effect is a mathematical artefact which occurs when axis two is compressed and becomes arched as a function of axis one (Hill & Gauch, 1980). A DCA allows the axes to be interpreted separately and independent (Hill & Gauch, 1980).

A DCA was performed on all diatom and pigment taxa using the software PAST. No taxa were down weighted. DCA assumes the taxa are responding in a unimodal manner to the environmental variables (Ammann et al., 2000). Therefore, if the axis one gradient length was <0.3 s.d. then a linear ordination was deemed appropriate and Principal Components Analysis (PCA) was performed (Ammann et al., 2000; ter Braak & Prentice, 1988). Axis 1 scores were normalised into z-scores to allow comparisons to be made across cores, these are presented against raw axis 1 values within the pigment and diatom data.

Cluster analysis extracts information from a data set by forcing 'objects', e.g. the sample dates with which taxa data sets are assigned, into discrete groups (Shi, 1993). The output from a cluster analysis is a dendrogram where the clusters can be interpreted as representing similar communities, e.g. similar taxa. Constrained Incremental Sums of Squares cluster analysis (CONISS) was performed on pigment and diatom assemblages to identify samples (dates) that were most similar to each other. By constraining the analysis, only stratigraphically adjacent samples can be clustered, this allowed temporal changes in assemblages to be determined (Grimm, 1987). CONISS distances were presented as sum of squares, the smaller the sum of squares distance, the more similar the samples are to each other.

DCA, PCA and CONISS methods can be used to analyse and summarise large, complex, multidimensional data sets (Shi, 1993). These techniques extract directions of variation within data sets to help understand how environmental changes have occurred over time (Shi, 1993).

3.7 Secondary data

Much of the secondary data used in this research was extracted from published sources as summarised in Table 3.7.

Table 3.7: Sources of secondary data.

Secondary data	Source
Precipitation	Met Office (2017, 2018)
Temperature	Met Office (2018)
Sea level	Haigh et al., (2009)
Agriculture	Grabowski and Gurnell (2016) Bowers (1985) Brassley (1996)
River Frome flow	Centre for Ecology and Hydrology (2017)
River Frome nitrate and phosphorus concentrations	Poole Harbour catchment Initiative (2014)

The Poole Harbour catchment is not a defined area that population is calculated for within censuses, e.g. parish or county. Thus, population for the Poole Harbour catchment was calculated from census data.

Catchment population changes over the past ca. 250 years are detailed in Figure 2.16. Where possible, parish level data was used to provide catchment population estimates for given census years. This was calculated by comparing parish boundaries with the Poole Harbour catchment boundary; for those boundaries which fell within the catchment the population was counted as whole and for those which fell on the boundary, the percentage of parish area within the catchment was calculated and such percentage was taken as the population within that parish. It is noted this does assume an even distribution of population within a parish but the population numbers were not of significant numbers that it would alter the population trends by any magnitude.

For years where parish level data was not available, 31% of the county level data for Dorset was calculated and 31% of Wrigley's (2007) Dorset county data was used, Poole Harbour accounts for 31% of Dorset. Parish and county level data was obtained from A Vision of Britain Through Time (Southall & University of Portsmouth, 2017).

3.8 Statistical methods used to identify transitions in water quality

A water quality indicator proxy was established for each core (Section 7.2.3). Three methods were applied to the water quality time series data to identify breakpoints which could be used to determine if transitions in the water quality trajectory could be statistically determined, e.g. a decline in water quality.

The first of these methods was the sequential algorithm presented by Rodionov (2004) to detect significant climate regime shifts. Since its introduction, the technique has been used by Zhang et al., (2015) to identify tipping points within time series data. The method utilises the Student's t-test to determine if the difference between the mean of two subsequent regimes, or time periods of data, is statistically significant (Rodionov, 2004). Any significant change indicates a regime shift occurred (Rodionov, 2004). This method can be applied using different cut-off lengths, e.g. sequential 10 or 20 year intervals, to assess the significance of the breakpoint (Zhang et al., 2015). Sampling resolution only allowed water quality values to be determined for certain years within the studied time period, i.e. where a sample was measured. Linear interpolation between these dated water quality data points was used to establish a yearly water quality time series data set. Equation 3.4 was used to determine what difference ($diff$) in mean water quality between regimes would qualify as a significant change in water quality (Rodionov, 2004). In this case, if the $diff$ was greater than the difference between the mean water quality of two sequential 10 or 20 year periods, then the water quality would be significantly different between the regimes and a breakpoint had occurred in the time series; where t is the critical value of student's t-distribution with $2l - 2$ degrees of freedom at a given probability level p, in this case p=0.05 was used, σ is the average variance for running $l -$ year intervals (Rodionov, 2004).

$$diff = t\sqrt{2\sigma/l} \qquad \text{Equation 3.4}$$

The second method used to determine a change in trajectory within the water quality time series data was segmented regression. This statistical method was carried out using the package 'segmented' in the statistical software R (Muggeo, 2017). This method identifies the location within the time series data where there is a change between two different linear relationships. Where the change in linear relationships is found, identifies a transition to a new water quality trajectory, e.g. a change to a decline in water quality.

The final statistical approach used to identify breakpoints within the water quality data was breakpoint analysis which was carried out using the package 'strucchange' in the statistical software R (Zeileis et al., 2015). This method identifies the location, or date, where there is a deviation from stability within the linear regression model of the data, i.e. the breakpoint point (Zeileis et al., 2015).

3.9 Conclusion

Table 3.8 provides a summary of the analyses used within this research and the sample resolution carried out on each core. These methods have been outlined in this chapter and have been justified to be used to address the aims of this study. Following exploratory data analysis, undated samples were discarded and are not presented within this thesis.

Table 3.8: Summary of analyses for each core with sampling resolutions.

	River Frome **FRM4**	**River Piddle** **PID1**	**Holes Bay** **HB1**	**Arne** **ARNE5**
Spheroidal carbonaceous particles	4cm until reached 3 zero counts and 2cm either side of start of record and peak concentration.			
^{137}Cs **^{210}Pb**	2cm until no counts continuous measured and evident end of the record had been reached.			
Itrax	200µm			
Magnetic susceptibility	1cm			
Loss-on-ignition	1cm			
Stable isotopes	2cm commencing from 1cm			
Pigments	1cm until 1850, 8cm thereafter			
Diatoms	0-16cm at 4cm 24-48cm at 8cm 64-128cm at 32cm	-	-	0-16cm at 4cm 24-72cm at 8cm 104-264cm at 32cm

Chapter 4 Chronology

4.1 Introduction

It is important to determine the chronology of sediments in order to date events within the sedimentary record. Within estuarine systems, it is also particularly important to establish good chronologies of sediment cores in order to determine if the records are chronologically intact and that estuarine processes, e.g. tidal action, have not disturbed the accretion of sediments.

As discussed in Chapter 3, the chronological methods undertaken in this study were Spheroidal Carbonaceous Particles (SCPs) analysis, Caesium-137 (^{137}Cs) and Lead-210 (^{210}Pb). Dates derived from the three-point SCP method, ^{137}Cs markers and simple (CF:CS) ^{210}Pb models were used in the Bayesian modelling package 'Bacon' to establish age-depth models for the River Frome (FRM4) and River Piddle (PID1) estuary, Holes Bay (HB1) and Arne (ARNE5).

4.2 Chronological methods

4.2.1 SCP analysis

Two methods were used to analyse SCP concentration profiles established for each core (Figure 4.1); the 10% cumulative concentration method and the three-point method (Rose et al., 1995; Rose & Appleby, 2005). For cores which exhibited a 'double peak' in SCP concentration (PID1, HB1 and ARNE5 (Figure 4.1B, C and D)), the greatest SCP concentration was taken as 'the peak', i.e. the 1970±5 chronological marker.

The 10% cumulative concentration method allows a date to be assigned to each 10% increase in SCP concentration from the 0% start of record (SoR) to the 100% peak (Rose & Appleby, 2005). Therefore, there is no user subjectivity in the assignment of a depth to a date. The three-point SCP method assigns a date to the SoR, peak and the depth at where there is a transition between the gradients of slow and fast rises in SCP concentrations, the mid-point 1950s date (Rose et al., 1995). While an ideal SCP concentration profile would exhibit no uncertainty as to the depth where this transition occurs (Figure 3.9), some SCP concentration profiles demonstrate multiple possibilities for the transition between the slow and rapid gradients, hence the placement of this mid-point 1950s date may be subjective (Figure 4.2).

SCPs were present in all cores. HB1 exhibited the greatest concentration of SCPs (734909 SCPs/g), up to nearly five times greater at the peak in comparison with the other cores (272991, 159858 and 147327 SCPs/g for FRM4, PID1 and ARNE5 respectively). A greater sediment accumulation rate (SAR) in Holes Bay could facilitate the trapping of contaminants and other environmental markers, e.g. SCPs, at a greater abundance relative to the other sites (Balachandran et al., 2005, 2008; Martin et al., 2012). Reasons behind high SARs in Holes Bay, e.g. land reclamation and catchment erosion, are explored in detail in Chapter 5. Poole Power Station was built in the late 1940s-1950 next to Holes Bay (Martin, J. (Borough of Poole), pers. comm. 2018). The close proximity of the power station to Holes Bay could have increased the source of SCPs which were deposited within Holes Bay, accounting for the higher abundance of SCPs counted in HB1.

FRM4 exhibits the closest resemblance to an ideal SCP concentration profile of the four cores (Figure 4.1A). PID1 shows a rapid increase in SCP concentration from the initial slow rise between 32.5-28.5cm (Figure 4.1B). The rapid increase is likely a result of a low SAR at PID1 around this time. Other proxies (^{137}Cs, ^{210}Pb, magnetic susceptibility and calcium concentration) present a record of environmental change across 32.5-28.5cm (Figure 4.3), suggesting no hiatus took place, as hiatuses can also lead to rapid changes in SCP concentration. HB1 and ARNE5 demonstrate a long 'tail' of low SCP concentrations before a gradual then rapid rise in SCP concentrations to the peak, likely an artefact of faster SARs experienced in these areas (Figure 4.1C and D).

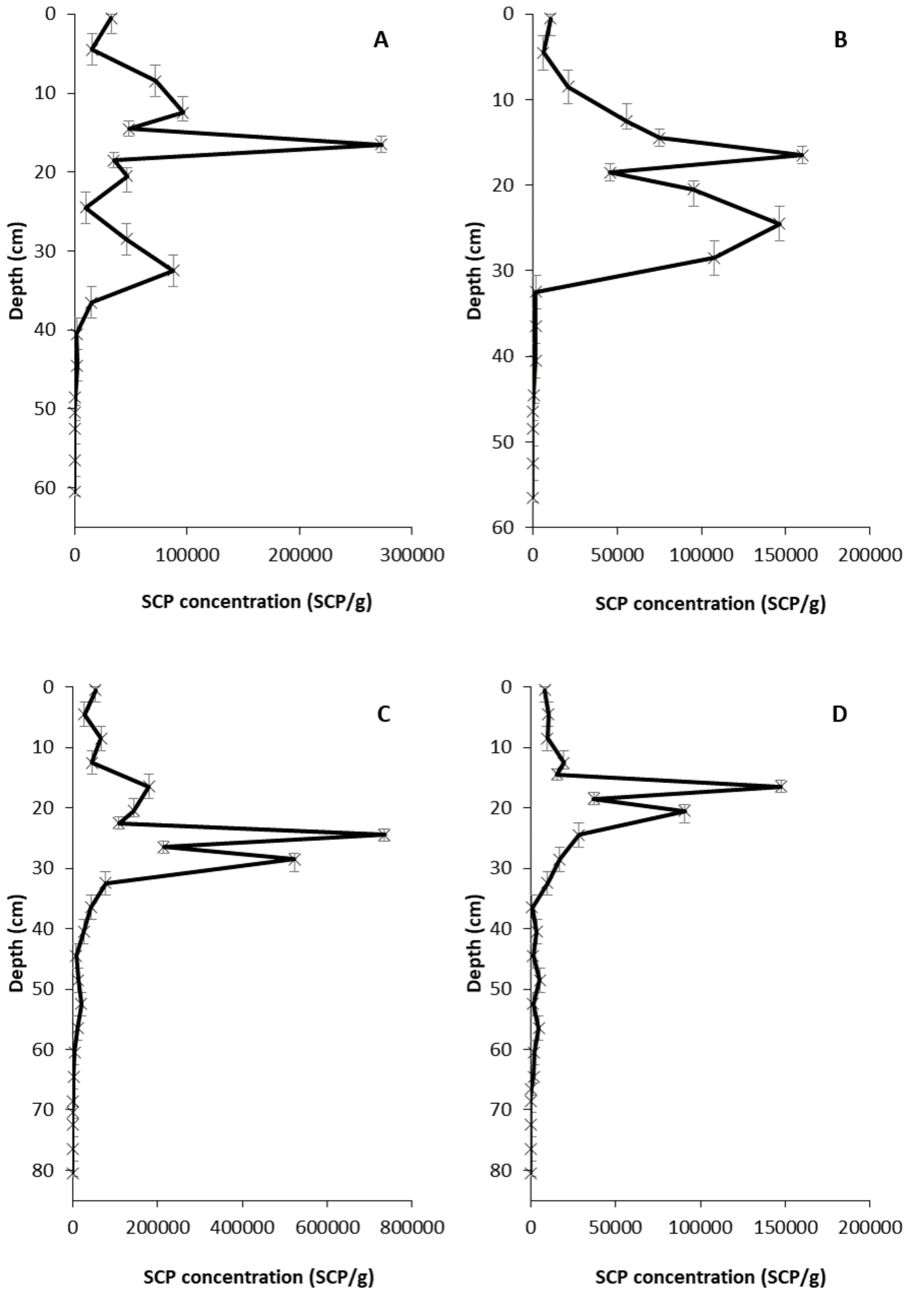


Figure 4.1: SCP concentration profiles for A: FRM4, B: PID1, C: HB1 and D: ARNE5. Y-axis error bars indicate sampling error.

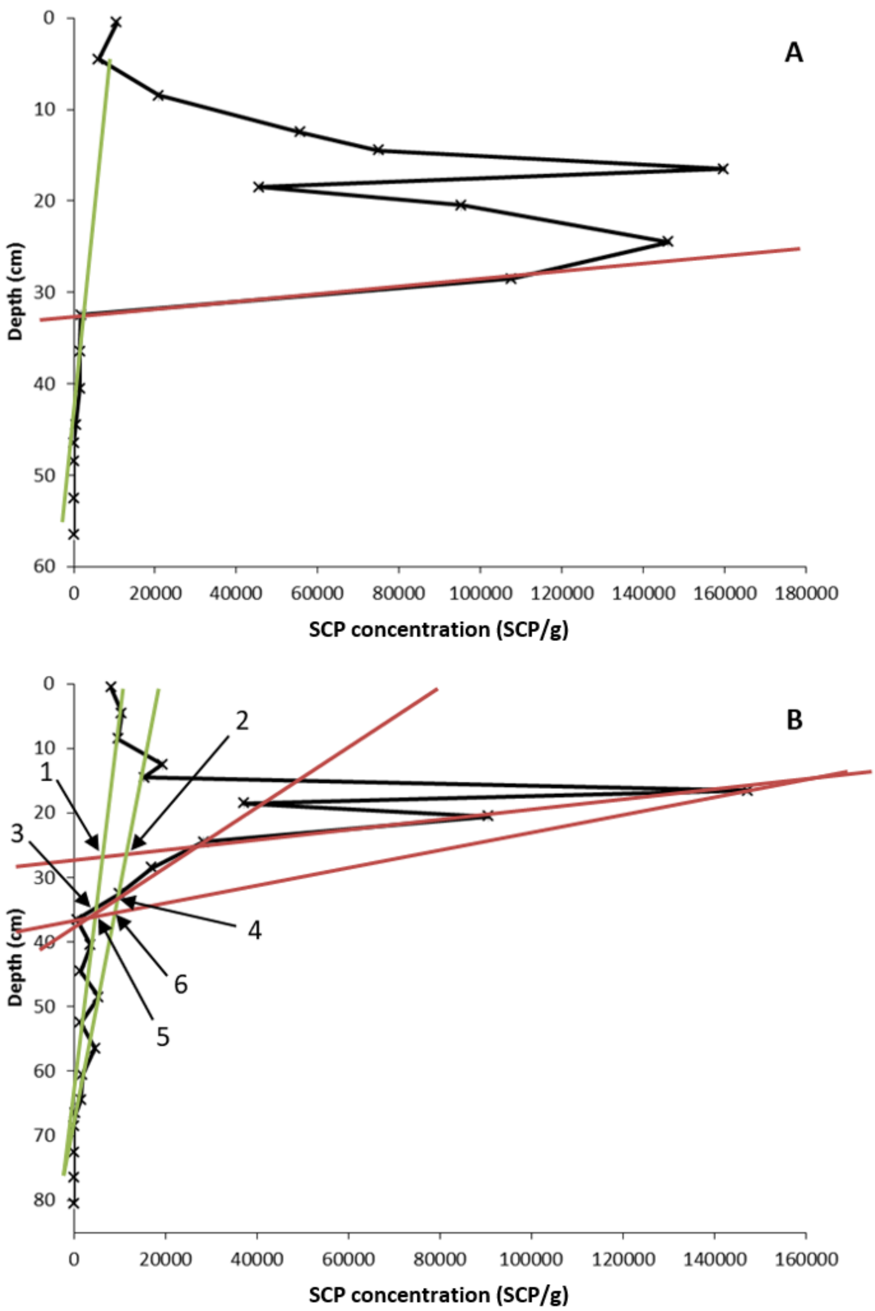


Figure 4.2: SCP concentration profiles for A: PID1 and B: ARNE5 with green lines indicating the slow rise in SCP concentration and the red lines indicating the fast rise in SCP concentration. The depth at where these lines meet is the mid-point 1950s date for the 3-point SCP dating method. Note that ARNE5 has 6 possibilities for the mid-point date as there is uncertainty as to where the slow and fast gradients lie whereas PID1 only has one possibility for the mid-point date.

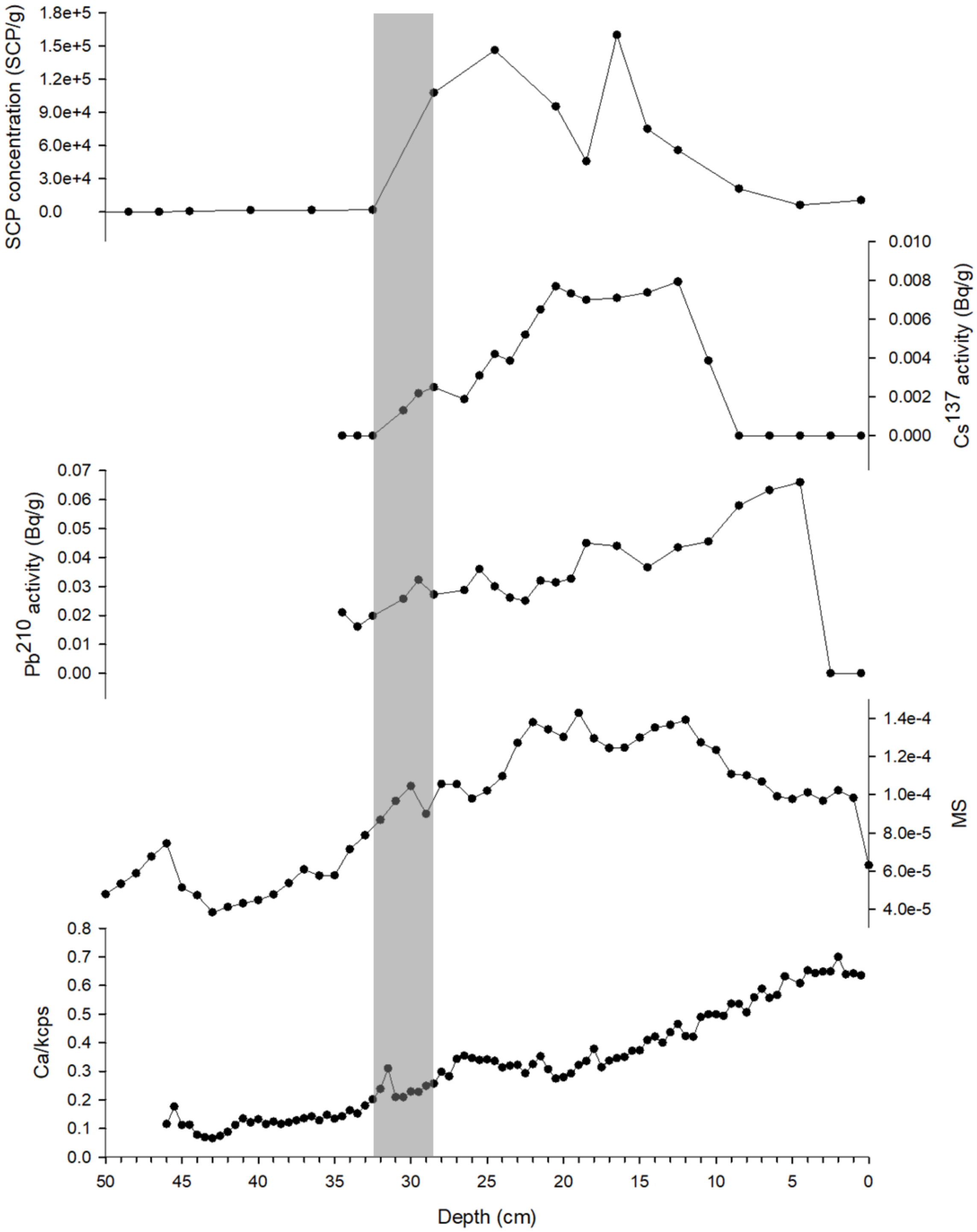


Figure 4.3: PID1 proxy data illustrating no hiatus between 28.5-32.5cm (grey shaded area).

4.2.2 Radionuclide analysis

^{137}Cs detected in sediments from Poole Harbour could have originated from global fallout and locally from discharges associated with the Atomic Energy Establishment at Winfrith, the latter hereafter termed the 'local source' (Section 3.3.3.1). The local source is more likely to be found in sediments close to the sea entrance (ARNE5) and in well-mixed waters (FRM4 and PID1) where the pollutants from the discharge can deposit (Figure 3.8).

^{137}Cs and ^{210}Pb activity were detected in all cores except ARNE5 where only ^{137}Cs was detected (Figure 4.4 and Figure 4.5). Only the ARNE5 Russian core was analysed for chronological markers, hence only a ^{137}Cs profile was obtained (Section 3.3.3.3). UWITEC core measurements for PID1 and HB1 were matched with the partial ^{137}Cs profile of the Russian cores to provide a full ^{137}Cs profile. For FRM4, only UWITEC core measurements were used because the Russian core exhibited no features to match against.

Data collected from ^{137}Cs and ^{210}Pb analysis were used to establish a standard radionuclide age-depth relationship for each core. Characteristic markers, i.e. peaks and increases, in ^{137}Cs activity were assigned estimated dates from global fallout: 1953 (start of atmospheric testing) and 1963 (nuclear weapons peak), and the local source: 1975/1978 (mid peak discharge) and 1990 (Winfrith closure). Simple (CF:CS) ^{210}Pb models were also calculated for each core. The dated features for the ^{137}Cs profiles were compared to the estimated date for that depth according to the simple (CF:CS) ^{210}Pb model. This comparison was performed to examine the reliability of ^{137}Cs dating as the start of the ^{137}Cs profile, i.e. the start of atmospheric testing, would not necessarily be detected in some of the samples due to their minimal mass (Croudace, I. pers. Comm. 2017; Figure 4.4A and C). Good agreement was found in all cases between the ^{137}Cs estimated date and that date estimated by the simple (CF:CS) ^{210}Pb models. As such, ^{137}Cs dates were included in the final age-depth model for each core (Section 4.2.3). Errors were calculated to consider the estimated ^{210}Pb simple model date and time taken for the ^{137}Cs to become deposited within the sediment. The narrow entrance between Holes Bay and the rest of Poole Harbour likely reduces the mixing between these two areas; detection of ^{137}Cs in this area is limited to global fallout and shows no record of the local discharge when checked with the simple (CF:CS) ^{210}Pb model.

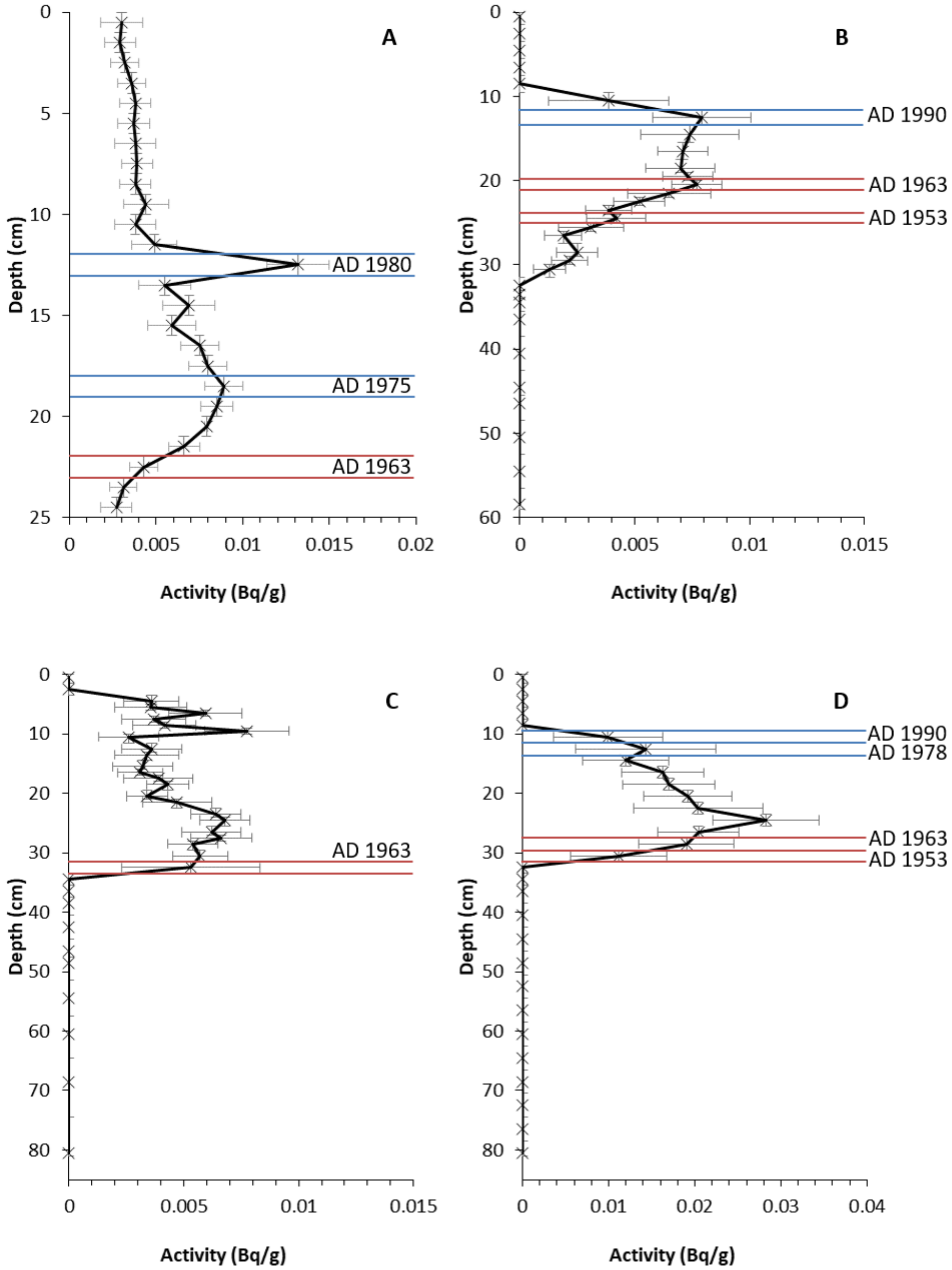


Figure 4.4: Distribution of the radionuclide ^{137}Cs for: A: FRM4, B: PID1, C: HB1 and D: ARNE5. X-axis error bars indicate analytical error and Y-axis error bars indicate sampling error. Red lines indicate dateable horizons from global fallout whereas blue lines indicate dates established from local source. Dates have been confirmed using the simple (CF:CS) ^{210}Pb age-depth models except ARNE5 where dates have been confirmed against SCPs.

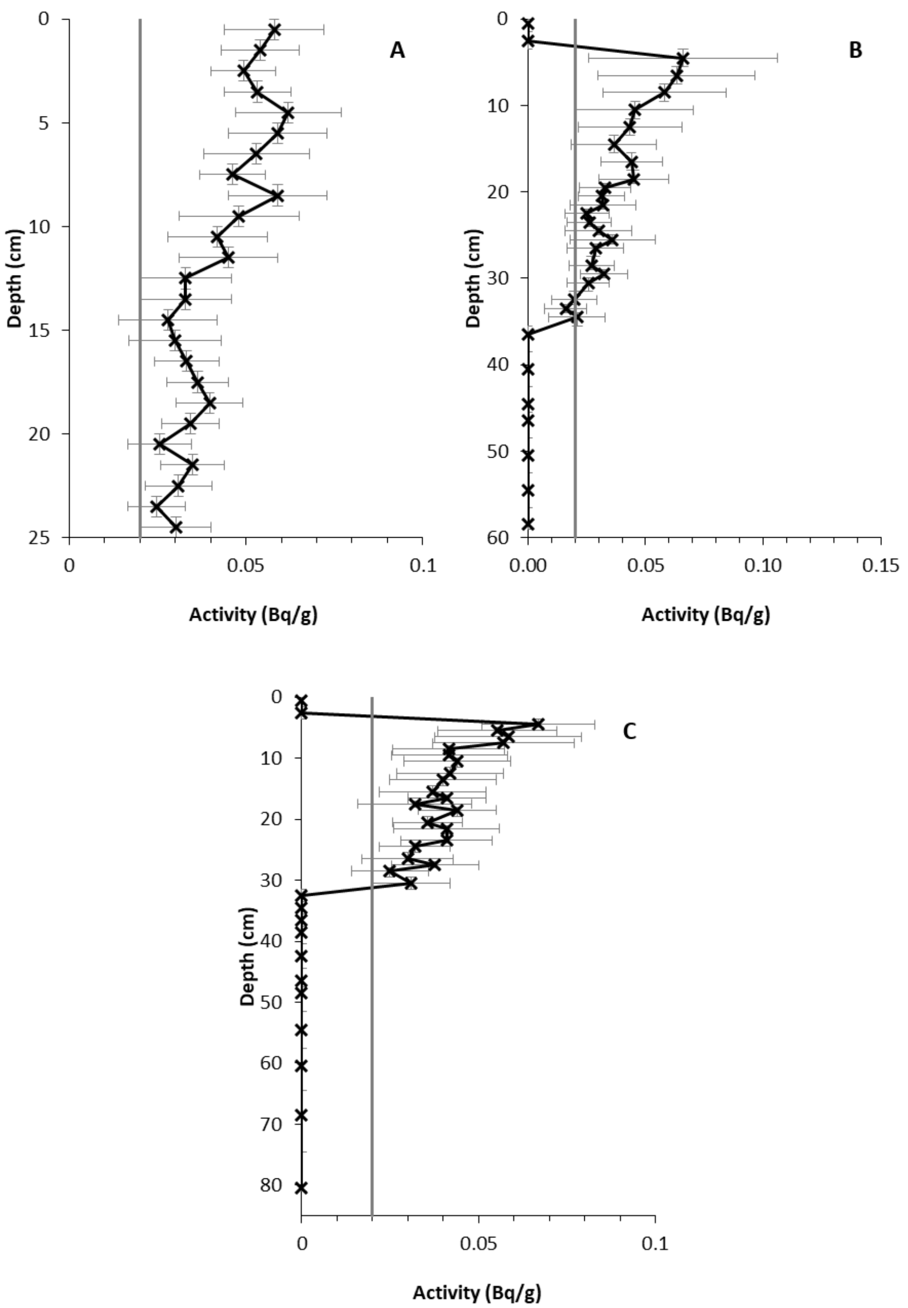


Figure 4.5: In black, the distribution of the radionuclide ^{210}Pb for: A: FRM4, B: PID1 and C: HB1. In grey, the supported ^{210}Pb values used in the simple (CF:CS) model. X-axis error bars indicate analytical error and vertical error bars indicate sampling error.

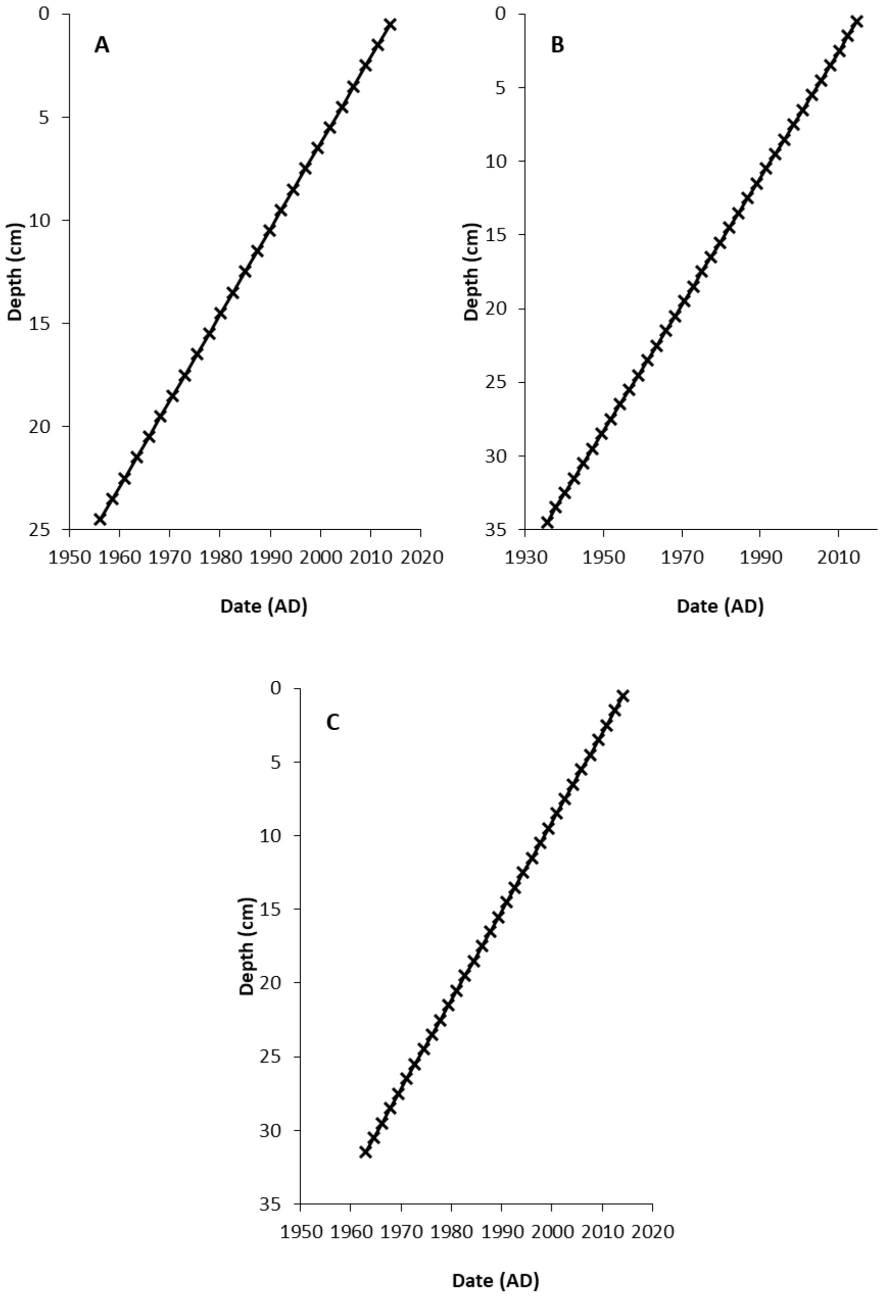


Figure 4.6: Simple (CF:CS) 210Pb age-depth models for: A: FRM4, B: PID1 and C: HB1. Note: dates only calculated to the depth of last 210Pb detection.

4.2.3 Age-depth modelling

Final age-depth models were established using Bayesian modelling. Dates used within the model were derived from the 3-point SCP method and the final ^{137}Cs dates which had been checked against simple (CF:CS) ^{210}Pb models (see above). Given the ambiguity with the placement of the mid-point SCP date using the 3-point method, all possibilities (see above) were used within the Bayesian model. The process behind developing the age-depth models for each core is expanded on below.

As demonstrated in Figure 4.7, the two SCP methods, the 10% cumulative concentration and 3-point method, produced age-depth models that were not in complete agreement with each other. While both SCP methods for FRM4 are similar (Figure 4.7A), PID1 (Figure 4.7B), HB1 (Figure 4.7C) and ARNE5 (Figure 4.7D) show there is deviation between the two SCP methods, most notably after the 1950s mid-point.

In all the cores, except FRM4, the multiple possibilities for the mid-point SCP date derived from the 3-point method agree more with each other than for the equivalent time marker (1955) in the 10% cumulative concentration method. Age-depth models using the 3-point method agree more with the ^{137}Cs independent markers relative to the poorer agreement between the ^{137}Cs independent markers and the SCP 10% cumulative concentration model. Therefore, as the 3-point SCP method provides dates that are in agreement with the independent radionuclide chronological markers, the 3-point SCP derived dates and the ^{137}Cs independent markers were carried forward for use in the Bayesian age-depth modelling.

The final age-depth models were derived using Bayesian modelling with the 'Bacon' package in the statistical software R. Bayesian modelling was used as it can account for uncertainties regarding depths (e.g. sampling resolution) and the variations in ages produced via the different methods, i.e. the 3-point SCP method and radionuclide independent markers. All possibilities for the 1950s mid-point markers within each core were included in the age-depth modelling to account for uncertainties surrounding the depth at where this date lies.

The final age-depth models are presented in Figure 4.8, see Appendix A for full Bacon outputs. The model uses a weighted mean to establish the 'best' model, i.e. the most likely age-depth relationship (Blaauw & Christen, 2013).

Figure 4.9 illustrates the similarities between the final age-depth models and the simple (CF:CS) ^{210}Pb models. The Bayesian derived models provide a chronology of greater duration than the simple (CF:CS) ^{210}Pb models. Where both the simple (CF:CS) ^{210}Pb model and final model have chronologies (FRM4 ca. 1956, PID1 ca. 1935 and HB1 1962 onwards), they demonstrate good similarity, thereby supporting the Bacon output as being the most likely age-depth model. This supports the use of the age-depth models presented in Figure 4.8 as they can be used to date sediment records of the last ca. 150 years which is necessary to understand the multi-decadal relationships between catchment drivers and ecological responses in Poole Harbour.

The weighted mean model output from Bacon is used through the rest of the thesis. Using these age-depth models, the SARs for each site were calculated and their results are discussed in Chapter 5.

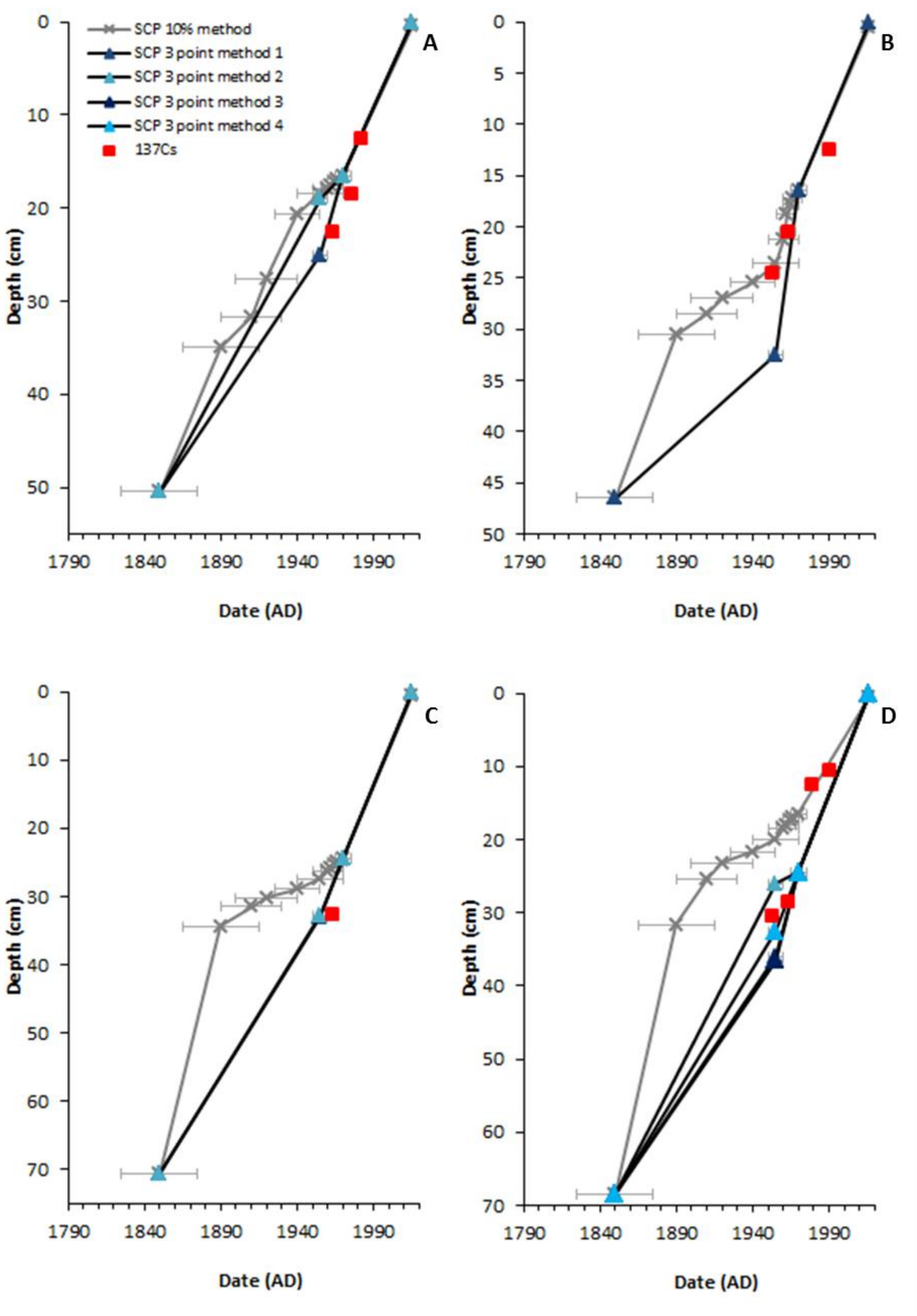


Figure 4.7: Comparison of the two SCP models (cumulative 10% concentration and all possibilities of the 3-point method) and dates derived from radionuclide analysis for: A: FRM4, B: PID1, C: HB1 and D: ARNE5. X-axis error bars indicate the dating error of the assigned age to a depth.

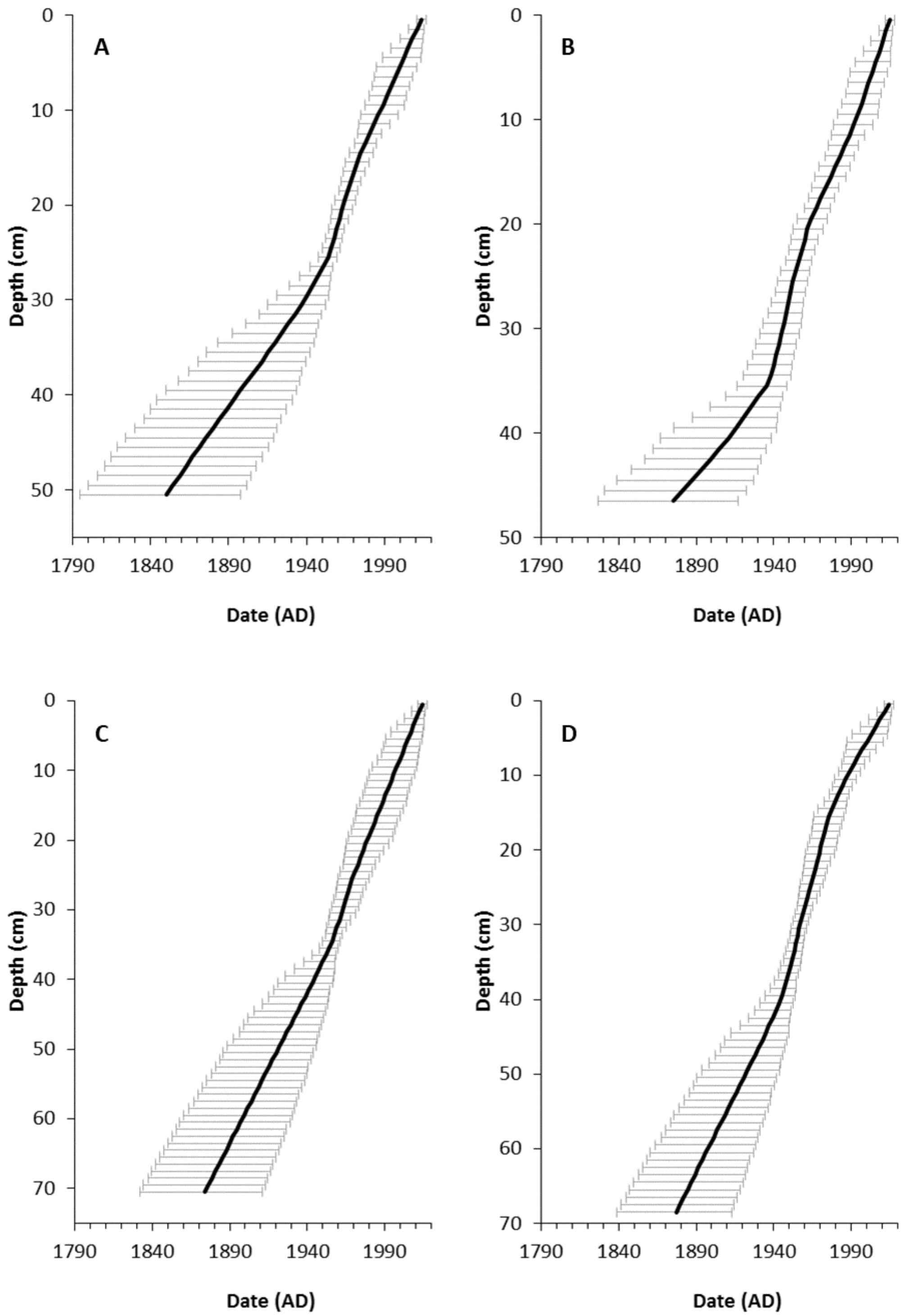


Figure 4.8: Final age-depth models for: A: FRM4, B: PID1, C: HB1 and D: ARNE5. Black line represents the weighted mean age for each depth. X-axis error bars represent the minimum and maximum date that the true age may lie within at a given depth.

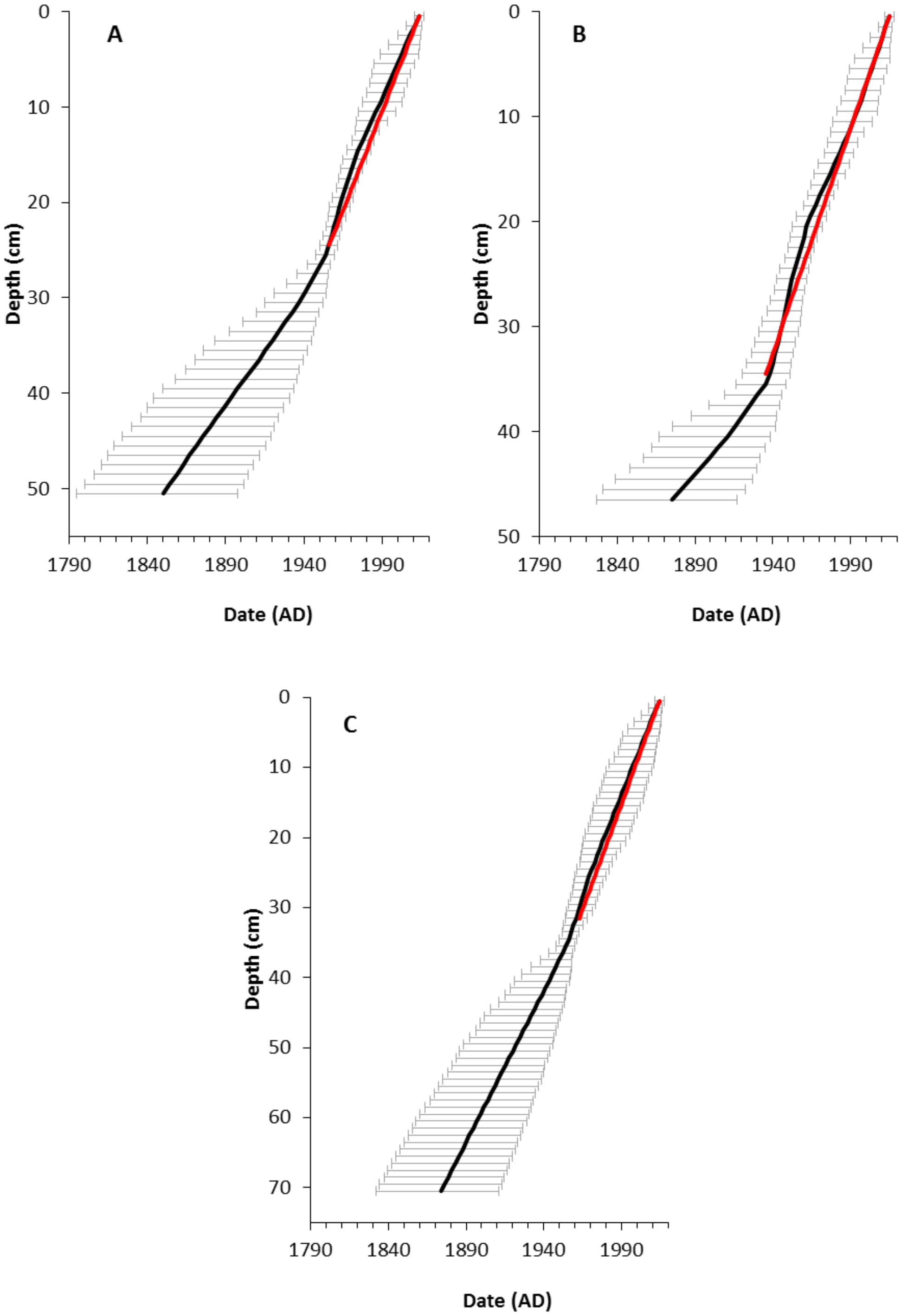


Figure 4.9: Final age-depth models for: A: FRM4, B: PID1 and C: HB1 as demonstrated by the black line with red lines representing the simple (CF:CS) ^{210}Pb model. Both models are in agreement with each other where they both span the same time length.

Chapter 5 Spatial and temporal variations of Sediment Accumulation Rates (SARs) within Poole Harbour

5.1 Introduction – drivers of change in sediment accumulation rates

The development of marshes within estuaries typically follows an initial rapid period of sediment accumulation which slows as the surface of the marsh becomes elevated from the tidal range and it's flooding frequency reduces (Cundy et al., 2002). Aside from autogenic changes in marsh sediment accumulation rates (SARs), SARs may change due to variations in the inputs and outputs of sediment or the trapping efficiency of a given point within an estuary (Bell et al., 2000; French, 2006; Mudd, 2011). There are many allogenic drivers of SAR change within estuaries, e.g. sea level rise and land use changes (farming, industrial development, urbanisation, shipping traffic) (Gedan et al., 2009; Bell et al., 2000).

While there is limited long term tide gauge data for Poole Harbour, data are available to 1935 for Southampton, the longest closest record (Haigh et al., 2009). The Southampton data suggest that while there has been fluctuation in levels, mean sea level for the south coast is increasing (Figure 5.1). Agricultural practices have changed within the catchments of the Rivers Frome and Piddle, e.g. post WWII intensified cereal crop farming (Bowers, 1985). As will be discussed in subsequent sections, changes in agricultural practices within the catchments of the River Frome and Piddle alter sediment delivery to Poole Harbour and consequently effect SARs within the estuary. Urban and industrial development in and around Holes Bay has altered sediment source and deposition, the effects of which shall be explored within this chapter.

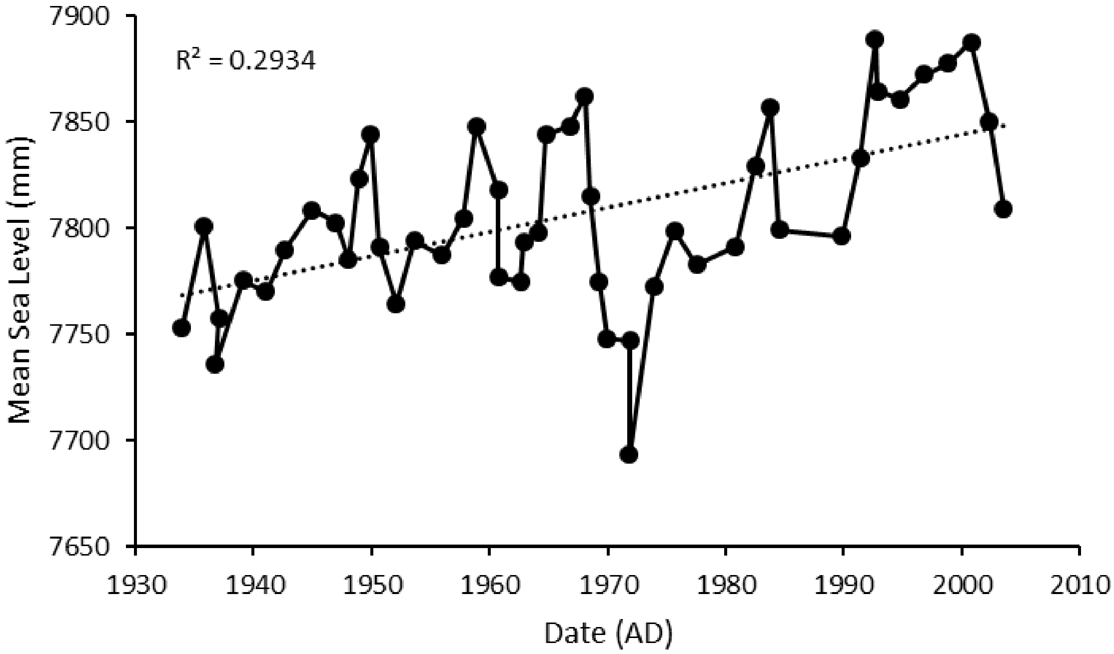


Figure 5.1: Mean sea level for Southampton, the closest longest record to Poole Harbour (Haigh et al., 2009).

Estuarine sediments and their SARs have been the subject of many studies, for example to investigate landscape evolution and to determine sediment sources, e.g. Bartholdy and Madsen (1985), Nichols (1989), French and Spencer (1993), Allen and Longworth (1993), Andersen et al., (2000), Flemming and Delafontaine (2000), Madsen et al., (2005). Studies on SARs in Poole Harbour have previously focused on the Arne Peninsula, e.g. Cundy (1994), Cundy and Croudace (1996), Long et al., (1999), Marshall et al., (2007). This chapter will further develop these by discussing the temporal and spatial variations of SARs at multiple sites within Poole Harbour, the River Frome and Piddle estuary, Holes Bay and Arne (Figure 3.1).

This chapter shall explore why changes in the SARs of Poole Harbour have occurred using data collected from the sediment cores. A summary of the data used to explain changes in potential drivers of SARs are given in Table 5.1.

Table 5.1: Proxies that can be used as indicators for drivers of changes in sediment accumulation rates.

Proxy	Indicator
Magnetic Susceptibility (MS)	Catchment erosion – an increase in low frequency MS suggests more minerogenic material is entering the system, e,g, erosion of top soils within the catchment, (Dearing, 1994).
Ca	Poole Harbour's catchment is mainly chalk. An increase in Ca could indicate an increase in catchment erosion or dissolution of the chalk during wet periods.
Zr/Rb	Indicator of grain size, higher ratio indicating a larger grain size (Schillereff et al., 2014). Change in grain size could indicate change in sediment source, e.g. increase in grain size could indicate more sediment from the sea and a decrease in sediment could indicate more sediment from the rivers (Bell et al., 2000).
Organic matter	Increase in OM can indicate increase in sewage input. It can also be an indicator of increased productivity within the water, e.g. algal growth or changes in vegetation (e.g. *Spartina*).
Pb	Indicator of industrial activity (Renberg et al., 2001).
Cu	Element in antifouling paint used on the hull of ships (Ytreberg et al., 2010). The use of Cu in antifouling paints has increased in the last 20 years as TBT has been phased out (Jones & Bolam, 2007). An increase in Cu could suggest increase in shipping traffic within the harbour.
Cl Br	Indicators of increased salt water content from the sea.

5.2 How have SARs changed in Poole Harbour?

SARs were calculated for the four study sites using the final age-depth models presented in Figure 4.8 (Figure 5.2). All cores demonstrate similar patterns of SARs throughout the record suggesting catchment wide changes affecting the whole harbour (Figure 5.2). All cores exhibit a broadly constant SAR until ca. 1940s where SARs increase by ca. 3-6 mm/yr. SARs remain greater relative to the pre-1940s rates until ca. 1970s. SARs decline post ca. 1970s and remain stable to present save for PID1 where the SAR increases ca. 2000 by ca. 1.1mm/yr. For FRM4, PID1 and HB1 the post ca. 1970s SARs are higher (ca. 1-1.5mm/yr increase) than pre-ca. 1940s but ARNE5 post ca. 1970s SAR falls to a lower SAR (ca. 0.5mm/yr decrease) compared to pre-ca. 1940s rates.

Wider catchment changes may explain SAR variability over the dateable period. Figure 5.3, Figure 5.4, Figure 5.5 and Figure 5.6 provide proxy records which may be used to help identify catchment scale environmental changes. Changes in SARs of FRM4 and PID1 are likely a result of changes in agricultural practices (e.g. WWII intensification in farming and draining of agricultural fields). SAR variability in HB1 is likely a consequence of land reclamation within Holes Bay and an increase in infrastructure whilst a combination of changes within the River Frome and Piddle catchments combined with periodic pulses in sea level rise (SLR) influence SARs in ARNE5. The following sections (5.2.1, 5.2.2, 5.2.3 and 5.2.4) discuss these forcings on SARs as determined using a suit of proxy records and secondary data.

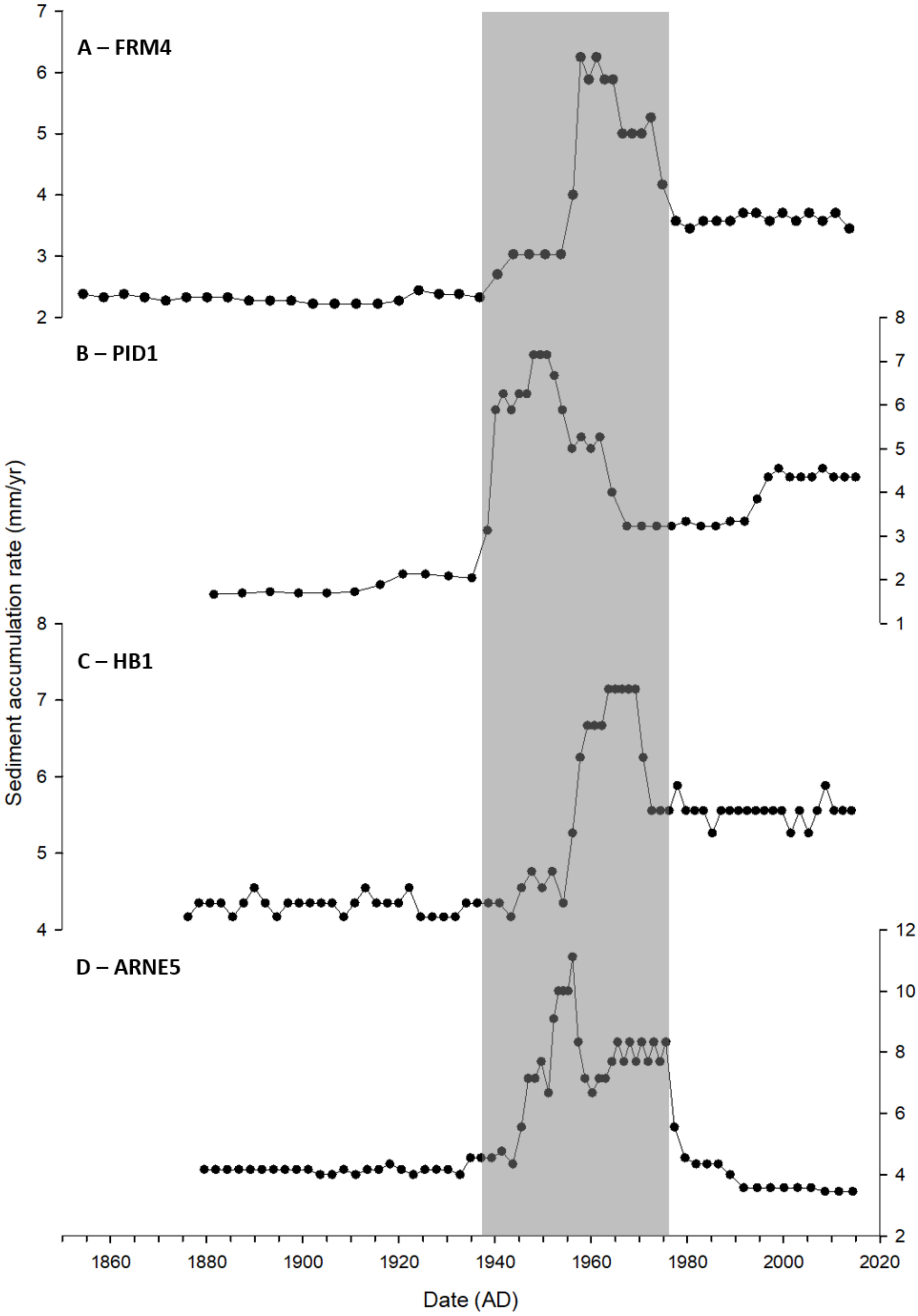


Figure 5.2: Sediment accumulation rates for A:FRM4, B:PID1, C: HB1 and D:ARNE5. Grey shading indicates period of higher SARs ca. 1940s-1970s.

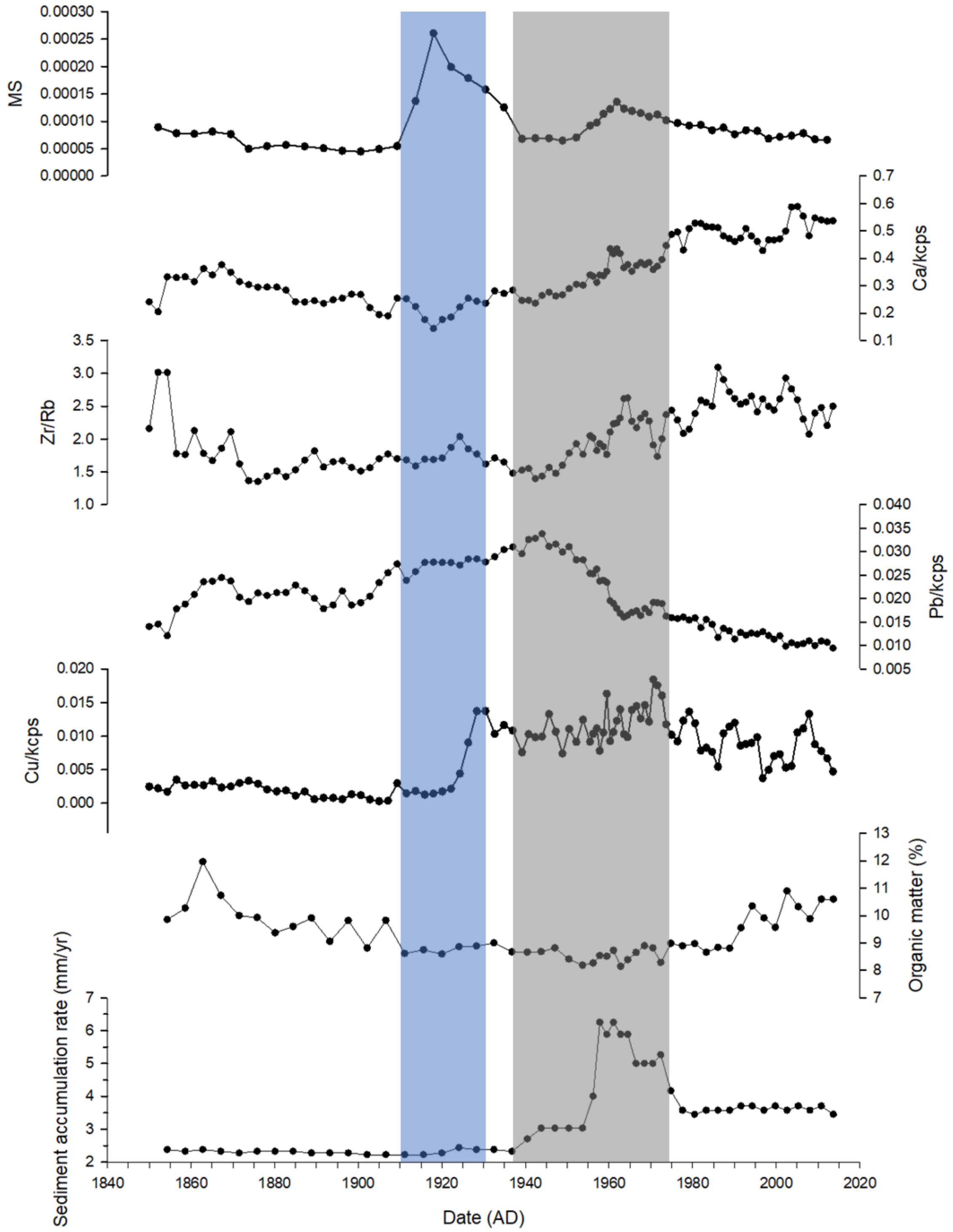


Figure 5.3: Proxies to demonstrate reasons for change in FRM4 sediment accumulation rates. Blue shading represents the rapid increase in magnetic susceptibility event and grey shading represents the ca. 1940s-1970s period of high sediment accumulation.

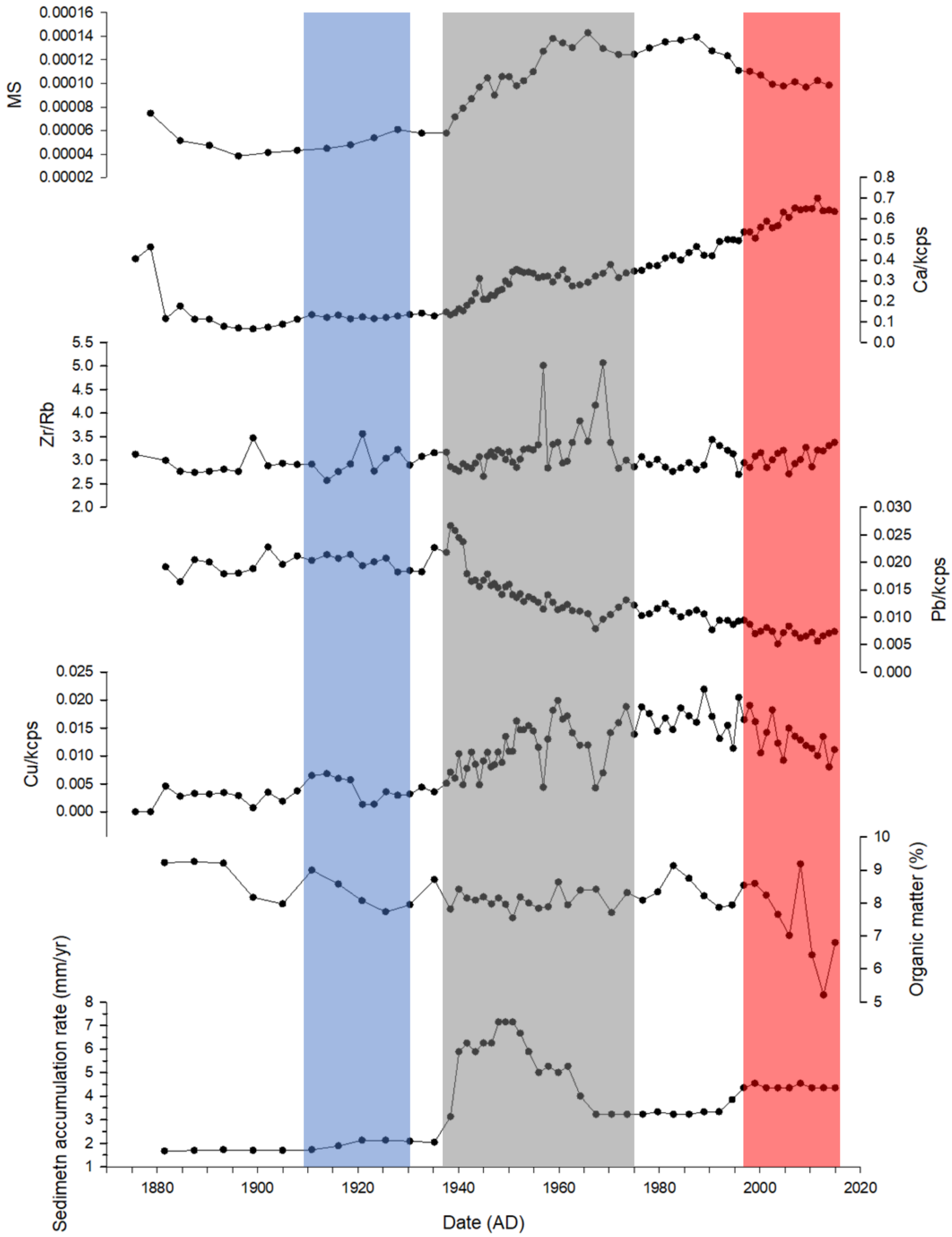


Figure 5.4: Proxies to demonstrate reasons for change in PID1 sediment accumulation rates. Blue shading represents the FRM4 rapid increase in magnetic susceptibility event, grey represents the ca. 1940s-1970s period of high sediment accumulation and red represents the post ca.2000s PID1 increase in sediment accumulation rate.

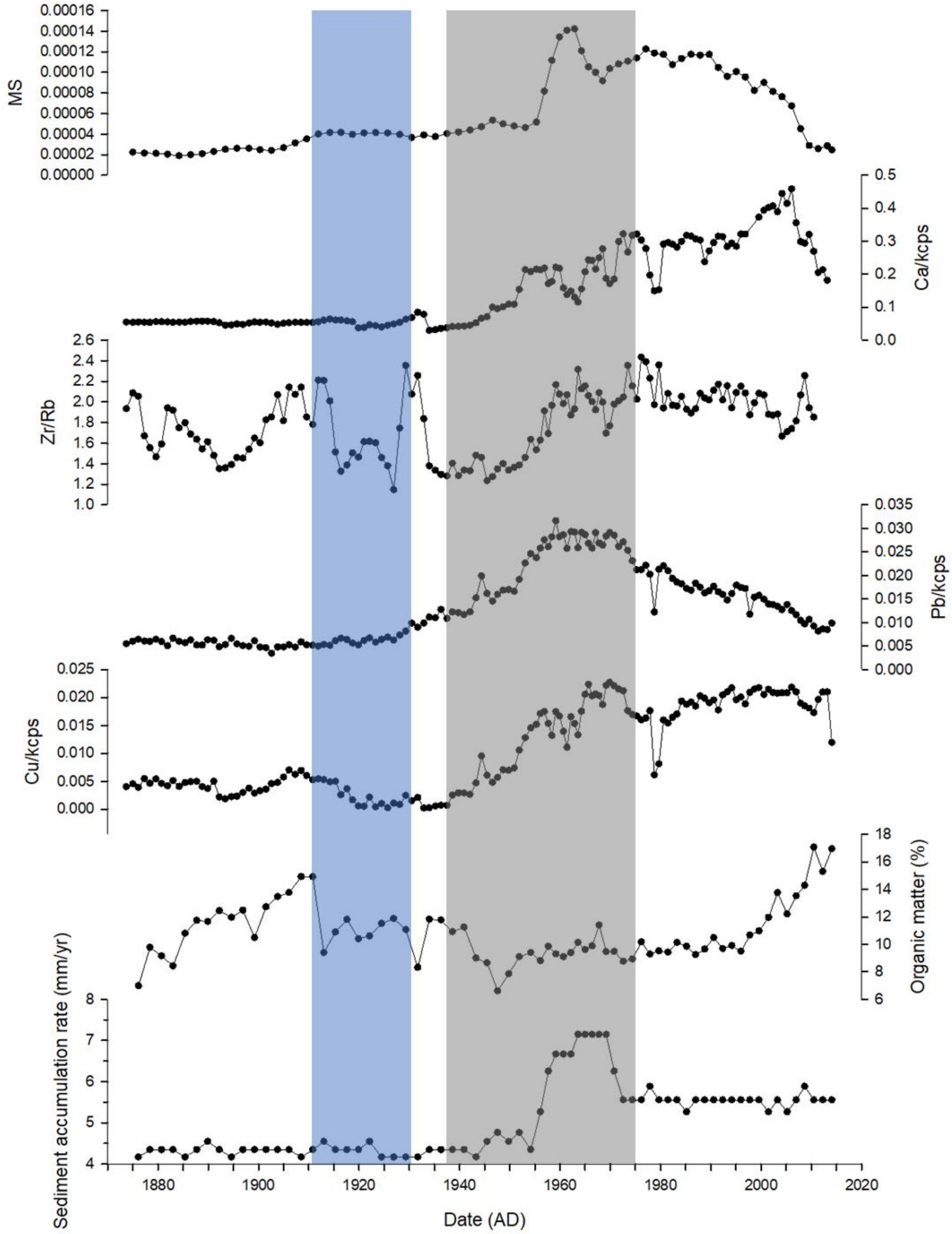


Figure 5.5: Proxies to demonstrate reasons for change in HB1 sediment accumulation rates. Blue shading represents the FRM4 rapid increase in magnetic susceptibility event and grey shading represents the ca. 1940s-1970s period of high sediment accumulation.

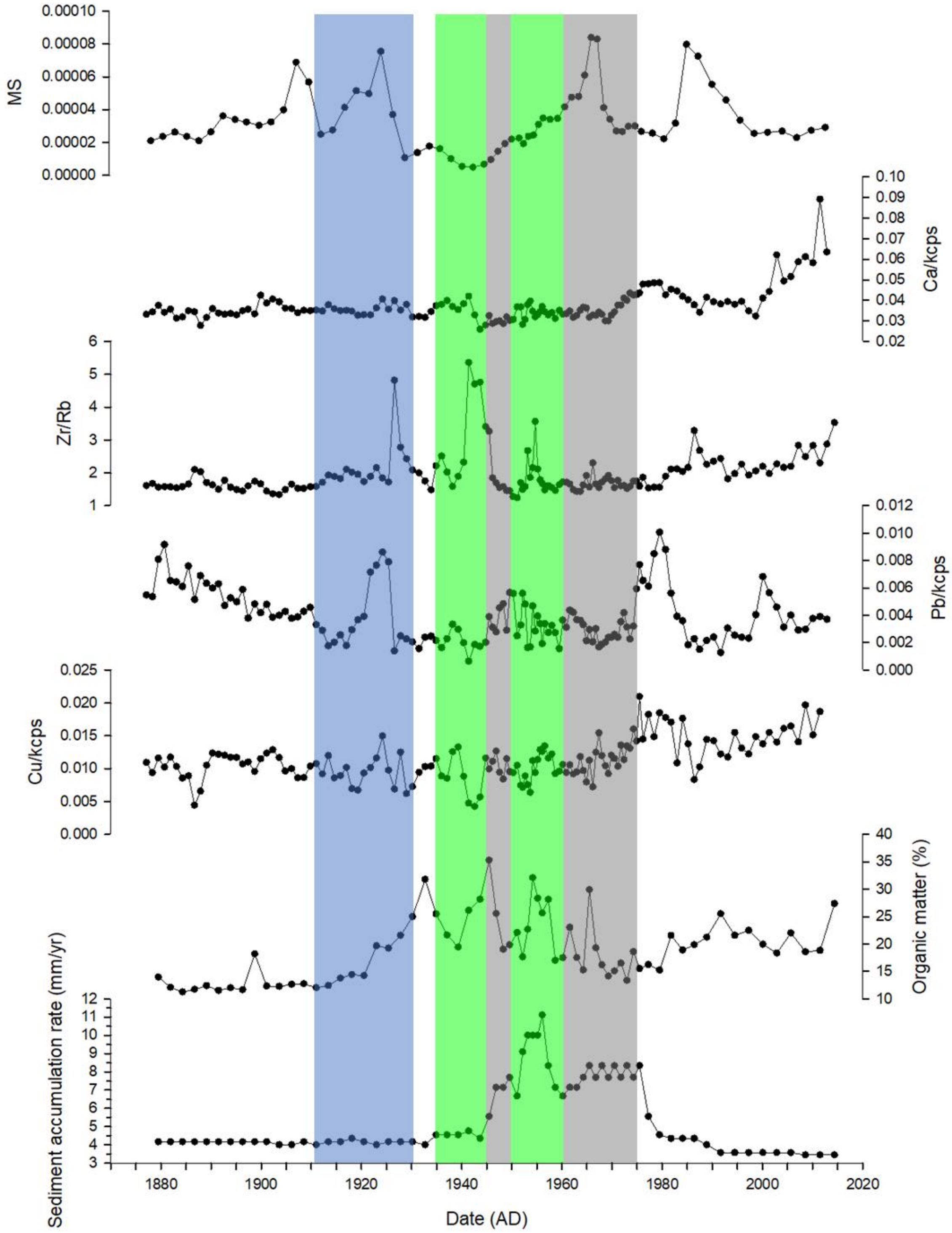


Figure 5.6: Proxies to demonstrate reasons for change in ARNE5 sediment accumulation rates. Blue shading represents the FRM4 rapid increase in magnetic susceptibility event and grey shading represents the ca. 1940s-1970s period of high sediment accumulation with green to indicate periods of increased influence from the sea.

5.2.1 The River Frome 1910-1930s high magnetic susceptibility event

Data presented for the River Frome (Figure 5.3) indicate a period of high MS dated to ca. 1910-1930, with a peak ca. 1920, from the age model.

During this ca. 1910-1930 period, the MS record indicates an increase in minerogenic material entering the estuary from the River Frome catchment, peaking ca. 1920s. Increased MS readings are not associated with an increase in Ca, which instead declines ca. 1910-1930. There is no notable (i.e. >1mm/yr) change in SARs at this time. The increase in MS would suggest an increase in top soil erosion from the catchment (Dearing, 1994). The decline in Ca suggests this erosion is not within the chalk area of the catchment, e.g. it could be erosion of the sandstone in the catchment below Dorchester (Figure 5.7). With little to no change in SAR detected in the River Frome estuary, or within any core at this time (Figure 5.2), data suggests material is being stored within the river itself. Some material must still be transported to the estuary for the increase in MS to be detected.

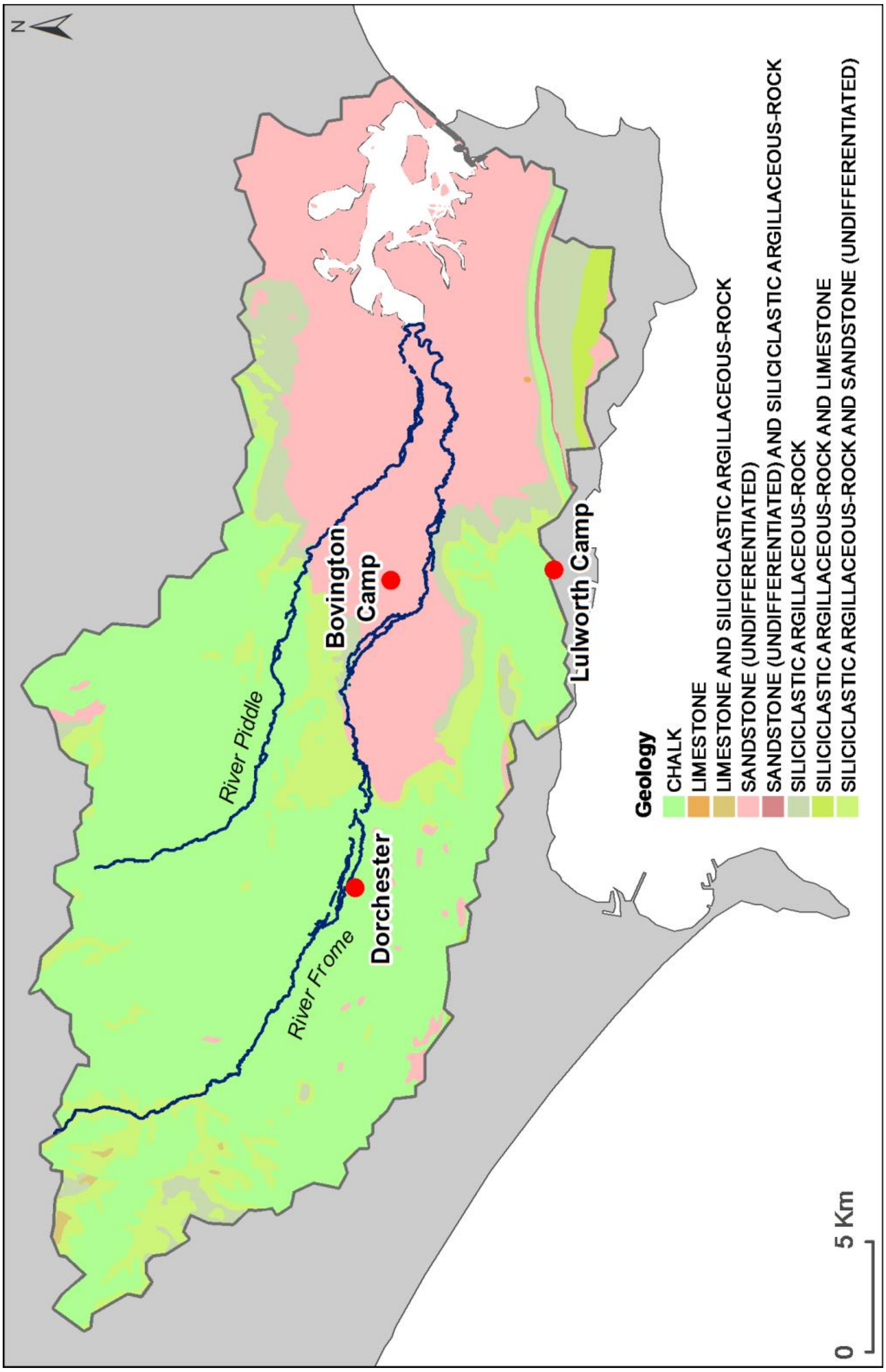


Figure 5.7: Geology map of the Poole Harbour catchment with the Rivers Frome and Piddle, Dorchester and the Ministry of Defence (MoD) training camps highlighted.

While not used in general practice until WWII, mechanised farming, e.g. tractors, were available from the early 1900s (Brassley, 1996; Whetham, 1970; Long, 1963; Figure 5.8). Mechanised approaches would be expected to increase catchment erosion of agricultural fields compared to manual farming. One would expect the increase in mechanised farming to be detected throughout the duration of its usage, e.g. increased MS, Ca from erosion of other agricultural fields in chalk areas of the catchment and SAR. As can be seen in Figure 5.3 this period of magnetic susceptibility change only lasts ca. 20 years. Therefore, it can be assumed the increase in minerogenic material detected in FRM4 is not a product of the introduction of mechanised farming practices ca. 1910-1930s.

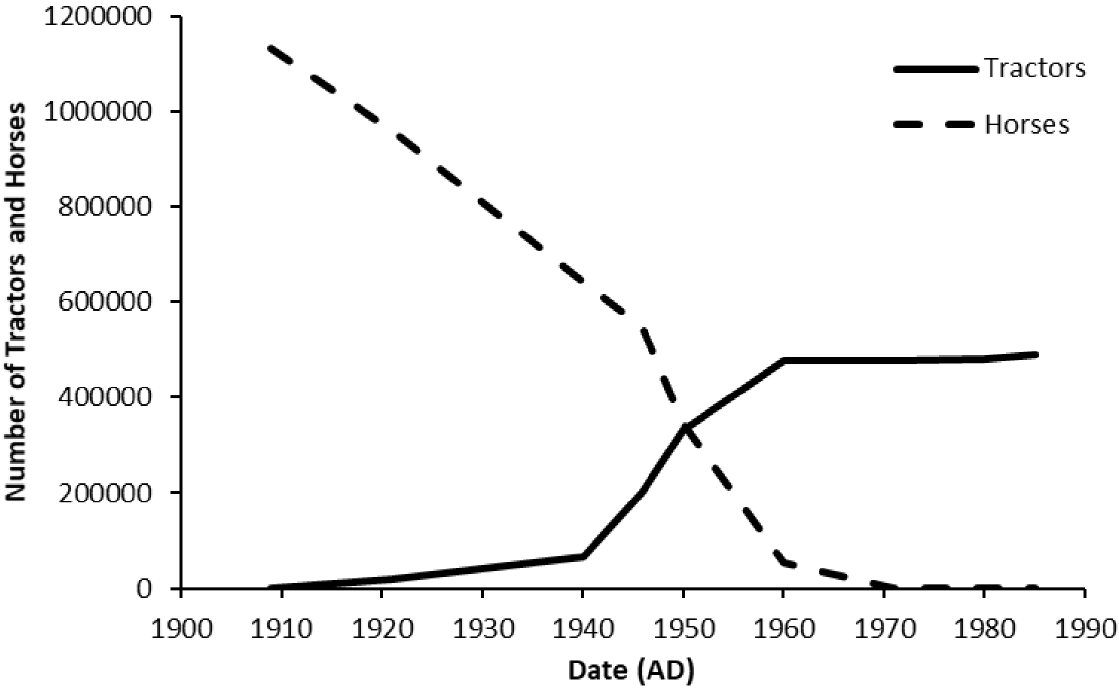


Figure 5.8: Change in the number of tractors and horses used in farming during the 1900s in Great Britain (Brassley, 1996). From WWII the number of tractors increases rapidly until ca. 1960 when tractor numbers remain similar and horses are no longer used.

During July 1909, 9.5cm of rainfall fell over the course of one day causing Dorset to flood (British Hydrological Society, 2017). While this was one of the largest daily rainfall events on record in Dorset, it was not the greatest, e.g. November 1894 30.5cm (12 inches) fell (Table 5.2). However, flooding in July 1909, likely brought more sediment from the catchment due to the drier antecedent conditions of summer compared to wetter winter conditions, meaning sediment from the catchment is more likely to be washed off the land and brought into the river where it can be both stored and transported further downstream to the estuary.

Flood driven erosion would be expected to transport more top soil to the estuary, thereby increasing minerogenic material content in cores, resulting in greater MS values. FRM4 demonstrates higher MS values ca. 1910 to the peak ca. 1920, indicating more minerogenic top soil has been washed into the river and deposited in the estuary, with it decreasing when the excess of more minerogenic topsoil within the stores of the river decrease. PID1 does not exhibit a large/peak increase in MS values post ca. 1910 (Figure 5.4), which would be expected if flooding was causing catchment scale increases in erosion. There is also no increase in Ca post ca. 1910, which would be expected during flooding events given the catchment of the River Frome is largely chalk (Gray, 1985; Casey & Newton, 1973). This could be because only the top soil was washed into the river as it was dry and therefore more mobile, diluting the Ca concentration within the elemental profile of the core. It could also be an indication the flooding was located mainly in the sandstone geology area of the catchment. The date of 1909 for the flooding event is also prior to the intensification of farming (as discussed in Section 5.2.2.1). Intensified farming practices, e.g. ploughing, may increase Ca concentration in the soil washed off from the land as deeper sediment, higher in Ca, could be lifted to the surface and reach the water course when transported during erosion events, e.g. floods. The Zr/Rb ratio of FRM4 ca. 1910-1930 increases towards the end of the twenty year period, indicating larger sized sediment deposited in the estuary. If there is an increase in the quantity of sediment reaching the river, more sediment will reach the estuary before being eroded by riverine processes and thus larger sediment grain size will be deposited in the estuary. A sudden increase in catchment erosion should also be detected in SARs, but no core demonstrates an increase ca. 1910 with FRM4 and PID1 SARs only increasing ca. 0.15mm/yr and ca. 0.3mm/yr respectively. Alongside the slight increase in SAR, the MS of PID1 slightly increases ca. 1910-1930. ARNE5 also exhibits an increased MS across this period. The appearance of greater change in MS ARNE5 than PID1 could be a consequence of the greater SAR at ARNE5 than PID1, storing more of the material from the River Frome. No changes are detected in HB1 at this time. This supports the assertion that this period of MS change is a result of discrete changes within the River Frome catchment, or at least a change outside the catchment of Holes Bay.

No other flooding event (Table 5.2) prior to the Dorset flooding of July 1909 is detected within the records of the sediment cores. With little supporting evidence from the other proxies, e.g. sudden increase in SARs and no major changes in

PID1, it can be assumed that the change during the period ca. 1910-1930 within the FRM4 record is not a consequence of the 1909 flood of Dorset.

Table 5.2: Climate events in the Poole Harbour catchment (British Hydrological Society, 2017).

Year	Month	Condition
1866	September	Wet month (23.1cm)
1868	December	Wet month (19.8cm)
1873	January	Low ground flooded
1875	October	Wet month (21.0cm)
1875	July	High floods, higher than for many years including winter
1875	July	Dorchester low lying land flooded
1876	December	Wet month (26.0cm)
1884	August – November	Very dry, wells became exhausted
1887	December	Poole, low springs
1894	November	Weymouth, flooding (30.5cm in one day)
1908	October	Weymouth, flooding (10.2cm in two days)
1909	July	Dorset, flooding (10.0cm in one day)
1921	February	Drought
1955	July	Weymouth flood

The River Frome catchment is home to several Ministry of Defence (MOD) training areas. Bovington and Lulworth training camps were established in 1899 and were adopted by the Tank Corps in 1917 (Figure 5.7). Use of tanks in the catchment would increase erosion of the top soils (Tilney, 2009) and could account for the increase and subsequent peak in MS detected in FRM4 ca. 1920s, however, it does not explain the decrease in MS post ca. 1920s suggesting less erosion. During 1921, there was a drought within Britain (British Hydrological Society, 2017). This drought coincides with the peak MS of FRM4 ca. 1920. The dry conditions combined with increased military activity within the catchment could cause an increase in top soil erosion in comparison to wetter conditions when deeper soils, with potentially lower MS, could be eroded.

During the 1920s, silviculture was practised on heathlands in the River Frome (Puddletown, Moreton and Hethfelton) and Piddle (Wareham Forest) catchments. While there may be an increase in soil disturbance with the planting of the trees, once finished, the forested areas would decrease sediment erosion. Silviculture, stabilising soil matrices could explain the decrease in MS seen post ca. 1920s.

During the mid-1920s, *Spartina* reached its maximum extent within Poole Harbour (Table 2.5). The increase in *Spartina* would prevent sediment reaching the waters of Poole Harbour as it would be stored by the vegetation (Lacambra et al., 2004; Marshall et al., 2007). It was not until the late 1920s/early 1930s that *Spartina* was in decline, allowing sediment that was stored by the Spartina to enter the harbour (Lacambra et al., 2004; Marshall et al., 2007). Sediment released by the decline in Spartina may be recorded in the SARs of FRM4 and PID1 where there is an increase of ca. 0.15mm/yr and ca. 0.3mm/yr respectively ca. 1920s-1930s (Figure 5.2). However, the die back of *Spartina*, and thus the increase in sediment in the harbour, should be detected in all cores, including HB1 and ARNE5 where there is no sustained increase in SARs from ca. 1920s.

The period of MS change ca. 1910-1930 is mainly found in FRM4 with some detection in PID1 and ARNE5. This suggests that River Frome catchment changes were driving changes in proxy records during this ca. twenty-year period. No one cause may explain all change evidenced in FRM4 ca. 1910-1930. Several catchment activities may have driven changes in sediment delivery to the estuary ca. 1910-1930s. Increased sediment erosion from flooding and military activity could have caused the initial increase in MS. The peak of MS ca. 1920 could be the transition to tank based training at the military training camps increasing top soil erosion. The decline in MS post ca. 1920 may be a response to more sediment being captured by silviculture plantations established during the 1920s.

5.2.2 Ca. 1940s-1970s period of greater sediment accumulation

Greater SARs are detected in all cores ca. 1940s-1970s, dated from the age-depth models (Figure 5.2). Increased SARs in these cases are a result of activity within the agricultural landscape (River Frome and Piddle), the industrial area of Poole Harbour (Holes Bay) and influence from the sea at Arne. Sections 5.2.2.1, 5.2.2.2 and 5.2.2.3 discuss how changes within these areas of the catchment resulted in higher SARs throughout Poole Harbour.

5.2.2.1 Agricultural intensification

As discussed above, the Rivers Frome and Piddle drain the agricultural landscape of Poole Harbour's catchment and meet in their mutual estuary in the harbour. Thus, any changes within agricultural practices are likely to be recorded in FRM4 and PID1.

Both FRM4 and PID1 exhibit increased SARs ca. 1940-1970s, with FRM4 SARs increasing two-fold, an initial increase to 3mm/yr ca. 1940-1960 and another increase to 6.25mm/yr ca. 1960-1970 (Figure 5.2). PID1 SARs increase to a maximum of 7.1mm/yr during the ca. 1940-1970 (Figure 5.2).

During WWII, to reduce dependence on imported animal feed, British farmers increased the cereals and root crops they grew, e.g. during 1939-1942 wheat and barley increased by 66%, oats by 75% and potatoes doubled (Bowers, 1985). These changes are reflected in the agricultural land use data for the Poole Harbour catchment in Figure 5.9 and Figure 2.14B where arable land use increased alongside the aforementioned crops during this time period. This was at the expense of livestock and in consequence the number of sheep reduced (Bowers, 1985; Figure 2.14C). The Agriculture Act of 1947 encouraged the production of cheaper food (Angus et al., 2009; Robinson & Sutherland, 2002). 'Deficiency payments' were used when markets fell below guaranteed levels and subsides were available for fertilisers and grants for the drainage and ploughing of permanent pasture (Angus et al., 2009). Government grants for drainage, started in 1939, instigated an increase in drained land until the activity peaked in the ca. 1970s (Robinson, 1990). Walford (2013) stated that within the South Downs, most of the land 'ploughed up' was chalk. Chalk being 'ploughed up' was likely the case within the River Frome and Piddle catchments were the catchments are also highly comprised of chalk. The installation of drains meant the agricultural land was deeply ploughed (Robinson, 1990). Evans (2006) reports that during 1970s erosion events, more sediments were sourced from subsoils than top soils. Subsoil erosion is detected in the data for FRM4 and PID1 (Figure 5.3 and Figure 5.4). From the ca. 1940s, both FRM4 and PID1 exhibit an increase in Ca suggesting deeper soils are being transported to the estuary, increasing past ca. 1970. The Zr/Rb ratio for FRM4 suggests grain size continues to increase throughout the ca. 1940s-1970s period, potentially a result of the greater quantities of sediment reaching the estuary before it can be eroded, i.e. reduced in size, by riverine processes. The Zr/Rb ratio of PID1, while remaining relatively stable throughout the period, does have some sizeable fluctuations, ca. 1958 and

1965/70, suggesting influxes of larger material (Figure 5.4). The SARs of both FRM4 and PID1 increase during the ca. 1940s-1970s, with FRM4 SARs increasing again ca. 1960s-1970s. These increases could be an artefact of intensified farming practices after the Common Agricultural Policy (CAP) was introduced in 1962. FRM4 exhibits a small peak in Ca and a peak in MS ca. 1960s, suggesting increased erosion from the River Frome catchment following the introduction of the CAP.

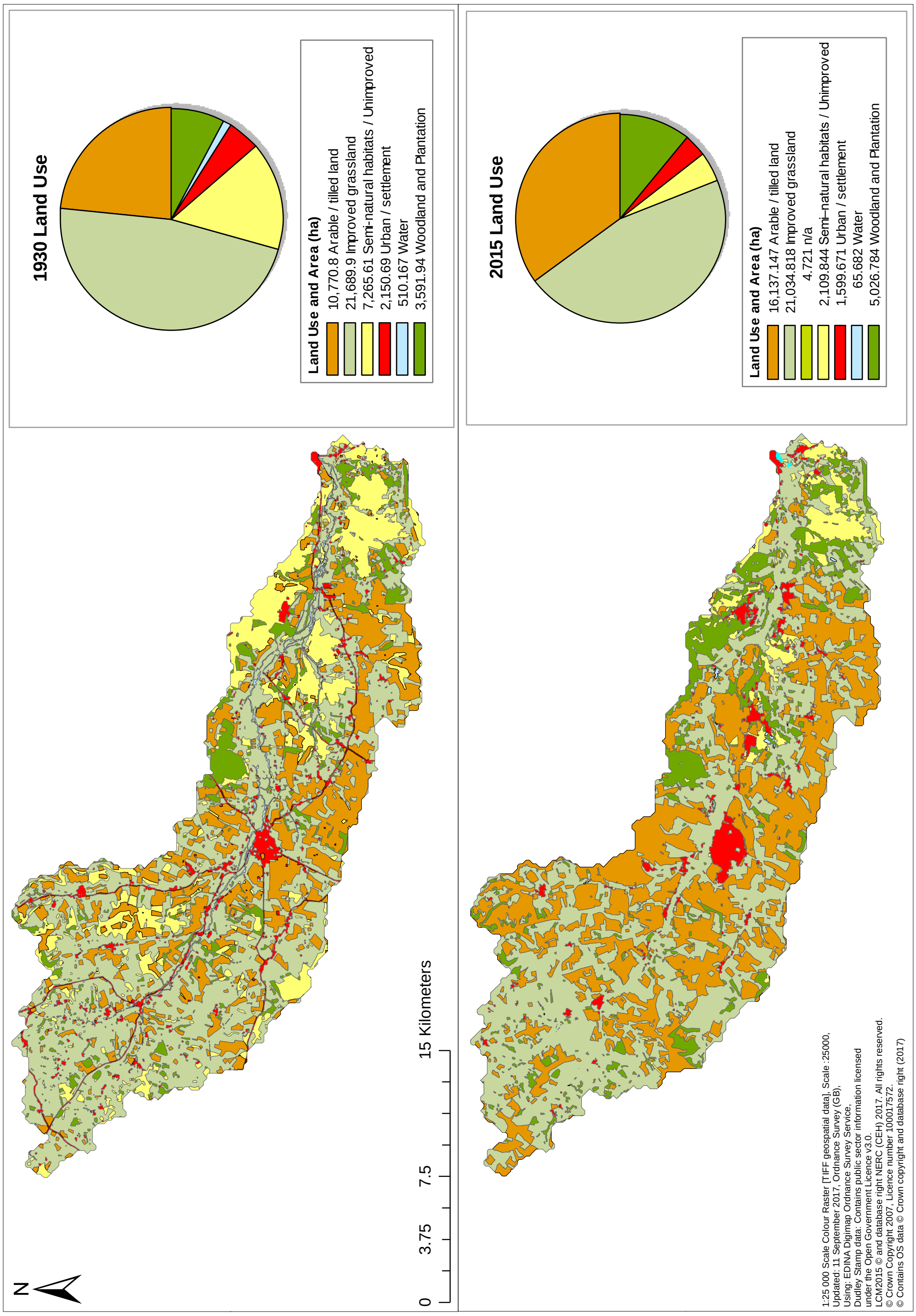


Figure 5.9: 1930 and 2015 land use data for the River Frome catchment.

The drive for increased food production through agricultural activity meant the catchments of the Rivers Frome and Piddle were subjected to activities which disturbed the top- and subsoils, e.g. ploughing and drainage. The increasing use of tractors ca. 1940s to ca. 1960s (Figure 5.8) allowed agricultural land to be ploughed deeper than before, as reflected in the Ca profiles of FRM4 and PID1 (Figure 5.3 and Figure 5.4). An increase in agricultural activity can be responsible for an increase in sediment contribution to the rivers as the sediments are more mobile and thus greater quantities can be removed from the catchment's land and deposited downstream, as evidenced by the increased SARs of FRM4 and PID1 during ca. 1940s-1970s.

Grabowski and Gurnell (2016) suggest the change in farming due to WWII and government policies resulted in unintentional soil loss, thus an increase in sediment load to the rivers and consequently the estuary. During this time there was also an increase in livestock numbers, increasing the pressure on the land from grazing (Grabowski & Gurnell, 2016; Figure 2.14C). The intensification of grazing influences the vegetation cover and biomass, soil properties and surface hydrology resulting in the increase of sediment delivery to the river channel (Grabowski & Gurnell, 2016; Trimble, 1994; Trimble & Mendel, 1995). An increase in cattle stocking can also cause river bank degradation when they access the river for drinking, e.g. via cow ramps, and thus an increase of sediment input into the rivers (Grabowski & Gurnell, 2016). The combination of these land use changes would lead to an increase in sediment production from the 1940s (Grabowski & Gurnell, 2016), increasing sediment load to the rivers and thus to the estuary and Poole Harbour.

Another reason SARs could increase post ca. 1940s is changes in vegetation in the harbour. As discussed in Section 2.4.5.3, vegetation influences sediment accumulation. Within Poole Harbour, the history of the vegetation *Spartina* is of relevance here (Table 2.5). An increase in *Spartina* would trap sediment and reduce deposition in the estuary. From the 1930s, *Spartina* was in widespread decline across Poole Harbour, giving potential to the sediment held by the vegetation to be released back into the waters (Lacambra et al., 2004). It is estimated that 4 million m^3 of sediment accumulated by *Spartina* has been released back into Poole Harbour as a result of its die back (Hübner et al., 2010). This would result in an increase in SARs within the cores collected on mudflats as agreed by Marshall et al., (2007) whom carried out an SAR investigation of Arne which shall be discussed in more detail in Section 5.3.1.

There is evidence that an increase in sediment contribution to the waters of Poole Harbour occurred ca. 1940-1970 from the agricultural landscape of the catchment. This finding is based upon an increase in magnetic susceptibility and Ca indicating catchment erosion. The Zr/Rb ratios suggest this sediment was of larger grain size, possibly a result of more sediment not being trapped in the river and being subject to erosional processes before it was deposited in Poole Harbour. The timing of this change in SAR coincides with intensification of farming practices due to WWII and government policies and the decline of *Spartina*.

5.2.2.2 Industrial intensification

HB1 (Figure 5.5) provides a record of industrial activity within the catchment of Poole Harbour, as evidenced in the elemental record of HB1. Pb increases from ca. 1930s to ca. 1960s, where it remains at its peak until ca. 1970s when it starts to decline. Changes in Pb reflect the increase in leaded fuel used post ca. 1920s and tighter controls on air pollution from regulations post 1956, e.g. Clean Air Act of 1956, amendments and extensions of the Clean Air Act 1968, Control of Pollution Act 1974 (Rose et al., 1995). Cu also increases from ca. 1930s, the main biocide in antifouling paints used on the hull of ships (Ciriminna et al., 2015; Jones & Bolam, 2007; Ytreberg et al., 2010). The area of Holes Bay has a history of boat yards making and repairing boats, e.g. the opening of J. Bolson and Sons boat building business in 1931 and the British Power Boat company in 1940/41 (Andrews & Henson, 2010). The increase in boating manufacturing business in the first half of the 20th century, especially during WWII, accounts for the increase in Cu. Ca increases throughout ca. 1940s-1970s and continues to do so until ca. 2000s. Increased Ca concentrations likely reflect the increase in land reclamation within Holes Bay for industrial building and infrastructure where chalk was brought in to reclaim the land, e.g. in 1946 250000 tonnes of chalk was brought in for the building of Poole Harbour Power Station and the construction of Holes Bay Road and Upton Bypass in the 1980s (Martin, J. (Borough of Poole), pers. comm. 2018; Figure 5.10).

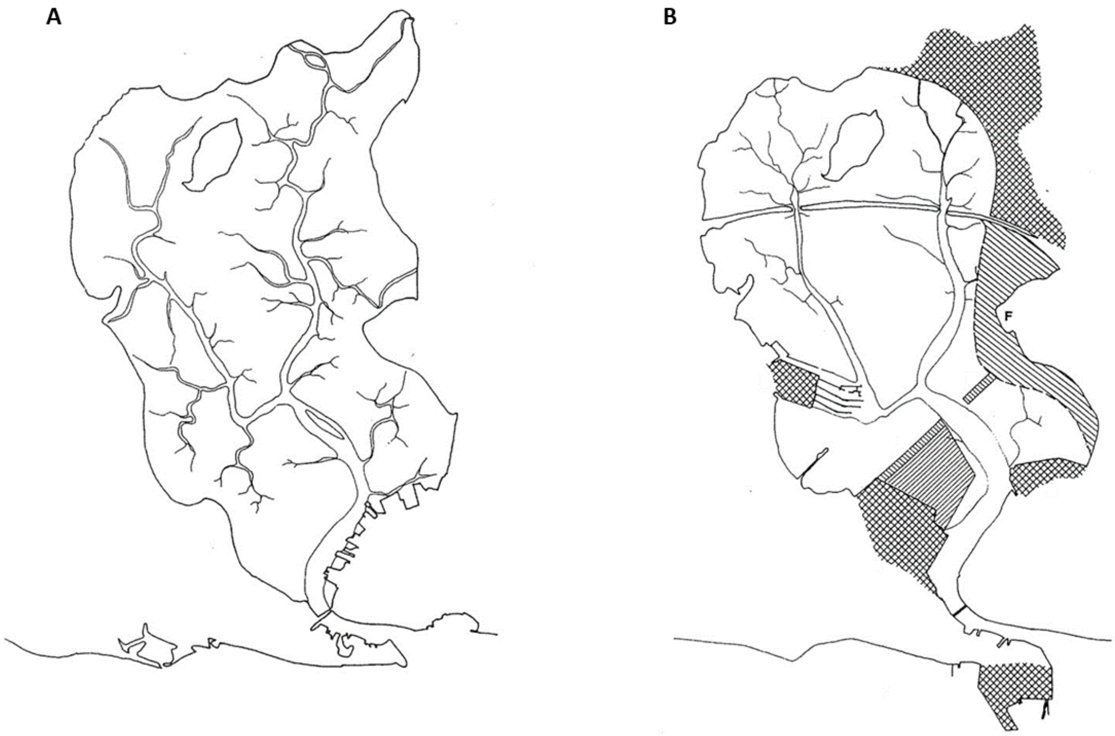
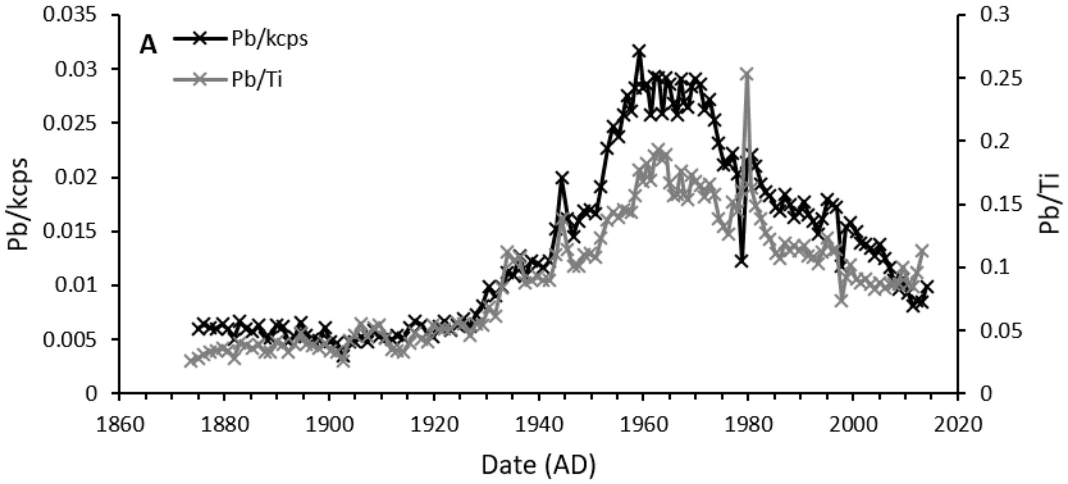
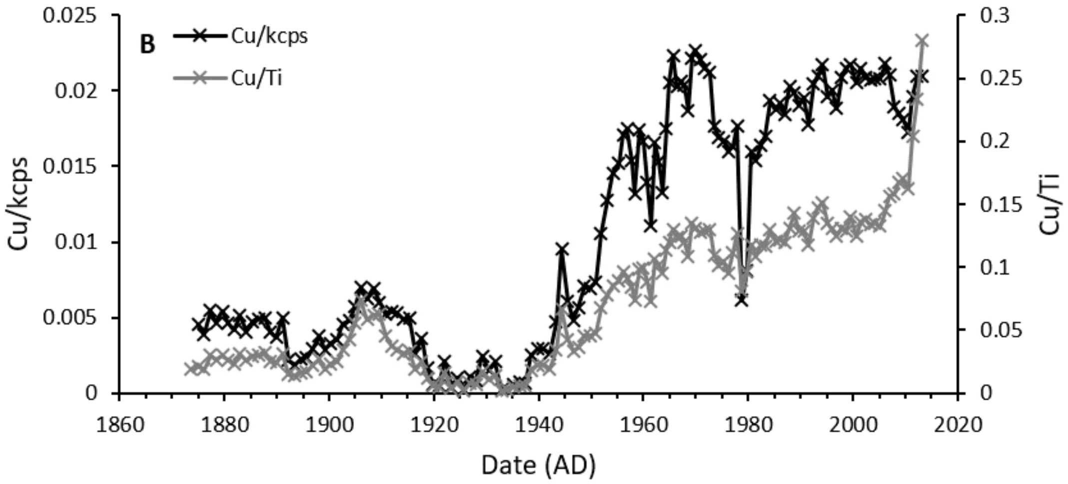


Figure 5.10: Holes Bay land reclamation from A: 1849 to B: 1982 (Dyrynda, 1985).

These trends in Pb, Cu and Ca as a reflection of industrial activity are further supported by enrichment data. The element Ti is an indicator of catchment inwash. Normalising Pb, Cu and Ca against Ti aid in determining the source of the element ((Kylander et al., 2009)), i.e. if Pb, Cu and Ca when normalised against Ti increase, it indicates the source of that element is not from the catchment, e.g. via erosion, as Ti would also increase and thus the normalised relationship would not increase. Pb/Ti (A), Cu/Ti (B) and Ca/Ti (C) trends replicate those of the non-normalised elements (Figure 5.11). These replication of trends further strengthens the notion that; the trend of Pb is likely an industrial response, i.e. the use of leaded fuels and the subsequent decline in lead in fuels, the increase in Cu from ca. 1930s is likely a result of the increased presence of antifouling paints present in the harbour due to the increase in boating manufacturing, and the increase in Ca is likely due to the use of chalk for land reclamation.





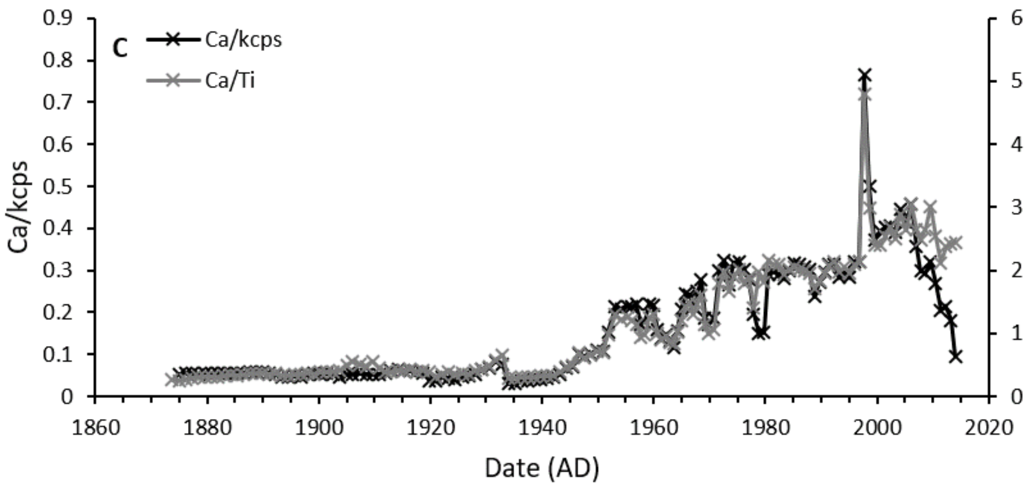


Figure 5.11: HB1 enrichment data; A) Pb, B) Cu and C) Ca.

The increase in industrial activity in and around Holes Bay not only contributed an increase of pollutants but also increased SARs ca. 1940-1970. The SAR of HB1 increased in the mid-1940s from ca. 4.3mm/yr to 4.7mm/yr followed by a second increase ca. mid-1950s to 7.1mm/yr. This second SAR increase coincides with an increase in the Zr/Rb ratio and MS suggesting a greater proportion of larger minerogenic material being supplied to Holes Bay.

Cranford Heath, a heathland area around Holes Bay, was used during WWII by the military, for mineral extraction (sand, clay and gravels) and illegal motorcycling after WWII (Martin, J. (Borough of Poole), pers. comm. 2018). It was also subject to heath fires. These activities would have caused an increase in erosion of the heathland which could have brought in larger, minerogenic sediment into Holes Bay and caused SARs to increase. Increased catchment erosion is recorded in the MS and Zr/Rb record of HB1 where they both increase ca. mid-1950s with the increase in SARs during the ca. 1940s-1970s period suggesting larger, minerogenic sediment deposited in Holes Bay. Ca also increases during this period. These phenomena may have resulted from the increase in chalk brought into Holes Bay for land reclamation or from increased land erosion from the activities on the heathlands.

Another reason for the increase in SAR in HB1 post ca. mid-1940s is the aforementioned land reclamation in Holes Bay. While areas within Holes Bay were filled in by chalk, this meant there was less area for the sediment to deposit in the water. From 1924 to 1980, the total intertidal area within Holes Bay decreased from 329 to 273ha, a 17% reduction as a result of land reclamation for urban, industrial and port development (Doody, 1984). Combined with increased erosional activities from the heathland surrounding Holes Bay, this would cause an increase in SARs in HB1.

As previously discussed, vegetation, in particular *Spartina*, plays an important role in sediment accumulation in Poole Harbour. Figure 5.12 illustrates the loss of *Spartina* in Holes Bay from 1924 to 1980. In 1924, *Spartina* covered 63% of the total intertidal area of Holes Bay and by 1980 this had reduced to 29%, a loss of 128ha (Doody, 1984). The decline of *Spartina* should have meant sediment stored within the vegetation was released into Holes Bay (Lacambra et al., 2004; Marshall et al., 2007). However, SARs of HB1 do not reflect this. There are no increases in SARs from ca. 1920s-1980s except that of ca. 1940s-1970s which has already been explained previously within this section as a result of industrial development as evidenced from the elemental proxy record (see above). The sediment stored within the *Spartina* will likely have redistributed within Holes Bay or out into the rest of the harbour via the narrow entrance between Holes Bay and the rest of Poole Harbour meaning the loss of *Spartina* may not be explicitly recorded in the SARs of HB1.

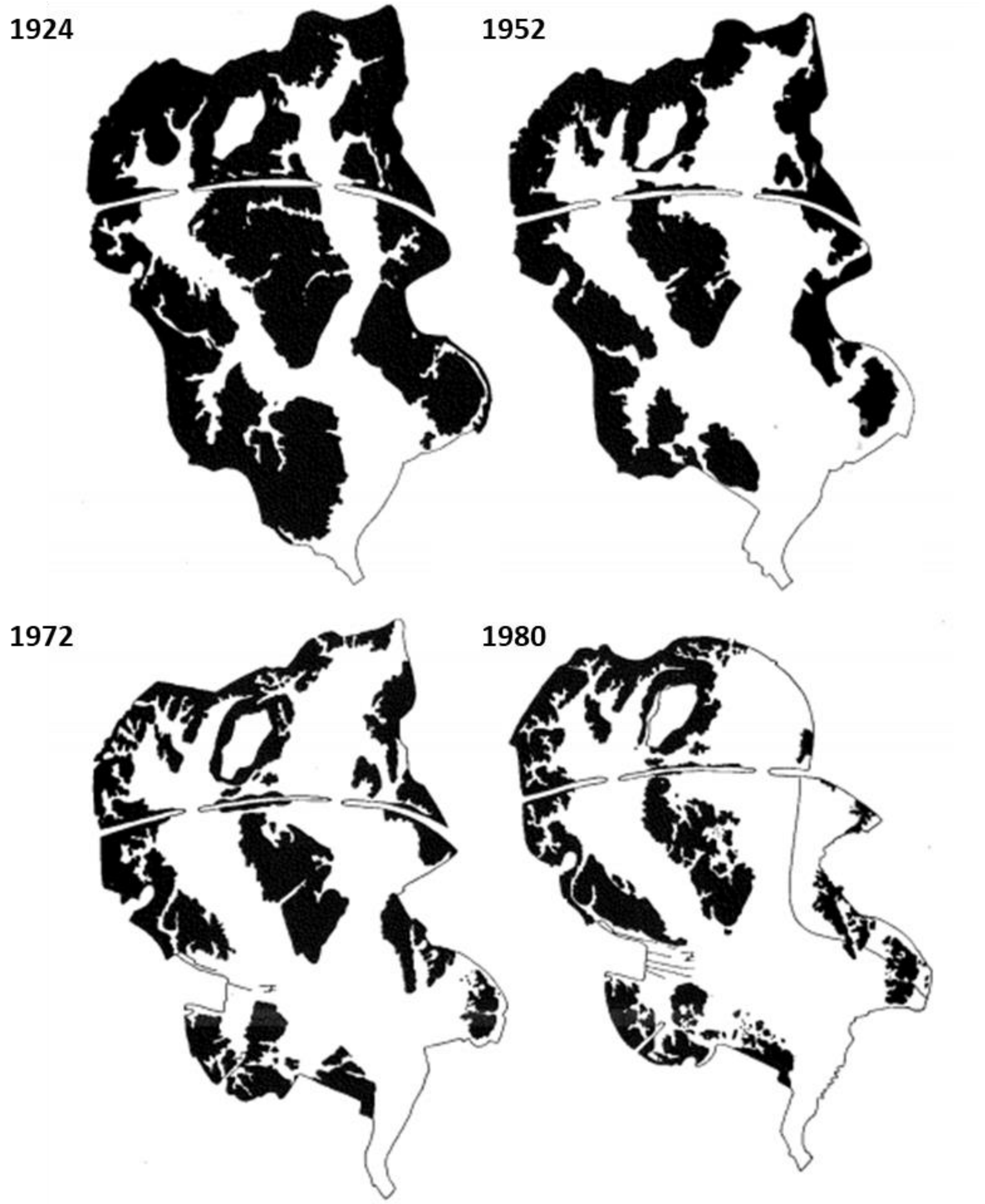


Figure 5.12: *Spartina* dominated salt marsh loss from 1924 to 1980 (Doody, 1984).

From the evidence provided within this section, the probable cause for the increase in SARs during the ca. 1940s-1970s period detected in HB1 was a result of industrial development within Holes Bay. During ca. 1940s-1970s erosional activities took place on heathlands in the Holes Bay catchment supplying large quantities of sediment to the water. Land was reclaimed within Holes Bay for construction of infrastructure and industrial buildings, reducing the area of water for the sediment to be deposited in. A combination of these activities in turn caused an increase in SAR in Holes Bay ca. 1940s-1970s.

5.2.2.3 Marine influence

Various studies have been carried out in Poole Harbour regarding the relationship between sea level and SARs, e.g. Marshall et al., (2007), Long et al., (1999), Cundy & Croudace (1996) and Edwards (2001). Comparison of published SARs from the area with this study are further explored in Section 5.3. They concluded that increases in SARs can be attributed somewhat to increases in sea level but SARs in Poole Harbour may also be influenced by local changes, e.g. the expanse and decline of *Spartina*.

ARNE5 is located in a well-mixed area of Poole Harbour and is the closest core recovered where the harbour meets the sea, driven not only by changes in the catchment but also by the sea. The mean sea level for the south coast increased from the ca. 1940s until ca. 1970 whereupon it declined for ca. 5 year period (Figure 5.1). An increased sea level means more sediment could be supplied from the sea and also be deposited on higher ground where the potential for reworking is reduced.

During the ca. 1940s-1970s, ARNE5 SAR increases, though not in a uniform manner (Figure 5.6). Ca. 1935-1945, the SAR increases from 4.1mm/yr to 4.5mm/yr, only a 0.4mm/yr increase. The 0.4mm/yr increase is likely a result of increased sediment supply from the sea as indicated by an increase in Cl and Br (indicators of sea water) and an increased Zr/Rb ratio indicating sediment of larger grain size is being deposited (Figure 5.13). Ca does not increase at this time suggesting the increase in SAR is not a result of catchment erosion (Figure 5.6).

Ca. 1945-1950, the SAR increases to 7.1-7.6mm/yr. Cl, Br and the Zr/Rb ratio decline suggesting the increase in SAR is not a result of increased sediment contribution from the sea (Figure 5.13). This is supported in the small decline of mean sea level from ca. 1945 before it increases again by ca. 1950 (Figure 5.1). During this time, MS starts to increase suggesting an increase in the supply of minerogenic material, possibly an artefact of the increased agricultural activity within the River Frome and Piddle catchments (Section 5.2.2.1).

Ca. 1950-1960, the ARNE5 SAR increases to its peak of 11.1mm/yr. Peaks in the Zr/Rb ratio and Cl accompany the SAR increase, alongside increased variability in

Br, suggesting an increase in sediment size which was supplied from the sea (Figure 5.13). Figure 5.1 demonstrates an increase in mean sea level ca. 1950-1960, supporting the link between sediment supply increases and sea level change. MS increases ca. 1950-1960 (Figure 5.6), suggesting a supply of material from the agricultural catchments of the harbour to Arne; however, the quantity of material from the sea is more influencing on the elemental record and thus SAR.

Ca. 1960-1975, the SAR reduces but is still high, fluctuating between 7.7 and 8.3mm/yr. Br increases throughout this period, as does Cl to the end of the period, suggesting an increase of sediment from the sea. The impact of intensified farming practices under the CAP are recorded in FRM4 during the ca. 1960s (Figure 5.3). The MS of ARNE5 also peaks during the ca. 1960s (Figure 5.6), suggesting that while there is still a large supply of sediment from the sea to Arne, the supply of sediment from the agricultural catchments has increased as the Zr/Rb ratio remains low and stable (Figure 5.13).

ARNE5 exhibits little change in Pb or Cu throughout the ca. 1940s-1970s (Figure 5.6). There is likely little ship activity on the Arne side of the harbour as the main shipping channels are on the eastern side into Holes Bay. The lack of Pb and Cu change in ARNE5, combined with the narrow entrance between Holes Bay and the rest of Poole Harbour, suggests the industrial development around Holes Bay did not have a great effect on the SAR of ARNE5 ca. 1940s-1970s.

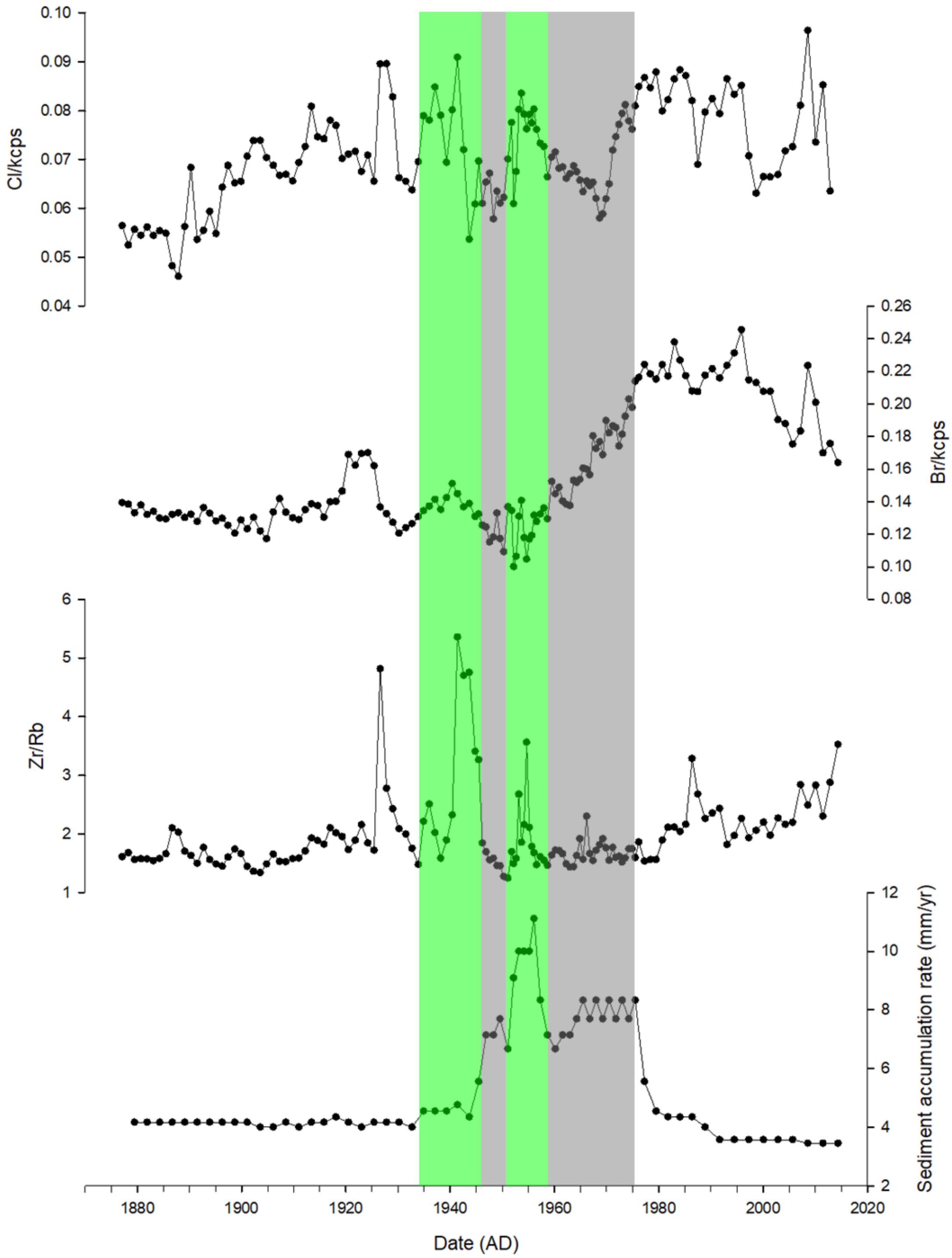


Figure 5.13: ARNE5 elemental proxies to indicate periods of influence from the sea. Grey shading represents the ca. 1940s-1970s period of high sediment accumulation rate with green to indicate increased influence from the sea.

5.2.3 The 1970s decline

All cores demonstrate a decline in SARs post ca. 1970s, as determined by the age-depth models. At this time, activity within the Poole Harbour catchment changed, e.g. decline in agricultural practices and changes in building around Holes Bay. This section will discuss how these changes caused the SARs of all cores to decline.

5.2.3.1 Agricultural decline

As discussed, the environmental histories of FRM4 and PID1 reflect agricultural changes in the catchment. Post ca. 1970 both FRM4 and PID1 record a decline in SARs (Figure 5.2). FRM4 declines to ca. 3.7mm/yr, a 2.5mm/yr reduction from the maximum SAR during ca. 1940s-1970s period. FRM4 SARs remain steady at ca. 3.7mm/yr to present. PID1 declines to 3.2mm/yr, a 3.9mm/yr reduction from the maximum SAR during ca. 1940s-1970s period. PID1 SARs remain at this rate until ca. 2000s where SARs increase again by 1.1mm/yr to 4.3mm/yr.

Vegetation and arable crop growth changes in the catchment are noted in the work of Grabowski and Gurnell (2016). Figure 2.14 illustrates a shift in crops grown ca. 1970s with an increase in wheat and a decline in barley. Figure 2.15 shows an increase in the percentage land covered by forest, shrub and heath in 1990 compared to that of 1940. Increases in these vegetation cover could reduce soil erosion from the catchment, thus reducing the sediment reaching watercourses and being transported into Poole Harbour, thereby causing a decline in SARs.

During the 1970s, there was a reduction in farming as a result of the end of the ‘war effort’. Areas that were difficult to farm, e.g. chalk slopes, were left to form back to grass (Kite, D. (Natural England), pers. comm. 2018). From the 1970s, there was no increase in land drained and from the 1980s drainage rates reduced as the Government reduced its support of grants (Robinson, 1990; Robinson & Gibson, 2011). The reduction in agricultural activity, e.g. ploughing and draining, would reduce soil erosion and thus the sediment supply to the rivers and estuary. Collins et al., (2008) reports sediment from agriculture in water courses declined on a national scale from 1970-2004. The decline is reflected in the fall of MS in FRM4 from ca. 1970s and PID1 ca. mid-1980s (Figure 5.3 and Figure 5.4). The Zr/Rb ratio fluctuates somewhat for FRM4 but PID1 records a low and steady ratio post ca. 1970s. These data suggest a decline in larger sediment from the catchment and possibly a supply of smaller sized material sourced from the river.

The form of the Rivers Frome and Piddle changed post ca. 1970s. Grabowski and Gurnell (2016) discuss the narrowing of the channel of the River Frome by 5-15%, due to the increase in fine sediment storage within the river. An increase in sediment storage within the river, e.g. sediment trapped by aquatic vegetation (Grabowski & Gurnell, 2016), reduces downstream sediment transport to Poole Harbour. After the 'war effort', water meadow management ceased in the Rivers Frome and Piddle and the vegetation within the rivers were no longer cut back to allow the meadows to flood. This practice, where meadows were flooded to enrich the land with silt and nutrients to aid agriculture, kept the rivers clear of vegetation and thus sediments were able to be transported relatively freely to the estuary. The ceasing of meadow management meant the sediment would be able to be trapped and stored within the riverine vegetation of the river which was no longer being cleared to aid meadow flooding. However, with a reduction in sediment coming from the agricultural fields, the sediment stored within the river becomes a more substantial source of sediment transported to the estuary. This is reflected particularly in the Zr/Rb ratio of PID1 where the ratio has declined suggesting the fine material once flooded on to the meadows can now be transported to the estuary where they can be deposited.

Sediments stored in the river could act as a sink for pollutants and nutrients transported from agricultural land within the catchment (Evans, 2006). If these sediments become mobile, they could promote an increase in productivity and possible algal blooms if transported to Poole Harbour. Such a phenomena will be discussed in subsequent chapters.

Another change post ca. 1970s that is apparent in the catchment of Poole Harbour is the increase in population (Figure 2.16). An increase in urbanisation could both increase SARs (an increase in tarmac promotes runoff which transports sediment to the estuary) or decreases SARs (tarmacked areas reduce exposed soil, thus limiting sediment transport in erosion events). Urbanisation is minor, in the catchments of the River Frome and Piddle, compared to other areas surrounding Poole Harbour, e.g. the town of Poole itself. Therefore, the effect of urbanisation as a result of increasing population may not influence the SAR of FRM4 and PID1 greatly.

A further effect of an increase in population is an increase in sewage. The catchments of the River Frome and Piddle have several Sewage Treatment Works (STWs) which discharge into the rivers (Figure 2.10). An increase in population would be expected to increase effluent discharges from the STWs to the harbour.

An increase in STW effluent could increase the organic matter within the sediments. However, increases in organic matter post ca. 1970s in FRM4, and variability in organic matter in PID1 (Figure 5.3 and Figure 5.4), do not affect SARs in these cores.

Post ca. 1970s SARs of FRM4 and PID1 remain higher than pre-ca. 1940s SARs, likely a result of post 1970s farming practices being more intensive relative to pre-1940s practices. During the early-mid 2000s, investigations into the source of sediments found in the Rivers Frome and Piddle concluded that pasture and cultivated land were the highest contributors of sediment compared to that of woodland, bank erosion and subsurface sediments (Collins & Walling, 2007b; Walling et al., 2008). The high abundance agricultural sediments suggests that while farming practices have declined post ca. 1970s, they are still a primary contributor of sediment to the Rivers Frome and Piddle. Changes in agricultural practices also mean that silt that was once deposited on the water meadows during the ca. 1940s-1970s was now able to be stored in the river itself due to the decline in water meadow management. This fine sediment therefore has more potential mobility to be transported to the estuary than during ca. 1940s-1970s when it was frequently moved and stored on the water meadows when flooded.

The reduction in SARs recorded in FRM4 and PID1 post ca. 1970s were a result of the decline in agricultural intensity at the end of the 'war effort'. Not only has farming intensity reduced, reducing the source of the sediment, but management practices, e.g. water meadow flooding, had ceased, allowing sediment to be stored in the vegetation of the river before being transported to the estuary.

5.2.3.2 Changes around Holes Bay

Post ca. 1970s, the SAR of HB1 reduces from 7.1mm/yr during the ca. 1940s-1970s to 5.5mm/yr, a 1.6mm/yr reduction (Figure 5.2).

As discussed above, Holes Bay is the industrial area of Poole Harbour and while industrial activity increased during ca. 1940s-1970s, it did not cease post ca. 1970s. During the 1970s, Cranford Heath and another heathland Creekmoor were built on (Martin, J. (Borough of Poole), pers. comm. 2018), stopping the erosional activities that were prominent here during ca. 1940s-1970s, e.g. military activity, heath fires, illegal motorcycling and mineral extraction. A decline in erosion of the land is detected in HB1, where the SAR reduces post ca. 1970 as the eroded sediment supply is reduced. MS also decreases suggesting less minerogenic top soil is reaching Holes Bay (Figure 5.5). The Zr/Rb ratio slightly declines post ca. 1970s suggesting a decline in sediment size that enters Holes Bay.

The industrial activity in and around Holes Bay supplies Holes Bay with pollutants, e.g. Cu from antifouling paints from ship manufacturing companies. As well as industrial pollutants entering Holes Bay, Poole STWs effluent drains directly into Holes Bay. Poole STW has been in existence since 1922 but has been extended in several phases throughout the decades. With an increase in population, it is expected that there would be an increase in effluent from the STW contributing to greater organic matter. This could increase the SAR in Holes Bay. Post ca. 1970s, the population of the Poole Harbour catchment increased (Figure 2.16) which should increase the effluent discharged from Poole STW. The organic matter record for HB1 shows an increase in organic matter in the ca. 2000s (Figure 5.5), three decades after the initial rise in population. The change in organic matter does not relate to any changes in the SAR, which remains stable from the ca. 1970s to present and therefore it is assumed industrial activity, e.g. building on heathland, is responsible for the change in SAR in HB1 post ca. 1970s.

The SAR of HB1 post ca. 1970s declines relative to the higher SARs during the ca. 1940s-1970s but remains greater than pre-ca. 1940s SARs. While it has been discussed that a main sediment supply to Holes Bay has reduced, i.e. the ceasing of the erosional activities of the heathland which has now been built on, Holes Bay itself is smaller than prior to ca. 1940s due to the land reclamation (Figure 5.10). Therefore, the SAR of HB1 remains higher than pre-ca. 1940s because there is less area for the sediment to be deposited within Holes Bay. The SAR of HB1 post ca. 1970s is higher than any of the other cores at this time (Figure 5.2). This is likely a consequence of the narrow entrance between Holes Bay and the rest of Poole Harbour limiting the ability of the sediment to leave Holes Bay and thus it deposits within its own area rather than freely mixing with the rest of the harbour.

5.2.3.3 Arne

Post ca. 1970s, the SAR of ARNE5 reduces from a peak of 11.1mm/yr during the ca. 1940s-1970s high SAR phase to 3.5mm/yr (Figure 5.2). This new rate, unlike FRM4, PID1 and HB1, is lower than the pre-ca. 1940s SAR by 0.6mm/yr.

As discussed in Section 5.2.2.3, Arne is influenced by changes in the sea and more so from the agricultural catchment than the industrial catchment surrounding Holes Bay. While the mean sea level does decrease ca. 1970s (Figure 5.1), it increases from ca. mid-1970s to present.

The decline in SAR of ARNE5 ca. 1970s is at the same time as the declines in SAR of the other cores. At this time, there was also a drop in mean sea level, to the lowest in the record (Figure 5.1). A combination of reduced sediment from the sea, the agricultural landscape and potentially from areas surrounding Holes Bay, resulted in the reduction of the SAR of ARNE5.

While a reduction in sea level reduced the sediment supply from the sea to Arne post ca. 1970s, ARNE5 SAR did not reach its lowest level instantaneously. ARNE5 SAR reduced initially to 4.3mm/yr before declining to 3.5mm/yr at ca. 1990 to present. While the initial drop in SAR was a partial result in the drop in mean sea level, after the drop in mean sea level the sea level quickly began to rise again. The initial SAR drop to 4.3mm/yr occurred during a peak of Cl and Br alongside a Zr/Rb ratio increase, indicating sediment contribution from the sea was greater than that from the catchment (Figure 5.13). A decline in farming in the catchments of the Rivers Frome and Piddle post ca. 1970s means this is a reasonable proposition.

While the SAR of ARNE5 post ca. 1970s (3.5mm/yr) is lower than pre-ca. 1940s rates, it is not that different to the SARs of FRM4 and PID1 (3.7 and 3.2mm/y respectively) across the ca. 1970s-present period. From the evidence presented in this section, it is assumed that the reduction in SARs across all cores, except HB1, is in some way influenced by the changes in farming in the agricultural catchments. While the initial drop in SAR in ARNE5 ca. 1970s coincided with the drop in mean sea level, it also coincided with the decline in farming intensity ca. 1970s. The sediment deposited in ARNE5 during the initial decline in SARs post ca. 1970s is interpreted as being comprised mainly of sea sourced sediment due to the elemental record. However, while the sea level continues to increase, the SAR of ARNE5 resides a stable low, thus suggesting the decline in sediment from the agricultural catchment plays an important part in sediment deposition in the Arne area.

5.2.4 The River Piddle post-ca. 2000 increase

From ca. 2000 PID1 exhibits an increase in SAR by ca. 1mm/yr (Figure 5.2). This change is not detected within any of the other cores. The increase is therefore likely due to a change within the River Piddle catchment, not the wider catchment of Poole Harbour.

In 2000, Piddlehinton, a village by the River Piddle, was subject to a flooding event that caused 54 properties to flood (Dorset County Council, 2016). This would likely cause an increase in sediment transportation within the River Piddle and into its estuary. However, the magnetic susceptibility at this time does not increase, it decreases to a stable lower level, and the Zr/Rb ratio does not alter. These signals are the opposite to what would be expected from a flooding event where it would be expected larger grained sediment and more minerogenic material would be transported to the estuary. The increased SARs is also sustained to the end of the PID1 record. The SAR does not therefore reflect a high, temporary increase as expected during flood events.

As previously discussed, following the ceasing of water meadow flooding, vegetation was allowed to grow in the rivers and thus provide a trap for fine sediment that was once deposited on the water meadows. Walling and Amos (1999) also suggest the River Piddle is a store of fine sediment which is of high organic content. While there does not seem to be a signal from the 2000 Piddlehinton flood recorded in the PID1, a possibility could be the flood caused a disturbance of the fine sediment stored within the river to be released. If the fine sediment was mobilised, it could take some time for it to reach the estuary, hence the longer period of increased SAR than expected with a flood event. The MS decreases post-ca. 2000 and then remains stable but slightly lower. This could suggest that less of the sediment being deposited in the estuary has originated from the catchment but instead that the sediment is sourced from within the river. The Zr/Rb ratio does not change post-ca. 2000 suggesting the sediment composition of PID1 has remained similar and of fine nature, there are just larger quantities of it. The organic matter post ca. 2000s fluctuates more than previously (Figure 5.4), a potential indication that the sediment being delivered to the estuary is of mixed organic content. This could be because while the fine sediment within the river is of high organic content, that which comes from the agricultural fields of the catchment is of even higher organic content. Thus, with an increase in sediment that has been remobilised from the river reaching the estuary, there is more sediment that has spent longer in the river reaching the estuary which potentially has lower organic content than that from the catchment. This could explain why the organic matter of PID1 initially quickly drops ca. 2000 (Figure 5.4).

The SAR increase post-ca. 2000 is only detected in PID1 and is not detected in any of the other cores. The cause of this increase is likely limited to changes within the River Piddle and its catchment. Changes in farming practices locally within the River Piddle catchment could account for changes in SARs of only PID1. Collins & Walling (2007a) provide evidence that the sediment within the River Piddle is composed majority of agricultural sourced material. The River Piddle catchment is smaller than that of the River Frome, 437km^2 versus 918km^2 respectively (Collins & Walling, 2007a). Therefore, changes within the smaller River Piddle catchment are likely to account for a greater change in the river itself when compared to the River Frome. Collins & Walling (2007a) determined the River Piddle fine grained bed sediment storage was over double that of the River Frome. Thus, small changes in farming practices within the River Piddle could have contributed to more fine grained sediment in the river and recorded in PID1 as a small increase in SARs.

The increase in PID1 post ca. 2000s is likely a result of local catchment changes. A change in farming practices may have resulted in increased fine grained sediment being delivered to the river which in turn increased the SARs of PID1. This could have been facilitated by the flooding event in 2000 which may have increased the transport of the sediment, however, PID1 record does not support the notion of a flooding event due to the lack of temporary changes in the record.

5.3 Calculated sediment accumulation rates and their comparison to other published data

5.3.1 Comparison to other Poole Harbour studies

As discussed within Section 2.4.5.3, there have been several other studies carried out within Poole Harbour to reconstruct SARs. This section will discuss how these compare to the SARs calculated for ARNE5. The SARs of Cundy (1994), Cundy and Croudace (1996), Long et al., (1999) and Marshall et al., (2007), which have all been taken around the Arne Peninsula of Poole Harbour (Figure 2.24), are presented in Figure 5.14 alongside that of ARNE5.

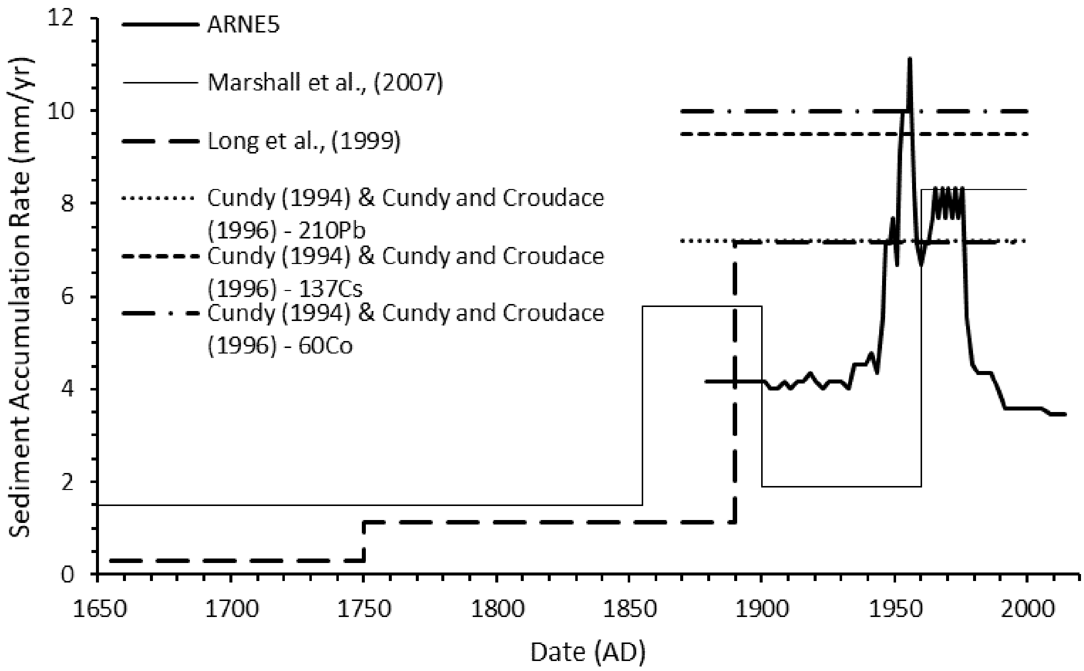


Figure 5.14: Published sediment accumulation rates of Poole Harbour and ARNE5.

The SARs published by Cundy (1994) and Cundy and Croudace (1996), demonstrate a constant SAR whereas those by Marshall et al., (2007) and Long et al., (1999) show variability throughout their record. The SARs provided by Cundy (1994) and Cundy and Croudace (1996) have been derived using radionuclide dating and their models, e.g. simple (CF:CS) ^{210}Pb model; these provide a constant SAR across the record. Marshall et al., (2007) and Long et al., (1999) used other techniques such as chronostratigraohic markers, e.g. SCPs, and biostratigraphic markers, e.g. pollen changes of *Pinus* and *Spartina*, and radiocarbon dating. These techniques facilitate the dating of sediment that accumulated prior to the range of ^{210}Pb dating and also to model age-depth relationships in a non-linear manner. Both Marshall et al., (2007) and Long et al., (1999) used linear interpolation between the chronological and biostratigraphic markers to complete their age-depth models. Long et al., (1999) used radiocarbon dating to obtain a basal age of 1510-1260BC, pollen *Pinus* to establish the 1750 pine introduction and establishment and the pollen of *Spartina* to detect 1890 *Spartina* establishment, SARs were calculated between these dates. Marshall et al., (2007) used more dating markers within their linear interpolation which has potentially picked up more changes in SARs than those of Long et al., (1999), e.g. Marshall et al., (2007) detects a shift to a higher SAR at 1855, which then declines at 1900 before increasing again at 1960, whereas Long et al., (1999) detects a shift to a higher SAR later at 1890 which remains constant to the end of the record (Figure 5.14).

The SARs of Marshall et al., (2007) and Long et al., (1999) are 'jumpy' in nature as only a few points were used to calculate the SARs. The ARNE5 SARs appear 'noisy' relative to these records as the SARs have been calculated for every 1cm with the aid of Bayesian age-depth modelling. While the record of ARNE5 does not extend as far back as those of Marshall et al., (2007) and Long et al., (1999), some similarities can be seen between the published SARs and the SAR of ARNE5. ARNE5 remains at a low, stable SAR until ca. 1940s, during this time Marshall et al., (2007) shows a drop in SAR ca. 1900, coinciding with the low SAR of ARNE5, however their SAR is ca. 2mm/yr lower than that of ARNE5. During the start of ARNE5 SAR record where the SAR is stable and low, ca. 1980-1940, Long et al., (1999) shows an earlier increase to a higher SAR than both Marshall et al., (2007) and ARNE5 at ca. 1890. As mentioned, this higher SAR is an artefact of the age-depth model used by Long et al., (1999). While ARNE5 SAR increases earlier than that of Marshall et al., (2007) their ca. 1960 increase shows a similar SAR of 8.3mm/yr for ARNE5 ca. 1960-1975. After ca. 1975 ARNE5 decreases whereas Marshall et al., (2007) and Long et al., (1999) remain at a higher SAR, an artefact of limited chronostratigraphic and biostratigraphic markers post 1890 for Long et al., (1999) and 1960 for Marshall et al., (2007). The ^{137}Cs and ^{60}Co derived SARs of Cundy (1994) and Cundy and Croudace (1996) are higher than other published SARs, these SARs are similar to the peak of ARNE5 ca. mid-1950s. However, if the SAR of Cundy (1994) and Cundy and Croudace (1996) are averaged for their timespan, this is a very high average as no other record shows similar SARs for an extended period of time. The averaged SAR for ARNE5 is 5mm/yr, this is even lower than the ^{210}Pb SAR which is similar to Long et al., (1999) for this time but higher than Marshall et al., (2007) for the period 1900-1960.

An important factor to consider when comparing SARs of multiple sources is the locations of the recovered sediment cores (Figure 2.24). The cores retrieved from Long et al., (1999), Marshall et al., (2007) and that of ARNE5 were all recovered within approximately 100m distance of each other. ARNE5 was taken along the transect that was used by Long et al., (1999) while the core of Marshall et al., (2007) was taken 50m southwest where it is more terrestrial. This means that the location of Marshall et al., (2007) core would likely only receive sediment to be deposited at higher tides than from Long et al., (1999) and ARNE5 and thus could account for the lower SARs detected in this record. As ARNE5 was taken along the transect of Long et al., (1999), it would be expected that their SARs would be similar. However, for ca. 1890 to the top of the record, Long et al., (1999) provides a higher SAR than the averaged SAR of ARNE5 by ca. 2.1mm/yr. Long et al., (1999) recovered multiple cores along a transect whereas ARNE5 has been calculated from a single core, therefore the SARs of ARNE5 may not adequately reflect SAR variability across this area of the Arne peninsula. Averaged for the length of record of ARNE5, ca. 1880 to the top of record, the average SAR of Marshall et al., (2007) is ca. 4.7mm/yr, only ca. 0.3mm/yr less than ARNE5 average. These two values are similar and it has been discussed the use of more chronological and biostratigraphic markers by Marshall et al., (2007) provides a SAR profile most like that of ARNE5 out of the published SARs of the area. The core collected by Cundy (1994) and further used in the work of Cundy and Croudace (1996), was retrieved ca. 2km southwest from the other cores studied within the Arne peninsula. Therefore, it is likely there will be different SARs detected in the work of Cundy (1994) and Cundy and Croudace (1996). While this site is further inland and thus sediment delivery from tidal activity within the harbour will be less, Figure 2.22 suggested this area has a fluvial sediment source. Thus, a source of sediment and limited tidal activity will promote higher SARs as the sediment can accumulate and be disturbed less by the tides of the harbour.

In comparison of ARNE5 to other published SARs of the area, ARNE5 is most like the SARs produced by Marshall et al., (2007). The similarity likely arises due to the higher number of chronostratigraphic and biostratigraphic markers used by Marshall et al., (2007) relative to other published works, allowing more accurate changes in SARs to be detected. When the SARs are averaged, ARNE5 is again most similar to that of Marshall et al., (2007) even though ARNE5 was taken along the transect of Long et al., (1999). However, Long et al., (1999) used multiple cores to calculate the SAR and thus individual changes within each core may exhibit different SARs and unique changes, like that of ARNE5. Little comparison can be made to the work of Cundy (1994) and Cundy and Croudace (1996) as only constant SARs were provided which were higher than that of ARNE5 averaged and the core was taken some distance from the other cores studied, thus a different SAR for Cundy (1994) and Cundy and Croudace (1996) is expected.

5.3.2 Comparison to other estuaries

SARs have been calculated for other estuaries of southern England (Figure 5.15 and Table 5.3). The SARs presented have all been calculated using radionuclide dating and provide a constant SAR for each site. These have been presented with the SAR of ARNE5 and the mean averaged SAR of ARNE5 to allow comparison to be made with the other estuaries (Figure 5.16).

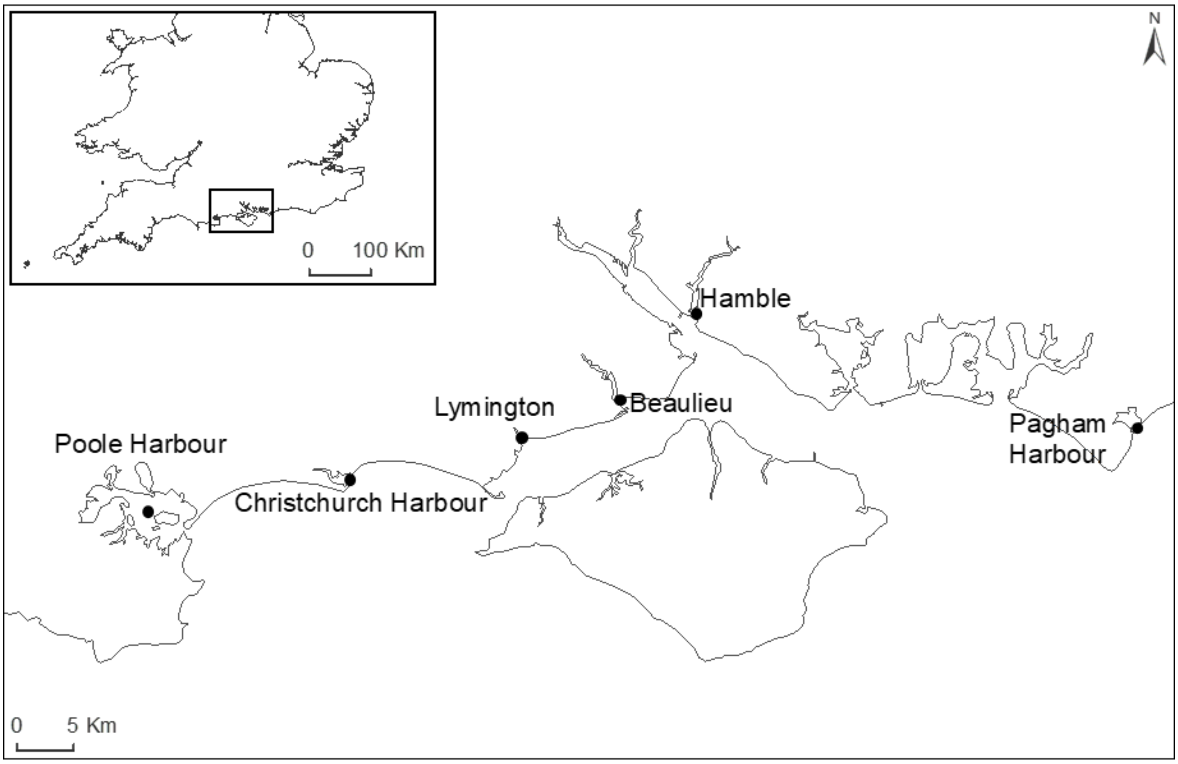


Figure 5.15: Locations of other SAR studies in estuaries within southern England.

Using the mean SAR for ARNE5, it can be assumed Poole Harbour has a similar SAR to other estuaries within southern England as it lies within their range (Figure 5.16). ARNE5 shows most similarity to Pagham Harbour. Like Poole Harbour, Pagham Harbour has a narrow entrance (100m) between the estuary and the sea, limiting the exchange of sediment between the two bodies of water (Cundy et al., 2002). While Poole Harbour's entrance is wider (350m), it has a larger freshwater catchment, >770km^2 (Humphreys & May, 2005), bringing in fine sediment required for salt marsh construction. Pagham Harbour has a limited freshwater input and thus fine sediment sources are limited to remobilised sediments within the estuary and that from the sea that can be transferred through the narrow entrance (Cundy et al., 2002). So, while sediment source is limited within Pagham Harbour, it is more constrained to the estuary by the narrower entrance than Poole Harbour which has more sediment sources. This provides a possible reasoning for the similar SARs of ARNE5 and Pagham Harbour. The next two similar SARs to Poole Harbour are Lymington estuary and Christchurch Harbour. Lymington estuary has more connection with the sea which likely results in more sediment loss within the estuary. Christchurch harbour has a freshwater supply providing fine sediment and a narrow entrance of 47m, narrower than that of Poole Harbour, allowing it to retain sediment within the estuary (Gao & Collins, 1997). Therefore, the narrower entrance of Christchurch Harbour provides the ability to maintain a higher SAR than ARNE5 and the good connection between Lymington estuary and the sea allows for a lower SAR.

The chronology of ARNE5 was established using Bayesian modelling which allowed for a 1cm resolution age-depth model and thus a 1cm resolution SAR. This high resolution has allowed trends within the SAR of ARNE5 to be found. Trends cannot be found within the given SARs of published studies of the other estuaries presented in Figure 5.16 because only a constant SAR is given. Therefore, comparisons cannot be made using the given SARs to determine if the estuaries of southern England have behaved in similar ways as Poole Harbour to historic events, e.g. colonisation of *Spartina* and the intensification of farming and industrialisation. Therefore, the use of Bayesian modelling appears to be a novel approach to producing SARs for estuarine sediments within southern England.

Table 5.3: Sediment accumulation rates for other estuaries within Southern England. Adapted from Cundy et al., (2002). Note: where catchment and mouth size was not stated in publication, river catchments which flow into the estuaries were summed (Environment Agency, 2018) and measurements of the estuary mouth were made using Google Earth.

Estuary	**Date first colonised by *Spartina***	**Average SAR (mm/yr)**	**Method**	**Catchment size (km^2)**	**Mouth size (m)**	**Reference**
Pagham Harbour, southern England	1919	5	^{210}Pb and ^{137}Cs dating	72	100	Cundy et al., (2002)
Hamble estuary, southern England	1907	4-8.4	^{210}Pb and ^{137}Cs dating	190	485	Cundy and Croudace (1995b)
Christchurch Harbour, southern England	1913	4-8	^{210}Pb and ^{137}Cs dating	227	47	Cundy and Croudace (1996) Gao and Collins (1997)
Lymington estuary, southern England	1893	3-5.2	^{210}Pb and ^{137}Cs dating	49	>800	Cundy and Croudace (1996)
Beaulieu estuary, southern England	1898	2-5	^{210}Pb and ^{137}Cs dating	58	520	Cundy and Croudace (1996)

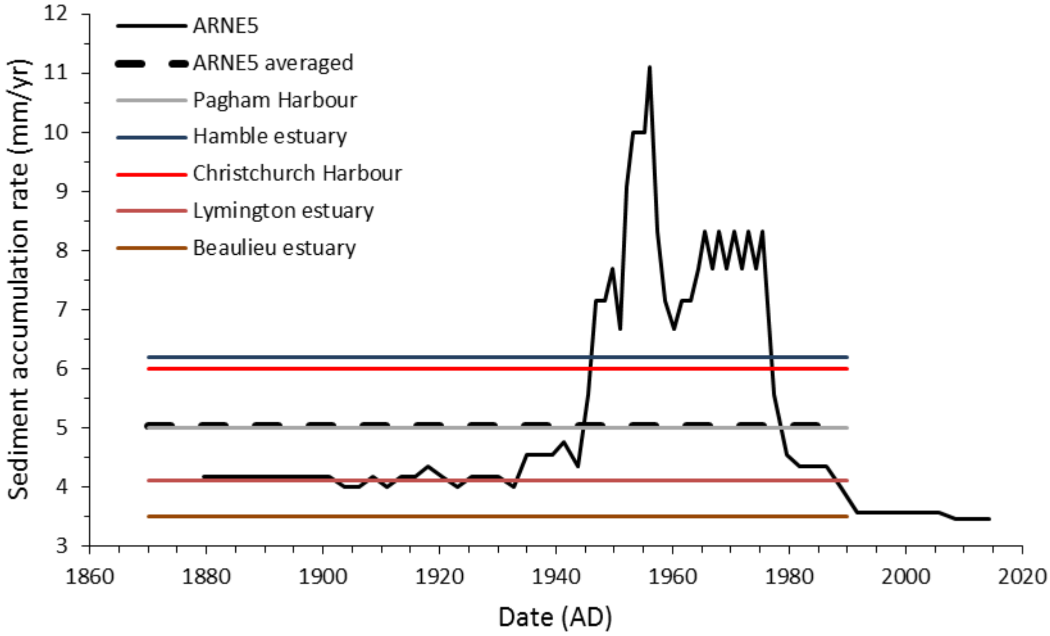


Figure 5.16: Sediment accumulation rates for estuaries presented within Table 5.3, ARNE5 and averaged ARNE5 SAR. Where SAR ranges have been given for estuaries, the mid-SAR value was used.

5.4 Conclusions

This chapter has discussed the SARs of the four cores from the sites of the River Frome and Piddle estuary (FRM4 and PID1respectively), Holes Bay (HB1) and Arne (ARNE5). The main periods of change were highlighted and evidence was presented for the reasoning behind these changes as summarised below:

- Ca. 1910-1930s there was a brief high MS event within the River Frome. No firm conclusion has been given for this event but flooding, military activity and a drought within the River Frome catchment likely caused increased erosion at this time resulting in more minerogenic top soil reaching the estuary causing an increase in MS. Post ca. 1920s, forestry plantations occurred within the River Frome catchment which could have decreased sediment transport to the watercourse, resulting in the lowered MS.
- Ca. 1940s-1970s there was a high SAR period across all cores. For FRM4 and PID1, this was a result of increased catchment erosion from the intensification of farming as a result of WWII and subsequent government policies (e.g. CAP 1962). The increase in industrialisation and land reclamation within Holes Bay accounted for the increase of SAR in HB1. The increase of SAR in ARNE5 was attributed to influences from the sea but

more so from the intensification in farming bringing finer sediment to the area.

- Post ca. 1970s there was a decline in SAR seen across all cores. For HB1, this was a result of building on heathland that previously was subject to heavy erosive activity. Within the catchments of the River Frome and Piddle, the 'war effort' ceased meaning intensified farming reduced and water meadows were no longer managed. This reduced catchment erosion, thus the supply of sediment reaching the watercourse, and sediment within the rivers could be more easily stored within the increasing vegetation which was not being cleared for the water meadow management. The decline in SAR in ARNE5 has again been assumed to mainly be a result of the decline in farming practices.
- Ca. 2000s there was a sustained increase in the SAR of PID1, not seen across any other core, thus this increase is likely due to local changes in the River Piddle catchment. Such changes may include changes in farming practices which may have increased the delivery of fine grained sediment to the river, thus the estuary. The transport of this material may have been facilitated by a flooding event in 2000 but PID1 does not show a temporary fluctuation in its record which would be expected during a flooding event.

The SAR of ARNE5 was compared to SARs of other published studies from both within Poole Harbour and from other estuaries within southern England. Methods for establishing age-depth models, from which SARs can be calculated, have been shown to show the greatest difference between the SAR of ARNE5 and those of published studies both within Poole and other southern estuaries. ARNE5 showed some similarity to other SARs of Arne, more so to Marshall et al., (2007) in particular with regards to patterns of change and averaged SARs. When averaged, the SAR of ARNE5 was within the range of other estuaries within southern England, being most similar to those that also had large freshwater inputs and/or had narrow entrances between the estuary and the sea.

Chapter 6 Spatial and temporal variations of nutrient loads to Poole Harbour and the effects on algal blooms

6.1 Introduction

Poole Harbour is a complex system with multiple sources of nutrients within its catchment and multiple pathways for these sources to enter the harbour. As evidenced by the data explored in Chapter 5, agricultural practices are the main control on sediment dynamics in the Rivers Frome and Piddle. It is thought that the Rivers Frome and Piddle predominantly supply nutrients associated with agriculture to the Poole Harbour system. Nutrients may also be associated with the sewage treatment works (STWs) within the River Frome and Piddle catchments. Poole STW adds human derived nutrients via effluent which drains directly into Holes Bay. Within Chapter 5, it was determined marine processes also drove changes in Poole harbour thus it is assumed marine derived nutrients also influence the productivity of this estuarine environment.

This chapter shall present evidence obtained from the palaeoenvironmental reconstructions of the sediment cores collected from the four study sites within Poole Harbour, the River Frome and Piddle estuary (FRM4 and PID1), Holes Bay (HB1) and Arne (ARNE5). The analysis of these cores demonstrates how different sources of nutrients have varied over time, influencing algal productivity across Poole Harbour.

Throughout this chapter the use of geochemical and palaeoecological proxies will be used to provide evidence of change within Poole Harbour. While the justification of using these proxies has been explained in Chapter 3, a summary of what each of the proxies indicate are shown in Table 6.1.

Table 6.1: Summary of proxies used to determine source of nutrients and productivity.

Proxy	Indication
Organic matter	A predictor of organic carbon and thus indicator of productivity. Increase in productivity would produce more organic matter (Craft et al., 1991).
%C	Indicator of productivity, an increase in %C suggests an increase in productivity.
%N	Indicator of productivity, an increase in %N suggests an increase in productivity.
C/N	Indicator of the source of productivity. Lower C/N suggests more autochthonous (internal productivity, e.g. within the water) while higher C/N suggests more allochthonous (externally sourced productivity, e.g. sourced from the catchment) (Leng & Lewis, 2017).
$\delta^{13}C$	Carbon has many sources. Changes in the C12:C13 ratio can be tracked by measuring $\delta^{13}C$. Higher $\delta^{13}C$ values can be interpreted to suggest an input of more terrestrial material (Leng & Lewis, 2017) or an increase in productivity. To determine the source of carbon and the nature of $\delta^{13}C$ changes, $\delta^{13}C$ needs to be analysed alongside other isotopic proxies.
$\delta^{15}N$	Indicator of productivity with an increase in $\delta^{15}N$ representing more productivity (Talbot, 2001). Also an indicator of the source of N, e.g. values of $\delta^{15}N$ greater than 8 indicating the source of N is potentially derived from sewage (Heaton, 1986; Bedard-Haughn et al., 2003). To determine the source, $\delta^{15}N$ needs to be analysed alongside other isotopic proxies.
Si	Silica is a productivity or terrigenous indicator (Croudace et al., 2006). Silica concentrations can provide some indication of algae (diatom) production, with an increase in silica suggesting an increase in diatom production. Note, diatoms use biogenic silica for which data is lacking in this study. Increases in elemental silica may also relate to increased terrestrial in wash. Therefore, the use of elemental silica here will only be used as a tentative indication of diatom productivity.
Pigments	Produced by algae and can provide an indication of algal communities (McGowan, 2007, 2013).
Diatoms	Group of algae where species display affinity to specific environmental conditions. Studying the species assemblage changes of diatoms can indicate environmental changes.

6.2 How do the sources of nutrients differ across Poole Harbour and how does algal productivity respond?

This section shall explore how nutrient source differs across Poole Harbour depending on historical activities within the catchment. Chapter 5 provides a history of the catchment of Poole Harbour and its effects on sediment accumulation rates (SARs) across the harbour. This section shall further draw upon the information and data presented in Chapter 5 to provide reasoning for the changes in nutrient source across Poole Harbour and the effect this has had on algal productivity. First, a comparison of all the sites will be presented to show their variation before detailed discussions are given for site specific changes.

6.2.1 How does source differ across Poole Harbour?

The Rivers Frome and Piddle both drain the agricultural landscape of the catchment. Within Chapter 5 it was discussed how agricultural practices were the dominant drivers of SARs in FRM4 and PID1, explaining why similar SAR variability is exhibited in both cores since ca. 1880. It is therefore a logical extension that changes in agricultural practices would account for changes in nutrient delivery to the River Frome and Piddle estuary. If the River Frome and Piddle estuary is influenced by the same dominant environmental driver, i.e. changes in agricultural practices across both river catchments, then one would expect the respective cores of FRM4 and PID1 to exhibit similar nutrient histories. SARs in HB1 were determined to reflect changes in industry and infrastructure, both by changing the sediment delivery to the area and reducing the ratio of water area to the catchment through land reclamation within Holes Bay. These changes in industrial development would also be expected to influence nutrient dynamics in Holes Bay, especially the effluent associated with the development of the Poole STW. Changes in ARNE5 SARs were determined to be a result of both marine influence and changes within the agricultural landscape. Therefore, changes in nutrients in ARNE5 are likely to be driven by the Rivers Frome and Piddle but also be associated with nutrients that enter the harbour from the sea.

As discussed in Section 3.5.2, the relationship between C/N and $\delta^{13}C$ can help determine the source of nutrients which have been recorded within a sediment core. Figure 6.1 illustrates this relationship for the four cores studied. This figure does not indicate the exact temporal range over which these changes occur.

Changes in the relationship between C/N and $\delta^{13}C$ over time are discussed for each core in subsequent sections (6.2.2.1, 6.2.3.1 and 6.2.4.1).

FRM4 and PID1 are shown in Figure 6.1 to be similar to each other, likely a result of the shared agricultural nutrient supply. The nutrient source of HB1 is different to that of those cores recovered from agriculturally driven components of Poole Harbour, as its data series is set apart from cores FRM4 and PID1. HB1 has higher $\delta^{13}C$ values which suggest a relatively enhanced marine influence, expected given the lower freshwater contribution in Holes Bay compared with the Rivers Frome and Piddle. ARNE5, exhibits predominantly higher $\delta^{13}C$ which suggests this area is driven more by marine sourced nutrients. Freshwater sourced nutrients have been in effect here with the lower $\delta^{13}C$ values detected within ARNE5. ARNE5 also demonstrates during its record higher C/N values suggesting that sources of carbon have been sourced from terrestrial plants. The following sections will discuss in detail the reasoning for the differences between the cores and how nutrient delivery has changed over time at each site.

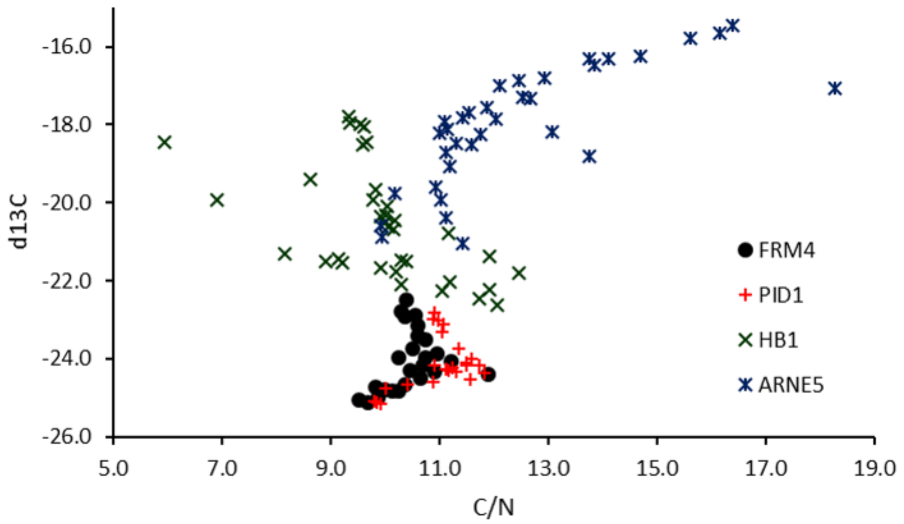


Figure 6.1: Site differences in C/N vs $\delta^{13}C$ for FRM4, PID1, HB1 and ARNE5 demonstrating the similarity between the river (FRM4 and PID1) and marine (HB1 and ARNE5) sourced nutrients.

6.2.2 The agricultural catchment

6.2.2.1 Nutrient source

Palaeoenvironmental evidence for FRM4 and PID1 exhibit similar changes through the record (Figure 6.2, Figure 6.3, Figure 6.4 and Figure 6.5). The similarity is likely a result that both the Rivers Frome and Piddle, which feed into their mutual estuary, drain agricultural catchments. This section explains how these two rivers have supplied nutrients to Poole Harbour and how they have changed over time.

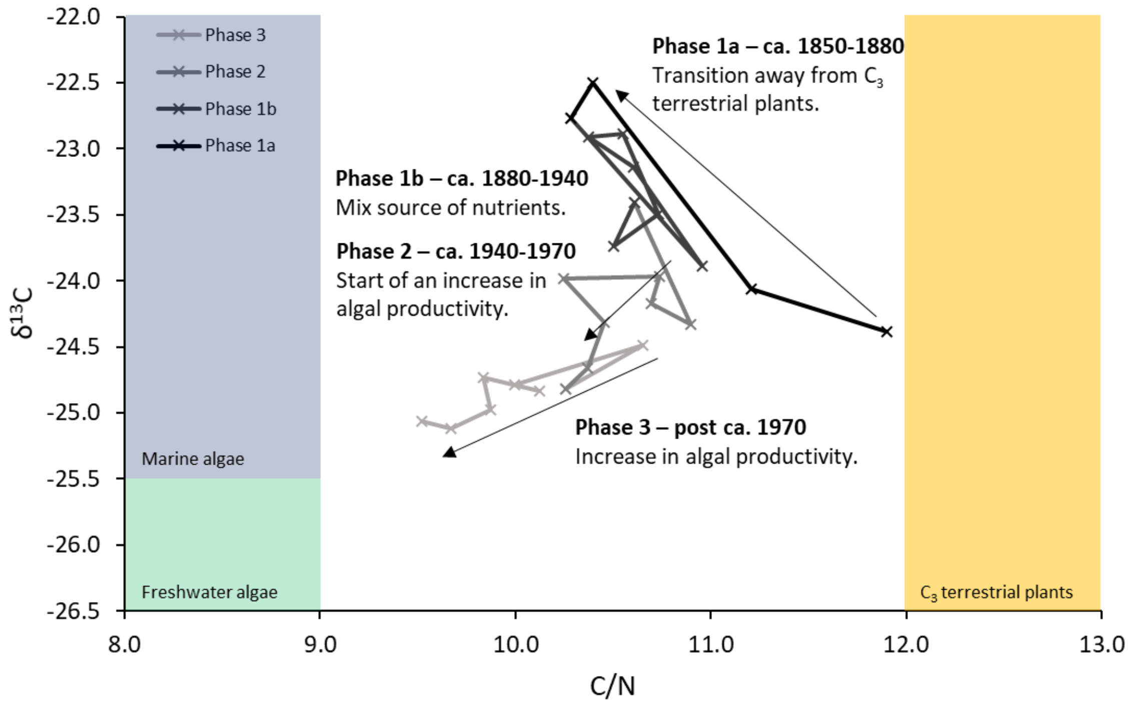


Figure 6.2: FRM4 C/N vs $\delta^{13}C$ represented with shaded line demonstrating change over time with regards to phases discussed within the text: Phase 1a – ca. 1850-1880, Phase 1b – ca. 1880-1940, Phase 2 – ca. 1940-1970 and Phase 3 – post ca. 1970. Note: boxes illustrate the $\delta^{13}C$ and C/N typical ranges for organic inputs to coastal environments (Lamb et al., 2006).

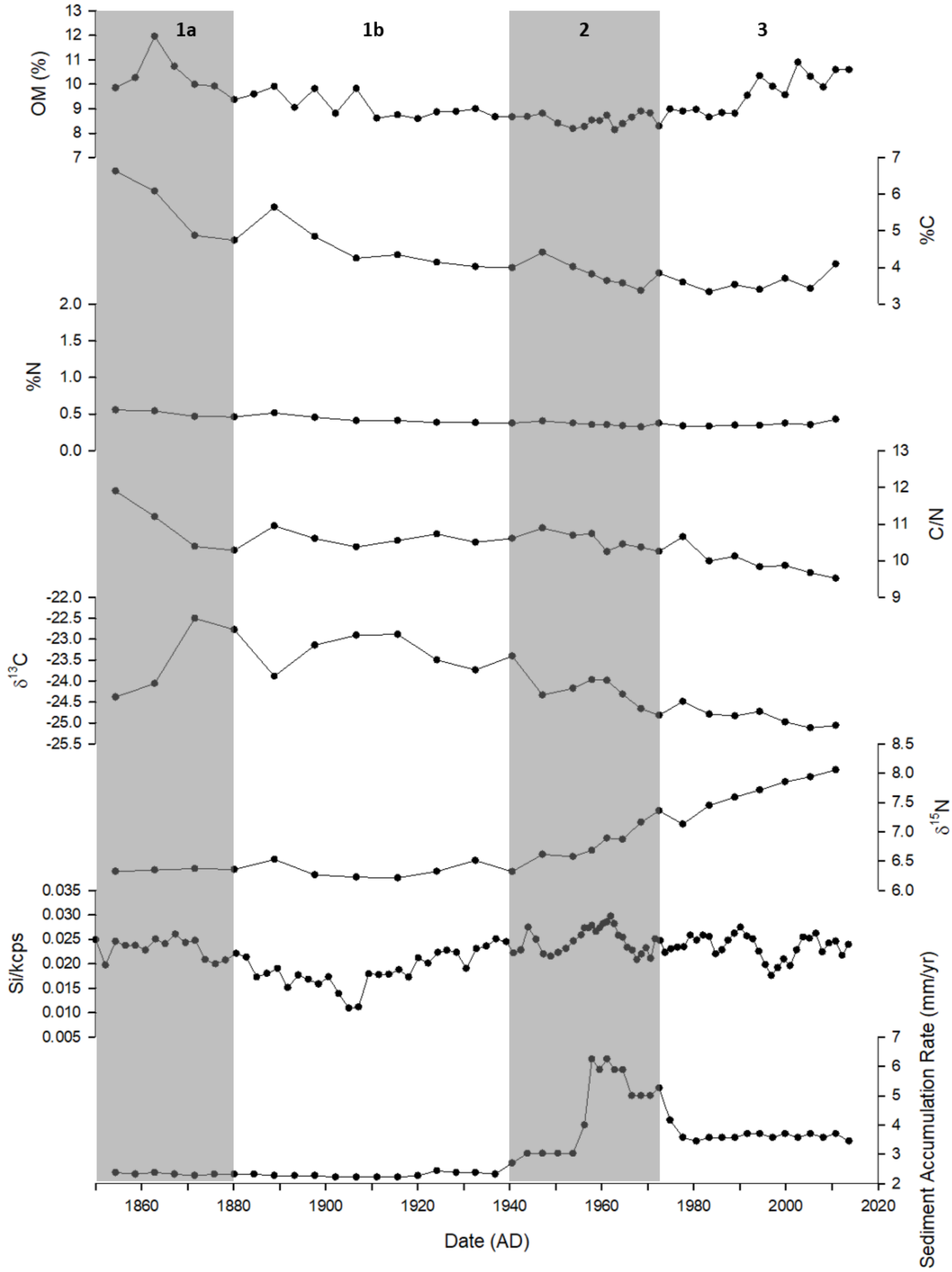


Figure 6.3: FRM4 geochemical data and sediment accumulation rates with shading to indicate phases discussed within text. Note: %N shows little variation over the record.

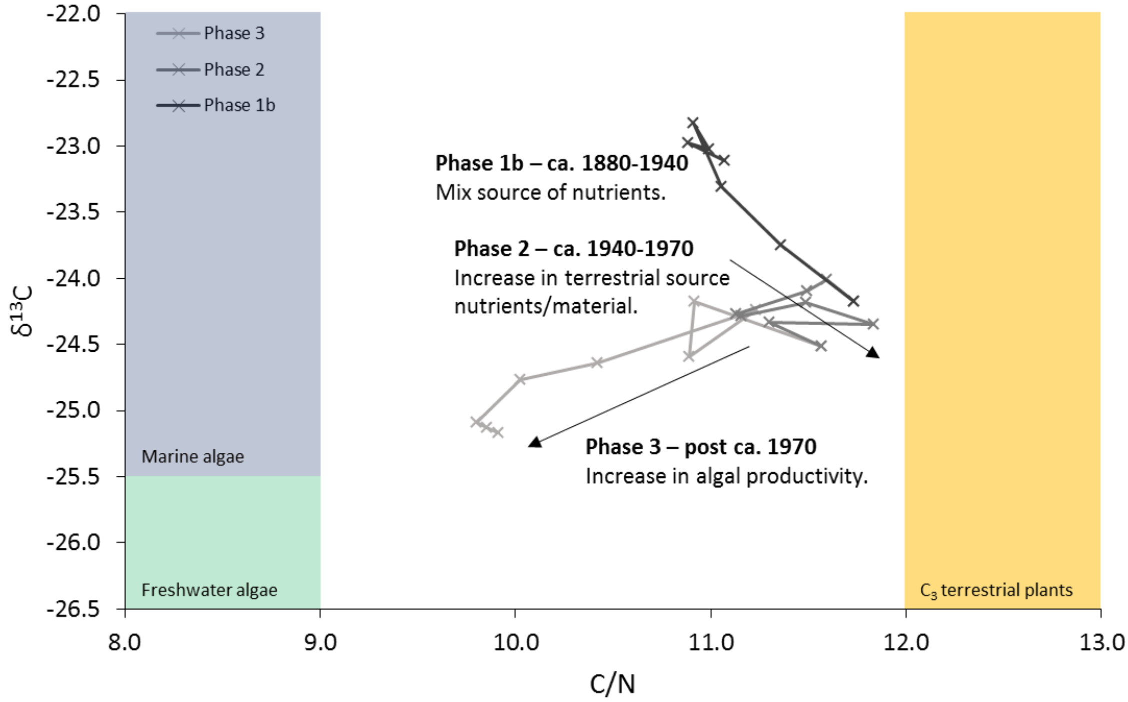


Figure 6.4: PID1 C/N vs $\delta^{13}C$ represented with shaded line demonstrating change over time with regards to phases discussed within the text: Phase 1b – ca. 1880-1940, Phase 2 – ca. 1940-1970 and Phase 3 – post ca. 1970. Note: boxes illustrate the $\delta^{13}C$ and C/N typical ranges for organic inputs to coastal environments (Lamb et al., 2006).

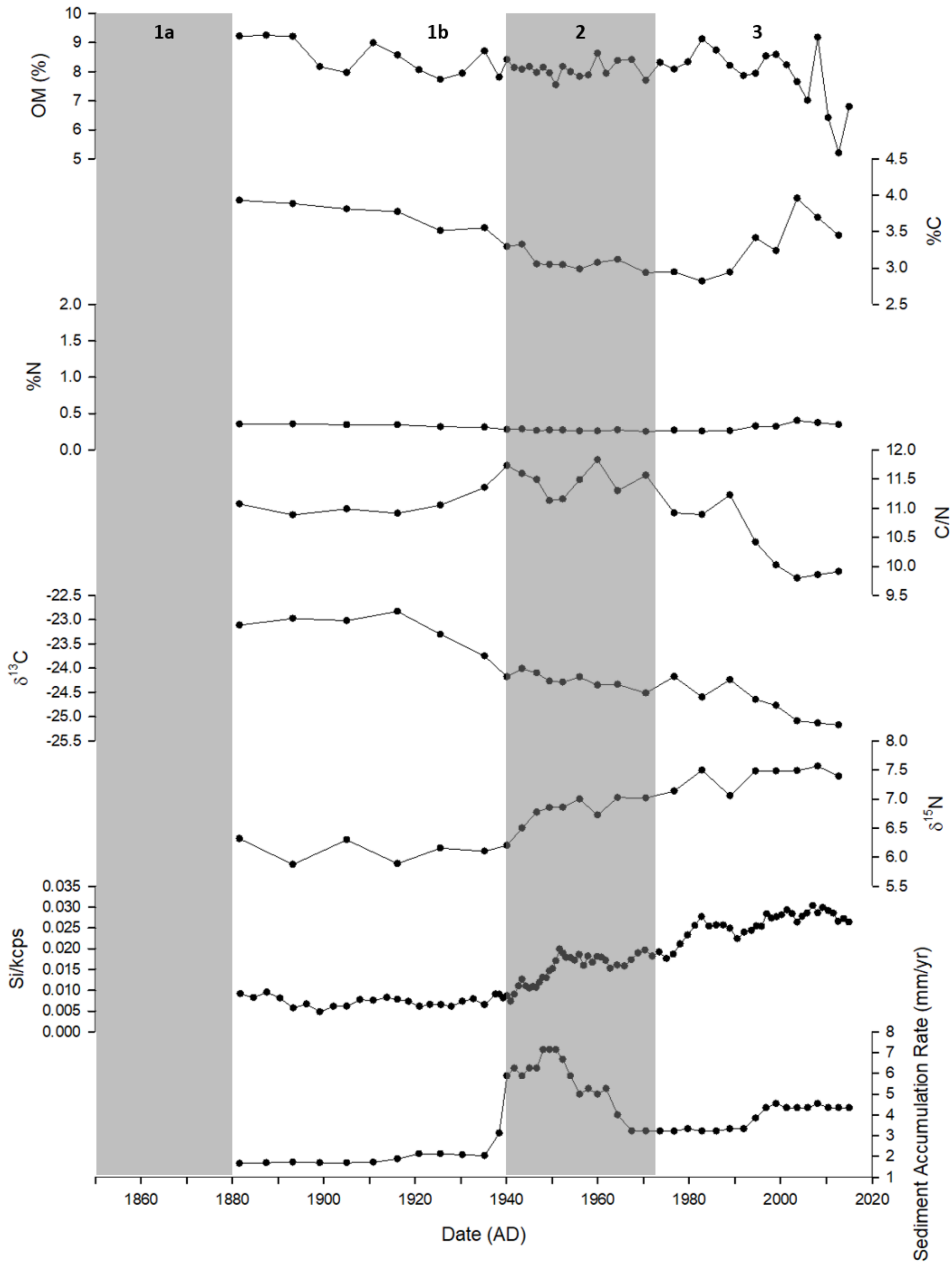


Figure 6.5: PID1 geochemical data and sediment accumulation rates with shading to indicate phases discussed within text. Note: %N shows little variation over the record.

6.2.2.1.1 Phase 1a – ca. 1850-1880

FRM4 is the only core which provides palaeoenvironmental evidence ca. 1850-1880 (Figure 6.3). Moving from the bottom of this phase, ca. 1850, to the top, ca. 1880, there is a progressive transition from a terrestrial source of nutrients to more productivity within the water. The productivity increase is evidenced by the decrease in C/N suggesting more autochthonous productivity and an increase in $\delta^{13}C$ which when coupled with a declining C/N suggests more autogenic productivity is occurring at this time rather than an increase in input of terrestrial sourced material.

Nitrogen and phosphorus are important nutrients which are essential for algal growth, however algal productivity also depends on the availability of other resources, e.g. silica for diatom production (Kilham & Hecky, 1988; Tilman et al., 1986; Rocha et al., 2002). An increase in diatom production will be recorded as an increase in silica preserved within the sediment record (Rocha et al., 2002). As diatom production continues, silica reservoirs within the water column will deplete as it is not added to the system in the same abundance as nitrogen and phosphorus, which also recycle faster than silica and thus are available for algae productivity at a faster rate (Sommer & Stabel, 1983; Rocha et al., 2002). Non-diatom algae do not require silica for production, thus if a clear increase in silica is not detected, it does not mean there is not an increase in productivity, just that the algal productivity is not diatom dominant (Rocha et al., 2002). It should be noted that diatoms utilise biogenic silica for production, for which data within this study is lacking. Here, elemental concentrations of silica have been used as an indicator of productivity but consideration has also been given to the potential source of terrestrial silica from the catchment. The Si concentration during Phase 1a remains relatively stable and starts to decline ca. 1875. This suggests that Si could be associated with terrestrial in wash and that the decline in Si is associated with a decrease in terrestrial input when the autochthonous productivity commences.

The transition from terrestrially sourced nutrients to increased autogenic productivity suggests that by ca. 1880, anthropogenic activities had already influenced the system.

6.2.2.1.2 Phase 1b – ca. 1880-1940

A directional change in the C/N vs $\delta^{13}C$ relationship can provide evidence for a changing source of nutrient supply (Leng & Lewis, 2017). Figure 6.2 and Figure

6.4 show the change in C/N vs $\delta^{13}C$ for FRM4 and PID1 respectively, with the gradual change in the colour of the line of dark to light representing the transition within the record of older to younger sediment. The directional change within FRM4 and PID1 post ca. 1940 suggests an increasing contribution from freshwater. However, both FRM4 and PID1 during Phase 1b demonstrate the source of carbon, and associated nutrients, have likely been derived from multiple sources. The placement of the C/N vs $\delta^{13}C$ values ca. 1880-1940 suggest the source is a composite of terrestrial plants, bacteria and freshwater.

Si concentrations during Phase 1b in PID1 (Figure 6.5) remain low and stable indicating either little change in productivity or source of nutrients. Within FRM4 (Figure 6.3), Si concentrations decrease to ca. 1905 after which it then increases to pre-existing concentrations. This could be an indication of a decrease in terrestrial sourced nutrients to ca. 1905 and then an increase in terrestrial sourced nutrients to ca. 1940, or ca. 1905 there could be an increase in diatom production. However, C/N, OM and $\delta^{13}C$ in both FRM4 and PID1 remain relatively stable throughout Phase 1b suggesting productivity remains stable.

6.2.2.1.3 Phase 2 – ca. 1940-1970

Ca. 1940-1970, FRM4 and PID1 SARs sustainably increase, likely due to the intensification of farming practices during and post WWII (Section 5.2.2.1). Phase 2 also exhibits a change in the geochemical record. $\delta^{15}N$ increases throughout Phase 2 (Figure 6.3 and Figure 6.5). Estuaries can retain and recycle nitrogen effectively, e.g. via dentrification and phytoplankton assimilation, but the removal capability of nitrate within estuaries is overwhelmed by excessive reactive nitrogen loading from anthropogenic forcings, e.g. urbanisation and intense agricultural activities (Wong et al., 2014). The increased $\delta^{15}N$ detected in FRM4 and PID1 is likely a result of increased application of fertilisers within the agricultural land of the catchment and the associated leaching into the rivers and the estuary, where the input of increased nitrates cannot be removed at the same rate.

$\delta^{13}C$ decreases in FRM4 and PID1 ca. 1940-1970 despite the SAR increasing as a result of increased sediment erosion in the catchment (Section 5.2.2.1). The inverse relationship between $\delta^{13}C$ and SAR would not typically be expected due to the associated increase in terrestrial input. Algal production utilises ^{12}C preferentially to ^{13}C, and as the productivity increases, the reservoir of ^{12}C depletes and algae are required to use more ^{13}C (Meyers, 2002). The expected response with this changing relationship therefore manifests as an increase in $\delta^{13}C$ in the sediment record as the algae die and become part of the organic matter (Meyers, 2002). However, when nutrient loading is in excess, less fractionation of carbon is required for productivity as there is an abundance of ^{12}C, thus the $\delta^{13}C$ values of the sediment decrease. As demonstrated by the $\delta^{15}N$ (Figure 6.3 and Figure 6.5), there is an increase in nutrients coming into the water meaning there is less fractionation of carbon as productivity can utilise the greater quantities of ^{12}C before it is required to depend more on the ^{13}C. The increasing C/N in PID1 (Figure 6.5) also supports the notion of an increased supply of terrestrial sourced material during Phase 2, replicated in the move towards more terrestrially sourced carbon in Figure 6.4 during the ca. 1940-1970s.

From ca. 1940, PID1 demonstrates an increase in silica (Figure 6.5), suggesting more silica rich algae, i.e. diatoms, are being preserved in the sediment due to increased productivity and/or an increase in terrestrial in wash from the catchment. While this trend is not as prominent within FRM4 (Figure 6.3), the values of silica are higher than previous within the record. The change in silica concentration within FRM4 and PID1 post ca. 1940 also support the notion of increased terrestrial in wash and increased algal productivity during Phase 2.

6.2.2.1.4 Phase 3 – post ca. 1970

SARs decline post ca. 1970s in both FRM4 and PID1 (Section 5.2.3.1). $\delta^{15}N$ continues to increase post ca. 1970s alongside the declining intensity of agricultural practices reducing the quantity of artificial fertilisers applied to the catchment. Within FRM4, the increase in $\delta^{15}N$ is supported by the increasing dissolved nitrate concentrations recorded at the East Stoke River Monitoring Station since 1965 (Figure 2.19). As discussed (Section 2.4), Poole Harbour is a groundwater fed system (PHCI, 2014), meaning application of fertilisers during the intensified farming period (ca. 1940-1970) are still within the extended Poole Harbour hydrological system and may not have yet entered the estuary. Such a lag time could explain why $\delta^{15}N$ continues to increase post ca. 1970. Another explanation for an increase in $\delta^{15}N$ could be an increase in population post ca. 1970 (Figure 2.16). While STWs have been in operation in the River Frome and Piddle catchments prior to ca. 1970, e.g. Wool STW constructed in 1954 and Dorchester STW constructed in 1959, it is not common practice for STWs to have nitrate removal (Jones, D. (Wessex Water) pers. comm. 2018). Therefore, an increasing population would result in an increase in nitrates from STW effluent which drain into the Rivers Frome and Piddle. Biotic and abiotic processes result in the fractionation of ^{15}N which return different ^{15}N:^{14}N ratios for different nitrogen sources (Bedard-Haughn et al., 2003). The value of $\delta^{15}N$ can indicate its source. Values <8 suggest the source of $\delta^{15}N$ is from agricultural fertilisers and soils while values >8 suggest the source of $\delta^{15}N$ is from animal waste and sewage (Heaton, 1986; Bedard-Haughn et al., 2003). $\delta^{15}N$ values remain below 8 post ca. 1970, with both FRM4 and PID1 values only nearing or reaching 8 post ca. 2000. This suggests that the source of $\delta^{15}N$ still remains to be from agricultural fertiliser and soils during Phase 3, with sewage becoming the more prominent source of $\delta^{15}N$ post ca. 2000.

$\delta^{13}C$ continues to decrease during Phase 3 as large quantities of nutrients promote little fractionation of carbon for algal productivity. However, in PID1, post ca. 2000, both $\delta^{13}C$ and $\delta^{15}N$ begin to stabilise, suggesting nutrients within the groundwater of the catchment of the River Piddle are starting to diminish. A diminished nutrient supply would not necessarily reduce algal productivity as fractionation of carbon would allow the algae to grow using the ^{13}C. Future trends may exhibit increased $\delta^{13}C$ when fractionation of carbon will be required to sustain algal productivity. The decline in C/N post ca. 1970 suggests increased autochthonous productivity as the supply of nutrients from the catchment itself diminishes and algal productivity relies primarily upon the nutrient availability within the water column. The C/N vs $\delta^{13}C$ for both FRM4 and PID1 also suggests a transition to freshwater and/or freshwater algae source of carbon post ca. 1970s, suggesting catchment sourced nutrients are declining (Figure 6.2 and Figure 6.4).

Si concentrations in FRM4 remain high and stable post ca. 1970 (Figure 6.3). It has been determined terrestrial input has reduced post ca. 1970 so the high Si concentrations could be an indication of increased diatom productivity. Within PID1, the Si concentrations increase post ca. 1970 to its peak ca. 2000 (Figure 6.5). Again, it has been determined terrestrial contribution to PID1 has reduced post ca. 1970 so it can be assumed the increase in Si concentrations could be an indication of increased diatom productivity.

6.2.2.2 Algal response

Pigments have been measured in both FRM4 (Figure 6.6) and PID1 (Figure 6.7), with FRM4 also being subjected to diatom analysis (Figure 6.8). This section discusses the drivers of algal community change within the FRM4 and PID1 records.

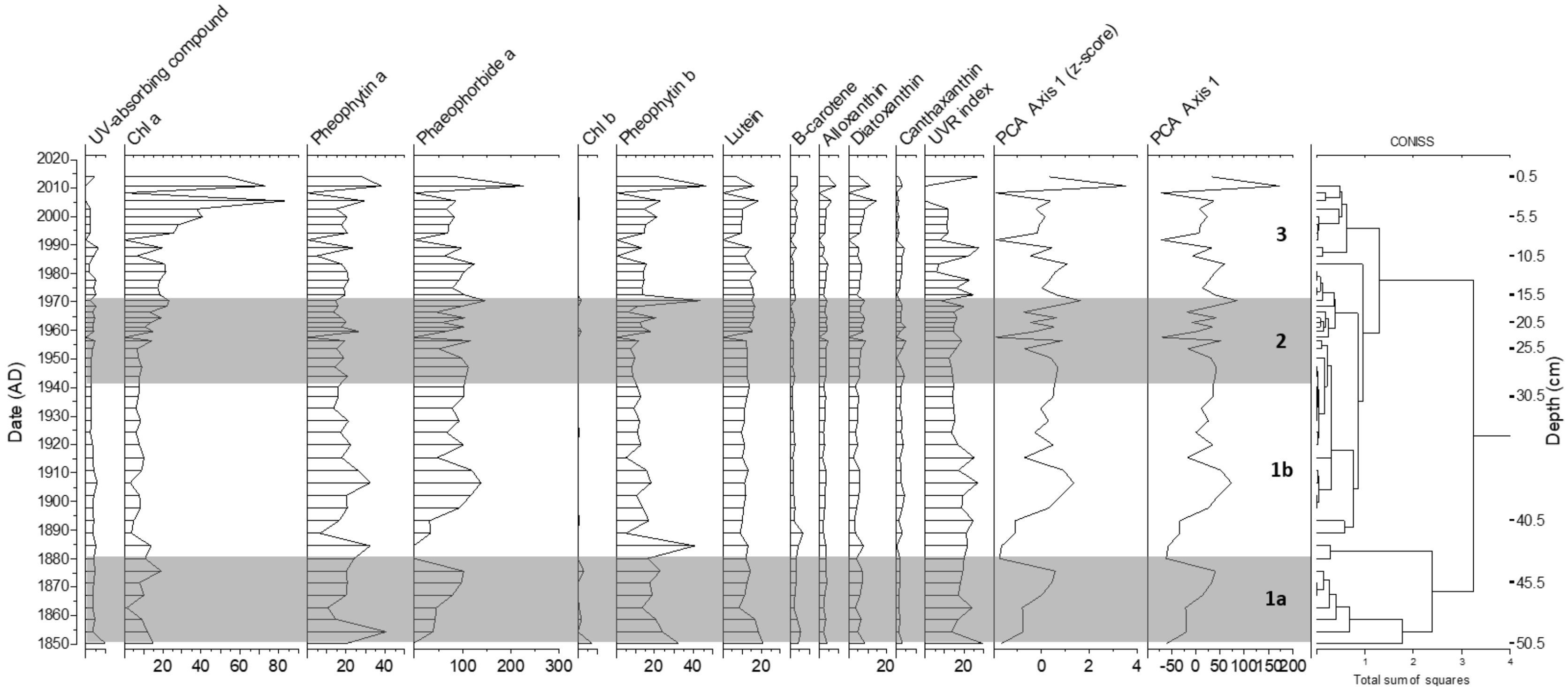


Figure 6.6: FRM4 pigments, PCA axis 1 and CONISS (right) with shading to indicate phases discussed within the text. Units: nmol pigment g^{-1} organic matter.

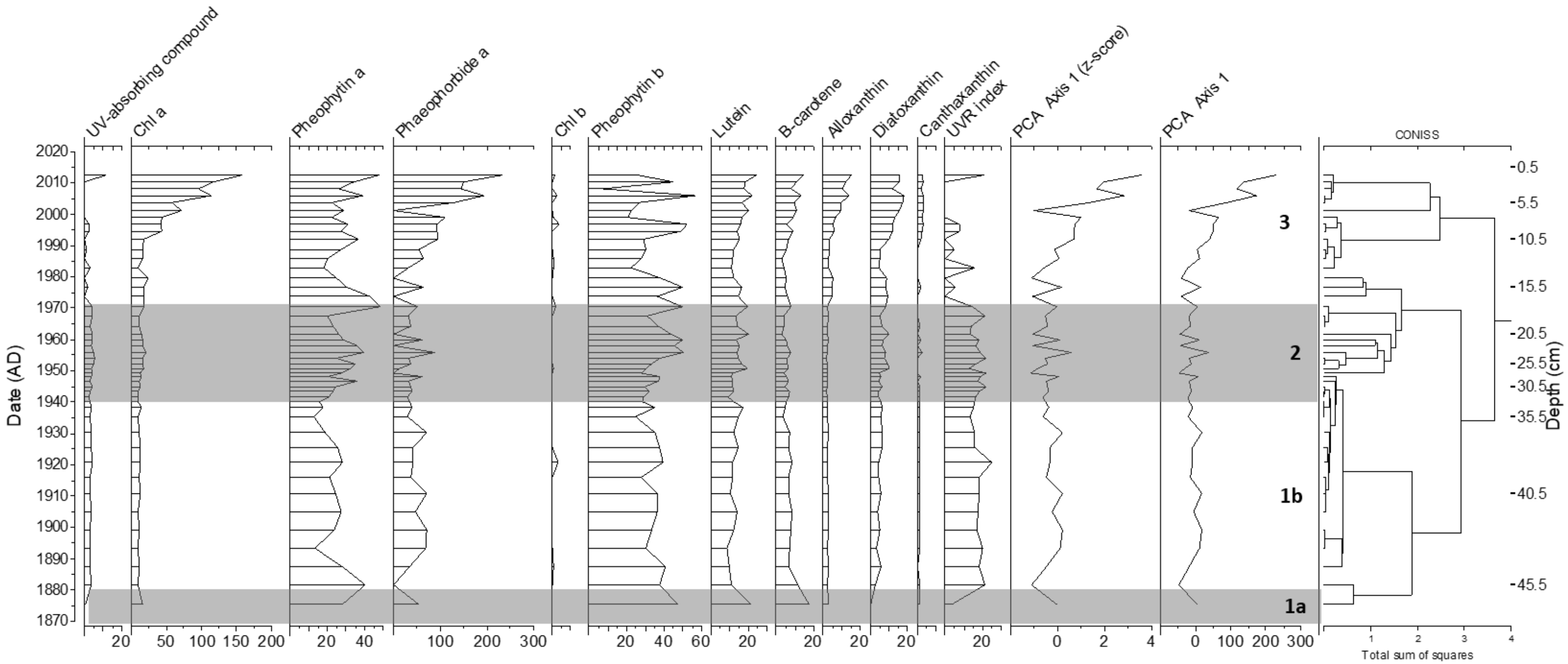


Figure 6.7: PID1 pigments, PCA axis 1 and CONISS (right) with shading to indicate phases discussed within the text. Units: nmol pigment g^{-1} organic matter.

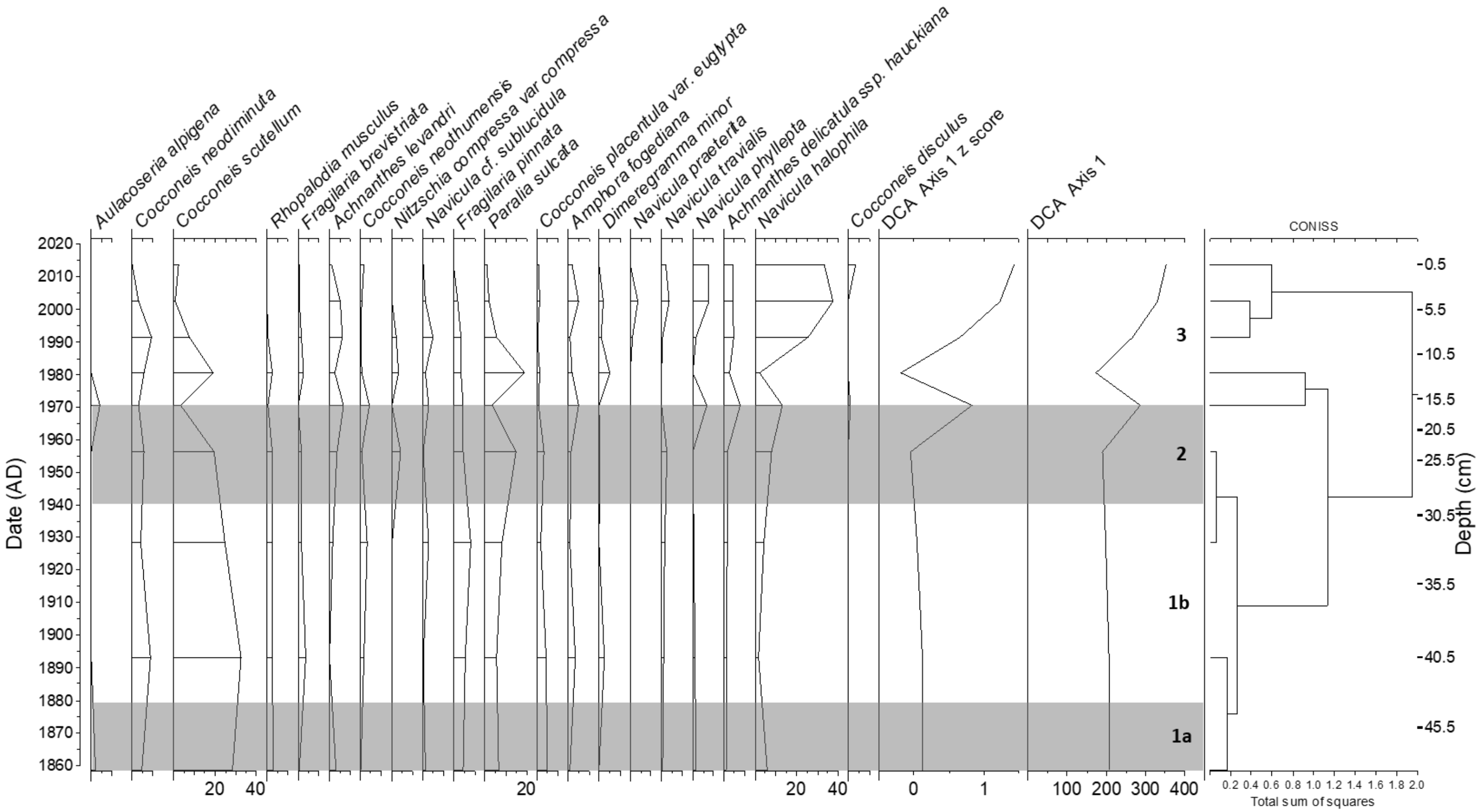


Figure 6.8: FRM4 diatom counts (%) for species occurring >3%, DCA axis 1 and CONISS (right) with shading to indicate phases discussed within the text.

6.2.2.2.1 Phase 1a and b ca. 1850-1940

Figure 6.6 shows stability within the algal record through Phase 1a with the exception of Pheophorbide a which peaks ca. 1875. The isotope data for FRM4 suggests productivity may increase towards the top of Phase 1a which could be potentially driven by the increase of Pheophorbide a which is affined to algae.

Stability continues through Phase 1b for both FRM4 (Figure 6.6) and PID1 (Figure 6.8) as indicated by the limited variability within the pigment assemblages for both records (Figure 6.6 and Figure 6.7) and the diatom species composition in FRM4 (Figure 6.8). This is supported by the relative stability within the geochemical record ca. 1880-1940.

6.2.2.2.2 Phase 2 – ca. 1940-1970

Phase 2 of PID1 demonstrates a relatively stable environment with regards to algal production. There is a slight increase in algal pigments such as Diatoxanthin suggesting a slight trend towards increased algal productivity during this phase. Within FRM4 there are signs that ca. 1955 there is a transition to more algal production as evidenced by increased Chl *a* which indicates higher plants or photosynthetic algae (Table 3.5). The presence of other algal pigments, Lutein/Zeaxanthin, β-carotene and Diatoxanthin, suggests that the increase in Chl *a* is not a function of increased plant matter but an increase in algal productivity. Pigment quantities were standardised against organic matter and should therefore negate a change in pigment numbers as a result of increased SAR, i.e. the increase in pigments during the ca. 1940-1970s high SAR period should not be a result of increased sedimentation storing more pigments.

The diatom species assemblage of FRM4 within Phase 2 demonstrates a shift in species composition with a decrease in species which are abundant within the older part of the record, e.g. *Cocconeis scutellum*, and an increase in species which become more abundant towards the top of the record, e.g. *Navicula halophila*. Even minor changes in environmental factors, e.g. nutrient availability and salinity, usually result in measurable shifts in diatom species (Snoeijs, 1999), therefore any transition in species composition within FRM4 during Phase 2 suggests a change in environmental conditions. The change in diatom species assemblage also supports the notion that the increase in Chl *a* is not a result of increased plants rather than an increase in algae as there is a move to more unattached diatom species rather than diatoms which attach to plants (Figure 6.9). During Phase 2 there is an increase in *Paralia sulcata*, until ca. 1970 when it declines and increases again. *Paralia sulcata* is often associated with brackish and marine environments (Mcquoid & Nordberg, 2003), the increase of this species during this period could indicate increased marine influence within the River Frome estuary area. Sea level does increase until ca. 1970 when it declines and then increases again (Figure 5.1). However, *Paralia sulcata* is also associated with periods of increased vertical mixing which bring nutrient rich, saline water to the surface (Gebühr et al., 2009). It has already been discussed that post ca. 1940s there was an increase in nutrients entering the estuary due to the intensification of agriculture, this coupled with an increasing sea level rise could have promoted the development of *Paralia sulcata* during Phase 2 and again after the decrease in sea level ca. 1970.

FRM4 and PID1 SARs increased ca. 1940-1970 due to increased sediment source from the catchment due to intensified agricultural practices (Section 5.2.2.1). The geochemical record of FRM4 (Figure 6.3) and PID1 (Figure 6.5) suggested an increase in terrestrially sourced nutrients ca. 1940-1970 (Section 6.2.2.1.3), e.g. from artificial fertilisers and sediment. The algal record ca. 1940-1970 supports the notion of a changing environment, e.g. increased nutrients, with a change in diatom species composition and the beginning of a transition to an increase in algal affined pigments.

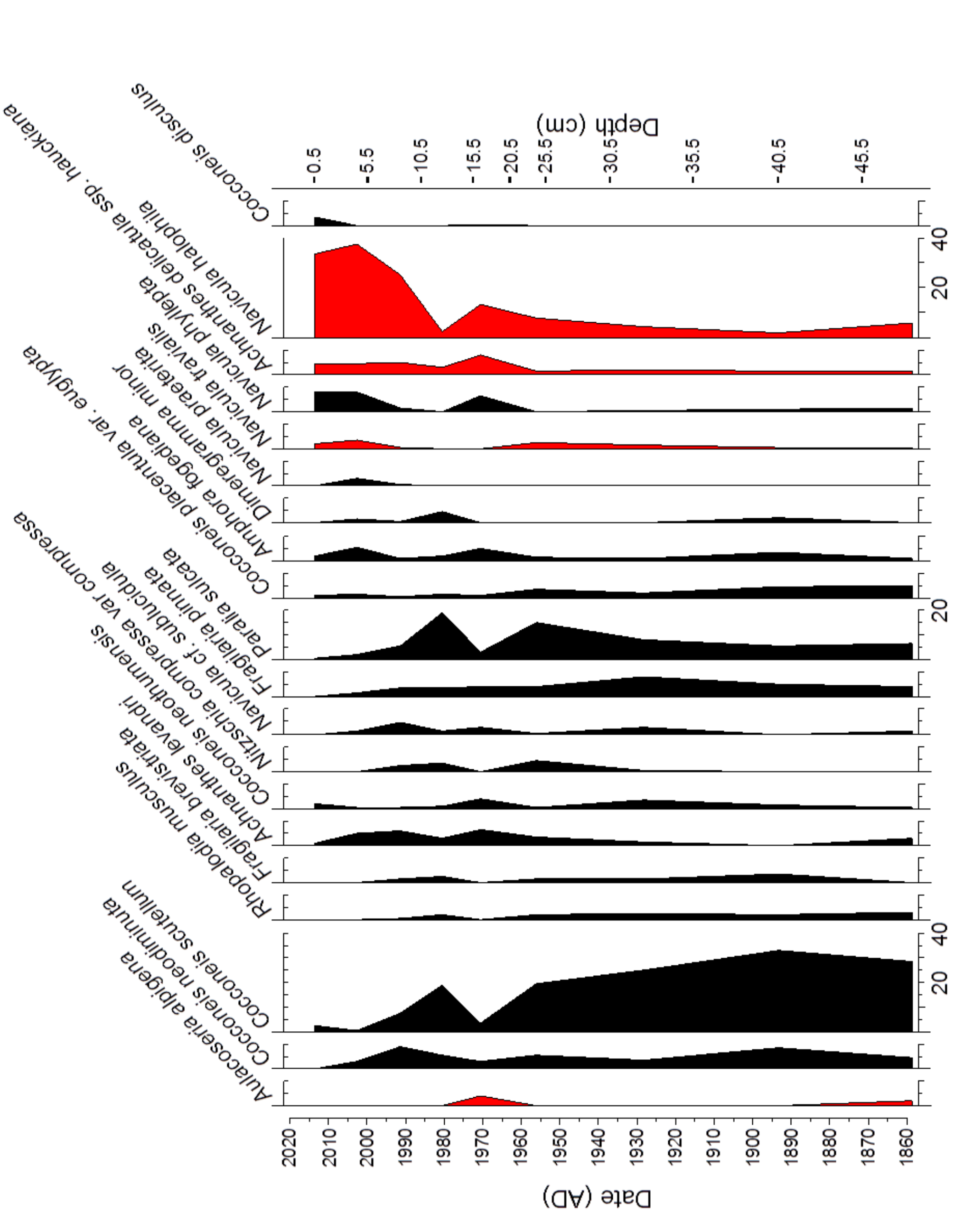


Figure 6.9: FRM4 diatom counts (%) for species >3%. Red shading indicates unattached diatoms.

6.2.2.2.3 Phase 3 – post ca. 1970

FRM4 and PID1 exhibit increased algal production over time through Phase 3 with indicators of eutrophication from ca. 2000s. Eutrophication is indicated within PID1 by the increase in pigments, noticeably of Chl *a* post ca. 1990 (Figure 6.7). After ca. 1990, the majority of all pigments increase in quantity in FRM4 and PID1, including those derived from algae (Figure 6.6 and Figure 6.7).

The increase in Diatoxanthin supports the notion that the increase in algae associated pigments is a product of increased algal production rather than an issue with sample contamination due to the sole measurement of living algae on the surface of the core. Diatoxanthin is produced as part of the degradation of the pigment Diadinoxanthin due to the latter's exposure to light (Kooistra et al., 2007). Therefore, the presence of Diatoxanthin, i.e. the degradative product, provides evidence that the pigment present within the sediment is a record of older, dead diatoms, not currently living diatoms.

PID1 pigment Principal Components Analysis (PCA) axis 1 scores increase post ca. 1980, with the most notable axis score increase occurring post ca. 2000 (Figure 6.7). FRM4 pigment axis 1 scores change most notably ca. 2010 when it peaks (Figure 6.6). These shifts in PCA axis 1 scores suggest the composition of the pigments most noticeably change in PID1 post ca. 1980 and ca. 2000 and in FRM4 ca. 2010, in accordance with increased pigment numbers, i.e. a result of increased productivity. Detrended Correspondence Analysis (DCA) axis 1 scores for FRM4 diatoms suggests a change in community composition ca. 1990 (Figure 6.8). This shift ca. 1990 suggests the driver of diatom species composition has continued throughout the rest of the record due to the ever-diverging axis 1 scores. A likely driver could be the continual increase in nutrients supporting the notion of increased algal blooms post ca. 1990.

The isotope record of PID1 suggests stabilisation of nutrient enrichment post ca. 2000 (Section 6.2.2.1.4). Productivity may though increase should algae start to use $\delta^{13}C$ for production. Should ^{12}C:^{13}C reach equilibrium, and therefore appear to suggest $\delta^{13}C$ is stabilising, productivity may therefore become $\delta^{13}C$ dominated. An increase in pigment abundance post ca. 2000 in FRM4 and PID1 implies the commencement/intensification of eutrophication (Figure 6.6 and Figure 6.7). The UVR index of both FRM4 and PID1 decreases at this time suggesting the water clarity has decreased. A decline in water clarity would be an expected result of an increase in algal blooms preventing sunlight to penetrate into the water column.

Within FRM4, ca. 2000 there is a decline in Canthaxanthin, an indicator of cyanobacteria. Within the diatom record, there is also a decrease in *Rhopalodia musculus*. This species of diatom and cyanobacteria are nitrogen fixing (Stancheva et al., 2013). The decrease in these suggests there may be an increase in nitrogen within the system which allows other species to outcompete for resources and thrive, reducing the population of *Rhopalodia musculus* and cyanobacteria.

Within Phase 3, the abundance of *Cocconeis scutellum* is less than previous in the record as its abundance notably declines post ca. 2000 (Figure 6.8). *Cocconeis scutellum* is a tightly attaching epiphyte which thrives in lower nutrient conditions where there is less competition (Buric et al., 2004). The decline in *Cocconeis scutellum* towards the top of the record suggests that there is an increase in nutrient availability, allowing other diatom species to outcompete *Cocconeis scutellum*, therefore reducing its abundance during eutrophication. *Navicula halophila* is a diatom species which tolerates high nitrogen concentrations and is an indicator of eutrophic state (Van Dam et al., 1994) and its abundance increases within Phase 3 ca. 1990 and reaches its peak abundance ca. 2000 (Figure 6.8). The increase in *Navicula halophila* during Phase 3 provides further evidence of increased algal productivity in nutrient rich waters and eutrophication.

Changes within the algal record of both FRM4 and PID1 within Phase 3 discussed above are corroborated by the constrained cluster analysis (CONISS) of the pigments and diatom records. The CONISS of PID1 pigments suggest a change ca. early 1990s from preceding pigment communities, given the separation between pre- and post ca. 1990 samples at the greatest sum of squares difference, ca. 3.75 (Figure 6.7). Post ca. 1990, there is again a difference between pre- and post 2000 communities at the ca. 2.75 sum of squares difference. These temporal markers agree with the increase in pigment abundance from the ca. 1990s before they peak from ca. early 2000s, further suggesting eutrophication from ca. 2000s. The CONISS of FRM4 (Figure 6.6) suggests a split post ca. early 1990s, this is when the pigments, in particular Chl *a* and Diatoxanthin, start to increase. There is also a split between pre- and post ca. 2000s pigment communities in the CONISS, coinciding with the increase to peak abundance in nearly all pigments. The CONISS of FRM4 diatoms, while recorded at a lower resolution than the pigments, also shows a split pre- and post ca. 1990s communities and pre- and post ca. 2000s communities (Figure 6.8) further supporting the notion of eutrophication within the Rivers Frome and Piddle estuary.

The isotopic records for FRM4 and PID1 provides evidence of continued supply of nutrients post ca. 1970, likely a result of the groundwater nature of Poole Harbour's catchment resulting in lag times between supply and effect. The continued nutrient supply is likely to result in further increased algal productivity. This notion is supported by the algal records presented within this section. Pigment records for PID1 (Figure 6.7) and pigment and diatom records for FRM4 (Figure 6.6 and Figure 6.8) suggest an increasing abundance of algae post ca. 1990 with signs of eutrophication ca. 2000s.

6.2.2.3 Summary

The intensification of agricultural practices ca. 1940-1970s caused SARs to increase in FRM4 and PID1 (Section 5.2.2.1) but SARs declined post ca. 1970s when farming intensity declined (Section 5.2.3.1). The isotope record demonstrates the period of intensified farming ca. 1940-1970 resulted in increased nutrient supply to the estuary. These nutrients promoted algal productivity that continued post ca. 1970, as the groundwater dominated catchment mean causes and effects do not occur over identical temporal scales. Ca. 1990, an increase in algal productivity occurred with post ca. 2000s identified as eutrophic conditions. Eutrophication is evidenced by the greatest abundance of algal derived pigments and indicators within the diatom species assemblage, e.g. the decline in *Rhopalodia musculus* and *Cocconeis scutellum* and increase in *Navicula halophila*. The C/N vs $\delta^{13}C$ of FRM4 and PID1 suggests that in recent decades, the contribution of nutrients has derived from an increase in freshwater algae supporting the notion of eutrophication.

6.2.3 The industrial catchment

6.2.3.1 Nutrient response

Holes Bay is surrounded by urban and industrial activity, the pollutants from which enter Holes Bay. Within Chapter 5 it was discussed how changes in the industrial development around Holes Bay influenced SARs in HB1. This section presents palaeoenvironmental evidence to demonstrate how industrial development has also affected nutrient dynamics within Holes Bay (Figure 6.10 and Figure 6.11).

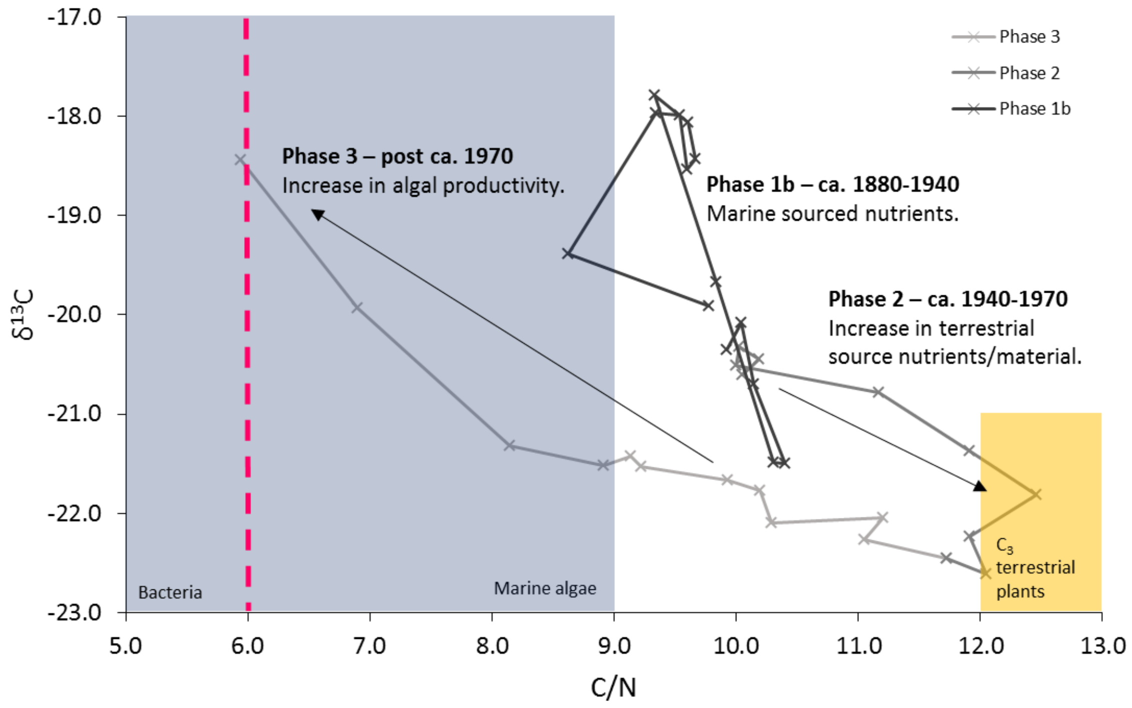


Figure 6.10: HB1 C/N vs $\delta^{13}C$ represented with shaded line demonstrating change over time with regards to phases discussed within the text: Phase 1b – ca. 1880-1940, Phase 2 – ca. 1940-1970 and Phase 3 – post ca. 1970. Note: boxes illustrate the $\delta^{13}C$ and C/N typical ranges for organic inputs to coastal environments (Lamb et al., 2006).

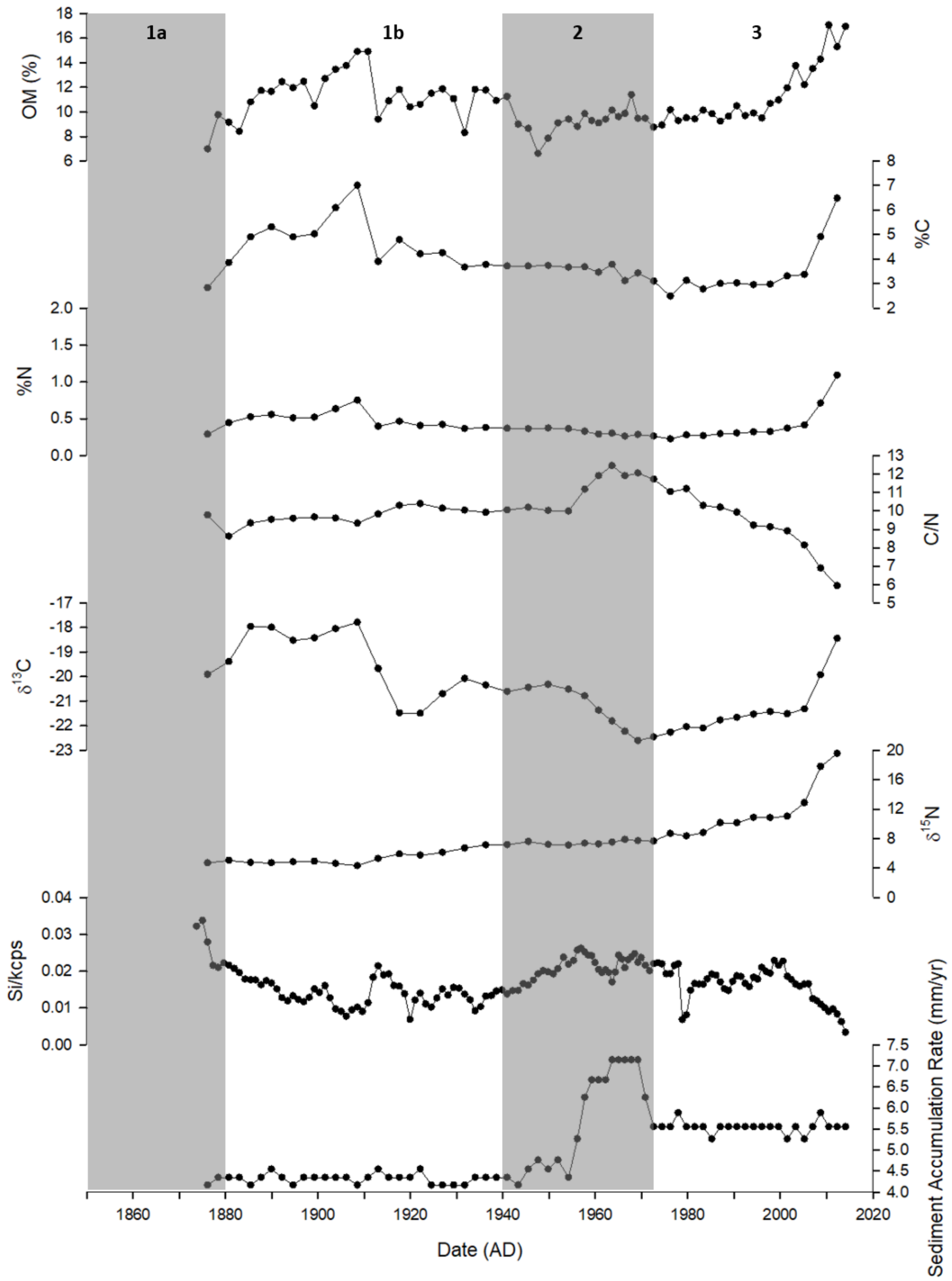


Figure 6.11: HB1 geochemical data and sediment accumulation rates with shading to indicate phases discussed within text.

6.2.3.1.1 Phase 1b – ca. 1880-1940

Figure 6.10 illustrates nutrient sources are more marine driven than freshwater when compared with FRM4 and PID1 (Figure 6.2 and Figure 6.4). A marine dominance is expected as Holes Bay does not have a major freshwater supply. From ca. 1880-1940, Phase 1b, HB1 is dominantly marine sourced.

High $\delta^{13}C$ from ca. 1880-1910 could either indicate high terrestrial input or high productivity (Figure 6.11). As stated, C/N vs $\delta^{13}C$ suggests nutrient input is predominantly marine rather than terrestrially sourced (Figure 6.10). High %C suggests that the high values of $\delta^{13}C$ are an indication of increased productivity causing an increase in organic matter (Figure 6.11). Ca. 1920s, there is a decline in $\delta^{13}C$, %C, organic matter and a slight decline in %N, suggesting a decrease in productivity. In 1922, Poole STW was constructed with a biofilter (Jones, D. (Wessex Water) pers. comm. 2017). The addiction of a biofilter can explain the decline in productivity as it would have reduced the nutrient content of the sewage, thereby restricting algal productivity.

6.2.3.1.2 Phase 2 – ca. 1940-1970

During ca. 1940-1970, the SAR of HB1 increased, driven by increased shipping manufacturing, erosion on the heathlands surrounding Holes Bay and land reclamation for increased infrastructure (Section 5.2.2.2).

The HB1 geochemical record shows $\delta^{13}C$ values are higher ca. 1940 – mid-1950s, suggesting an increase in terrestrial material (Figure 6.11). Ca. mid-1950s, $\delta^{13}C$ values decrease while C/N increases (Figure 6.11) alongside the second SAR increase (Section 5.2.2.2). The increased SARs and C/N values suggest a further increase in terrestrial sourced material entering Holes Bay ca. mid-1950s supported by the transition to more terrestrial sourced material in HB1 during Phase 2 in Figure 6.10. As discussed, an increase in $\delta^{13}C$ values would be expected to accompany an increase in terrestrial material. However, in HB1, $\delta^{13}C$ decreases alongside the C/N increase ca. mid-1950s. As in Section 6.2.2.1.3, decreased $\delta^{13}C$ values could indicate an excess of nutrients entering the system, meaning less fractionation of carbon is required for productivity. $\delta^{15}N$ values are high and increasing, suggesting an increase in productivity ca. mid-1950s. The notion of increased productivity is further supported by an increase in silica which indicates an increase of related siliceous algae, i.e. diatoms. The lack of biogenic silica and diatom analysis on HB1 prevents this relationship to silica being explored further. The increase in silica could also be related to the increased terrestrial material entering Holes Bay from the catchment.

High $\delta^{15}N$ values (>8) suggest the source of the nitrogen is sewage related as opposed to purely soil and/or fertiliser (Heaton, 1986; Bedard-Haughn et al., 2003). The expansion of Poole STW ca. late 1950s/early 1960s would reduce nutrients from sewage entering Holes Bay, but it would not completely eradicate them as nitrogen removal was not introduced until 2008 (Jones, D. (Wessex Water) pers. comm. 2017). Figure 2.16 shows population post ca. 1950s continually increased, which would be expected to apply associated pressure on Poole STW and perhaps an associated increase in nutrients from sewage entering Holes Bay. The expansion of Poole STW would account for the gradual increase in $\delta^{15}N$ rather than a dramatic shift in accordance with increasing population demands.

6.2.3.1.3 Phase 3 – post ca. 1970

HB1 SARs declined post ca. 1970 (Section 5.2.3.2) mainly as a consequence of reduced erosion on the surrounding heathlands.

A continually increasing population post ca. 1970s (Figure 2.16), would be expected to place further demand on Poole STW. $\delta^{15}N$ values continue to increase through Phase 3 (Figure 6.11), indicating increased productivity likely resulting from sewage based on the $\delta^{15}N$ values (Heaton, 1986; Bedard-Haughn et al., 2003).

$\delta^{13}C$ increases throughout Phase 3 also suggesting an increase in productivity supported by an increasing organic matter content and decreasing C/N (Figure 6.11). Increasing $\delta^{13}C$ and decreasing C/N suggests productivity is requiring the fractionation of carbon and the productivity is autochthonous.

Post ca. 2000s, the geochemical record dramatically shifts with $\delta^{13}C$, $\delta^{15}N$, %C, %N and organic matter all increasing rapidly coupled with a decrease in C/N (Figure 6.11). The rapid nature of these changes suggests Holes Bay became eutrophic post ca. 2000s. Figure 6.10 supports this notion with the directional change of the C/N vs $\delta^{13}C$ moving towards marine algae and bacteria post ca. 2000.

An increase in silica concentration of the sediment would be expected with an increase in algal productivity during eutrophication. However, as indicated in Figure 6.11, the silica concentration declines post ca. 2000s. The silica decline may be a result of increased water content in the top of the core reducing element detection, as supported with the increased concentrations of Cl and Br post ca. 2000 (Figure 6.12). The decrease in silica could also correspond to the decrease in terrestrial material entering Holes Bay as catchment erosion decreases.

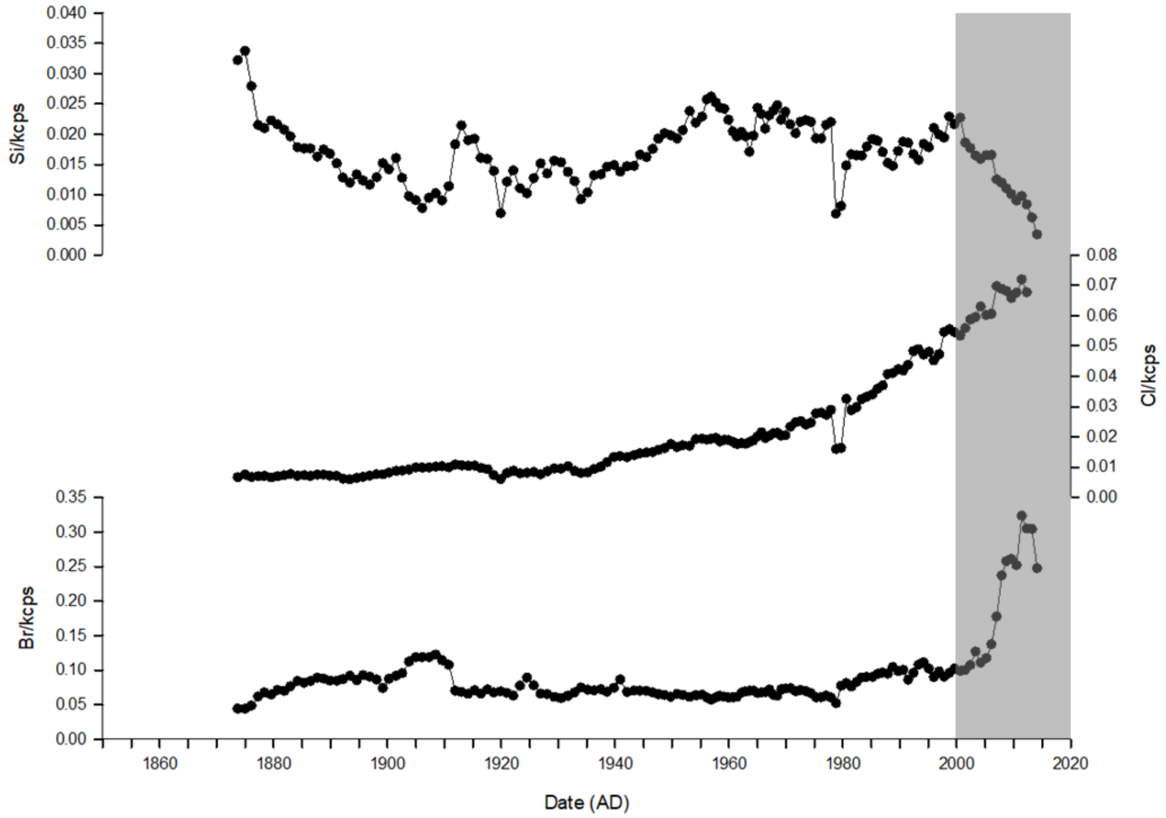


Figure 6.12: Itrax element concentration data of Si, Cl and Br for HB1 with shading to indicate high water content at the top of the core.

6.2.3.2 Algal response

Pigments have been measured in HB1 and provide a record of algal productivity change over time (Figure 6.13). This section discusses algal productivity response to changes in nutrient supply to Holes Bay.

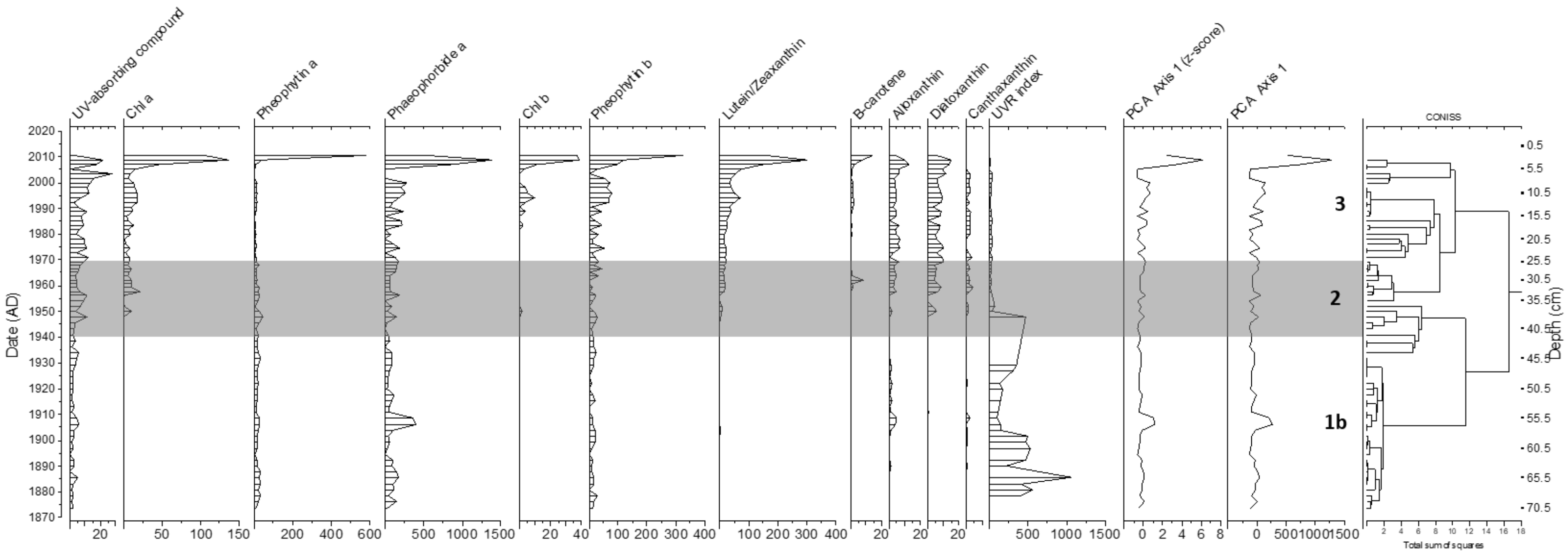


Figure 6.13: HB1 pigments, PCA axis 1 and CONISS (right) with shading to indicate phases discussed within the text. Units: nmol pigment g^{-1} organic matter.

6.2.3.2.1 Phase 1b – ca. 1880-1940

Activity within the pigments during Phase 1b is masked by the high values detected at the top of the core (Figure 6.13). Therefore Figure 6.14 shows HB1 pigments with post ca. 2000 measurements removed to allow the exaggeration of the pigment measurements during Phase 1b.

The high UVR index within Phase 1b suggests this is the period with the greatest water clarity (Figure 6.14). There is little activity within the pigments suggesting this is a stable phase with regards to algal productivity except a peak in Pheophorbide a ca. mid-1900 to ca. 1910. During this peak there is also an increase in Alloxanthin. These pigments are affined to algal productivity and their increase suggests a temporary increase in algal productivity ca. mid-1900 to ca. 1910. This notion is supported by the geochemical record which at the same time detects the peak of Phase 1b in %c, %N, $\delta^{13}C$ and organic matter content (Figure 6.11).

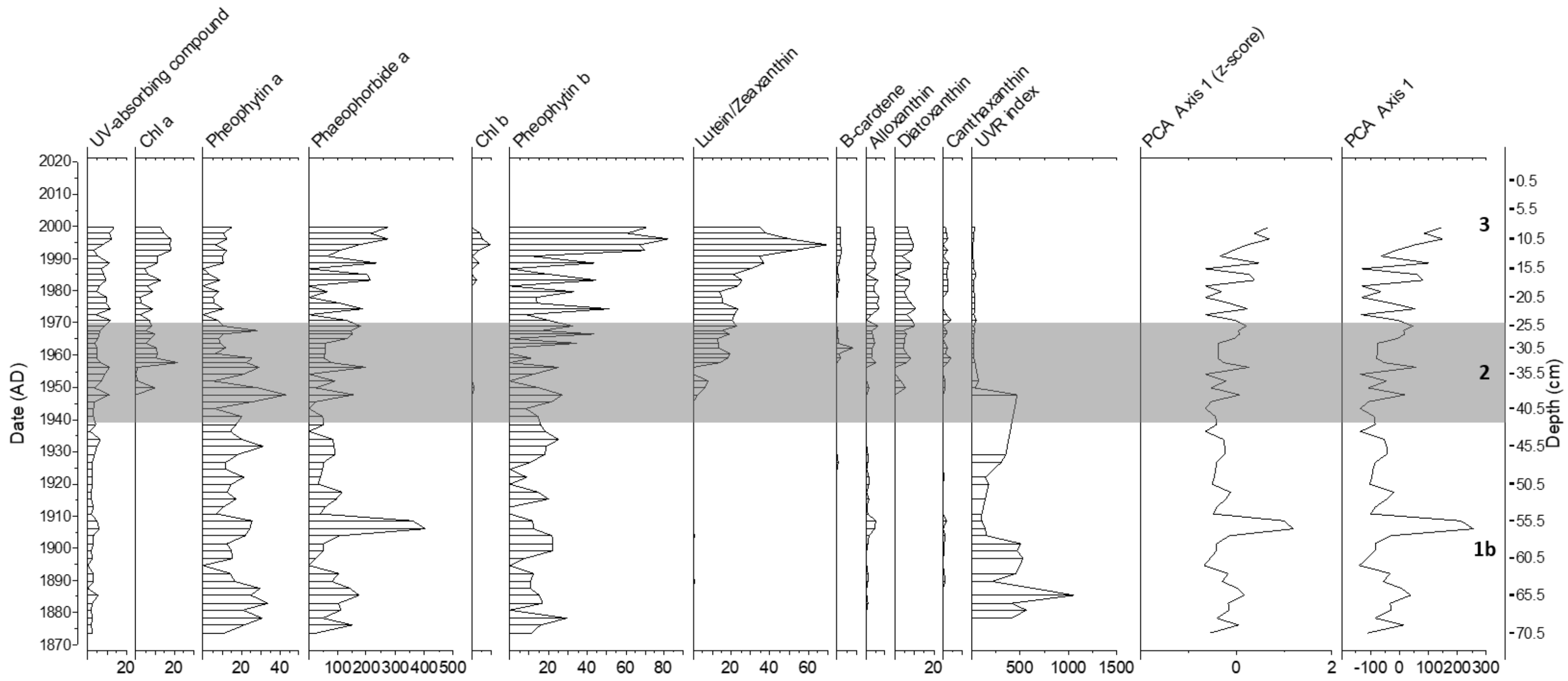


Figure 6.14: HB1 pigments and PCA axis 1 with shading to indicate phases discussed within the text. Post ca. 2000 measurements have been removed to allow exaggeration of pigment measurements. Units: nmol pigment g^{-1} organic matter.

6.2.3.2.2 Phase 2 – ca. 1940-1970

Chl *a* increases through Phase 2 (Figure 6.14), likely a result of an increase in algal productivity given the accompanying increase of pigments with algal affinity (Lutein/Zeaxanthin, Alloxanthin, Diatoxanthin and Canthaxanthin). The UVR index also declines during Phase 2 suggesting an increase in algae preventing sunlight penetrating the water column.

The pigment record (Figure 6.14) supports the geochemical evidence (Section 6.2.3.1.2) in that both datasets suggest an increase in productivity during Phase 2.

6.2.3.2.3 Phase 3 – post ca. 1970

The UVR index remains low throughout Phase 3, suggesting algal presence reduced light within the water column (Figure 6.13). All pigments are present within Phase 3, increasing in abundance towards the top of the phase, i.e. towards present. Ca. mid-2000s there is a peak in all pigments except Canthaxanthin, which declines in nitrogen rich environments (Stancheva et al., 2013). The high abundance of algae affined pigments and decline in Canthaxanthin therefore indicates a signal of eutrophication post ca. mid-2000s. The onset of eutrophication is also identified by the PCA axis 1 z-scores which demonstrate a divergence from the norm ca. mid-2000s, indicating a shift in pigment composition, i.e. as likely caused by eutrophication (Figure 6.13). HB1 CONISS demonstrates a split pre- and post ca. 2000s pigment communities (Figure 6.13), e.g. as a likely result of eutrophication.

The geochemical record suggests an increase in algal productivity throughout Phase 3, with indicators of eutrophication when productivity peaks post ca. 2000s (Section 6.2.3.1.3). The pigment record supports this notion with increased algal abundance during Phase 3 and dramatic increases in pigments ca. 2000s (Figure 6.13).

6.2.3.3 Summary

The source of nutrients within Holes Bay has been determined to principally derive from sewage treatment effluent. While Poole STW has expanded, it cannot remove all nutrients due to economic constraints (Barden, R. (Wessex Water) pers. comm. 2014, Isgar, L. (Wessex Water). pers. comm. 2017 and Jones, D. (Wessex Water) pers. comm. 2018). Thus, with an increase in population, an increase in nutrient supply has been detected within the sedimentary record of HB1.

The HB1 pigment record indicates increased algal productivity ca. mid-1950s, continuing to present. Ca. mid-2000s, there is evidence that Holes Bay has become eutrophic due to nutrient enrichment promoting algal productivity.

The dramatic shift in the geochemical record and increase in pigment abundance post ca. 2000s suggests that nutrient enrichment within Holes Bay reached a critical point which caused a shift to a eutrophic state.

The directional changes in the geochemical record suggest Holes Bay is driven by productivity rather than the source of the nutrients. A productivity driver differs to that of FRM4 and PID1, where the source of nutrients drives the geochemical record as the excess supply of nutrients allows for little fractionation of carbon and increase in productivity.

6.2.4 Arne – the control site

6.2.4.1 Nutrient source

Chapter 5 discusses how SARs in ARNE5 are influenced by marine sources and agricultural activities within the River Frome and Piddle catchments. This section presents palaeoenvironmental evidence to demonstrate how marine and agricultural changes have influenced nutrient dynamics at Arne (Figure 6.15 and Figure 6.16).

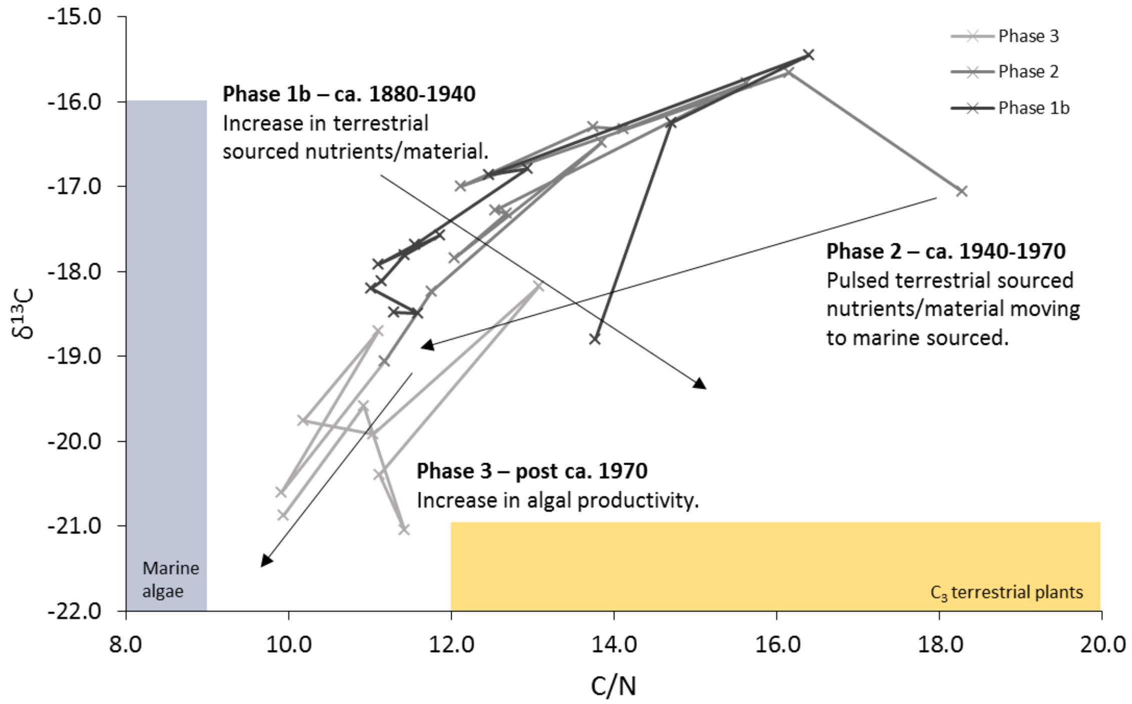


Figure 6.15: ARNE5 C/N vs $\delta^{13}C$ represented with shaded line demonstrating change over time with regards to phases discussed within the text: Phase 1b – ca. 1880-1940, Phase 2 – ca. 1940-1970 and Phase 3 – post ca. 1970. Note: boxes illustrate the $\delta^{13}C$ and C/N typical ranges for organic inputs to coastal environments (Lamb et al., 2006).

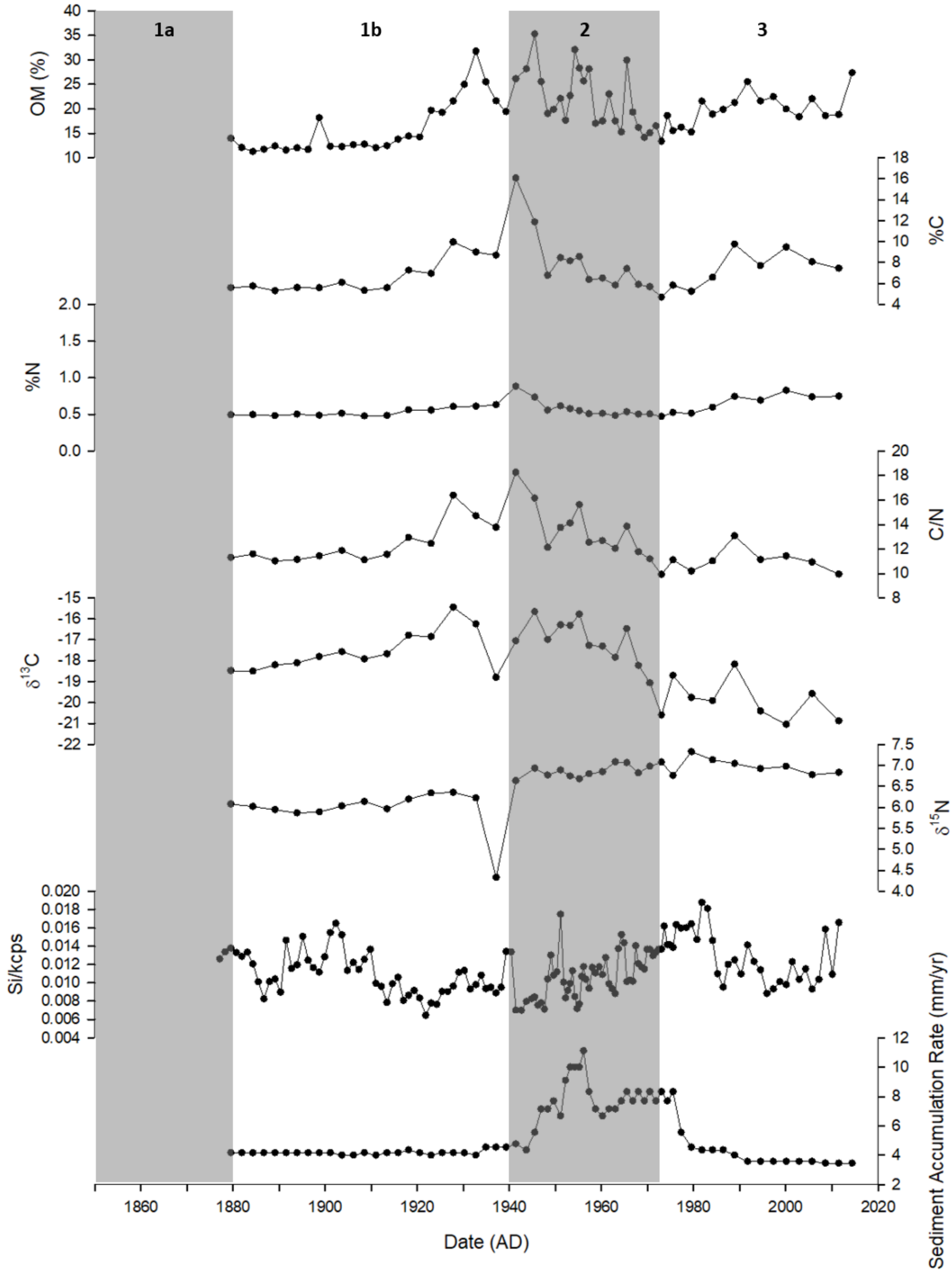


Figure 6.16: ARNE5 geochemical data and sediment accumulation rates with shading to indicate phases discussed within text. Note: %N shows little variation over the record.

6.2.4.1.1 Phase 1b – ca. 1880-1940

Terrestrial sourced material increased ca. 1920, as indicated by increasing C/N, $\delta^{13}C$ and organic matter (Figure 6.16) and the shift towards C_3 terrestrial plants sourced carbon in Figure 6.15.

Increased terrestrial inputs ca. 1910-1930 could be associated with those processes within the River Frome catchment that increased top soil erosion, e.g. military practices and flooding (see Section 5.2.1). These temporary increases in top soil delivery to the harbour were detected in ARNE5 sediment dynamics (Section 5.2.1) and would logically explain the increase in terrestrial sourced material within the harbour and therefore ARNE5.

Figure 5.13 shows increases in Cl and Br and a peak in Zr/Rb indicating an increase in marine influence ca. 1920-1930. It cannot be determined if this is a response to sea level rise as such data are lacking for this time. However, an increase in sea level rise ca. 1920 would allow excess terrestrial material from the River Frome catchment to be easily transported around Poole Harbour and to Arne.

6.2.4.1.2 Phase 2 – ca. 1940-1970

Throughout Phase 2, C/N decreases suggesting an increase in productivity (Figure 6.16). Figure 6.15 demonstrates a directional change towards marine algae, supporting the notion of increased productivity ca. 1940-1970. Silica concentrations also increase ca. 1940-1970 suggesting an increase in siliceous algae, i.e. diatoms, or an increase in terrestrial material from the catchment.

Peaks in organic matter, $\delta^{13}C$ and C/N (Figure 6.16) suggest pulsed spikes of terrestrial sourced material. SARs in ARNE5 increase ca. 1940-1970 as a result of increased agricultural activity within the River Frome and Piddle catchments (Section 5.2.2). Figure 6.17 shows there are peaks in sea level around the same time as the peaks detected in the geochemical record, ca. 1945, 1955 and 1965. Increased sea level could have facilitated the transport of increased sediment from the River Frome and Piddle, resulting in increased terrestrial material reaching Arne.

High levels of $\delta^{15}N$ are detected throughout Phase 2 (Figure 6.16), a likely consequence of increased agricultural activity ca. 1940-1970 within the River Frome and Piddle catchments. Increased nutrient supply likely caused the increase in productivity as suggested by the decline in C/N (Figure 6.16).

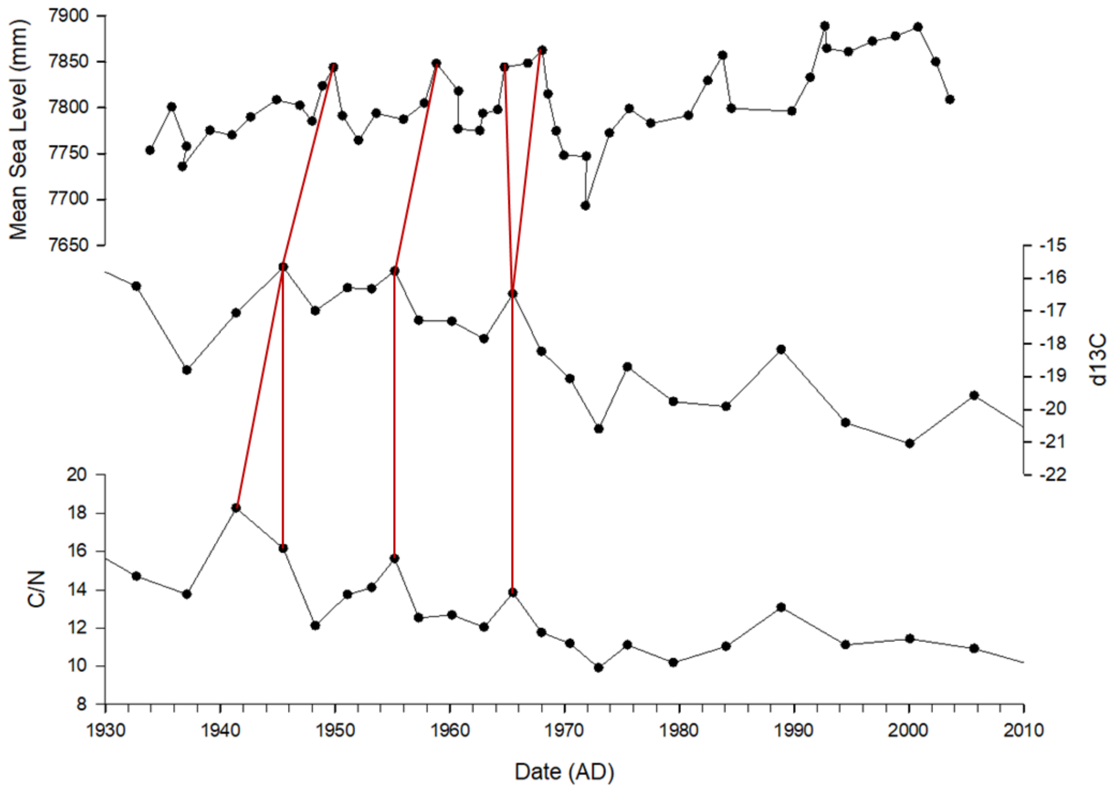


Figure 6.17: Mean sea level for Southampton (Haigh et al., 2009) and ARNE5 $\delta^{13}C$ and C/N. Red lines indicate peaks in sea level coincide with indicators of pulsed terrestrial material spikes ($\delta^{13}C$ and C/N). Where peaks in sea level and geochemical proxies are not at the exact same date, they lie within the date range presented in the age-depth model in Figure 4.8.

6.2.4.1.3 Phase 3 – post ca. 1970

Post ca. 1970, C/N is at its lowest level (Figure 6.16). Continual C/N declines suggest productivity is at its highest post ca. 2000. The C/N vs $\delta^{13}C$ relationship in Figure 6.15 suggest the productivity is being driven primarily by marine algae.

Ca. 1940-1970, organic matter is at its highest level as a combined result of increased productivity and increased terrestrial material. While the organic matter content is lower post ca. 1970, it is increasing throughout Phase 3. The lower values detected are because the organic matter is now primarily being driven by productivity only as the productivity increases. Silica declines post ca. 1980, possibly a result of either decreased productivity of siliceous algae or a decrease in terrestrial material from the catchment. SARs decline in ARNE5 post ca. 1970 likely a result of decreased agricultural activity within the River Frome and Piddle catchments (Section 5.2.3.3) which could account for the decrease in silica post ca. 1980. Silica increases ca. mid-2000s indicating either an increase in diatom productivity or increased terrestrial in wash from the catchment. SARs remain stable in ARNE5 post ca. 1990 (Figure 6.16) and limited changes in $\delta^{13}C$ and a declining C/N suggest the increased silica is not a product of increased terrestrial material from the catchment. Thus, the increase in silica post ca. mid-2000s could be a consequence of increased diatom productivity.

$\delta^{13}C$ declines through Phase 3 (Figure 6.16), the opposite response expected with an increase in productivity. $\delta^{15}N$ values remain high as effects from the increase in agriculture ca. 1940-1970 are still detected. Excess nutrient supply means productivity does not require the fractionation of carbon, thus $\delta^{13}C$ values decrease while excess ^{12}C is used for productivity (Section 6.2.2.1.4). As with FRM4 and PID1, the decrease in $\delta^{13}C$ alongside increased productivity suggests the source of nutrients has greater control on the geochemical record than productivity itself.

6.2.4.2 Algal response

Pigments and diatoms have been analysed in ARNE5 (Figure 6.18 and Figure 6.19). This section discusses how changes in nutrient dynamics drive the algal response of ARNE5.

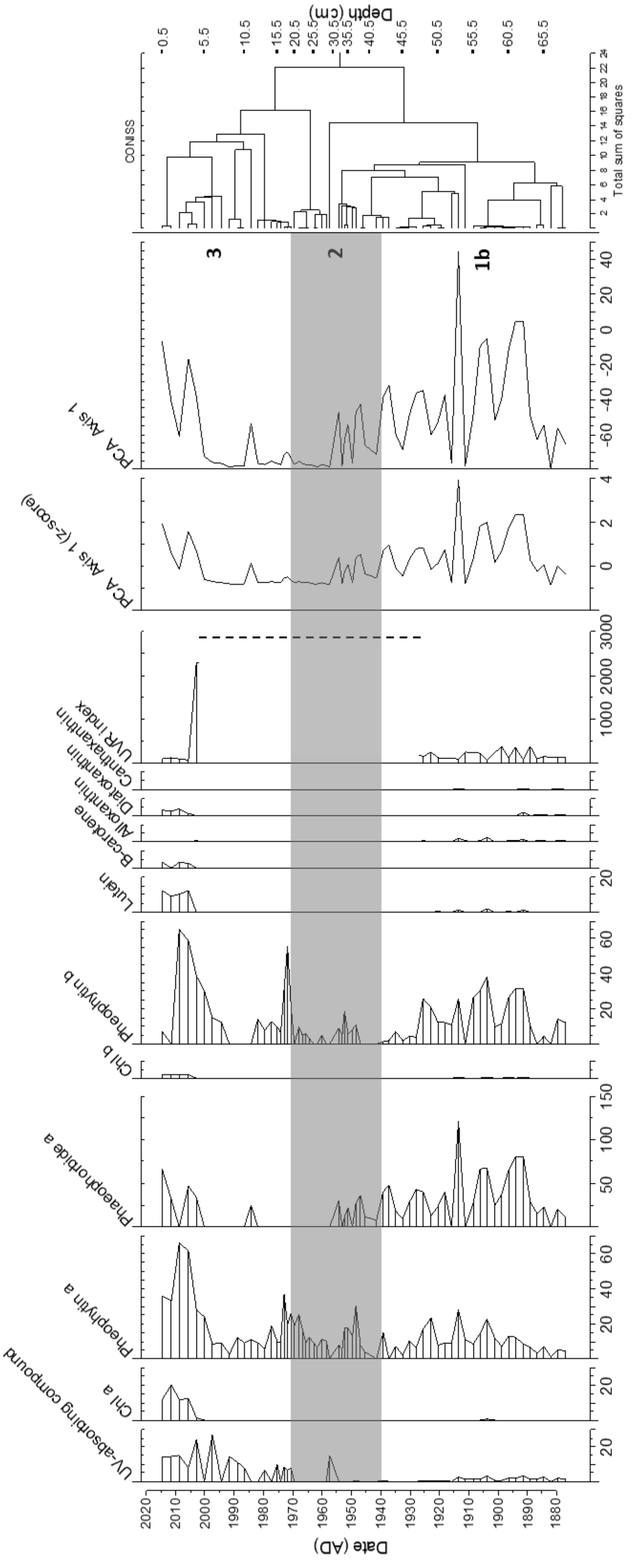


Figure 6.18: ARNE5 pigments, PCA axis 1 and CONISS (right) with shading to indicate phases discussed within the text. Units: nmol pigment g^{-1} organic matter. Note: black dashed line indicates high UVR index where no pigments are present to allow the UVR index to be calculated.

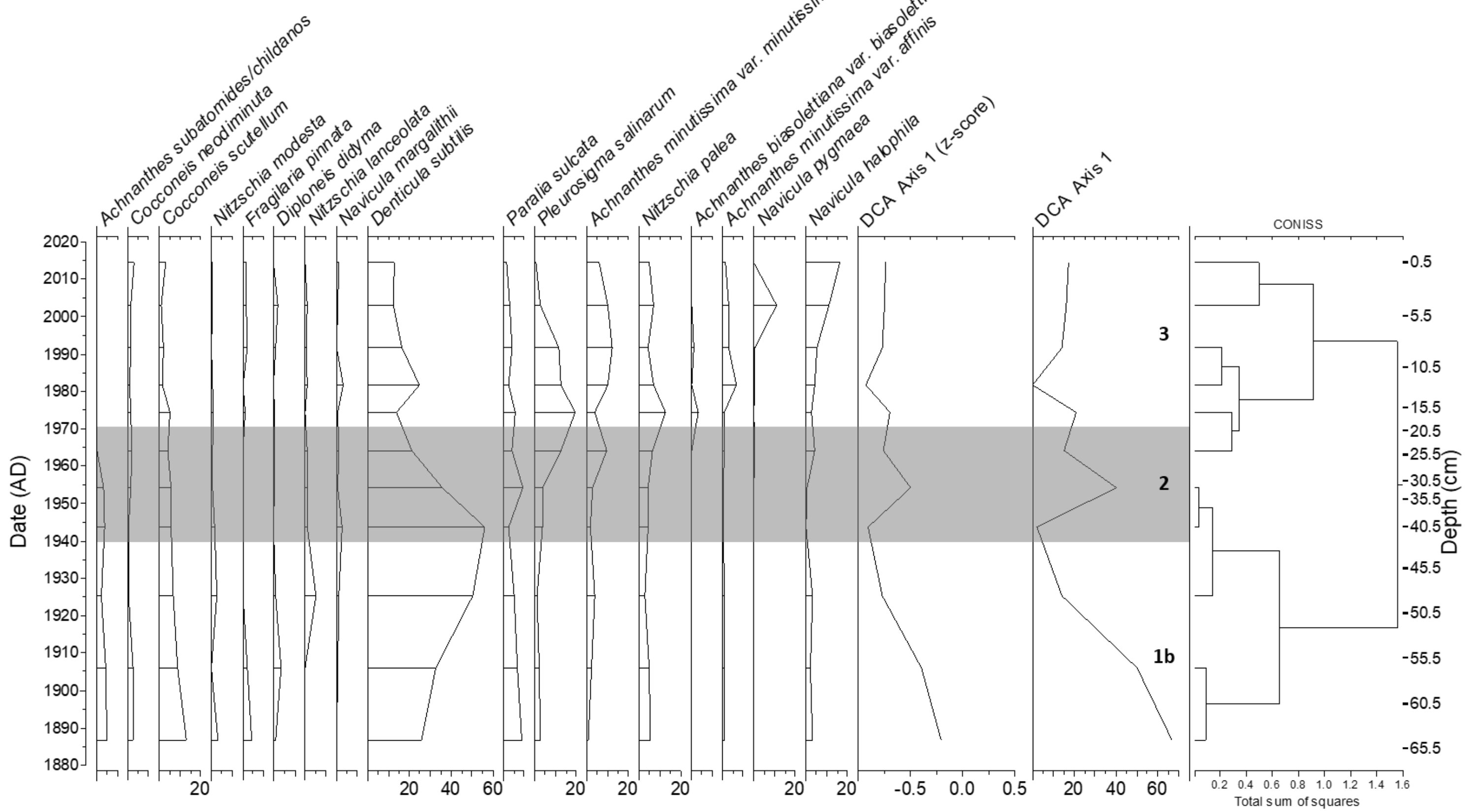


Figure 6.19: ARNE5 diatom counts (%) for species occurring >3%, DCA axis 1 and CONISS (right) with shading to indicate phases discussed within the text.

6.2.4.2.1 Phase 1b – ca. 1880-1940

Ca. 1880-1940, the pigment record suggests relatively stable productivity with little change in the abundance of pigments present (Figure 6.18). However, Figure 6.19 indicates there is a shift in diatom species composition, most noticeably the increase in *Denticula subtilis*, peaking ca. 1940s.

The geochemical record suggested an increase in terrestrial material being deposited in ARNE5 towards the end of Phase 1b (Section 6.2.4.1.1). An increased supply of material could increase the size of the mudflats at Arne. *Denticula subtilis* grows on mudflat habitats (Desianti et al., 2017), supporting the notion that increased terrestrial material provided a larger habitat for *Denticula subtilis* to thrive and increase in abundance.

6.2.4.2.2 Phase 2 – ca. 1940-1970

Ca. 1940-1970, nutrient rich sediment was being sourced from the River Frome and Piddle catchments during a period of intensified agricultural activity, which increased SARs in ARNE5. Agricultural activity drove an increase in diatom species which thrive in nutrient rich conditions ca. mid-1950s, i.e. *Navicula halophila*, *Navicula pygmaea* and *Nitzschia palea* (Figure 6.19) (Van Dam et al., 1994).

The notion that increased SARs drove mudflat expansion is supported by the high abundance of *Denticula subtilis* (see above) and an increase in *Achnanthese minutissima var. minutissima* which live in terrestrial environments (Figure 6.19).

Denticula subtilis, while high in abundance, declines throughout Phase 2 (Figure 6.19). The decline could be a response to increased nutrient levels which could promote competition from diatoms which thrive in high nutrient environments, e.g. *Navicula halophila*. The latter end of Phase 1b and some duration of Phase 2 have the highest C/N vs $\delta^{13}C$ (Figure 6.15), this suggests there could be C4 plants within the Arne area at this time. This is supported by the higher values of *Denticula subtilis* at this time as this species of diatom thrives on *Spartina*, a C4 plant (Stowe, 1980). As detailed in Figure 2.23, the colonisation of *Spartina* in the Arne area occurred ca. 1914, towards the end of Phase 1 when there is an increase in *Denticula subtilis*. The maximum extent of *Spartina* in Poole Harbour occurred ca. mid-1920s (Table 2.5), when *Denticula subtilis* was increasing. The decline in *Denticula subtilis* after ca. 1940, could be a result in the decline of *Spartina* during the ca. 1930s.

With regards to the quantity of algal productivity, pigment abundance, including those affined to algae, does not increase during Phase 2 (Figure 6.18).

6.2.4.2.3 Phase 3 – post ca. 1970

Ca. 2005 there is an increase in pigment abundance, including Diatoxanthin which indicates an increase in algal productivity (Figure 6.18). The UVR index also declines ca. 2005 as a result of increased pigments affined to algae. Post ca. 2000s, CONISS suggests a shift in pigment composition, likely due to increased algal productivity (Figure 6.18). The shift in pigment composition is supported by an increased PCA axis 1 z-score ca. 2000s (Figure 6.18). The diatom CONISS also shows a split pre- and post ca. 2000s, suggesting a change in environmental conditions (Figure 6.19).

The diatom assemblage (Figure 6.19) post ca. 1990 displays an increased abundance of species associated with nutrient enriched/eutrophic conditions, i.e. *Navicula halophila*, *Navicula pygmaea* and *Nitzschia palea* (Van Dam et al., 1994) and a decline in *Cocconeis scutellum* which also indicates increased nutrient supply (Buric et al., 2004).

Increased pigment abundance and nutrient affiliated diatom species suggests a post ca. early 2000s increase in algal productivity and possible eutrophication at Arne. However, the quantity of pigments measured in ARNE5 are not as great as those in FRM4, PID1 and HB1, e.g. up to ca. 80% less in Diatoxanthin. The difference may suggest that while there is increased algal productivity in ARNE5, it is not of the same magnitude as other areas within Poole Harbour. Arne is not the location of a main nutrient source, hence its ecological history may be expected to differ to elsewhere in Poole Harbour. However, the increase in algal productivity indicates that the increased nutrients from the agricultural catchment are promoting algal productivity elsewhere within Poole Harbour, not just locally in the River Frome and Piddle estuary. The lower pigment abundance could be caused by poorer pigment preservation in ARNE5 than compared to the other cores. Pheophytin *a* and *b* are the degradation products of Chl *a* and *b*. Poor preservation of pigments, such as Chl *a* and *b*, would result in increased abundance of Pheophytin *a* and *b*. ARNE5 does not exhibit abundances of Pheophytin *a* and *b* which are much different to the other cores, thus it can be determined the lower abundance of pigments is not a result of poor pigment preservation.

The notion of increased algal productivity post ca. 1970s, especially post ca. mid-2000s is supported by the geochemical record presented in Section 6.2.4.1.3.

6.2.4.3 Summary

The geochemical record of ARNE5 demonstrates a response to changes within the agricultural catchment of the Rivers Frome and Piddle, facilitated by periodic sea level rise ca. 1945, 1955 and 1965. Productivity is deemed to be the driver of the geochemical record of ARNE5 when excess supply of nutrients promotes little fractionation of carbon for productivity.

The pigment and diatom analysis indicate a response to nutrient dynamics with an increase in algal productivity ca. early-mid 2000s. However, while there is an increase in algal productivity, pigment abundance suggests productivity in ARNE5 is not as great as at other sites.

6.2.5 River Frome vs Arne diatom species composition

Both FRM4 and ARNE5 diatom species composition show a response to nutrient availability. The species which respond are not though the same at both sites likely a result of different microhabitats, e.g. salinity. Figure 6.20 shows the DCA where diatom data for FRM4 and ARNE5 were combined in the same ordination space. The DCA demonstrates that the species composition of the two cores are not overly similar as they are separated by at least ca. 1 standard deviation unit on axis 1.

The difference in species composition in FRM4 and ARNE5 is likely a result in salinity. FRM4 has a large freshwater supply whereas ARNE5 is close to the entrance of Poole Harbour and the sea. As FRM4 and ARNE5 are separated along the axis 1, this could indicate axis 1 represents salinity.

Within Figure 6.20, directional change in both FRM4 and ARNE5 over time, in particular post ca. 2000s, shows a transition in the same direction, i.e. toward less axis 1 values and greater axis 2 values. This suggests that both FRM4 and ARNE5 are responding in the same manner to the environmental controls at each site. Increased axis 2 values over time suggests axis 2 could indicate nutrient availability, hence increased axis scores reflect nutrient enrichment at both sites.

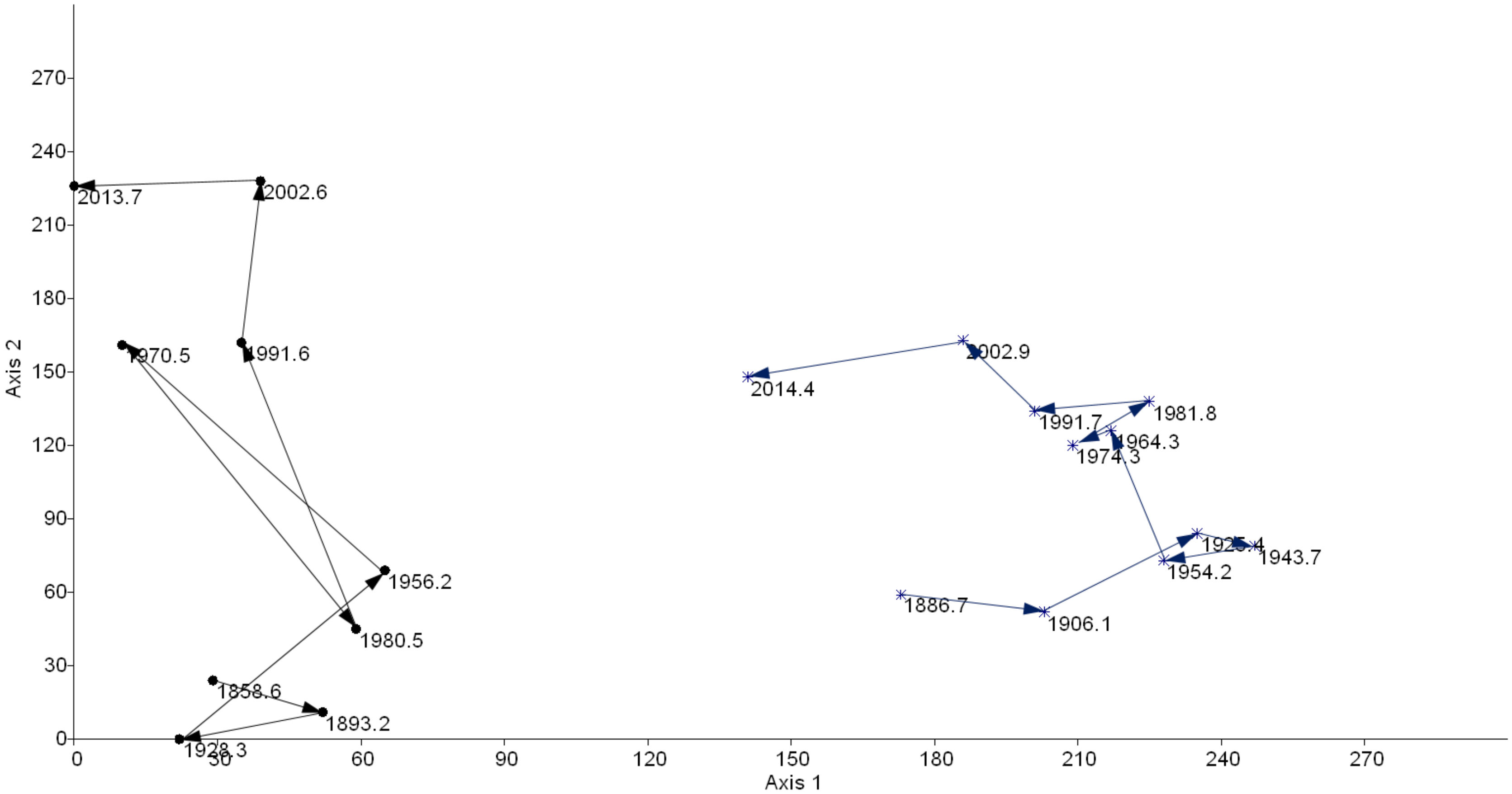


Figure 6.20: FRM4 (black dots) and ARNE5 (blue stars) DCA plot with arrows to show temporal change.

Axis 1 = 0.496 s.d.

6.2.6 Conclusions

This chapter has presented palaeoenvironmental records for the River Frome and Piddle estuary (FRM4 and PID1 respectively), Holes Bay (HB1) and Arne (ARNE5) to determine changes in nutrient dynamics and the algal response to such changes. The following points summarise the findings in this chapter:

- Nutrient delivery to the River Frome and Piddle estuary increased during ca. 1940-1970 as a result of increased agricultural activity within their catchments. Due to the groundwater nature of Poole Harbour's catchment, the delivery of these nutrients likely continued after a decline in agricultural activity post ca. 1970.
- ARNE5 demonstrated an increase in nutrient levels in response to the increased agricultural activity within the River Frome and Piddle catchments. This was facilitated by periodic increases in sea level.
- HB1 nutrient levels have been found to be primarily driven by the Poole STW effluent which drains directly into Holes Bay with increased population increasing the nutrient levels within HB1 as a result of increased demand on the STW.
- FRM4, PID1 and ARNE5 geochemical records were determined to be a response of source of nutrients rather than a result of productivity, a conclusion reached due to the decline in $\delta^{13}C$ during increased productivity as fractionation of carbon was not required due to the excess of nutrients within the system. In HB1, the $\delta^{13}C$ provided a productivity signal rather than a source of nutrients signal.
- FRM4, PID1 and HB1 demonstrated an increase in algal productivity in response to increased nutrients. These sites showed signs of eutrophication ca. 2000s. While algal productivity increased in ARNE5 ca. 2000s, the abundance of algae present within the sediment core suggested productivity was not as abundant in ARNE5 when compared with the other cores.

Chapter 7 The controls on Poole Harbour water quality and implications for catchment managers

7.1 Introduction

Poole Harbour is a dynamic system with a complex problem of increased algal presence, first noted in the 1960s and increased blooms since ca. 2000s. Key environmental indicators have been taken from Chapter 5 and Chapter 6 to assess the long-term changes in Poole Harbour water quality and to discuss possible strategies to mitigate poor water quality. The palaeoenvironmental data considered to be representative of water quality and the controls upon it are organic matter, $\delta^{15}N$, C/N, pigment PCA Axis 1 scores and sediment accumulation rates (SARs).

$\delta^{13}C$ response to environmental change varies across Poole Harbour, thus $\delta^{13}C$ has not been included as a water quality indicator. HB1 exhibits an expected response of $\delta^{13}C$ to increased algal productivity in that $\delta^{13}C$ increases alongside algal productivity. Due to excessive nutrient loading in FRM4, PID1 and ARNE5, there is little fractionation of carbon during algal productivity and a reversed relationship is recorded, i.e. decreasing $\delta^{13}C$ with increasing algal productivity until the abundant ^{12}C is diminished. Therefore, the response of $\delta^{13}C$ to productivity was not consistent across all sites and was not included as a water quality indicator.

The aims and objectives of this thesis were:

- To reconstruct Poole Harbour's historic water quality and assess the drivers of change using palaeoenvironmental reconstruction techniques.
- To determine when and where tipping points in water quality occurred and establish the driver/response interactions of them.
- To determine how the system responds to catchment drivers, i.e. in bifold, step change or linear manner.
- To establish the safe operating space (SOS) for Poole Harbour water quality, determine if good water quality can be restored and what implications this poses on the management of the Poole Harbour catchment.

This chapter addresses each of these objectives in turn using summary data for each site which have been presented in this chapter.

7.2 Reconstruction of Poole Harbour's historic water quality and assessment of the drivers of change

7.2.1 How do key water quality indicators vary across Poole Harbour?

Figure 7.1 presents radar diagrams for the four cores to demonstrate how the key indicators of water quality compare across Poole Harbour. Z-scores were calculated for each proxy and averaged across each phase (duration of these phases are detailed in Figure 7.1 below).

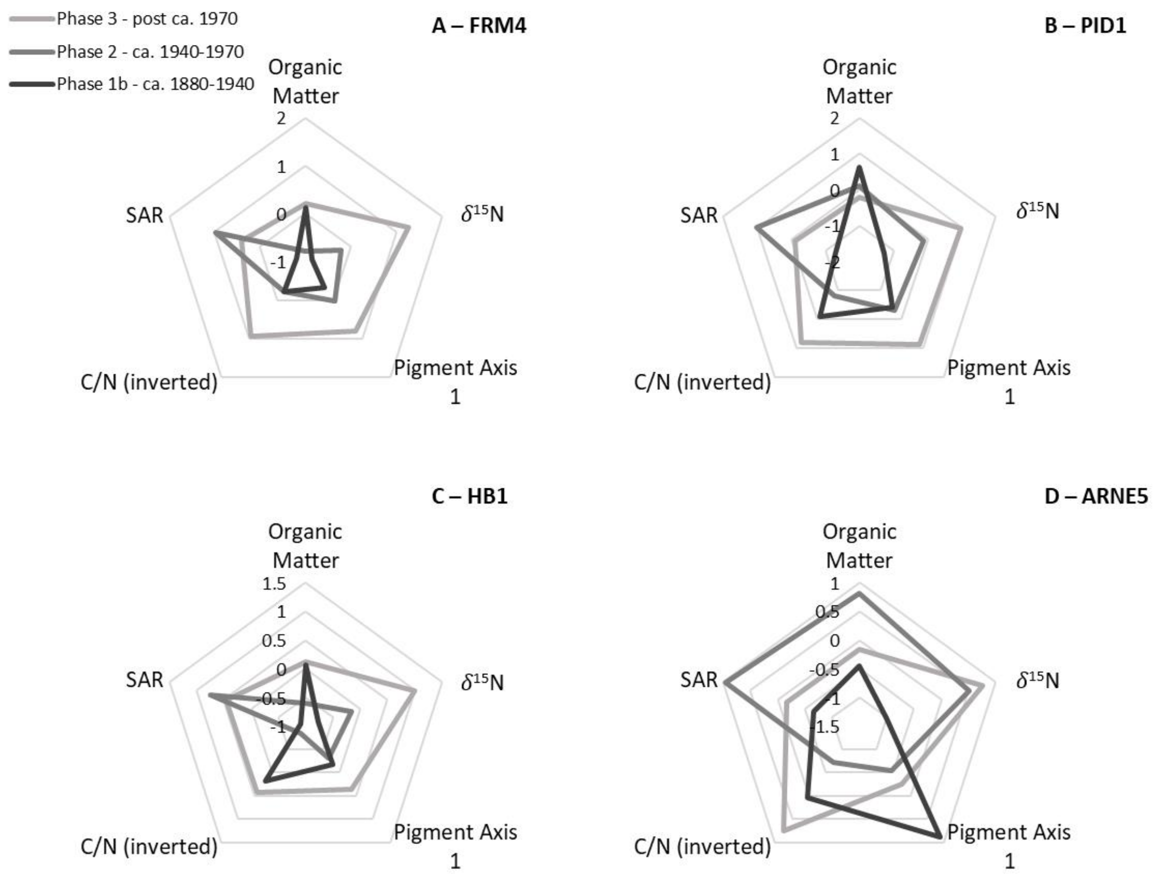


Figure 7.1: Radar diagrams showing z-scores for key indicators of water quality and controls for A – FRM4, B – PID1, C – HB1 and D – ARNE5, colour coded to correspond with phases discussed within the text. Note: Phase 1a is only present in FRM4 and so has been removed to allow for easier comparison across all cores and C/N z-scores have been inverted so positive z-scores suggest increase in productivity.

Cores which display greater responses to nutrient sources (FRM4, PID1 and HB1), demonstrate similar directional change in terms of proxy behaviour over time, with these trajectories differing notably when compared with ARNE5 (Figure 7.1). ARNE5 proxy records likely display differing directions of change as the core was recovered from an area where the impacts of nutrients are controlled by both catchment and marine changes/influences, rather than primarily changes in the former (or industrial development in the case of HB1).

All cores demonstrate an increase in $\delta^{15}N$ over time, suggesting that nitrogen supply has continued to increase from the Rivers Frome and Piddle and Holes Bay, with this supply also being detected in ARNE5. As previously discussed, the Rivers Frome and Piddle are likely to have more influence on ARNE5 than Holes Bay due to the greater potential of mixing by the River Frome and Piddle estuary with the rest of the harbour.

SARs across all cores demonstrate the highest z-scores during Phase 2, ca. 1940-1970. These scores suggest, ca. 1940-1970, SARs across Poole Harbour were notably different than compared with any other period within the study's time window, supporting evidence presented in Section 5.2.2.

There is a change in algal composition to more productive and eutrophic conditions in Phase 3, post ca. 1970, as indicated by high inverted C/N and pigment axis 1 z-scores in FRM4, PID1 and HB1 (Figure 7.1). In ARNE5, while Phase 1b ca. 1880-1940 has the greatest z-scores, Phase 3, post ca. 1970 is the second highest in pigment axis 1 and this is coupled with the highest inverted C/N values suggesting post ca. 1970 there is increased algal productivity. The high pigment axis 1 z-scores in ARNE5 during Phase 1b, ca. 1880-1940, suggests there was a change in algal assemblage between Phase 1b and Phase 2, ca. 1940-1970. Phase 1b inverted C/N scores are the second highest suggesting the productivity at this time is likely autochthonous, coupled with high pigment axis 1 z-scores suggests that ca. 1880-1940 was also a period of more algal productivity in ARNE5. This is supported by the pigment abundance affined to algae during Phase 1a and 3 compared with Phase 2 (Figure 6.18).

Organic matter varies over time across all cores and shows no consistent pattern between phases. Organic matter is an indicator of organic carbon, thus there are many controls on the value of organic matter, e.g. algal productivity and terrestrial input from the catchment. ARNE5 suggests Phase 2, ca. 1940-1970, is the time where the greatest supply of organic matter occurs, likely a result of the increased terrestrial material from the agricultural catchment being deposited at

Arne during the period of increased agricultural activity. Phase 3, post ca. 1970, exhibits the second greatest input of organic matter in ARNE5, likely sourced from increased algal productivity. The organic matter z-scores for FRM4, PID1 and HB1 do not vary greatly over time, ca. 1 z-score, suggesting that while algal productivity has changed over time at these sites, it is not the main control on organic matter.

7.2.2 Poole Harbour – the whole system

The impacts of the different types of catchments that supply nutrients to Poole Harbour, i.e. agricultural and industrial, have been examined throughout Chapter 5 and Chapter 6 and it has been discussed how they have impacted the control site Arne. This section attempts to determine how Poole Harbour as a whole has changed over time.

The z-scores for each Phase, 1b, 2 and 3, were averaged across all four sites to create a whole Poole Harbour system radar diagram (Figure 7.2). The results demonstrate an increase in $\delta^{15}N$, not unexpected as this was recorded across all cores (FRM4, PID1, HB1 and ARNE5). The SAR z-scores demonstrate Phase 2, ca. 1940-1970, of being the greatest difference, also expected as ca. 1940-1970 was the period of greatest change in SARs across the studied time period.

Inverted C/N and pigment PCA axis 1 z-scores are greatest during Phase 3, indicating greatest algal productivity across the harbour post ca. 1970.

There is little fluctuation in organic matter values over the record, ca. 0.1 z-score. This suggests that while productivity may increase, or SARs may increase, it does not have a notable influence on organic matter values.

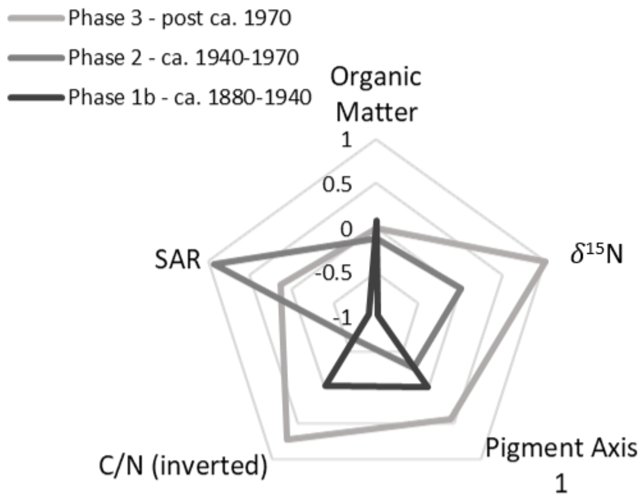


Figure 7.2: Whole Poole Harbour radar diagram showing the z-scores for key indicators of water quality and controls which have been averaged across all sites.

It is important to consider when analysing the data in Figure 7.2 how representative it is of Poole Harbour as a whole system. It is a simplistic view in that it is not very representative as no weighting to the averaging of each core is considered, i.e. it does not take into account what proportion of the harbour each core represents. For example, changes in Holes Bay may be prominent in the record of HB1, e.g. eutrophication post ca. 2000s, but with the limited mixing between Holes Bay and the rest of the harbour, HB1 likely represents a small proportion of the whole harbour. On the other hand, the Rivers Frome and Piddle are more able to freely mix with the rest of the harbour, so FRM4 and PID1 may represent a greater proportion of the whole system. However, FRM4 and PID1 may show greater changes than are actually occurring in the whole harbour as they are directly by main nutrient sources. Therefore, it seems more likely that the whole system should exhibit similarity to ARNE5, where nutrients from all sources, e.g. the Rivers Frome and Piddle and the sea, have the potential to mix and result in algal productivity changes.

To provide a better estimation of what the whole Poole Harbour system looks like, consideration would have to be given to the contribution of each source of nutrients (Rivers Frome and Piddle, Holes Bay and the sea) has to Poole Harbour. This has been attempted in Figure 7.3 which represents the estimated proportion each main nutrient source which has been measured within this study provides to the harbour, FRM4, PID1 and HB1.

To obtain water quality proxy measurements for each year throughout the record of FRM4, PID1 and HB1, linear interpolation was carried out between years that data was present for. Proportional estimations were calculated based on the inorganic nitrogen contributions from each Poole Harbour catchment source using the 2013-2017 data as a proxy for how much each source contributes to the harbour (Kite et al., 2018). It is realised there are limitations using the data provided by Kite et al., (2018), i.e.:

- using nitrogen as a proxy is not representative of all key indicators as other key indicators may contribute in different proportions
- using only 2013-2017 is not representative of how contributions vary over time
- other contributors, e.g. other smaller catchments and the sea influence are not included in this estimation
- Poole Harbour direct sources was used as a proxy for HB1 as this source included STW of which Poole STW is the largest within the catchment and is within the Holes Bay catchment.

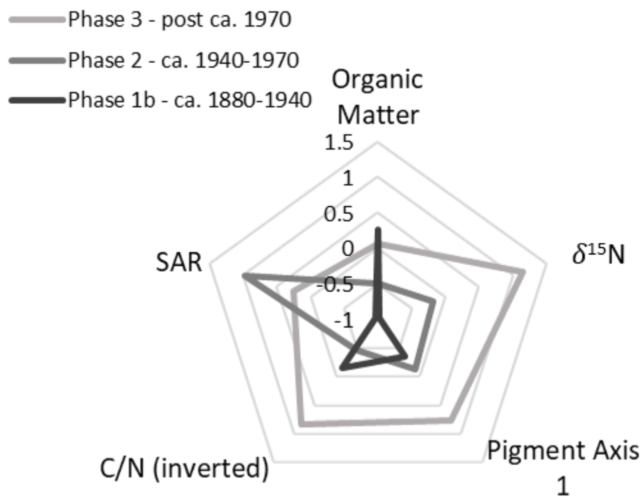


Figure 7.3: Poole Harbour main nutrient contribution radar diagram using proportional representation of FRM4, PID1 and HB1.

The shape of the new proportionally represented radar (Figure 7.3) is similar to that using equal proportions (Figure 7.2). Again, $\delta^{15}N$ increases from ca. 1880-present, i.e. post ca. 1970. While values slightly differ, ca. 0.5 z-scores, organic matter, SAR and C/N change in the same manner as those in Figure 7.2. Pigment Axis 1 z-scores demonstrate a constant increase in change over time, ca. 1880-post ca. 1970, in the proportionally representative diagram (Figure 7.3) which differs to that of Figure 7.2 where variation in change was detected over time. This could be because ARNE5 has not been included in the proportionally representative diagram as it is not a main source of nutrients to the harbour which demonstrated greatest change in Phase 1b, ca. 1880-1940, in Figure 7.1.

To provide a better estimation of what the whole Poole Harbour system looks like, more investigation would be required to better determine the contribution of each source, River Frome, River Piddle and Holes Bay, including contribution from the sea and other smaller catchments, e.g. the Rivers Corfe and Sherford. This would involve using flow rates of the Rivers Frome and Piddle to estimate their contribution to Poole Harbour and also calculating how much exchange there is between Holes Bay and the rest of Poole Harbour and also account for the exchange between Poole Harbour and the sea, i.e. how much is brought in from the sea and how much from Poole Harbour is flushed out.

7.2.3 Calculations of water quality

A water quality indicator proxy was established for each core. The indicator was calculated by averaging the z-scores of proxies that were determined to be indicators of water quality across the recovered cores, these being:

- $\delta^{15}N$ – indicator of nutrient loading.
- Organic matter – indicator of productivity.
- Pigment PCA axis 1 scores – indicator of productivity.
- C/N – indicator of autogenic productivity.

C/N z-scores were inverted, i.e. negative C/N z-scores were made positive, as lower C/N values suggest increased productivity. C/N z-scores were inverted for consistency so that larger z-scores indicated increased productivity and/or nutrient loading, i.e. poorer water quality. To make the water quality proxy easier for the reader, the averaged z-scores for the suite of proxies used was inverted so that lower z-scores suggest poorer water quality.

As discussed in Section 7.2.1, $\delta^{13}C$ response to environmental change varies across Poole Harbour, thus it was not used as a water quality proxy.

7.2.4 Water quality across Poole Harbour

A water quality indicator has been established for each core (Figure 7.4). Through Phases 1a, 1b and 2 (ca. 1850-1970), all cores demonstrate relatively stable water quality. Post ca. 1960, FRM4 and PID1 and ca. 1970 HB1 show a decline in water quality most notably post ca. 2000s in FRM4 and HB1. ARNE5 shows little variability throughout the record but values are slightly lower post ca. 1970 by a maximum of 1 z-score.

FRM4, PID1 and HB1 likely show a larger relative decline in water quality than ARNE5 as they are sites of main nutrient sources for the harbour, thus stronger signals of pollution and/or environmental change are likely to be detected in these three cores. ARNE5 is primarily influenced by the agricultural catchments of the Rivers Frome and Piddle and more marine influence from the sea than compared with the other sites (Chapter 5 and Chapter 6). Therefore, changes in the water quality indicator proxy in ARNE5 are likely to be less dramatic and slower in nature as the concentration of pollutants/nutrients is lower than compared with the main sources of nutrients FRM4, PID1 and HB1.

FRM4 reduces by ca. 2 z-scores and PID1 by ca. 1.6 z-scores. In contrast, HB1 shows the greatest change in water quality, reduction by ca. 4 z-scores from ca. 1970 to ca. 2010. The more dramatic change in HB1 to ca. 2010 is likely a result of relatively limited mixing between Holes Bay and the rest of the harbour due to its narrow entrance. While declines in water quality are detected in FRM4 and PID1 to ca. 2010, these sites are more open than Holes Bay and therefore more able to freely mix with the rest of the harbour. The limited mixing with the rest of the harbour likely limits the dispersion of contaminants/nutrients from Holes Bay, thereby constraining the effects of pollution, e.g. increase in algal productivity are constrained primarily to Holes Bay. The source of nutrients in Holes Bay post ca. 1970 are also more direct, e.g. from Poole STW effluent discharge, than compared with FRM4 and PID1 whose nutrients are more diffuse from the agricultural land and groundwater which would be expected to produce a more discrete signal in geochemical records, and by extension, a more muted change in the developed water quality indicator (Figure 7.4).

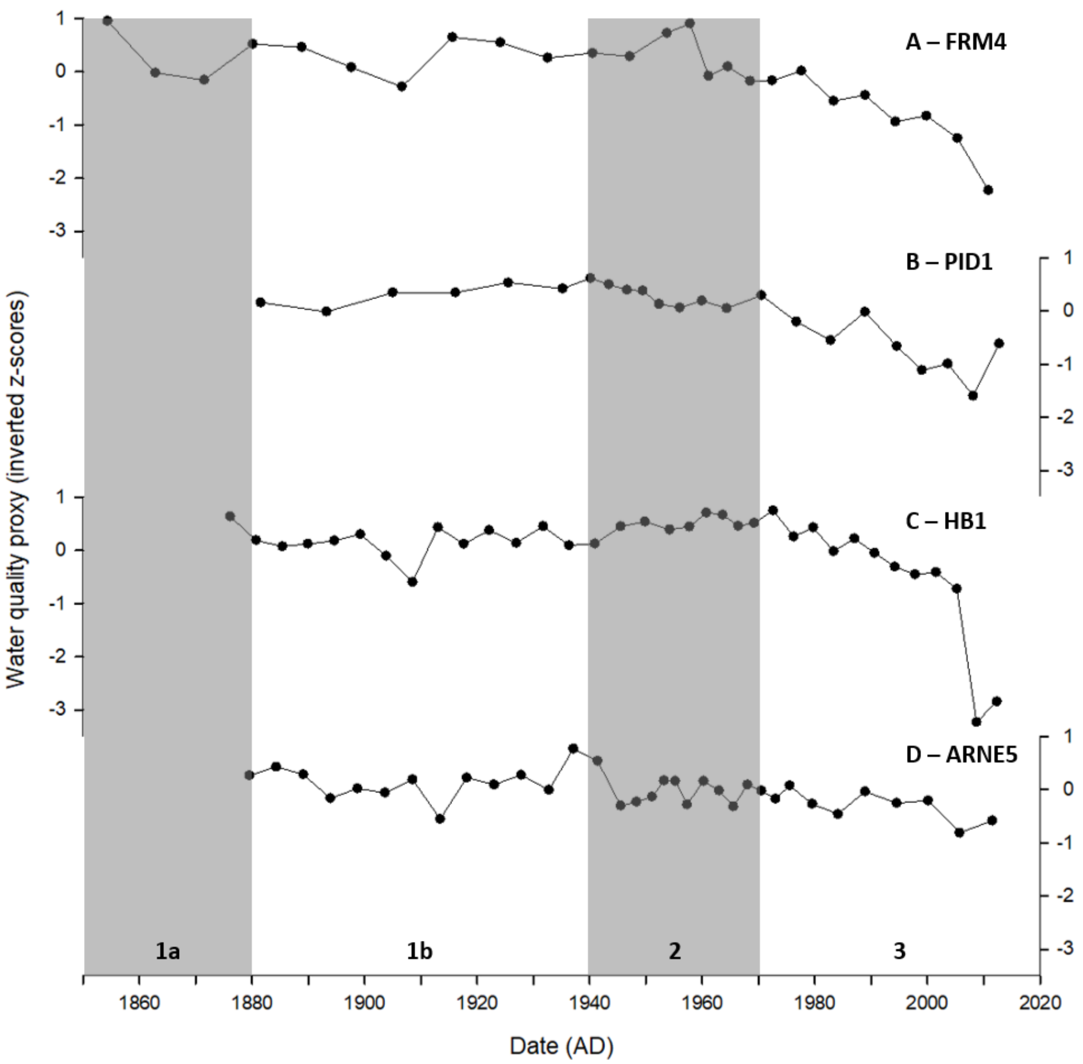


Figure 7.4: Water quality proxy (inverted z-score) for A – FRM4, B – PID1, C – HB1 and D – ARNE5. Note: scales kept the same for each core to show how water quality compares across Poole Harbour.

7.2.5 What controls the water quality in Poole Harbour?

The water quality indicator proxy for each core has been plotted against potential drivers of water quality change, e.g. population and fertiliser application. Water quality scores for FRM4, PID1 and ARNE5 (Figure 7.4) were compared against artificial nitrate fertiliser application (Figure 2.18) and the East Stoke River Monitoring Station nitrate (Figure 2.19) and phosphorus (Figure 2.20) concentrations to examine the influence of agricultural practices on water quality. All cores have been compared against population (Figure 2.16), including HB1 whose main nutrient source is population driven by the STW effluent. ARNE5 has also been compared against sea level (Figure 5.1) as it has been previously determined ARNE5 is also subject to marine influence (Figure 6.17), more so than the other cores.

FRM4 and PID1 suggest relatively stable water quality until post ca. 1960 when it declines (Figure 7.5 and Figure 7.6). Population increases ca. 1970 which likely altered the water quality, e.g. from increased STW effluent, but as determined in Chapter 6, the level of $\delta^{15}N$ found in the sediments suggest the source of nitrogen was from the agricultural soils and fertilisers. While artificial nitrogen fertiliser applications have decreased since ca. 1980, the concentration of nitrates in the River Frome have continued to increase, likely a result of the groundwater nature of the Poole Harbour catchment. Phosphorus concentrations declined post ca. 2000s, but this has apparently had no or little influence on water quality which has continued to decline after the phosphorus reductions. From these drivers, it is apparent that nitrogen has been the main control on water quality in FRM4 and PID1.

Holes Bay is surrounded by industrial and urban development. The main source of nutrients into Holes Bay derives from the STW effluent which drains directly into the body of water. The levels of $\delta^{15}N$ in the sediments of HB1 suggest the main source of nitrogen in Holes Bay is sewage. Therefore, an increase in population will result in increased amounts of STW effluent flowing directly into Holes Bay. As can be seen in Figure 7.7, HB1 water quality starts to decline ca. 1970, when the population continues to increase. The water quality of HB1 most notably declines post ca. 2010, as previously stated as a result of eutrophication in Holes Bay at this time.

There is little change in the water quality of ARNE5 but towards present, post ca. 1970, the value of the water quality is declining (Figure 7.8). As stated, phosphorus concentrations decline post ca. 2000 but population and nitrate concentrations continue to increase. Sea level also increases post ca. 1970, likely facilitating the transport of nutrients from the Rivers Frome and Piddle but also bringing more sources of nutrients from the sea.

Looking at the drivers of water quality, it is apparent nitrogen is a key driver in the water quality across all cores, either from agricultural or sewage sources. Sea level is also deemed to have more of an influence on ARNE5 than any of the other cores. While phosphorus does not seem to be a key controller of water quality at present, its high concentrations to ca. 2000s may have contributed to the decline in water quality post ca. 1970 when it could have promoted the growth of more algae.

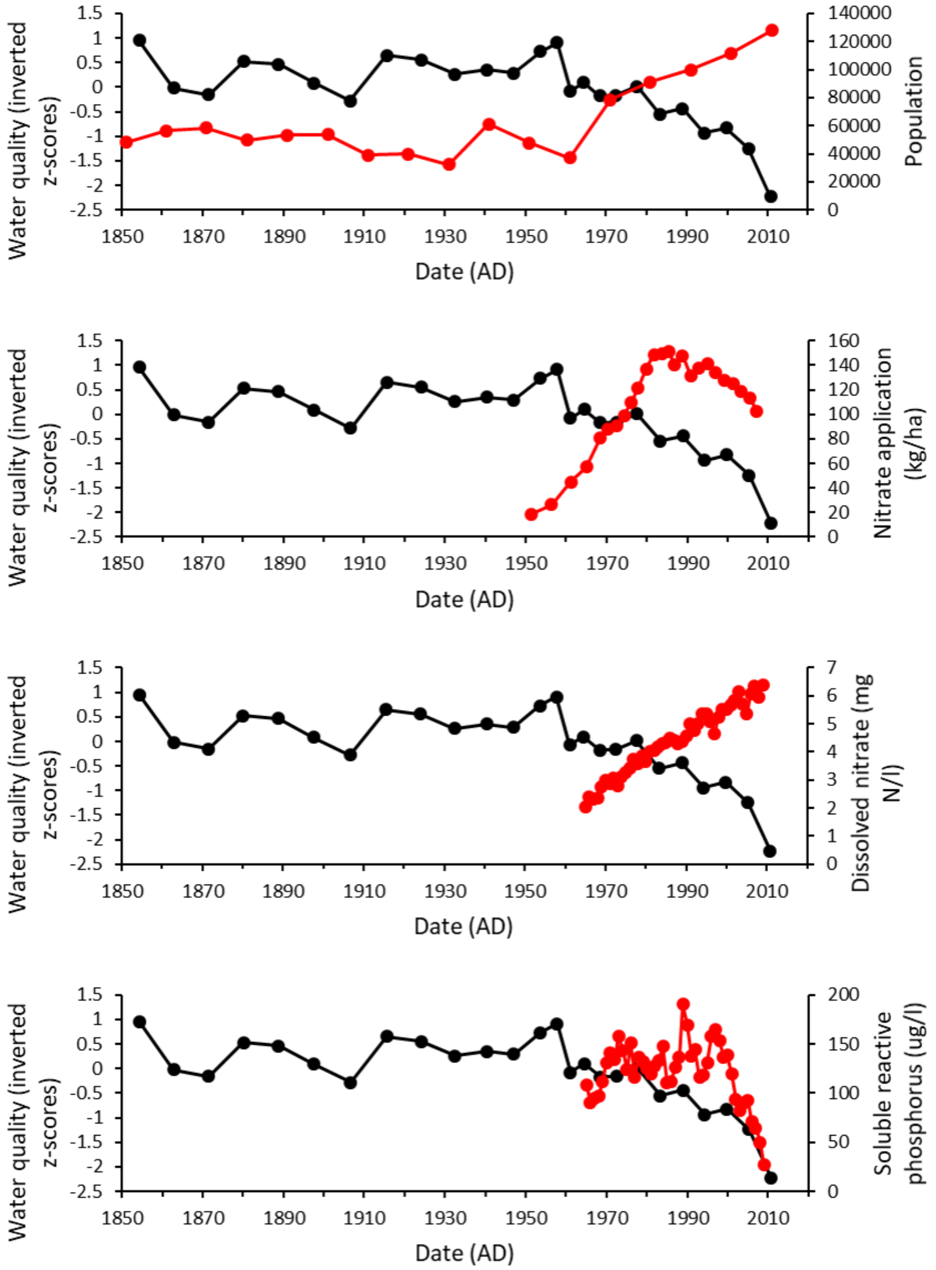


Figure 7.5: FRM4 water quality (black) versus potential drivers of water quality (red).

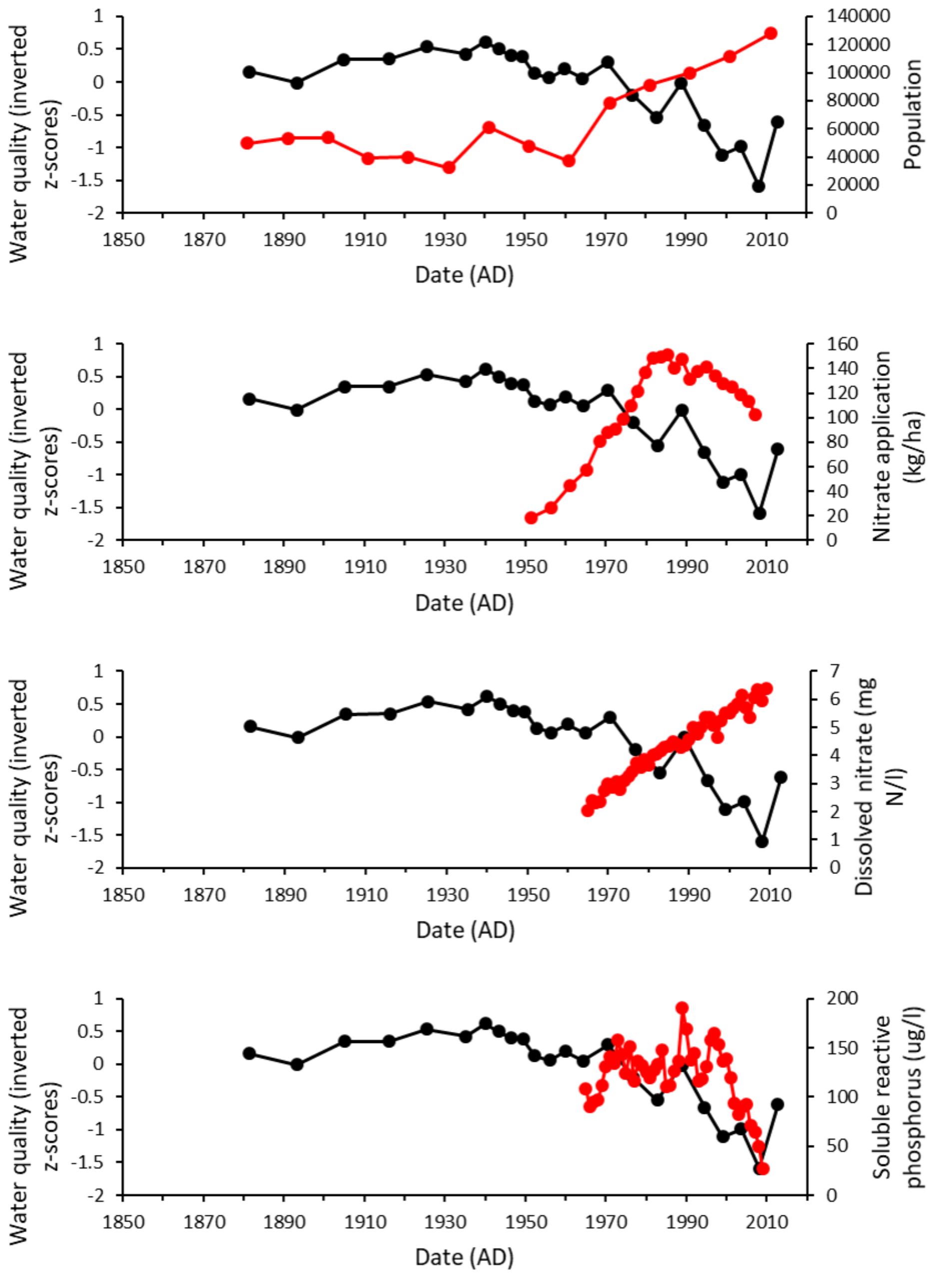


Figure 7.6: PID1 water quality (black) versus potential drivers of water quality (red).

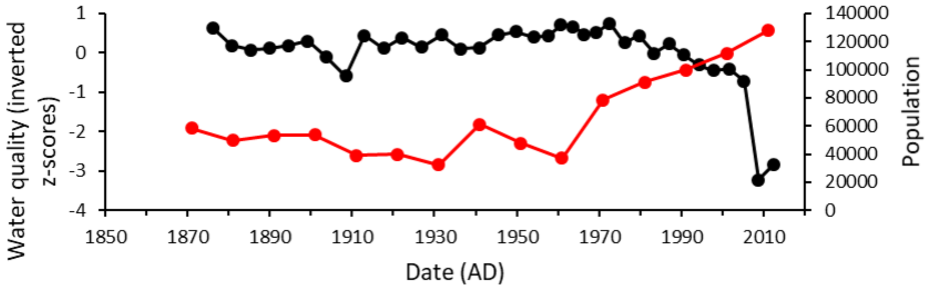


Figure 7.7: HB1 water quality (black) versus population (red), a potential driver of water quality.

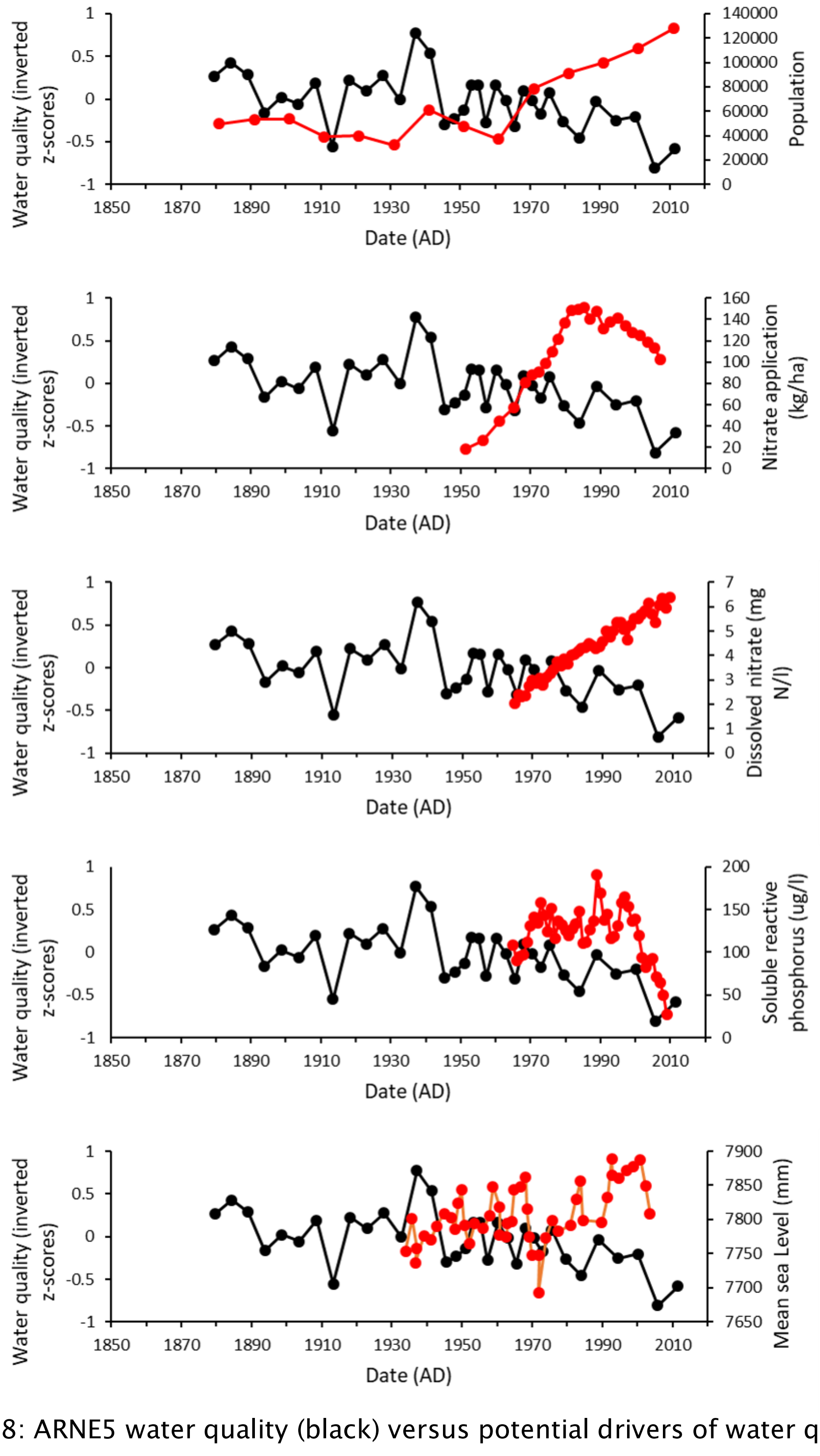


Figure 7.8: ARNE5 water quality (black) versus potential drivers of water quality (red).

7.3 Identifying when and where tipping points in water quality occur and the drivers of them

7.3.1 Drivers of water quality

Agricultural and industrial catchments surround Poole Harbour. The estuary is also influenced by the sea. Algal growth requires the macronutrients nitrogen and phosphorus. Both nitrogen and phosphorus increased post ca. 1970s (Figure 2.19 and Figure 2.20) when an increase in algal productivity was detected in cores determined to be influenced by the agricultural catchment, FRM4, PID1 and ARNE5 (Sections 6.2.2.2.3 and 6.2.4.2.3). While phosphorus concentrations within the River Frome have continued to decline post ca. 2000s (Figure 2.20), nitrogen concentrations have continued to increase (Figure 2.19).

The decline in phosphorus in the River Frome may not inherently indicate a decline in average phosphorus in the estuary itself. As discussed, Poole Harbour is a groundwater fed estuary. Thus, any declines in phosphorus supplied to the harbour by the Frome may be offset by maintained/increased supplies of phosphorus delivered to the estuary by groundwater. Without direct measurements of phosphorus in the harbour waters, this possibility cannot be tested. The decline in phosphorus in the River Frome may though indicate that groundwater phosphorus concentrations in some parts of the Poole Harbour watershed have declined as the River Frome itself is also groundwater fed, meaning its post ca. 2000 decline in phosphorus concentration may reflect a) a decline in phosphorus supplied by runoff from agricultural activities and/or b) a decline in phosphorus in the groundwater that enters it along its course. In any case, the nitrogen: phosphorus ratio within Poole Harbour will continue to increase while phosphorus declines. As discussed in Section 2.4.5.2, within coastal environments, like Poole Harbour, nitrogen becomes the limiting macronutrient for algal growth as phosphorus can be more easily recycled compared to freshwater systems (Conley et al., 2009; Blomqvist et al., 2004; Howarth & Marino, 2006). In some reported cases, a decline in phosphorus within a source river for an estuary has resulted in increasing algal blooms within the estuary itself (Paerl et al., 2004). As the overall quantity of phosphorus reaching Poole Harbour has likely declined since ca. 2000s when there has been noted increases in algal productivity, this thesis thus far has determined that nitrogen has been the primary control on water quality across the cores recovered.

Phase plots for the agricultural catchment (FRM4 and PID1), the industrial catchment (HB1) and the control site (ARNE5) show how drivers of nitrogen, from either agricultural practices or sewage (population), and phosphorus have affected water quality (Figure 7.9, Figure 7.10 and Figure 7.11 respectively). All cores demonstrate that water quality declines as nitrogen levels increase (nitrates and population). Phosphorus and water quality exhibit a similar relationship with the exception that when phosphorus concentrations decline, water quality continues to decline.

The linear relationship between increasing nitrogen and declining water quality suggests nitrogen is a direct driver of water quality (Table 7.1). Phosphorus and water quality exhibit a weak linear relationship (Table 7.1), implying a relationship between phosphorus and water quality, with this linear component constrained to pre- ca. 2000s, after which phosphorus declines and water quality continues to decline. The relationship of these macronutrients to water quality suggests that while phosphorus may contribute to poorer water quality, nitrogen is the primary driver of water quality in Poole Harbour.

Water quality of the four cores were also plotted against the long term precipitation and temperature data presented in Figure 3.5 and Figure 3.7 respectively (see Appendix C). However, no correlation was found between these two external drivers and water quality (Table 7.2). Therefore, it is assumed catchment drivers, e.g. nitrogen fertilisers, have greater control on water quality than climate, and/or any climatic impacts are likely minimised by the nutrient drivers.

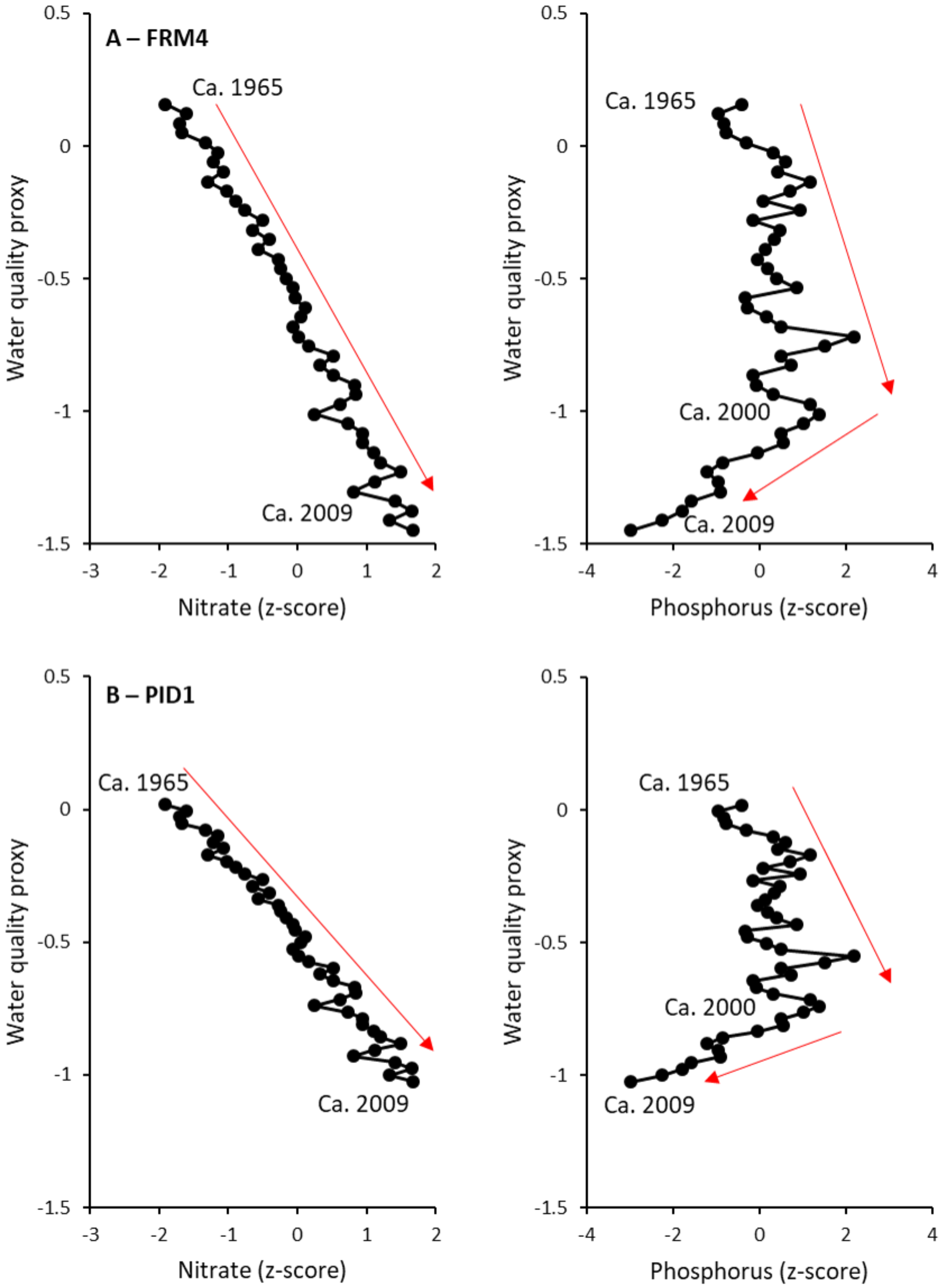


Figure 7.9: Phase plots of nitrate and phosphorus against water quality of A – FRM4 and B – PID1 for ca. 1965-2009. Red arrows show the direction of change through time. Note: Nitrate and phosphorus z-scores have been calculated from the East Stoke River Monitoring Station.

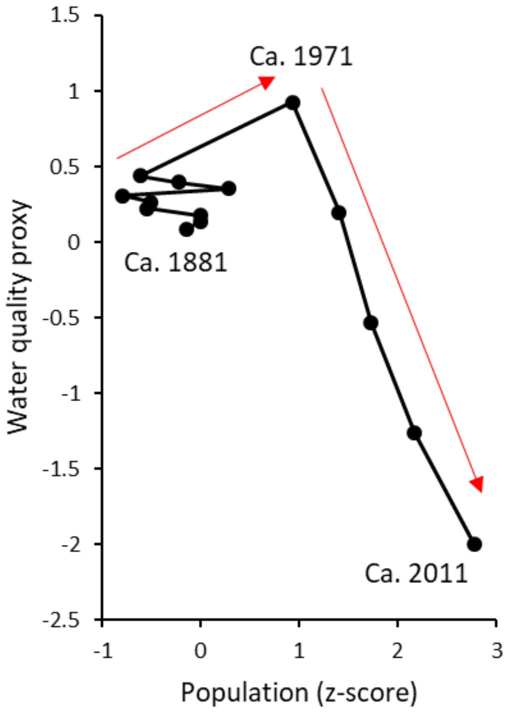


Figure 7.10: Phase plot of Poole Harbour catchment human population and water quality of HB1 for ca. 1881-2011. Red arrows show the direction of change through time.

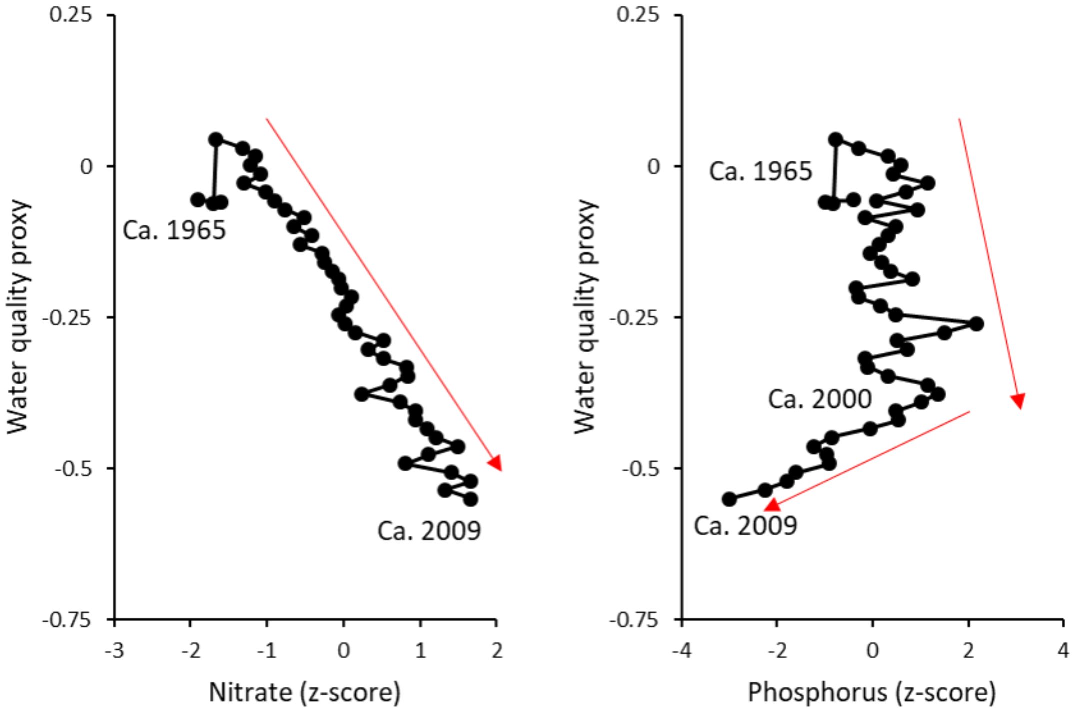


Figure 7.11: Phase plots of nitrate and phosphorus against ARNE5 water quality for ca. 1965-2009. Red arrows show the direction of change through time. Note: Nitrate and phosphorus z-scores have been calculated from the East Stoke River Monitoring Station.

Table 7.1: R^2 values of linear regression for FRM4, PID1 and ARNE5 water quality against nitrate and pre-ca. 2000s phosphorus from the East Stoke River Monitoring Station.

	FRM4	**PID1**	**ARNE5**
Nitrate	0.966	0.966	0.922
Phosphorus pre-ca. 2000s	0.235	0.235	0.160

Table 7.2: R^2 values of linear regression for FRM4, PID1, HB1 and ARNE5 water quality against long term precipitation (Figure 3.5) and temperature (Figure 3.7) climate data.

	FRM4	PID1	HB1	ARNE5
Precipitation	0.0098	0.0161	0.0002	0.0023
Temperature	0.0486	0.0439	0.0041	0.0573

7.3.2 When did water quality decline in Poole Harbour?

Figure 7.5 to Figure 7.11 demonstrate that across all sites water quality has declined over time; however, the time at which water quality began to decline differs between sites.

There is no defined method for establishing a tipping point of a system. This section shall explore the results established from using multiple methods for identifying breakpoints which locate where there is a statistical change in the data in FRM4, PID1, HB1 and ARNE5. By looking at where there is a breakpoint within the data, it can be used to determine where a change in trajectory within the water quality of each site occurred, e.g. started to decline. The statistical methods used for identifying the breakpoints, i.e. Rodionov's (2004) sequential algorithm, segmented regression and breakpoint analysis, are detailed in Section 3.8 and their results are presented in Table 7.3.

Table 7.3: Summary of water quality breakpoints obtained from several methods.

	FRM4	PID1	HB1	ARNE5
10 year sequential algorithm (p=0.05)	-	-	2004, 2005, 2006	-
20 year sequential algorithm (p=0.05)	-	-	-	-
Segmented regression (Standard Error)	1958 (6.523)	1941 (6.451)	1996 (1.733)	1970 (15.309)
Breakpoint analysis	1977.6	1988.9	1994.2	1975.5

Table 7.3 identifies no consistency between the methods to identify the date of the breakpoints within the water quality of FRM4, PID1, HB1 and ARNE5. However, the date ranges obtained from the methods can be used to guide the placement of the SOS for the water quality proxy of these cores, i.e. the end of the SOS may

lie within the range of dates given by the different statistical methods after which a decline in water quality is noted.

Water quality of FRM4 and PID1 declines post ca. 1960 (Figure 7.12A and B). This is 20 years after the onset of intensified agricultural practices in the Rivers Frome and Piddle catchments. This suggests it took 20 years between changes in the catchment and increases in nutrient loads to affect the water quality. The lagged relationship between the start of intensified agricultural practices, and thus nutrient loading, and the decline in water quality could be due to internal system dynamics trying to maintain good water quality, e.g. feedback loops (Scheffer et al., 2001). However, ca. 1940s-1970s was a period of high SARs. The excess sediments deposited in FRM4 and PID1 would contain nutrients from the catchment. The combined abundance of nutrients within the excess sediment deposited during the high SAR period and the nutrients from the agricultural practices, e.g. artificial fertilisers, may have caused an internal system threshold, thus tipping point, to be crossed which triggered the decline in water quality (Scheffer & Carpenter, 2003). It could be suggested that without the increased SARs, the system may have exhibited good water quality with only the increase in nutrient loading from intensified agricultural practices, e.g. artificial fertilisers. The increase in sediment deposition may have made the system more susceptible/sensitive to change as the sediment acted as an additional nutrient source which, when combined with nutrient loading from agriculture, triggered a state shift in water quality.

Water quality of HB1 declines post ca. 1970, as catchment population increases. Figure 7.10 suggests a negative linear relationship between population and water quality in HB1, suggesting population has a direct effect on water quality in HB1. The increased population likely promoted nitrogen loading to Holes Bay from increased volumes of STW effluent. While water quality declined post ca. 1970, ca. 2010, water quality declines further, ca. 2.5 z-scores (Figure 7.12C). This suggests a tipping point was reached which caused the water quality to decline at a faster rate than ca. 1970-2010.

While there is little change in ARNE5 water quality, less than 1 z-score, post ca. 1970 values suggest water quality has declined relative to earlier periods in the record (Figure 7.12D). Changes in agricultural practices in the Rivers Frome and Piddle catchments have been deemed to be the primary control on ARNE5 water quality. ARNE5 was not recovered from a main nutrient source location and water at Arne is able to freely mix with the rest of the harbour, particularly when compared with water flow at FRM4 and PID1. Therefore, it could be expected that there is a lag time between changes in water quality detected in FRM4 and PID1 and that of ARNE5. Thus, it is possible that changes detected in FRM4 and PID1 offer an insight into changes that may occur in ARNE5.

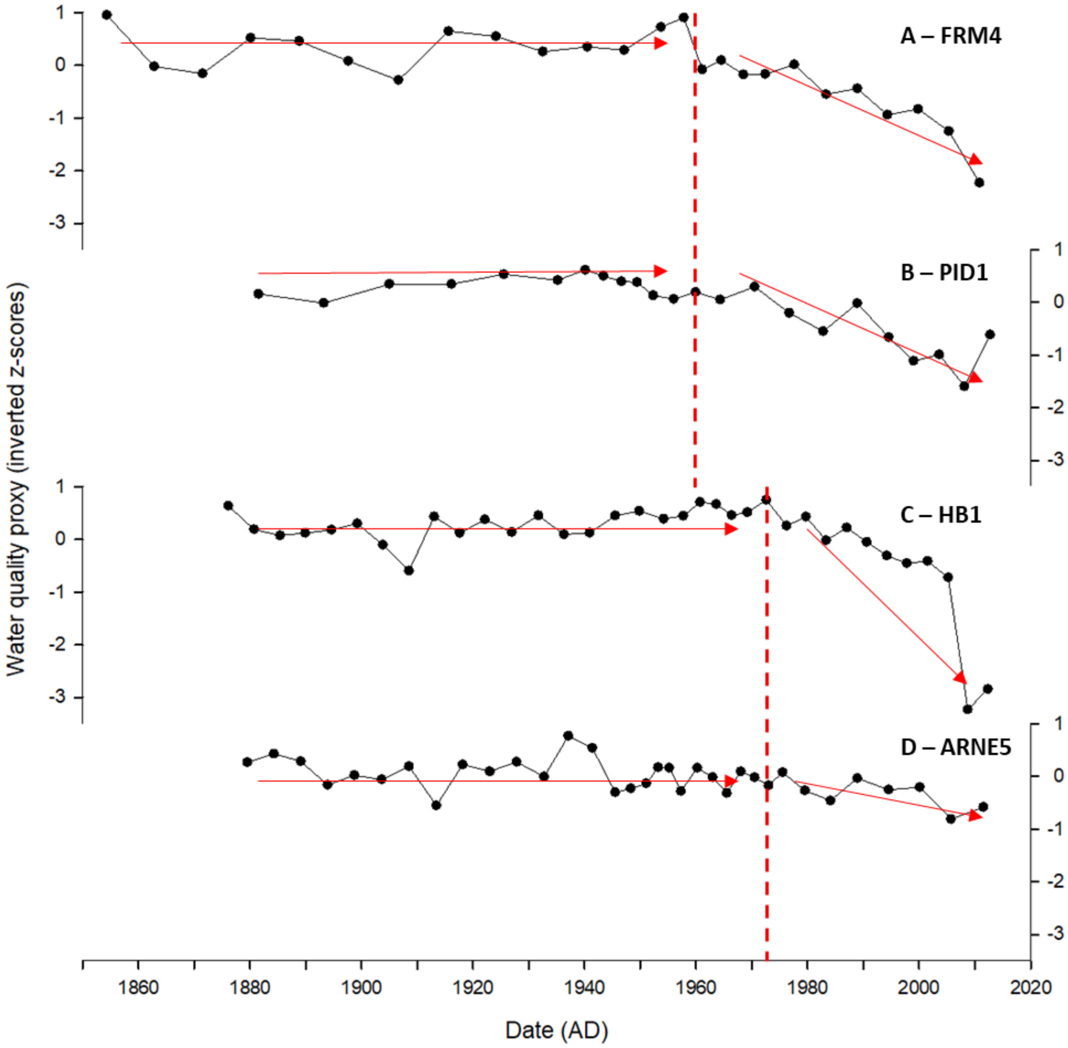


Figure 7.12: Water quality for A – FRM4, B – PID1, C – HB1 and D – ARNE5 with red arrows to show direction of change of the water quality and dashed lines to show when visually direction changes.

7.4 Understanding the system dynamics of Poole Harbour

It is important to understand what type of estuary-catchment system Poole Harbour is to better inform catchment practices to improve water quality. The three types of system, linear, step-change and bifold (Figure 2.3) have been detailed in Section 2.2.

Figure 7.10 illustrates a direct, linear relationship between driver and environmental response in HB1, i.e. an increase in nitrogen from increased population caused a decline in water quality. However, as previously stated, ca. 2010, water quality declines further, ca. 2.5 z-scores. This suggests a step change in water quality in response to nitrogen loading in the system.

There is likely a linear relationship between nitrate concentrations and water quality in FRM4, PID1 (Figure 7.9) and ARNE5 (Figure 7.11). However, Figure 7.12 demonstrates a lag time between an increase in nutrient loading from the agricultural catchment ca. 1940 and a decline in water quality ca. 1960. The lag time between driver and response suggests a step change system, i.e. the water quality can be somewhat maintained while nitrogen increases, but water quality declines once nitrogen reaches a critical level and the threshold is passed.

Within a step change system there are two steady states over a range of conditions (Scheffer & Carpenter, 2003). If Poole Harbour is a step change system, then it suggests that it has not reached its new steady state and the water quality will continue to decline until it reaches a new plateau.

7.5 Management implications – identifying the water quality Safe Operating Space for Poole Harbour

7.5.1 Where is the SOS for water quality in Poole Harbour?

The work of Rockstrom et al., (2009a, 2009b) and Dearing et al., (2014) respectively proposed global and regional SOS taking into account multiple variables, e.g. climate change, air pollution, sediment and soil stability, to define a SOS of a whole system. This study has been limited to the drivers of historic water quality of Poole Harbour. Therefore, the SOS proposed here for Poole harbour only accounts for the safe zone of one variable of the system, water quality.

FRM4 and PID1 water quality decline ca. 1960 and HB1 and ARNE5 water quality decline ca. 1970 (Figure 7.12 and Figure 7.13). Figure 7.13 illustrates that prior to the decline, the water quality fluctuated but remained stable within an envelope of variability of ca. 1-1.25 z-scores (Dearing et al., 2014; Figure 2.6 and Figure 2.30). This envelope of variability could be classified as the SOS as the water quality is maintained with some fluctuation until a system shift which resulted in a decline in water quality, i.e. outside the SOS. FRM4 and PID1 SOS end dates, ca. 1960, while not mutually agreed upon by the statistical methods as the date at which a transition in water quality occurs, is a date which is within the range provided by the methods (Table 7.3). The breakpoint date supplied by the statistical methods for HB1 are ca. 20 years later than the suggested SOS end date of ca. 1970 (Table 7.3). The ca. mid-1990s dates suggest by the statistical methods likely produce later dates for the transition as the most present water quality values, post ca. 2000s, are much lower than previous, by ca. 3 z-scores (Figure 7.13C). These extreme low values likely skew the statistics towards a later date. However, ca. 1990s has not been taken as the SOS end date as post ca. 1970s the water quality does not recover from its continuous decline and thus cannot be classified as ‘safe’. It is harder to define the end of the SOS in ARNE5 as the decline in water quality is not as prominent (Figure 7.13D). However, both the segmented regression and breakpoint analysis suggest the trend in water quality changes ca. 1970 (Table 7.3) at which time the variability within the water quality has reduced, i.e. variable within ca. 0.5 z-scores rather than 1.5 z-scores (Figure 7.13). Therefore, the SOS of ARNE5 has been determined to end ca. 1970.

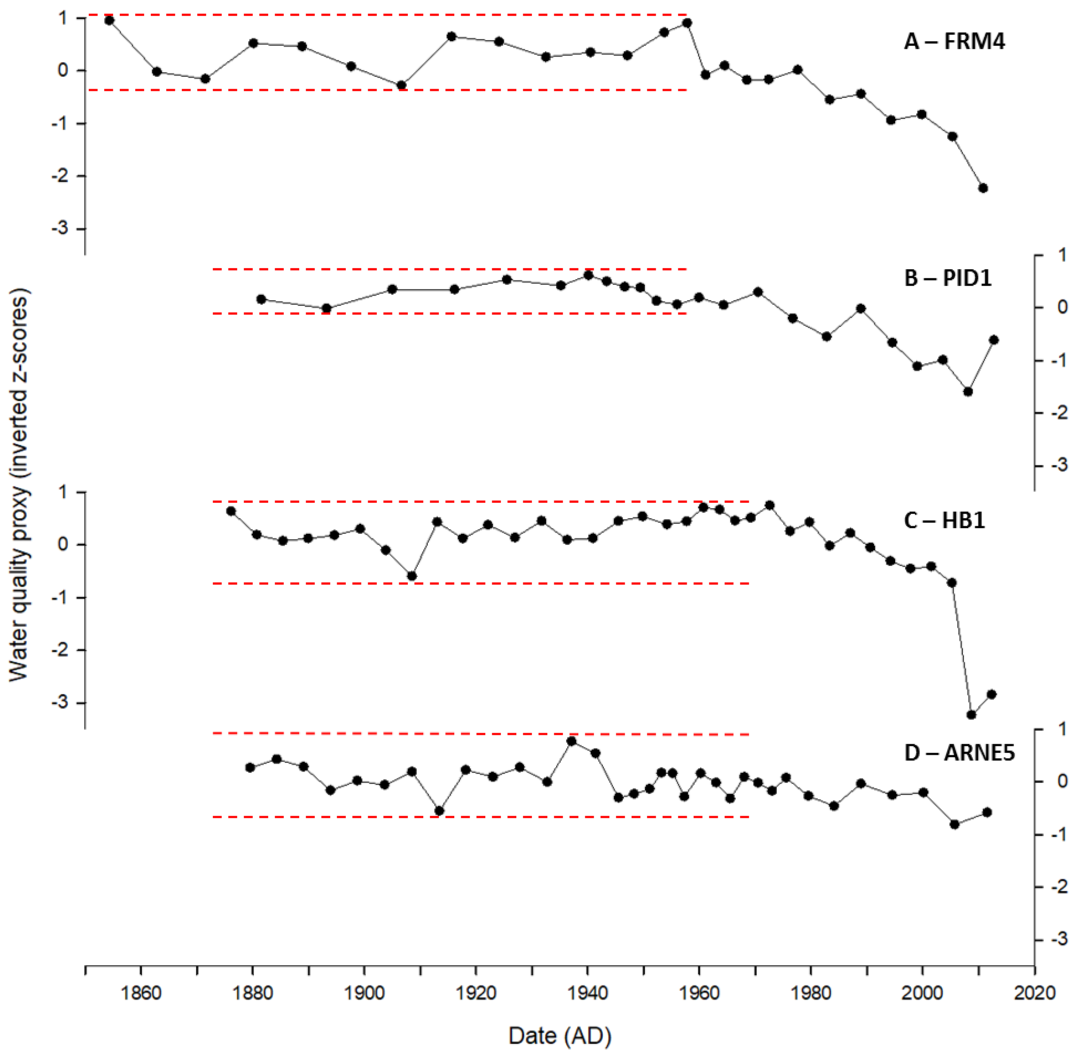


Figure 7.13: Water quality for A – FRM4, B – PID1, C – HB1 and D – ARNE5 with red dashed lines to indicate the envelope of good water quality variability.

The SOS could be argued to be the space of good water quality for the period of the study as it does not reach higher water quality values throughout the record. However, prior to the record starting, ca. 1880 (1850 FRM4) the water quality could have been higher as the system ca. 1880 had already been influenced by anthropogenic activities. Therefore, the envelope of variability likely does not reflect the natural good water quality of Poole Harbour but could be regarded as an acceptable water quality given the relatively limited chronology employed in this study when considered against the overall development of Poole Harbour.

Within the SOS, water quality does not continuously decline until ca. 1960 for FRM4 and PID1 and ca. 1970 for HB1 and ARNE5. While the water quality remains in the envelope of variability, the system can maintain a relatively constant water quality under changing drivers, e.g. increasing nitrogen loads.

If the envelope of variability for HB1 was extended over a greater time scale, i.e. post ca. 1970, it could be argued that water quality does not decline until later in the record, ca. 2005, because the water quality values remain within the envelope (Figure 7.14). However, post ca. 1970, while the water quality may remain within the envelope there is minimal variability, i.e. there is a constant decline in water quality, suggesting the system can no longer support the good water quality and the threshold to poorer water quality has been passed. In the case of ARNE5, if the envelope of variability was extended for the whole length of the record, the water quality in fact does not decline past its limits until ca. 2005 at which, even post this date it is not continuously below the lowest limits of the envelope of variability (Figure 7.15). This suggests that while ARNE5 water quality appears to be declining post ca. 1970, it can still be classed as acceptable water quality. However, as the water quality has breached the lower limits of the envelope of variability in the past ca. 10 years, ca. mid-2000s, it is likely it will surpass the lowest limit of the SOS in the near future when it can no longer be classed as acceptable water quality. Therefore, as the water quality has surpassed the lowest boundary of the SOS already, the water quality cannot be classed as 'safe'.

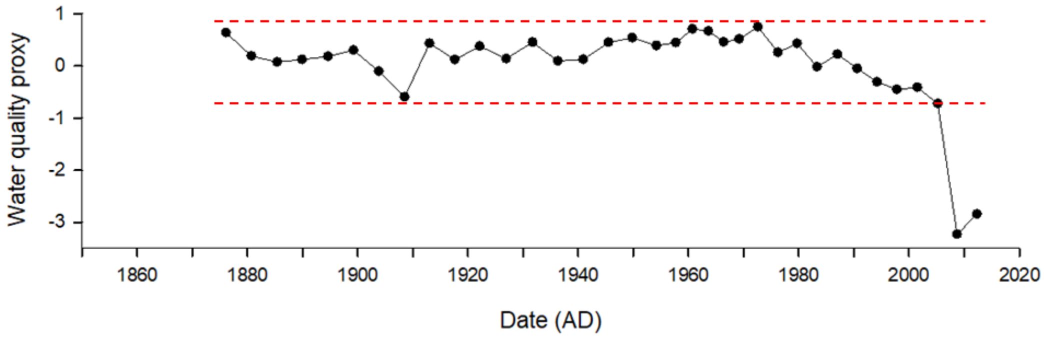


Figure 7.14: HB1 water quality with envelope of variability indicating good water quality extended to the length of the whole record to show water quality does not fall below the lower limits of the envelope until ca. 2005.

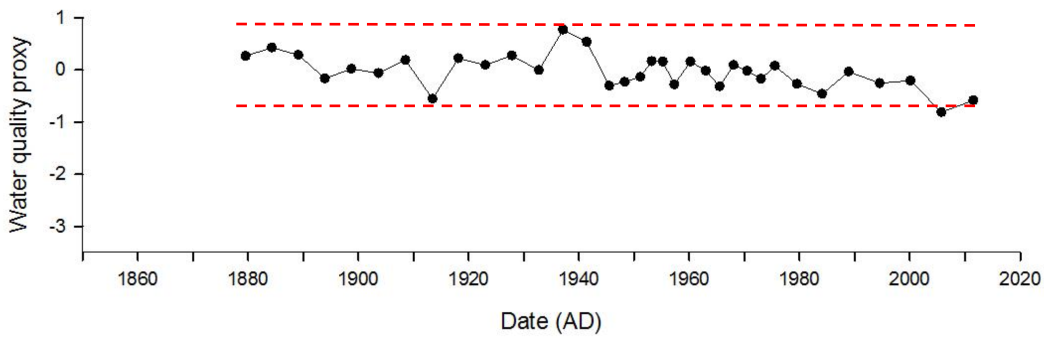


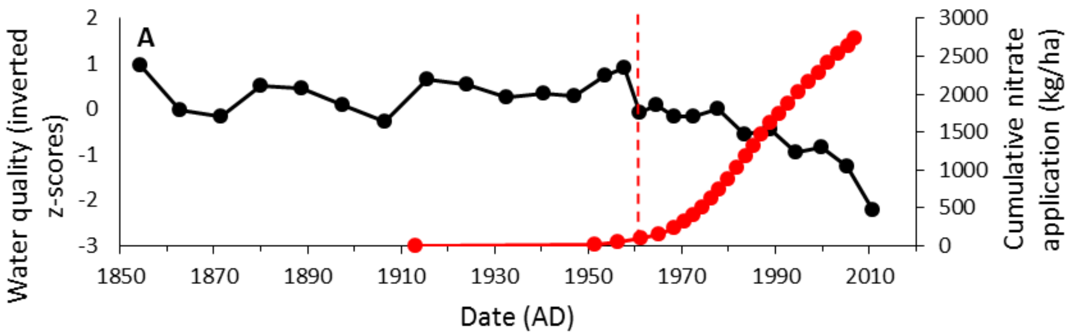
Figure 7.15: ARNE5 water quality with envelope of variability indicating good water quality extended to the length of the whole record.

7.5.2 How can acceptable water quality be restored?

It has been determined nitrogen is the primary driver of water quality change in the estuary of Poole Harbour. However, increasing nitrogen loads to Poole Harbour do not exhibit a linear relationship with water quality. Therefore, it is likely that cumulative nitrogen levels stress the system until a critical threshold is reached and water quality begins to decline.

FRM4 has been used to demonstrate the relationship between nitrogen loading and water quality as this core, along with PID1, demonstrates a decline in water quality earlier than the other sites. FRM4 also arguably shows the transition to poorer water quality more clearly as it reduces by ca. 2.5 z-scores compared to ca. 2 z-scores in PID1.

Figure 7.16A illustrates the relationship between FRM4 water quality and the cumulative stress from nitrate application. At the time of the transition to a decline in water quality, the cumulative nitrate application was ca. 90kg/ha. This corresponds to a river concentration of ca. 2mg N/l (Figure 7.16B), ca. 9mg N/l below the DWI standards (Table 2.1).



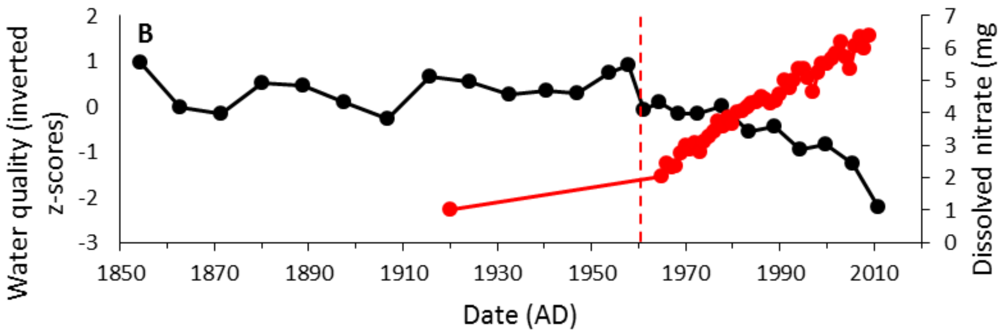


Figure 7.16: FRM4 water quality (black) verses A – cumulative nitrate application (red) (Smith et al., 2010) and B – dissolved nitrate concentration in the River Frome from the East Stoke River Monitoring Station, with red dashed line indicating the transition to poorer water quality ca. 1960. Note: A – 1913 has been assigned 0kg/ha as this is when artificial nitrogen fertiliser were manufactured (Cocking, 2000) and B – early 20th century has been assigned 1 mg N/l, the reported concentration for Dorset (Edmunds et al., 2002).

It can be argued that pre- ca. 1940s is the true acceptable water quality for the period of study as this is prior to the increased SARs which likely contributed to the water quality decline. However, it is not a reasonable management decision to reinstate conditions prior to ca. 1940 as sediment has already been deposited in Poole Harbour and is now part of the system. Therefore, to go back to acceptable water quality space, conditions should be returned to pre- ca. 1960, when the system could maintain acceptable water quality with the increased SARs before the water quality declined.

Ca. 1960 has been determined to be the transition date of water quality decline meaning river nitrate concentrations need to be <2mg N/l which equates to a cumulative total <90kg/ha of artificial nitrate fertiliser application. Current artificial nitrate fertiliser applications are ca. 100 kg/ha (Smith et al., 2010), however, due to the groundwater nature of the catchment, applications would have to be reduced further than <90kg/ha as it will take several decades for any reductions to take effect on the water quality. This nitrate target does not account for the contribution from natural sources of nitrogen, either from the agricultural catchment, sewage or from the sea. It may be possible to return to preferable conditions by returning the dissolved nitrate concentration to <4mg N/l as this lies below the envelope of acceptable water variability. However, it should be taken into consideration this is an overview of the Poole Harbour system, it does not take into account all possible drivers and interactions of water quality, these being discussed below.

Other variables which may affected water quality are fish stocks, salinity incursions and air quality. These variables are not necessarily independent of water quality but are key parts of the system. Fish species, abundance and biomass can provide an indicator of water quality within an estuary as fish species thrive in their preferred environments (Whitfield & Elliott, 2002). The knowledge of what environmental parameters, e.g. salinity, a fish species thrives in, changes within the fish species composition, e.g. abundance and biomass, can provide an indication of water quality. Fish could therefore be used as any other ecological proxy, e.g. diatoms, although they are typically harder to measure in palaeoenvironmental analyses (Davidson et al., 2003). An increase in salinity may increase the amount of phosphorus readily available to be used for algal production within the estuary and thus result in more algal blooms and eutrophication (Blomqvist et al., 2004). Estuaries receive nitrogen not only from the sources discussed within this research, namely agricultural and STW effluent, but also from the atmosphere (Paerl, 1997). The atmosphere contains reactive nitrogen which comes from a variety of sources, including fossil fuels (Howarth et al., 2002). Estuaries can receive direct deposition of the reactive nitrogen from the atmosphere (Howarth et al., 2002), thus changes in the amount of nitrogen in the atmosphere, for example from an increase in the use of fossil fuels, can result in an increase of nitrogen in the estuary.

Climate change is an external driver to the Poole Harbour system. Whilst this research has found no correlation between climate (temperature and precipitation) and water quality, it is not to say that future climate change will not have an impact. Temperature has a strong influence on phytoplankton growth and algal blooms are promoted by higher temperatures (Moore et al., 2008; O'Neil et al., 2012). Thus, hotter temperatures will likely increase algal productivity. Predicated sea level rises for Poole Harbour (Drake & Bennett, 2006) could potentially decrease the nutrient and pollution concentrations within the estuary. However, associated sea level rise would likely increase both a) the duration that certain areas subject to tides are inundated and b) expose new areas to submersion (following Pickering et al., (2017)). Both of these effects would increase sediment disturbance, potentially releasing nutrient rich sediments back into the system, thus promoting algal productivity and eutrophication. An increase in sea level rise would also likely increase the salinity of the Poole Harbour system, thus allowing phosphorus to become more readily available for algal production. However, as this research found no correlation between climate and Poole Harbour water quality, it suggests local drivers, e.g. catchment changes, may have had a greater influence on the estuarine system over the studied period. This lack of correlation does not provide a precedent for future interactions between climate and water quality, but rather shows that as boundary conditions move, new relationships could develop and climate may become a more active driver of system change.

Whilst these are important variables which may affect Poole Harbour water quality, their lack of quantification does not preclude the usefulness of this study in identifying trends in water quality and may be used for foci of future investigation.

7.5.3 What does the future look like for Poole Harbour?

Using the same key drivers that were used to establish a water quality proxy indicator for FRM4, PID1, HB1 and ARNE5 (Figure 7.4), a whole Poole Harbour water quality was calculated. Two methods were used to establish this whole system:

1. The linear interpolated water quality measurements for each year were averaged across all four cores.
2. Using the same proportions used to create Figure 7.3, the proportion of the linear interpolated water quality measurements for FRM4, PID1 and HB1 were calculated and summed.

The results of these two methods are shown in Figure 7.17 which demonstrates the two methods produce similar results. From this point forward, the averaged water quality proxy of all four cores will be used.

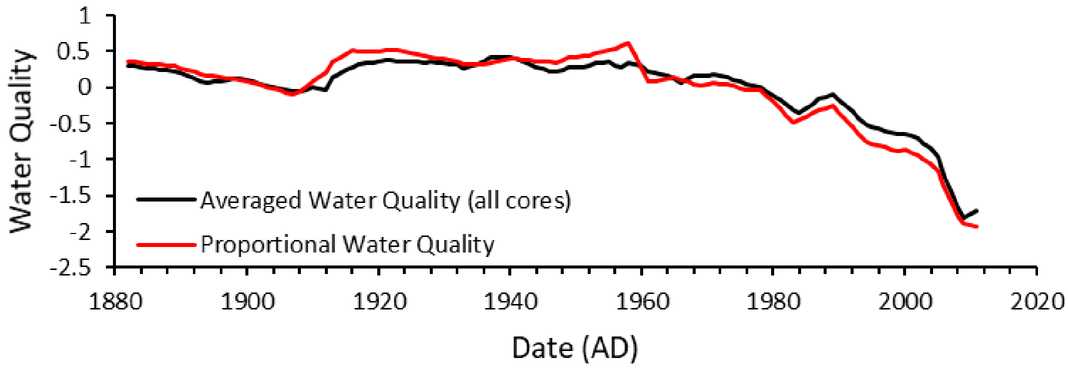


Figure 7.17: Whole Poole Harbour system water quality proxy indicator.

Statistical breakpoint analysis was calculated on the Poole Harbour water quality proxy (Table 7.4). The methods do not mutually agree on a breakpoint. The water quality starts to continuously decline ca. 1960 (Figure 7.18). Prior to ca. 1960, the water quality remains relatively stable within an envelope of variability of ca. 0.5 z-scores, this can be defined as good water quality and the SOS.

There is no set method for defining the transition to a dangerous/critical state system. Here, it has been taken as 1 z-score (1 standard deviation) below the bottom boundary of the SOS (Figure 7.18). Using this value as a boundary defines Poole Harbour transitioned towards a dangerous state ca. mid-2000s, this is in agreement with the 10 year sequential algorithm and is only 10 years after the suggested break date of the breakpoint analysis (Table 7.4). However, it is stressed this analysis has used a very general and simplistic model of the Poole Harbour system. For a better estimation further investigation is required as stated in Section 7.2.2 and expanded upon in Section 8.3.

Table 7.4: Summary of Poole Harbour water quality breakpoints obtained from several methods.

	Poole Harbour water quality
10 year sequential algorithm (p=0.05)	2004, 2005
20 year sequential algorithm (p=0.05)	-
Segmented regression (Standard Error)	1974 (1.339)
Breakpoint analysis	1992

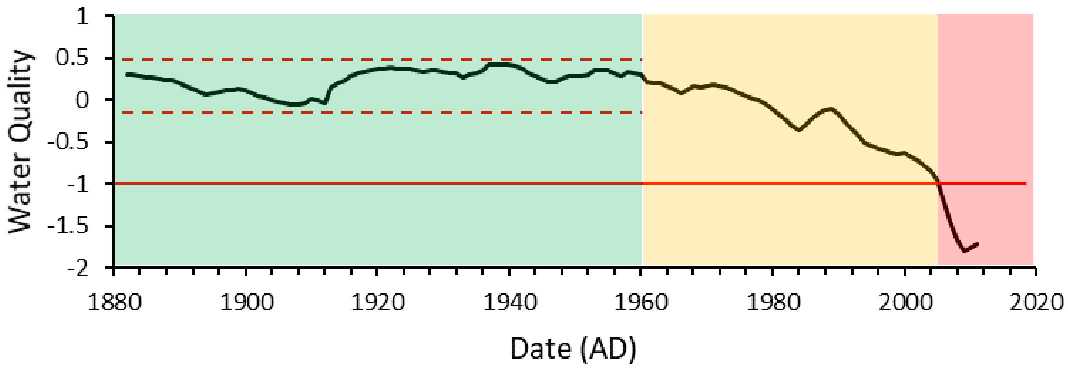


Figure 7.18: Water quality for Poole Harbour with envelope of good water quality variability (dashed red line) and transition to critical system state (solid red line). The diagram has been colour coded to represent the safe (green), cautious (yellow) and dangerous (red) stages of the system.

The analysis within this chapter suggests Poole Harbour is in a critical system state, i.e. it has become eutrophic as a consequence of excess nitrogen loading. It is apparent that for Poole Harbour to be restored to historical acceptable water quality levels, nitrogen loading will likely need to be reduced. This would involve reducing nitrogen loading from point and diffuse sources within the system.

Strict nitrogen removal processes would be required at all STWs in the catchment, this has already started at Poole STW in 2008 (Jones, D. (Wessex Water) pers. comm. 2017) but would have to be a standard process for most, if not all, STWs within the Poole Harbour catchment.

Agricultural management would be required to reduce not only nitrogen leaching into the rivers, thus the estuary but also to reduce the potential of sediment erosion from the catchment into the estuary. Some mitigation measures have already been tested to combat these issues, e.g. sediment reduction from the Win catchment, a tributary of the River Frome (PHCI, 2014).

The sediments of Poole Harbour are found to contain high nitrogen levels as detected by the increasing $\delta^{15}N$ values post ca. 1940, with the highest levels detected at present, i.e. post ca. 2010 (Figure 7.19). Sediments may provide nutrients which stimulate algal productivity during periods of sediment disturbance, e.g. tidal activity and dredging, or during biogeochemical processes. Dredging and removal of these sediments from the estuary may prevent further algal blooms by removing the nutrients sequestered in the sediments. The long term benefits of this strategy must be balanced against the potential short term negative impacts for algal blooms driven by nutrients released during dredging.

Reducing the nitrogen within the system, e.g. reducing agricultural fertilisers, strict nitrogen removal at STWs and/or dredging of high nitrogen containing sediments, may aid the reversal of eutrophic status within Poole Harbour by reducing the limiting macronutrient required for algal productivity within estuarine systems.

Due to the groundwater nature of the Poole Harbour catchment, catchment managers should be aware that changes within the agricultural landscape of the catchment, e.g. sensitive farming and reducing artificial nitrogen fertilisers, may take several decades to reduce the nitrogen load to Poole Harbour itself. Poole Harbour has been defined as a step change system (Section 7.4), which means that nitrogen reduction processes may reduce or reverse the eutrophic status of the estuary, but it will likely take several years, if not decades, to potentially reverse the eutrophication. Evidence presented within this chapter suggests that there is a 20-30 year lag time between drivers and water quality response, thus nitrogen reducing practices put into effect now may not cause an increase in water quality response until ca. 2040-2050.

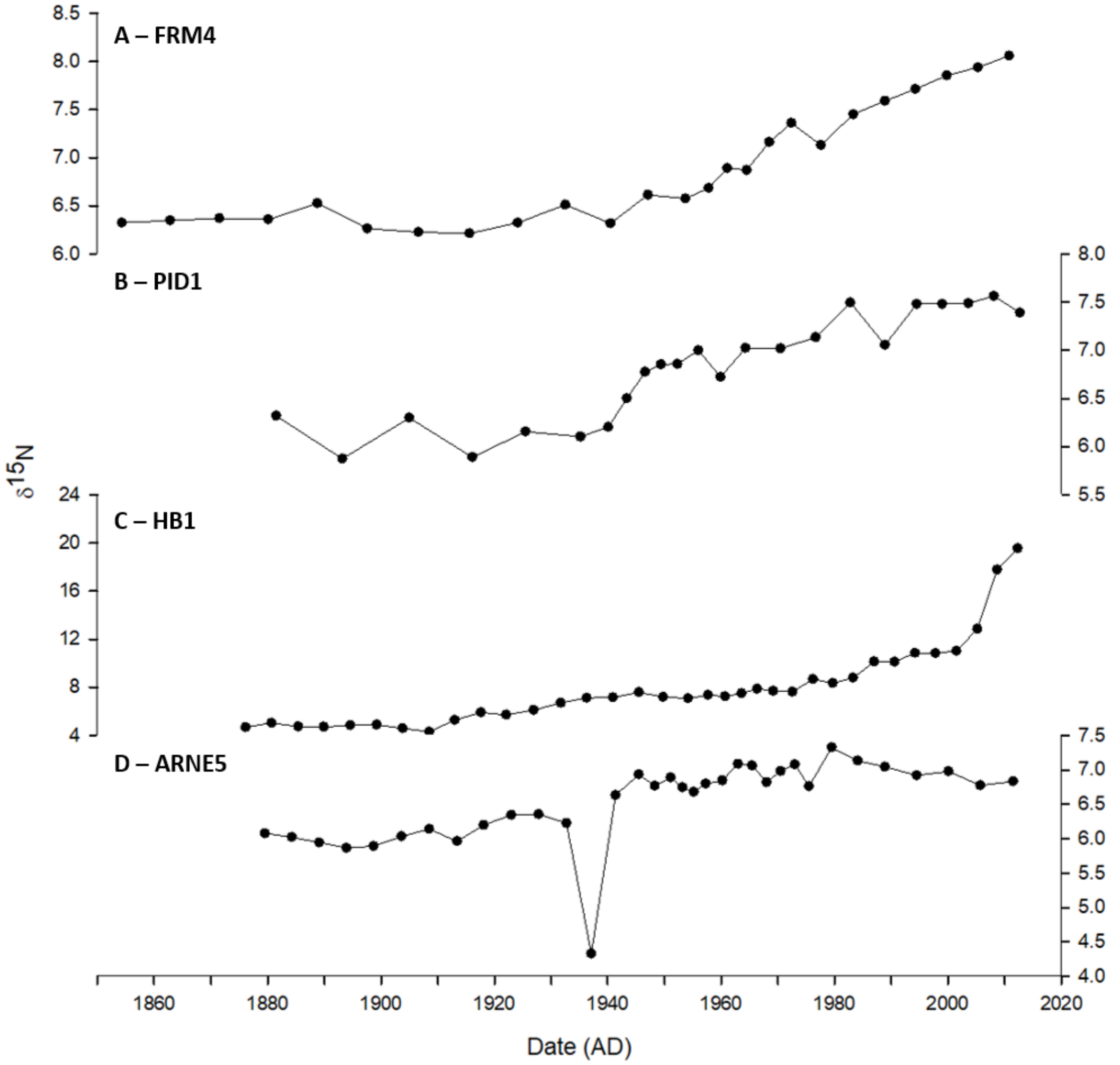


Figure 7.19: $\delta^{15}N$ values for A: FRM4, B: PID1, C: HB1 and D: ARNE5.

Chapter 8 Conclusions

8.1 Introduction

The aim of this thesis was to establish a safe operating space (SOS) for Poole Harbour water quality, to determine if the good water quality can be restored and implications of these findings for the management of the Poole Harbour catchment. Three objectives were set to achieve this overall aim:

- To reconstruct Poole Harbour's historic water quality and assess the drivers of change using palaeoenvironmental reconstruction techniques.
- To determine when and where tipping points in water quality occurred and establish the driver/response interactions of them.
- To determine how the system responds to catchment drivers, i.e. in bifold, step change or linear manner.

This chapter commences by reviewing the principal findings of this research which allowed the aim and objectives to be met (Section 8.2). Following this, recommendations for future research with regards to determining the future for Poole Harbour water quality and ecology will be discussed (Section 8.3).

8.2 Principal findings

Four cores were retrieved from within Poole Harbour. FRM4 and PID1 were taken from where the Rivers Frome and Piddle respectively meet their mutual estuary, these cores represent the agricultural contribution to Poole Harbour from the catchment. HB1 was retrieved from within Holes Bay into which the sewage treatment effluent from Poole Sewage Treatment Works (STW) drains; this core represents industrial changes within the catchment. ARNE5 was taken from the Arne Peninsula and was selected as a control site for the study. The analysis of these cores has allowed for a holistic reconstruction of Poole Harbour environmental change considering the relative contributions of differing catchment drivers. The conclusions drawn from the analysis of these four cores are presented in the following Sections (8.2.1, 8.2.2 and 8.2.3).

8.2.1 Sediment accumulation rates

Analysing the changes in the sediment accumulation rates (SARs) of FRM4, PID1, HB1 and ARNE5 allowed catchment scale drivers of environmental change within Poole Harbour to be identified. These were as follows:

- Ca. 1940-1970s, the Poole Harbour catchment underwent changes that resulted in an increase in SARs within Poole Harbour.
    - The intensification in agriculture due to the 'war effort' resulted in increased erosion and transport of agricultural soils within the Rivers Frome and Piddle catchments, accounting for the increase in SARs in FRM4 and PID1 ca. 1940-1970s.
    - Erosional activities on the heathlands in the Holes Bay catchment supplied large quantities of sediment to the water. The volume of water within Holes Bay was reduced due to land reclamation to allow for the construction of industrial buildings and infrastructure. Thus, an increase in supply of sediment and a reduction in water volume increased SARs in HB1.
    - The increase in ARNE5 SARs ca. 1940-1970s was attributed primarily to the increase in fine material brought to the harbour as a result of the intensification of agriculture in the River Frome and Piddle catchments. The industrial signal recorded at Holes Bay was not detected in ARNE5, likely due to the narrow entrance between Holes Bay and the rest of the harbour reducing the potential for transfer of material between the two bodies of water.
- Post ca. 1970s, a shift in catchment activities caused a reduction in SARs across Poole Harbour.
    - Post ca. 1970s, the 'war effort' and the subsequent elevated agricultural activity ceased, meaning the intensification in agriculture declined, reducing the amount of sediment erosion from the agricultural catchment. With this decline in agricultural practices, water meadow management ceased, which meant sediment could be more easily stored within the Rivers Frome and Piddle. Thus, the decline in agricultural activities reduced the SARs of FRM4 and PID1. These SARs remained higher than pre- ca. 1940s as the agricultural activity was still higher post ca. 1970 than pre-ca. 1940s.

  - Heavy erosional activities on the heathlands within the Holes Bay catchment reduced post ca. 1970s when the areas were built on, reducing the supply of material to Holes Bay. However, post ca. 1970s SARs remain higher than pre- ca. 1940s SARs as there is now less volume for sediment to be deposited due to the land reclamation.
  - The decline in ARNE5 SARs post ca. 1970 has been associated to the decline in agricultural activity within the Rivers Frome and Piddle catchments.

ARNE5 SARs were compared to SARs of other published studies within Poole Harbour and other southern England estuaries.

- Bayesian age-depth modelling produced SARs with increased variation when compared to other published SARs.
- ARNE5 showed some similarity to other published SARs of the Arne area, more so to Marshall et al., (2007) likely due to the close proximity the cores were taken from each other and that Marshall et al., (2007) used more chronological markers than other published records of the area meaning their SARs showed more variability, somewhat similar to those of ARNE5.
- When averaged across the time period ca. 1880-2015, the SAR of ARNE5 showed most similarity to other southern England estuaries with a notable freshwater supply and/or narrow entrance between the estuary and the sea.

8.2.2 Nutrient and ecological changes over the last ca. 150 years

Catchment drivers were responsible for an increase in nutrient delivery to the estuary post ca. 1940s. These changes were within the boundary of natural variability until major changes in ecological state occurred ca. 2000s.

- Agriculture intensification ca. 1940-1970s increased the nutrient delivery to FRM4 and PID1. Due to the groundwater nature of the catchment, nutrient levels continued to increase post ca. 1970s after the decline in agricultural practices after the ‘war effort’, as evidenced by the increasing value of $\delta^{15}N$ from ca. 1940s to present.
- Increasing population post ca. 1970s increased the $\delta^{15}N$ detected in HB1 due to the added pressure on the Poole STW.

- Increased nutrient supply to ARNE5 post ca. 1940 was primarily driven by the agricultural intensification in the Rivers Frome and Piddle catchments. The transport of the nutrients to ARNE5 was facilitated by periodic increases in sea level.
- The source of nutrients was the main control on the geochemical record of FRM4, PID1 and ARNE5, determined by the decline in $\delta^{13}C$ during increased productivity as fractionation of carbon was not required due to the excess nutrients within the system. The HB1 geochemical record was determined to be controlled by productivity within the water.
- Algal productivity (diatoms and pigments) within FRM4, PID1 and HB1 demonstrated a response to changes in nutrients, i.e. increased nutrients produced higher algal abundance. These sites showed signs of eutrophication ca. 2000s by an increased abundance in algae and shifts within statistical measurements (PCA and DCA axis 1 z-scores). Algal productivity also increased in ARNE5 ca. 2000s, however the abundance of algae was less than that of other cores suggesting the productivity in ARNE5 is not as great as the other sites.

8.2.3 Changes in Poole Harbour's water quality over the last 150 years

Causes of the change in Poole Harbour water quality over the last ca. 150 years were reconstructed using the drivers of nutrient and ecological change discussed in Section 8.2.2 above. A water quality proxy indicator was created for each core using the averaged z-scores of $\delta^{15}N$, organic matter, pigment PCA axis 1 scores and inverted C/N. Findings from the water quality indicator are summarised below:

- An estimated whole system model was established using estimated proportions of each main source of nutrients, FRM4, PID1 and HB1, contributed to the harbour. However, the model was a simplistic representation with several limitations. To provide a better estimated whole system model, more investigation would be required to better determine source contributions, including the sea. Investigation would also be required to determine the exchange between the estuary and the sea, i.e. how much comes in from the sea and how much of the nutrients gets flushed out to the sea.
- Each core demonstrated an envelope of variability which was determined to be the good/acceptable water quality for Poole Harbour, or the SOS. Water

quality for FRM4 and PID1 remains within the SOS from the start of their records to ca. 1960 and for HB1 and ARNE5 the SOS extends to ca. 1970. The dates at which the water quality leaves the envelope of variability are considered to be tipping points as water quality declines to present.

- The lag time between changes in the catchment, i.e. agricultural intensification onset ca. 1940 and industrial changes ca. 1940, and the decline of water quality, ca. 1960 (FRM4 and PID1) and ca. 1970 (HB1 and ARNE5), demonstrates that the aquatic environment in the Poole Harbour system can be classified as a step change system.
- A step change system can potentially be reversed, i.e. return to good water quality. It was determined that the increased SARs of the sites provided a source of excess nutrients, in addition to those supplied directly via the watercourse, meaning that achieving a pre- ca. 1940s water quality state would not be possible. Therefore, ca. 1960s/1970s has been considered as a target system state as this was during the high SARs period and before the tipping point when the water quality declined. Therefore, returning to just prior to the conditions of these dates could potentially reverse the water quality decline.
- A very general and simplistic view of the system indicates that water quality could be restored to pre- ca. 1960s/1970s values if dissolved nitrate concentrations remained below 2mg N/l which equates to a cumulative total <90kg/ha of artificial nitrate fertiliser application. However, current artificial nitrate fertiliser applications are only ca. 100kg/ha and the cumulative total is ca. 2750kg/ha. This suggests that applications would have to be reduced further than <90kg/ha as it will take several decades for any reductions to take effect on the water quality due to the groundwater nature of the catchment. Further reductions in nitrogen loading of the system would also be required as this nitrate target does not account for the contribution from other sources of nitrogen, e.g. STW effluent or from the sea. This could be done, for example, by having nitrogen removal processes at STWs within the Poole Harbour catchment like those introduced at Poole STW in 2008.
- FRM4 and PID1 may provide an indication as to the future development of ARNE5 given ARNE5's tendency to respond to changes within the agricultural catchment, with environmental change lagging behind change recorded in FRM4 and PID1. However, no estimates have been given as to precise future of the Poole Harbour system given modelling would be required to look at system responses under different scenarios (see below).

8.3 Recommendations for future research

Any future research in Poole Harbour should focus on modelling and predicting environmental change given such analysis would have the most applied relevance to catchment managers, i.e. Wessex Water. These are as follows:

- This research has primarily looked at catchment changes and their impact on water quality within Poole Harbour. However, within an estuarine system, consideration should be given to the contributions of the sea and its effect on the estuarine environment. Thus, it is recommended that the exchange of nutrients, pollutants, etc, entering and leaving Poole Harbour via the sea are investigated. Marine sediment cores should supplement such an investigation and be recovered in close proximity to the estuary mouth both within, and external, to the estuary. Such marine cores could evidence historic changes in nutrient dynamics which could be compared to the cores recovered in this study to further constrain the relative importance of terrestrial and marine drivers of the Poole Harbour system.
- Tidal patterns should be investigated with regards to their flow and exchange with the different areas of Poole Harbour. For example, whether the exchange between Holes Bay and the rest of the harbour means that Holes Bay has a potential to influence other areas of Poole Harbour, or if it is the harbour that is a driver of Holes Bay environmental change. By determining these exchanges, the relative influence of each nutrient source (Rivers Frome and Piddle, Holes Bay and the sea) on the harbour can be examined.
- An integrated catchment-estuary model to quantify the contribution of groundwater and surface flow to the estuary should help catchment managers understand how long it will take for changes in policies to have an effect on water quality.
- Modelling should be used to develop a holistic Poole Harbour system, within which future estimates of water quality and ecosystem state can be provided under different scenarios of change, e.g. catchment sensitive farming, implementation/increased STW nitrogen removal. The outcomes of such modelling may facilitate catchment management policies by enabling them to investigate how different possible future policies will influence the water quality, e.g. reducing artificial fertiliser application to <90kg/ha.

- This thesis has focused on providing a SOS for Poole Harbour only regarding water quality and its drivers. For a holistic Poole Harbour SOS, other variables should also be examined with regards to their safe, cautious or dangerous state, e.g. fish stocks, air pollution, salinity incursions and climate change. These variables are not necessarily independent of water quality but are key parts of the system. By investigating how these other variables interact with the Poole Harbour system will allow for more accurate future modelling scenario prediction.

Future research assessing the past and future water quality of Poole Harbour may wish to exploit additional palaeoenvironmental techniques to better refine historic environmental change, and in doing so, better parametrise models of Poole Harbour future development. These techniques are detailed below.

- Supplementary cores should be retrieved and analysed from the areas studied to better explore the spatial variability of Poole Harbour environmental development, and to test the replicability of results presented in this thesis. Recovering cores from additional locations within the harbour would also contribute toward an improved understanding of the Poole Harbour system.
- Further chronological methods could be used to improve the dating of environmental change reported in this thesis. Radiocarbon dating can be used both as an additional temporal marker across the studied time period, i.e. post 1850, and to date sediment which accumulated prior to SCP base date of ca. 1850±25 years. Dating of older sediment within Poole Harbour using radiocarbon dating has been carried out by Long et al., (1999) and Marshall et al., (2007). Pollen analysis could also be used as a chronological marker to identify dateable changes in catchment and estuarine flora, i.e. *Pinus* and *Spartina*, which could be used to refine age-depth models (Long et al., 1999). The usefulness of dating sediments older than the pre- ca. 1940s increase in SARs is somewhat academic if the system cannot be restored to pre- ca. 1940s state, i.e. before the increased SAR period. However, it may allow for further understanding of catchment drivers and water quality responses to events that may have occurred pre- ca. 1850.
- This research has utilised a wide range on palaeoenvironmental reconstruction techniques to determine nutrient and ecological dynamics within Poole Harbour. However, further research could include increasing the sampling resolution of diatom analysis to identify smaller scale

changes rather than general changes which may help identify ecological response to catchment drivers on a shorter time scale. Other techniques may also be deployed to better understand ecosystem responses and biodiversity changes that cannot be identified solely using diatoms and pigments, e.g. ancient DNA (aDNA) and biomarkers.

Appendix A

Bacon output graphs showing dateable features, i.e. SCP and radionuclide dates, (transparent blue) and the age-depth model (darker grey indicates more likely calendar ages, grey dotted lines shows 95% confidence intervals and red line shows the 'best' model based on the weighted mean age for each depth).

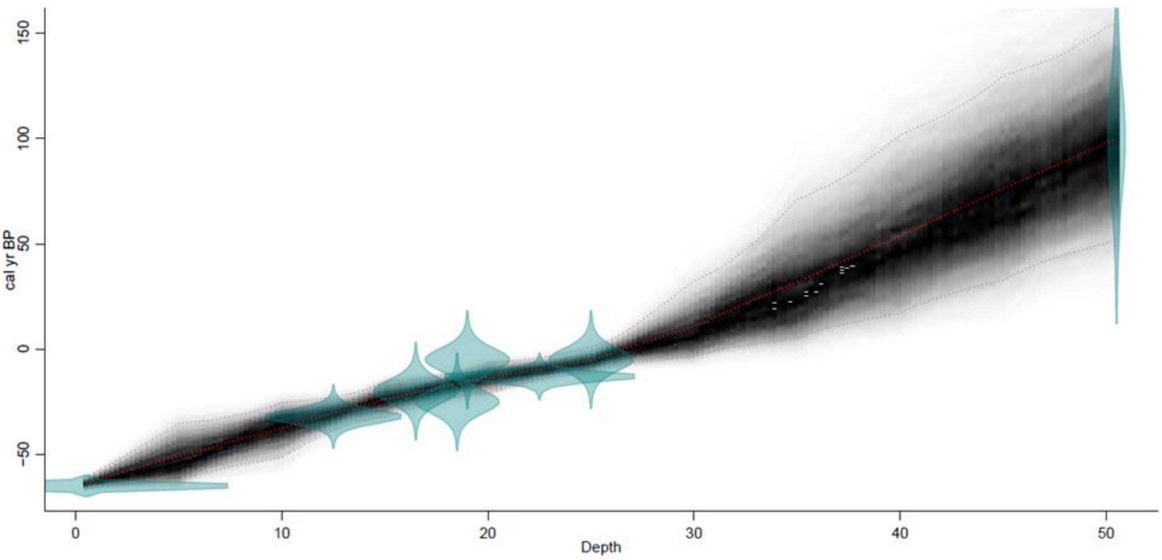
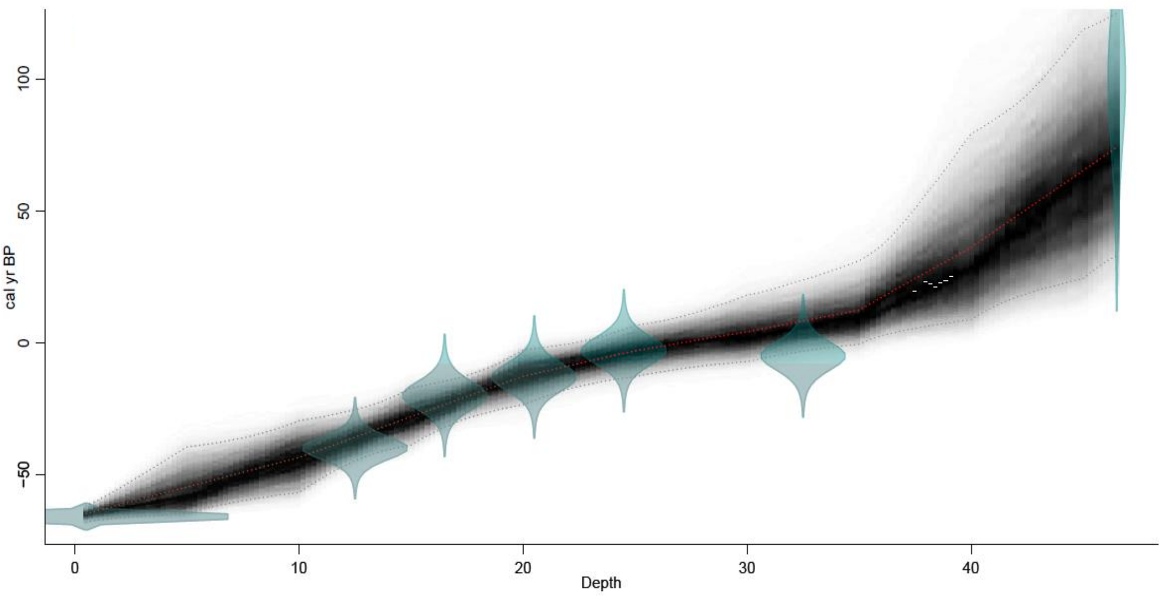


Figure A.1: FRM4.



Appendix A

Figure A.2: PID1.

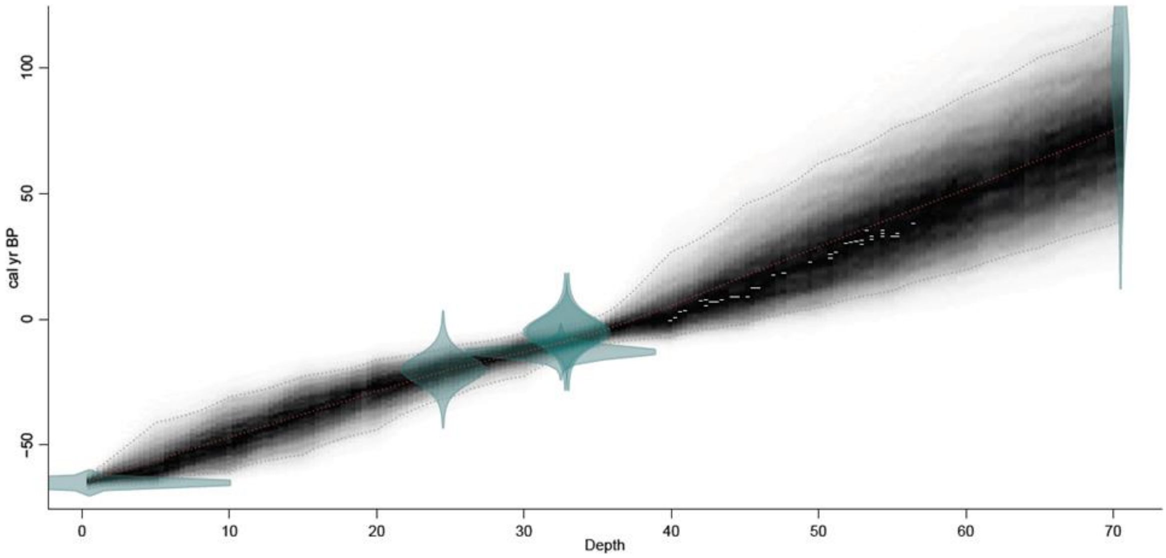


Figure A.3: HB1.

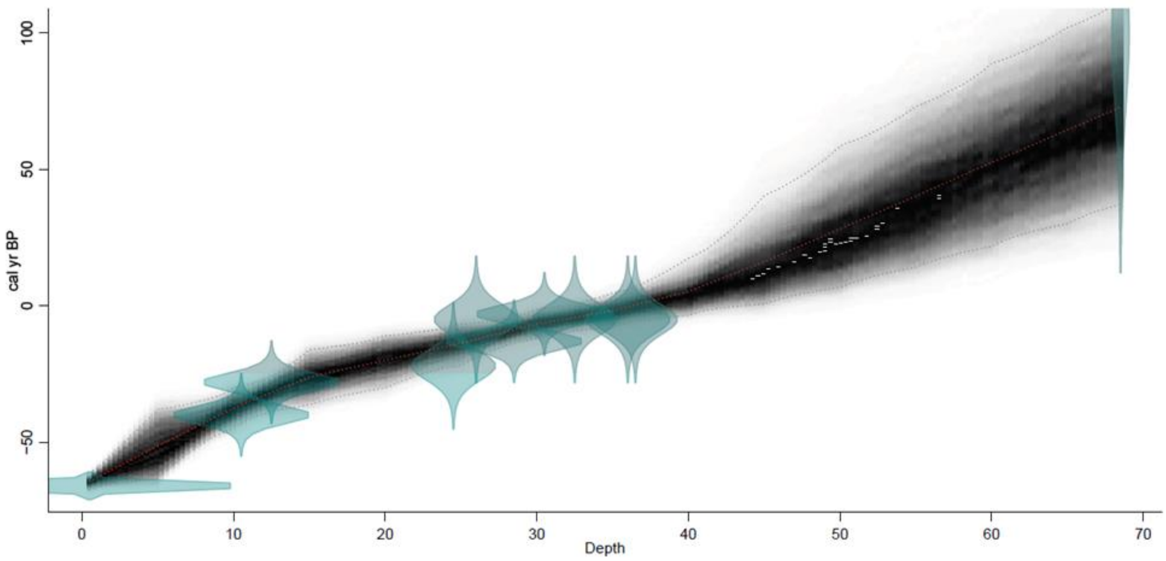
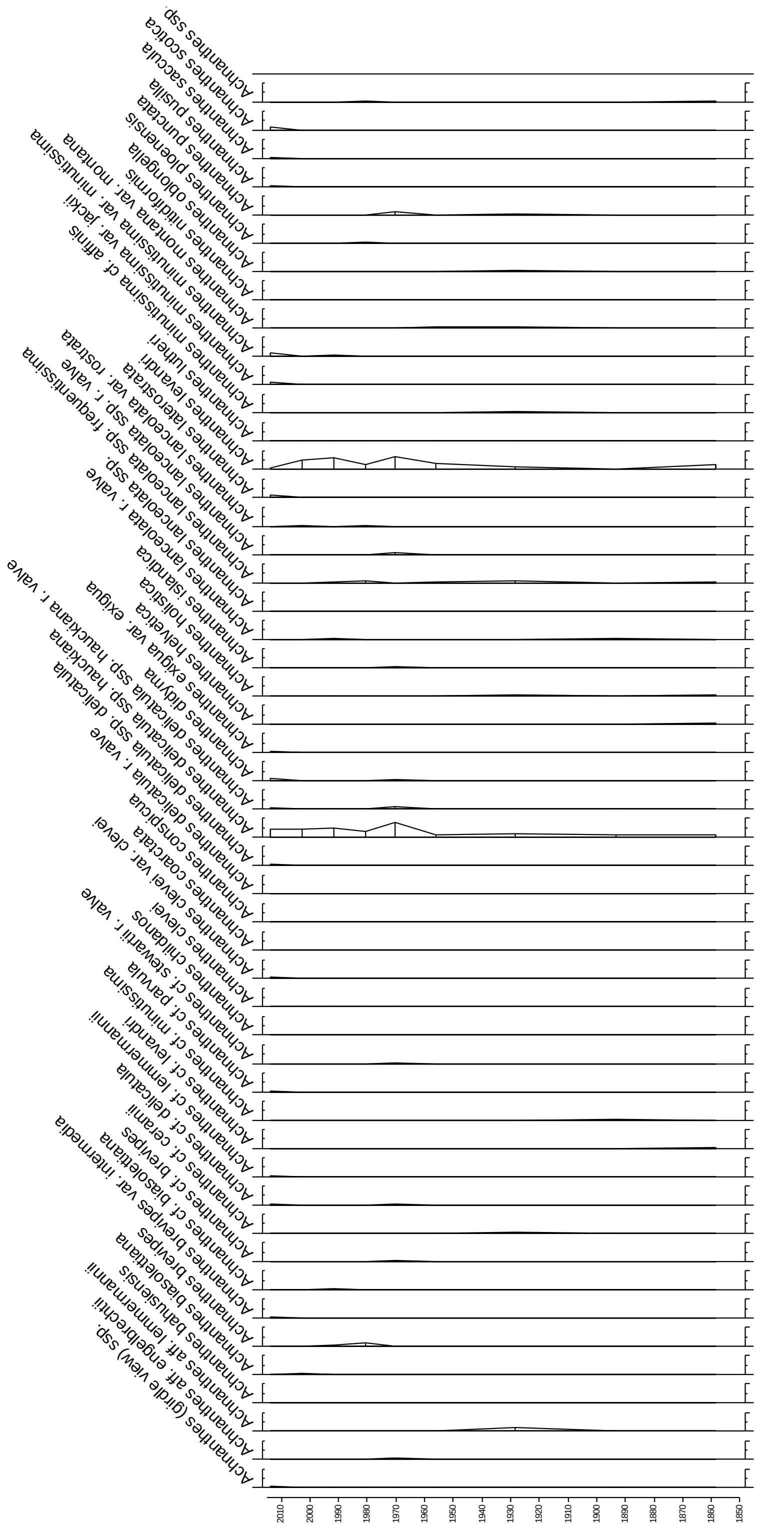


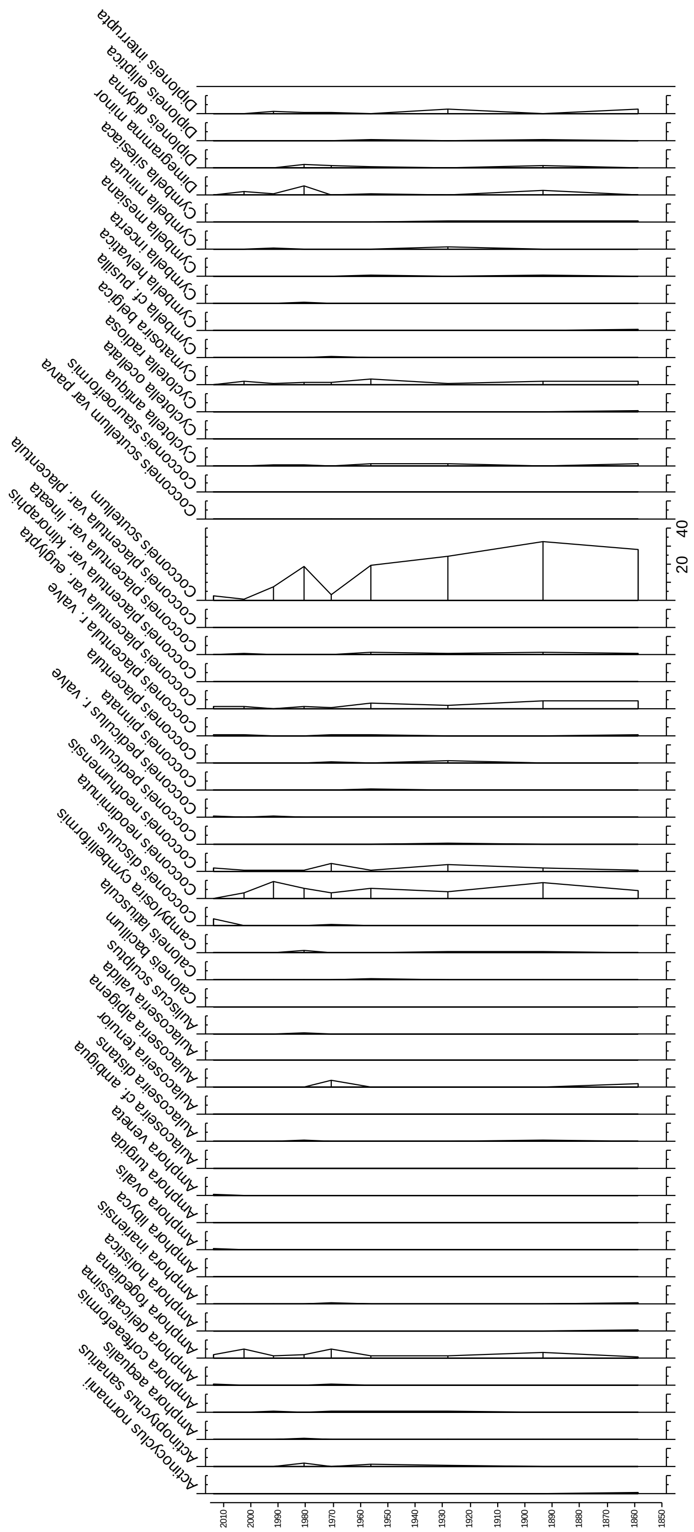
Figure A.2: ARNE5.

Appendix B

The following diagrams are the full diatom counts (percentage) for FRM4.



Appendix B


Diploneis interrupta
Diploneis elliptica
Diploneis didyma
Dimeregramma minor
Cymbella silesiaca
Cymbella minuta
Cymbella mesiana
Cymbella inerta
Cymbella helvatica
Cymbella cf. pusilla
Cymatosira belgica
Cyclotella radiosa
Cyclotella ocellata
Cyclotella antiqua
Cocconeis stauroneiformis
Cocconeis scutellum var parva
Cocconeis scutellum
Cocconeis placentula var. placentua
Cocconeis placentula var. lineata
Cocconeis placentula var. klinoraphis
Cocconeis placentula var. euglypta
Cocconeis placentula r. valve
Cocconeis placentula
Cocconeis pinnata
Cocconeis pediculus r. valve
Cocconeis pediculus
Cocconeis neothumensis
Cocconeis neodiminuta
Cocconeis disculus
Campylosira cymbelliformis
Caloneis latiuscula
Caloneis bacilium
Auliscus sculptus
Aulacoseira valida
Aulacoseira alpigena
Aulacoseira tenuior
Aulacoseira distans
Aulacoseira cf. ambigua
Amphora veneta
Amphora turgida
Amphora ovalis
Amphora libyca
Amphora inariensis
Amphora holsatica
Amphora fogediana
Amphora delicatissima
Amphora coffeaeformis
Amphora aequalis
Actinoptychus senarius
Actinocyclus normanii
20
40
2010
2000
1990
1980
1970
1960
1950
1940
1930
1920
1910
1900
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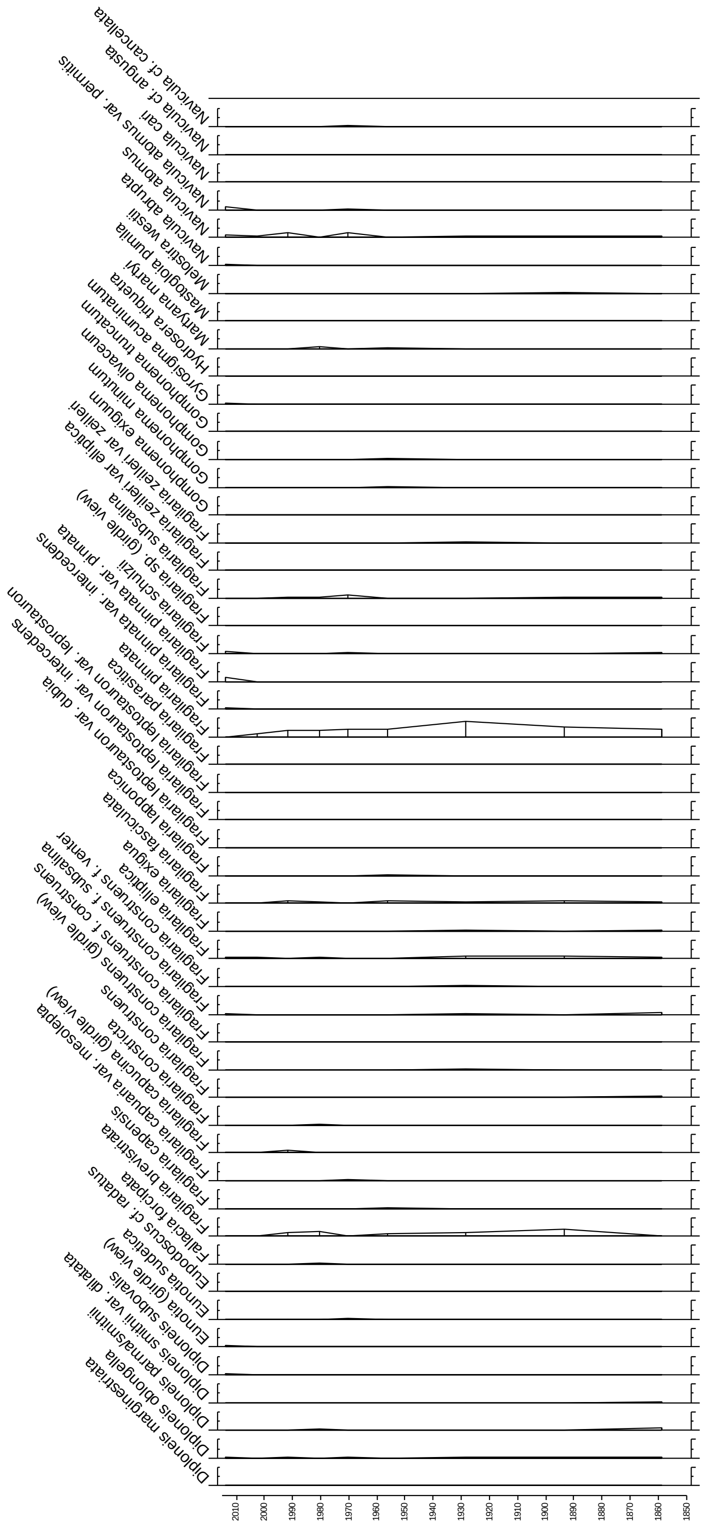
1880
1870
1860
1850


Navicula cf. cancellata
Navicula cf. angusta
Navicula cari
Navicula atomus var. permitis
Navicula atomus
Navicula abrupta
Navicula westii
Melosira pumila
Mastogloia martyi
Martyana martyi
Hydrosera triquetra
Gyrosigma acuminatum
Gomphonema truncatum
Gomphonema olivaceum
Gomphonema minutum
Gomphonema exiguum
Fragilaria zeilleri var zeilleri
Fragilaria zeilleri var elliptica
Fragilaria subsalina
Fragilaria sp. (girdle view)
Fragilaria schulzii
Fragilaria pinnata var. pinnata
Fragilaria pinnata var. intercedens
Fragilaria pinnata
Fragilaria parasitica
Fragilaria leptostauron var. leprostauron
Fragilaria leptostauron var. intercedens
Fragilaria leptostauron var. dubia
Fragilaria leptonica
Fragilaria lapponica
Fragilaria fasciculata
Fragilaria exigua
Fragilaria elliptica
Fragilaria construens f. venter
Fragilaria construens f. subsalina
Fragilaria construens f. construens
Fragilaria construens (girdle view)
Fragilaria construens
Fragilaria constricta
Fragilaria constricta (girdle view)
Fragilaria capucina var. mesolepta
Fragilaria capuana
Fragilaria capensis
Fragilaria brevistriata
Fragilaria forcipata
Fallacia forcipata
Eupodoscus cf. radiatus
Eunotia sudetica
Eunotia (girdle view)
Diploneis subovalis
Diploneis smithii var. dilatata
Diploneis parma/smithii
Diploneis parmella
Diploneis oblongella
Diploneis marginestriata
2010
2000
1990
1980
1970
1960
1950
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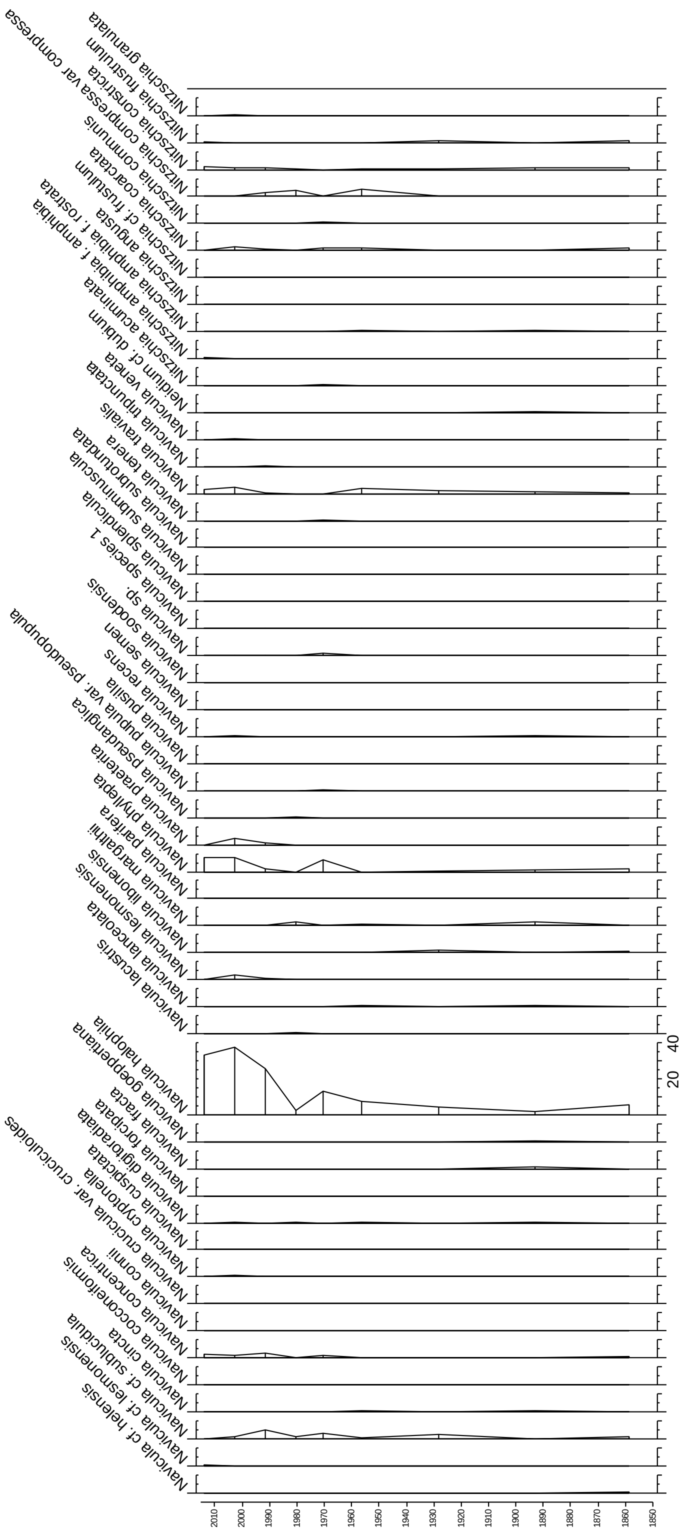
Appendix B



Nitzschia granulata
Nitzschia frustulum
Nitzschia constricta
Nitzschia compressa var compressa
Nitzschia communis
Nitzschia coarctata
Nitzschia cf. frustulum
Nitzschia angusta
Nitzschia amphibia f. rostrata
Nitzschia amphibia f. amphibia
Nitzschia acuminata
Neidium cf. dubium
Navicula veneta
Navicula tripunctata
Navicula trivialis
Navicula tenera
Navicula subrotundata
Navicula subminuscula
Navicula splendicula
Navicula species 1
Navicula sp.
Navicula soodensis
Navicula semen
Navicula recens
Navicula pusilla
Navicula pupula var. pseudopupula
Navicula pseudanglica
Navicula praeterita
Navicula phyllepta
Navicula parifera
Navicula margalithii
Navicula libonensis
Navicula lesmonensis
Navicula lanceolata
Navicula lacustris
Navicula halophila
Navicula goeppertiana
Navicula facta
Navicula forcipata
Navicula digitoradiata
Navicula cuspidata
Navicula cryptonella
Navicula cruciculia var. cruciculoides
Navicula connii
Navicula concentrica
Navicula cocconeiformis
Navicula cincta
Navicula cf. subbicudula
Navicula cf. lesmonensis
Navicula cf. helensis
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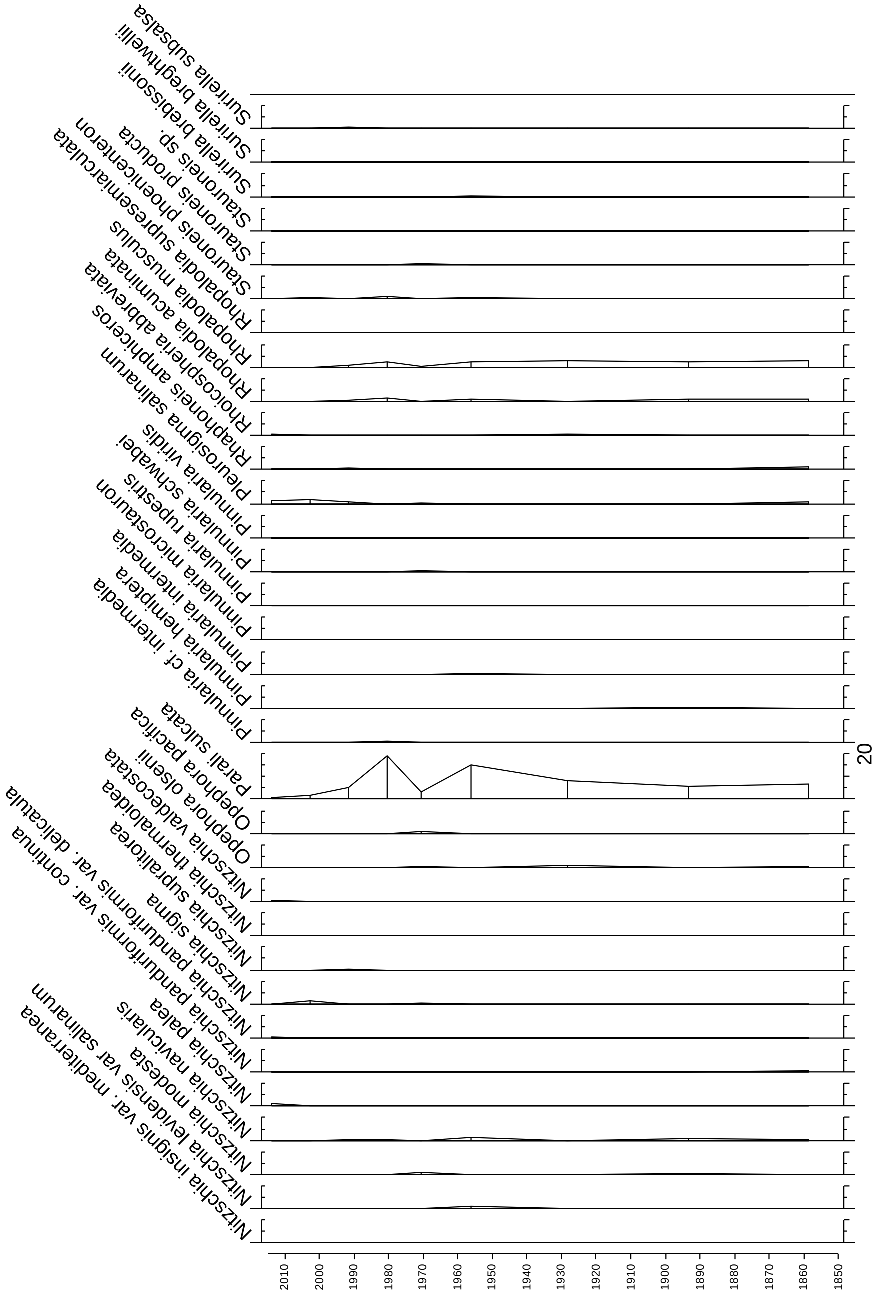
Surirella subsalsa
Surirella brightwellii
Surirella brebissonii
Surirella sp.
Stauroneis producta
Stauroneis phoenicenteron
Staurosira supersemiarculata
Rhopalodia musculus
Rhopalodia acuminata
Rhopalodia abbreviata
Rhoicosphenia amphiceros
Rhaphoneis salinarum
Pleurosigma viridis
Pinnularia schwabei
Pinnularia rupestris
Pinnularia microstauron
Pinnularia intermedia
Pinnularia hemiptera
Pinnularia cf. intermedia
Parali sulcata
Opephora pacifica
Opephora olsenii
Nitzschia valdecostata
Nitzschia thermaloidea
Nitzschia supralitorea
Nitzschia sigma
Nitzschia panduriformis var. continua
Nitzschia panduriformis var. delicatula
Nitzschia palea
Nitzschia navicularis
Nitzschia modesta
Nitzschia levidensis var salinarum
Nitzschia insignis var. mediterranea
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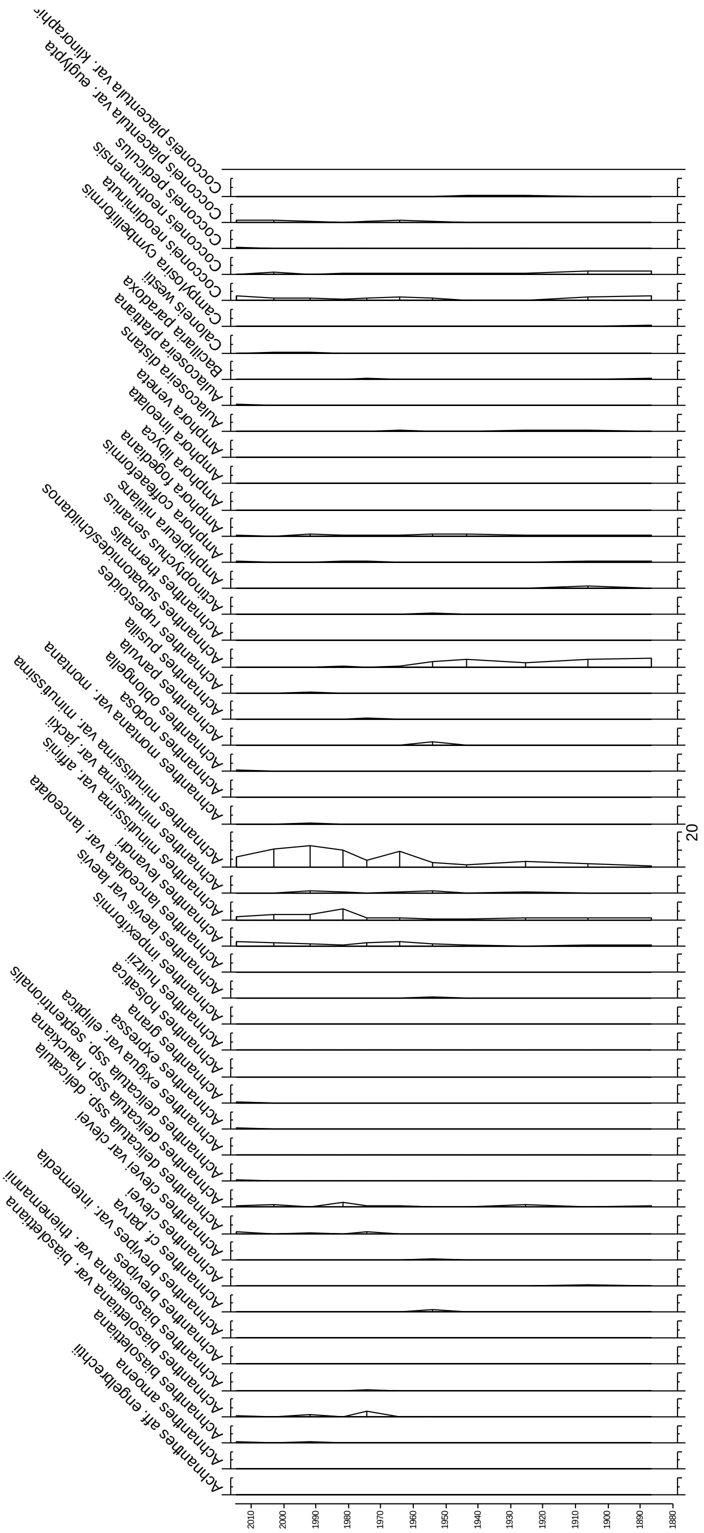
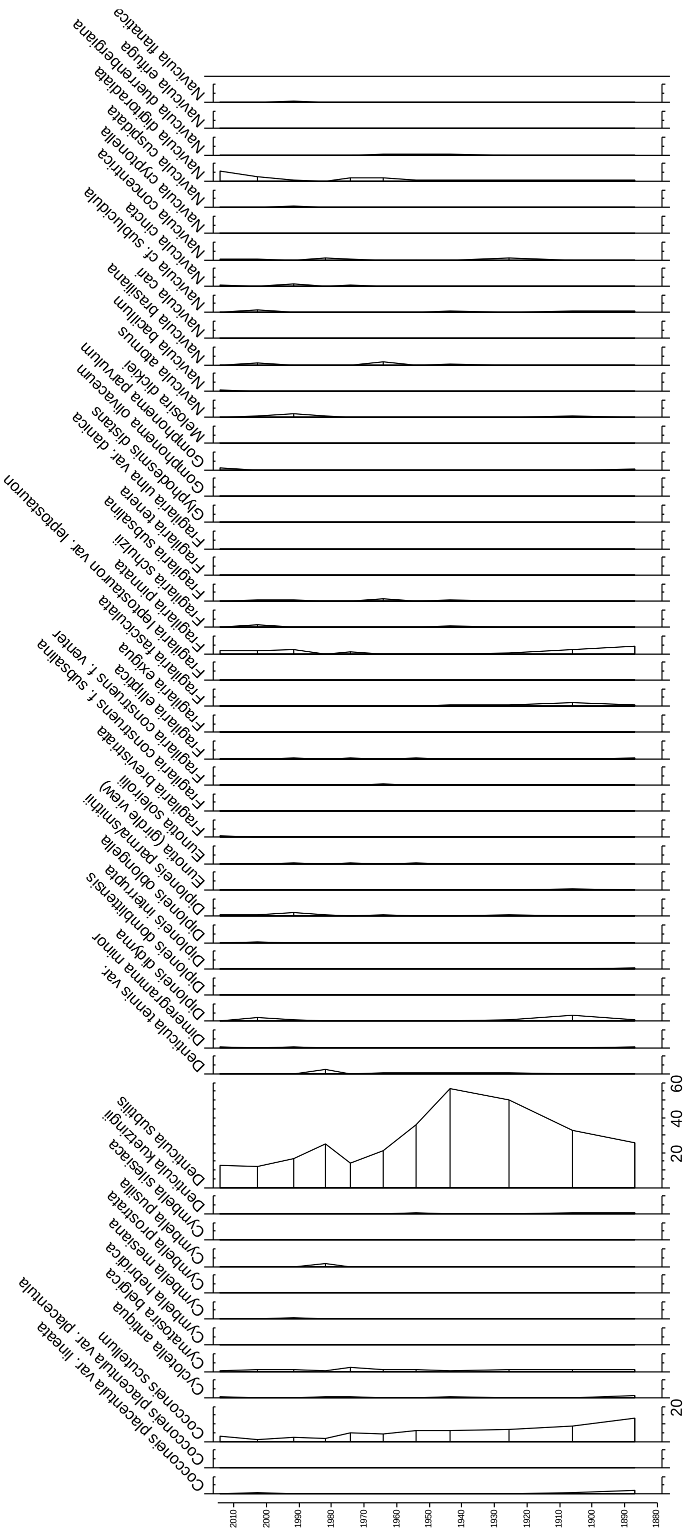
Appendix B

The following diagrams are the full diatom counts (percentage) for ARNE5.




Navicula flanatica
Navicula erifuga
Navicula duerrenbergiana
Navicula digitoradiata
Navicula cuspidata
Navicula cryptonella
Navicula concentrica
Navicula cincta
Navicula cf. sublucidula
Navicula cari
Navicula brasiliana
Navicula bacillum
Navicula atomus
Melosira dickiei
Gomphonema parvulum
Gomphonema olivaceum
Gomphonemis distans
Gomphodesmis distans
Glyphodesmis ulna var. danica
Fragilaria tenera
Fragilaria subsalina
Fragilaria schulzii
Fragilaria pinnata
Fragilaria leptostauron var. leptostauron
Fragilaria fasciculata
Fragilaria exigua
Fragilaria elliptica
Fragilaria construens f. venter
Fragilaria construens f. subsalina
Fragilaria brevistriata
Fragilaria soleirolii
Eunotia (girdle view)
Eunotia parma/smithii
Diploneis parmella
Diploneis oblongella
Diploneis interrupta
Diploneis dombilitensis
Diploneis didyma
Diplonegramma minor
Dimeregramma minor
Denticula tennis var.
Denticula subtilis
Denticula kuetzingii
Cymbella silesiaca
Cymbella pusilla
Cymbella prostrata
Cymbella mesiana
Cymbella hebridica
Cymatosira belgica
Cyclotella antiqua
Cocconeis scutellum
Cocconeis placentula var. placentula
Cocconeis placentula var. lineata
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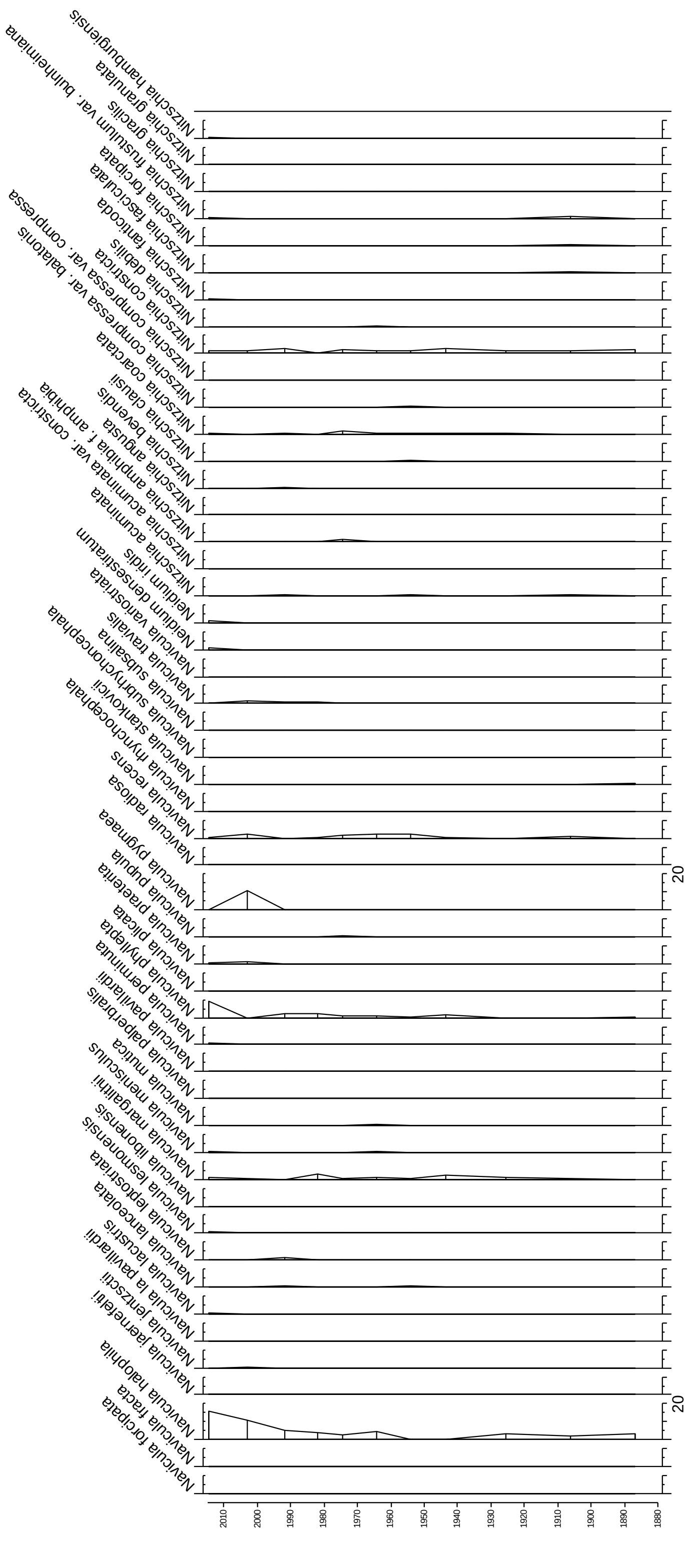
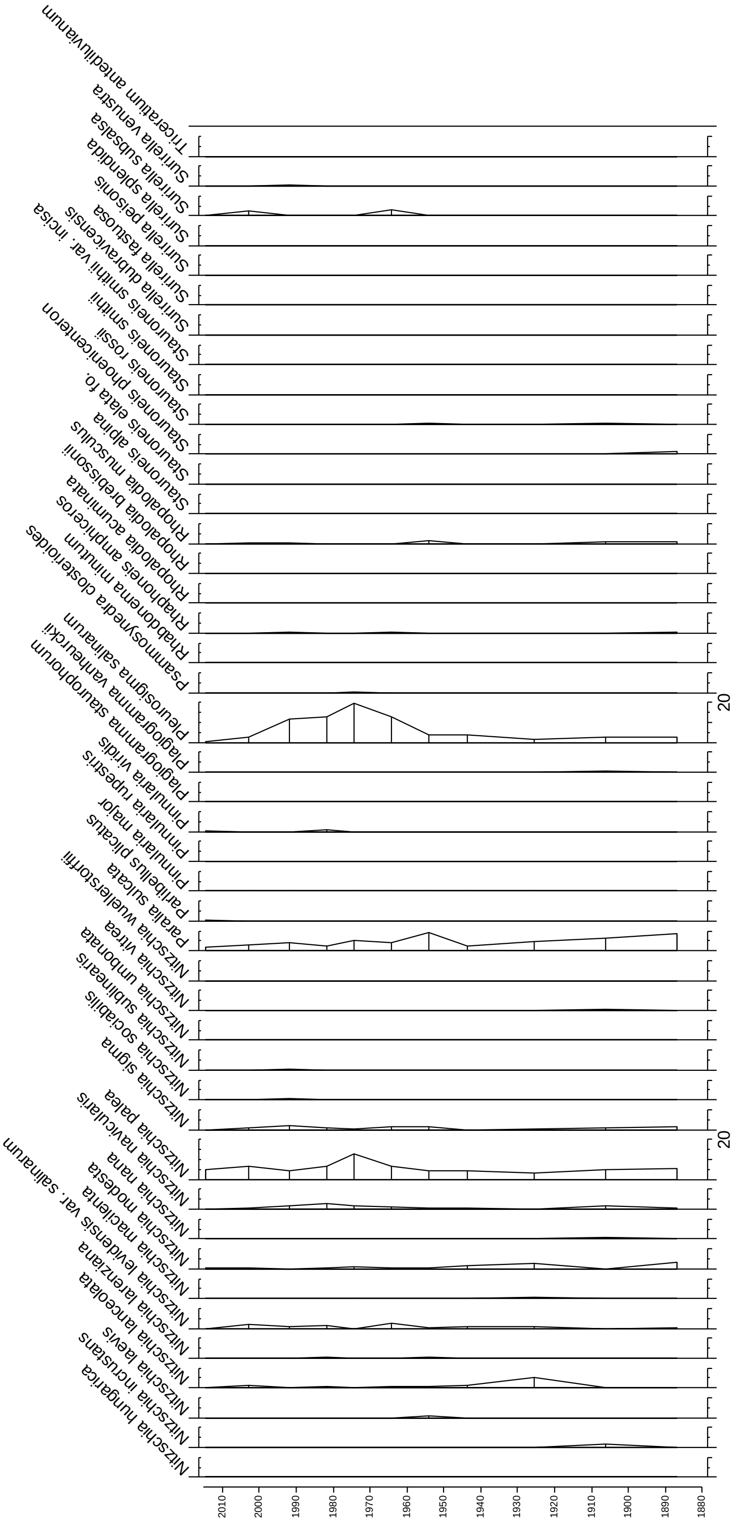
Appendix B




Triceratium antediluvianum
Surirella venusta
Surirella subsalsa
Surirella splendida
Surirella peisonis
Surirella fastuosa
Surirella dubravicensis
Surirella smithii var. incisa
Stauroneis smithii
Stauroneis rossii
Stauroneis phoenicenteron
Stauroneis elata fo.
Stauroneis alpina
Staurosira musculus
Rhopalodia brebissonii
Rhopalodia acuminata
Rhaphoneis amphiceros
Rhabdonema minutum
Rhabdonema closterioides
Psammosynedra salinarum
Pleurosigma vanheurckii
Plagiogramma staurophorum
Plagiogramma viridis
Pinnularia rupestris
Pinnularia major
Parlibellus plicatus
Paralia sulcata
Nitzschia wuellerstorffii
Nitzschia vitrea
Nitzschia umbonata
Nitzschia sublinearis
Nitzschia sociabilis
Nitzschia sigma
Nitzschia palea
Nitzschia navicularis
Nitzschia nana
Nitzschia modesta
Nitzschia macilenta
Nitzschia levidensis var. salinarum
Nitzschia lorenziana
Nitzschia lanceolata
Nitzschia laevis
Nitzschia incrustans
Nitzschia hungarica
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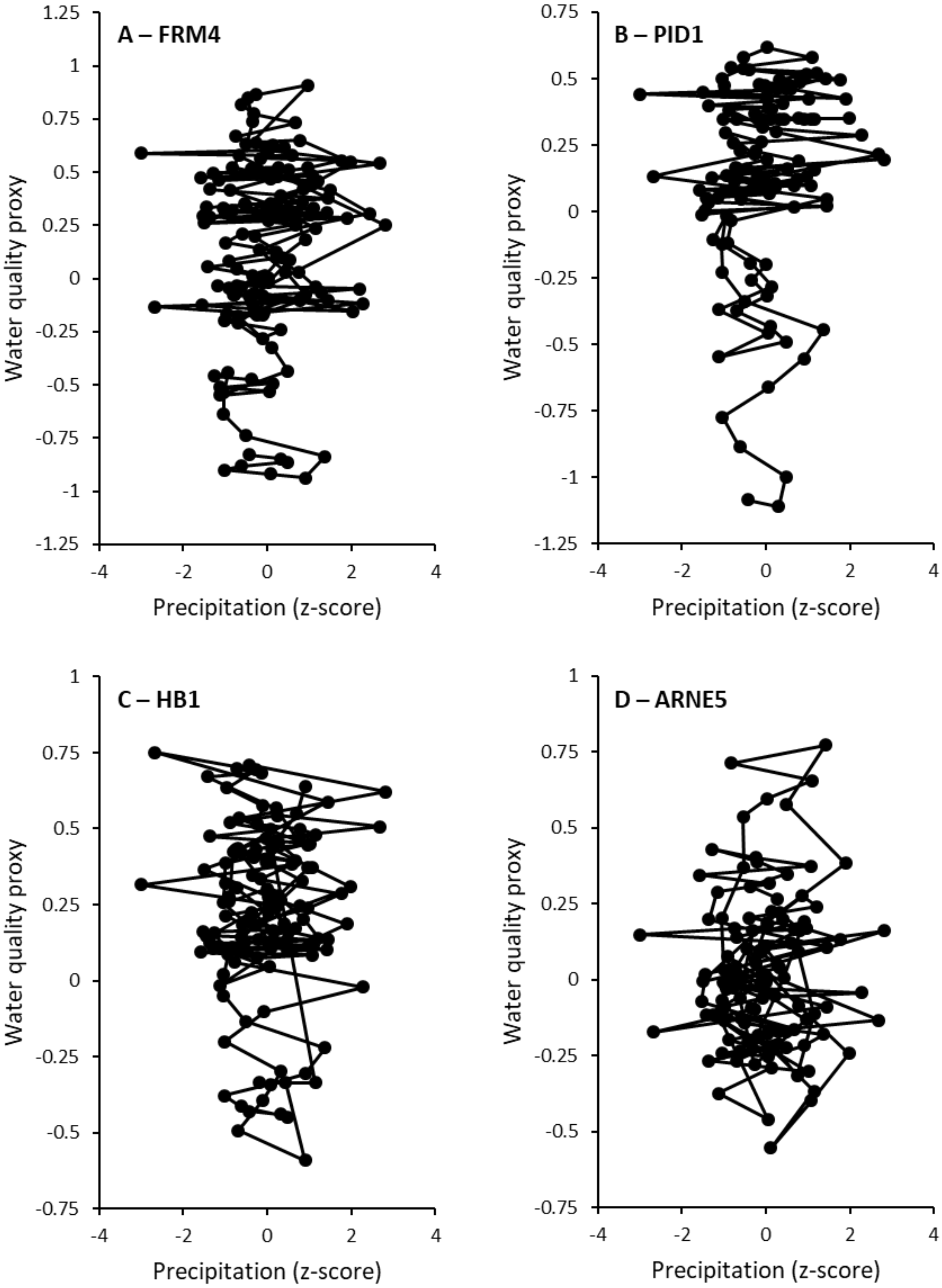
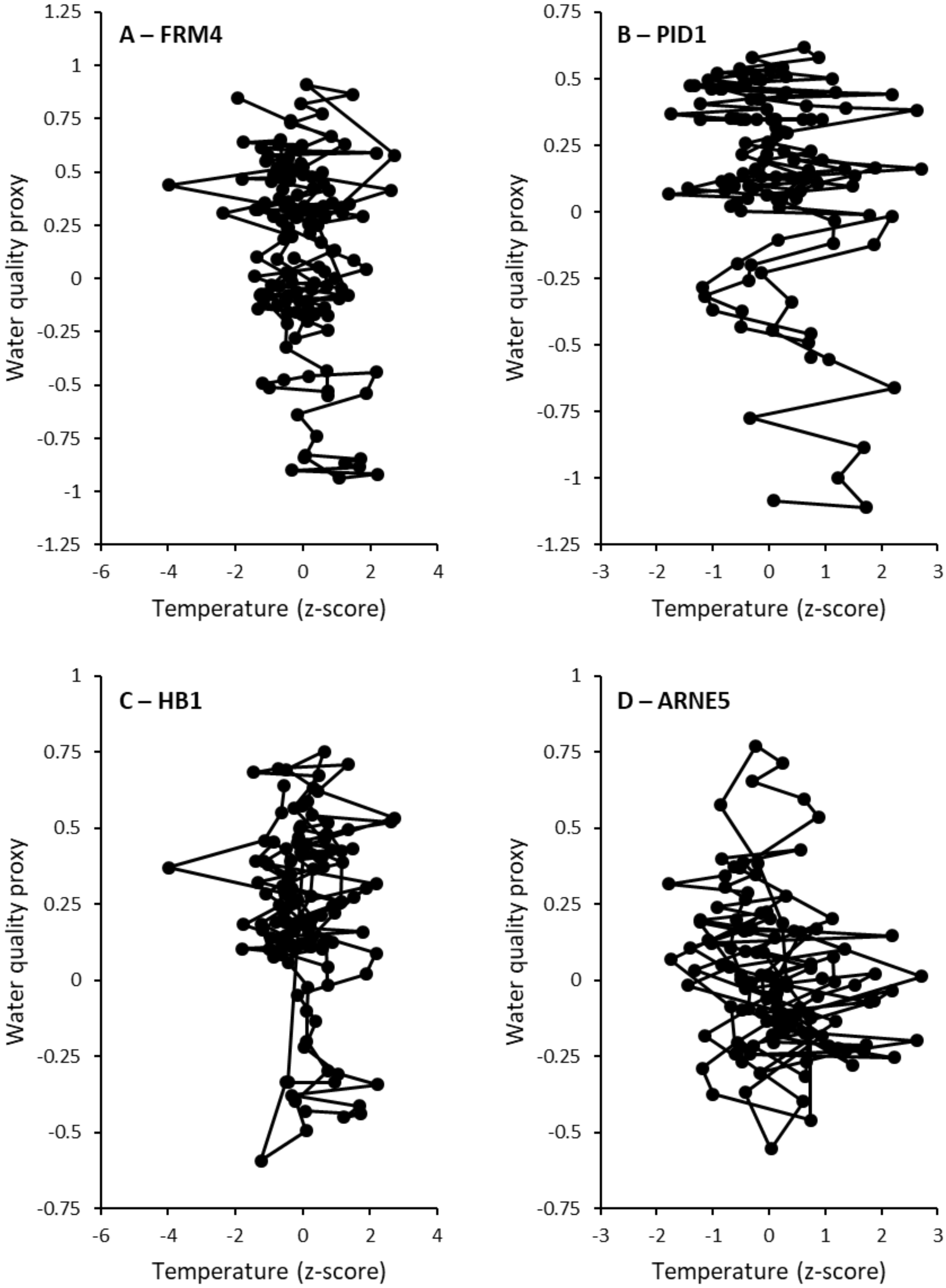
Appendix C

Water quality for A: FRM4, B: PID1, C: HB1 and D: ARNE5 against long term precipitation, for correlation scores see Table 7.2.



Water quality for A: FRM4, B: PID1, C: HB1 and D: ARNE5 against long term temperature, for correlation scores see Table 7.2.



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