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Phosphorus fate and management on the Somerset Levels and Moors Ramsar ditch systems

By

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… Ryan Letourneau

Author's Declaration

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other University award without prior agreement of the Doctoral College Quality Sub-Committee.

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Phosphorus fate and management on the Somerset Levels and Moors Ramsar ditch systems

RY CROCKER

Abstract

Fundamental to all life, phosphorus is an essential nutrient and, contrastingly, a significant threat to surface water biodiversity globally as one of the most common causes of eutrophication in surface waters worldwide. Freshwater wetland ditches afflicted by these conditions undergo a shift from primarily submerged aquatic vegetation to algae or duckweed dominance, leading to excessive shading and anoxic conditions.

Phosphorus, from both point (e.g., wastewater treatment works) and diffuse (largely agricultural runoff) sources, is currently the central reason for failure in the majority of surface water bodies in England to meet required water quality guidelines. Historic data indicate that surface waters within the ditch systems of the Somerset Levels and Moors, a listed Ramsar site (no. 914) under the Ramsar Convention and designated Special Protection Area (SPA) under the Habitat Regulation 2017, are elevated in nutrients with potential for total phosphorus to be above the current Common Standards Monitoring Guidance target of <0.1 mg L^{-1} set out by the Joint Nature Conservation Committee in 2005.

However, there is a general lack of up-to-date consistent monitoring data for the ditch systems and few comprehensive datasets are available, which cover an extended time period with good spatial coverage, leading to a lack of knowledge as to how the complex seasonal water flow paths and levels affect transport of phosphorus, from both point and diffuse sources, throughout the wetland ditch systems. This thesis pursues the closure of this knowledge gap through investigations conducted on West Sedgemoor, a designated site of special scientific interest and part of the Somerset Levels and Moors Ramsar site.

Firstly, an investigation assessed the spatial distribution of sediment phosphorus storage in the ditch systems, as freshwater sediment acts as an internal source of legacy bound phosphorus that can induce production of algal and duckweed blooms beyond what may be expected from external loading of phosphorus alone. Elevated phosphorus concentrations in sediment were observed throughout the Moor up to 4,220 mg Kg^{-1}, almost 10 times that which may be expected from background levels. The highest concentrations were generally observed at the more intensively farmed sites in the north of the moor, near key inlets and the outlet. Based upon their chemical and physical properties, clear distinction was observed between sites outside and within the Royal Society of the Protection of Birds nature reserve, using principal component analysis.

Secondly, an investigation assessed the chemical speciation of sediment phosphorus in the ditch systems. Based upon their associations with different phosphorus species, clear distinction was observed between sites outside and within the Royal Society of the Protection of Birds nature reserve, using principal component analysis. Sites outside the nature reserve, typically wet and damp grassland used for arable use and grazing, were generally correlated to higher non-apatite inorganic phosphorus (associated with iron and aluminium minerology) and higher total phosphorus levels, associated with algal and duckweed blooms.

Thirdly, an investigation assessed the seasonal variation in spatial distribution and chemical fractionation of surface water phosphorus, as well as surface biomass abundance and total phosphorus content in the ditch systems. Elevated phosphorus concentrations in the surface water were observed across the site, the highest being 1.88 mg L^{-1} during the summer, over 10 times the Common Standards Monitoring Guidance target of <0.1 mg L^{-1}. Sites lacking hydrological flow connectivity with freshwater inputs, typically had lower surface water phosphorus concentrations than the rest of the moor. Summer and autumn were determined as the dominant duckweed growth seasons, in which an estimated 39 kg of phosphorus could be removed via duckweed biomass harvesting, per harvest period. The study has demonstrated that there is an undoubted need for practical management options to help mitigate phosphorus in eutrophic freshwater ditch systems.

Evidence has been reviewed which demonstrates that appropriate and targeted ditch management practices can play a significant role in reducing both phosphorus load and legacy phosphorus concentrations. A wide variety of management options exist (e.g.; water level management; dredging, emergent macrophyte harvesting and channel widening (two-stage channels); algae/duckweed harvesting; and filter substrates), although some are best suited to particular environments and landscapes, some to accelerating recovery rate rather than initialising recovery, and data regarding the efficiency of certain approaches is rather limited. The development of the management options into functioning phosphorus mitigation solutions requires determination of likely costs, implementation timescales, maintenance requirements, and delivery mechanisms, at site specific level. Further studies are necessary to generate data useful to the development of mitigation schemes.

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List of Abbreviations

AP	Apatite Inorganic Phosphorus
APA	Alkaline Phosphatase Activity
ASSI	Areas of Special Scientific Interest
ATP	Adenosine Triphosphate
BA&NSSmc	Bristol Avon and North Somerset Streams management catchment
CRM	Certified Reference Material
CSF	Catchment Sensitive Farming
CSM	Common Standards Monitoring
Defra	Department for Environment, Food and Rural Affairs
DM	Dry Mass
DNA	Deoxyribonucleic Acid
DRP	Dissolved Reactive Phosphorus
Dutch-N	Dutch Nitrogen Case
EA	Environment Agency
EU	European Union
GCS	Good Chemical Status
GES	Good Ecological Status
GTP	Guanosine Triphosphate
HDPE	High Density Polyethylene
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometry
IDB	Internal Drainage Board
IP	Inorganic Phosphorus
JNCC	Joint Nature Conservation Committee
LBDB	Lower Brue Drainage Board
LOD	Limit of Detection
LOI	Loss on Ignition
LWA	Lightweight Aggregates
NAIP	Non-Apatite Inorganic Phosphorus
nv	No values
OP	Organic Phosphorus
PCA	Principal Component Analysis
PE	Polyethylene

POPs	Persistent Organic Pollutants
PRP	Particulate Reactive Phosphorus
RBMP	River Basin Management Plan
RGR	Relative Growth Rate
RNA	Ribonucleic Acid
ROL	Radial Oxygen Loss
RP	Orthophosphate Reactive as Phosphorus
RSPB	Royal Society for the Protection of Birds
RWLA	Raised Water Level Area
SAC	Special Areas of Conservation
SFCA	Surfactant Free Cellulose Acetate
SMT	Standards, Measurements and Testing Program
SPA	Special Protection Area
SRP	Soluble Reactive Phosphorus
SSC trigon	Sand, Silt, and Clay Trigon
SSSI	Sites of Special Scientific Interest
STWs	Sewage Treatment Works
SuDS	Sustainable Drainage Systems
SWAT	Soil Water Assessment Tool
S&WSmc	South & West Somerset management catchment
SWT	Somerset Wildlife Trust
TAA	Taunton Angling Association
TP	Total Phosphorus
TRP	Total Reactive Phosphorus
TSP	Total Soluble Phosphorus
TSS	Total Suspended Solids
uPBTs	Ubiquitous, Persistant, Bioaccumilative, and Toxic substances
WD-XRF	Wavelength Dispersive X-Ray Fluorescence
WFD	Water Framework Directive
WwTW	Wastewater Treatment Works

1 Introduction

1.1 Overview

Phosphorus (P) was discovered by the alchemist Hennig Brandt in Hamburg, Germany in 1669. He unintentionally extracted 120 g of P after evaporating 5500 L of urine and heating the remaining residue up until it was red hot, at which point P vapour distilled that he promptly collected through condensing with water. Brandt thought he had discovered the Philosopher's Stone, the mythical alchemical substance surmised to be capable of turning base metals into gold (Kleinman et al., 2019; Royal Society of Chemistry, 2022; Sharpley et al., 2018). Today his discovery is known as the chemical element with atomic number 15.

For life, P is an essential element and the sixth most abundant in living organisms. Within important biomolecules, P is foundational for both structure and function, appearing in the sugar-phosphate backbone of both deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) for biological information coding, phospholipids for the structure of cell membranes, adenosine triphosphate (ATP) and guanosine triphosphate (GTP) for energy metabolism, and numerous other molecules of biological significance (Heaney and Graeff-Armas, 2018; Sharpley et al., 2018). Hence, it is commonly recognised that P availability is a significant factor that limits the rate of algae and macrophyte growth within aquatic ecosystems. Eutrophication of surface water is a significant threat to biodiversity worldwide, with excessive P concentrations being among the most common causes (Comber et al., 2015a; Dodds et al., 2009; Pretty et al., 2003; Zhang et al., 2017). Conditions of surface water systems deviate under these conditions from primarily submerged aquatic vegetation to algae or duckweed dominance, leading to shading, potentially anoxic conditions, and the deterioration of aquatic ecosystems (Zhang et al., 2017). Algal and duckweed blooms produce heavy shading, via surface coverage, and excessive amounts of organic matter undergoing bacterial degradation, which causes depletion of oxygen in the water column, giving rise to fish kills and the evolution of bad odours (Padedda et al., 2017; Riley et al., 2018; Zhang et al., 2017).

A multitude of valuable ecological services for people and wildlife are provided by wetland ecosystems worldwide. They are habitats of rich biological diversity serving important hydrological functions such as, water storage; storm protection and flood mitigation; and water purification. Economic benefits include supporting water supply; agriculture; fisheries and recreational fishing; tourism; and wetland products such as herbal medicines (Hughes and Heathwaite, 1995; Ramsar Convention Secretariat, 2016). Regrettably however, wetlands are also amongst the most threatened ecosystems owing to loss and degradation. 87% of wetlands globally have been lost in the last 300 years, with 54% being lost since 1900 (IPBES, 2018). The principal drivers of wetland degradation are human activities. Agriculture intensification has seen appreciably enhanced crop and livestock yields worldwide, yet under improper management, can give rise to soil erosion and eutrophication of aquatic systems by way of diffuse pollution (IPBES, 2018; Ockenden et al., 2014). Objectives of the European Habitats Directive (Council of the European Communities, 1992) and the Water Framework Directive (WFD) (Council of the European Communities, 2000) demand action to restore waterbodies that are either not meeting good status, WFD, or need to meet favourable conservation status, Habitats Directive. Wetland areas are also protected under the Ramsar Convention (Ramsar, 1994).

Considerable advancements have been achieved to reduce the proportion of P input from point source discharges to water courses, such as wastewater treatment Works (WwTW), and farming best management practices are being encouraged by land management policy to reduce biogeochemical flows (Ockenden et al., 2014). Specifically, P's linear biogeochemical flow from mineral reserves, to agriculture, and subsequently into catchments and oceans, which is deemed to be exceeding the planetary boundary, consequently inducing eutrophication (Carpenter and Bennett, 2011; Ockenden et al., 2014). Even so, waterfowl nature reserve managed wetland has the potential to be a cause of P loading through bird excreta (guanotrophication). Alas, degradation, and loss of freshwater bodies, such as wetlands, that were previously breeding grounds and migratory stopovers, has necessitated the intensified use of the remaining habitat. The resulting disproportionately prodigious waterfowl populations, in comparison to the expanse and capacity of the waterbody, can have a significant fraction of the internal P load cycling through their diet. Wetland P cycling can potentially be considerably affected by waterfowl through the alteration of the forms of P present and the input and/or export of P to and/or from external locations to the wetland (Adhurya et al., 2020; Scherer et al., 1995).

The Somerset Levels and Moors Ramsar site consists of the largest area of lowland wet grassland and wetland habitat remaining in the UK. The Somerset Levels are not only internationally important for the populations of wintering wildfowl (waders) they support, but are also nationally important for assemblages of plants, insects, and breeding birds, as well as for their landscape, historical, and wetland heritage (Bowers, 2022; Natural England, 2019). Draining activity and land reclamation on the Somerset Levels has been going on since at least the 1400's, facilitated in part by digging ditches, locally referred to as rhynes (Williams, 1970). In the present day the landscape is dominated by artificially drained, irrigated and otherwise modified rivers and wetlands, to allow high-yielding farming (predominantly pasture), as well as restored wetland bird habitat (Bowers, 2022; Parrett IDB, 2009; Williams, 1970). During the time of the drainage and reclamation of the Somerset Levels, many other wetland areas were undergoing the same treatment across vast stretches of western and northern Europe, such as the coasts of northern France, Belgium, Netherlands, Germany, and Denmark, and the inland swamps of the Polish Urstromtäler and the Russian Pripet marshes. Each of these areas of draining being distinct and a result of the endeavours of different peoples, engaging at separate times and with varying levels of technology, dependant of different institutions. Hence, the draining of the Somerset Levels was one part of a significant development in land reclamation which transpired amid the medieval and later centuries in Europe (Williams, 1970). Not only clearly embodying the continental occurrence, the Somerset Levels also more narrowly exemplifies one of the several UK regions reclaimed in this manner; the Fens, the Isle of Axholme, the Hull valley, the Vale of York and the Humberhead Levels, the Norfolk Broads, the Essex marshes, Romney Marsh, the Pevensey Level, Lancashire Mosses, and the Somerset Levels (Darby, 1956; Gramolt, 1961; Hallam, 1965; Hardman, 1961; Lambert et al., 1960; Rollinson, 1964; Sheppard, 1966, 1958; Smith, 1940; Thirsk, 1953; Williams, 1970).

Evidently, the UK regions are all essentially flat tracts of wetland, however, coupled with their shared characteristics of susceptibility to flooding and ensuing requirement for remedial action, these wetlands present a special distinctiveness emulated within their explanatory local names such as the Fens, the Carrs, the Broads, the Mosses, and the Levels (Williams, 1970). Regardless of broad correspondence, nonetheless, there are a few differences with regards to their physical setting and flood complications, such as the existence of a coastal clay belt and peat at lower level (the Fens, the Hull valley, the Levels); the principal source of flooding being either tidal flooding (the Essex marshes, Romney Marsh, the Pevensey Level) land floods (the Lancashire Mosses, the Vale of Pickering, the Isle of Axholme) or both tidal and land floods (the Fens, the Levels); the land utilization being either predominantly arable (the Fens) or pastoral (the Levels) (Broadmeadow and Nisbet, 2010; Cooper et al., 2001; Hartmann, 2017; Kenyon, 1991; Prime et al., 2016; Thirsk, 1953; Thompson, 1957; Williams, 1970; Williams and Worth, 2003).

The balance of evidence indicates that surface waters in the ditch systems of the Somerset Levels and Moors Ramsar are elevated in P, with associated biological evidence of hyper-eutrophication. A recent study undertaken by Taylor et al. (2016) on West Sedgemoor SSSI (Site of Special Scientific interest) involved routine water spot sampling, performed fortnightly between August 2015 to June 2016, to assess nutrient chemistry of the water in the ditch system, coupled with continuous monitoring of supporting parameters (dissolved oxygen, turbidity, conductivity, and stage). The results revealed the majority of monitoring sites exceeded the Common Standard Monitoring target for ditches of <0.1 mg P L^{-1} as total phosphorus (TP), with significant spatial differentiation observed across the site. Assessment in line with historic data suggests several factors that can potentially influence nutrient concentrations on site, including water level and flow management, surrounding land management, and seasonal cycles. Across the system, the highest concentrations of P were observed in August, with key inlet sites exhibiting consistently higher concentrations of P in relation to sites further within the ditch system which, in comparison, are less connected to surface drainage inputs. Sporadic increases in nutrient concentrations observed at some sites during the winter period were proposed to be related to drainage management. However, greater detail with regard to management operations is required to support this with confidence.

The work by Taylor et al. (2016) identified further possible research:

- Additional monitoring to fill in gaps in source data and seasonality, including summer penning winter draining.
- Spatial coverage of water chemistry spot sampling is extended to include minor ditch areas to aid condition assessment.
- The impact of the River Parrett inflows are studied given that this is a key inlet and it was not possible to assess these inflows during the study period.
- Further monitoring is undertaken at key inlet sites to aid assessment of key sources and improve estimates of load inputs.

1.2 Aims and objectives

Based upon prior investigations and consultations with stakeholders, Natural England (the UK government's adviser for the natural environment in England) has concluded that the greatest chance for improving the Somerset Levels and Moors situation, with regards to the eutrophication pressure, depends upon a number of actions:

1) Seeing what can feasibly be done to reduce P inputs across the catchments of the feeder rivers - implementing improvements at sewage treatment works (STWs), alongside changes in land management through catchment sensitive farming (CSF), Countryside Stewardship, innovative approaches such as EnTrade (a Wessex Water business) and possibly enhanced regulation of non-STW sources.

2) Looking at ways of intercepting P before it enters the ditch system from the rivers (e.g., constructed wetlands).

3) **Looking at how ditch management can be modified to accelerate recovery, including dealing with the existing burden of P in the system.**

The studies presented in this thesis focus on **(3)**, covering: the partitioning of P between sediment, water column, and algae/duckweed, and the factors affecting this, such as flow, water levels, seasonality, and physicochemical interactions.

Potentially feasible ways of mitigating the internal cycling and bioavailability of P are also explored, including: investigation into the interactions between water level management and the operation of structures on nutrient dynamics, the effects of winter flooding, de-silting and weed cutting in the ditches (typical ditch management practices) as ways of exporting nutrients from the system, and the possibility of harvesting duckweed and algae to reduce internal cycling and to export nutrients.

1.3 Thesis structure

The structure of this thesis is as follows:

- Chapter 1 introduces context and the rationale for the study through defining its aims and objectives.
- Chapter 2 reviews water quality policy, the current condition of the Somerset Levels and Moors, and historical phosphorus eutrophication data relating to the Ramsar ditch systems.
- Chapters 3 – 5 are experimental investigations addressing the objectives outlined above.
- Chapter 6 reviews potentially feasible ways of reducing the internal cycling and bioavailability of P within wetland ditch systems through ditch management techniques, based on best available evidence.
- Chapter 7 presents the main conclusions of the study and identifies potential avenues for further investigations.

1.4 Research hypotheses

The hypotheses for the research chapters are as follows:

Chapter 3 - Spatial distribution of sediment phosphorus in a Ramsar wetland

- Legacy phosphorus concentrations in sediment are higher in ditches adjacent to agricultural land than wetland bird nature reserve land.

Chapter 4 - Chemical speciation of sediment phosphorus in a Ramsar wetland

- Chemical speciation of sediment phosphorus in ditches is influenced differently by adjacent agricultural land than wetland bird nature reserve land.

Chapter 5 - Seasonal cycling of phosphorus within a UK Ramsar wetland: Impacts of land use and hydrology on algal and duckweed growth and implications for management

- Duckweed harvesting can be used as an effective method of phosphorus mitigation.

2 Review of Eutrophication on the Somerset Levels and Moors Ramsar Ditch Systems

2.1 Introduction

Within this review, context will be given to the regulation and monitoring of eutrophication and the current condition of the Somerset Levels and Moors Ramsar site. Background is provided regarding conservation objectives pertaining freshwater ditches within designated sites in the UK.

2.2 Ramsar Convention

Adopted in Ramsar, Iran on February 3rd, 1971, the Convention on Wetlands of International Importance especially as Waterfowl Habitat ('Ramsar Convention' or 'Wetlands Convention') was the first of the modern intergovernmental treaties pursuing the conservation of natural resources at the global scale (Joint Nature Conservation Committee, 2019; Matthews, 2013). Concerned with wetland habitats, the mission of the Ramsar Convention is stated as "the conservation and wise use of all wetlands through local and national actions and international cooperation, as a contribution towards achieving sustainable development throughout the world" (Ramsar Convention Secretariat, 2016). Article 1 of the Ramsar Convention defines wetlands as "areas of marsh, fen, peatland or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt, including areas of marine water the depth of which at low tide does not exceed six metres" (Ramsar, 1994). Initially, the signatures of representatives from 18 nations endorsed the treaty (Matthews, 2013). Since then, 172 nations have acceded to become "Contracting Parties" (Ramsar Convention Secretariat, 2021). Subscriptions of the Ramsar Convention's Parties fund an active organization with a staffed secretariat, the Convention Bureau, based in Gland, Switzerland (Ramsar Convention Secretariat, 2016).

Contracting Parties that have affiliated with the Ramsar Convention undertake four fundamental commitments outlined in Articles of the Convention (Ramsar Convention Secretariat, 2016):

- Article 2, Listed sites.
- Article 3, Wise use.
- Article 4, Reserves and training.
- Article 5, International cooperation.

Article 2.4 outlines the initial obligation of each Contracting Party to designate a minimum of one wetland, at the time of signing the Convention or depositing an instrument of ratification or accession, to be included in the List of Wetlands of International Importance. Article 2.1 outlines the need for the promotion of the conservation of designated wetlands, and the expectation for the continual addition of further designated wetlands for the List (Ramsar, 1994; Ramsar Convention Secretariat, 2016). These 'Ramsar Sites' are chosen based off of their ecological, botanical, zoological, limnological, and/or hydrological significance. Article 3.1 details an expected general obligation of the Contracting

Parties to "formulate and implement their planning so as to promote the conservation of the wetlands included in the List, and as far as possible, the wise use of wetlands in their territory" (Ramsar, 1994). With "wise use" being understood as synonymous with "sustainable use". This calls for the consideration, at a national planning level (e.g., land-use, water-resource management, etc.), of matters regarding wetland conservation (Ramsar Convention Secretariat, 2016). Under Article 4, Contracting Parties are obliged to establish wetland nature reserves, regardless of international importance, with adequate wardening provided (Article 4.1), and to raise the populations of waterfowl through the management of appropriate wetlands (Article 4.4) (Matthews, 2013; Ramsar, 1994; Ramsar Convention Secretariat, 2016). Subject to Article 5, Contracting Parties are to consult with each other on the implementation of the Convention obligations, particularly when wetlands spanning the territories of multiple Contracting Parties or the shared water systems of Contracting Parties are concerned. Contracting Parties are to endeavour to participate in internationally coordinated policies and regulations having to do with conservation of wetlands including their flora and fauna (Matthews, 2013; Ramsar, 1994; Ramsar Convention Secretariat, 2016).

Ratified in 1976, the UK designated its first Ramsar Sites as a Contracting Party: Broadland, Cors Fochno & Dyf, Lindisfarne, Loch Leven, Loch Lomond, Lough Neagh & Lough Beg, Minsmere – Walberswick, North Norfolk Coast, Ouse Washes, Rannoch Moor, Severn Estuary, and South Uist Machair & Lochs. The UK's ratification further comprises its Overseas Territories and Crown Dependencies, inside which the first Ramsar site was the North, Middle & East Caicos Islands, in the administrative region Turks and Caicos Islands, designated in 1990. The Somerset Levels and Moors were designated as a Ramsar site in 1997. Presently the UK has 175 designated Ramsar Sites covering a combined 1,283,040 ha (Joint Nature Conservation Committee, 2019; Ramsar Convention Secretariat, 2018). UK Ramsar Sites are typically derived through designation of existing Sites of Special Scientific Interest (SSSIs) (Areas of Special Scientific Interest (ASSIs) being the Northern Ireland equivalent). In accordance, SSSIs (and ASSIs) secure statutory protection under the Wildlife & Countryside Act 1981 (as amended) (HM Government, 1981), the Nature Conservation (Scotland) Act 2004 (as amended) (Scottish Parliament, 2004), and the Nature Conservation and Amenity Lands (Northern Ireland) Order 1985 (as amended) (Northern Ireland Assembly, 1985). The Department for Environment, Food and Rural Affairs (Defra) acts as the Designated Ramsar Administrative Authority of the UK.

2.3 Water Framework Directive

The primary objective of the European Union (EU) Water Framework Directive (WFD: 2000/60/EC) is to establish a system to improve and/or maintian the quality of waterbodies, so that all waterbodies achive 'Good Ecological Status' (GES) and 'Good Chemical Status' (GCS) by 2027 at the latest (Council of the European Communities, 2000). Status is graded in a classification system ranging from high to good, moderate, poor, and bad for biological (e.g., phytoplankton, benthic flora, benthic invertebrate, and fish fauna), physico-chemical and hydro-morphological factors; with the worst performing factor defining the overall status (Carvalho et al., 2019; Council of the European Communities, 2000; Goddard et al., 2020; Poikane et al., 2019). Physico-chemical parameters include nutrient conditions which are required to "not exceed the levels established so as to ensure the functioning of the ecosystem and the achievement of values specified (for good status) for the biological quality elements" (Annex V, 1.2). Hence, nutrient concentration targets are not provided within the WFD, instead requiring EU countries to determine type-specific nutrient criteria to eunsure GES (Council of the European Communities, 2000; Poikane et al., 2019). UK Government agreed, under the EU WFD, to water policy environmental quality standards and chemical analysis technical specifications for the monitoring of water status in the UK. The WFD was retained in UK law following the UK's exit from the EU.

The UK Government's 25 Year Environment Plan sets the target for 75% of waters (including rivers, lakes, groundwater aquifers, estuaries and costal waters) to be as near as possible to natural state as early as possible, based upon River Basin Management Plans (RBMPs) (Department for Environment Food and Rural Affairs, 2018). The majority of waters are not meeting this target; surface waters in Engalnd and Wales currently meeting the criteria for GES under WFD currently total 16%. For 2019, 0% of surface water bodies met the criteria for achieving GCS under WFD, compared to 97% meeting criteria in 2016. This is due to the 2019 inclusion of new assessments for ubiquitous, Persistant, Bioaccumilative, and Toxic substances (uPBTs), as well as new standards, improved techniques and methods. Data on European protected nature sites showed that 79% of all SSSI wetlands are classified as unfavourable declining, with only 14.8% being in favorable condition. However, this figure includes sites designated for birds that may be in favourable condition without assessment of water quality (Environment Agency and Natural England, 2022).

2.4 Common Standards Monitoring guidance for ditch systems

Guidelines for the regular monitoring and condition assessment of freshwater and brackish UK ditch systems, within designated sites (e.g., SSSI), has been established by the Joint Nature Conservation Committee (JNCC). The Common Standards Monitoring (CSM) guidance outlines a structured walk across the entirety of a given site to assess overall status of a ditch network, coupled with a comprehensive survey monitoring of ditch vegetation and physico-chemical indicators, at 20 m sampling intervals. Seven attributes and their constituent elements are used for ditch system monitoring (Joint Nature Conservation Committee, 2005). Table 2.1 shows the attributes and their associated targets.

These seven attributes and their targets are considered to reflect both the reasons for designation and the significant pressures affecting ditch systems. At the minimum, assessment of sites occurs once throughout the duration of each 6-year reporting period for SSSIs. However, some ditches may not be comprehensively assessed frequently along their entirety, considering the relatively large size of numerous sites and therefore the length of ditches. Thus, the CSM guidance attempts to rectify this by proposing in depth survey of 20 m sample ditch lengths (Clarke, 2015). Hamilton (2009) undertook an evaluation of the CSM guidance at three SSSIs which revealed some variation in the recording of qualitative attributes, this accentuated the requirement of training for surveyors. However, following multivariate analysis, quantitative data presented in the evaluation indicate that the recorded environmental variables were the key factors determining vegetation within the ditches, although a significant amount of unexplained variability remained within the data and water chemistry was not assessed (Hamilton, 2009).

Table 2.1: Attributes and targets assessed to determine the condition of ditch systems at designated sites (Joint Nature Conservation Committee, 2005).

Attribute		Targets
Extent of the ditch feature		No reduction in channel length.
Habitat functioning: water availability		Characteristic water levels to be maintained. Generally, in wet ditches summer water depth at least 0.5 m in minor ditches and 1 m in major drains. 90% of channel length should reach this target.
Habitat functioning: water quality	Water clarity	Water clear or only slightly turbid / discoloured in at least 90% of channel length.
	Algal dominance	Mean cover of filamentous macro-algae not more than 10% (mid June to end August).
	Water chemistry	Total phosphorus <0.1 mg L^{-1}; water quality equivalent to at least Chemical Class 2 of the England and Wales River Quality Classification.
Habitat structure	Channel form	A range of variation in ditch profiles. If ditches are the only wetland feature, no more than 75% of ditch length with a trapezoidal cross-section. (This target may be adjusted according to the characteristics of the site).
	Extent and composition of in-channel vegetation	Mix of early, mid and late succession ditches: 10–25% early, 35–75% mid, 10–25% late.
	Extent and composition of bankside vegetation	Where aquatic vegetation is a key feature of the site, no more than 10% of the channel length should be heavily shaded.
Aquatic vegetation composition: native species richness		Native aquatic flora of ditches species-rich: freshwater ditches – mean at least 7 species per 20 m; brackish ditches – mean at least 5.
Indicators of negative change: introduced/non-native plants		Mean cover of each very aggressive non-native plant not exceeding 1%. Mean total combined cover of all non-native species and introduced species less than 30%.
Indicators of local distinctiveness	Salinity gradient: conductivity, botanical indicators	Where saline influences are characteristic, the existing salinity gradient across the site to be maintained. Plant communities to reflect the fresh/brackish transition.
	Presence of rare species and quality indicators	Populations of rare species and other species / communities characteristic of high quality ditch systems should persist.

2.5 Current condition

The Somerset Levels and Moors (51°06'N 02°51'W; Somerset, UK) are listed as a Ramsar Site (no. 914) under the Ramsar Convention and are designated as a Special Protection Area (SPA) under the Habitat Regulation 2017 (HM Government, 2017; Ramsar, 1994). Both designations generally cover the same area, with the Ramsar designation owing to the site's internationally important wetland features such as floristic and invertebrate diversity and species present within the ditch systems. These features are also mutual for the designation of the many SSSIs present on the Levels, designated under the Wildlife & Countryside Act 1981 (as amended) (HM Government, 1981). These SSSIs are situated within the largest area of lowland wet grassland and wetland habitat in Britain (Bowers, 2022).

Draining activity and land reclamation on the Somerset Levels has been going on since at least the 1400's, facilitated in part by digging ditches, locally referred to as rhynes (Williams, 1970). In the present day the landscape is dominated by artificially drained, irrigated and otherwise modified rivers and wetlands, to allow high-yielding farming (predominantly pasture), as well as restored wetland bird habitat (Bowers, 2022; Parrett IDB, 2009; Williams, 1970). The Ramsar Site consists of 6,388 ha (non-contiguous) of wet grassland, peat bog, fen, and reedbed, within the larger Somerset Levels catchment of approximately 70,000 ha, which covers the approximately 35,000 ha combined area of the catchments of the River Parrett, River Tone, River Brue, and River Axe, and their associated tributaries (Bowers, 2022; Ramsar, 2005).

Favorable condition classification of the Ramar Site ditch systems is in part dependant on water quality. However, a great majority of ditches within the Ramsar designation are classified as being unfavourable in condition or at risk due to excessive phosphorus (P) concentrations causing eutrophication. Water quality at SSSI sites, which form part of the Ramsar Site, show total phosphorus (TP) concentrations in exceedance of the CSM guidance target of <0.1 mg P L^{-1} as TP (Taylor et al., 2016). A significant threat to biodiversity worldwide, surface water systems under eutrophic conditions deviate from primarily submerged aquatic vegetation to algae or duckweed dominance, leading to deterioration of aquatic systems via shading and therefore anoxic conditions (Bowers, 2022; Crocker et al., 2021; Zhang et al., 2017). This depletion of oxygen in the water column can bring about fish kills and development of bad odours (Padedda et al., 2017; Riley et al., 2018). Various sources contribute to the P pollution present on the Somerset Levels, although wastewater treatment works (WwTW) and livestock farming contribute the vast majority with onsite wastewater treatment, urban, and arable also contributing significantly (Bowers, 2022). Monitoring and modelling investigations performed by Wessex Water, and concurred by the Environment Agency, concluded that annual mean phosphate concentrations of the river inputs into all the SSSIs are at minimum 3 times the CSM target. Following this, Natural England took the decision to downgrade the condition of the Somerset Levels and Moors Sites of SSSI to unfavourable declining in June 2021 (Bowers, 2022; Natural England and Environment Agency, 2021).

2.6 Condition of sub-catchments

The Somerset Moors and Levels Ramsar site is situated within the aforementioned catchments of the Rivers Parrett, Tone, Brue and Axe. Each of these catchments contain numerous surface water bodies failing to achieve GES. As previously mentioned, 0% of surface water bodies investigated by the Environment Agency met the criteria for achieving GCS under WFD.

The River Parrett catchment (Figure 2.1), situated in the southern area of Somerset, is mainly rural, besides the urban area of Yeovil. Tributaries of the Parrett generally flow towards a north and westerly direction from steep uplands towards the expansive lowland floodplain; the major tributaries are the Rivers Isle, Tone, Yeo and Cary. The catchment is approximately 1,700 km^2 (Tone catchment included). The River Parrett is 60 km long and has a tidal reach of 30 km from the Severn Estuary up to Oath. Environment Agency WFD data (as set out in the South West River Basin Management Plan (RBMP)) states that there are 56 water bodies in this operational catchment, with only one being classified as meeting GES, eight being classified as poor, one as bad, and the remainder moderate. Elevated phosphate concentrations are partly responsible for this, with no sites achieving good status for phosphate. Pollution from rural areas as well as from towns and wastewater dominate the reasons for not achieving good status (Bowers, 2022; Environment Agency, 2022).

The River Tone catchment (Figure 2.1), situated in the western area of Somerset, has two major urban influences, with the River Tone running north of Wellington and through Taunton. Tributaries of the Tone drain Exmoor, the Brendon, Quantock and Blackdown Hills; the major tributaries are the Hillfarrance Brook, Halse Water, Haywards Water and Broughton Brook. The catchment is approximately 414 km^2. The River Tone is 33 km long and is tidal up to the Newbridge Sluice in North Curry Parish, joining the main channel of the River Parrett at Burrowbridge. Predominant land uses in the catchment are permanent pasture, arable and sheep and cattle grazing and woodland. Environment Agency WFD data states there are 16 water bodies in this operational catchment, with only one being classified as meeting GES, six being classified as poor, and the remainder moderate. Elevated phosphate concentrations are partly responsible for this, with only three sites achieving good status for phosphate or TP. Pollution from rural areas as well as from wastewater dominate the reasons for not achieving good status (Bowers, 2022; Environment Agency, 2022).

The Brue and Axe Operational Catchment (Figure 2.1), situated in the northern area of Somerset, constitutes the River Brue and the River Axe which are interconnected by sluice controlled rhynes, establishing a complex artificial drainage system. The River Brue flows west from the catchments

Eastern clay towards the sea, entering at Highbridge. The River Axe flows west from limestone springs at Wookey Hole on the Mendips towards the sea through the Somerset Levels and Moors. The major tributaries are the South drain and North drain that directly provide flow to the Ramsar sites and the River Sheppey. Land use is predominately agricultural, with water for public supply provided by the Mendip Hills. The River Axe is currently within the Bristol Avon and North Somerset Streams management catchment (BA&NSSmc). Proposed changes by the Environment Agency would see the BA&NSSmc boundary amended so that the River Axe would be included in the South & West Somerset management catchment (S&WSmc). Environment Agency WFD data states there are 27 water bodies in this operational catchment, with only one being classified as meeting GES, two being classified as poor, and the remainder moderate. Pollution from rural areas as well as from wastewater dominate the reasons for not achieving good status (Bowers, 2022; Environment Agency, 2022).

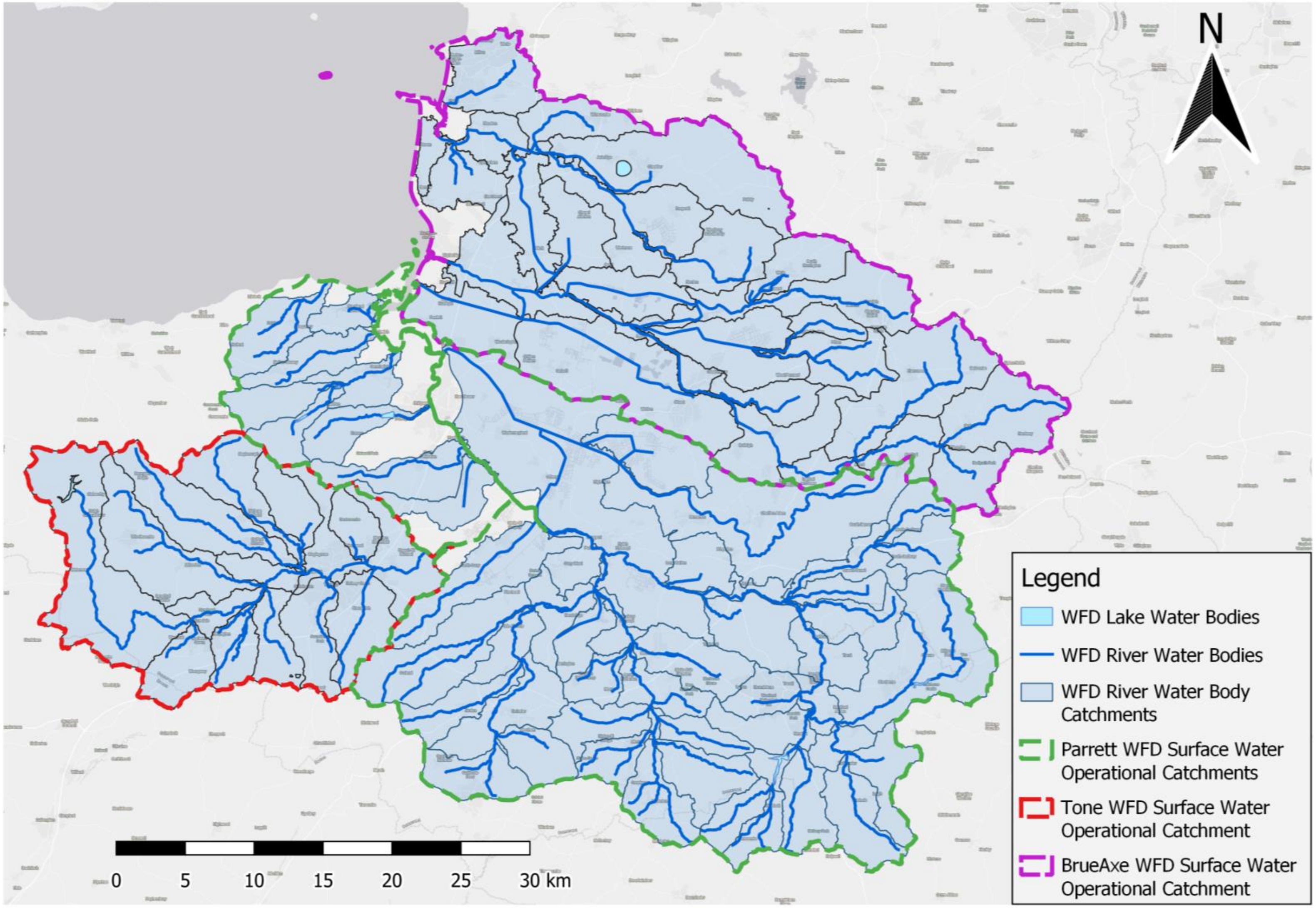

Figure 2.1: South & West Somerset management catchment under the Water Framework Directive (WFD). WFD Operational Catchments of the River Parrett, River Tone, and the Rivers Brue & Axe.

2.7 Historic ditch system data

Phosphorus is often the growth limiting nutrient in freshwater systems such that biologically available forms of P are naturally in short supply and become quickly exhausted by biological uptake. Freshwater systems are sensitive to changes in the natural balance of available P, which is commonly affected by human inputs, particularly those derived from agricultural practice and WwTWs. Diffuse input of P via runoff from agricultural land and direct point source inputs from effluent discharges can potentially increase the bioavailable pool of P (eutrophication), leading to excessive algal and duckweed growth and associated ecological impacts. In turn, impact upon ecosystem function disrupts the flow of services and benefits to society (such as those associated with recreation and health) and can lead to increased cost of water treatment (Withers and Jarvie, 2008).

Natural England have contracted or collaborated on a number of projects over a number of years on the Somerset Levels to monitor water quality and identify sources of eutrophication. The Environment Agency also routinely monitor water quality at a limited number of sites across the S&WSmc. However, there is a general lack of up-to-date consistent monitoring data for the ditch systems and few comprehensive datasets are available, which cover an extended time period with good spatial coverage.

2.7.1 Catcott Lows ditch system

The Catcott Lows (51°10'10.776"N 2°51'35.334"W) consists of 0.52 km^2 of re-wetted basin fen managed as wet grassland nature reserve, bordered by fields supporting permanently grazed pasture and arable crops. The site forms part of the Catcott Complex (alongside Catcott Heath), also forming part of the Catcott, Edington and Chilton Moors SSSI, which also forms part of the Somerset Levels and Moors Ramsar site. The reserve was acquired by the Somerset Wildlife Trust (SWT) in 1990 and is managed primarily as a wet grassland habitat for wintering waterfowl and waders with conservation grazing and grass cutting taking place in the summer and autumn. Prior to SWTs acquisition, the site had been deep drained and fertilised intensively for arable use over a period spanning approximately 20 years (Hill and Robinson, 2012a; Niedermeier and Robinson, 2009). However, the original reclamation drainage of the site likely occurred between 1600 to 1640 as part of the draining developments in the Brue valley. Further parochial reclamations followed in 1798 and 1799 which altered the drainage pattern of the moor (Williams, 1970).

Whereas the internal ditches of the reserve are managed by the SWT, the larger arterial ditches (‘viewed rhynes’) that form the boundaries on the east (Black Ditch) and west (Lady’s Drove Rhyne) of the site are managed by the Lower Brue Drainage Board (LBDB). Viewed rhynes water levels are ‘penned’ high (1.56–1.60 m above mean sea level) during the summer season, providing a wet fencing within the reserve to contain grazing livestock. During the winter season the viewed rhynes are penned much lower (1.20 m above mean sea level) to avoid excessive flooding with agricultural drainage water in the wetter months. The site also receives calcium-enriched water input drained from White Lias–basal Blue Lias limestone scarp known as the Polden Hills located to the south of the site (Hill and Robinson, 2012a; Niedermeier and Robinson, 2009).

Niedermeier and Robinson (2009) reports on surface water monitoring carried out for two ditches (Higher Stubbylawn Rhyne and Black Ditch; Figure 2.2) on the Catcott Lows site between 2001 to 2002, for the assessment of the impacts of managed and seasonal fluctuations of hydrology on site. The influence of pump drainage on Higher Stubbylawn Rhyne was observed. Throughout the duration of a 7-day water table drawdown via intermittent pump drainage, it was estimated approximately 45 g ha^{-1} of dissolved reactive phosphorus (DRP) entered Higher Stubbylawn Rhyne from the degraded peat of the field adjacent to it and Black Ditch. At the onset of pumping, increases in ditch DRP concentration were observed up to 0.4 mg L^{-1}, with increases up to 0.7 mg L^{-1} also seen during subsequent rewetting in the autumn (Niedermeier and Robinson, 2009). DRP concentrations in Higher Stubbylawn Rhyne were consistently exceeding the current CSM guidance target of <0.1 mg TP L^{-1}, while Black Ditch exceeded during peaks in the summer and autumn months. While this report does indicate how ditch systems on the Somerset Levels can become eutrophic (exceeding the current CSM guidance target set in 2005) the water data presented is not comprehensive. The report states that water samples were analysed for TP but fails to present that temporal data. The study is also lacking good spatial coverage with only two ditches sampled at three points each, with the data from those three sites each not reported separately.

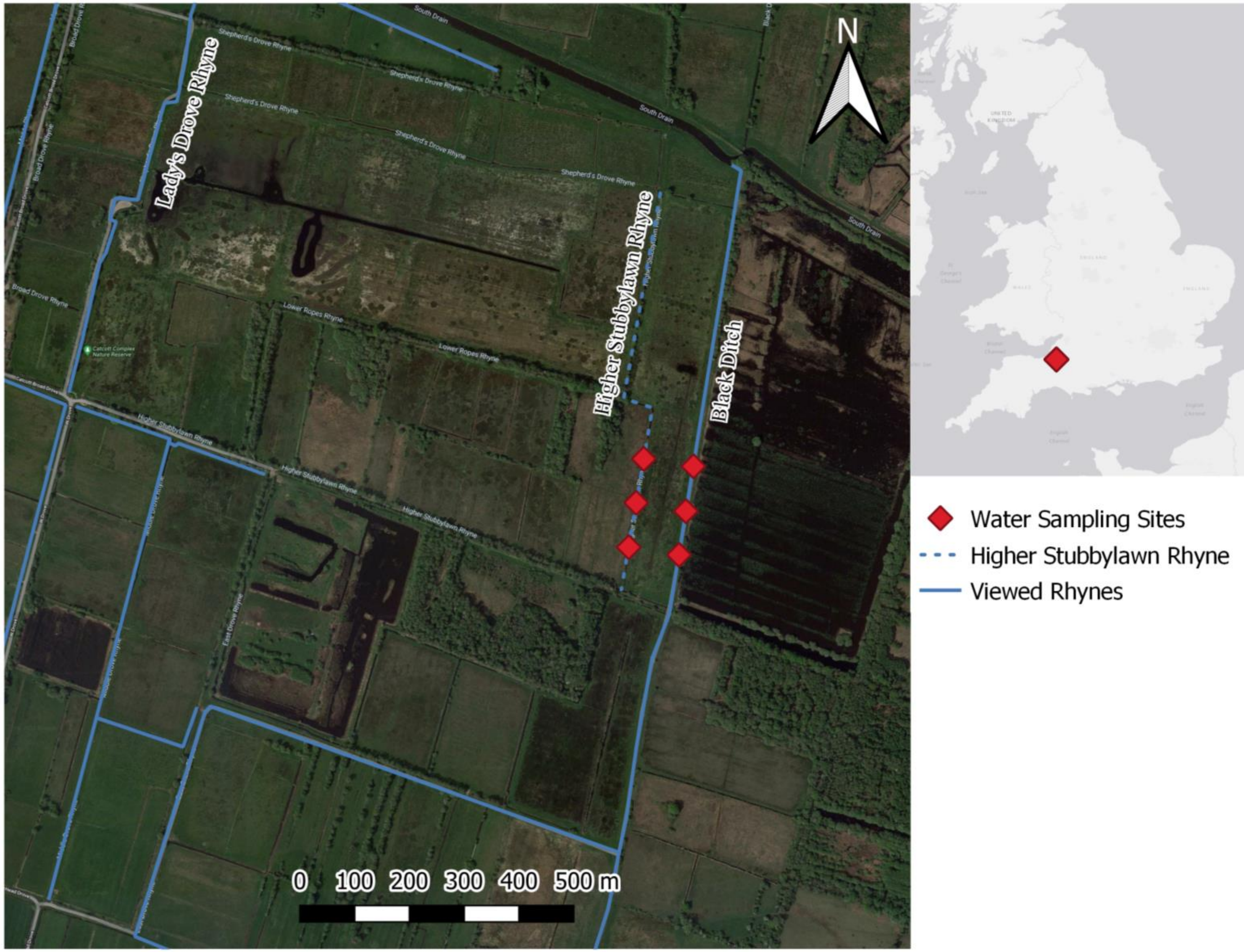

Figure 2.2: Historic water sampling sites at the Catcott Lows site investigated by Niedermeier and Robinson (2009). Upper right inset shows the study area within South West England.

2.7.2 West Sedgemoor ditch system

West Sedgemoor SSSI (51°01'40.8"N 2°54'45.2"W) is an area of the Somerset Levels and Moors Ramsar site and SPA site in Somerset, England; Figure 3. The site consists of 10.16 km^2 of low-lying fields and meadows, typically 5 m above sea level, separated by narrow water-filled ditches locally referred to as rhynes. Although the only outlet from the site, West Sedgemoor Pumping Station, which drains into the River Parrett (tidal), is operated by the Environment Agency (EA), it is the Parrett Internal Drainage Board (IDB) which manage water levels and flow circulation on the moor.

Drained in 1816, West Sedgemoor was one of the final moorland reclamations of the Somerset Levels. The high ground surrounding the site limited how the area could be dealt with, this provided the drainage scheme a certain unity, which other schemes on the Levels lacked. Furthermore, the relatively late reclamation resulted in ability to apply experience gained from previous drainage scheme endeavours from across the Levels. Splitting the moor more or less in half, the judiciously labelled Middle Rhyne was the first ditch implemented on the moor, swiftly followed by the addition of the North Drove Rhyne that was dug in parallel to Middle Rhyne (Williams, 1970). This arterial ditch system is still in operation in the present day; however, the pumping station was only constructed in 1944, enabling stricter control over water levels (Parkin et al., 2004; Williams, 1970).

One of West Sedgemoor's major water sources is runoff, supplied by a relatively small catchment of roughly 41 km^2. Widness Rhyne, situated to the southwest of the site at Helland, supplies the majority of runoff water entering West Sedgemoor. Both Sedgemoor Old Rhyne and West Sedgemoor Main Drain are provided with direct runoff from the North Curry and Stoke St Gregory ridge. Wickmoor Rhyne also supplies runoff water from Curry Rivel ridge, and Wick Moor (also fed directly by the River Parrett; nontidal). The Site is also provided water directly from the River Parrett (nontidal) by a culvert throughout the summer flow period. Winter flood risk is reduced via the lowering of water levels, although, a raised water level area is maintained year-round in the interest of nature conservation efforts (Parrett IDB, 2009). The Royal Society for the Protection of Birds (RSPB) is the majority land owner on West Sedgemoor, managing a nature reserve which supports England's largest breeding population of waders such as Lapwing (*Vanellus vanellus*), Snipe (*Gallinago gallinago*) and Curlew (*Numenius arquata*) making the site internationally important for supporting wintering waterfowl populations (Natural England, 2019). Additionally, West Sedgemoor is abundant with rare and scarce invertebrate fauna, especially water beetles, partly justifying the Somerset Levels Ramsar status under Ramsar criterion 2 (Drake et al., 2010).

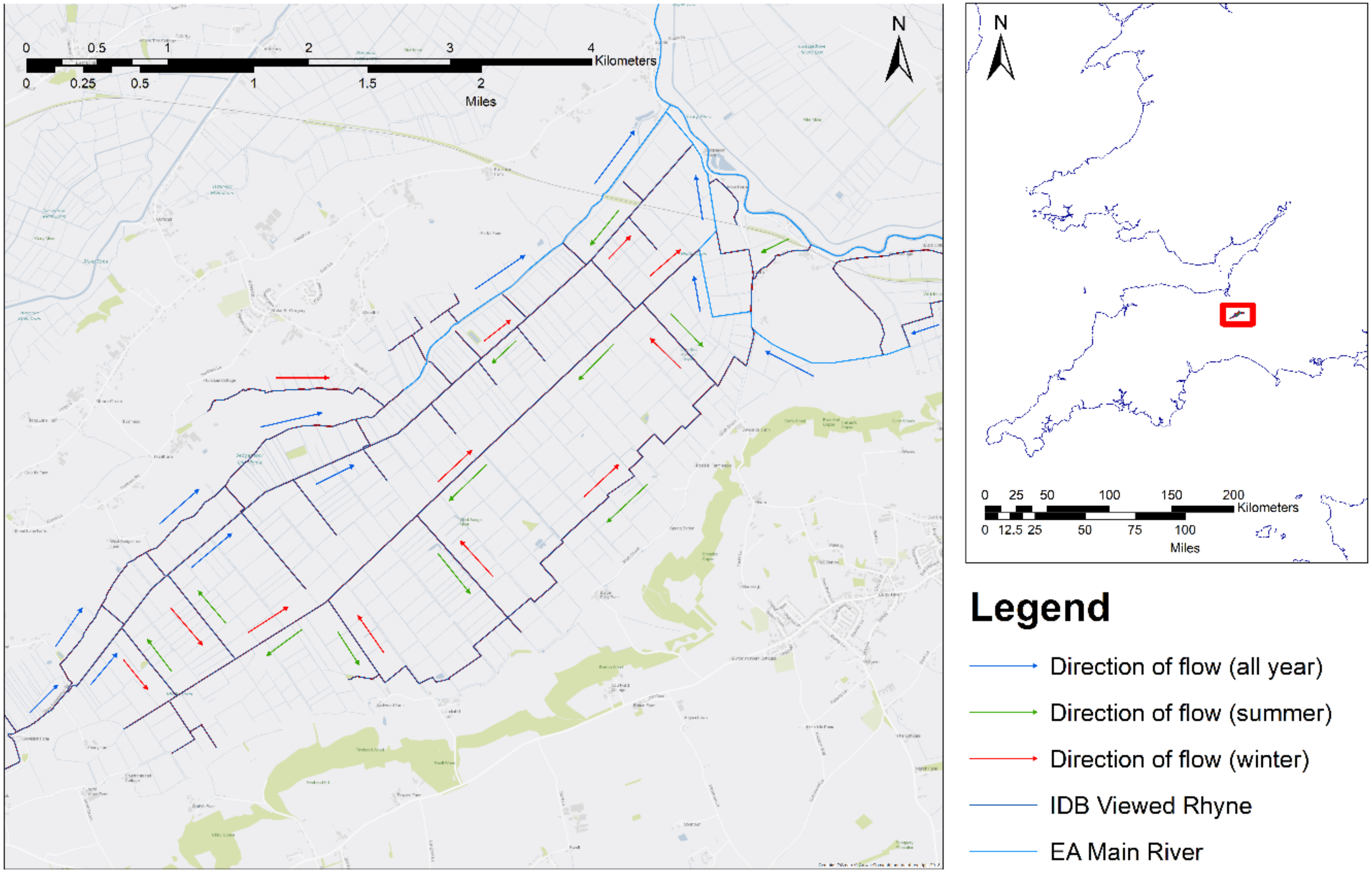

Figure 2.3: Location and controlled water flows of West Sedgemoor SSSI. Upper right inset shows the study area within South West England (red box). Left panel shows seasonal dependant water flow directions, indicated by coloured arrows (blue, all year; green, summer; red, winter).

Taylor et al. (2016) reports on surface water monitoring carried out across West Sedgemoor Levels on behalf of Natural England. The study updated a monitoring programme first undertaken in by Dawe and Rowe in 2001 (in an internal Environment Agency report) and by the Environment Agency in 2005 and 2009 (Dawe and Roe, 2001; Taylor et al., 2016). The study by Dawe and Roe (2001) constitutes a comprehensive dataset of water chemistry data derived from fortnightly sampling between May 1999 to June 2000. The other Environment Agency datasets are relatively smaller, derived from sampling between March to June 2005 and between May to July 2009. Sampling sites investigated by Dawe and Roe (2001) do not overlap with sites investigated by the Environment Agency in subsequent studies (Figure 4), and taking into account the complexity of the water flow paths through the ditch system (Figure 3) it is difficult to produce robust comparisons in these data regarding spatiality. Small sample sizes and lack of data continuity also hinder the ability to analyse long-term trends in water quality (Taylor et al., 2016).

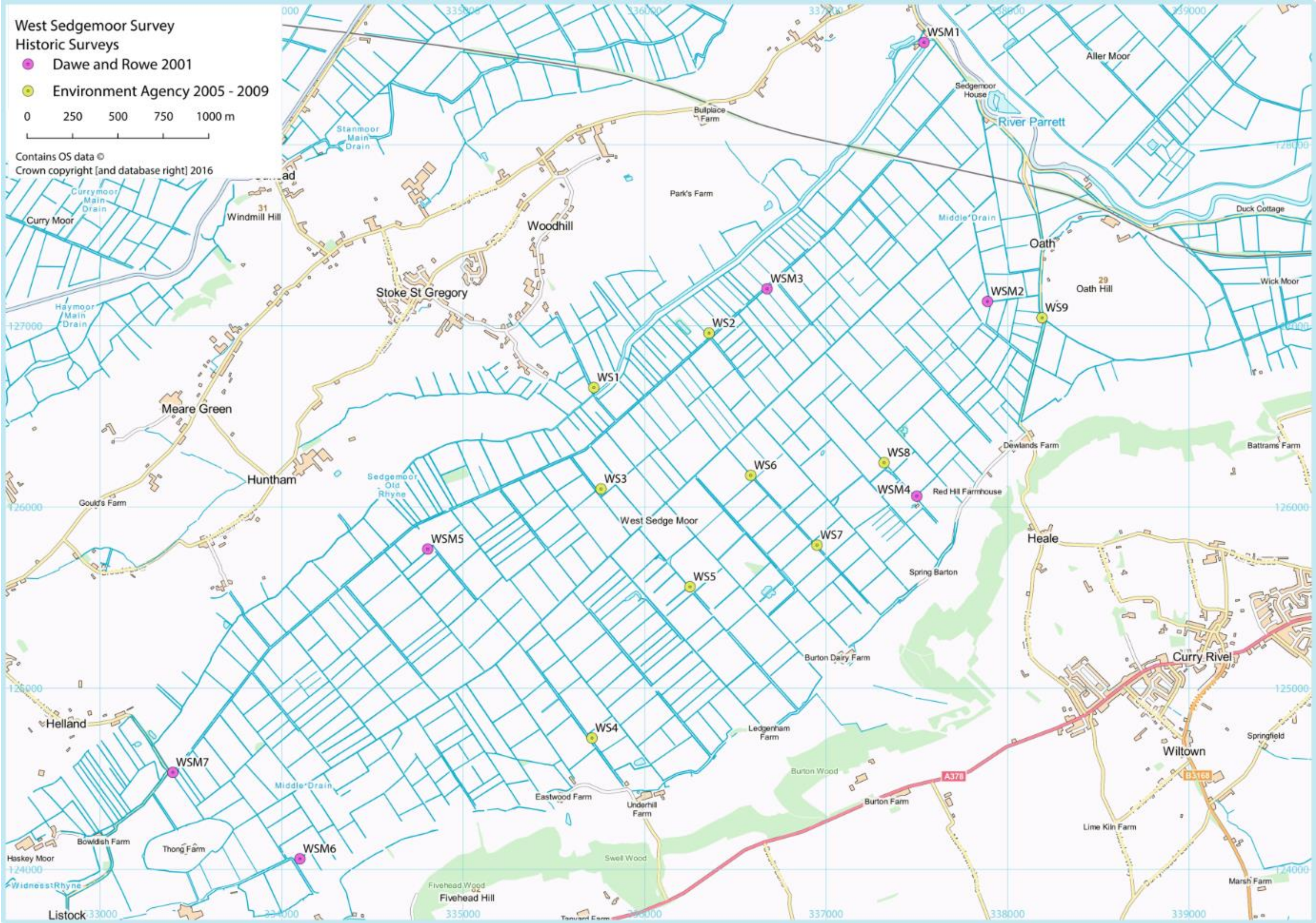

Figure 2.4: Historic monitoring sites across West Sedgemoor undertaken by Dawe and Rowe in 2001 and by the Environment Agency from 2005 to 2009. Figure reproduced from Taylor et al. (2016).

Orthophosphate data produced by Dawe and Roe (2001) is presented in Figure 5. TP data were not provided in the report; however, it is clear that the median orthophosphate concentration values observed were all in exceedance of the current CSM guidance target of <0.1 mg TP L^{-1}. Therefore, it is likely that the TP concentrations were substantially above this target. The majority of the sites showed a seasonal elevation of orthophosphate concentrations in the summer months. Taylor et al. (2016) propose numerous factors that have the potential to influence this observed summer peak including (i) increase in microbial activity (Jarvie et al., 2008), (ii) reduction in dilution of point source inputs under low water conditions, and (iii) sediment bound P release to the overlying waters under changing redox conditions (Van der Perk et al., 2007). The discernible issue with the proposed factor (ii) is that water levels on West Sedgemoor are in actual fact penned higher during the summer flows than during the winter flows. Although, flood events are more common during winter flows.

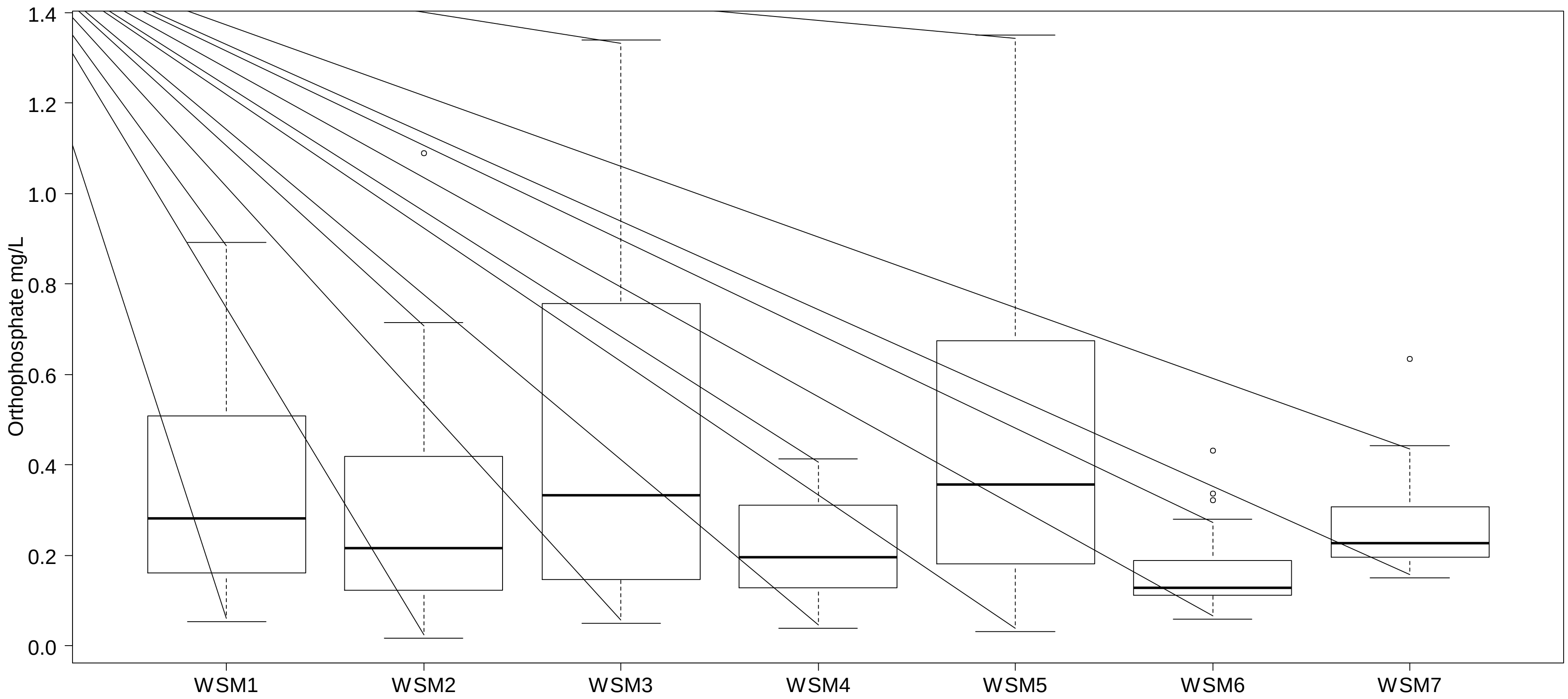

Figure 2.5: Boxplot of orthophosphate for West Sedgemoor derived from data reported by Dawe and Roe (2001). The bottom and top of the boxes represent the 25th and 75th percentiles respectively. The horizontal line across the box is the median value (50th percentile). The top whisker extends to the maximum value or the 75th percentile + (1.5 x the interquartile range), whichever is smaller. The bottom whisker extends to the minimum value or the 25th percentile – (1.5 x the interquartile range), whichever is larger. Circles represent values outside of the whisker limits. Figure reproduced from Taylor et al. (2016).

Orthophosphate data produced from Environment Agency sampling campaigns in 2005 and 2009 is presented in Figure 6. Overall, the median orthophosphate concentration values observed are lower than those reported by Dawe and Roe (2001), albeit several sites still exhibit orthophosphate concentration values in exceedance of the current CSM guidance target of <0.1 mg TP L^{-1}. As seen with the Dawe and Roe (2001) dataset, seasonal elevation peaks of orthophosphate concentrations in the summer months is observed within the 2009 dataset.

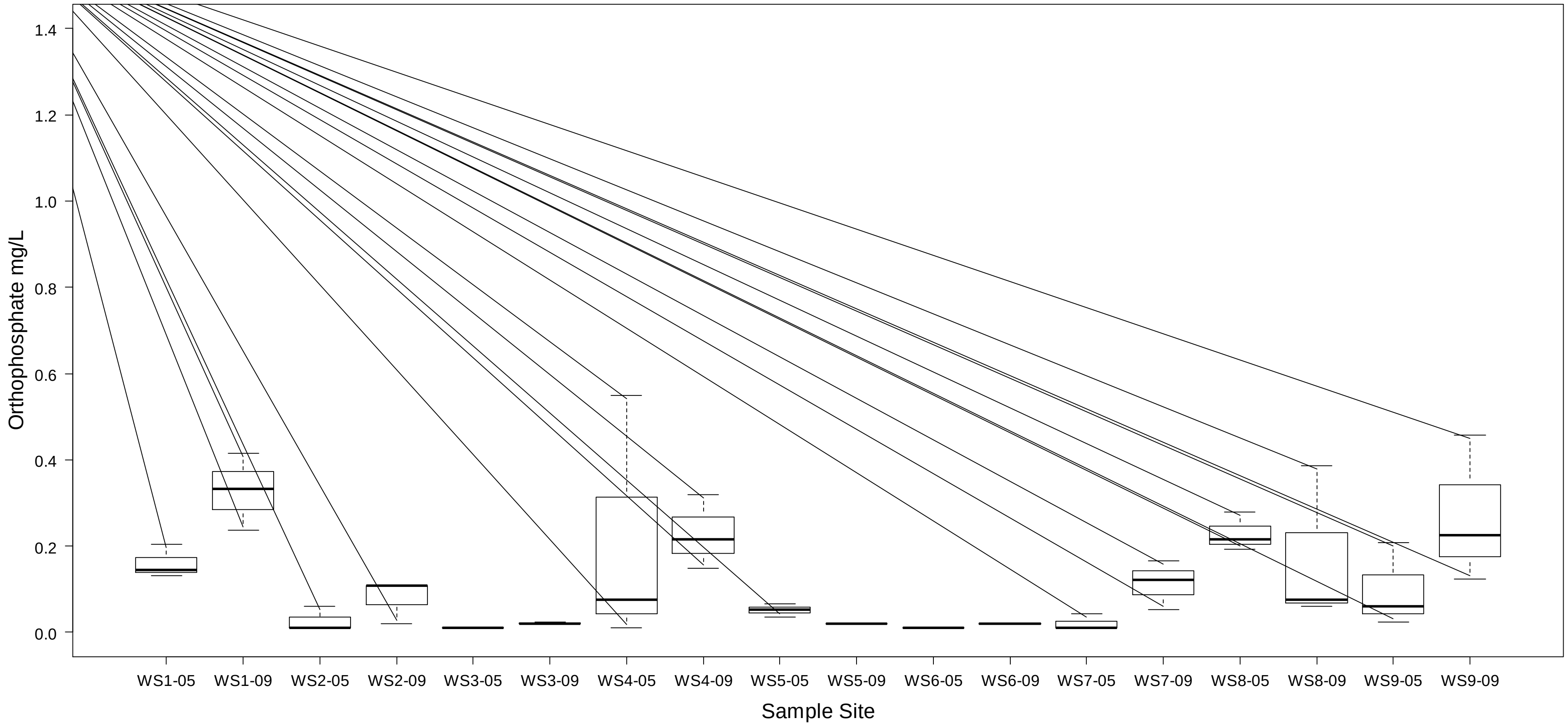

Figure 2.6: Boxplot of orthophosphate for West Sedgemoor derived from Environment Agency data from 2005 (05) and 2009 (09) sampling campaigns. The bottom and top of the boxes represent the 25th and 75th percentiles respectively. The horizontal line across the box is the median value (50th percentile). The top whisker extends to the maximum value or the 75th percentile + (1.5 x the interquartile range), whichever is smaller. The bottom whisker extends to the minimum value or the 25th percentile – (1.5 x the interquartile range), whichever is larger. Circles represent values outside of the whisker limits. Figure reproduced from Taylor et al. (2016).

In the routine sampling investigation by Taylor et al. (2016), sixteen monitoring sites were selected in agreement with Natural England and the Parrett IDB (Figure 7). The sampling sites of the study are mostly situated on the IDB viewed rhynes so that water quality could be assessed in the arterial ditch system. Some sites were chosen for overlapping data points with the monitoring sites of the previous investigations on West Sedgemoor. Routine (fortnightly) sampling was performed between August 2015 and June 2016 for assessment of nutrient chemistry (e.g., orthophosphate reactive as phosphorus (RP), total phosphate as P) in the system. Additional spot sample determinations of RP were taken from minor ditches using a portable Jenway 6051 colorimeter to improve spatial coverage. To assess the extent to which eutrophication is occurring, percentage cover of filamentous algae and Lemna was recorded in channel sections corresponding to water chemistry sampling points in line with CSM guidance for ditch systems (Joint Nature Conservation Committee, 2005).

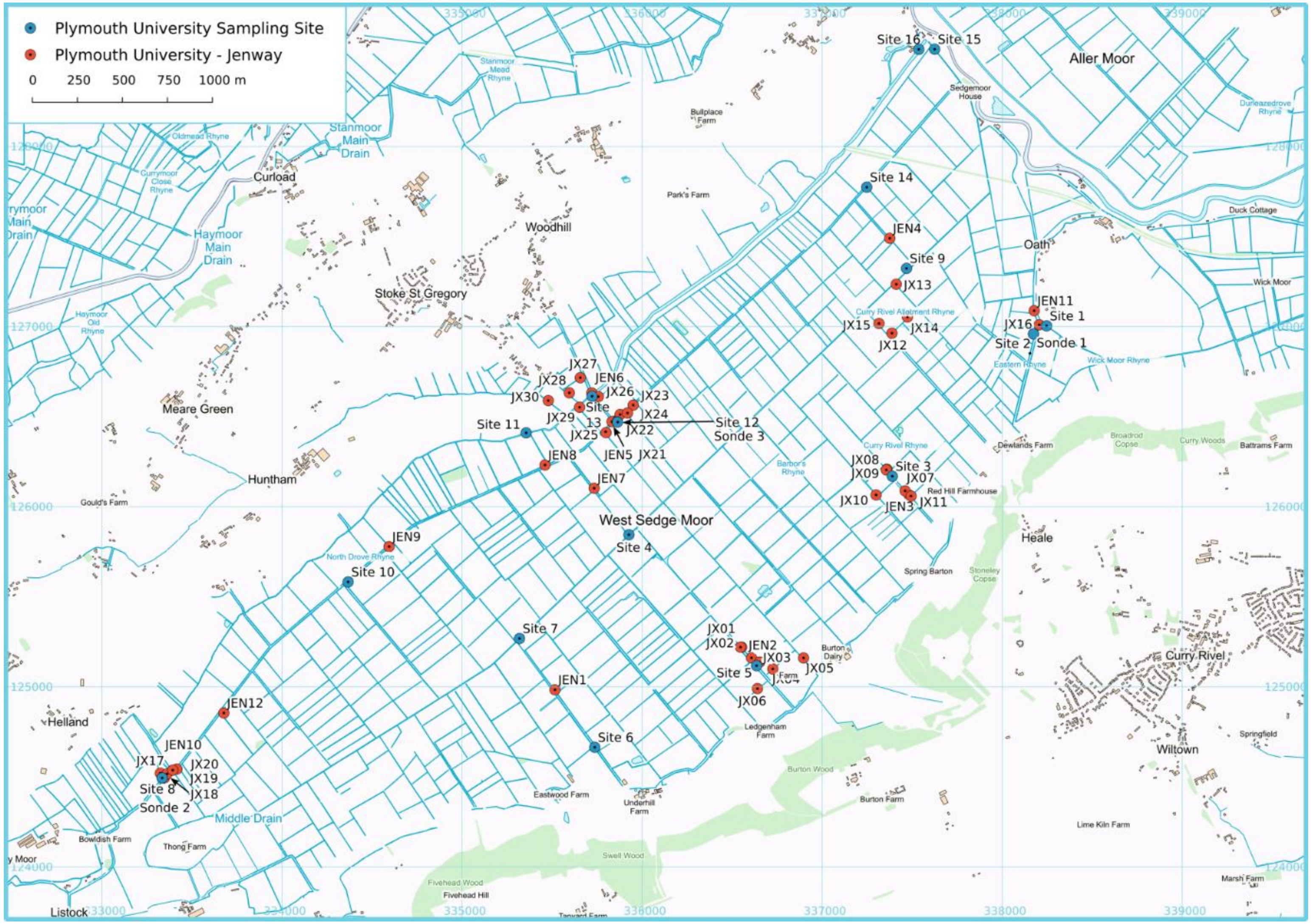

Figure 2.7: Historic monitoring sites across West Sedgemoor undertaken by Taylor et al. (2016). The sites indicated in blue are the routine monitoring sites and those in red are the additional points sampled using the portable instrument (Jenway 6051). Figure reproduced from Taylor et al. (2016).

Concentrations of total phosphate as P produced by Taylor et al. (2016) are shown in Figure 8. It is observed that all sites have the potential to be in exceedance of the CSM guidance target of <0.1 mg TP L^{-1}. The highest concentrations were generally observed at the sites situated at or below the key inlets (sites 1, 2, 3, 8, 12, 13) and at the outlet (sites 15, 16). The lower concentration data values at sites 6 and 14 are less robust as sampling at these sites ceased after the first three campaigns. The possible factors influencing the concentration gradient are unclear; Taylor et al. (2016) propose that P concentrations decrease with increased distance from inlets, owing to dilution and uptake by flora and sediment as water flows through the system. Sites 12 and 13 had the largest observed ranges of total phosphate as P concentration; Taylor et al. (2016) propose that this could reflect sporadic drainage inputs from agricultural land on the northern boundary of the site. This is supported by relatively lower concentrations being observed at site 11 which is upstream of a tributary inlet ditch that flows toward sites 13 and 12 draining runoff from North Curry and Stoke St Gregory ridge during the winter.

Concentrations of RP produced by Taylor et al. (2016) are shown in Figure 9. Concentrations of RP across the site were considerably lower than those reported by Dawe and Roe (2001) and comparable to those shown by the Environment Agency in 2005 and 2009.

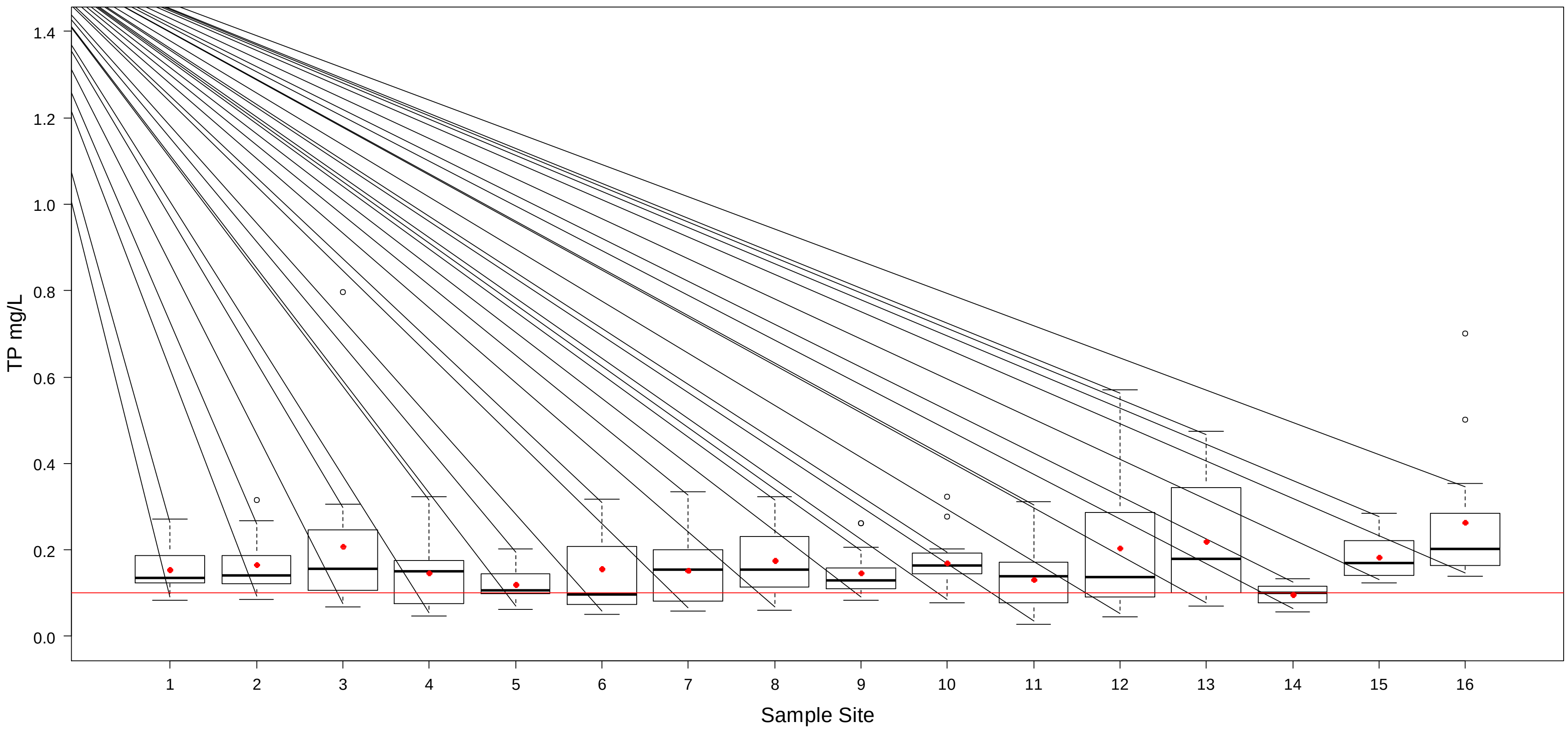

Figure 2.8: Total phosphate as P concentrations for sites 1-16 for sample campaigns from August 2015 to June 2016. The red line denotes the current CSM target of 0.1 mg L-1. Note that concentrations for sites 6 & 14 are based upon 3 samples. The bottom and top of the boxes represent the 25th and 75th percentiles respectively. The horizontal line across the box is the median value (50th percentile). The red points denote the mean values. The top whisker extends to the maximum value or the 75th percentile + (1.5 x the interquartile range), whichever is smaller. The bottom whisker extends to the minimum value or the 25th percentile – (1.5 x the interquartile range), whichever is larger. Circles represent values outside of the whisker limits. Figure reproduced from Taylor et al. (2016).

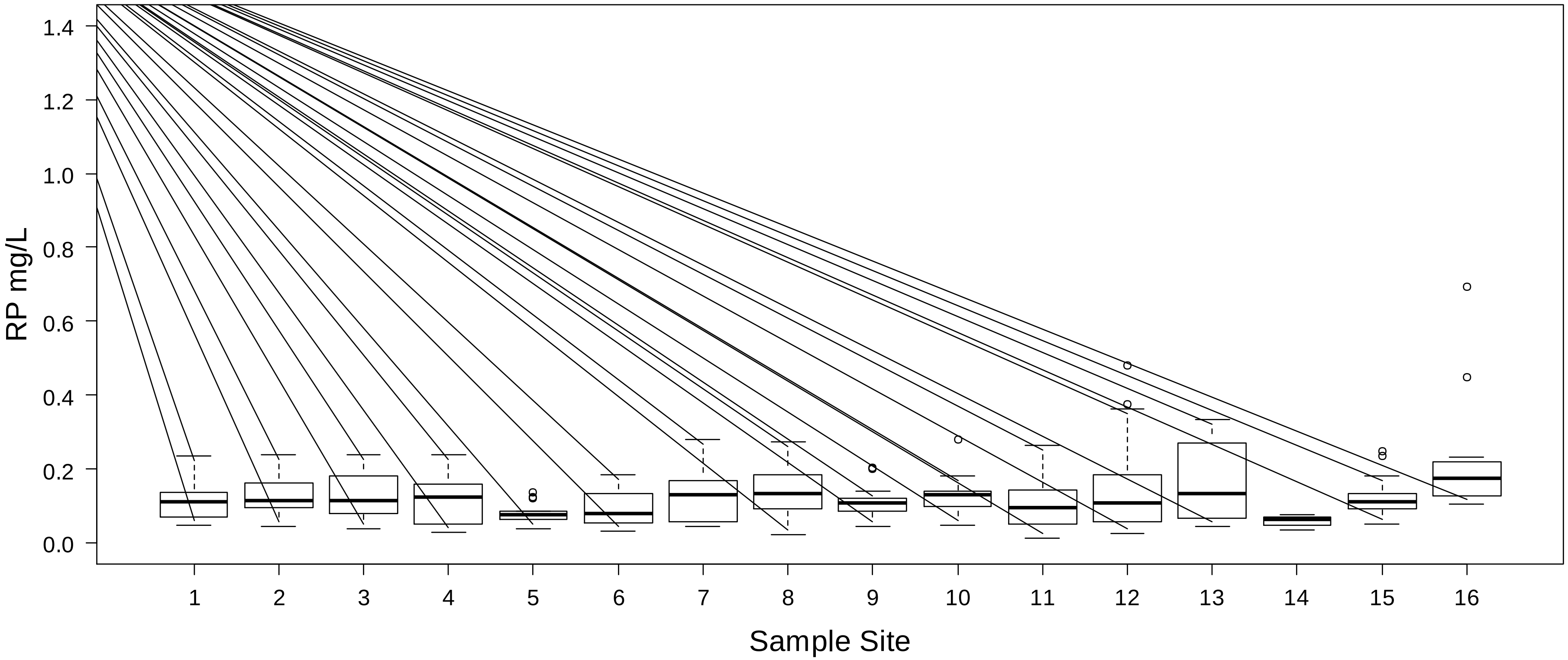

Figure 2.9: Orthophosphate reactive as P concentrations for sites 1-16 for sample campaigns from August 2015 to June 2016. Note that concentrations for sites 6 and 14 are based upon 3 samples. The bottom and top of the boxes represent the 25th and 75th percentiles respectively. The horizontal line across the box is the median value (50th percentile). The top whisker extends to the maximum value or the 75th percentile + (1.5 x the interquartile range), whichever is smaller. The bottom whisker extends to the minimum value or the 25th percentile – (1.5 x the interquartile range), whichever is larger. Circles represent values outside of the whisker limits. Figure reproduced from Taylor et al. (2016).

Concentrations of soluble reactive phosphorus (SRP) produced by Taylor et al. (2016) are shown in Table 2.2. In practice, the difference between SRP and RP is minimal (UKTAG, 2013). Concentrations at these sites indicate how minor ditches can have comparable reactive P concentrations to the arterial ditches. In particular, the ability to far exceed the CSM guidance target of <0.1 mg TP L^{-1}. High concentrations observed in minor ditches situated close to sites 12 and 13 further support the Taylor et al. (2016) proposal of eutrophic nutrient enrichment of this area by sporadic agricultural runoff.

Table 2.2 Soluble reactive phosphate (SRP) concentrations in minor ditches. Samples analysed using the Jenway 6051 colorimeter on filtered (< 0.45 µm) waters. No values (nv) for some sites in March 2016 owing to restricted access to avoid disturbance to nesting birds. Some analysis were below the limit of detection (LOD) for the instrument. Table reproduced from Taylor et al. (2016).

Site	SRP µg/L		Site	SRP µg/L		
	12/03/16	17/03/16		17/11/15	02/02/16	12/04/16
JX01	45	60	Jen1	246	48	21
JX02	<LoD	40	Jen2	40	8	56
JX03	92	179	Jen3	31	33	14
JX04	115	37	Jen4	149	57	21
JX05	47	7	Jen5	149	424	92
JX06	86	421	Jen6	219	204	77
JX07	167	nv	Jen7	79	236	192
JX08	112	nv	Jen8	172	204	70
JX09	72	nv	Jen9	312	155	84
JX10	102	nv	Jen10	165	32	35
JX11	95	nv	Jen11	106	57	120
JX12	82	428	Jen12	nv	294	152
JX13	87	137				
JX14	20	22				
JX15	12	<LoD				
JX16	65	132				
JX17	194	60				
JX18	30	<LoD				
JX19	62	127				
JX20	107	152				
JX21	750	799				
JX22	675	989				
JX23	147	501				
JX24	329	530				
JX25	234	346				
JX26	595	645				
JX27	613	565				
JX28	583	341				
JX29	451	254				
JX30	650	595				

Data for algal and duckweed coverage produced by Taylor et al. (2016) are shown in Table 3. The data constitutes sites where coverage of filamentous algae and Lemna was >10% and >50% respectively. Algal dominance would have been expected during the summer months and although the survey was hampered by water clarity (colour) during the August 2015 campaign, the data for June 2016 clearly showed increased coverage. As would be expected, data showed decreasing coverage in the winter months. Site 1 showed the most consistent algal coverage above the threshold values during the first half of the sampling period (August 2015 to January 2016), and this is in line with elevated nutrient concentrations shown at this site across that sampling period. From March 2016 site 1 showed lower nutrient concentrations, which corresponded to reduced algal growth. Other locations, which consistently demonstrated nutrient elevation above required standards (sites 2, 3, 13, 15 and 16) showed sporadic periods of high algal coverage highlighting that whilst significantly elevated nutrients promote algal blooms a number of factors will affect the local occurrence of algal growth.

Table 2.3: Sites where coverage of filamentous algae and Lemna spp. was deemed to be >10% and >50% respectively from August 2015 to February 2016. Table reproduced from Taylor et al. (2016).

Site	27th Aug		23rd Sep		6th Oct		21st Oct		4th Nov		17th Nov		1st Dec		19th Jan		2nd Feb	
1																		
2			c															
3	c																	
4																		
5	c																	
6																		
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14	c																	
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[c] assessment hampered by high water colour

Site	1st March		15th March		12th April		26th April		10th May		24th May		7th June		21st June	
1																
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	Filamentous algae >10%
	Lemna spp. >50%

2.8 Summary

This review has highlighted the importance of the regulation and monitoring of eutrophication, the current condition of the Somerset Levels and Moors, and the general lack of up-to-date consistent and comprehensive monitoring data for the Ramsar ditch systems. It is recognised that there is not enough research concerning P dynamics specific to drainage ditch processes and management, leading to a lack of knowledge as to how the complex seasonal water flow paths and levels affect transport of P, from both point (e.g., WwTWs) and diffuse (largely agricultural runoff) sources, throughout the wetland ditch systems. The closure of this knowledge gap is pursued within the research presented in this thesis.

3 Spatial distribution of sediment phosphorus in a Ramsar wetland

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Authorship contribution statement:

- Ry Crocker – Conceptualization, Methodology, Data Curation, Formal analysis, Writing.
- Sean Comber – Conceptualization, Review, Resourcing, Managing.
- William Blake – Sediment geochemistry technical input, Review, Conceptualization, Managing.
- Tom Hutchinson – Conceptualization, Review, Technical input on ecology, Managing.

Research Hypothesis:

- Legacy phosphorus concentrations in sediment are higher in ditches adjacent to agricultural land than wetland bird nature reserve land.

3.1 Abstract

Eutrophication is a significant threat to surface water biodiversity worldwide, with excessive phosphorus concentrations being among the most common causes. Wetland ditches under these conditions shift from primarily submerged aquatic vegetation to algae or duckweed dominance, leading to excessive shading and anoxic conditions. Phosphorus, from both point (e.g., wastewater treatment works) and diffuse (largely agricultural runoff) sources, is currently the central reason for failure in the majority of surface water bodies in England to meet required water quality guidelines. This study assesses phosphorus storage in the ditch systems at West Sedgemoor, a designated site of special scientific interest. Elevated phosphorus concentrations in sediment were observed across the Moor up to 4,220 mg kg^{-1}, almost 10 times that which may be expected from background levels. The lowest observed total phosphorus concentration was 957 mg kg^{-1}, while the mean concentration for the whole site was 1870 mg kg^{-1}. The highest concentrations were generally observed at the more intensively farmed sites in the north of the moor, near key inlets and the outlet. Based upon their chemical and physical properties, clear distinction was observed between sites outside and within the Royal Society of the Protection of Birds nature reserve, using principal component analysis.

3.2 Introduction

Wetland ecosystems are important worldwide, providing numerous valuable ecological services for people and wildlife. They are biologically diverse habitats serving hydrological functions, including water storage; storm protection and flood mitigation; and water purification. Economically, wetlands benefit water supply; agriculture; fisheries and recreational fishing; tourism; and wetland products such as herbal medicines (Hughes and Heathwaite, 1995; Ramsar Convention Secretariat, 2016). However, wetlands are one of the most threatened ecosystems due to loss and degradation, with 87% lost globally in the last 300 years, and 54% since 1900 (IPBES, 2018). Human activities are the main driver of wetland degradation. Intensified agriculture has seen considerably increased crop and livestock yields across the world, but when managed inappropriately, can cause soil erosion, and eutrophication of aquatic systems via diffuse pollution (IPBES, 2018; Ockenden et al., 2014). Objectives of the European Habitats Directive (Council of the European Communities, 1992) and the Water Framework Directive (WFD) (Council of the European Communities, 2000) demand action to restore waterbodies that are either not meeting good status, WFD, or need to meet favourable conservation status, Habitats Directive. Wetland areas are also protected under the Ramsar Convention (Ramsar, 1994).

Eutrophication of surface water is a significant threat to biodiversity worldwide, with excessive phosphorus (P) concentrations being among the most common causes (Comber et al., 2015a; Zhang et al., 2017). Surface water systems under these conditions deviate from primarily submerged aquatic vegetation to algae or duckweed dominance, leading to shading and potentially anoxic conditions and therefore deterioration of aquatic ecosystems (Zhang et al., 2017). Heavy shading via surface coverage, and bacterial degradation of excessive amounts of organic matter, produced by algal and duckweed blooms, causes depletion of oxygen in the water column, bringing about fish kills and development of bad odours (Padedda et al., 2017; Riley et al., 2018; Zhang et al., 2017).

Significant improvements have been made to reduce the amount of P input from point source discharges to water courses, such as wastewater treatment Works (WwTW), and land management policy is encouraging farming best management practices to reduce biogeochemical flows (Ockenden et al., 2014). Specifically, the linear biogeochemical flow of P from mineral reserves to agriculture and then into catchments and oceans is considered to be exceeding the planetary boundary, thence leading to eutrophication (Carpenter and Bennett, 2011; Ockenden et al., 2014). In arable catchment, surface runoff is an important driver of erosion damage and of fertilizer P export to waterbodies. Phosphorus contributions from pasture catchment include dissolution of cow manure from overland flow or from subsurface flow (Verheyen et al., 2015). However, wetland managed as waterfowl nature reserve can potentially cause P loading through bird droppings (guanotrophication). Sadly, the degradation and loss of wetlands and other freshwater bodies that were once breeding grounds and migratory stopovers have forced intensified use of the surviving habitat. These large bird populations, relative to the size and/or volume of the waterbody, can have a significant fraction of the internal P load cycling through their diet. Waterfowl have the potential to affect wetland P cycling by altering the form of P and by inputting and/or exporting P to and/or from external areas to the wetland (Adhurya et al., 2020; Scherer et al., 1995).

However, measures put in place to reduce P loads discharged to a catchment could be negated as legacy P bound in sediment has the potential to act as a secondary source of P to the water column, following disturbance (Collins and McGonigle, 2008; Van der Perk et al., 2007) or in response to changes in condition of overlying waters (Jarvie et al., 2005; Reynolds, 1992). This ability of sediment to release stored P to the water column could significantly delay the recovery and compliance with water column-based standards, and give rise to algal and duckweed bloom production in excess of what may be expected from external loading alone (Heaney et al., 1992). Therefore, it is crucial to generate data on particulate P storage in sediments in systems that are failing to meet WFD requirements.

In this study, the spatial distribution of surface sediment P is examined across West Sedgemoor, a Site of Special Scientific Interest (SSSI) and part of the Somerset Levels and Moors, Ramsar site no. 914.

Water quality across a number of sites on the moor has already been shown to exceed the Common Standards Monitoring Guidance for P (>0.1 mg-P l^{-1} as total P) set as part of the Natura 2000 series of which include Special Protection Areas (SPAs), designated under the European Birds Directive, and Special Areas of Conservation (SACs), designated under the European Habitats Directive (Council of the European Communities, 1992; European parliament and the council of the European Union, 2009; Taylor et al., 2016). This eutrophication necessitates the requirement to identify the sources of contamination and to put in measures to remediate the situation. Understanding the potential sediment contribution to this overlying water exceedance is crucial and so for the first time a systematic sediment sampling exercise was planned and undertaken.

Ditch sediment samples were collected from a range of locations, corresponding with different land uses, from agricultural to Royal Society for the Protection of Birds (RSPB) nature reserve areas. In order to assess potential factors of P loading in sediments, sediments were also analysed for a range of major and minor element constituents and particle size. Multivariate principal component analysis was used to determine whether land use impacts ditch surface sediment geochemistry.

3.3 Material and methods

3.3.1 Study area

West Sedgemoor SSSI (51°01'40.8"N 2°54'45.2"W) is an area of the Somerset Levels and Moors Ramsar site and a Special Protection Area (SPA) site in Somerset, England; Fig. 3.1. This inland wetland has a total area of 10.16 km^2 and consists of many small, low-lying fields and meadows separated by narrow water-filled ditches, locally called rhynes. Water levels and the circulation of water flow on the moor is managed by the Parrett Internal Drainage Board (IDB), although the only water outlet is via West Sedgemoor Pumping Station, discharging to the River Parrett (tidal), which is operated by the Environment Agency (EA). The site is of a maritime temperate climate, typically 5 m above sea level with the average monthly temperature ranging from 8.3 °C (January) to 21.8 °C (July) with an annual mean temperature of approximately 14.6 °C. The area receives a mean annual precipitation of 708.5 mm (Met Office, 2019).

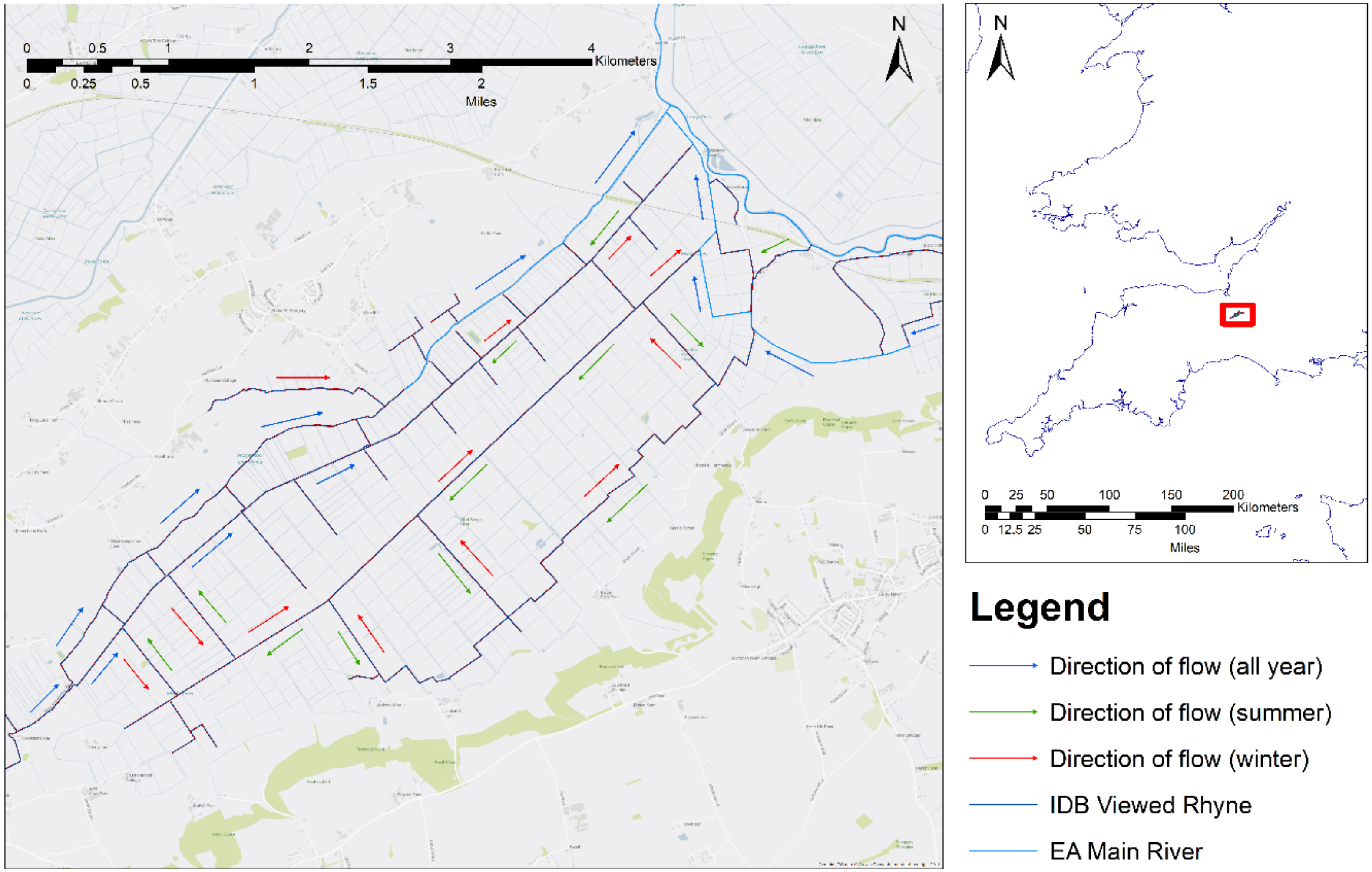


Figure 3.1: Location and controlled water flows of West Sedgemoor SSSI. Upper right inset shows the study area within South West England (red box). Left panel shows seasonal dependant water flow directions, indicated by coloured arrows (blue, all year; green, summer; red, winter).

Lowland wet grassland in the UK usually consists of reclaimed floodplain land managed as grazing marshes with some being cut for hay or silage (Jefferson and Grice, 1998; Williams, 1970). West Sedgemoor was drained in 1816, making it one of the last moorland reclamations of the Somerset Levels. The surrounding higher ground gave limitations to how the area could be dealt with, this gave a certain unity to the drainage scheme, which other areas in the Levels lacked. Also, the relatively late reclamation meant experience from previous drainage schemes across the Levels could be applied. Dividing the moor nearly in half, the aptly named Middle Rhyne was the first to be implemented on the moor, swiftly followed by the addition of the North Drove Rhyne which was dug parallel to the Middle Rhyne (Williams, 1970). This arterial ditch system is still in operation today; however the pumping station was not constructed until 1944, allowing for stricter control over water levels (Parkin et al., 2004; Williams, 1970).

Runoff provides one of the main sources of water to West Sedgemoor, from a relatively small catchment (roughly 41 km^2). Widness Rhyne in the west contributes most of the runoff water entering the moor. Other runoff water sources include the North Curry and Stoke St Gregory ridge, draining directly to both Sedgemoor Old Rhyne and West Sedgemoor Main Drain, and Wick Moor (fed also by the River Parrett; nontidal) and Curry Rivel ridge, draining to Wickmoor Rhyne. During the summer, a culvert allows the moor to be supplied with water direct from the River Parrett (nontidal) via the Oath Farm Inlet. Although the area is still often flooded, water levels are lowered in the winter to reduce flood risk by allowing better drainage. However, most watercourses retain low pen level in the interest of conservation efforts and in order to reduce frost damage and bank erosion. Winter target water levels in Raised Water Level Area (RWLA) blocks range from 4.65 m to 5.15 m ODN (Ordnance Datum Newlyn). Outside of RWLAs, winter target water levels range from 4.20 m to ~4.70 m ODN, barring flood events. Circulation of water flow changes drastically in the summer months, the emphasis changing from drainage to irrigation, barring high flood risk conditions (e.g., heavy rainfall). During the period of early April to late November, water levels are allowed to rise in rhynes and ditches. Summer target water levels range from 4.65 m to 5.30 m ODN. These higher levels provide ‘wet fences’ around fields to contain livestock, maintain the groundwater table for the growing period and continue the watercourse conservation interest (Parrett IDB, 2009).

West Sedgemoor is internationally important for supporting wintering waterfowl populations such as Wigeon (*Anas penelope*), Teal (*Anas crecca*) and Lapwing (*Vanellus vanellus*). The moor also supports England’s largest breeding population of waders such as Lapwing (*Vanellus vanellus*), Snipe (*Gallinago gallinago*) and Curlew (*Numenius arquata*) (Natural England, 2019). Additionally, Fivehead Woods and Meadow on the southern edge of the moor has one of the largest heronries in the UK with more than 100 breeding pairs of Grey Heron (*Ardea cinerea*) (Drewitt et al., 2008). West Sedgemoor is also the location for the Great Crane Project aimed to secure the future for the Crane (*Grus grus*) in the UK, after a five year reintroduction was completed in 2015 (The Great Crane Project, 2014). West Sedgmoor Drain, Stathe, to the north of the moor is a recreational fishing site managed by the Taunton Angling Association (TAA). Fish species present include Common Bream (*Abramis brama*), Tench (*Tinca tinca*), European Perch (*Perca fluviatilis*), Common Roach (*Rutilus rutilus*), Northern Pike (*Esox lucius*), Common Carp (*Cyprinus carpio*), Gudgeon (*Gobio gobio*), Rudd (*Scardinius erythrophalmus*), Sunbleak (*Leucaspius delineatus*), Stone Loach (*Barbatula barbatula*), 3-Spined Stickleback (*Gasterosteus aculeatus*), 10-Spined Stickleback (*Pungitius pungitius*) and Eels (*Anguilla anguilla*) (Environment Agency, 2020). Finally, the site is also rich in rare and scarce invertebrate fauna, particularly water beetles (Drake et al., 2010).

3.3.2 Sampling and chemical analyses

Surface sediment samples were collected in March 2018. 59 sampling sites (Fig. 3.2) were chosen based upon (1) coverage of IDB viewed rhynes and potential inputs (2) site accessibility/access permission (3) minimal disturbance to nature conservation efforts of the RSPB. Samples were collected using a Van Veen Grab sampler and transferred into hydrochloric acid (10% - Fisher Scientific Primar Plus) and ultra high purity water (>18 Mohm.cm) soaked HDPE 500 ml Nalgene bottles and stored frozen at -18°C in the dark until further analysis.

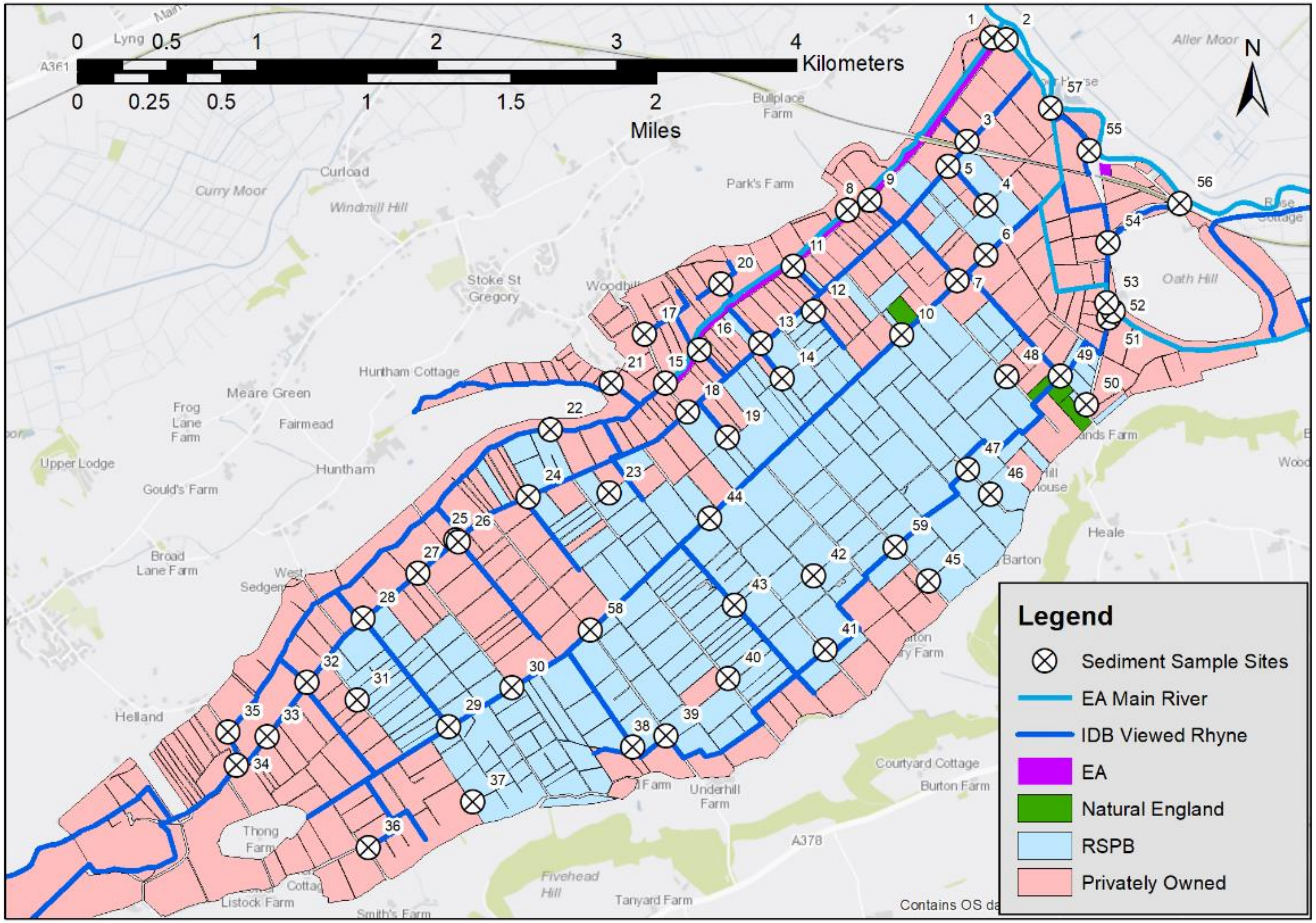


Figure 3.2: Sediment sampling sites and land ownership on West Sedgemoor SSSI.

Once thawed, samples were centrifuged at 4000 rpm for 10 minutes, and the majority of the pore water was poured off. At this stage samples were individually mixed and had subsamples taken for particle size analysis. Roots and other large plant material were either not present or removed from samples manually. These subsamples of sediment were pushed through a stainless steel mesh sieve with a 1.00 mm aperture, and then pretreated with H_2O_2 to remove organic constituents. Particle size analysis was measured using a Malvern Mastersizer 2000. Particle size analysis data were analysed using GRADISTAT (Blott S.J. and Pye K., 2001).

The remaining sediment was frozen, freeze-dried, disaggregated, and sieved to the <63 µm fraction. Subsamples were then taken, milled and pressed into pellets for analysis using a PANalytical Wavelength Dispersive X-Ray Fluorescence Spectrometer (WD-XRF) (Axios Max); the concentrations of a range of major and minor element constituents (F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Br, Rb, Sr, Y, Zr, Nb, Ba, Ce, Pb, As, Au, Bi, Ge, Ir, Mo, Nd, Pr, Se, Tl and V) were measured (Blake et al., 2013). These elemental constituents were measured alongside P so that correlations could be analysed, and potential biogeochemical flow pathways of P could be identified. Sites 12, 46 & 50 were unable to be analysed by WD-XRF due to an insufficient amount of <63 µm fraction available.

3.3.3 Principle Component analysis

Principal component analysis (PCA) of the WD-XRF and particle size analysis data was conducted using Minitab 17. No outliers were observed from examining the Mahalanobis distances plotted in Fig. A.1 of Appendix A (Brereton, 2015). The grouping of the sites was visualized with a scatterplot of the scores of the second principal component versus the scores of the first principal component. The variables responsible for the grouping of sites were identified by plotting the coefficients of each variable for the first component versus the coefficients for the second component.

3.4 Results and discussion

3.4.1 Spatial phosphorus distribution in sediment

The spatial distribution of total phosphorus (TP) in sediments is shown in Fig. 3.3. The highest TP content of 4220 mg kg^{-1}, around 10 times that which may be expected from background levels (Owens and Walling, 2002), was recorded at site 53 located on the section of Wickmoor Rhyne that intersects Eastern Rhyne, south of the Oath Supply Ditch. Site 30, on the southern end of the Middle Rhyne, had the lowest observed TP concentration of 957 mg kg^{-1}, while the mean concentration for the whole site was 1870 mg kg^{-1}. Higher TP concentrations were generally observed in the north of the moor, near key inlets (sites 33, 35, 51, 53, 54, 56) and the outlet (sites 1 and 2). The mean TP concentration in the north of the site (sites 1-22, 48-57) was 2140 mg kg^{-1}, in the south (sites 23-47, 58 & 59) It was 1560 mg kg^{-1}. Lower TP concentrations were generally observed around winter roost sites with a mean concentration of 1460 mg kg^{-1}, compared to 1960 mg kg^{-1} for the rest of the site. However, most of these winter roost samples are taken from the ditches that outline the boarder of the winter roost sites (Fig A.2); this was done to cause minimal disturbance to the roosting birds and the nature conservation efforts of the RSPB. Table 3.1 compares the TP concentration range, in ditch sediment, of this study to other literature data for similar rural ditch environments. West Sedgemoor had the highest single observed TP sediment concentration, of all the compared sites TP ranges, and the second highest low-end concentration. Even compared to other man-made managed aquatic ecosystems, West Sedgemoor can be considered to have exceedingly high TP concentrations; a study of fishponds in the Czech Republic observed an average sediment TP concentration of 1113.2 mg kg^{-1}, across 28 sites, with a highest concentration of 3020 mg kg^{-1} (Baxa et al., 2019). Although the analytical method of this study differs from that of the other literature data, previous studies have shown that the methods are equivalent (Blake et al., 2013; Matsunami et al., 2010).

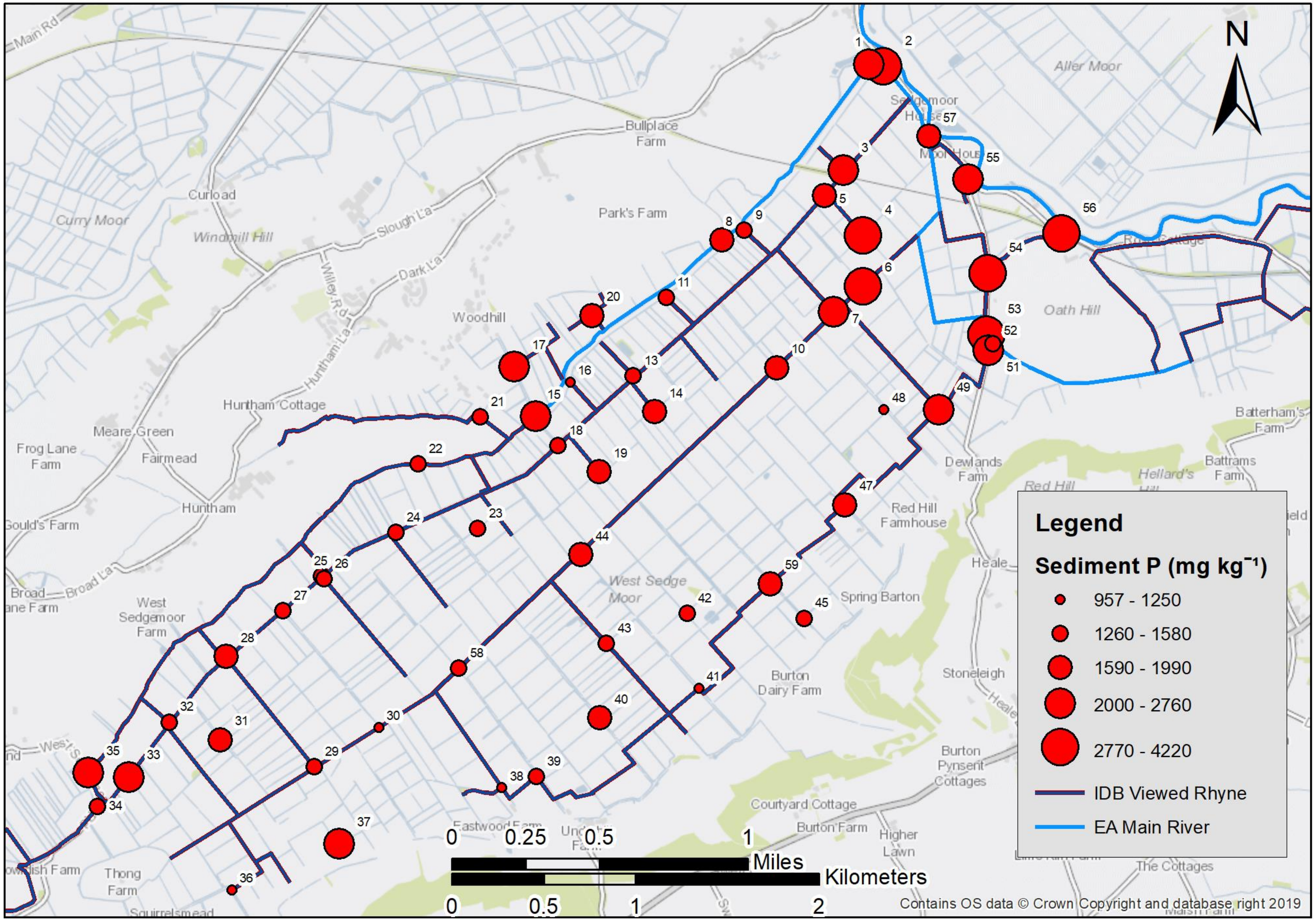


Figure 3.3: Distribution of total phosphorus (TP) in sediments at West Sedgemoor SSSI. Data are displayed using the Jenks natural breaks classification method.

Table 3.1: Comparison of the total phosphorus (TP) concentration range, in ditch sediment, of this study to other literature data for similar environments.

Site	TP Range (mg kg^{-1})	Analytical Method	Reference
West Sedgemoor, Somerset, UK	957 - 4220	Wavelength dispersive x-ray fluorescence spectrometer	This study
Catcott Lows, Somerset, UK	414 - 2065	Sequential extraction; molybdenum blue colorimetric method	(Hill and Robinson, 2012a)
Cumbria, UK	220 - 4000	Acid digestion; molybdenum blue colorimetric method	(Ockenden et al., 2014)
South-East Ireland	200< - 1790	Aqua regia digestion; inductively coupled plasma atomic emission spectroscopy	(Shore et al., 2016)
Noordplas polder, Netherlands	673 - 3575	Acid digestion; molybdenum blue colorimetric method	(Van der Grift, 2017)
Quarles van Ufford polder area, Netherlands	1712 - 3287	Acid digestion; molybdenum blue colorimetric method	(Van der Grift, 2017)
Everglades Agricultural Area, Florida, USA	220 - 2889	Acid digestion; molybdenum blue colorimetric method	(Capasso et al., 2020)
Jieliu Catchment, central Sichuan Basin, China	427 - 718	Acid digestion; molybdenum blue colorimetric method	(Wang et al., 2012)

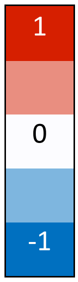
3.4.2 Main factors affecting phosphorus storage in sediment

3.4.2.1 Correlation coefficient analysis

The correlation coefficients between P, Fe, S, Al, Ca and % mud (<63 µm) particle size, for West Sedgemoor SSSI, are shown in Table 3.2. Sediment P was not correlated with Fe (r = 0.169), Al (r = 0.261), Ca (r = -0.051) or % mud (r = -0.066). This varies from data reported for other rivers in England for example where a stronger correlation was observed (Burns et al., 2015) between P and Ca. The reasons for a lack of correlation potentially reflects the varying sources and magnitudes of the elements across the wetland site including agricultural runoff, inflows from the main river, including wastewater treatment works effluents and avian deposition via faeces.

Table 3.2: Correlation matrix of Pearson's correlation coefficients between P, Fe, S, Al, Ca and % mud (<63 µm) in West Sedgemoor surface sediments.

Parameter	P	Fe	S	Al	Ca
Fe	0.169				
S	-0.400**	0.218			
Al	0.261	0.204	-0.826**		
Ca	-0.051	-0.195	0.427**	-0.627**	
% Mud (< 63 µm)	-0.066	0.233	0.21	0.003	0.052



Note: * p<0.05; ** p<0.01

Seasonal increases in temperature and biological activity influences internal loading, retention capacity and release mechanisms. Increasing temperatures stimulate mineralisation of organic matter and the release of soluble inorganic phosphate. Increased sediment respiration during mineralisation processes causes decline in oxygen and nitrate sediment penetration depth. As oxygen and nitrate have the capability to keep iron in its oxidised form, their decline can cause redox-sensitive release of P. Under oxic conditions, P is bound to Fe(III) compounds; under anoxic conditions, both P and Fe are released to the water column as insoluble Fe(III) compounds are reduced to soluble Fe(II) (Søndergaard et al., 2003). Additionally, low nitrate and high sulphate concentrations, combined with a large supply of biodegradable organic matter, enables dissimilatory sulphate reduction (desulphurication) and sulphide-mediated chemical iron reduction. This sulphide precipitation depletes the amount of Fe available for P binding, influencing both short- and long-term P retention in sediments (Søndergaard et al., 2003; Wu et al., 2019; Zhao et al., 2019). A weak negative correlation was observed between P and S (r = -0.400), suggesting a possible S interference in iron-phosphorus cycling by sulphide-mediated chemical iron reduction. However, there is a general lack of significant correlations observed, for the site as a whole, from which to draw conclusions.

The study site was therefore split into three designations in order to observe the influence of land management on P storage in sediment. Sites surrounded by RSPB nature reserve land, sites surrounded by land that is not RSPB nature reserve, and sites adjacent to both land that is RSPB nature reserve and land that is not RSPB nature reserve were analysed for correlations as separate groups (Table 3.3).

Table 3.3: Correlation matrix of Pearson's correlation coefficients between P, Fe, S, Al, Ca and % mud (<63 µm) in surface sediments of sites surrounded by RSPB nature reserve land, sites surrounded by land that is privately owned and sites adjacent to both land that is RSPB nature reserve and land that is privately owned.

Parameter	P	Fe	S	Al	Ca
RSPB Land					
Fe	0.682*				
S	-0.905**	-0.894**			
Al	0.764*	0.956**	-0.955**		
Ca	-0.758*	-0.720*	0.752*	-0.761*	
% Mud (< 63 µm)	-0.055	0.291	-0.161	0.339	-0.384
Private Land					
Fe	-0.12				
S	-0.397*	0.659**			
Al	-0.012	0.105	-0.444*		
Ca	0.174	-0.003	0.254	-0.650**	
% Mud (< 63 µm)	-0.263	0.395*	0.483*	0.099	0.097
RSPB and Private Land					
Fe	0.635**				
S	-0.009	0.324			
Al	0.124	0.147	-0.822**		
Ca	-0.007	-0.158	0.297	-0.573**	
% Mud (< 63 µm)	0.213	0.089	0.273	-0.25	0.176

Note: * p<0.05; ** p<0.01

In surface sediments of sites surrounded by RSPB nature reserve land, P showed significant positive correlations with Fe (r = 0.682) and Al (r = 0.764) and significant negative correlations with S (r = -0.905) and Ca (r = -0.758). This suggests P at these sites is primarily stored in the sediment bound to Fe and Al, not Ca. The moderate P-Fe positive correlation along with significant negative correlations between S-P (r = -0.905) and S-Fe (r = -0.894) suggest that sulphide interference of iron-phosphorus cycling is happening, but Fe concentration is high enough that, in RSPB surrounded sites, Fe storage of P is still a primary pathway (Fig. A.3-A.7 of Appendix A). Phosphorus retention from co-precipitation with Fe oxides may be more prevalent in RSPB surrounded sites due to a larger influence of rooted macrophyte radial oxygen loss (ROL) induced oxidised chemical conditions in the sediment rhizosphere. Most macrophytes shield against harmful Fe sulphide precipitates via the ROL process, in which the roots release oxygen into the rhizosphere forming protective plaques of Fe oxides (LaFond-Hudson et al., 2018; Smith and Luna, 2013). These Fe oxides would then be available for co-precipitation with P (Petkuviene et al., 2019). This larger influence of ROL in RSPB surrounded sites may be due to higher S concentrations at these sites and/or the RSPB land management as marsh and wet hay meadow, as this could be supporting a larger amount of macrophytes and/or macrophytes species with higher radial oxygen rates (Smith and Luna, 2013). Many of the plant species at West Sedgemoor are described in Table A.1.

Surface sediments of sites surrounded by land that is not RSPB nature reserve showed less significant correlations than in RSPB surrounded sites. Phosphorus concentrations were not correlated to Fe ($r = -0.120$), Al ($r = -0.012$), Ca ($r = 0.174$) or % mud ($r = -0.263$). A weak negative correlation was observed between P and S ($r = -0.400$) and a moderate positive correlation between Fe and S ($r = 0.659$) suggest that sulphide interference of iron-phosphorus cycling is occurring (Fig. A.8 and A.9). A potentially high input of organic matter, such as cow manure from pasture or leaf-fall from arable land withy (willow) beds, could be increasing mineralisation, decreasing oxygen and nitrate sediment penetration depth, and subsequently enabling sulphide-mediated chemical iron reduction, at these sites. Sulphide interference of P retention from coprecipitation with Fe oxides may be more prevalent in sites surrounded by land that is not RSPB nature reserve due to less rooted macrophyte ROL. As this land is typically managed as agricultural pasture, it could be supporting a smaller amount of macrophytes and/or species with lower radical oxygen rates than the marsh and wet hay meadow managed RSPB land. However, it is unclear what mechanisms affect P storage for sites that don't boarder RSPB land.

Surface sediments of sites adjacent to both land that is RSPB nature reserve and land that is not RSPB nature reserve showed less significant correlations than in RSPB surrounded sites and sites that don't boarder RSPB land. Therefore, the sites bordering both types of land are relatively more different from each other geochemically, which suggests that the dominate land management influence varies for these sites. Phosphorus showed a significant moderate positive correlation with Fe ($r = 0.635$) (Fig. A.10). Phosphorus concentrations were not correlated to S ($r = -0.009$), Al ($r = 0.124$), Ca ($r = -0.007$) or % mud ($r = 0.213$). This suggests P at these sites is primarily stored in the sediment bound to Fe, not Al or Ca.

As sites surrounded by land that is not RSPB nature reserve had no significant positive correlations between P and the selected parameters, it indicates that these sites have a lower chemical ability to bound P in the sediment when compared to sites surrounded by or partially adjacent to RSPB nature reserve land. Correlations between P and Fe, indicating P bound to Fe(III) compounds and a greater chemical ability to bound P, was observed in sites surrounded by or partially adjacent to RSPB nature reserve land.

The lack of significant correlations observed for % mud (< 63 µm) in the correlation coefficient analysis, is most likely due to the lack of variance in particle size of the sediments. Fig. 3.4 is a sand, silt, and clay trigon (SSC trigon) showing sediment classification schemes based on the relative percentages of sand, silt and clay (Blott S.J. and Pye K., 2001). Most sediment samples were classified as sandy silt with only four sites being classified as silty sand. Of the silty sand sites, 46 and 50 were unable to be analysed by WD-XRF due to an insufficient amount of <63 µm fraction available; sites 31 and 57 are located at opposite ends of the West Sedgemoor, so it's unlikely their increased particle size is linked. Localised bank collapses could be a possible explanation for these sites having coarser sediment. A relatively consistent particle size distribution suggests that variance in the P concentrations across the site cannot be attributed to a bias towards higher concentrations being associated with finer sediment (Capasso et al., 2020; Xiao et al., 2013).

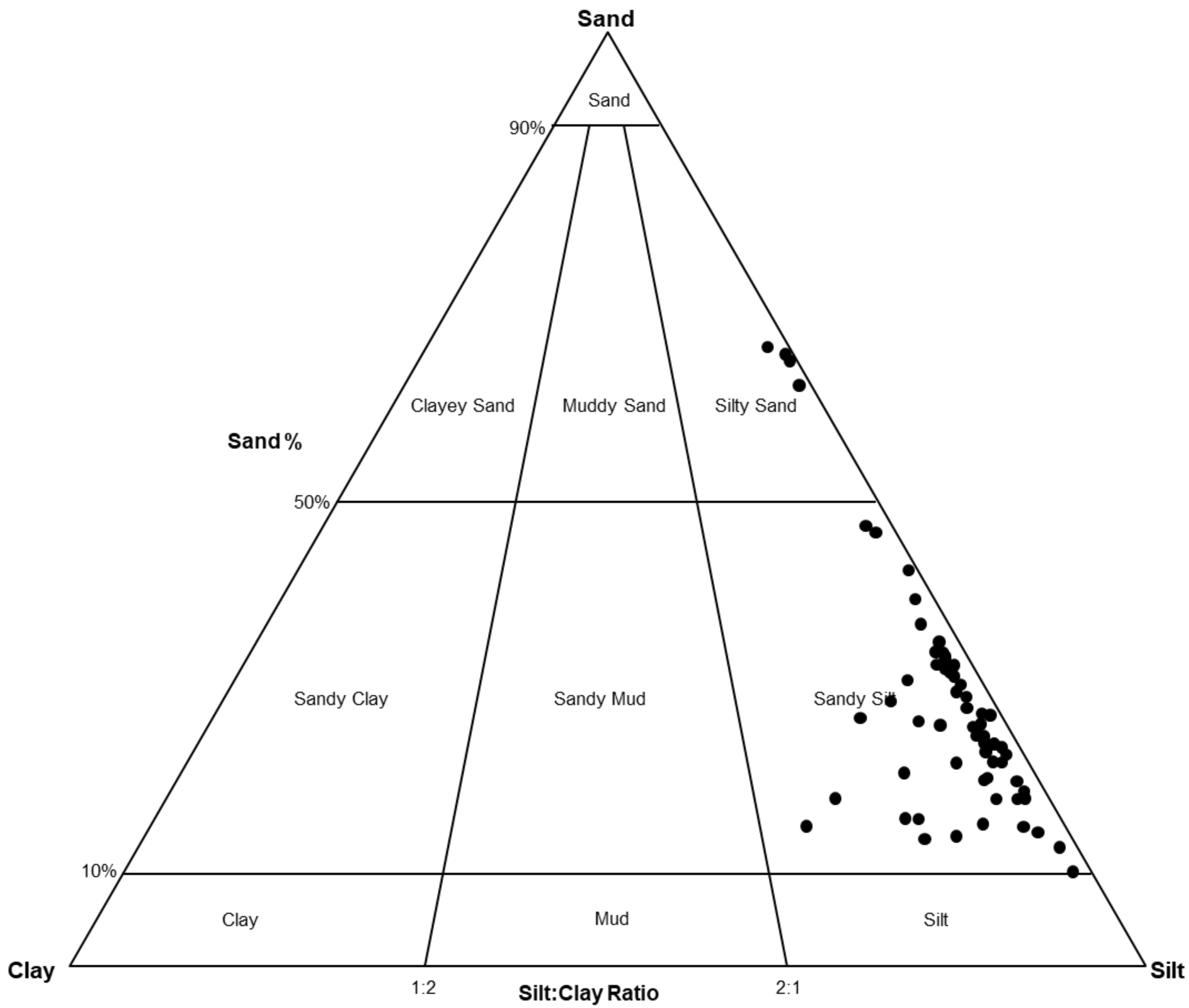


Figure 3.4: Sand, silt, and clay trigon (SSC trigon) of West Sedgemoor SSSI sediment samples.

3.4.2.2 Principal components analysis

A principal component analysis was conducted to determine whether the three designations of sample sites (sites surrounded by RSPB nature reserve land, A; sites surrounded by land that is not RSPB nature reserve, B; and sites adjacent to both land that is RSPB nature reserve and land that is not RSPB nature reserve, C) could be distinguished from each other using their chemical and physical properties. The first principal component explains 28.3% of the variation (Eigenvalue = 11.309) and is mainly based on Al, Si, S, Cl, K, Ti, Br, Sr, Y and Zr (factor loadings = -0.273, -0.289, 0.274, 0.259, -0.213, -0.284, 0.262, 0.246, -0.248 and -0.226, respectively). The second principal component explains 8.5% of the variation and is mainly based on Na, Mg, K, Ca, Fe, Co, Cu, Ga, Rb, Ge and Ir (factor loadings = -0.239, 0.200, 0.246, -0.227, 0.234, 0.220, 0.211, 0.208, 0.410, 0.205 and -0.208, respectively). Eigen values, explained variance, and cumulative variance of subsequent principal components is provided in Table A.2.

The principal component analysis score plot of West Sedgemoor SSSI surface sediment sample sites (Fig. 3.5a) is shown bassed on chemical and physical differences illustrated in the occompaning loading plot (Fig. 3.5b). A clear distinction can be seen between sites surrounded by RSPB nature reserve land and sites surrounded by land that is not RSPB nature reserve, based on separation along the first principal component axis. Sites of group A are generally positively correlated with the first principal component, although site 37 appears to be an outlier in this case. Sites of group B are generally negatively correlated with the first principal component. This suggests that land management influences ditch surface sediment geochemistry, which could have the potential to affect P storage in sediments. However, sites of group C are spread relatively evenly across the first principal component axis, most likely owing to the groups varying land management influences. This shows that some group C sites are more similar to group A sites than others, suggesting that certain sites are less influenced by land that is not RSPB nature reserve than others, and vice versa. Group A sites were characterised by relatively higher concentrations of S, Br, Cl and Sr, whereas the group B sites had higher Si, Ti, Al, and Y (Fig. 3.5b). Of these, S and Cl are likely associated with avian guano input on RSPB nature reserve land (Chen et al., 2020; Schnug et al., 2018), while Sr has been reported to accumulate in egg shells which suggests an input from migratory breeding (Kitowski et al., 2014; Mora et al., 2007). Si, Ti and Al are related to terrigenous watershed input (Sabatier et al., 2014), whereas Y is present in agricultural fertilisers which can cause diffuse pollution of rare earth elements in runoff and surface water in rural areas (Möller et al., 2014; Otero et al., 2005). This suggests that Si, Ti, Al, and Y are enriched in the group B sites due to soil runoff. Although correlation coefficient analysis indicated that group B sites have a lower chemical ability to bound P in the sediment, compared to groups A and C, P has a weak negative loading on the first component which suggests that P concentrations tend to be slightly higher outside of the RSPB nature reserve (Fig. 3.5b). This suggests that higher P concentrations at group B sites is due to higher P input from the surrounding agricultural land. However, the P concentrations did not significantly differ between the site groups (Table A.4, Appendix A).

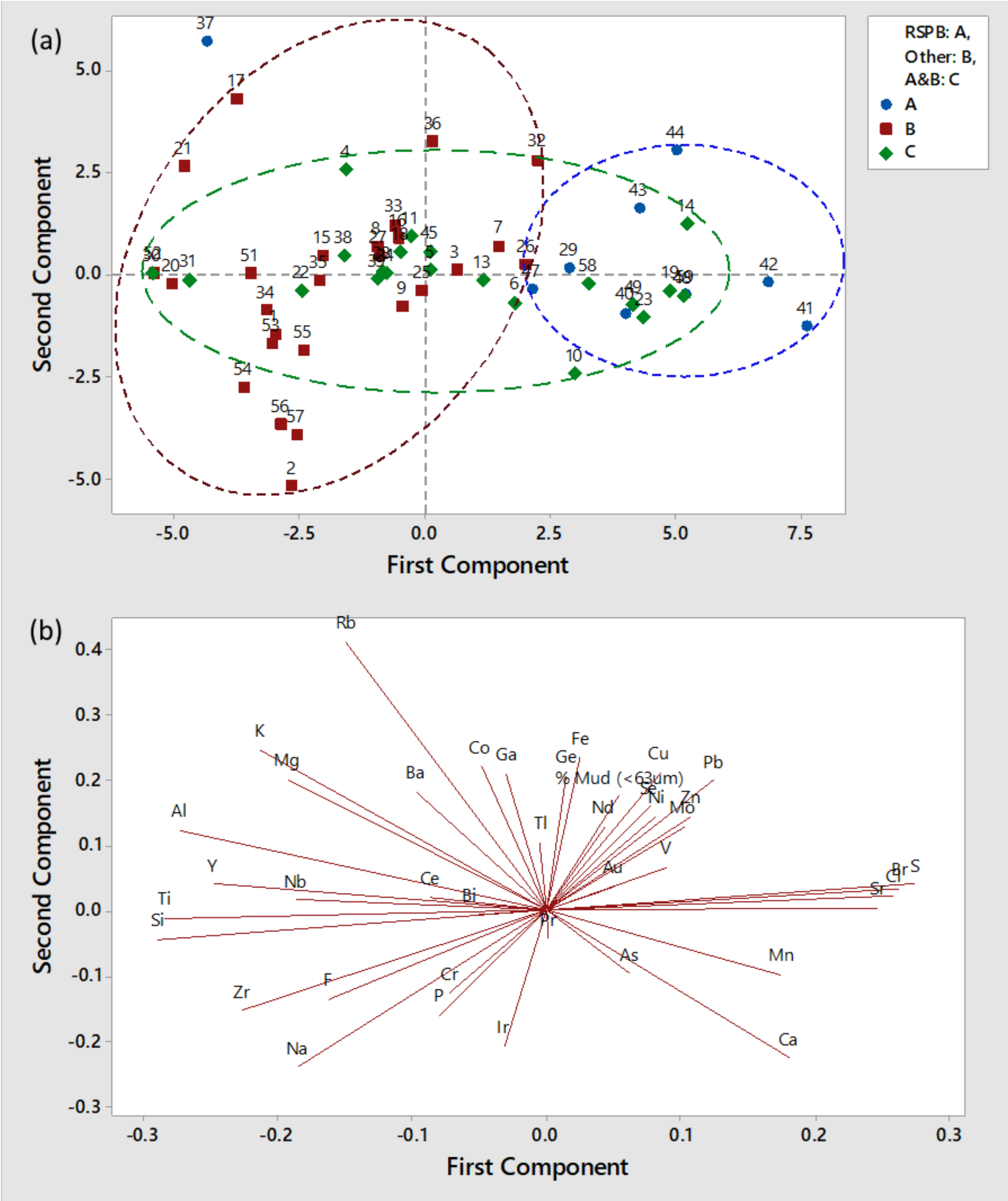


Figure 3.5: (a) principal component analysis score plot of West Sedgemoor SSSI surface sediment sample sites bassed on chemical and physical differences. Scores for the first two pricipal components are plotted. (Sites surrounded by RSPB nature reserve land, A; sites surrounded by land that is not RSPB nature reserve, B; and sites adjacent to both land that is RSPB nature reserve and land that is not RSPB nature reserve, C). (b) Principal component analysis loading plot of West Sedgemoor SSSI surface sediment chemical and physical properties. The coefficients of each variable for the first component versus the coefficients for the second component are plotted.

3.5 Conclusions

The main findings of the research are as follows:

- The analysis of total phosphorus (TP) in sediments show that all the sites have elevated concentrations, when compared with expected background concentrations, with sites in the north of the moor, near key inlets and the outlet generally showing the highest concentrations. Mean TP concentration in the north of the site (sites 1-22, 48-57) was 2140 mg kg^{-1}, in the south (sites 23-47, 58 & 59) it was 1560 mg kg^{-1}.
- Based on correlation coefficient analysis, sediments phosphorus (P) storage mechanisms vary across the site depending on the influence of differing land management between Royal Society of the Protection of Birds (RSPB) nature reserve and privately owned land. Correlations between P and Fe, indicating P bound to Fe(III) compounds and a greater chemical ability to bound P, was observed in sites surrounded by or partially adjacent to RSPB nature reserve land. As opposed to sites surrounded by land that is not RSPB nature reserve that had no significant positive correlations between P and the selected parameters. Also, the lack of significant correlations observed for % mud (< 63 µm) in the correlation coefficient analysis, is most likely due to the lack of variance in particle size of the sediments.
- Principal component analysis showed clear distinction between sites surrounded by RSPB nature reserve land and sites surrounded by land that is not RSPB nature reserve, based upon their chemical and physical properties. RSPB nature reserve land surrounded sites were characterised by relatively higher concentrations of S, Br, Cl and Sr, whereas sites surrounded by land that is not RSPB nature reserve had higher Si, Ti, Al, and Y concentrations. This suggests that differing land management between Royal Society for the Protection of Birds (RSPB) nature reserve and privately owned (e.g. agricultural) land influences ditch surface sediment geochemistry, which could have the potential to affect P storage in sediments. Phosphorus has a weak negative loading on the first component suggesting that P concentrations tend to be slightly higher outside of the RSPB nature reserve. Therefore, the hypothesis 'legacy phosphorus concentrations in sediment are higher in ditches adjacent to agricultural land than wetland bird nature reserve land' is accepted.

4 Chemical speciation of sediment phosphorus in a Ramsar wetland

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Authorship contribution statement:

- Ry Crocker – Conceptualization, Methodology, Data Curation, Formal analysis, Writing.
- Sean Comber – Conceptualization, Review, Resourcing, Managing.
- William Blake – Sediment geochemistry technical input, Review, Conceptualization, Managing.
- Tom Hutchinson – Conceptualization, Review, Technical input on ecology, Managing.

Research Hypothesis:

- Chemical speciation of sediment phosphorus in ditches is influenced differently by adjacent agricultural land than wetland bird nature reserve land.

4.1 Abstract

Phosphorus (P) is an essential nutrient, which, at excessive concentrations can cause eutrophication of aquatic ecosystems. In freshwater wetlands, water quality deteriorates under these conditions, succumbing to algal or duckweed dominance, over the biodiversity of other aquatic vegetation. Freshwater sediment acts as an internal source of legacy bound P that can induce production of algal and duckweed blooms beyond what may be expected from external loading of phosphorus alone. This study assesses the mobility, bioavailability, and origin of phosphorus in wetland ditch systems at the designated site of special scientific interest, West Sedgemoor. Comparing the values of total phosphorus (TP) from the sequential extraction with the corresponding Wavelength Dispersive X-Ray Fluorescence (WD-XRF) TP value reveals that the sequential extraction procedure extracted on average 40% less TP than what was observed using WD-XRF, despite previous studies observing high correlation between the two techniques. While the sequential extraction data cannot be considered reliably quantitative, the sites with acceptable modified Z-scores (for the sum of the determined values of component fractions as a percentage of the determined value of their sum fraction) can still be observed qualitatively and a comparison of relative values across the sites remains valid. Based upon their associations with different phosphorus species, using principal component analysis, clear distinction was observed between sites outside and within the West Sedgemoor Nature Reserve (managed by the Royal Society of the Protection of Birds). Sites outside the nature reserve, typically wet and damp grassland used for arable use and grazing, were generally correlated to higher non-apatite inorganic phosphorus (associated with iron and aluminium minerology) and higher total phosphorus levels, associated with algal and duckweed blooms.

4.2 Introduction

Phosphorus (P) is well known for being an essential nutrient and for its role in the eutrophication of freshwater ecosystems when present in excessive concentrations (Harrison, 1999). Aquatic ecosystems deteriorate under these conditions as they deviate from primarily submerged aquatic vegetation to algae or duckweed dominance, potentially leading to anoxic conditions (Zhang et al., 2017). Sources of P to water can be either external or internal to the system. External inputs of P can come from point source discharges, such as industrial and domestic effluents, or from diffuse sources e.g., natural, or agricultural (Wang et al., 2013). Although, as sediment acts as an internal source of legacy bound P, expected improvements to water quality from reductions in external inputs discharged to catchments can be significantly delayed. Phosphorus released from sediment to the water column can induce production of algal and duckweed blooms beyond what may be expected from external loading alone (Heaney et al., 1992; van Liere et al., 2007).

However, not all P species contribute towards eutrophication due to differences in sediment release mobility and bioavailability. Hence, the ability of a sediment to store or release P is dependant not only on the amount of P, but also the proportions of different P species present. Consequently, it is crucial to determine P fractionation, not just total P content, in the planning of water management and restoration of water bodies (González Medeiros et al., 2005; Ruban et al., 2001a).

Environmental studies often use sequential extraction schemes to quantify discrete chemical fractions and assess the mobility and bioavailability of a given element, and many extraction schemes have been developed for P (Martin et al., 1987; Ruban et al., 2001a; Wang et al., 2013). These methods can also allow for the assessment of the origin of P in the sediment. Despite many developed extraction schemes for P speciation, there is no widely acceptable standardised method largely due to its variety and changeability in sediments. Data comparability is, however, possible only based on standardized procedures requiring collaborative verification by group(s) of researchers (González Medeiros et al., 2005; Ruban et al., 2001a; Wang et al., 2013). Therefore, a proposed harmonised sequential extraction scheme for P in freshwater sediments was produced by the European Commission through the Standards, Measurements and Testing (SMT) Program. Referred to as the SMT method, it has the added advantage of an associated certified reference material (CRM), BCR 684, for quality control (González Medeiros et al., 2005; Ruban et al., 2001b; Wang et al., 2013). Table 4.1 summarises and compares the SMT method to several other sediment P sequential extraction procedures. Both the Golterman (Golterman, 1996) and SEDEX (sequential extraction method) (Ruttenberg, 1992) methods have the benefit of separating out more specific P fractions. However, both of these schemes have been seen as impractical and otherwise difficult to perform. Alternately, the Hieltjes and Lijklema (Hieltjes and Lijklema, 1980) method is simple and practical but is limited in the useful information it can provide as it only determines three separate fractions directly, none of which are an organic P (OP) fraction; although, OP can be calculated as the difference between total P (TP) and inorganic P (IP). The extraction scheme of Williams (Williams et al., 1976) as modified by Burrus (Burrus et al., 1990) is simple and practical, involving two independent procedures, determining NaOH-P (non-apatite inorganic phosphorus, NAIP), HCl-P (apatite inorganic phosphorus, AP), OP, and TP. As a modified version of the Williams (Burrus et al., 1990) scheme, the SMT extraction method builds upon its predecessor, adding a third independent procedure and yielding an IP fraction in addition to NAIP, AP, OP, and TP. The SMT method was therefore chosen for this study owing to its simplicity, practicality, and how it allows laboratories to generate reproducible and comparable results using its associated CRM (Ruban et al., 2001a, 2001b; Wang et al., 2013).

Table 4.1: Sediment phosphorus sequential extraction schemes for the determination of fractional composition.

Method	Extraction Procedure	Proposed fraction	Advantages	Disadvantages
Williams (Burrus et al., 1990; Williams et al., 1976)	a. NaOH 1 M (Extract + 3.5 M HCl) b. 1 M HCl c. Calcination + HCl 3.5 M d. Calcination + HCl 1 M	Non-apatite P Apatite P Total P Organic P	Simple, practical	Partial resorption of NaOH extracted P on $CaCO_3$
SMT (Ruban et al., 2001a)	a. NaOH 1 M (Extract + 3.5 M HCl) b. 1 M HCl (a. residue) c. Calcination + HCl 3.5 M d. 1 M HCl e. Calcination + HCl 1 M (d. residue)	Non-apatite inorganic P Apatite P Total P Inorganic P Organic P	Simple, practical	Partial resorption of NaOH extracted P on $CaCO_3$
Hieltjes and Lijklema (Hieltjes and Lijklema, 1980)	a. NH_4Cl 1 M pH 7 b. NaOH 0.1 M c. HCl 0.5 M	Labile P Fe- and Al-bound P Ca-bound P	Simple, practical	Dissolution of small amounts of Fe–P and Al–P by NH_4Cl; hydrolysis of organic P; no relation with bioavailability
Golterman (Golterman, 1996)	a. H_2O b. Ca-EDTA 0.05 M + dithionite c. Na_2-EDTA 0.1 M d. H_2SO_4 0.25M e. NaOH 2 M reductant	Labile P bioavailable Fe-P bioavailable Ca–P nonavailable Acid-soluble Organic P bioavailable Organic P non-available	Extracts specific compounds; permits extraction of organic P fractions; provides information on bioavailable fractions	Not practical; EDTA interferes with P determination; complicated solution preparation; in some sediments, extraction must be repeated
SEDEX (Ruttenberg, 1992)	a. $MgCl_2$ 1 M b. Na_3-citrate 0.3 M + $NaHCO_3$ 1 M c. Na-acetate 1 M d. HCl 1 M e. Calcination + HCl 1 M	Loosely sorbed P Ferric Fe-bound P Authigenic apatite, Ca-bound P, biogenic apatite Detrital apatite P Organic P	Separating between different apatite forms; no redistribution of P on to residual solid surfaces	Very long; not practical; very difficult to achieve butanol extraction

In this study, using the SMT method, the chemical speciation of surface sediment P is examined across West Sedgemoor, a Site of Special Scientific Interest (SSSI) and part of the Somerset Levels and Moors, Ramsar site no. 914. West Sedgemoor experiences both algal and duckweed blooms with eutrophic water quality exceeding the Common Standards Monitoring Guidance for P in ditches (>0.1 mg-P l^{-1} as total P) in a previous study (Taylor et al., 2016). The site requires sources of contamination to be identified, including the sediment contribution, and measures to restore the water bodies. Ditch sediment samples were collected across the moor at varying locations corresponding to different surrounding land management, from agricultural to Royal Society for the Protection of Birds (RSPB) nature reserve. Multivariate principal component analysis was used to assess the origin of P in the sediment with regards to surrounding land management.

4.3 Material and methods

4.3.1 Study area

West Sedgemoor SSSI (51°01'40.8"N 2°54'45.2"W) is an area of the Somerset Levels and Moors Ramsar site and a Special Protection Area (SPA) site in Somerset, England; Fig. 4.1. It has a total area of 10.16 km^2, typically 5 m above sea level, consisting of low-lying fields and meadows separated by narrow water-filled ditches locally referred to as rhynes. The Parrett Internal Drainage Board (IDB) manage water levels and flow circulation, while the Environment Agency (EA) operate the only outlet from the site, West Sedgemoor Pumping Station, which drains into the River Parrett (tidal).

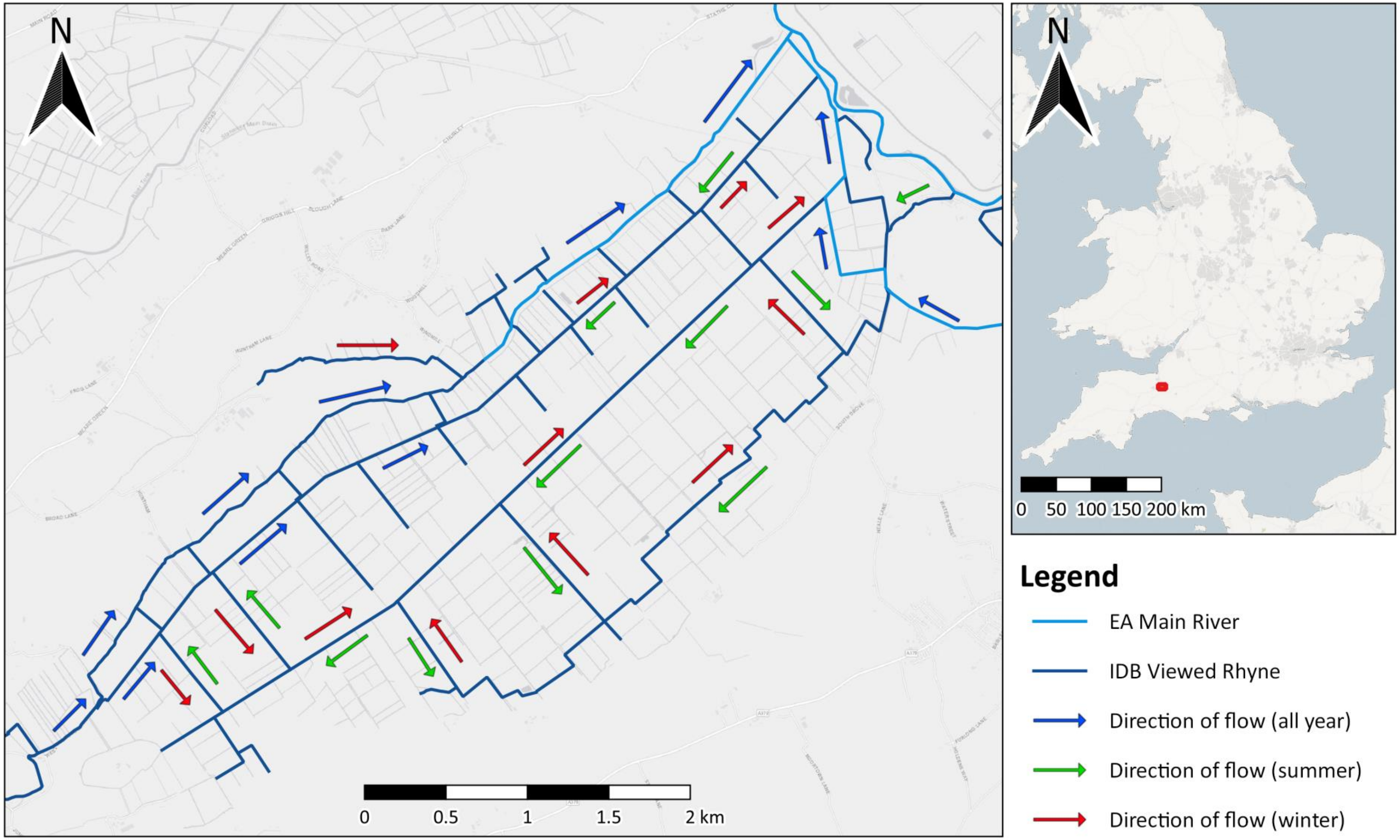

Figure 4.1: Location and controlled water flows of West Sedgemoor SSSI. Upper right inset shows the study area within Southwest England (red box). Left panel shows seasonal dependant water flow directions, indicated by coloured arrows (blue, all year; green, summer; red, winter). Reproduced from (Crocker et al., 2021).

Runoff provides one of the main sources of water to West Sedgemoor, from a relatively small catchment (roughly 41 km^2). Most of the runoff water entering the moor is provided by Widness Rhyne, located southwest of the site. North Curry and Stoke St Gregory ridge drain runoff directly to both Sedgemoor Old Rhyne and West Sedgemoor Main Drain. Runoff water is also provided by Wick Moor (fed also by the River Parrett; nontidal) and Curry Rivel ridge, draining to Wickmoor Rhyne. The moor can also be supplied with water direct from the River Parrett (nontidal) via a culvert, during the summer. An annotated map of West Sedgemoor's notable features can be seen in Fig. B.1 of Appendix B. Water levels are lowered in the winter to reduce flood risk, although, a raised water level area is maintained year-round in the interest of nature conservation efforts (Parrett IDB, 2009). The moor hosts England's largest breeding population of waders such as lapwing, snipe and curlew, making the site internationally important for supporting wintering waterfowl populations (Natural England, 2019). Rare and scarce invertebrate fauna are also abundant, particularly water beetles, in part justifying the Somerset Levels' Ramsar status under Ramsar criterion 2 (Drake et al., 2010).

4.3.2 Sampling and chemical analyses

Surface sediment samples were collected using a Van Veen Grab sampler in March 2018 at 59 sampling sites (Fig. 4.2). Sites were chosen based upon (1) coverage of IDB viewed rhynes (2) site accessibility/access permission and (3) minimal disturbance to RSPB nature conservation efforts. Samples were collected in HDPE 500 ml Nalgene bottles pre-soaked in hydrochloric acid (10% - Fisher Scientific Primar Plus) and ultra high purity water (>18 Mohm.cm) and stored frozen at -18°C in the dark. Unwanted material (e.g., fragments of vegetation) was removed from the sediment grab samples prior to collection.

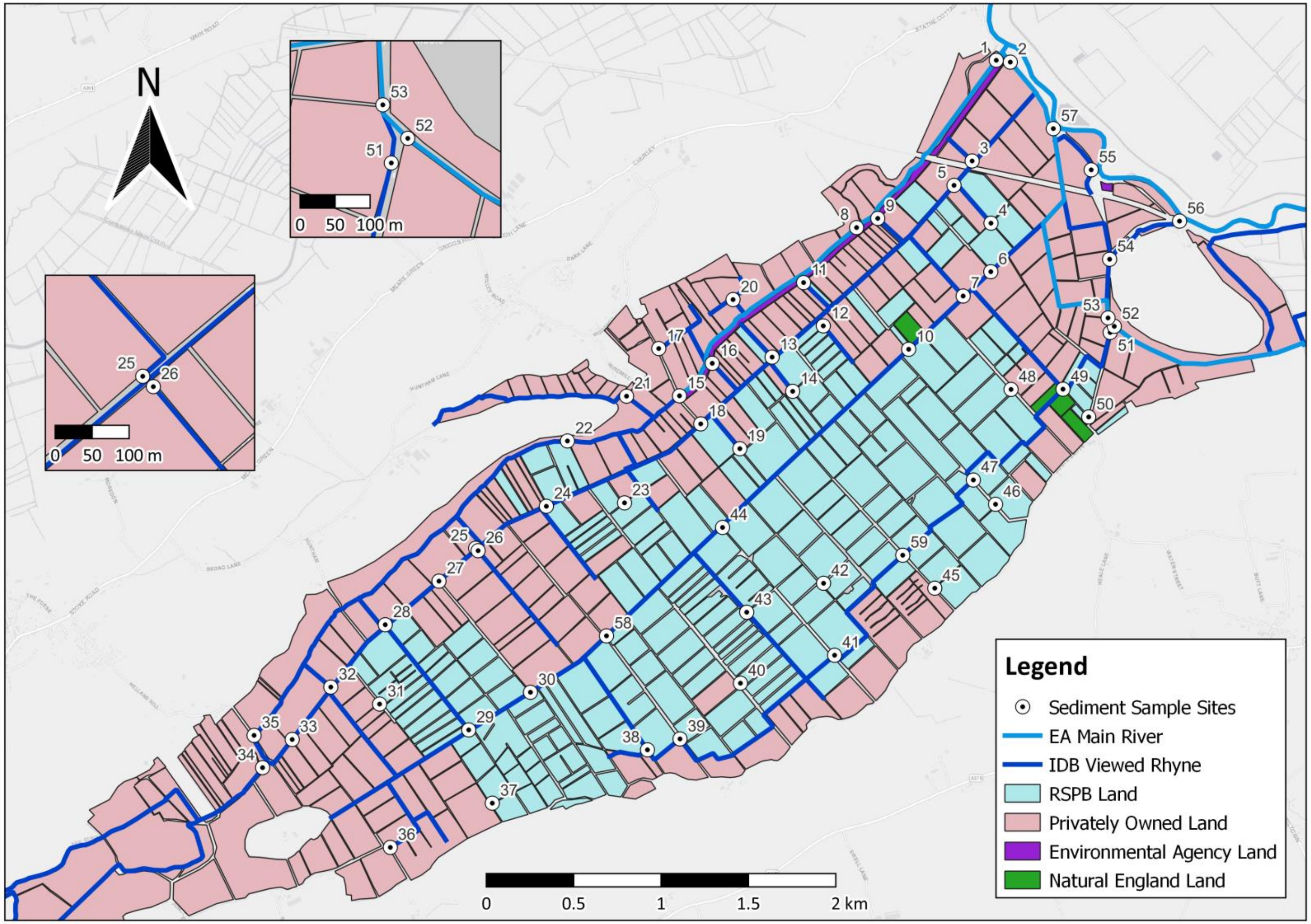

Figure 4.2: Sediment sampling sites and land ownership on West Sedgemoor SSSI. Reproduced from (Crocker et al., 2021). Insets present a magnified highlight of sites that otherwise appear to overlap at the scale of the main map.

Total elemental concentrations were determined as described in a previous paper (Crocker et al., 2021), using Wavelength Dispersive X-Ray Fluorescence Spectrometer (WD-XRF) (using a PANalytical Axios Max) for a range of major and minor element constituents (F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Br, Rb, Sr, Y, Zr, Nb, Ba, Ce, Pb, As, Au, Bi, Ge, Ir, Mo, Nd, Pr, Se, Tl and V) and by particle size analysis (using a Malvern Mastersizer 2000). These elemental constituents were measured alongside P so that correlations could be analysed, and potential biogeochemical flow pathways of P could be identified.

For sequential extraction analysis, post thawing, samples were centrifuged at 4000 rpm for 10 minutes, and much of the pore water was poured off, prior to refreezing and subsequent freeze-drying, after which samples were homogenised and subsequently sieved to the <63 µm fraction. 0.2g subsamples of sediment were then taken and were sequentially extracted following the Standards Measurements and Testing Program of the European Commission (SMT) method (Fig. 4.3). The SMT method is not completely sequential, involving three independent procedures, allowing the separation of the following sedimentary fractions: NaOH-P (non-apatite inorganic phosphorus, NAIP), HCl-P (apatite inorganic phosphorus, AP), IP, OP and TP. NAIP is the fraction associated with Fe, Al and Mn oxides and hydroxides (typically bioavailable), while the AP fraction is associated with Ca-bound P (typically non available) (Pardo et al., 1999; Ruban et al., 2001b; Wang et al., 2013). All P determination was made by either Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES; Thermo Scientific ICAP 7400 Series) or Inductively Coupled Plasma - Mass Spectrometry (ICP-MS; Thermo Scientific X 199 Series 2).

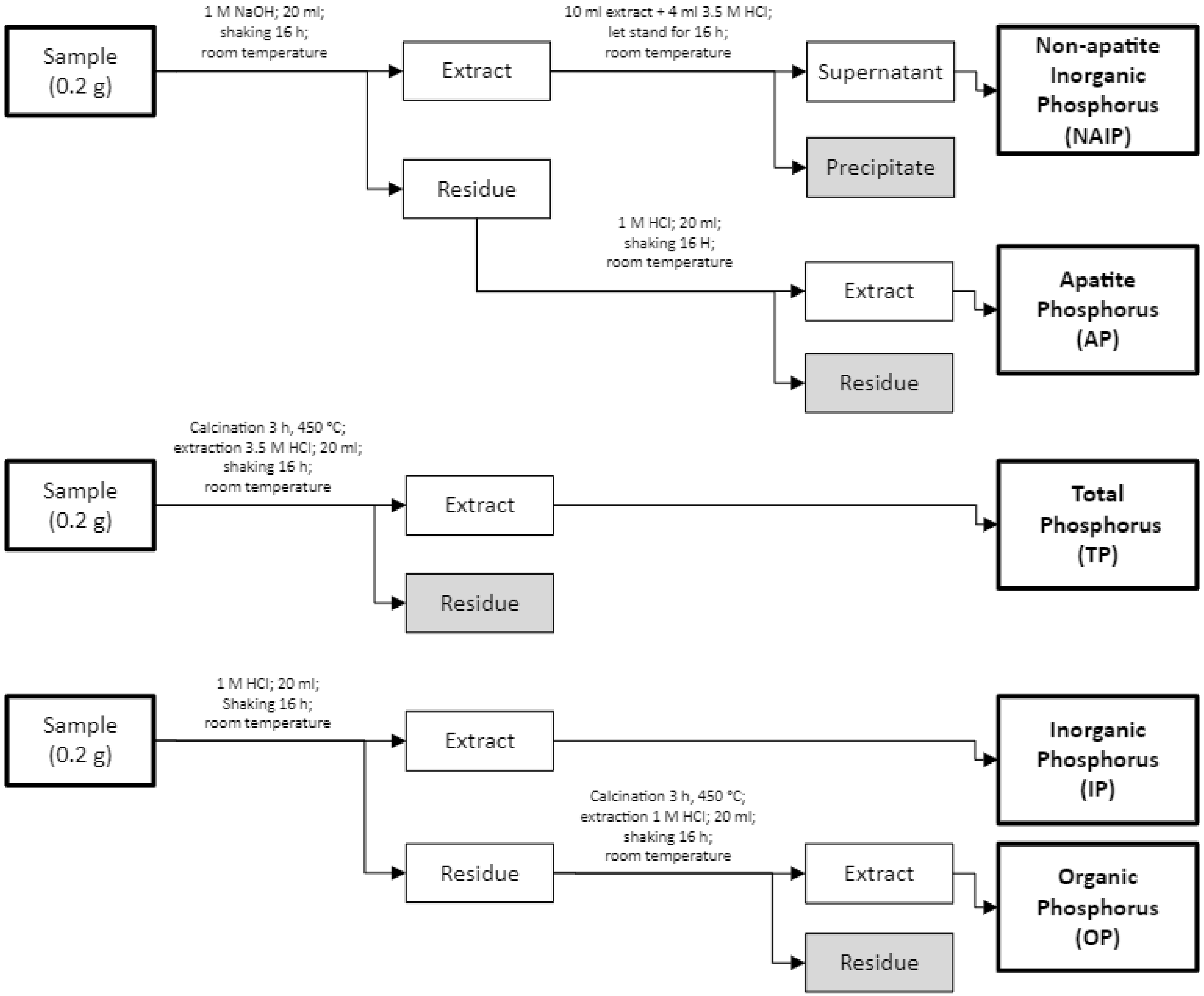

Figure 4.3: Standards Measurements and Testing Program of the European Commission (SMT) extraction method protocol flow chart.

4.3.3 Data analysis

Modified Z-scores were calculated using the sum of the determined values of component fractions as a percentage of the determined value of their sum fraction (e.g., the sum of NAIP and AP should equal IP). Absolute values of greater than 2.7 were labelled as potential outliers, and corresponding sites were set aside from the data set (Iglewicz and Hoaglin, 1993; NIST/SEMATECH, 2013).

Principal component analysis (PCA) of the sequential extraction data and previously determined WD-XRF and particle size analysis data was conducted using Minitab 19. No outliers were observed from examining the Mahalanobis distances plotted in Fig. B.2 of Appendix B (Brereton, 2015). The grouping of the sites was visualised with a scatterplot of the scores of the second principal component versus the scores of the first principal component. The variables responsible for the grouping of sites were identified by plotting the coefficients of each variable for the first component versus the coefficients for the second component.

4.4 Results and discussion

4.4.1 Reliability of the sequential extraction

Modified Z-scores identified potential outliers in thirteen of the fifty-two sites sampled; sites 2, 6, 8, 10, 26, 28, 30, 34, 40, 42, 43, 46 & 50 which were therefore removed from the data set. Comparing the values of TP from the sequential extraction with the corresponding WD-XRF TP value reveals that the sequential extraction procedure extracted on average 40% less TP than what was observed using WD-XRF, despite previous studies observing high correlation between the two techniques (Pardo et al., 2003). WD-XRF has previously been shown to be a reliable technique for P analysis (Blake et al., 2013).

In spite of the development of many extraction procedures, P extraction has no standardised method in part because of the variation in sediment compositions (calcareous, siliceous, organic rich, etc.). Hence, extraction procedures are designed for specific sediment types. The SMT method is most suited to siliceous sediments, although it has been shown to be satisfactory in the analysis of various sediment types (Pardo et al., 2003; Wang et al., 2013). Advantages of the SMT method include being more economic and simpler to use than other methods and that it has an associated certified reference material (CRM), BCR 684, which was used in this study and acceptable recoveries were obtained (Table. B.1 of Appendix B) (Pardo et al., 2003, 1999; Wang et al., 2013). Procedurally analysed CRM recoveries therefore show that the method performed accurately in this study. A representative subsample of 10 sites (sites 5, 18, 20, 29, 35, 39, 44, 52, 55 & 59) analysed for organic matter by loss on ignition (LOI) showed 53.1-92.1% combustion (average 71.1%, median 69.2%; Table. B.2 of Appendix B), indicating that the sediment at West Sedgemoor is organic rich, this is unsurprising as the area is a fen peat environment and the majority of the sediment is classified as sandy silt (Crocker et al., 2021; Ross and Heathwaite, 1984). To assess the possibility that high organic matter content of the West Sedgemoor sediments caused low recoveries of TP by the siliceous sediment suited SMT method, the correlation between % recovery (between SMT and WD-XRF) and organic matter content (% LOI) was analysed. A strong positive correlation of $R = 0.904$ with a p-value significance level of <0.01 was observed between % recovery and % LOI showing that SMT extraction TP values were closer to the corresponding WD-XRF TP value in sediments with higher organic matter content. Alternatively, P mineralisation could be the cause of low TP recoveries. One of the known shortcomings of the SMT method is the partial resorption of P extracted by NaOH on $CaCO_3$, a common problem with sequential extraction methods for sediment P (Wang et al., 2013). No significant correlation was observed between % recovery and Ca concentration ($R = -0.593$, p-value = 0.071), however it is noted that Ca concentrations (29,600 – 99,500 mg kg^{-1}) are well in excess of P concentrations. Both Cl and Pb were observed to have strong negative correlations with % recovery (Cl; $R = -0.888$, p-value <0.01) (Pb; $R = -0.703$, p-value <0.05). This suggests the presence of pyromorphite, a highly insoluble lead phosphate mineral that is chemically and biologically stable which forms in surface soil environments with the chemical formula $Pb_5(PO_4)_3Cl$ (Tai et al., 2013). It's likely that sequential extraction techniques would have difficulty extracting P from minerals such as pyromorphite. Whereas, XRF techniques have been demonstrated to be effective at analysing phosphate rock (Amar et al., 2022; Hasikova et al., 2014; Safi et al., 2006) This could also explain the large number of outliers observed through modified Z-scores. While the sequential extraction data cannot be considered reliably quantitative, the sites with acceptable modified Z-scores (for the sum of the determined values of component fractions as a percentage of the determined value of their sum fraction) can still be observed qualitatively and a comparison of relative values across the sites remains valid. It is only in comparison with other data reported using the same methodology, should caution be used in interpretation.

4.4.2 Qualitative analysis of sediment phosphorus fractions

The spatial distribution between sum fractions NAIP & AP (Fig. 4.4a) and IP & OP (Fig 4.4b), are shown in Fig. 4.4 through pie chart symbol maps. The partitioning between NAIP & AP were observed to have no correlation with spatial distribution. This suggests that differing land management, between private and nature reserve land, on the site does not affect the distribution of IP between NAIP (Al and Fe bound P) and AP (Ca bound P). However, proportions of IP & OP were observed to vary spatially, with higher concentrations of IP than OP in the north of the moor, near key inlets (sites, 21, 33, 35, 51-56) and the outlet at site 1. These observations are complemented by the results of the principal component analysis performed previously which determined that three designations of sample sites (sites surrounded by the RSPB West Sedgemoor Nature Reserve land; sites surrounded by land outside of the RSPB Nature Reserve; and sites adjacent to both land inside and outside the RSPB Nature Reserve) could be distinguished from each other based on their chemical and physical properties (Crocker et al., 2021).

Figure 4.4: (a) distribution of the partitioning between sum fractions non-apatite inorganic phosphorus (NAIP) & apatite inorganic phosphorus (AP) at West Sedgemoor SSSI. (b) distribution of the partitioning between sum fractions inorganic phosphorus (IP) & organic phosphorus (OP) at West Sedgemoor SSSI. Insets present a magnified highlight of sites that otherwise appear to overlap at the scale of the main map.

The principal component analysis score plot of West Sedgemoor SSSI surface sediment sample sites observed in this study (Fig. 4.5a) is shown based on chemical and physical differences illustrated in the accompaning loading plot (Fig. 4.5b), using previously published XRF and particle size analysis data (Crocker et al., 2021), and sequential extraction data from this study. The first principal component explains 34.7% of the variation (eigenvalue = 12.146) and is mainly based on Al, Si, S, Cl, Ti, Br, Sr, Y and Zr (factor loadings = 0.257, 0.278, -0.267, -0.251, 0.279, -0.246, -0.245, 0.228 and 0.219, respectively). The second principal component explains 11.6% of the variation (eigenvalue = 4.056) and is mainly based on NAIP, AP, TP, IP, XRF TP, Mg, K, Cr, Rb and Ba (factor loadings = 0.257, 0.285, 0.297, 0.293, 0.329, -0.313, -0.324, 0.235, -0.287 and -0.222, respectively). Eigenvalues, explained variance, and cumulative variance of subsequent principal components is provided in Table B.3 of Appendix B. Between sites surrounded by RSPB nature reserve land (group A) and sites surrounded by land that is not RSPB nature reserve (group B), a clear distinction can be observed based on separation along the first principal component axis (Crocker et al., 2021). Sites of group A are generally negatively correlated along the first principal component, although site 37 appears to be an outlier in this case. Sites of group B are generally positively correlated along the first principal component. Of the P variables, OP is the only one to not have a strong positive PC2 eigenvector (factor loading = -0.031) and to have a negative PC1 eigenvector (factor loading = -0.159). This indicates that sites surrounded by RSPB nature reserve land are more associated with higher OP levels while sites surrounded by land that is not RSPB nature reserve are generally correlated with higher IP and TP levels.

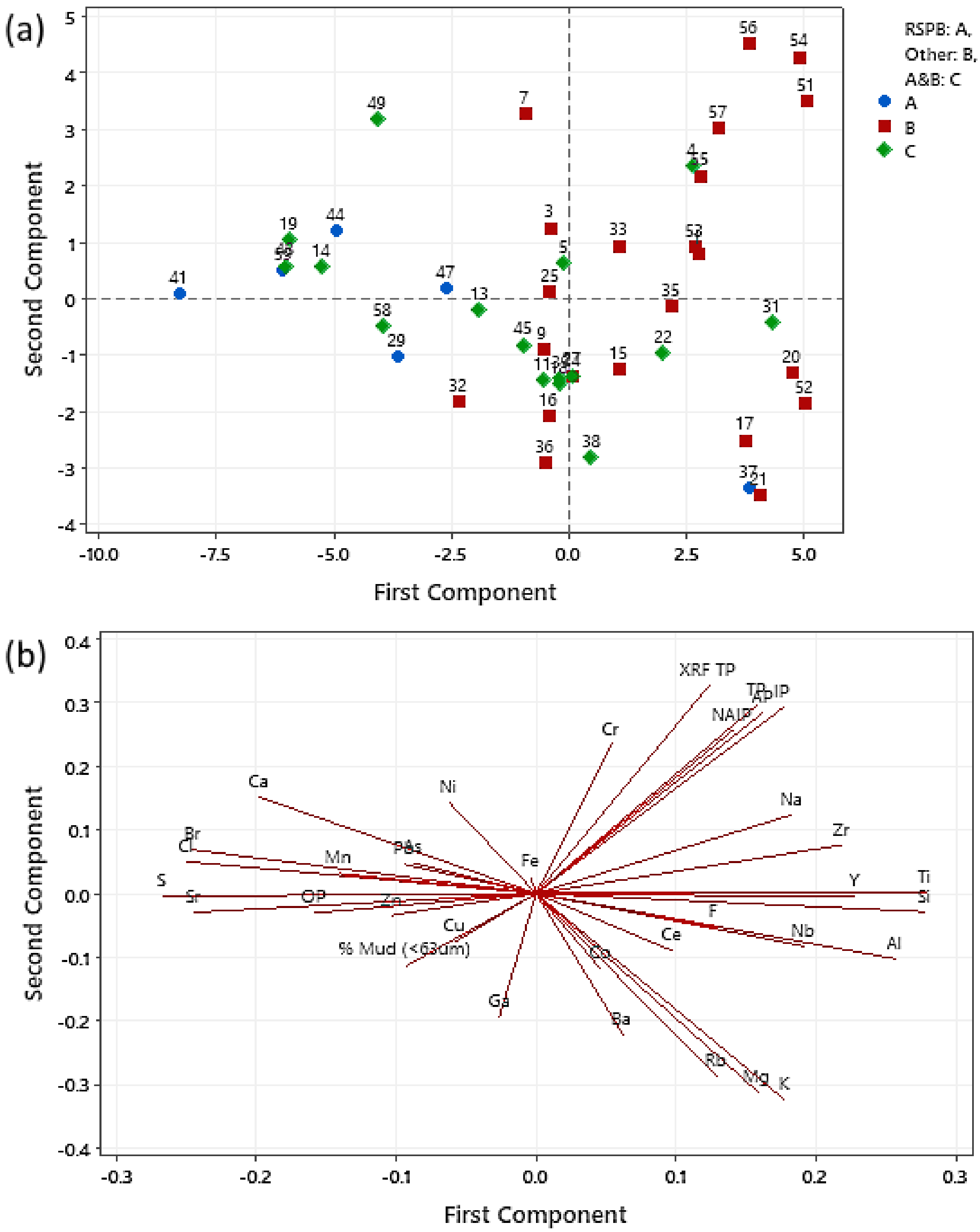

Figure 4.5: (a) principal component analysis score plot of West Sedgemoor SSSI surface sediment sample sites based on chemical and physical differences. Scores for the first two principal components are plotted. The first principal component explains 34.7% of the variation (eigenvalue = 12.146). The second principal component explains 11.6% of the variation (eigenvalue = 4.056). Sites are defined by surrounding land management (sites surrounded by RSPB nature reserve land, A; sites surrounded by land that is not RSPB nature reserve, B; and sites adjacent to both land that is RSPB nature reserve and land that is not RSPB nature reserve, C). (b) principal component analysis loading plot of West Sedgemoor SSSI surface sediment chemical and physical properties. The coefficients of each variable for the first component versus the coefficients for the second component are plotted.

Land surrounding group B sites is typically wet and damp grassland suitable for arable use and grazing. Much of this land is used for grazing dairy cattle, together with a limited amount of beef cattle farming and crop farming (typically associated with willow production). In agricultural soils, the major input of IP are P fertilizers, with approximately 70-80% of P being IP in cultivated soils (Foth, 1990). Within hours of application, fertilizer P is converted into water-soluble IP as orthophosphate ions $H_2PO_4^-$ and HPO_4^{2-} (Schute and Kelling, 1996). Available moisture in the soil dissolves fertilizer particles, increasing IP concentrations in solution. Relatively insoluble complexes are then formed between negatively charged IP and positively charged Fe, Al and Ca ions (Bhattacharya, 2019). Runoff water can then carry this IP adsorbed to particles of soil or manure into nearby water bodies such as wetland ditches. This is likely to cause IP enrichment of ditch sediments on West Sedgemoor, at sites surrounded by agricultural land and at inlet sites allowing water in from intensely farmed catchment areas. Manure and urine from large numbers of livestock kept in small areas can also result in excess P (both organic and inorganic) leaching into the surrounding environment when not managed efficiently (Barnett, 1994; Department for Environment Food and Rural Affairs, 2006).

The RSPB managed land surrounding group A sites is typically unimproved hay meadows on damp peat soils, as part of a managed raised water level area. To create ideal habitats for ground-nesting birds, the RSBP perform hay cutting and utilise aftermath grazing with beef cattle. Artificial fertilisers are not applied as it can promote a thick sward which nesting birds will avoid, as well as reducing floral and invertebrate biodiversity, both of which negatively affect bird foraging (Vickery et al., 2001). This avoidance of artificial fertilisers, unlike group B sites, is likely to be why group A sites are not associated with IP. However, group A sites are broadly associated with the OP fraction which includes nucleic acids, phospholipids, inositol phosphates, phosphoric amides, phosphoproteins, sugar phosphates, amino phosphoric acids, and organic condensed P species (Worsfold et al., 2008). Many of the 'biogenic' P compounds geologically have relatively short turnover times in freshwater sediment, with estimated half-lives of 10-12 years for pyrophosphate and 20-23 years for orthophosphate mono- and diesters, after which they mineralise into orthophosphate (Ahlgren et al., 2005; Özukundakci et al., 2014; Turner and Weckstrom, 2009). One of the more stable fractions of OP, and therefore abundant, is phytate which is the primary form of P storage in seeds and is introduced to the environment through plant residues and animal manure. Phytate accumulates in soils and sediments as a result of strong interactions with clays and other abiotic soil components (Gerke et al., 2015; Turner and Weckstrom, 2009). It is possible that the land management of the RSPB Nature Reserve, which is in part designed to promote plants in the swards to flower and seed for food for seed-eating birds, causes increased concentrations of phytate (and therefore OP) in adjacent ditch sediments. The stability of phytate in the environment and it's use as a novel P-specific paleo-indicator suggest that it is not of major concern for eutrophication mitigation (Turner and Weckstrom, 2009).

Through measurement of sediment P uptake by algae in culture with sediments as the sole source of P, Williams et al., (1980) found that P uptake by the algae was related to the amount of NAIP in the sediments. Neither AP nor OP was utilised by the algae. Algal cell P uptake was generally highest when TP concentration in the sediments was itself high (Williams et al., 1980). However, it is known that some algal groups can excrete alkaline phosphatases that catalyse the release of IP (as orthophosphate) from OP compounds containing P-O-P and C-O-P bonds (Jansson et al., 1988; Worsfold et al., 2008). Synthesis of excretory alkaline phosphatases is typically related to phosphate concentrations. With production being repressed at high and derepressed at low phosphate concentrations, alkaline phosphatase activity (APA) can be used as an indicator of P deficiency in algae (Jansson et al., 1988). Newman and Reddy, (1992) found that suspension of surface sediment resulted in an immediate increase in APA and TP in overlying waters. Although, post turbulence and sediment settling, these concentrations decreased drastically (Newman and Reddy, 1992). Turbid conditions are unlikely on West Sedgemoor due to slow flow rates and ditch systems in general being less susceptible to factors such as wind causing wave action. Yet, turbid conditions are caused during a biennial vegetation clearing ditch maintenance process traditionally known as keeching, in which emergent macrophytes are cut and scooped out of the ditches to improve water flow management (Rippon, 2006; Somerset Drainage Boards Consortium, 2022). This operation is unlikely to significantly impact APA long term because of its infrequency. Overall, this suggests that group B site sediments, which are generally correlated with higher NAIP and TP levels, are more likely to facilitate eutrophic algal blooms on the overlying waters than group A sites. This hypothesis will be explored further as part of ongoing sampling and analysis and will be the subject of another manuscript.

4.5 Conclusions

The main findings of the research are as follows:

- The Standards Measurements and Testing Program of the European Commission (SMT) sequential extraction method was found to be less suited for the quantitative analysis of the sediments found on West Sedgemoor. The data were therefore examined qualitatively after removing identified outliers using modified Z-scores.
- Principal component analysis showed clear distinction between sites surrounded by differing land management, based upon their associations with different phosphorus species. Sites surrounded by land that is not RSPB Nature Reserve were generally correlated to higher IP and TP levels, while sites surrounded by RSPB nature reserve land were more associated with

higher OP levels. This suggests that P storage in sediments was directly affected by surrounding land management influences. Therefore, the hypothesis ‘chemical speciation of sediment phosphorus in ditches is influenced differently by adjacent agricultural land than wetland bird nature reserve land’ is accepted.

- The difference in IP enrichment between ditch sites could be caused by land management differences regarding phosphorus fertiliser application. Artificial fertilisers are not applied on the RSPB Nature Reserve land, where IP concentration in surrounding ditch sediments was relatively lower; while agricultural cultivated soils are typically IP enriched with fertiliser use, where surrounding ditch sediments were higher in IP concentration.
- Sites surrounded by land that is not RSPB Nature Reserve were generally correlated with higher NAIP and TP sediment levels, so are more likely to facilitate eutrophic algal blooms as a source of bioavailable P to the overlying waters than sites surrounded by RSPB nature reserve land.

5 Seasonal cycling of phosphorus within a UK Ramsar wetland: Impacts of land use and hydrology on algal and duckweed growth and implications for management

This experimental chapter was published on the 1st of October 2023 as:

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Authorship contribution statement:

- Ry Crocker – Conceptualization, Methodology, Data Curation, Formal analysis, Writing.
- Sean Comber – Conceptualization, Review, Resourcing, Managing.
- William Blake – Sediment geochemistry technical input, Review, Conceptualization, Managing.
- Tom Hutchinson – Conceptualization, Review, Technical input on ecology, Managing.

Research Hypothesis:

- Duckweed harvesting can be used as an effective method of phosphorus mitigation.

5.1 Abstract

Fundamental to all life, phosphorus is an essential nutrient and, contrastingly, a significant threat to surface water biodiversity globally as one of the most common causes of eutrophication in surface waters worldwide. Freshwater wetland ditches afflicted by these conditions undergo a conversion from primarily submerged aquatic vegetation to algae or duckweed dominance, leading to anoxic conditions. However, macrophyte biomass harvesting in eutrophic water systems is a promising means of remediation and nutrient recycling. This study seasonally assesses spatial distribution and chemical fractionation of surface water phosphorus, as well as surface biomass abundance and total phosphorus content in the ditch systems at West Sedgemoor (Somerset, UK), a designated site of special scientific interest. Elevated phosphorus concentrations in the surface water were observed across the site, the highest being 1.88 mg L^{-1} during the summer, over 10 times the Common Standards Monitoring environmental quality standard value of <0.1 mg L^{-1}. Sites lacking hydrological flow connectivity with freshwater inputs, typically had lower surface water phosphorus concentrations than the rest of the moor. Summer and autumn were determined as the dominant duckweed growth seasons, in which an estimated 39 kg of phosphorus could be removed via duckweed biomass harvesting, per harvest period, from yielding a total estimated biomass of 7770 kg dry mass.

5.2 Introduction

Phosphorus (P) is an essential element required for all life. Fundamental to the structure and function of important biomolecules, P is involved in biological information coding as the sugar-phosphate backbone of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), cell membrane structure as phospholipids, energy metabolism as adenosine triphosphate (ATP) and guanosine triphosphate (GTP), and many other biologically important molecules (Heaney and Graeff-Armas, 2018). For that reason, P availability has been broadly recognised as a factor limiting the rate of algae and macrophyte growth in aquatic ecosystems. Eutrophic conditions arise with excessive P enrichment of these ecosystems, a significant threat to biodiversity worldwide that also causes significant economic and social damage (Comber et al., 2015a; Dodds et al., 2009; Pretty et al., 2003; Zhang et al., 2017). Wetland ditches suffering these conditions undergo a conversion from primarily submerged aquatic vegetation to algae or duckweed dominance, which leads to excessive shading and potentially anoxic conditions and therefore deterioration of the aquatic ecosystem (Zhang et al., 2017). Shading of the water column due to dense surface coverage, and bacterial degradation of the excessive amounts of organic matter produced by algal and duckweed blooms, exhausts oxygen supply in the water column, causing fish kills and the development of unpleasant odours (Padedda et al., 2017; Riley et al., 2018; Zhang et al., 2017).

However, numerous studies report the implementation of duckweed as a treatment of various anthropogenic wastewater effluents (Bergmann et al., 2000; Cheng and Stomp, 2009; Culley et al., 1981; Dinh et al., 2020; Fernandez Pulido et al., 2021; Iqbal et al., 2019; Ishizawa et al., 2020; Li et al., 2020; Muradov et al., 2014; Willett, 2005; Zhou et al., 2019). Although, taking into consideration the broad-spectrum of experimental designs at varying scales, under various artificial and/or environmental conditions, it is tough to deduce substantial conclusions from comparisons of separate studies (Paterson et al., 2020). Nevertheless, harvesting of macrophyte biomass from eutrophic water systems has been advocated as a means of remediation and nutrient recycling (Grosshans, 2014; Quilliam et al., 2015). Duckweed harvested for this purpose can then be processed into products such as animal feed, fertiliser, and biofuel due to high levels of protein, fat, amino acids, and starch (Baliban et al., 2013; Cheng and Stomp, 2009; Kreider et al., 2019; Zirschky and Reed, 1988).

In this study, the spatial distribution and chemical fractionation of surface water P, as well as surface biomass abundance and total phosphorus (TP) content, is examined seasonally across West Sedgemoor, a Site of Special Scientific Interest (SSSI) and part of the Somerset Levels and Moors, Ramsar site no. 914. West Sedgemoor suffers from both algal and duckweed blooms, under eutrophic water conditions shown in a previous study to be in excess of the Common Standards Monitoring Guidance for P in ditches (>0.1 mg-P l^{-1} as TP) established as part of the Natura 2000 series which includes Special Protection Areas (SPAs), designated under the European Birds Directive, and Special Areas of Conservation (SACs), designated under the European Habitats Directive (Council of the European Communities, 1992; European parliament and the council of the European Union, 2009; Taylor et al., 2016). Identification of contamination sources and measures to remediate these eutrophic circumstances is a critical priority. Understanding the relationship between seasonal surface water P concentrations and seasonal surface water biomass growth is essential to determining the viability of floating macrophyte biomass harvesting as a means of remediation on the site, so a surface water and biomass sampling exercise was planned and undertaken. Samples were collected from ditches suitable for a potential surface biomass harvesting P mitigation plan. Multivariate principal component analysis was used to determine whether hydrological block water management on the site impacted surface water chemistry.

5.3 Material and methods

5.3.1 Study area

West Sedgemoor SSSI (51°01'40.8"N 2°54'45.2"W) makes up part of the Somerset Levels and Moors Ramsar site and is also a SPA in Somerset, UK; Fig. 5.1. The site consists of 10.16 km^2 of low-lying fields and meadows, typically 5 m above sea level, separated by narrow water-filled ditches locally referred to as rhynes. Although the only outlet from the site West Sedgemoor Pumping Station, which drains into the River Parrett (tidal), is operated by the Environment Agency (EA), it is the Parrett Internal Drainage Board (IDB) which manage water levels and flow circulation on the moor.

One of West Sedgemoor's main water sources is runoff, provided by a relatively small catchment of roughly 41 km^2. Widness Rhyne, located southwest of the site at Helland, provides most of the runoff water entering the site. Both Sedgemoor Old Rhyne and West Sedgemoor Main Drain receive direct runoff input from the North Curry and Stoke St Gregory ridge. Wickmoor Rhyne also provides runoff water from Wick Moor (also fed directly by the River Parrett; nontidal) and Curry Rivel ridge. West Sedgemoor is also supplied with water direct from the River Parrett (nontidal) via a culvert during the summer flows. Flood risk is reduced in the winter by lowering water levels, although, a raised water level area is maintained year-round in the interest of nature conservation efforts (Parrett IDB, 2009). The moor hosts a Royal Society for the Protection of Birds (RSPB) nature reserve and supports Englands largest breeding population of waders such as Lapwing (*Vanellus vanellus*), Snipe (*Gallinago gallinago*) and Curlew (*Numenius arquata*) making the site internationally important for supporting wintering waterfowl populations (Natural England, 2019). The site is also abundant with rare and scarce invertebrate fauna, particularly water beetles, in part justifying the Somerset Levels Ramsar status under Ramsar criterion 2 (Drake et al., 2010).

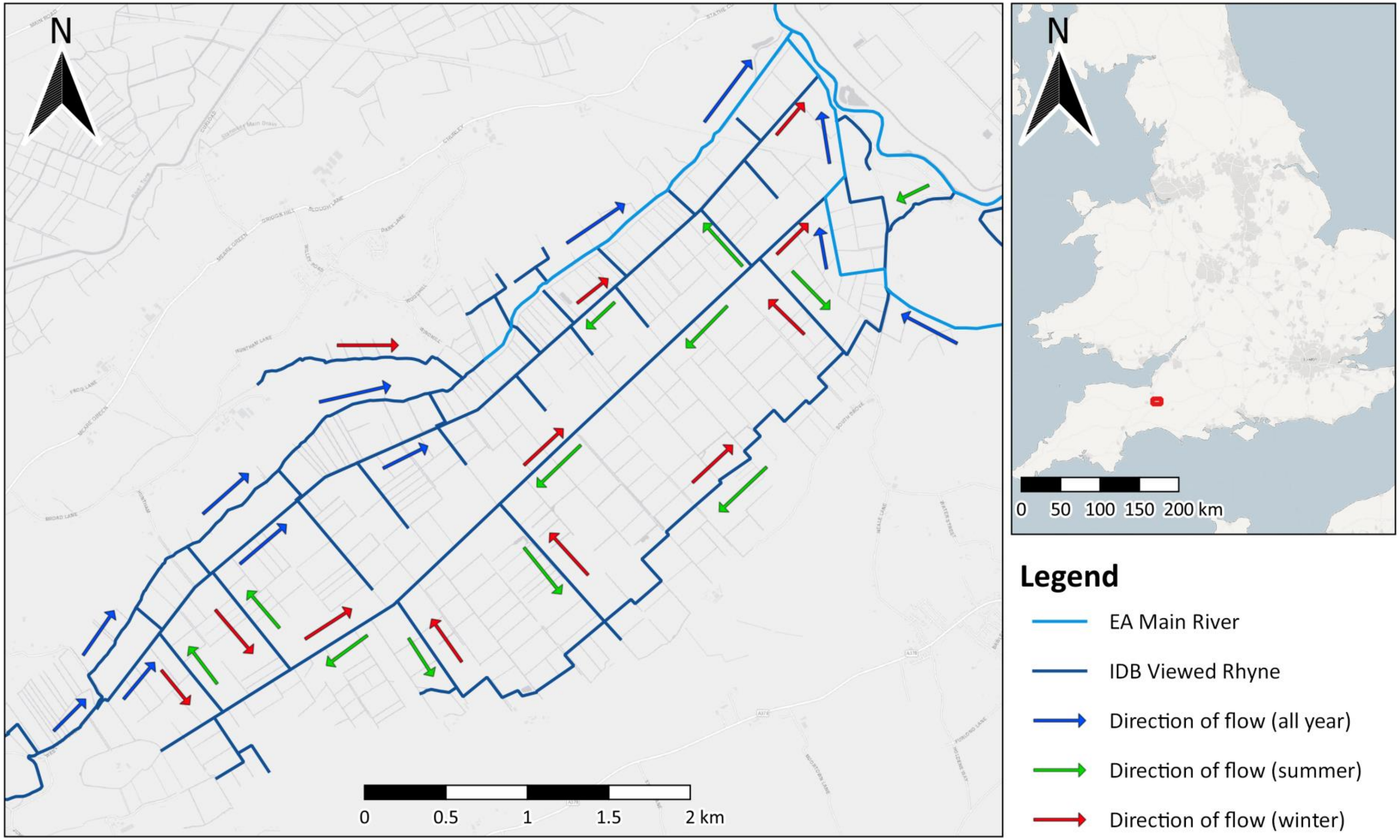

Figure 5.1: Location and controlled water flows of West Sedgemoor SSSI. Upper right inset shows the study area within Southwest England (red box). Left panel shows seasonal dependant water flow directions, indicated by coloured arrows (blue, all year; green, summer; red, winter). Reproduced from (Crocker et al., 2021).

5.3.2 Sampling and chemical analyses

Despite it being recommended that analysis be performed without delay following water sample collection to reduce microbial activity and subsequent changes in P fractions, circumstances such as the distance between sample sites and the laboratory accentuate the significant value of appropriate sample storage (Kalkhajeh et al., 2019). Prior to any collection of water samples for P analysis, it is imperative that a rigorous cleaning procedure is utilized, such as making sure the storage bottles have been cleaned with 10% HCl overnight, and then rinsed with ultra-high purity water, to prevent contamination of samples with P potentially sorbed onto the walls (Gardolinski et al., 2001). For the analysis of dissolved constituents, polycarbonate or cellulose acetate membrane filters are recommended (Hall et al., 1996). Literature has shown that freezing is not always appropriate for sample storage due to coprecipitation of inorganic phosphate and calcite following sample thawing (Gardolinski et al., 2001; House et al., 1986; Neal et al., 1998). However, refrigeration (typically around 4 °C) in darkness prior to analysis within 48 hours has been shown to be reliable at keeping P fractions stable, without the need for prior filtration on site (for soluble fractions) or the use of chemical preservatives (which in some cases can accelerate the release of P to soluble fractions) (Comber et al., 2015b; Haygarth et al., 1995).

Surface water and surface water biomass samples were collected seasonally in May; August; November 2019 and February 2020. A total of 27 sampling sites (Fig. 5.2) were chosen based upon (1) coverage of potential inputs (2) ditches suitable for a potential surface biomass harvesting P mitigation plan (3) minimal disturbance to nature conservation efforts of the RSPB. Surface water samples were collected mid-channel using a clean bucket or measuring jug and transferred into hydrochloric acid (HCl; 10% - Fisher Scientific Primar Plus) and ultra-high purity water (>18 Mohm.cm) cleaned HDPE (high density polyethylene) 500 ml Nalgene bottles and stored chilled at 2°C to 8°C in the dark until further analysis (within 48 hours). Surface water biomass samples were collected, across a 1 m stretch at each ditch sample site, using a hand net and transferred into PE (polyethylene) resealable bags, and stored frozen at -18°C in the dark until further analysis.

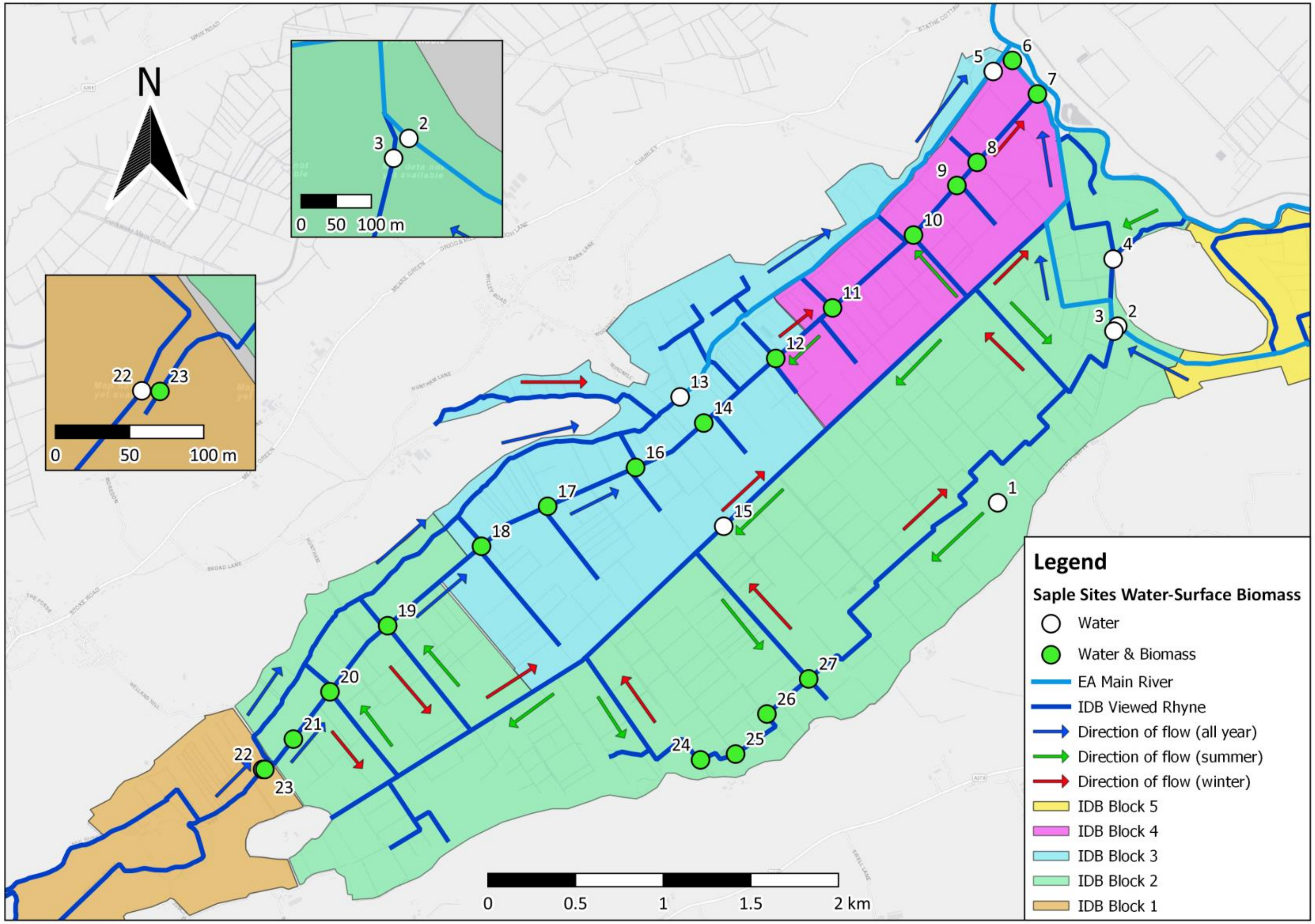

Figure 5.2: Surface water and biomass sampling sites, controlled water flows, and Parrett Internal Drainage Board (IDB) hydrological blocks on West Sedgemoor SSSI.

Water samples were analysed for soluble reactive phosphorus (SRP), total reactive phosphorus (TRP), total soluble phosphorus (TSP) and total phosphorus (TP), in triplicate. 12.5 ml samples for SRP and 9 ml samples for TSP were filtered into HCl (10% - Fisher Scientific Primar Plus) and ultra-high purity water cleaned centrifuge tubes using 0.45 µm non-sterile hydrophilic SFCA (surfactant free cellulose acetate) membrane disposable filters (Cole-Parmer) and syringes, pre-cleaned in HCl (2% - Fisher Scientific Primar Plus) and twice rinsed with ultra-high purity water. Unfiltered 12.5 ml samples for TRP and 9 ml samples for TP were transferred to centrifuge tubes using clean syringes. The TSP and TP 9 ml samples were acidified by adding 1 ml of concentrated HCl (Fisher Scientific Primar Plus). Analysis of the reactive P fractions (SRP and TRP) were performed using the molybdenum blue method (Appendix C, C.1) (Blue Book Method A) (HMSO, 1992). Analysis of TSP and TP was performed using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS; Thermo Scientific X 199 Series 2). EnviroMAT Drinking Water, Low (EP-L) and EnviroMAT Ground Water, High (ES-H) reference materials were used for quality control (supplier: Qmx laboratories).

Once thawed, surface water biomass samples were oven-dried at 80°C for 48 h after which a harvest dry mass was obtained. Triplicate 0.1 g subsamples were then quantitatively transferred into hydrochloric acid (HCl; 10% - Fisher Scientific Primar Plus) and ultra-high purity water cleaned digestion tubes. 5 ml of concentrated nitric acid (HNO_3; Fisher Scientific Primar Plus – Trace analysis grade) was then added to the tubes and samples were allowed to predigest for 30 min. Samples were then transferred to a Tecator Digestion System 12 1009 digestor, temperature ramped to 105°C, and then digested at 105°C for 1 hour. After cooling to room temperature, samples were filtered through manually fluted Whatman 541 filter paper. Analysis of biomass TP was performed using inductively coupled plasma - optical emission spectrometry (ICP-OES; Thermo Scientific ICAP 7400 Series). BCR-129 Hay Powder certified reference material (CRM) was used for quality control (supplier: European Commission, Joint Research Centre).

5.3.3 Data analysis

Principal component analysis (PCA) of the surface water sample data was conducted using Minitab 19. The data from 21 of the sites were used as 6 of the sites had missing data (Sites 1, 11, 12, 15, 16 and 17). No outliers were observed from examining the Mahalanobis distances plotted in Fig. C.1 of Appendix C (Brereton, 2015). The grouping of the sites was visualised with a scatterplot of the scores of the second principal component versus the scores of the first principal component. The variables responsible for the grouping of sites were identified by plotting the coefficients of each variable for the first component versus the coefficients for the second component.

5.4 Results and discussion

5.4.1 Seasonal fractionation of freshwater phosphorus

5.4.1.1 Total phosphorus (TP)

Concentrations of TP for each of the seasons: spring, summer, autumn, and winter, for West Sedgemoor water samples, are shown in Fig 5.3. The figure shows how all sites observed in this study have the potential for TP concentrations to be above the Common Standards Monitoring (CSM) environmental quality standard value of 0.1 mg L^{-1} with all sites exceeding the CSM target in the summer and autumn months. Temporal interpretations of this data should be taken with caution as seasonal spot samples may only represent a narrow period of time and not reflect weekly P dynamics of a site (Taylor et al., 2016). The highest TP concentration observed was 1.88 mg L^{-1} at Site 1 during the summer, over 10 times the CSM target value. Site 1 is located adjacent to a cattle shed, a possible source of this localised nutrient enrichment. North Drove Rhyne (sites: 7-12, 14, 16-21, 23) generally showed peak TP concentrations in the summer, the highest of which were directly fed by the input Site 22 at Helland. Site 22 feeds water, mostly agricultural land run off, into West Sedgemoor from the higher catchment. There are also several permitted sewage discharge points in the catchment from both sewage treatment works (including a sewer storm overflow at Meare Green, Wrantage), as well as smaller on-site domestic sewage treatment plants (domestic septic tanks). It is likely that the increased summer concentrations from Site 22 reflect increased agricultural activity in the catchment during that period. South Drove Rhyne (sites: 24-27) generally showed peak TP concentrations in the autumn. South Drove Rhyne boarders both RSPB nature reserve land and privately owned agricultural land that supports a cowshed (Fig C.2). Typically, during the autumn at West Sedgemoor, cattle grazing is intensified after summer hay cutting (Armstrong and Bradley, 2014; Kirkham, 1996). Therefore, the increased TP concentrations observed at South Drove Rhyne in the autumn could be caused by an increased presence of grazing cattle on the adjacent land. In the spring, only sites 9, 10 and 20 were significantly lower in concentration than the CSM target value of 0.1 mg L^{-1}, despite expected increase of nutrient uptake by ditch flora during spring growth (Taylor et al., 2016). Sites 11, 12, 15-17 were unable to be sampled during the winter, as the sites were inaccessible due to flooding and arboreal damage on site. Eight out of the twenty-two sites sampled during winter (sites: 1-5, 13, 22, 24) failed the CSM target, Site 13 having the highest concentration of 0.23 mg L^{-1}. Of these, sites 1 & 24, as mentioned previously, are adjacent to cowsheds which are likely acting as sources of nutrient enrichment locally to these sites throughout winter as cows are over-wintered there. Site 13 is located directly downstream of Broadmead/Sedgemoor Rhyne which inputs runoff water to West Sedgemoor, from Huntham on the North Curry and Stoke St Gregory ridge, during the wetter winter months. The Broadmead/Sedgemoor Rhyne also receives inputs from three permitted sewage discharge points,

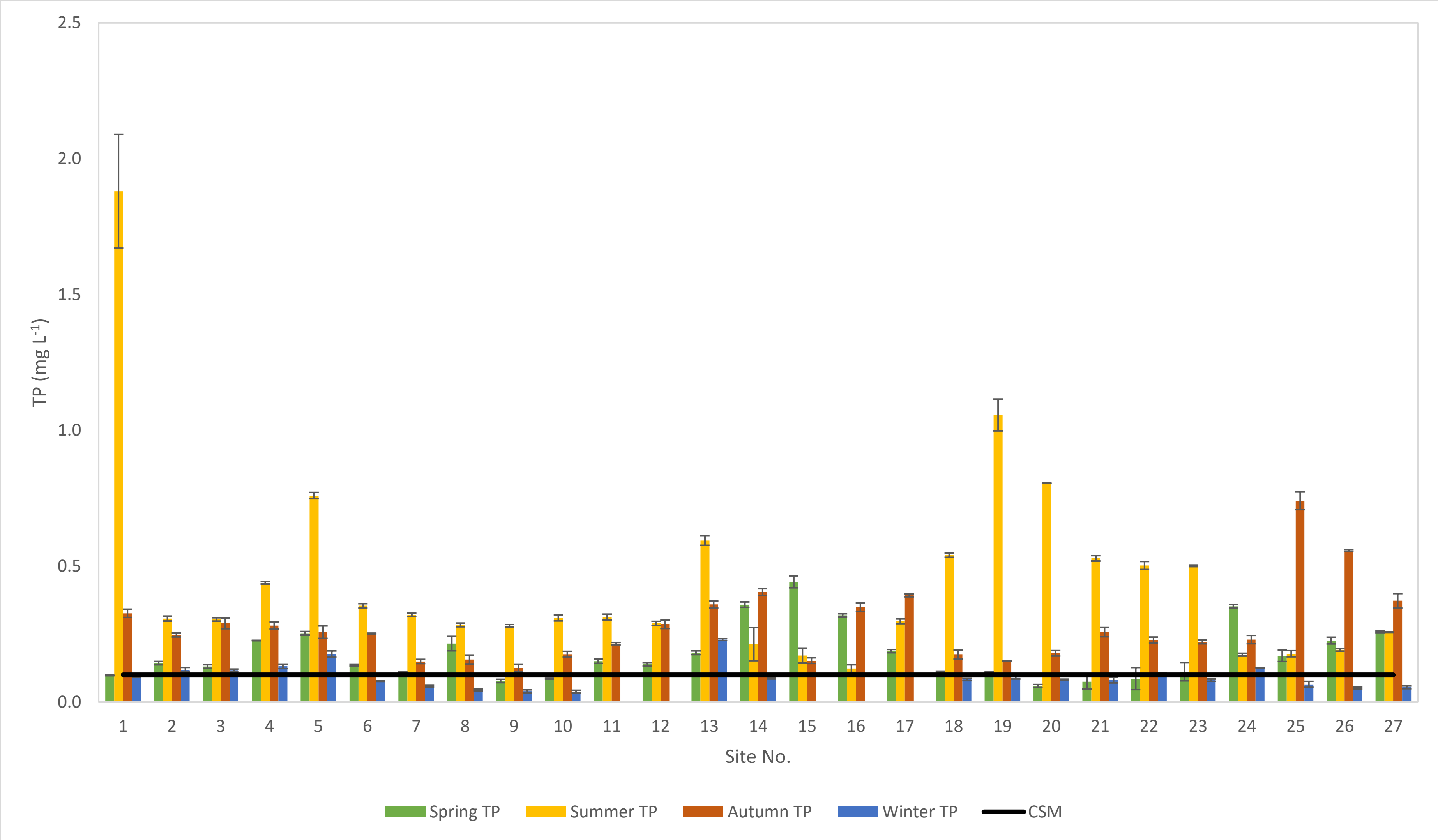

Figure 5.3: Total phosphorus (TP) concentrations in surface water at West Sedgemoor SSSI for the sample campaign from May 2019 to February 2020. The black line denotes the current Common Standards Monitoring (CSM) guidance for phosphorus of >0.1 mg-P l^{-1} as TP. Error bars represent 2 standard deviations.

including two sewer storm overflows. However, the large spike in TP concentration observed at Site 13 was likely due to a farm pollution event that took place around the time of sampling. On January 30th 2020, Environment Officers from the Environment Agency found that Broadmead/Sedgemoor Rhyne had been polluted with slurry from Huntham Farm. Slurry had been applied to nearby fields at such a high rate that it led to slurry run off entering the ditch. This was the third of three separate incidents where slurry had polluted the watercourse, attributed to Huntham Farm, Stoke St Gregory, the first and second events happening on June 19th and October 29th 2019 respectfully. The farm has a history of effluent discharge offences including events from August 2016 and December 1970 (Environment Agency, 2021). Site 5, located at the outlet West Sedgemoor Pumping Station, is directly downstream of Site 13, so increased concentrations here were also likely caused by the slurry pollution event (Environment Agency, 2021). Sites 2, 3 and 4 are located at and near the input at Wickmoor Rhyne, fed by Wick Moor and run off from Curry Rivel ridge. Increased TP concentrations at these sites and Site 22 in winter likely reflect increased run off input, from agricultural land in the catchment, due to increased rainfall (Hannah, 2022; Shigaki et al., 2007). However, increased rainfall and the flood event present during sampling, is likely the cause of most sites meeting the CSM target, as direct rainfall to the moor is a minimal input of P to the water column and higher water levels act to dilute the existing concentrations (Zhao et al., 2018).

5.4.1.2 Correlation coefficient analysis

The correlation coefficients between TP, TSP, TRP and SRP for each of the seasons: spring, summer, autumn, and winter, for West Sedgemoor SSSI, are shown in Table 1. TP, TSP, TRP and SRP were observed to be strongly positively correlated within each season with no strong or moderate correlations observed between the seasons. These correlations show that increases in TP across the site are not driven by any singular fraction but instead a combination of increases across all fractions TSP, TRP & SRP.

Table 5.1: Correlation matrix of Pearson's correlation coefficients between total phosphorus (TP), total soluble phosphorus (TSP), total reactive phosphorus (TRP) and soluble reactive phosphorus (SRP) for each of the seasons: spring, summer, autumn, and winter, for West Sedgemoor SSSI surface water samples.

	Spring TP	Summer TP	Autumn TP	Winter TP	Spring TSP	Summer TSP	Autumn TSP	Winter TSP	Spring TRP	Summer TRP	Autumn TRP	Winter TRP	Spring SRP	Summer SRP	Autumn SRP
Summer TP	-0.405														
Autumn TP	0.215	-0.160													
Winter TP	0.250	0.234	0.044												
Spring TSP	0.943	-0.333	0.262	0.263											
Summer TSP	-0.327	0.960	-0.177	0.362	-0.230										
Autumn TSP	0.168	-0.196	0.967	-0.022	0.217	-0.226									
Winter TSP	0.298	0.213	0.031	0.982	0.299	0.333	-0.026								
Spring TRP	0.986	-0.396	0.216	0.272	0.975	-0.297	0.168	0.313							
Summer TRP	-0.353	0.984	-0.375	0.396	-0.285	0.981	-0.396	0.379	-0.299						
Autumn TRP	0.113	0.131	0.899	0.089	0.166	0.049	0.891	0.068	0.106	-0.377					
Winter TRP	0.182	0.227	0.002	0.976	0.192	0.361	-0.058	0.959	0.208	0.450	0.027				
Spring SRP	0.933	-0.331	0.244	0.235	0.997	-0.222	0.197	0.272	0.971	-0.264	0.137	0.177			
Summer SRP	-0.317	0.979	-0.163	0.342	-0.228	0.991	-0.209	0.323	-0.296	0.984	0.098	0.337	-0.224		
Autumn SRP	0.260	-0.279	0.962	0.054	0.313	-0.270	0.972	0.060	0.275	-0.346	0.830	0.026	0.298	-0.263	
Winter SRP	0.247	0.208	0.024	0.979	0.255	0.348	-0.031	0.983	0.271	0.440	0.033	0.987	0.238	0.326	0.065

p value	<0.05	<0.01

1

0

-1

However, West Sedgemoor can be sectioned into different hydrological areas based off the water flows and levels. The IDB defines these areas as hydrological blocks (Fig. 5.2). Blocks 1 and 5 cover the inputs at Helland and Wick Moor respectfully, while Blocks 2, 3 and 4 cover various parts of West Sedgemoor SSSI. The correlation coefficients between TP, TSP, TRP and SRP for both block 2 and block 3 were similar to the site as a whole, showing the same observational pattern where TP, TSP, TRP and SRP were strongly positively correlated within each season with no strong or moderate correlations observed between the seasons (Tables C.1 and C.2). However, in block 4, only autumn and winter show strong positive correlations between all the fractions TP, TSP, TRP and SRP. Whereas, block 4 spring and summer only showed strong positive correlations between TP & TRP, and TSP & SRP, with the summer also showing strong positive correlation between TSP & TRP (Table 5.2). The strong positive correlations between block 4 spring and summer TP and TRP without significant correlation between TP and SRP shows that the block 4 spring and summer TP concentrations are driven by particulate reactive phosphorus (PRP) concentration. The PRP fraction, typically determined as the difference between TRP and SRP, represents inorganic and/or organic P compounds that are solubilised from particulate material, reacting with the colorimetric reagent in the molybdenum blue method (Surridge and Gittins, 2020). Increased PRP indicates an increase in turbidity and total suspended solids (TSS), with possible causes including change in water flow speed and direction, bank erosion, soil runoff and bioturbation (Green et al., 1999; Loperfido et al., 2010). Numerous strong positive correlations are also shown between winter and the other seasons; however, these correlations are likely an artifact of the lower number of sites sampled during the winter due to flooding. Hence why most of those correlations are not significant at a p value significance level of <0.01 despite R values ≥ 0.9.

Table 5.2: Correlation matrix of Pearson's correlation coefficients between total phosphorus (TP), total soluble phosphorus (TSP), total reactive phosphorus (TRP) and soluble reactive phosphorus (SRP) for each of the seasons: spring, summer, autumn, and winter, for Parrett Internal Drainage Board (IDB) hydrological block 4 surface water samples at West Sedgemoor SSSI.

	Spring TP	Summer TP	Autumn TP	Winter TP	Spring TSP	Summer TSP	Autumn TSP	Winter TSP	Spring TRP	Summer TRP	Autumn TRP	Winter TRP	Spring SRP	Summer SRP	Autumn SRP
Summer TP	-0.105														
Autumn TP	0.229	0.359													
Winter TP	0.156	0.894	0.79												
Spring TSP	0.214	0.331	0.773	0.97											
Summer TSP	-0.25	0.662	0.744	0.556	0.581										
Autumn TSP	0.182	0.179	0.958	0.694	0.739	0.682									
Winter TSP	-0.094	0.978	0.855	0.947	0.937	0.776	0.745								
Spring TRP	0.918	0.074	0.489	0.458	0.553	-0.006	0.451	0.196							
Summer TRP	-0.278	0.948	0.466	0.75	0.359	0.842	0.315	0.919	-0.082						
Autumn TRP	0.191	0.377	0.962	0.881	0.712	0.683	0.956	0.894	0.476	0.454					
Winter TRP	0.066	0.955	0.852	0.986	0.966	0.678	0.733	0.985	0.358	0.85	0.903				
Spring SRP	0.16	0.269	0.794	0.939	0.993	0.583	0.767	0.941	0.5	0.322	0.727	0.95			
Summer SRP	-0.289	0.537	0.732	0.474	0.551	0.976	0.732	0.696	-0.041	0.746	0.697	0.588	0.56		
Autumn SRP	0.1	0.241	0.958	0.771	0.722	0.698	0.99	0.838	0.387	0.373	0.976	0.814	0.754	0.741	
Winter SRP	0.044	0.968	0.898	0.966	0.936	0.747	0.786	0.99	0.323	0.889	0.931	0.994	0.923	0.663	0.859

p value	<0.05	<0.01

1

0

-1

Correlation coefficients were also calculated between the water data and sediment data for West Sedgemoor from a previous study (Crocker et al., 2021). However, no significant correlations were observed between the data (Table C.3).

5.4.1.3 Principal component analysis

A principal component analysis was conducted to determine whether the IDB hydrological blocks could be distinguished from each other using their chemical properties. The first principal component explains 40.7% of the variation (Eigenvalue = 6.504) and is mainly based on spring TP, summer TP, autumn TP, spring TSP, summer TSP, autumn TSP, spring TRP, summer TRP, autumn TRP, spring SRP, summer SRP and autumn SRP (factor loadings = -0.238, 0.336, -0.292, -0.214, 0.308, -0.291, -0.217, 0.331, -0.287, -0.205, 0.312, -0.285, respectively). The second principal component explains 34.1% of the variation and is mainly based on spring TP, winter TP, spring TSP, winter TSP, spring TRP, winter TRP, spring SRP and winter SRP (factor loadings = -0.253, -0.372, -0.275, -0.375, -0.272, -0.359, -0.269, -0.374, respectively). Eigen values explained variance and cumulative variance of subsequent principal components is provided in Table C.4.

The principal component analysis score plot of West Sedgemoor SSSI water sample sites (Fig. 5.4a) is shown based on chemical differences illustrated in the accompanying loading plot (Fig. 5.4b). A clear distinction can be seen between block 4 sites and the other blocks, based on separation along the second principal component axis. In contrast to the factor loadings which are all negative for the second principal component, the block 4 sites are all positively correlated with the second principal component and show little correlation to the first principal component. This shows that the block 4 sites have relatively lower concentrations of the P fractions, across all the seasons, compared with the rest of the sites. Other hydrological blocks have sites which were observed to have spikes in P concentrations during different seasons, such as block 3 sites 19 and 24 which had relatively higher P concentrations during summer and spring respectively. This indicates that block 4 is less at risk of seasonal spikes in P inputs compared to other hydrological blocks. This could be due the relatively high elevation of block 4 in comparison to block 3 (Fig. C.3) which causes difficulty in directing enough water to block 4 to reach penning level targets. During summer flows, block 4 is fed from the Wickmoor Rhyne input during which water tends to flow toward the lower elevation block 3 instead of deeper into block 4. During winter flows, block 4 is fed from the Widness Rhyne input during which water must flow up gradient from block 3 to reach block 4 causing low flow rates. However, during flood events, such as the one during winter sampling, West Sedgemoor's only water output the pumping station is inactive to prevent putting extra load into the River Parrett and risking burst banks. Without the through flow, this causes newly inputted water, and by extension P, to pool in block 3 without reaching block 4. The position of the EA main river West Sedgemoor Main Drain also acts a barrier to runoff inputs from the Stoke St Gregory ridge reaching block 4. This suggests that block 4 is less susceptible to external inputs of P to West Sedgemoor than the other hydrological blocks.

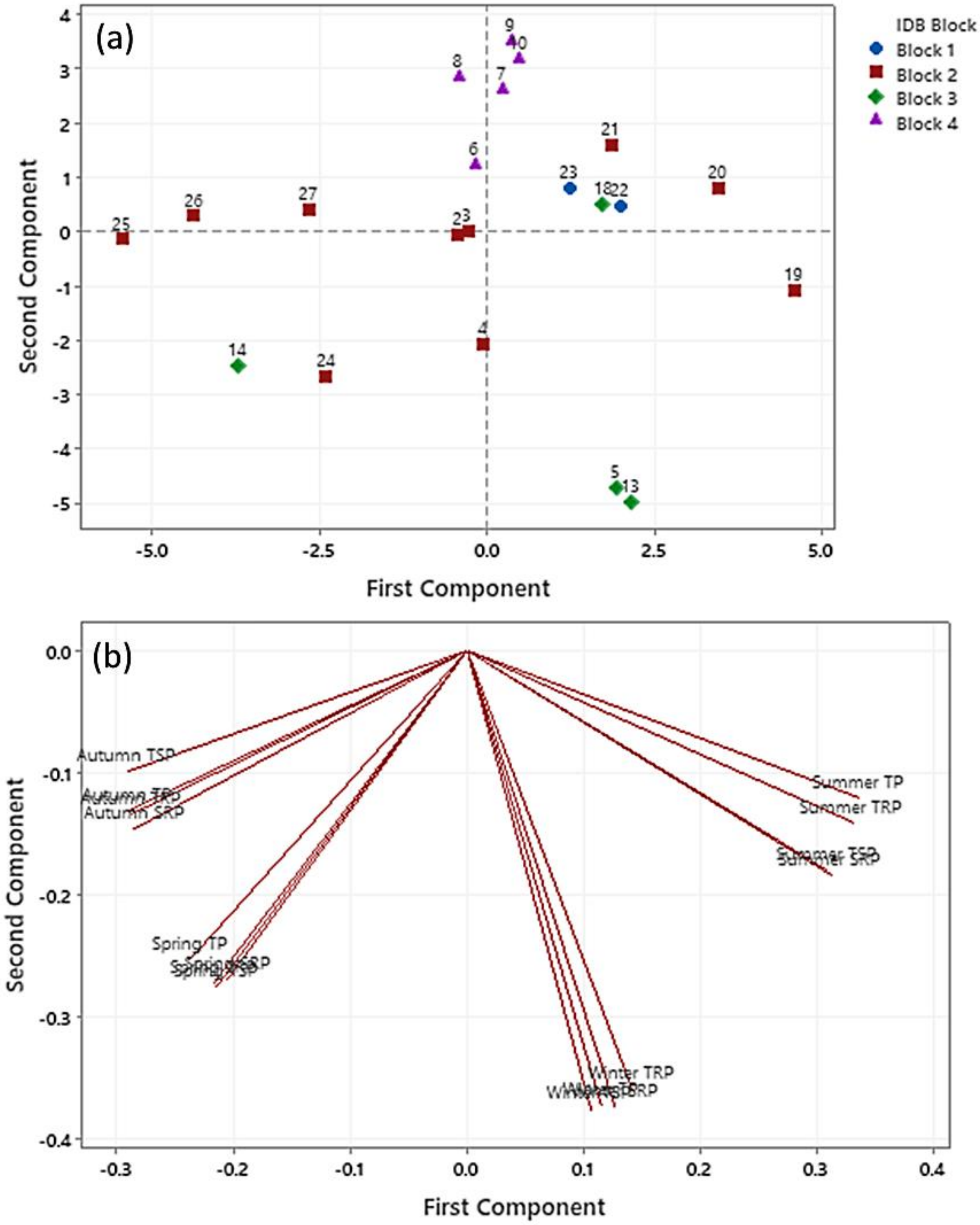

Figure 5.4: (a) Principal component analysis score plot of West Sedgemoor SSSI surface water sample sites based on chemical differences. Scores for the first two principal components are plotted. Markers indicate different Parrett Internal Drainage Board (IDB) hydrological blocks. (b) Principal component analysis loading plot of West Sedgemoor SSSI surface water chemical properties. The coefficients of each variable for the first component versus the coefficients for the second component are plotted.

5.4.2 Seasonality of surface water biomass phosphorus

5.4.2.1 Seasonal growth and phosphorus accumulation

Literature states that P typically makes up between 0.03 to 2.8% of a typical duckweed dry mass (DM) (Landolt and Kandeler, 1987). Percentage P concentrations of DM, for West Sedgemoor SSSI biomass samples, are shown in Fig. 5.5. The ranges of %P DM observed in this study were 0.18 to 0.62% in the spring, 0.39 to 0.63% in the summer, 0.28 to 0.64% in the autumn, and 0.45 to 0.66% in the winter. However, in spring sampling 9 of the 15 sites observed to have surface biomass were filamentous algal blooms (sites: 7, 8, 10, 14, 17, 20, 21, 23, 24) rather than duckweed blooms. In all other seasons, only duckweed (*L. minor*) blooms were observed. Of the duckweed spring sites, the range of %P DM was 0.26 to 0.46%. These %P DM values are on the lower end of the literature range most likely due to the duckweed collected in this study being wild, not purposely grown under controlled perfect conditions. This is reflected in the variance, between sites and seasons, in the amount of dry biomass collected (Fig. 5.6) in which some sites had upwards of 70-80 g m^{-2} DM sampled while other sites have no observed surface water biomass coverage. The largest amount of biomass observed was 86.4 g m^{-2} DM at site 26 during the winter. However, winter also had the lowest number of sites with surface water biomass observed with just 3 of the 19 having *L. minor* present. Therefore, winter also had the lowest average biomass at 11.4 g m^{-2} DM across all sites. Spring and summer had averages of 15.7 g m^{-2} DM and 16.0 g m^{-2} DM respectively, although summer was the only season in which all sites had observable surface water biomass. Despite having less sites with surface water biomass than both summer and spring, the highest average biomass of 17.7 g m^{-2} DM was observed in the autumn.

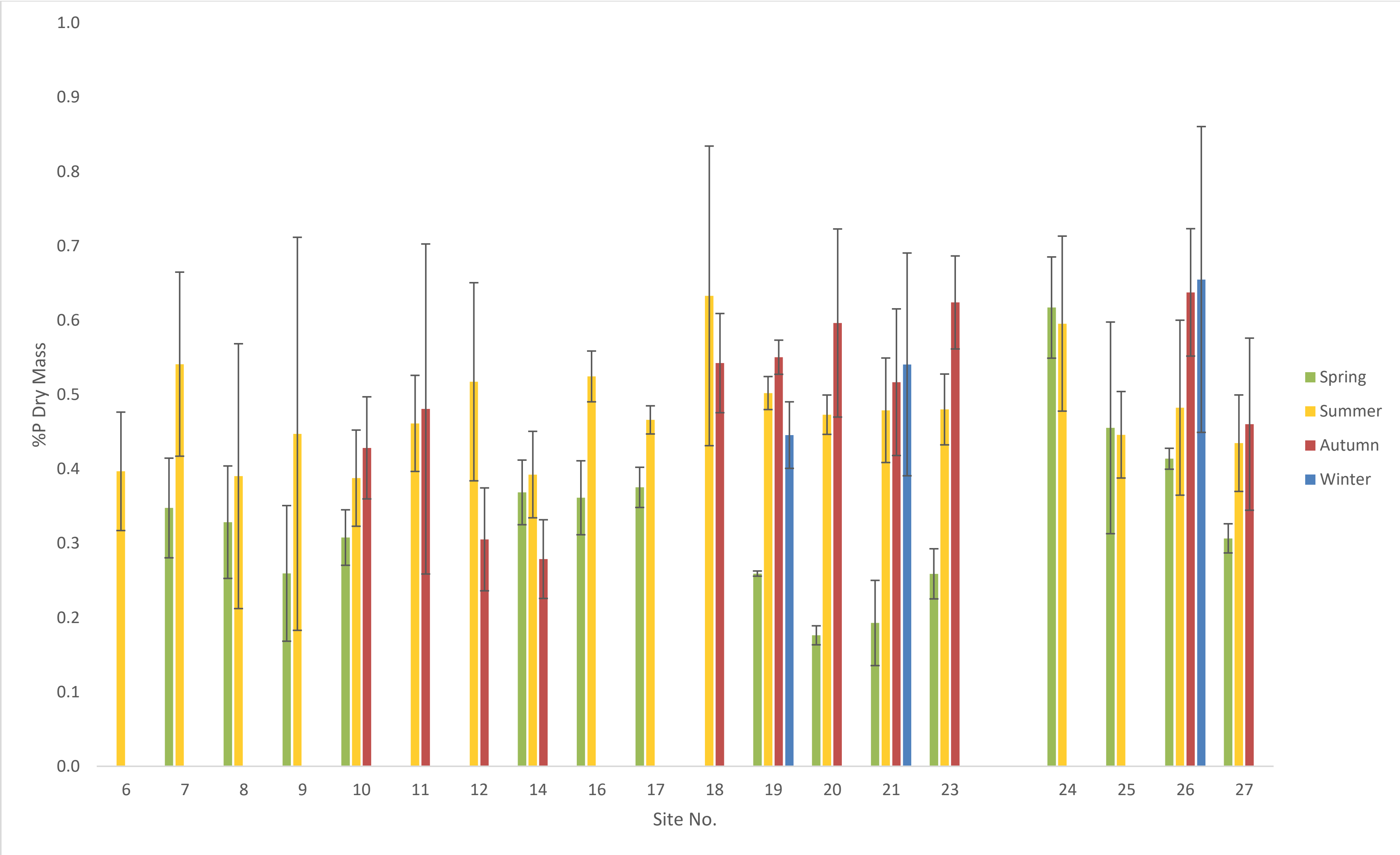

Figure 5.5: Percentage concentrations of total phosphorus in dry surface water biomass samples of West Sedgemoor SSSI. Error bars represent 2 standard deviations.

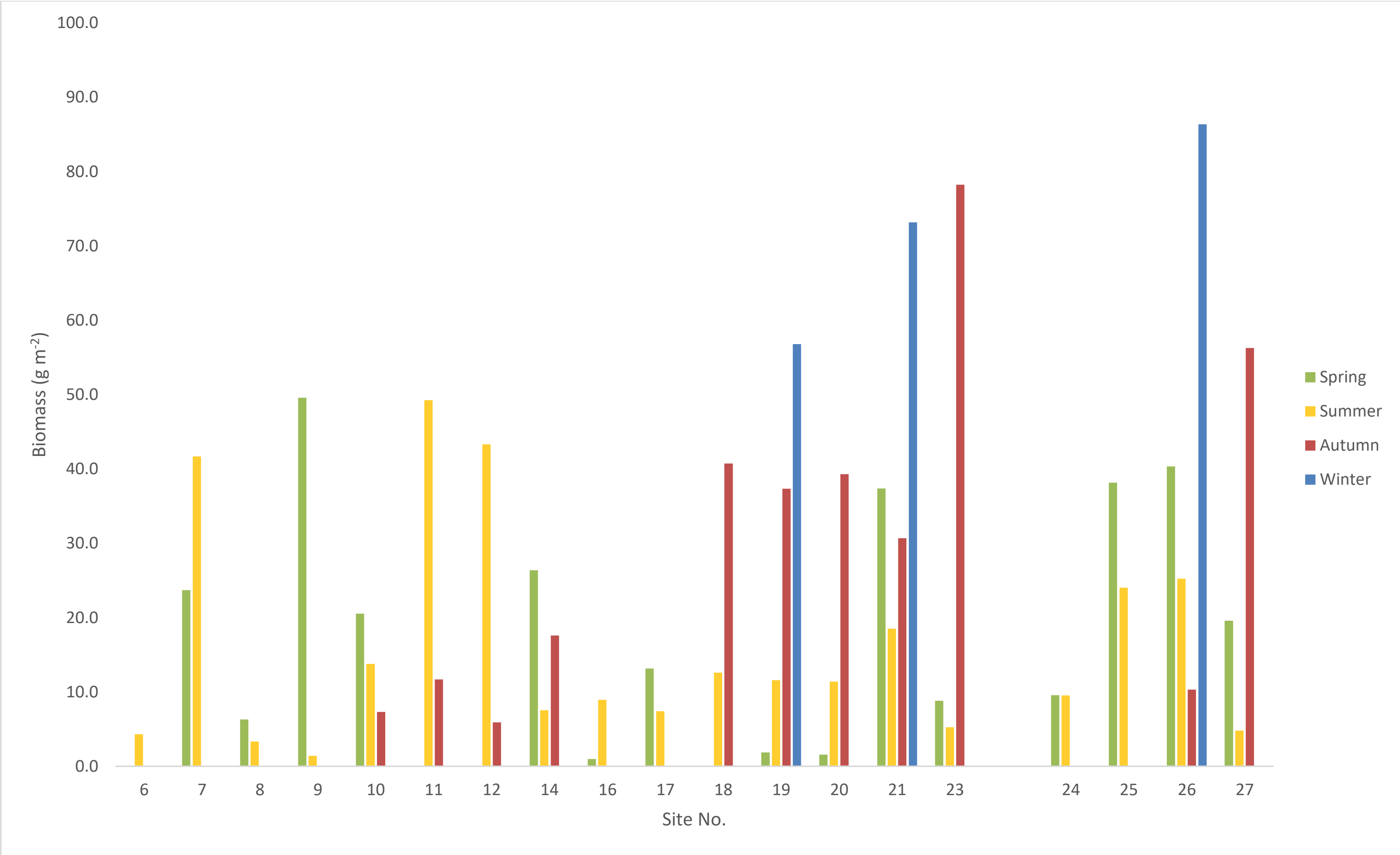

Figure 5.6: Distribution of surface water biomass coverage across the sample sites at West Sedgemoor.

Correlation coefficients calculated between the water data and surface water biomass data for West Sedgemoor had no observable correlations for the seasons summer, autumn, and winter (Table C.5). Spring however showed moderate positive correlations between P concentration in the biomass and TP, TSP, TRP and SRP concentrations in the water. By separating out the spring samples into duckweed and algal bloom sites, further correlation analysis (Table 5.3) shows no correlation between duckweed bloom P concentrations and water P concentrations. However, algal bloom P concentrations showed high positive correlations to TP, TSP, TRP and SRP concentrations in the water. Correlation between seasons were not performed as *L. minor* has a lifespan of approximately 30 days which is significantly shorter than the time between sampling (Lemon et al., 2001). The lack of correlations between the duckweed blooms and the water P concentrations suggest that the concentration of P in the water is high enough to not be limiting duckweed growth. Correlations between algal bloom P concentrations and water P concentrations, in contrast to duckweed, is likely due to how algal nutrient removal is significantly more intensive than that of duckweed fronds (Szabó et al., 1999). When growing in competition, algae significantly reduce the growth of duckweed by reducing the nutrient availability and by shading with dense floating algal beds which can form dense mats on the duckweed fronds. However, under eutrophic conditions duckweed can maintain growth despite a high algal presence. This then usually leads to duckweed dominating the surface and outcompeting algal blooms by completely shading out the algae (Roijackers et al., 2004). This is the case for ditch systems where wave action and high winds are unlikely factors to affect duckweed growth. In systems with open waters such as lakes, duckweed is prone to be layered up on itself by high winds and/or wave action. This prevents duckweed from becoming dominant as light is allowed to penetrate the water column in cleared areas, stimulating algal bloom production. Excessive layering also causes lower layers of duckweed to die-off as they are cut off from light (Hasan and Chakrabarti, 2009; Roijackers et al., 2004). This layering effect was observed during the winter sampling, enabled by the flood event at the time in which water levels rose above field level effectively turning the site from a ditch system to one resembling a lake. Therefore, the dominance of duckweed over algae when transitioning from spring to summer, and the die-off of duckweed during the winter, are likely in part caused by the insusceptibility of ditch systems to high winds and wave action, and the susceptibility of West Sedgemoor to these effects during flood conditions. Other limiting factors that can cause seasonal differences in duckweed growth include solar radiation and temperature. Landolt (1957) found the optimum temperature range for duckweed growth to be between 20°C to 30°C at light intensities between 1000 and 9000 lux. Although growth rates decrease below this range, *L. minor* has been found to have a permanent growth rate at temperatures less than 8°C and also has the tenacity to survive being enclosed in ice for an extended period (Hasan and Chakrabarti, 2009; Landolt, 1957;

Landolt and Kandeler, 1987; Paterson et al., 2020). Several studies have found that duckweed growth rates are influenced by seasonal changes in temperature and solar radiation, with lower growth and nutrient uptake rates observed during winter lows in temperature and solar radiation, compared to higher growth and nutrient uptake rates observed during summer highs in temperature and solar radiation (Hodgson, 1970; Muradov et al., 2014; Rejmánková, 1973). Table 5.4 shows the seasonal temperatures and sunshine hours at climate station Yeovilton (51°00'21.6"N 2°38'24.0"W) the nearest climate station to West Sedgemoor SSSI (Met Office, 2022). The UK seasonal temperature averages were 8.4°C during Spring 2019 (March, April and May), 15.1°C during Summer 2019 (June, July and August), 9.1°C during Autumn 2019 (September, October and November), and 5.3°C during Winter 2019/20 (December, January and February) (Kendon et al., 2021, 2020). Both the seasonal maximum temperatures at Yeovilton climate station and the UK seasonal averages show the temperature gradient Summer>Autumn>Spring>Winter, with air frost days at Yeovilton being in the reverse order. The same order Summer>Autumn>Spring>Winter is observed for the number of sites with duckweed (*L. minor*) blooms in this study. This agrees with the findings of Rejmánková (1973) in that temperature is the main factor controlling the growth rate of duckweeds in outdoor experiments.

Table 5.3: Correlation matrix of Pearson's correlation coefficients between total phosphorus (TP), total soluble phosphorus (TSP), total reactive phosphorus (TRP) and soluble reactive phosphorus (SRP) concentrations (mg L^{-1}) in surface water samples, and TP (g kg^{-1}) in surface water biomass samples and mass of surface water biomass samples during the spring season at West Sedgemoor SSSI.

Duckweed	Biomass g m^{-2}	Biomass g kg^{-1}	Spring TP (mg L^{-1})	Spring TSP (mg L^{-1})	Spring TRP (mg L^{-1})
Biomass (g kg^{-1})	0.26				
Spring TP (mg L^{-1})	-0.427	0.438			
Spring TSP (mg L^{-1})	-0.552	0.35	0.985		
Spring TRP (mg L^{-1})	-0.556	0.341	0.984	1	
Spring SRP (mg L^{-1})	-0.611	0.312	0.97	0.997	0.997
Algae	**Biomass (g m^{-2})**	**Biomass (g kg^{-1})**	**Spring TP (mg L^{-1})**	**Spring TSP (mg L^{-1})**	**Spring TRP (mg L^{-1})**
Biomass (g kg^{-1})	-0.145				
Spring TP (mg L^{-1})	-0.053	0.798			
Spring TSP (mg L^{-1})	0.037	0.77	0.921		
Spring TRP (mg L^{-1})	-0.019	0.783	0.988	0.968	
Spring SRP (mg L^{-1})	0.053	0.76	0.913	0.998	0.963

p value	<0.05	<0.01

Table 5.4: Met Office climate temperature and sunshine data for Yeovilton climate station between March 2019 to February 2020 (Met Office, 2022). *Data presented seasonally as Spring 2019 (March, April, and May), Summer 2019 (June, July, and August), Autumn 2019 (September, October, and November), and Winter 2019/20 (December, January, and February).*

Season	Maximum temperature (°C)	Minimum temperature (°C)	Air frost (days)	Sunshine (hours)
Spring 2019	17.3	4.7	6	462.5
Summer 2019	24.0	10.4	0	539.3
Autumn 2019	19.9	4.3	5	270.2
Winter 2019/2020	10.8	3.2	14	167.8

5.4.2.2 Biomass harvesting for phosphorus capture

Compared to other macrophytes, free-floating duckweed reproduces rapidly and is easily harvested from the surface, resulting in direct removal of nutrients from the water column (Roijackers et al., 2004; Willett, 2005; Zirschky and Reed, 1988). Once harvested, duckweed can be used to produce animal feed, fertiliser and biofuel products owing to its high contents of protein, fat, amino acids, and starch (Baliban et al., 2013; Cheng and Stomp, 2009; Kreider et al., 2019; Zirschky and Reed, 1988). These advantages make duckweed a promising candidate for phytoremediation of eutrophic surface waters. Optimising the production of duckweed requires regular harvesting, as overcrowding causes relative growth rate (RGR) to decrease as well as the formation of dense layered mats causing duckweed die-off, returning nutrients to the water column after degradation (Chakrabarti et al., 2018; Cheng and Stomp, 2009; Hasan and Chakrabarti, 2009; Roijackers et al., 2004). Frequent removal of duckweed could potentially have the benefit of providing submergent vegetation sunlight allowing for photosynthetic oxygen production in the water column, combating anoxic conditions. However, the removal of duckweed and its water shading effect can also allow for competitive algal bloom production (Farrell, 2012; Roijackers et al., 2004; Szabó et al., 1999).

The feasibility of harvesting wild duckweed (*L. minor*) blooms is assessed in this study. Under near optimum conditions for duckweed growth, Landolt and Kandeler (1987) found that 20 g DM m^{-2} day^{-1} (73 t DM ha^{-1} $year^{-1}$) had the potential to be produced. However, 5 to 20 t DM ha^{-1} $year^{-1}$ (1.4 to 5.5 g DM m^{-2} day^{-1}) is more realistic under less than optimal conditions based on field results (Leng, 1999). Hasan and Chakrabarti (2009) suggest 10 to 20 t DM ha^{-1} $year^{-1}$ (2.7 to 5.5 g DM m^{-2} day^{-1}) is potentially harvestable in environments with high nutrient concentrations and optimum environmental conditions. The RGRs of duckweeds is reported to be around 0.1 g DM m^{-2} day^{-1} to 0.3 g DM m^{-2} day^{-1} in less than optimal conditions (Chakrabarti et al., 2018; Njambuya et al., 2011; Oron, 1994). Rejmánková (1975) observed for *L. minor* an RGR of 0.20 g DM m^{-2} day^{-1} in a study under field conditions. As shown previously, the most optimum conditions for duckweed growth on West Sedgemoor happen during the seasons of summer and autumn due to higher temperatures and an established dominance over algae post spring. Across the summer and autumn, the average duckweed DM was 17 g DM m^{-2} and the average concentration of P in the duckweed biomass was 0.5% DM. The combined length of the North and South Drove Rhyne's is 7553 m with a total surface area estimated as 25,400 m^2. Therefore, assuming a harvest of 8.5 g DM m^{-2} leaving half of the duckweed to regrow what was harvested, assuming a RGR of 0.20 g DM m^{-2} day^{-1}, this would allow for 36 harvests to be achieved over the summer and autumn. This would yield a total estimated biomass of 7770 kg DM, removing an estimated total of 39 kg P from the system. To dilute 39 kg P to the CSM value of <0.1 mg L^{-1} TP, the volume of water required would be 3.9×10^8 L (309000 m^3). In comparison, at West

Sedgemoor, the available ditch channel storage during winter under current conditions, winter theoretical maximum and summer under current conditions are 315540 m^3, 408630 m^3, and 204315 m^3 respectfully (Stratford and Acreman, 2014).

If duckweed harvesting were to be implemented at West Sedgemoor, it is likely the techniques used would mirror those of current ditch maintenance. Overgrowth of vegetation in the wetland ditches and rivers is a constant threat to the functioning of the Somerset Levels drainage and flood defence system. Therefore, the IDB maintains its managed ditches, known locally as Viewed Rhynes, on West Sedgemoor every two years, by a vegetation clearing process traditionally known as keeching (Rippon, 2006; Somerset Drainage Boards Consortium, 2022). Once a process done by hand, keeching is now performed using excavators equipped with weed cutting buckets, in which emergent macrophytes are cut and scooped out of the ditches, with cuttings being left on the ditch banks close to the ditches (Schindler and Comber, 2021). Stacking the cuttings along the banks allows additionally dredged aquatic fauna, such as eels (*A. anguilla*), to make their way back into the ditches. The practice has also heightened the banks of the ditches, aiding watercourse management. Harvested duckweed would also likely be left on the ditch banks but for the purpose of drying, as sunlight is an efficient low-cost way of drying duckweed (Leng, 1999). This is due to duckweed lacking a waxy cuticle, present on terrestrial plants to prevent water loss, allowing duckweed to be dried rapidly (Cheng and Stomp, 2009). It would also have the added ecological benefit of allowing capable aquatic fauna the chance to return to the ditches, as during sampling in this study aquatic invertebrates were observed in and removed from the duckweed samples including many water beetles. Under Ramsar criterion 2, West Sedgemoor SSSI supports 17 species of British Red Data Book invertebrates, including 6 near threatened water beetle species (Drake et al., 2010; Pepler, 2019; Ramsar, 2005). While it is likely many of these species were present in the samples, prior to removing them, invertebrate identification and analysis was outside the scope of this research. It is therefore important not to impact these species negatively by removing the duckweed from the site too promptly. However, leaving the duckweed on the banks indefinitely could negate attempts of removing P from the water column as duckweed undergoes biodegradation releasing P (Schindler and Comber, 2021). The most feasible uses of the dried duckweed product in the surrounding West Sedgemoor catchment would be as cattle feed or as an agricultural amendment (Cheng and Stomp, 2009; Kreider et al., 2019).

5.5 Conclusions

The main findings of the research are as follows:

- The analysis of total phosphorus (TP) in surface waters show that all sites have the potential for TP concentrations to be above the Common Standards Monitoring (CSM) environmental quality standard value of <0.1 mg L^{-1}, with all sites exceeding the CSM target in the summer and autumn months. The highest concentration observed being 1.88 mg L^{-1} at Site 1 during the summer, over 10 times the CSM target value.

- Based on correlation coefficient analysis, across the site, surface water TP increases are not driven by any singular fraction but instead a combination of increases across all fractions total soluble phosphorus (TSP), total reactive phosphorus (TRP) & soluble reactive phosphorus (SRP). However, when sectioned into different hydrological block areas, hydrological block 4 spring and summer only showed strong positive correlations between TP & TRP, and TSP & SRP, with the summer also showing strong positive correlation between TSP & TRP. The strong positive correlations between TP & TRP without significant correlation between TP & SRP indicated that hydrological block 4 TP increases were driven by particulate reactive phosphorus (PRP) concentrations in the spring and summer.
- Principal component analysis (PCA) showed clear distinction between hydrological block 4 and the other hydrological blocks, based on their chemical properties. Hydrological block 4 sites were characterised by relatively lower concentrations of TP, TSP, TRP, and SRP, whereas a lack of clustering was observed for the other hydrological blocks. This suggests that the sites in hydrological block 4 are less susceptible to seasonal spikes in phosphorus concentration than sites in other hydrological blocks, likely due to the lacking flow connectivity of hydrological block 4 to the rest of the site and external runoff water phosphorus loadings.
- Duckweed dominance over algal blooms was observed on West Sedgemoor post spring. Correlation coefficient analysis of surface biomass showed a lack of correlations between the duckweed blooms and the water P concentrations. This suggests that phosphorus concentrations in the water are high enough not to be a limiting factor of duckweed growth on the site. This, coupled with ditches providing favourable growth conditions for duckweed to outperform algae, is likely why duckweed dominates West Sedgemoor.
- It was found that if biomass harvesting of duckweed over the dominant growth seasons of summer and autumn was implemented at West Sedgemoor, an estimated 39 kg of phosphorus could be removed per harvest period, which would otherwise require 3.9×10^8 L of water to dilute down to the CSM target of <0.1 mg L^{-1}. Therefore, the hypothesis ‘duckweed harvesting can be used as an effective method of phosphorus mitigation’ is accepted. However, this mitigation technique would have to be implemented in a way that was cost effective and did not negatively impact the nationally important ecology of the site.

6 Ditch Management for Phosphorus Mitigation: Accelerating the Recovery of the Somerset Levels and Moors Eutrophic Systems

6.1 Introduction

Wetland ditches arise from the desire of landowners for drainage and reclamation of swamplands and marshes to create new landscapes, sometimes establishing new societies and economies. Anthropogenic drainage of wetlands has occurred for many centuries, being considered one of the 'vertical-themes' in historical geography, alongside other major 'resource-converting', landscape changing processes operating in society, such as clearing woodland, reclaiming heath, irrigating desserts, and urban-industrial growth (Darby, 1953; Davidson, 2014; Williams, 1970). The underlying drivers of the continuous conversion and degradation of wetlands are economic development and population growth, with one of the most typical wetland conversions being first to extensive and then intensive agricultural land (both croplands and pasture) (Davidson, 2014; Millennium Ecosystem Assessment, 2005).

The Somerset Levels and Moors (51°06'N 02°51'W; Somerset, UK) are designated as a Ramsar site (Site No. 914) under the Ramsar Convention, as a Special Protection Area (SPA) under the Habitat Regulations 2017, and as a Site of Special Scientific Interest (SSSI) under the Wildlife & Countryside Act 1981 (as amended)(HM Government, 2017, 1981; Ramsar, 2005, 1994). The Ramsar Site designation recognises the site's important wetland features, attracting rare invertebrates and internationally important numbers of wintering wildfowl. This Ramsar Site consists of 6,388 ha (non-contiguous) of wet grassland, peat bog, fen, and reedbed, within the larger Somerset Levels catchment of approximately 70,000 ha (Ramsar, 2005). Draining activity and land reclamation on the Somerset Levels has been going on since at least the 1400's, facilitated in part by digging ditches, locally referred to as rhynes (Williams, 1970). In the present day the landscape is dominated by artificially drained, irrigated and otherwise modified rivers and wetlands, to allow high-yielding farming (predominantly pasture), as well as restored wetland bird habitat (Bowers, 2022; Parrett IDB, 2009; Williams, 1970). However, a great majority of ditches within the Ramsar designation are classified as being unfavourable in condition or at risk due to excessive phosphorus (P) concentrations causing eutrophication. A significant threat to biodiversity worldwide, surface water systems under eutrophic conditions deviate from primarily submerged aquatic vegetation to algae or duckweed dominance, leading to deterioration of aquatic systems via shading and therefore anoxic conditions (Bowers, 2022; Crocker et al., 2021; Zhang et al., 2017). Various sources contribute to the P pollution present on the Somerset Levels, although wastewater treatment works (WwTW) and livestock farming contribute the vast majority with onsite wastewater treatment, urban, and arable also contributing significantly (Bowers, 2022).

In the wake of the Dutch Nitrogen Case ('Dutch-N'), a 2018 ruling of the European Court of Justice on the implementation of the Habitats Directive clarified that where a site of international importance (i.e., SPAs and Ramsar Sites) fails to achieve an acceptable condition due to nutrient pollution, the potential of new developments to contribute to the nutrient load must be 'necessarily limited' (Bowers, 2022; House of Commons Environmental Audit Committee, 2022). This has therefore influenced how regulation 63 of the Habitats Regulation 2017 will apply to pollution related incidents and has resulted in Local Planning Authorities in Somerset being unable to grant new developments planning permission within the Somerset Levels and Moors Ramsar Site catchment unless they can clearly demonstrate that there will not be a nutrient loading increase to the protected area (Bowers, 2022).

It is therefore both ecologically and economically important to mitigate both existing and additional P loads within the Somerset Levels and Moors. Mitigation techniques for dealing with both diffuse and point pollution P are well documented in scientific literature (Bowers, 2022; Deasy et al., 2008; Environment Agency, 2019; Ngatia and Taylor, 2018). Many catchment-level nature-based solutions and non-catchment-based interventions have been identified as being potentially viable for use in the Somerset Levels catchment. The nature-based solutions include those that are implemented within catchments to reduce loadings from diffuse pollution P inputs, such as: taking land out of agricultural use; cessation of fertiliser; installation of riparian buffer strips; beaver reintroduction; and wetland creation. The non-catchment-based interventions are those that require local policy change and third-party interventions, such as: water usage restrictions; anaerobic digestors; package treatment plants; improvements to WwTWs and reductions of water company permit limits; sustainable drainage systems (SuDS); third party credit schemes; portable treatment works; and alternative wastewater treatment providers (Bowers, 2022). However, Natural England has identified that the best chance for improving the situation on the Somerset Levels and Moors, in terms of the eutrophication pressure, in part relies on looking at how ditch management can be modified to accelerate recovery to include dealing with the existing burden of P in the system. Therefore, this thesis investigates potentially feasible ways of reducing the internal cycling and bioavailability of P within wetland ditch systems through ditch management techniques, including: water level management; dredging, emergent macrophyte harvesting and channel widening (two-stage channels); algae/duckweed harvesting; and filter substrates.

6.2 Methodology

After a thorough review of the literature and best-practice guidance, a list of potential Short-term (immediate – 3 years), medium-term (3 – 10 years), and long-term (>10 years) P mitigation solutions revolving around ditch management have been identified. Generally, short-term solutions are those that are used as transitional steps toward long-term solutions that which are achiveable in perpetuity.

However, for a solution to meet the requirements set out in the habitats regulations, as viewed by Natural England, it will have to adequately fulfil these questions (Bowers, 2022; Wood et al., 2022):

- Is the solution based on best available evidence?
- Is the solution effective beyond reasonable scientific doubt?
- Does it apply a precautionary approach?
- Can it be secured in perpetuity?

Natural England defines 'in perpetuity' as lasting 80 – 125 years. In most cases mitigation required in perpetuity must be inplace for the lifetime of a proposed development. However, this does not imply that mitigation is not a requirement following that period (Wood et al., 2022). A combination of solutions can be utilsed in a mitigation scheme, in order to provide mitigation that is satisfatory over a required lifetime. Where uncertainty arises in a proposed long-term solution, transitional short and medium-term solutions may prove appropriate, until further investigation. Short-term solutions can also be utilised as an appropriate bridging step, where long-term solutions require extended periods to initialise (Bowers, 2022).

6.3 Mitigation Options

6.3.1 Water level management

The Somerset Levels and Moors, as typical of lowland wet grassland in the UK, consists of reclaimed floodplain land managed as grazing marshes with some being cut for hay or silage as well as land managed as wetland bird nature reserves (Jefferson and Grice, 1998; Parrett IDB, 2009; Williams, 1970). To facilitate conservation management and required maintenance such as mowing and grazing, wetland bird habitat restoration often involves intricate localised ditch water level management utilising sluices, weirs and pumping stations to produce a fluctuating water regime including raised water level areas (Niedermeier and Robinson, 2009; Parrett IDB, 2009). Despite seasonal wetlands being considered net biological and chemical sinks for P, literature evidence also indicates that alternating flood/drainage cycling of wetland ditches can accelerate the transport and cycling of nutrients within surrounding soils, threatening decreased water quality via eutrophication as a source of P (Fisher and Acreman, 2004; Meissner et al., 2008; Niedermeier and Robinson, 2009; Peterjohn and Correll, 1984; Rupp et al., 2004).

In laboratory conducted studies, a multitude of biological and chemical soil processes which transpire in response to flood/drainage cycling have been attributed with P release of seasonal wetlands, e.g., anoxic release of iron-bound P under flood conditions, and aerobic mineralisation of organic phosphorus (OP) in the time of draining (Aldous et al., 2005; Fisher and Reddy, 2001; Martin et al., 1997; Pant and Reddy, 2003, 2001; Reddy and Rao, 1983; Venterink et al., 2002). Also, as a consequence of elevated hydraulic conductivity and weak retention of P against mass flow, soil P losses are tough to control from fields containing highly macroporus layers of degraded peat adjacent to managed drainage ditches (Niedermeier and Robinson, 2009). Studies also show that the risk of P release is greater in wetlands restored from drained agricultural land than undisturbed wetlands, as farmed soils tend to have relatively high concentrations of legacy P (Aldous et al., 2005; Kinsman-Costello et al., 2014; Pant and Reddy, 2003; Wiegman et al., 2022). Restoration of peat wetlands, by the removal of unnatural intrasite hydrological differences and artificial drainage water flow paths (e.g., ceasing ditch management thereby allowing them to infill with sediment), can benefit the development of peatland ecosystems and reduce leaching of nutrients and dissolved organic carbon to downstream waters in the long term. Within 10 years, significant recovery of peatland hydrology can be predicted, with deviations from natural wetland hydrology to be expected (Allott et al., 2019; Haapalehto et al., 2014). Although, increased P mobilisation can occur for decades in previously agricultural wetlands post rewetting (Zak et al., 2008).

A rewetting programme that maintains wetland ditches, utilising extended periods of flooded or drained conditions through spring and summer to manage soil P losses, could also be deployed. However, management plans involving less intensive localised ditch water level management leading to perpetually raised water tables near or exceeding soil surface will inhibit maintenance such as mowing and grazing, consequently compromising managed habitat maintained for wetland bird populations (Niedermeier and Robinson, 2009). Rewetting of historically drained and farmed soils should be undertaken with precaution as the potential for previously agricultural land to liberate legacy P, as soluble reactive phosphorus (SRP), to surface waters can offset mitigation of P retained through sedimentation during flooding (Wiegman et al., 2022). Dredging of former agricultural land prior to rewetting can reduce sediment P flux, reducing liberation of P to overlying waters but also reducing P sorption capacities of the sediment (Oldenborg and Steinman, 2019). Long term monitoring of water quality should be incorporated into rewetting plans in estimates of net P balance, and as part of a decision support system to inform practitioners, reduce the costs, and avoid unwanted SRP losses causing eutrophication of surface waters (Kinsman-Costello et al., 2014; Meissner et al., 2008; Wiegman et al., 2022).

6.3.2 Sediment dredging

Sediment dredging is a common engineering practice utilised to remove sediments (and other material) from aquatic systems such as ditches and is generally undertaken to enhance the flow or to establish sufficient depth of overlying waters (Oldenborg and Steinman, 2019; Parrett IDB, 2009; Smith et al., 2006). Dredging can also be influential in nutrient mitigation by increasing water depth allowing for higher load via dilution and removing sediment rich P from the system (Oldenborg and Steinman, 2019; Smith et al., 2006; van Liere et al., 2007). Laboratory and *in-situ* studies have shown that sediment P flux in wetlands affected by long-term nutrient loading is explained by the relationship between P sorption of surface sediment and the concentration of P in overlying waters (Hill and Robinson, 2012a; Moore Jr. and Reddy, 1994; Mortimer, 1942). Therefore, sediment rich in legacy P has the potential to act as a secondary source of P to overlying waters, after disturbance of the sediment or changes in condition of the water column (Collins and McGonigle, 2008; Hill and Robinson, 2012b; Jarvie et al., 2005; Reynolds, 1992; Van der Perk et al., 2007). Phosphorus mitigation by removing sediment through dredging aims to prevent the reintroduction of sediment bound P to the water column. This is palliative in essence as it causes the effects of the problem to be less severe but does not actually solve cause of the problem.

Dredging of ditch sediments alone will have no effect on eutrophic algae and duckweed bloom production without first reducing the P concentration in the overlying water (van Liere et al., 2007). Through simulation with the ecological eutrophication model PCDitch, van Liere et al. (2007) found that simultaneously dredging sediments and reducing P load to overlying waters could accelerate the recovery of eutrophic ditches; after increasing the loading of a 'pristine' ditch from 1.3 g P m^{-2} $year^{-1}$ to 11 g P m^{-2} $year^{-1}$ for 20 years then reducing back to the original low loading rate, the addition of dredging sped up recovery time to 2 years as opposed to 15 years for reducing loading rate alone (van Liere et al., 2007). Dredging is, therefore, best utilised as a tool to accelerate the recovery response times of other mitigation techniques (Van der Does et al., 1992; van Liere et al., 2007; Wen et al., 2020).

Sediment dredging can be an effective technique for minimising sediment P release in wetland habitat systems undergoing restoration. However, dredging's limitations, both logistical and cost, should be considered before implementation. Sediments are naturally heterogeneous in chemical, physical and biological composition which can alter the effectiveness of dredging sediment for P release reduction. This variability necessitates pre-restoration monitoring of the sediment and overlying waters to inform development decisions based on; sediment P release risk; success probability of dredging; and the required depth of dredging (Oldenborg and Steinman, 2019). Also, sediment dredging, while often carried out, is widely considered to be an expensive option and often a last resort technique for nutrient mitigation (Newcombe et al., 2010; Oldenborg and Steinman, 2019; Sarvilinna and Sammalkorpi, 2010). The cost of dredging can be offset by utilising the dredged sediment as a product rather than conventional landfilling.

Landfilling of sediments high in trace elements and nutrients such as P leads to the loss of these resources, and the practice of landfill is accredited with climate change emissions, production of polluted leachate, and its large land requirements (Ferrans et al., 2022; Renella, 2021; Vervaeke et al., 2003). However, sediments not only act as a sink for nutrients but also pollutants emitted by both point and diffuse sources including water-soluble, hydrophobic, recalcitrant, and hazardous compounds. Persistent organic pollutants (POPs) listed in the EU Regulation 850/2004 are also accumulated in sediments. Reuse of sediments *in situ* is in general permitted when contaminant concentrations are under threshold limits defined in legislation. Although, contaminants still limit the reuse and recyclability of dredged sediment material, causing difficulty with regards to hazardous waste management and disposal (Renella, 2021; Vervaeke et al., 2003). Sediments have considerable potential for agricultural reuse and progressing toward a circular economy but without pre-treatment can potentially contaminate food crops with pollutants, such as cadmium, over health risk thresholds limiting use to ornamental and biofuel crop production (Ferrans et al., 2022; Matej-Łukowicz et al., 2021; Renella, 2021). Electrokinetic remediation is widely accepted process that can separate out heavy metal, radionuclide, and hydrocarbon pollutants from sediment matrix. The technology mobilises pollutants through electromigration, electroosmosis, and electrophoresis by utilising a direct low-intensity electric field (Acar and Alshawabkeh, 1993; Han et al., 2021; Mao et al., 2019; Renella, 2021). However, sediments are currently excluded from EU regulation on fertilisers forbidding sediments from use as a component material of EU fertilisers. Currently, this leaves sediments as only suitable to be recycled in some non-food agricultural sectors. For these cases, in use as a soil modifier, treated dredged sediments can be considered and environmental and economical alternative treatment (Huang et al., 2019; Renella, 2021).

6.3.3 Emergent macrophyte harvesting

Aquatic plants are indispensable within aquatic ecosystems, providing a primary food source and habitats for aquatic fauna, preventing erosion of the banks and beds of watercourses, and improving water quality through the uptake and/or degradation of pollutants (Barrett et al., 1999). Several studies have shown clear evidence that vegetated ditches, as opposed to unvegetated ditches, are an efficient strategy for mitigating agricultural diffuse pollution by providing effective removal of nutrients, suspended solids, and organics from the water column (Flora and Kröger, 2014; Jiang et al., 2007; Kröger et al., 2008; Moore et al., 2010; Vymazal and Březinová, 2018). Kröger et al. (2008) details that vegetated ditches were capable of decreasing total phosphorus (TP) loads in effluent by 45%, while Moore et al. (2010) reports reductions in SRP concentrations up to 52%. However, when excessive growth occurs, macrophytes can adversely affect habitat and channel functionality (Barrett et al., 1999).

Weed cutting is a common ditch maintenance practice undertaken for flood risk management purposes. Hydraulic conditions are influenced by aquatic plants as they impede water course capacity and increase the resistance against water flow, subsequently increasing water levels and siltation rates (Baattrup-Pedersen et al., 2018; Curran and Hession, 2013; Manolaki Paraskevi et al., 2022). Without maintenance such as aquatic weed management and desilting, the majority of Grade 1 agricultural land within England would undergo regular flooding causing loss of crops, livestock, and potentially the lives of the people in elevated risk areas (Barrett et al., 1999; Dunderdale and Morris, 1997). Weed cutting is, therefore, considered a necessary endeavour by the Environment Agency and other organizations responsible for drainage such as internal drainage boards and local government authorities (Dunderdale and Morris, 1997). On the Somerset Levels and Moors, the process involving cutting and removal of vegetation from within ditch channels is locally referred to as 'keeching' (Rippon, 2006; Somerset Drainage Boards Consortium, 2022). Originally work carried out by hand, keeching is now performed utilising excavators equipped with weed cutting buckets which cut and scoop emergent macrophytes out of the ditches. Vegetation cuttings are then typically deposited indefinitely on the banks of adjacent land to the ditches both to allow any aquatic fauna such as invertebrates and eels (*A. anguilla*) to return to the ditches, and to, overtime, heighten the ditch banks to aid watercourse management (Schindler and Comber, 2021). Much of this work is carried out by the Somerset Drainage Boards Consortium who operate and maintain a network of about 1185 km watercourses, locally known as 'viewed rhynes', designed to provide drainage, flood protection, irrigation, and environmental enhancement. Viewed rhynes are typically maintained on an annual basis between August and December, outside of the nesting season to minimise the disturbance to wetland bird populations. Although, some viewed rhynes are maintained earlier in the year for irrigation purposes. Maintenance work, where possible, is undertaken on alternating banks each year to aid wildlife and biodiversity. Maintenance of watercourses, outside of the viewed rhyne network, are the responsibility of those who own land adjoining, above or with a watercourse running through it. Owners of this land are defined as a 'riparian owner' and are responsible for maintaining and removing obstructions from the banks and bed that could cause an increased flood risk (Environment Agency, 2018; Somerset Drainage Boards Consortium, 2022, 2021). Every kind of landowner will bear their own specific interests and will manage ditches they are responsible for accordingly, although within any relevant enforced restrictions. Predominantly, pastoral farmers will lean toward managing ditches to preserve their utility and security as wet fences in addition to being a source of drinking water for their livestock. Separately, arable farmers and Internal Drainage Board (IDB) engineers are inclined to view adequate drainage as a first concern. Shifts in the agricultural economy, such as those actualised by bovine spongiform encephalopathy, consequently leading to a lack of grazing, and the probable problems induced by climate change and sea level rise are likewise expected to affect the condition of grazing marsh ditches, both directly and indirectly, by way of presumable alterations in the practice of ditch management (Mclaren et al., 2002).

Harvesting of macrophytes for nutrient removal is well documented in scientific literature (Bartodziej et al., 2017; Busnardo et al., 1992; Fletcher et al., 2022; Grosshans, 2014; Kuiper et al., 2017; Rezania et al., 2021). Through systematic harvesting of macrophyte biomass, 50% of P can be mitigated from inflow supply water (Bartodziej et al., 2017; Busnardo et al., 1992). Additionally, the removal of macrophyte biomass opens up the possibility of nutrient recovery as part of a circular agronomic model (Grosshans, 2014; Quilliam et al., 2015). Grosshans (2014) reports that by harvesting nutrient rich cattail (*Typha* spp.), permanent removal of an average 30 kg of P per hectare per year (kg P ha^{-1} $year^{-1}$) from aquatic systems was achievable, while recovering up to 88 % of TP retained in ash following combustion during biomass bioenergy production. In a study carried out at West Sedgemoor, one of the wetlands that makes up the Somerset Levels Ramsar site, Schindler and Comber (2021) found that bankside emergent vegetation removed during keeching operations stored significant amounts of potentially recoverable P (16 to 32 g kg^{-1}). Although, there was no observed correlations between emergent vegetation P concentrations and those of adjacent water, sediment, or soil. Variations in concentration were therefore thought to likely be reflective of the variety of species present in samples and their differing P accumulation rates/capacities (Schindler and Comber, 2021).

However, weed cutting operations have the potential to cause environmental incidents by disturbing habitats and suspending sediments. Directly after weed cutting, water level will decline, flow rate will increase, and sediment is resuspended (Baattrup-Pedersen et al., 2018; Kaenel et al., 1998; Manolaki Paraskevi et al., 2022; Rasmussen et al., 2021; Schindler and Comber, 2021). These changes are linked to longer term alterations in biodiversity leading to domination by fast-growing plant species with basal meristem growth, rhizomes and high dispersal capacities, and subsequent changes in invertebrate taxa occurrence naturally associated with macrophyte assemblage change (Baattrup-Pedersen et al., 2016, 2002; Kaenel et al., 1998; Manolaki Paraskevi et al., 2022). Also, the current keeching practice of leaving cuttings on the banks indefinitely could negate attempts of removing P from the water column as the macrophyte biomass undergoes biodegradation releasing P, this highlights the need for further investigation into the sustainability of the approach (Schindler and Comber, 2021).

6.3.4 Two-stage ditches

Unlike conventional trapezoidal drainage ditches, two-stage ditches are modified by the addition of adjacent floodplain grass benches formed within the land of the watershed. The implementation of benches dissipates surface runoff energy, reducing sediment load, and extends the interaction time of water with the bench vegetation and soil increasing nutrient uptake by vegetation (Hodaj et al., 2017; Vymazal and Březinová, 2018). The conversion of conventional ditches into two-stage ditches involves creation of floodplain benches dug out of either side of the original main channel. These benches are typically created to appear as natural floodplains created by fluvial processes, such as unmaintained vegetated ditches. The main channel is left in its original maintained state, allowing water to flow with higher velocity in the main channel than the floodplain benches (depending on vegetation cover) (Davis et al., 2015; Englund, 2020; Jordbruksverket, 2013; Mahl et al., 2015). As this process widens the existing ditch, it requires cooperation with adjacent landowners to implement (Ranjan and Witter, 2020).

Originally the conceptualised purpose of two-stage ditches was to stabilise the banks of drainage ditch channels. During high water flow the vegetated floodplain benches are inundated decreasing water flow velocity and increasing water retention time. This decrease in flow velocity increases ditch stability and reduces the rate of erosion (Christopher et al., 2017; D'Ambrosio et al., 2015; Roley et al., 2016). The added advantage of this is that, by increasing water retention time, nutrients and sediment also have increased retention times. Nutrients can be assimilated by floodplain bench vegetation, while sediment particulates have increased chance to undergo deposition (Davis et al., 2015; Englund, 2020; Hodaj et al., 2017; Mahl et al., 2015; Vymazal and Březinová, 2018).

Functionality of two-stage ditches is influenced by their dimensional design. Floodplain bench width and height influence ditch stability, the ability of ditches to sustain runoff, and nutrient and sediment retention (Mahl et al., 2015). Larger bench widths will cause lower water levels relative to water volume in the ditch, and studies show longer two-stage ditches have a larger impact on reducing high water flow velocity (Englund, 2020; Jordbruksverket, 2013). Inundation frequency of the floodplain benches is dependent on bench height, with frequency increasing for lower bench heights (Mahl et al., 2015).

However, as they are a relatively new concept, the potential water quality benefits of two-stage ditches in reducing P loads are less certain (Christopher et al., 2017; Englund, 2020; Hodaj et al., 2017). Several studies have reported on the P reduction of two-stage ditch systems with varying results (Christopher et al., 2017; Davis et al., 2015; Hodaj et al., 2017; Mahl et al., 2015). Mahl et al. (2015) details that, two-stage ditch systems SRP concentration reductions ranged between 3 to 53%, with only half of the ditches having significant reductions. However, samples were collected primarily at base flow, rather than during inundation of the floodplain benches when greater nutrient reductions are expected (Davis et al., 2015; Mahl et al., 2015; Mayer et al., 2007; Noe and Hupp, 2009). Davis et al. (2015) results showed a reduction in turbidity at all sites during floodplain bench inundation, but reductions in total suspended solids (TSS) and P concentrations (both soluble reactive and total) was only observed for sites with extended periods of inundation. Hodaj et al. (2017) report two-stage ditches reducing the loads of TP by 40% and SRP by 11%. Through the use of a Soil Water Assessment Tool (SWAT) model, Christopher et al. (2017) found two-stage ditches effective at reducing TP export in a watershed at varying levels of implementation; with two-stage implementation in 25, 50, and 100% of headwater reaches TP export was reduced by 12, 20 and 31%, respectively. However, while the nutrient percent load reduction and cost of two-stage ditch implementation was found to be good compared with other techniques, it requires watershed-scale adoption to significantly reduce nutrient concentrations in line with policymaker requirements (Christopher et al., 2017). Overall, two-stage ditches are a promising mitigation technique that require further studies to investigate their effectiveness and optimisation.

6.3.5 Duckweed harvesting

Eutrophication is characterised by excessive duckweed and algal growth as a consequence of one or more of the limiting growth factors of photosynthesis being present in excess, e.g., sunlight intensity; carbon dioxide; nutrients; temperature; pH (Ansari and Khan, 2008; Chislock et al., 2013; Schindler, 2006). A significant threat to biodiversity worldwide, algal and duckweed blooms limit light penetration through dense surface coverage, reducing submergent macrophyte growth. This, alongside microbial decomposition of excessive amounts of organic matter as these blooms die, causes depletion of oxygen in the water column (anoxic conditions), bringing about fish kills and development of bad odours (Chislock et al., 2013; Crocker et al., 2021; Padedda et al., 2017; Riley et al., 2018; Zhang et al., 2017).

However, the implementation of duckweed as a treatment of various anthropogenic wastewater effluents is well documented in scientific literature (Bergmann et al., 2000; Cheng and Stomp, 2009; Culley et al., 1981; Dinh et al., 2020; Fernandez Pulido et al., 2021; Iqbal et al., 2019; Ishizawa et al., 2020; Li et al., 2020; Muradov et al., 2014; Willett, 2005; Zhou et al., 2019). Albeit, considering the broad-spectrum of experimental designs at varying scales, under disparate artificial and/or environmental conditions, conclusions of considerable importance are difficult to decipher from comparisons of separate studies (Paterson et al., 2020). Nonetheless, macrophyte biomass harvesting from eutrophic water systems remains an advocated means of nutrient mitigation and recycling (Ansari and Khan, 2009, 2008; Grosshans, 2014; Quilliam et al., 2015).

Duckweed, as compared to other macrophytes, reproduces rapidly and is harvested with ease from the water's surface, resulting in removal of P directly from the water column (Roijackers et al., 2004;

Willett, 2005; Zirschky and Reed, 1988). Harvested duckweed can then be processed into products such as animal feed, fertiliser, and biofuel thanks to high contents of protein, fat, amino acids, and starch (Baliban et al., 2013; Cheng and Stomp, 2009; Kreider et al., 2019; Zirschky and Reed, 1988). On account of these advantages, duckweed is seen as a promising candidate for eutrophic surface water phytoremediation. Regular harvesting is a requirement for production optimisation, as duckweed overcrowding forms dense layered mats causing duckweed die-off decreasing the relative growth rate (RGR) and returning P to the water column following degradation (Chakrabarti et al., 2018; Cheng and Stomp, 2009; Hasan and Chakrabarti, 2009; Roijackers et al., 2004). This frequent duckweed removal may potentially provide the benefit of sunlight provision to submergent macrophytes permitting photosynthetic oxygen production within the water column, combating anoxic conditions. Although, removal of duckweed surface coverage and its heavy water shading effect has the potential to permit competitive algal bloom production (Farrell, 2012; Roijackers et al., 2004; Szabó et al., 1999). When growing in competition with algae in eutrophic ditch systems, duckweed typically dominates as factors that affect duckweed growth by reducing surface coverage are unlikely. Factors such as wave action and high winds are more prevalent in open water systems, such as lakes, and can cause excessive layering of duckweed allowing sunlight to penetrate the water column in cleared areas, stimulating algal bloom production, as well as die-off of lower layers of duckweed as they are cut off from light (Hasan and Chakrabarti, 2009; Roijackers et al., 2004).

Under near optimum duckweed growth conditions, Landolt and Kandeler (1987) found that the potential dry mass (DM) harvest of duckweed was 20 g DM m^{-2} day^{-1} (73 t DM ha^{-1} $year^{-1}$). However, field results in less than optimal conditions show 5 to 20 t DM ha^{-1} $year^{-1}$ (1.4 to 5.5 g DM m^{-2} day^{-1}) is more realistic (Leng, 1999). For eutrophic systems with optimum environmental conditions, Hasan and Chakrabarti (2009) suggest 10 to 20 t DM ha^{-1} $year^{-1}$ (2.7 to 5.5 g DM m^{-2} day^{-1}) is potentially harvestable. In less than optimal conditions, the RGRs of duckweeds is reported to be around 0.1 g DM m^{-2} day^{-1} to 0.3 g DM m^{-2} day^{-1} (Chakrabarti et al., 2018; Njambuya et al., 2011; Oron, 1994). Rejmánková (1975) observed for *L. minor* an RGR of 0.20 g DM m^{-2} day^{-1} in a study under field conditions.

In a study carried out at West Sedgemoor (Crocker et al., 2022), one of the wetlands that makes up the Somerset Levels Ramsar site, duckweed was harvested for P from the North and South Drove Rhynes. It was found that during the summer and autumn was the best time to implement a potential wild duckweed harvesting scheme, for P mitigation on the Somerset Levels. The seasons of summer and autumn had the most optimum conditions for duckweed growth, due to higher temperatures and an established dominance over algae post spring. Across these seasons, the average harvest of duckweed DM was 17 g DM m^{-2} and the average concentration of P in the duckweed biomass was

0.5% DM. Literature states that P typically makes up between 0.03 to 2.8% of a typical duckweed DM (Landolt and Kandeler, 1987). The West Sedgemoor value is on the lower end of the literature range, likely because of the duckweed being wild rather than purposely cultivated under optimal conditions. Assuming a harvest of 8.5 g DM m^{-2} leaving half of the available duckweed to allow for regrowth of what was harvested, assuming a RGR of 0.20 g DM m^{-2} day^{-1}, this allows for 36 harvests to be undertaken over the summer and autumn. North and South Drove Rhyne's combined length is 7553 m with a total surface area estimated as 25,400 m^2. Therefore, this would yield a total estimated biomass of 7770 kg DM, removing an estimated total of 39 kg P from the system. To dilute 39 kg P to the Common Standards Monitoring Guidance (CSM) for P in ditches of 0.1 mg L^{-1} TP, the volume of water required would be 3.9×10^8 L (309000 m^3). In comparison, at West Sedgemoor, the available ditch channel storage during winter under current conditions, winter theoretical maximum and summer under current conditions are 315540 m^3, 408630 m^3, and 204315 m^3 respectfully (Stratford and Acreman, 2014).

If duckweed harvesting were to be implemented across the Somerset Levels, it is likely the techniques used would mirror those of the current weed cutting ditch maintenance 'keeching'. Harvested duckweed could be left on the ditch banks, akin to emergent macrophytes removed during keeching, but for the purpose of drying as sunlight is an efficient low-cost way of drying duckweed (Leng, 1999). Duckweed lacking a waxy cuticle (present on terrestrial plants to prevent water loss) allows duckweed to be dried rapidly in sunlight (Cheng and Stomp, 2009). It would also have the added ecological benefit of allowing aquatic fauna the chance to return to the ditches. However, leaving the duckweed on the banks indefinitely could negate attempts of removing P from the water column as duckweed undergoes biodegradation releasing P (Schindler and Comber, 2021). The most feasible uses of the dried duckweed product in the Somerset Levels catchment would be as cattle feed or as an agricultural amendment (Cheng and Stomp, 2009; Kreider et al., 2019). Although, any industry setup to use duckweed would have to be made in understanding that the goal of P mitigation is to work towards and maintain non-eutrophic conditions that would not support duckweed blooms. Therefore, duckweed harvesting would be a short to medium term mitigation technique focusing on accelerating recovery of a given system.

6.3.6 Filter substrates

Over recent years, considerable work has been carried out in P removal utilising filter systems with active media. In contrast to traditional filtration, reactive media filtration relies on substrate materials which remove P by sorption or direct precipitation processes. In short, this involves mobilisation of inorganic P from the water column to the surface of the reactive components of the media (e.g., aluminium, calcium, iron) where accumulation of P occurs. Therefore, Ca, Fe and Al content is important in efficient P removal via sorption and precipitation processes (Brix et al., 2001; Bunce et al., 2018; Vohla et al., 2011).

Most prevalent materials used as P filter substrates are generally categorizable as either natural materials, industrial by-products, or man-made products. Natural materials used as filter media for P removal include alunite, apatite, bauxite, dolomite, gravels, laterite, limestone, maerl, opoka, calcined waste eggshells, oyster shells, sands, wollastonite, and zeolite (Belliera et al., 2006; Brogowski and Renman, 2004; Drizo et al., 1999; Gray et al., 2000; Hill et al., 2000; Karaca et al., 2004; Köse and Kıvanç, 2011; Özacar, 2006; Roy, 2017; Sakadevan and Bavor, 1998; Seo et al., 2005; Vohla et al., 2011, 2005; Wood and McAtamney, 1996). Industrial by-products used as filter media for P removal include coal ash, sediment of oil shale ash, furnace slags, and gypsum (Bryant et al., 2012; Drizo et al., 1999; Gustafsson et al., 2008; Roy, 2017; Vohla et al., 2011, 2005; Yan et al., 2007). Man-made products used as filter media for P removal include Filtra P, Filtralite™, Leca, Norlite, and other lightweight aggregates (LWA) (Gustafsson et al., 2008; Hill et al., 2000; Vohla et al., 2011, 2005; Zhu et al., 1997).

In a comprehensive review of media for P removal with regards to constructed wetlands, Vohla et al. (2011) found significant positive correlation between the P retention and CaO and Ca content of filter materials. Therefore, precipitation is the dominant P retention process in constructed wetlands. Various industrial by-products were found to have reported the highest P removal capacities (up to 420 g P kg^{-1} for some furnace slags), the next highest was by natural materials (maximum 40 g P kg^{-1} for heated opoka), and followed by man-made filter media (maximum 12 g P kg^{-1} for Filtralite™) (Vohla et al., 2011). Pre-treatment for some filter materials has the potential to enhance P adsorption and allow for a longer lifetime, by decreasing clogging risk, pH, and/or increasing surface area (Roy, 2017; Vohla et al., 2011). For instance, Köse and Kıvanç (2011) found that eggshells calcinated at increased temperatures (>800 ° C compared to ≤ 600 ° C) had substantially enhanced P adsorption. Pre-treatment processes can, however, increase the cost, energy use, greenhouse gas emissions, and material investments requiring further assessments of sustainability (Roy, 2017). Another primary concern when considering a filter media is potential influence of solution pH, which can be substantial and costly to correct. Thermal and chemical pre-treatment is a promising option to reduce this risk, although, the method requires further investigation at full-scale and over extended periods (Bunce et al., 2018; Roy, 2017; Wium-Andersen et al., 2012; Yin et al., 2017). Despite hardly any performed investigations of the long-term saturation time of materials, calculations base off of available data suggest the majority of filter materials decrease in P retention capacity after 5-years of continuous application (Vohla et al., 2011).

The further application of the technology is, therefore, dependant on the recyclability of saturated materials in use cases such as fertiliser. Recycling of P-rich materials and substrates as soil fertiliser has been the topic of several studies (Hylander et al., 2006; Hylander and Simán, 2001; Kõiv et al., 2012; Kvarnström et al., 2004; Roy, 2017; Vohla et al., 2011). These materials can be limited in potential for agricultural applications owing to low P content by mass and relative insolubility, but in some cases, slow-release fertilisation potential does exist (Kõiv et al., 2012). In an investigation utilising P-enriched filter mediums as fertiliser for growing barley in pots, Hylander et al. (2006) found the majority of them stimulated plant growth compared to a unfertilised control. However, further studies are needed to ensure applicability, understand fertilisation potential and potential impacts of their use. One concern is the potential of saturated materials to contain high concentrations of heavy metals, causing contamination of the surrounding environment (Roy, 2017; Vohla et al., 2011).

When applied for use in drainage ditches, P filter substrates are contained within P removal structures; essentially landscape-scale filters designed to trap dissolved P in drainage water. These structures are widely variable, requiring site specific design, but each comprise of several core components (Penn and Bowen, 2018):

- A sufficient mass of an unconsolidated P filter media.
- Located in a hydrologically active area that receives and/or exhibits dissolved P concentrations higher than 0.2 mg L^{-1}.
- The target water can flow through the P filter media at a suitable flow rate to maximise contact.
- The P filter media can be removed and replaced once its p retention capacity has decreased below the desired rate.

Following these requirements, P removal structures are best suited within the flowing ditches inputting water into wetland systems, rather than ditches within wetland systems which can be relatively stagnant. In a comprehensive review of media for P removal with regards to P removal structures, Penn et al. (2017) found that structures with longer retention times and inflow P concentrations were more efficient. Increased retention times allowed Ca-rich P filter media higher efficiency, while short retention time systems had higher cumulative removal efficiency using Fe-based filter media (Penn et al., 2017). Inherent variability of P removal structures, due to differing designs and environmental conditions, means their efficacy is widely variable. Due to maintenance and clean-out requirements, ditch filtration can be impractical and not cost effective depending on the availability and efficiency of the P filter media used (Bryant et al., 2012; Penn et al., 2017). However, modelling approaches have been developed allowing prediction of filter material effectiveness greatly aiding filter design and filter use decisions (Mcgrath et al., 2012; Penn and

McGrath, 2011). Additionally, water quality improvement benefits of P removal structures are easily quantified, as the amount of dissolved or total P removed, compared to estimation of potential P load reductions involved with other nonpoint management practices (Penn et al., 2007).

6.3.7 Next steps

The development of the solutions presented here into functioning P mitigation solutions (e.g., for the Somerset Levels and Moors) requires several steps be taken (Bowers, 2022):

- Desired solution identification and determination of likely costs, implementation timescales, maintenance requirements, and delivery mechanisms. This is site specific and likely to be undertaken by the formation of mitigation plans to draw up developer contributions perhaps established through supplementary planning documentation.
- Implementation of a database tracking to record P loading at developments and the mitigation solutions used. This tool can also be used to track secondary benefits such as biodiversity net gain and carbon offsetting.
- Standardised legal agreements should be composed and utilised as the basis in future mitigation schemes.

The list of potential P mitigation solutions revolving around ditch management that have been identified are explored and summarised in Table 6.1.

Table 6.1: Summary of in-ditch phosphorus (P) mitigation solutions.

Mitigation solution	Duration timescales	Best available evidence?	Effective beyond reasonable scientific doubt?	Precautionary?	In Perpetuity?
Raise water levels	Long-term	Yes	No – further assessment required to understand likely changes.	Yes	Yes
Sediment dredging	Short / medium-term	Yes	Yes	Yes	Yes
Emergent macrophyte harvesting	Short-term	Yes	Yes	Yes	Yes
Channel widening	Long-tern	Yes	Yes	Yes	Yes
Duckweed harvesting	Short-term	Yes	No - further assessment required	Yes	No
Filter substrates	Medium / long-term	Yes	No – monitoring required	Yes	Yes

6.4 Conclusions

Based on the material outlined in this review, there is an undoubted need for practical management options to help mitigate phosphorus in eutrophic freshwater ditch systems. Evidence has been reviewed that demonstrates that appropriate and targeted ditch management practices can play a significant role in reducing both phosphorus load and legacy phosphorus concentrations. A wide variety of management options exist, although some are best suited to particular environments and landscapes, some to accelerating recovery rate rather than initialising recovery, and data regarding the efficiency of certain approaches is rather limited. The development of the management options into functioning phosphorus mitigation solutions requires determination of likely costs, implementation timescales, maintenance requirements, and delivery mechanisms, at site specific level.

7 Conclusions

Presented within this thesis is research demonstrating the importance of the partitioning of phosphorus (P) between sediment, water column, and algae/duckweed, in the determination of how ditch management can be modified to accelerate recovery, including dealing with the existing burden of P, within a wetland ditch system. Factors affecting P partitioning, such as flow, water levels, seasonality, and physicochemical interactions are also considered.

The experimental investigations conducted during the project were designed with the aim of providing up-to-date consistent and comprehensive monitoring data for the Ramsar ditch systems, to tackle the issue of a lack of research concerning P dynamics specific to drainage ditch processes and management. The research presented within this thesis provides understanding as to how the complex seasonal water flow paths and levels affect transport of P throughout the wetland ditch systems, previously a recognised gap in knowledge of these systems. This will be useful information for future development of management options into functioning P mitigation solutions.

Land management practices of wetland fields were found to have a notable impact on the geochemistry of the adjacent surrounding ditches, with spatial variance observable in the chemical properties of the sediment. Elevated P concentrations in sediment were observed up to 4,220 mg Kg^{-1}, almost 10 times that which may be expected from background levels. In ditches adjacent to land managed as waterfowl nature reserve, correlations were observed P and Iron (Fe), indicating P bound to Fe(III) compounds, whereas ditches surrounded by agricultural land showed no correlations between P and selected parameters. Nature reserve land surrounded ditches were characterised by relatively higher concentrations of sulphur, bromine, chlorine, and strontium, whereas sites surrounded by agricultural land had higher silicon, titanium, aluminium, and yttrium concentrations. Ditches outside of the nature reserve were generally correlated to higher inorganic phosphorus (IP) and total phosphorus (TP) concentrations, so are more likely to facilitate eutrophic algal blooms as a source of bioavailable P to the overlying waters than sites surrounded by nature reserve land which were more associated with higher organic phosphorus (OP) concentrations. These findings support potential viability of the 'taking land out of agricultural use' catchment-level nature-based solution to reduce loadings from diffuse pollution P inputs.

Phosphorus water concentrations within the ditches were found to be both temporally and spatially variable, with the complex seasonal water flow paths, levels, and hydrological block management affecting this. Analysis of TP in surface waters indicated that all sites have the potential for TP concentrations to be above the Common Standards Monitoring (CSM) environmental quality standard value of <0.1 mg TP L^{-1}, with all sites exceeding the CSM target in the summer and autumn months. The highest concentration observed was 1.88 mg L^{-1} during the summer, over 10 times the CSM target value. Surface water TP increases were found to not be driven by any singular fraction but instead a combination of increases across all the observed fractions: total soluble phosphorus (TSP), total reactive phosphorus (TRP) & soluble reactive phosphorus (SRP). However, when sectioned into different hydrological block areas, the hydrological block 4 spring and summer data only showed strong positive correlations between TP & TRP, and separately TSP & SRP, with the summer also showing strong positive correlation between TSP & TRP. The strong positive correlations between TP & TRP without significant correlation between TP & SRP indicated that hydrological block 4 TP increases were driven by particulate reactive phosphorus (PRP) concentrations in the spring and summer. Clear distinction between hydrological block 4 and the other hydrological blocks, being characterised by relatively lower concentrations of TP, TSP, TRP, and SRP. This indicates that the sites in hydrological block 4 are less susceptible to seasonal spikes in P concentration than sites in other hydrological blocks, likely due to the lacking flow connectivity of hydrological block 4 to the rest of the site and external runoff water P loadings, owing to the higher elevation of the block. Understanding this connectivity between the ditches and external runoff water P loadings is important for effectively targeting appropriate P mitigation solutions, prioritising areas with higher P inputs and legacy burdens that have the potential to supply other locations within a site.

An assessment into the possibility of harvesting duckweed and algae to reduce internal cycling and to export nutrients, found that during the summer and autumn was the best time to implement a potential wild duckweed harvesting scheme, due to higher temperatures and an established dominance over algae post spring. If implemented at the ditches investigated at West Sedgemoor, an estimated 39 kg of P could be removed per harvest period, which would otherwise require 3.9×10^{8} L of water to dilute down to the CSM target of <0.1 mg L^{-1}. If duckweed harvesting were to be implemented across the Somerset Levels, it is likely the techniques used would mirror those of the current weed cutting ditch maintenance 'keeching'. Harvested duckweed could be left on the ditch banks, akin to emergent macrophytes removed during keeching, but for the purpose of drying as sunlight is an efficient low-cost way of drying duckweed prior to removal. Frequent duckweed removal from ditch systems may potentially provide the benefit of sunlight provision to submergent macrophytes permitting photosynthetic oxygen production within the water column, combating anoxic conditions. Although, removal of duckweed surface coverage and its heavy water shading effect has the potential to permit competitive algal bloom production. The most feasible uses of the dried duckweed product in the Somerset Levels catchment would be as cattle feed or as an agricultural amendment. However, any industry setup to use duckweed would have to be made in understanding that the goal of P mitigation is to work towards and maintain non-eutrophic conditions that would not support duckweed blooms, adding difficulty for achieving cost effective implementation of the technique. Harvesting of wild wetland duckweed would be a short to medium term mitigation technique focusing on accelerating recovery but requires implementation that is cost effective and does not negatively impact the important ecology of a given ditch system.

Undoubtedly, there is a requirement for practical management solutions for P mitigation in eutrophic freshwater ditch systems. Evidence demonstrates the significant role that appropriate and targeted ditch management practices can play in reducing concentrations of both P load and existing legacy P burden. A diverse range of management options exist including water level management; dredging, emergent macrophyte harvesting and channel widening (two-stage channels); algae/duckweed harvesting; and filter substrates. However, some are best suited to particular environments and landscapes, some to accelerating recovery rate rather than initialising recovery, and data regarding the efficiency of certain approaches is rather limited. To achieve functioning P mitigation solutions, management options require assessment to determine likely costs, implementation timescales, maintenance requirements, and delivery mechanisms, at site specific level.

7.1 Prospects for further research

This thesis study focused on looking at how ditch management can be modified to accelerate recovery, including dealing with the existing burden of P in the system. This research topic was one of three areas identified by Natural England as having the greatest chance for improving the Somerset Levels and Moors situation, with regards to the eutrophication pressure. Naturally, investigation into these other two identified topics would offer a deeper understanding of the eutrophication issue:

1) Seeing what can feasibly be done to reduce P inputs across the catchments of the feeder rivers - implementing improvements at sewage treatment works (STWs), alongside changes in land management through catchment sensitive farming (CSF) or taking land out of agricultural use, Countryside Stewardship, innovative approaches such as EnTrade (a Wessex Water business) and possibly enhanced regulation of non-STW sources.
2) Looking at ways of intercepting P before it enters the ditch system from the rivers (e.g., constructed wetlands).

As for continuation of the research topic focused on in this study; an investigation implementing and assessing the effectiveness of the various ditch management mitigation techniques, identified within this thesis, would better inform future mitigation planning in ditch systems.

7.2 Limitations of the study

This study was adversely impacted from restrictions imposed in response to the (as of the time of this writing, ongoing) COVID-19 pandemic. As the first lockdown measures legally came into force in the UK on the 26 March 2020, this project was at a point where the vast majority of the immediate work to be performed was laboratory analysis. This caused time constraints which were only exacerbated by restrictive working conditions imposed by necessary social distancing health and safety measures upon reoccupation of the laboratories. For chapter 4, this meant that other sequential extraction techniques could not be explored experimentally which could have resulted in quantitatively reliable P fraction concentration data.

In the initial plans for this study, a placement project was designed to take place at Wessex Water, entailing being involved in their investigations and helping deliver the objectives of this work. The data and findings gathered during this proposed work were intended to form a chapter of this thesis. Alas, this placement project was unable to commence due to the rise of the COVID-19 pandemic, as the project would have involved sampling and analysis unable to be performed remotely.

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Zhou, Q., Li, X., Lin, Y., Yang, C., Tang, W., Wu, S., Li, D., Lou, W., 2019. Effects of copper ions on removal of nutrients from swine wastewater and on release of dissolved organic matter in duckweed systems. Water Res. 158, 171–181. https://doi.org/10.1016/J.WATRES.2019.04.036

Zhu, T., Jenssen, P.D., Mæhlum, T., Krogstad, T., 1997. Phosphorus sorption and chemical characteristics of lightweight aggregates (LWA) - potential filter media in treatment wetlands. Water Sci. Technol. 35, 103–108. https://doi.org/10.1016/S0273-1223(97)00058-9

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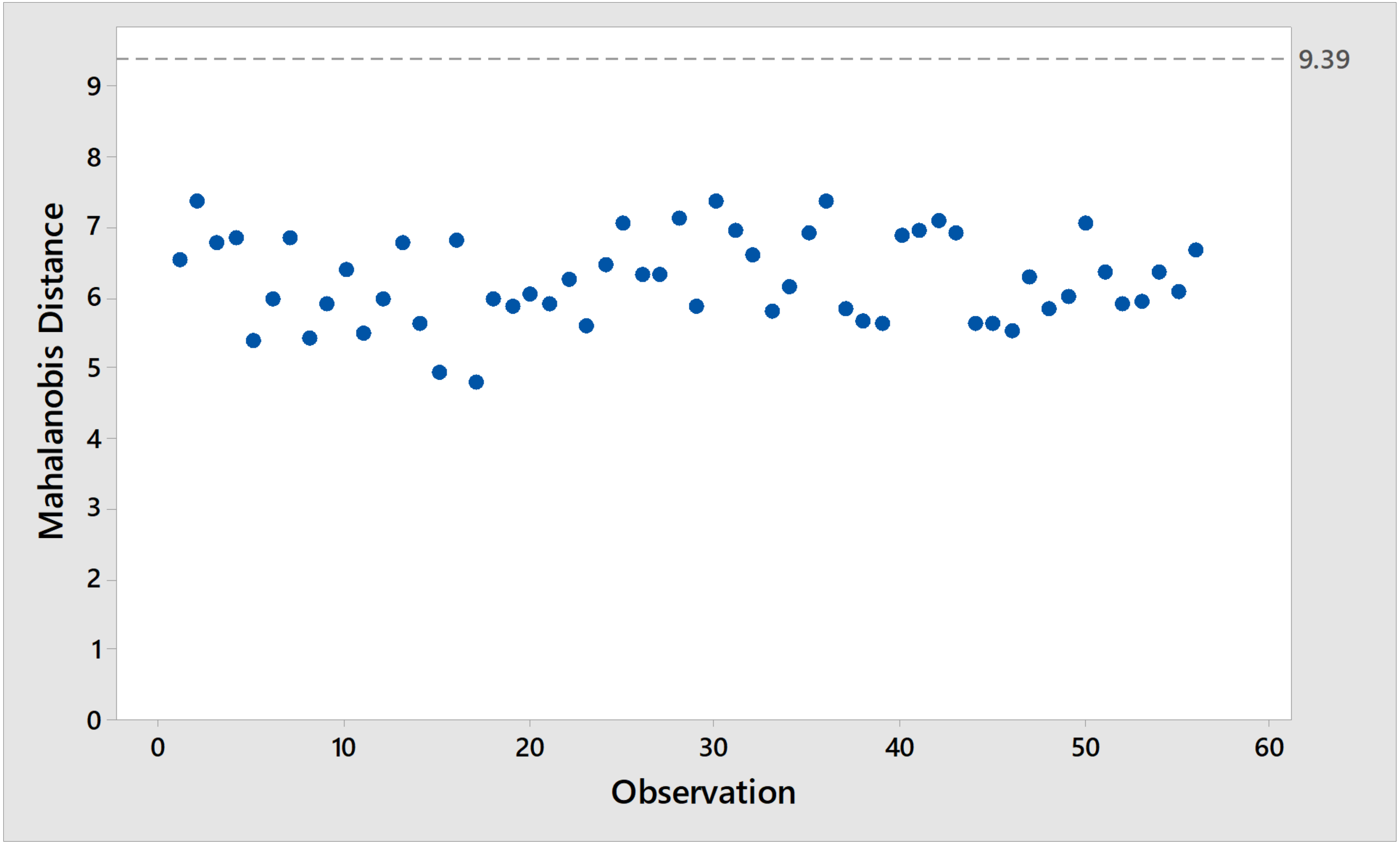
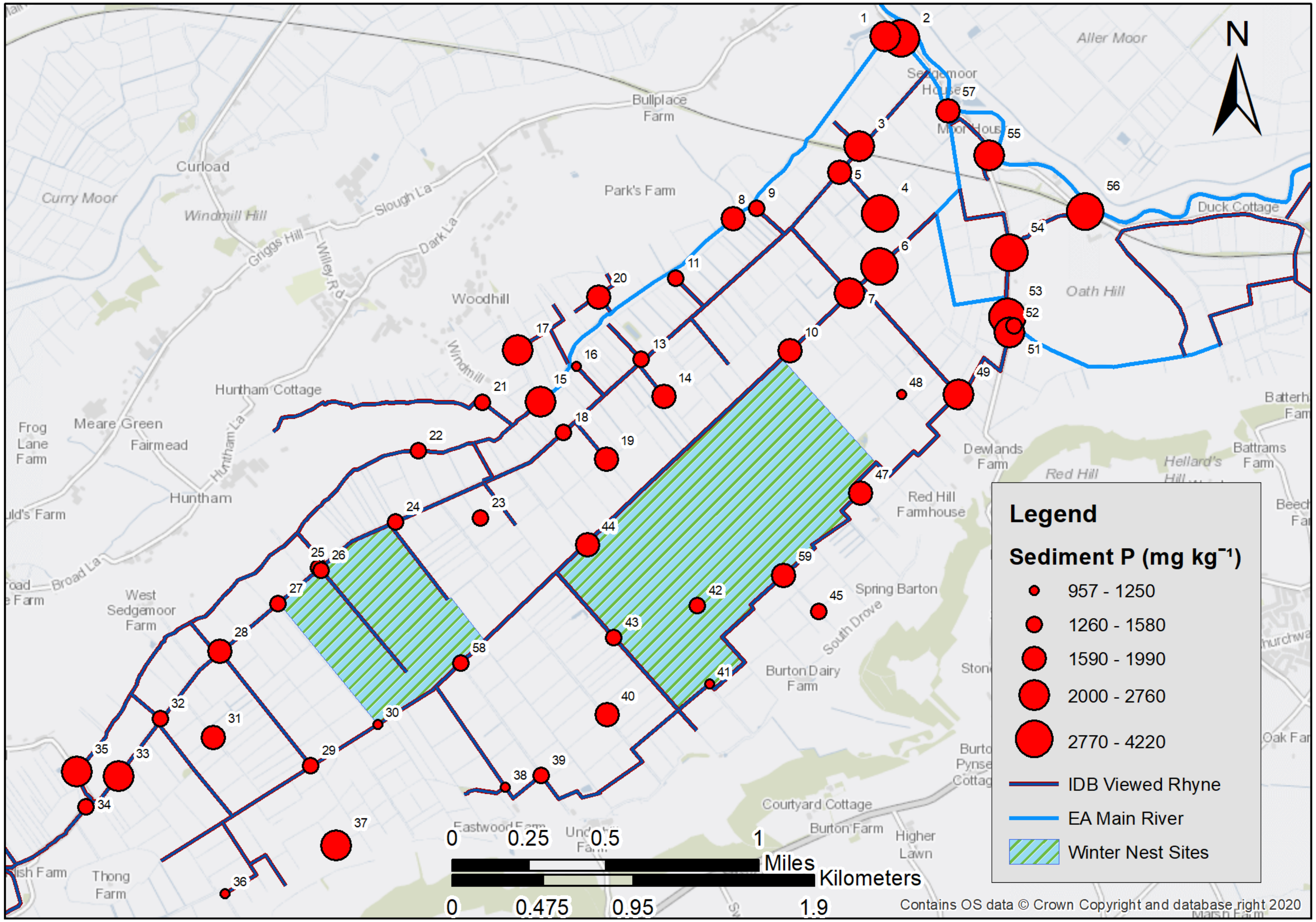
Appendix A.

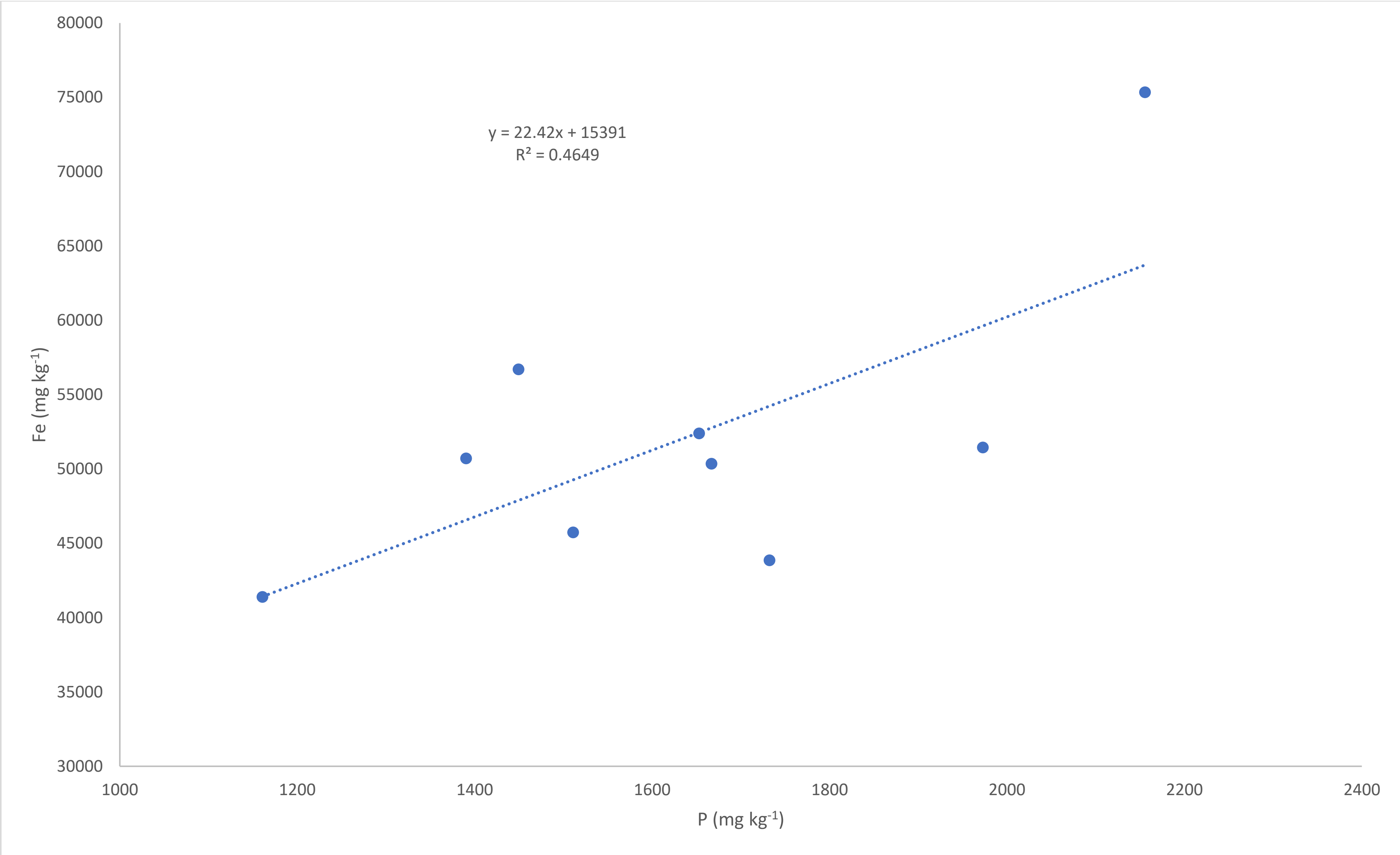
Spatial distribution of sediment phosphorus in a Ramsar wetland



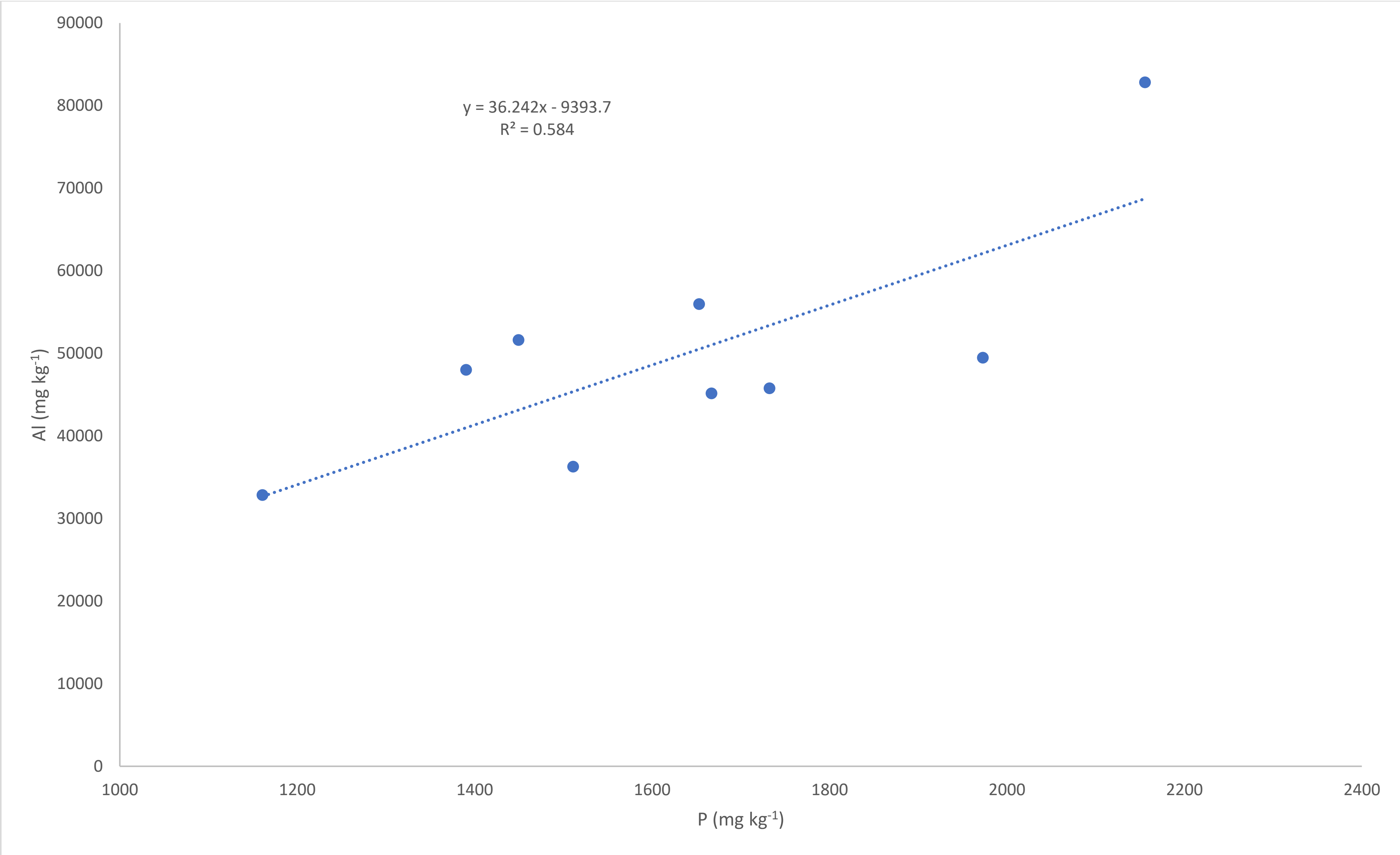
Appendix Figure A.1: Mahalanobis Distances plot of the data from principal component analysis of West Sedgemoor SSSI surface sediment samples. No outliers were observed.



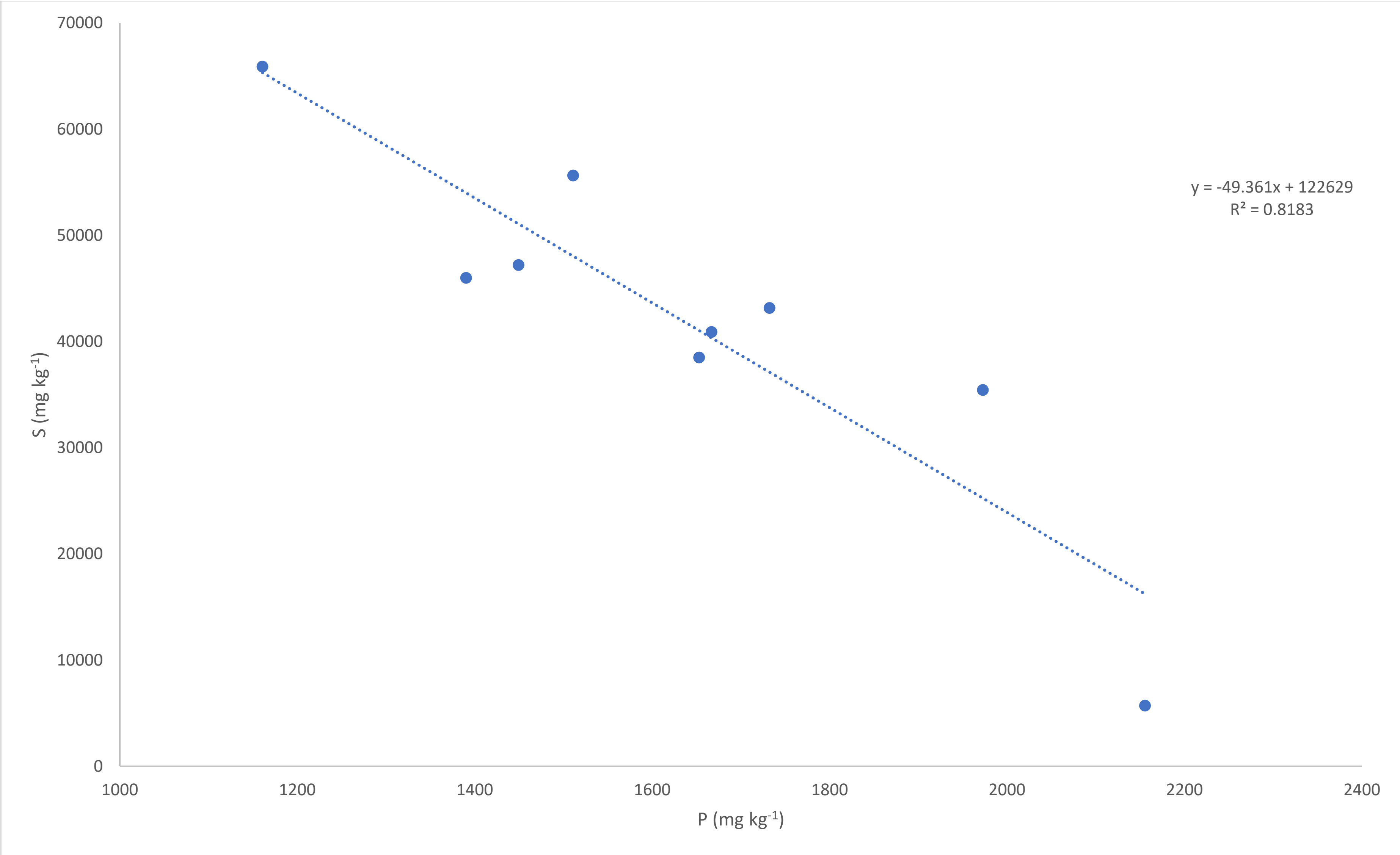
Appendix Figure A.2: Distribution of total phosphorus (TP) in sediments at West Sedgemoor SSSI, and winter nest site areas of wading birds. Data is displayed using the Jenks natural breaks classification method.



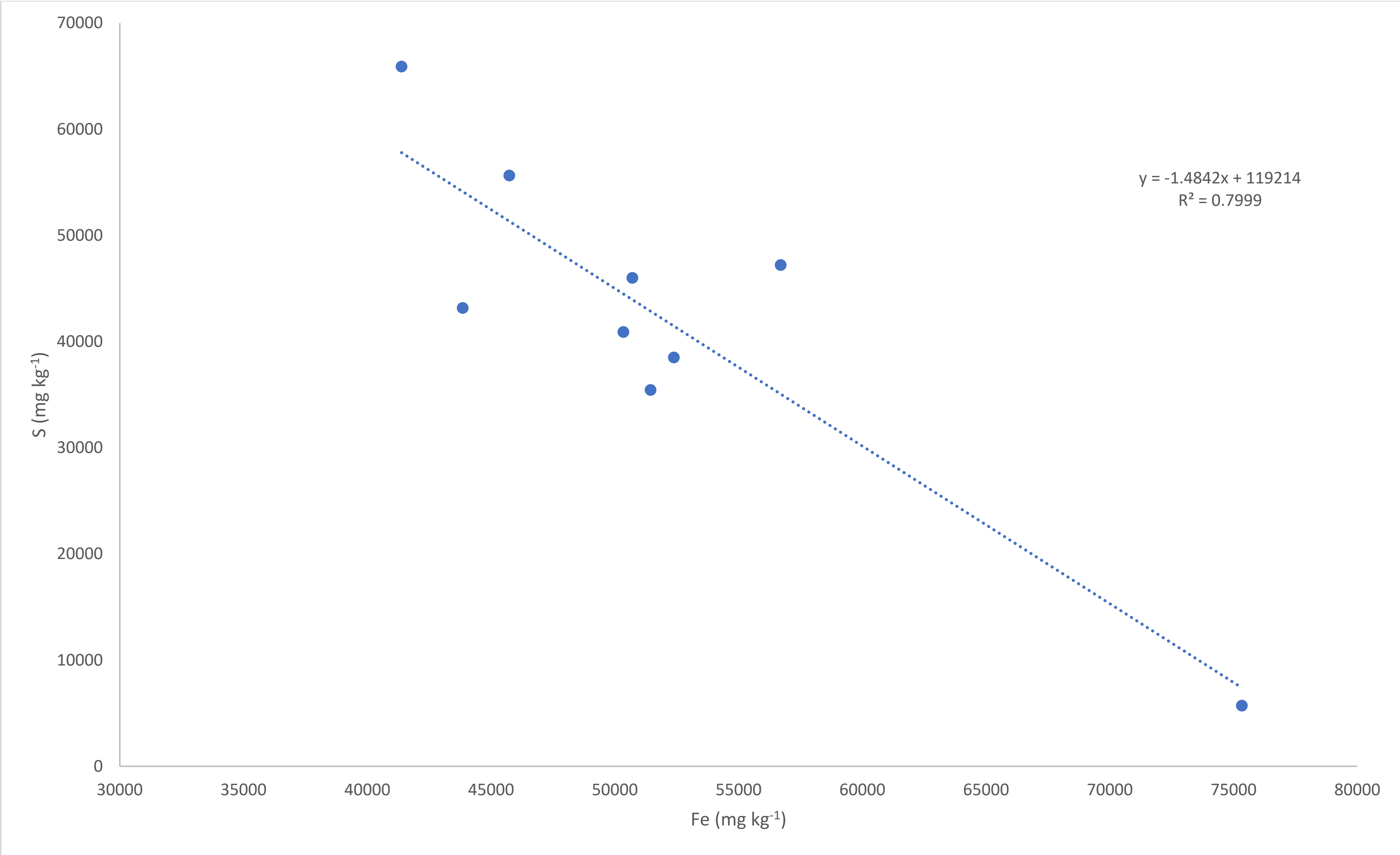
Appendix Figure A.3: Correlation scatter plot between P and Fe in surface sediments of sites surrounded by RSPB nature reserve land.



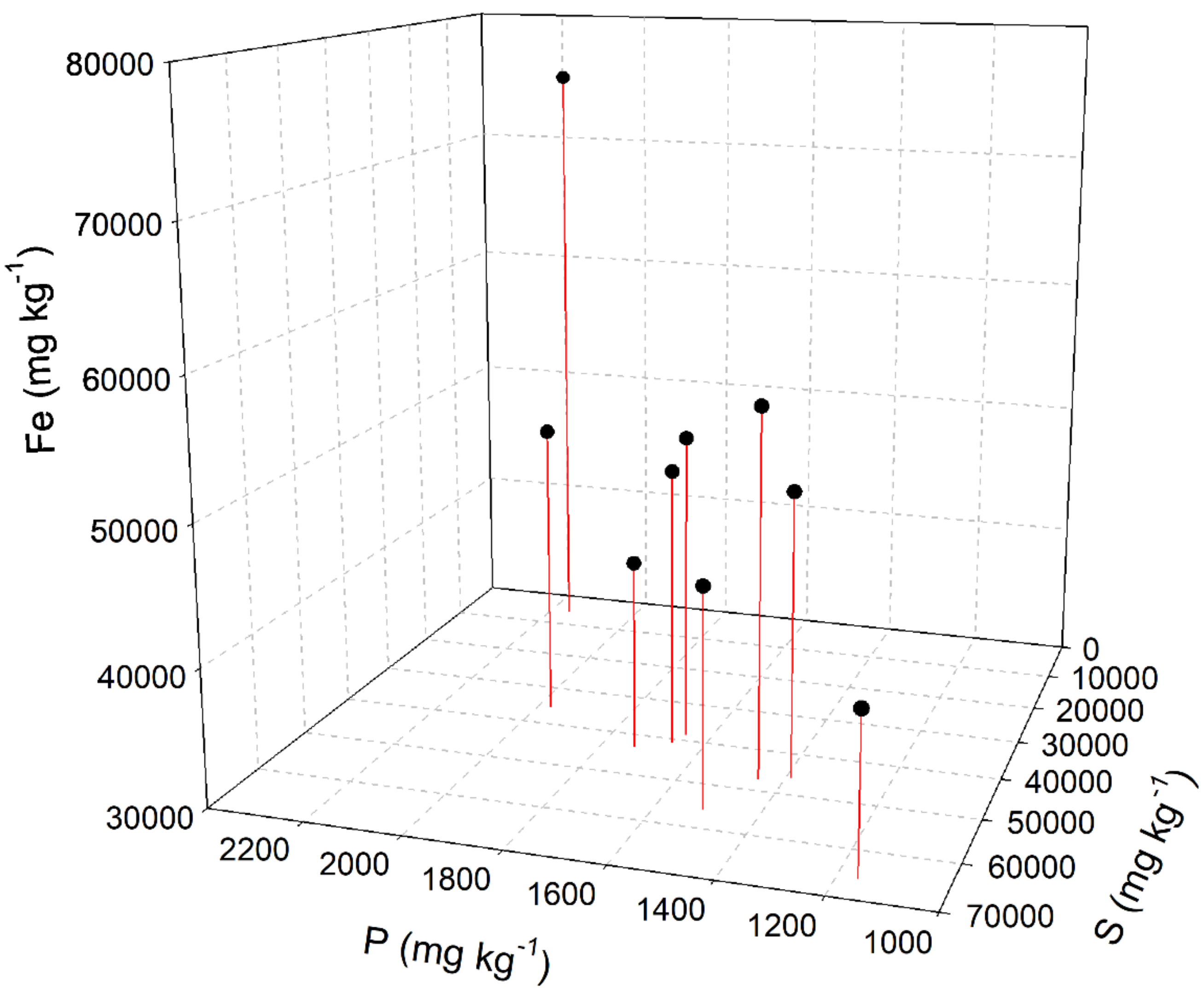
Appendix Figure A.4: Correlation scatter plot between P and Al in surface sediments of sites surrounded by RSPB nature reserve land.



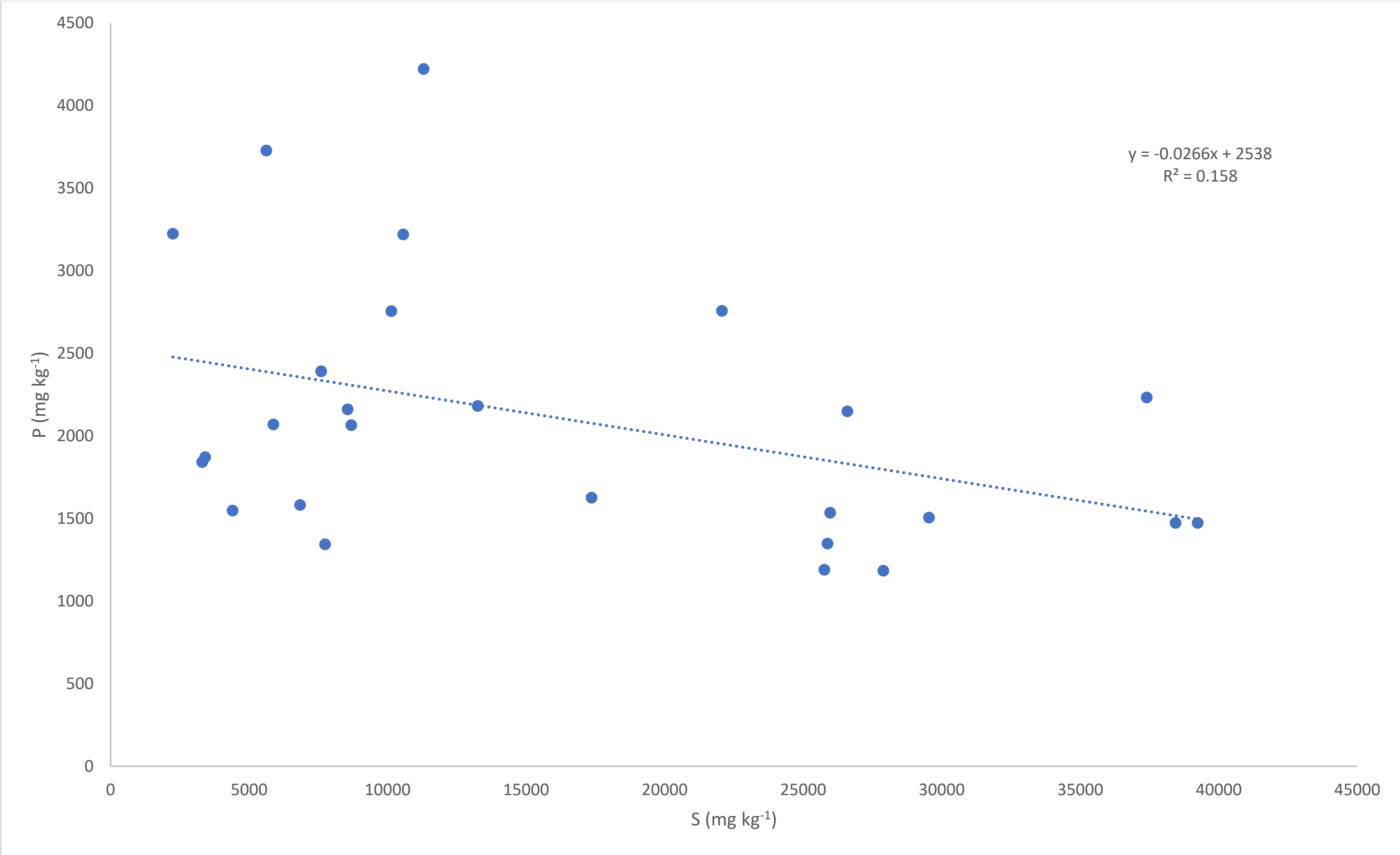
Appendix Figure A.5: Correlation scatter plot between P and S in surface sediments of sites surrounded by RSPB nature reserve land.



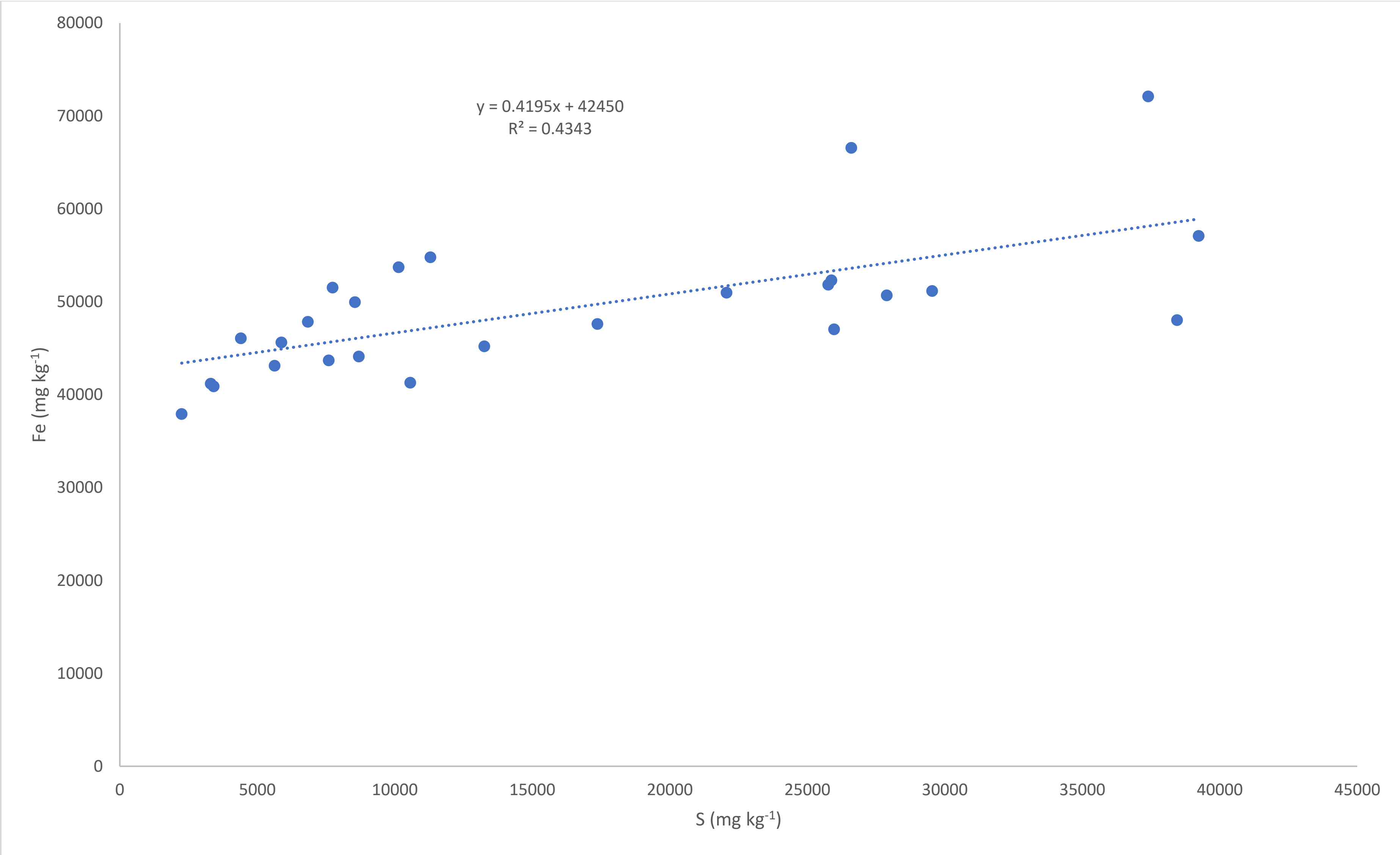
Appendix Figure A.6: Correlation scatter plot between Fe and S in surface sediments of sites surrounded by RSPB nature reserve land.



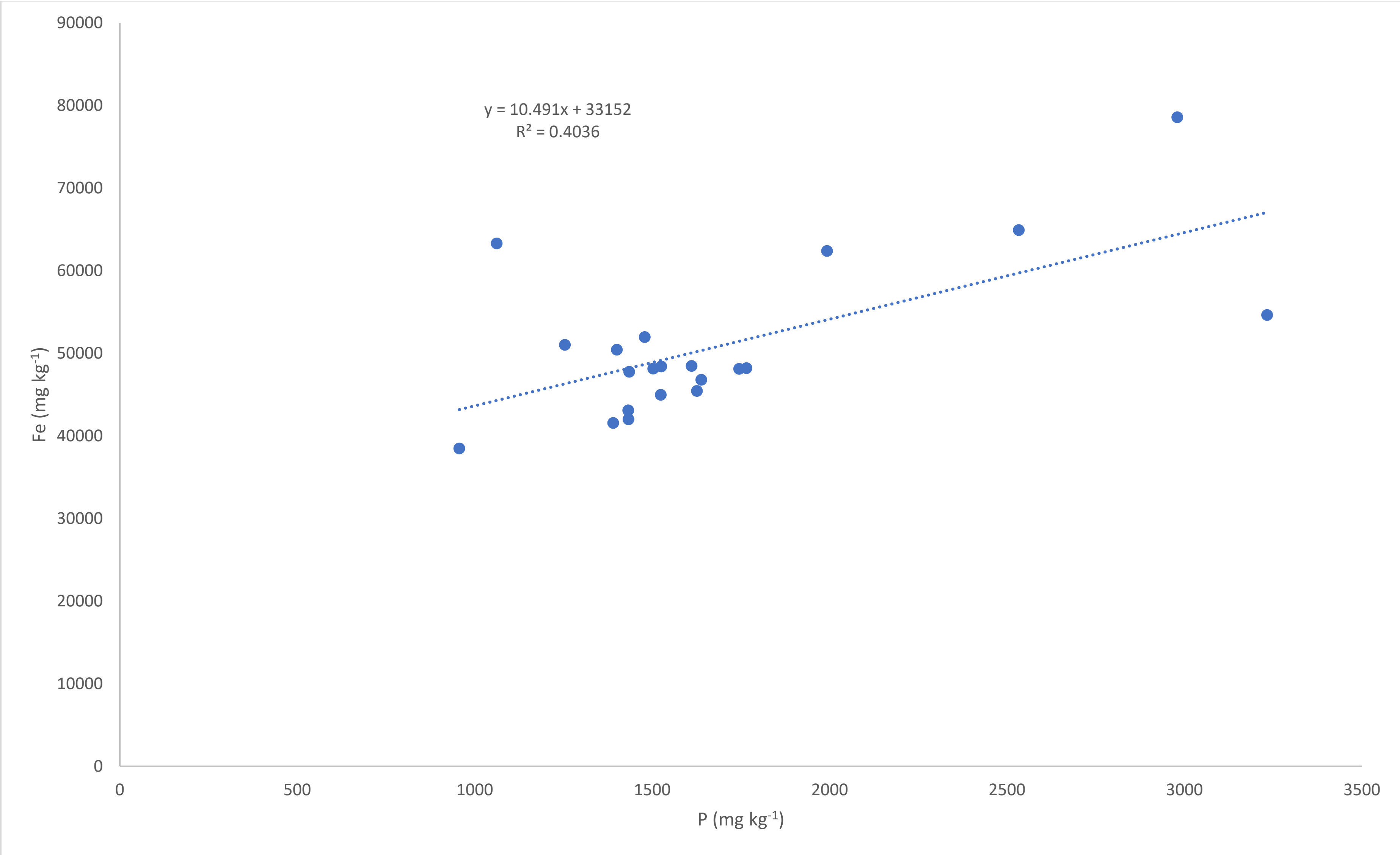
Appendix Figure A.7: 3D scatter plot of P, S and Fe in surface sediments of sites surrounded by RSPB nature reserve land.



Appendix Figure A.8: Correlation scatter plot between P and S in surface sediments of sites surrounded by land that is privately owned.



Appendix Figure A.9: Correlation scatter plot between Fe and S in surface sediments of sites surrounded by land that is privately owned.



Appendix Figure A.10: Correlation scatter plot between P and Fe in surface sediments of sites adjacent to both land that is RSPB nature reserve and land that is privately owned.

Appendix Figure A.11: Photograph examples of typical ditches on West Sedgemoor taken March 2018. (a) Site 32, (b) Site 30.

Appendix Table A.1: West Sedgemoor plant species and site localities.

Common Name	Latin Name	Site Location
Bullrush	*Typha latifolia*	Ditches
Soft rush	*Juncus effusus*	Ditches
Sea club rush	*Bolboschoenus maritimus*	Ditches
Reed canary grass	*Phalaris arundinacea*	Ditches
Hemlock waterparsnip	*Sium suave*	Ditches
Duckweed	*Lemna minor*	Ditches
Frogbit	*Hydrocharis morsus-ranae*	Ditches
Floating pennywort	*Hydrocotyle ranunculoides*	Ditches
Perennial ryegrass	*Lolium perenne*	Hay meadows
Southern marsh-orchid	*Dactylorhiza praetermissa*	Hay meadows
Marsh Marigold	*Caltha palustris*	Hay meadows
Cuckoo Flower	*Cardamine pratensis*	Hay meadows
Meadowsweet	*Filipendula ulmaria*	Hay meadows
Common meadow-rue	*Thalictrum flavum*	Hay meadows
Common knapweed	*Centaurea nigra*	Hay meadows
Meadow thistle	*Cirsium dissectum*	Hay meadows
Meadow foxtail	*Alopecurus pratensis*	Hay meadows
Willow trees	*Salicaceae*	Ditches, arable fields

Appendix Table A.2: Eigenvalues, explained variance and cumulative variance of the data from principal component analysis of West Sedgemoor SSSI surface sediment samples.

Order of Components	Eigenvalue	Explained variance /%	Cumulative variance /%
1	11.3	28.3	28.3
2	3.40	8.5	36.8
3	2.59	6.5	43.2
4	2.47	6.2	49.4
5	2.25	5.6	55.1
6	1.92	4.8	59.9
7	1.75	4.4	64.2

Appendix Table A.3: Target winter water levels and notable surroundings of sediment sampling sites.

Site	Raised Water Level Area (RWLA)	Winter Water Level (m ODN)	Notable Surroundings
1	Outside RWLA, West Sedgemoor Pumping Station	4.20	West Sedgemoor Pumping Station, Recreational Fishing Site, Road
2	Outside RWLA, West Sedgemoor Pumping Station	4.20	West Sedgemoor Pumping Station, Road
3	Outside RWLA	Not Penned ~4.20-4.70	Railway Track
4	Outside RWLA	Not Penned ~4.20-4.70	Railway Track
5	Outside RWLA	Not Penned ~4.20-4.70	Railway Track
6	Outside RWLA	Not Penned ~4.20-4.70	-
7	Outside RWLA	Not Penned ~4.20-4.70	-
8	Outside RWLA	Not Penned ~4.20-4.70	-
9	Outside RWLA	Not Penned ~4.20-4.70	-
10	Outside RWLA	Not Penned ~4.20-4.70	-
11	Outside RWLA	Not Penned ~4.20-4.70	-
12	17	4.95	-
13	Outside RWLA	Not Penned ~4.20-4.70	-
14	16	4.90	-
15	Outside RWLA	Not Penned ~4.20-4.70	North Curry and Stoke St Gregory Ridge Input
16	Outside RWLA	Not Penned ~4.20-4.70	-
17	Outside RWLA	Not Penned ~4.20-4.70	-
18	Outside RWLA	Not Penned ~4.20-4.70	-
19	15	4.90	-
20	Outside RWLA	Not Penned ~4.20-4.70	-
21	Outside RWLA	Not Penned ~4.20-4.70	North Curry and Stoke St Gregory Ridge Input
22	Outside RWLA	Not Penned ~4.20-4.70	-
23	Outside RWLA	Not Penned ~4.20-4.70	-
24	Outside RWLA	Not Penned ~4.20-4.70	-

Site	Raised Water Level Area (RWLA)	Winter Water Level (m ODN)	Notable Surroundings
25	Huntham	4.65	-
26	Huntham	4.65	-
27	Huntham	4.65	-
28	Huntham	4.65	-
29	12	4.85	-
30	Outside RWLA	Not Penned ~4.20-4.70	-
31	11	4.95	-
32	Outside RWLA	Not Penned ~4.20-4.70	-
33	Outside RWLA	Not Penned ~4.20-4.70	Widness Rhyne Input
34	Outside RWLA	Not Penned ~4.20-4.70	Widness Rhyne Input
35	Outside RWLA	Not Penned ~4.20-4.70	Widness Rhyne Input
36	Outside RWLA	Not Penned ~4.20-4.70	-
37	22	5.05	-
38	25	5.15	-
39	25	5.15	-
40	24	5.15	-
41	27	5.00	-
42	27	5.00	-
43	27	5.00	-
44	Outside RWLA	Not Penned ~4.20-4.70	-
45	30	4.90	-
46	Outside RWLA	Not Penned ~4.20-4.70	-
47	30	4.90	-
48	32	5.00	-
49	Outside RWLA	Not Penned ~4.20-4.70	Road
50	Outside RWLA	Not Penned ~4.20-4.70	Road
51	Outside RWLA	Not Penned ~4.20-4.70	Wickmoor Rhyne Input, Road
52	Outside RWLA	Not Penned ~4.20-4.70	Wickmoor Rhyne Input, Road

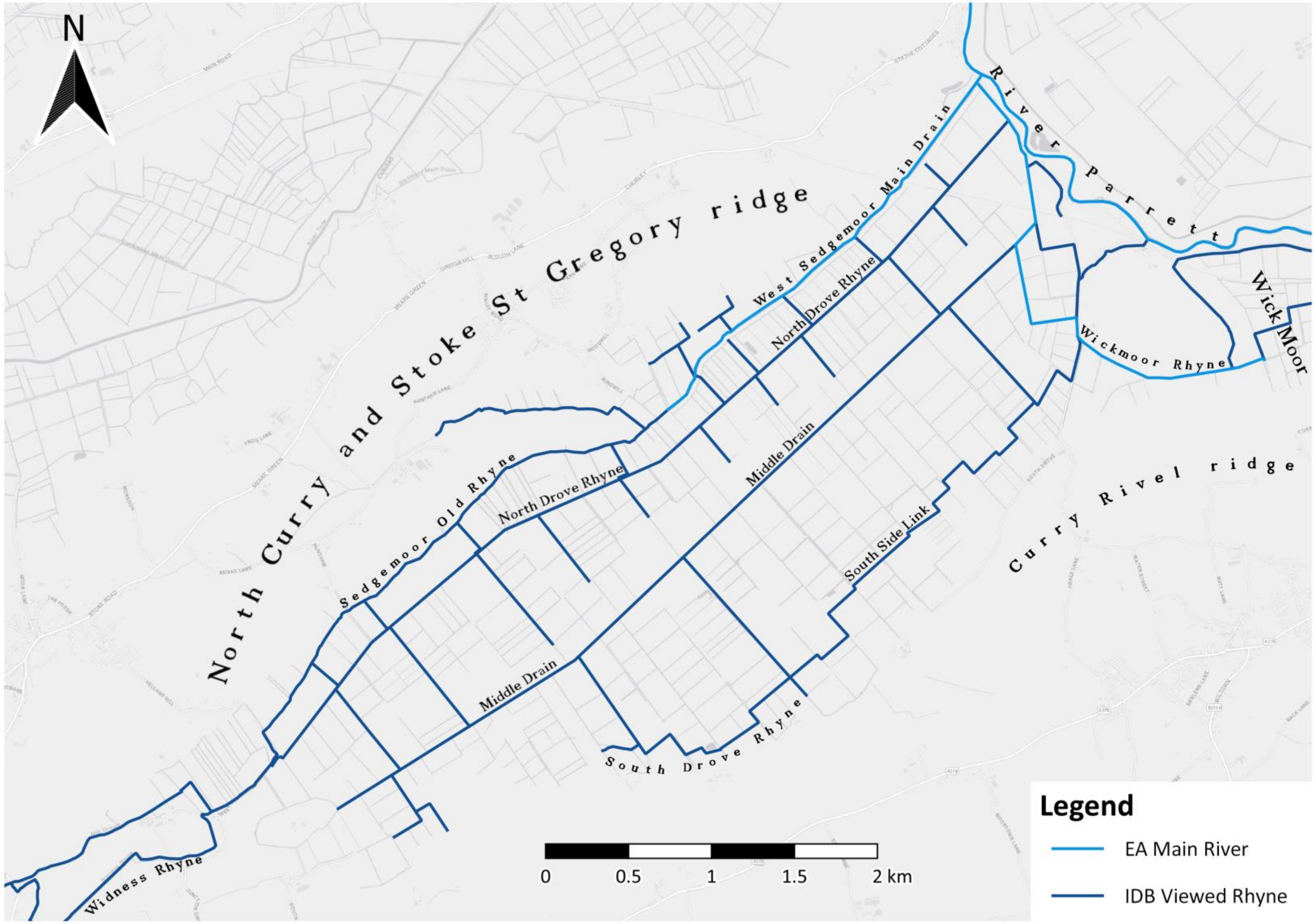
Site	Raised Water Level Area (RWLA)	Winter Water Level (m ODN)	Notable Surroundings
53	Outside RWLA	Not Penned ~4.20-4.70	Wickmoor Rhyne Input, Road
54	Outside RWLA	Not Penned ~4.20-4.70	River Parrett (Nontidal) Input, Road
55	Outside RWLA	Not Penned ~4.20-4.70	Road
56	Outside RWLA	Not Penned ~4.20-4.70	River Parrett (Nontidal) Input, Road
57	Outside RWLA	Not Penned ~4.20-4.70	Road
58	Outside RWLA	Not Penned ~4.20-4.70	-
59	30	4.90	-

Appendix Table A.4: Table of means and standard deviations (STD) for P, S, Fe, Al & Ca, and number of sites for each group of sites. (sites surrounded by RSPB nature reserve land, A; sites surrounded by land that is not RSPB nature reserve, B; and sites adjacent to both land that is RSPB nature reserve and land that is not RSPB nature reserve, C).

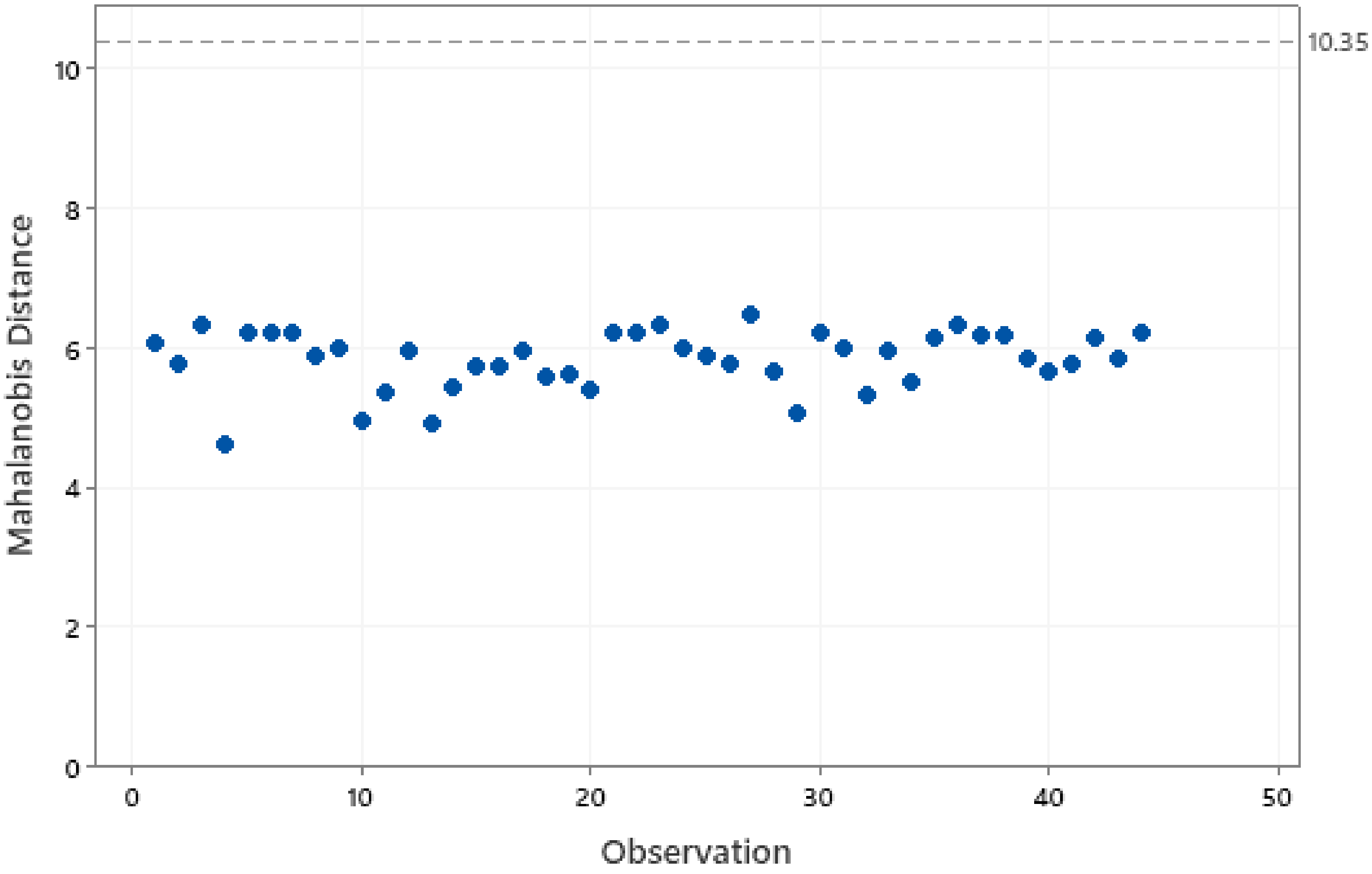
Group	No. of Sites	P		S		Fe		Al		Ca	
		Mean	STD	Mean	STD	Mean	STD	Mean	STD	Mean	STD
A	9	1630	±302	42100	±16400	52000	±9930	49800	±14300	66800	±25700
B	26	2100	±795	16400	±11900	49300	±7580	68700	±6000	54800	±16500
C	21	1690	±570	31400	±13200	50900	±9410	60000	±11100	60600	±23400

Appendix B.

Chemical speciation of sediment phosphorus in a Ramsar wetland



Appendix Figure B.1: Names of the notable rivers, rhynes, and ridges at West Sedgemoor SSSI.



Appendix Figure B.2: Mahalanobis Distances plot of the data from principal component analysis of West Sedgemoor SSSI surface sediment samples. No outliers were observed.

Appendix Table B.1: Certified values & uncertainty, and measured values & expanded uncertainty, of the BCR 684 certified reference material. Measured values are an average of 8 datasets. Expanded uncertainty of the measured values are estimated with the standard deviation of the measurements multiplied by a coverage factor of 2.

Certified parameters	Certified values (mg/kg)	Uncertainty (mg/kg)	Measured values (mg/kg)	Expanded uncertainty (mg/kg)
NAIP	550	21	467	108
AP	536	28	518	62
TP	1373	24	1143	163
IP	1113	9	1051	183
OP	209	35	211	37

Appendix Table B.2: Loss on ignition (LOI) values of West Sedgemoor SSSI surface sediment samples.

Site	LOI (%)	Standard deviation (%)	LOI (g)	Standard deviation (g)
5	66.2	0.326	0.667	0.00240
18	70.4	0.321	0.722	0.0214
20	88.7	0.283	0.937	0.00926
29	56.0	0.569	0.569	0.000252
35	84.5	0.162	0.881	0.0298
39	68.0	0.165	0.693	0.00742
44	46.4	0.575	0.468	0.00716
52	92.1	0.223	0.978	0.0358
55	85.9	0.032	0.877	0.00894
59	53.1	0.013	0.542	0.0132

Appendix Table B.3: Eigenvalues, explained variance and cumulative variance of the data from principal component analysis of West Sedgemoor SSSI surface sediment samples.

Order of Components	Eigenvalue	Explained variance (%)	Cumulative variance (%)
1	12.1	34.7	34.7
2	4.1	11.6	46.3
3	3.5	10.1	56.4
4	2.3	6.7	63.0
5	1.8	5.3	68.3
6	1.5	4.2	72.5
7	1.4	3.9	76.4

Appendix Table B.4: West Sedgemoor plant species and site localities.

Common Name	Latin Name	Site Location
Bullrush	*Typha latifolia*	Ditches
Soft rush	*Juncus effusus*	Ditches
Sea club rush	*Bolboschoenus maritimus*	Ditches
Reed canary grass	*Phalaris arundinacea*	Ditches
Hemlock waterparsnip	*Sium suave*	Ditches
Duckweed	*Lemna minor*	Ditches
Frogbit	*Hydrocharis morsus-ranae*	Ditches
Floating pennywort	*Hydrocotyle ranunculoides*	Ditches
Perennial ryegrass	*Lolium perenne*	Hay meadows
Southern marsh-orchid	*Dactylorhiza praetermissa*	Hay meadows
Marsh Marigold	*Caltha palustris*	Hay meadows
Cuckoo Flower	*Cardamine pratensis*	Hay meadows
Meadowsweet	*Filipendula ulmaria*	Hay meadows
Common meadow-rue	*Thalictrum flavum*	Hay meadows
Common knapweed	*Centaurea nigra*	Hay meadows
Meadow thistle	*Cirsium dissectum*	Hay meadows
Meadow foxtail	*Alopecurus pratensis*	Hay meadows
Willow trees	*Salicaceae*	Ditches, arable fields

Appendix C.

Seasonal variation of phosphorus within a UK Ramsar wetland: Impacts of land use and hydrology on algal and duckweed growth and implications for management

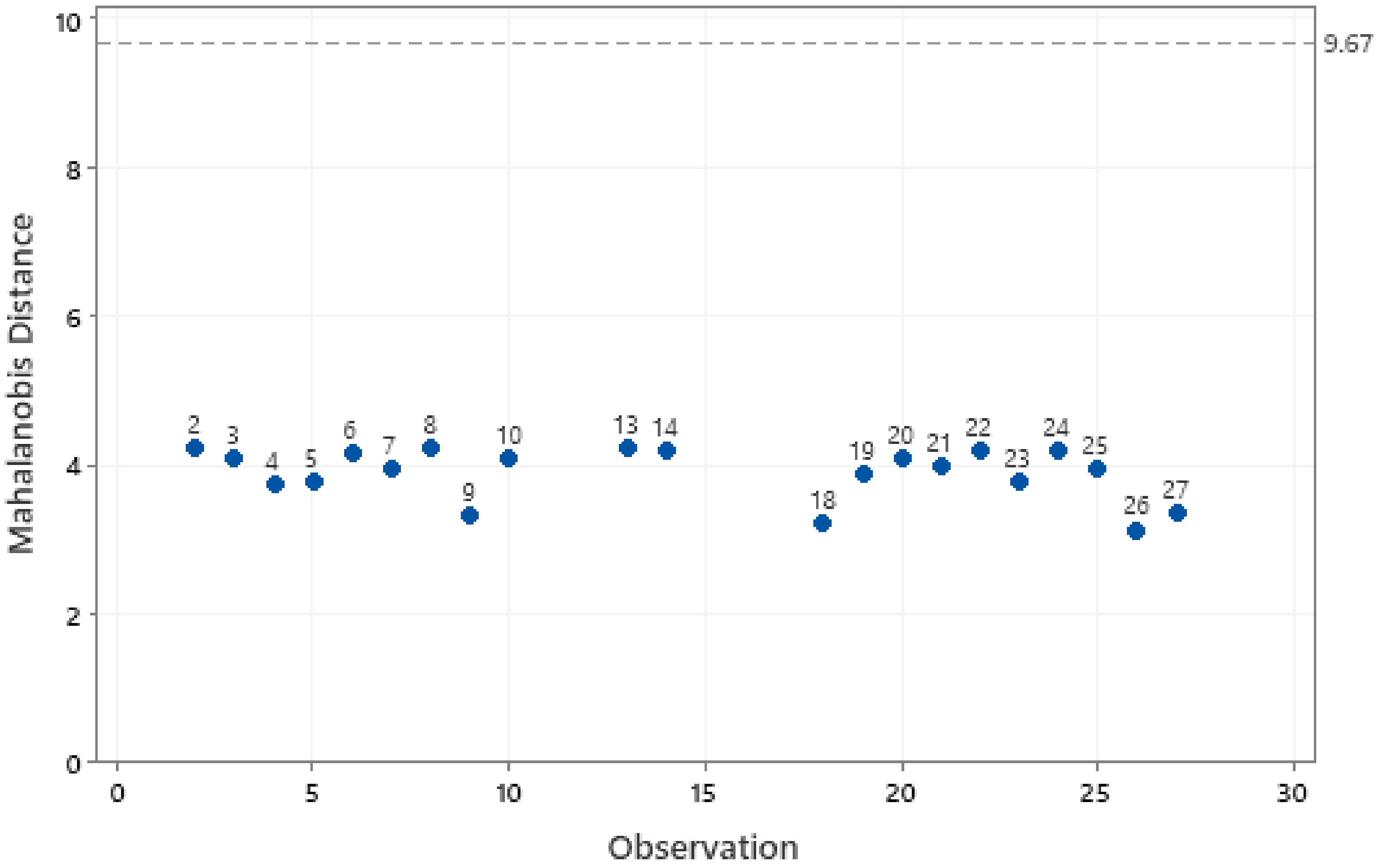
C.1 Molybdenum blue analysis for Soluble Reactive Phosphorus (SRP) and Total Reactive Phosphorus (TRP)

The following reagents were made up for the molybdenum blue analysis.

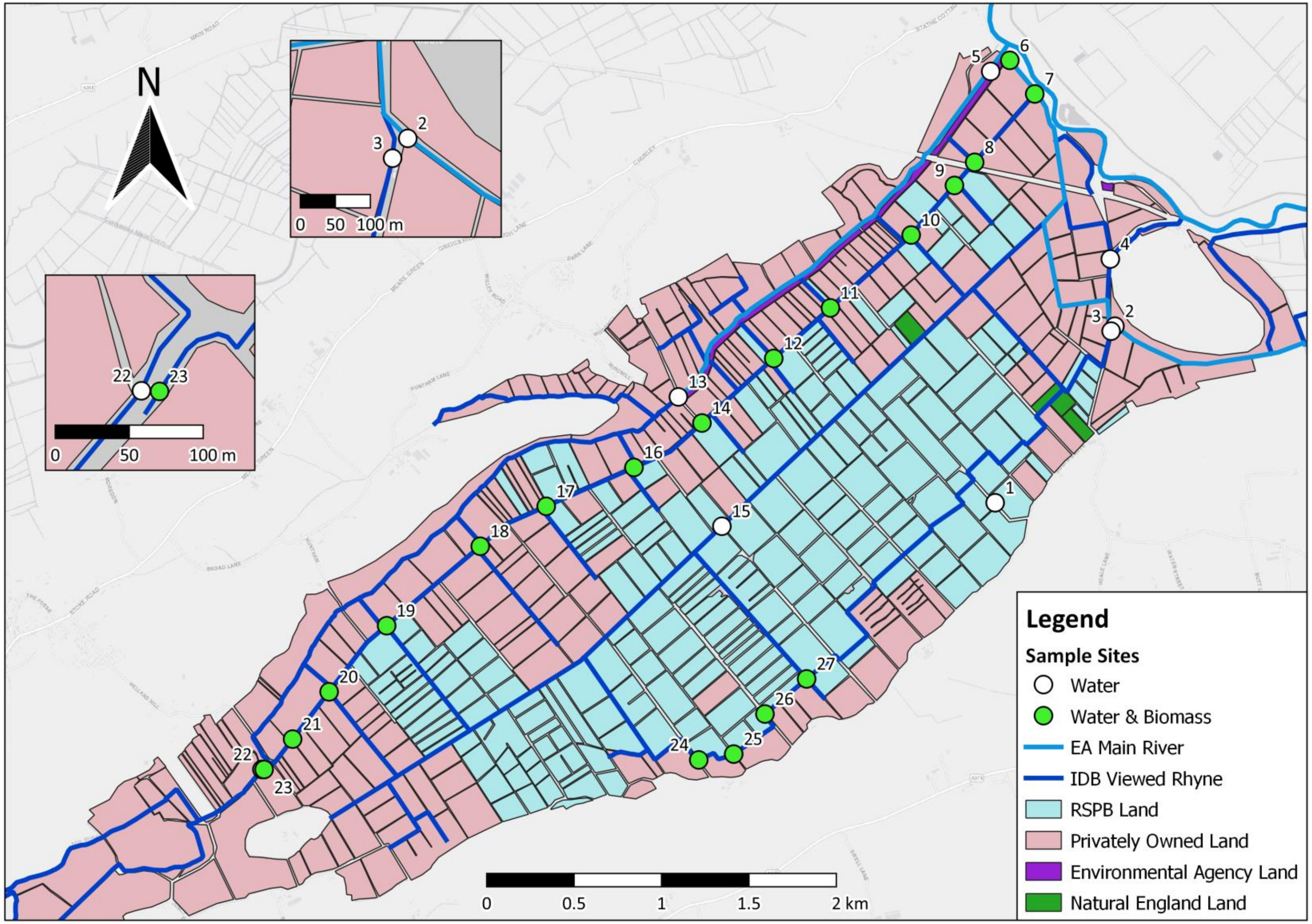
- 25% Sulphuric acid: 250 ml of concentrated sulphuric acid added to 750 ml of high purity water, allowed to cool then made up to 1 litre with further high purity water.
- Ascorbic acid: 2.5 g of ascorbic acid, $C_6H_8O_6$, dissolved in 12.5 ml of high purity water. 12.5 ml of diluted sulphuric acid (25%) solution (reagent 1) added and mixed well. This solution was made up before each analysis or stored in an amber lab glass bottle in a refrigerator at 2°C to 8°C in the dark, to be used within a week of preparation.
- Mixed Reagent: 12.5 g of ammonium heptamolybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}.4H_2O$ in 125 ml dissolved high purity water. 0.5 g of potassium antimony tartrate, $K(SbO)C_4H_4O_6$ (with/without ½ H_2O) dissolved in 20 ml high purity water. Molybdate solution added to 350 ml of dilute sulphuric acid solution (reagent 1) and stirred continuously. Tartrate solution added and mixed well. The reagent was stored in a lab glass bottle and was stable for several months.

Method:

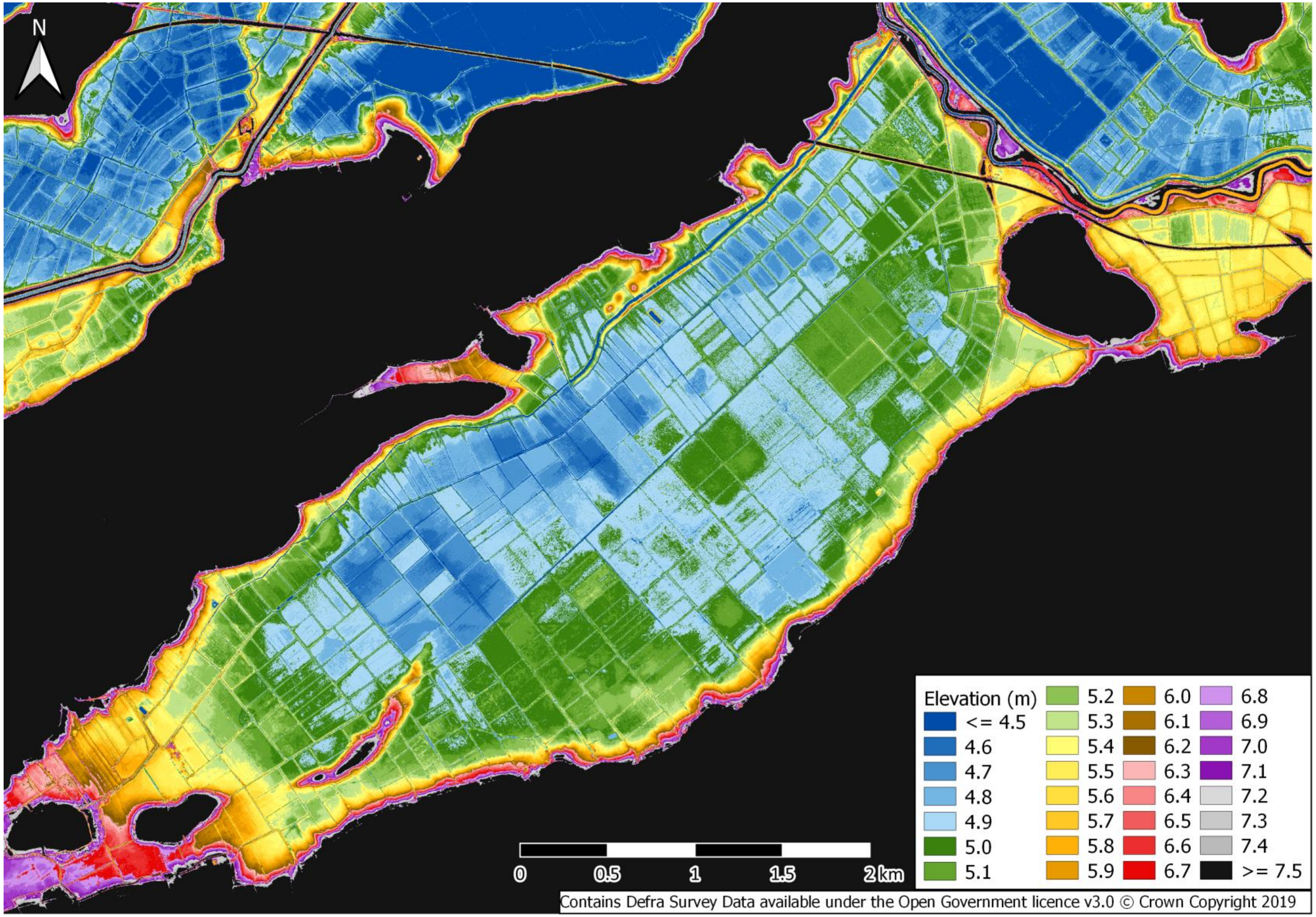
I. Add 0.25 ml of ascorbic acid to a 12.5 ml sample.
II. Add 0.25 ml of the mixed reagent to the solution.
III. Mix and leave for 10 minutes.
IV. Measure within 30 minutes by pouring the sample into 4 cm cuvette and placing in Cecil CE1010 colorimeter at 710 nm.



Appendix Figure C.1: Mahalanobis Distances plot of the data from principal component analysis of West Sedgemoor SSSI surface water samples. No outliers were observed.



Appendix Figure C.2: Surface water and biomass sampling sites and land ownership on West Sedgemoor SSSI.



Appendix Figure C.3: Lidar elevation map of West Sedgemoor SSSI.

Appendix Table C.1: Correlation matrix of Pearson's correlation coefficients between total phosphorus (TP), total soluble phosphorus (TSP), total reactive phosphorus (TRP) and soluble reactive phosphorus (SRP) for each of the seasons: spring, summer, autumn, and winter, Parrett Internal Drainage Board (IDB) hydrological block 2 surface water samples at West Sedgemoor SSSI.

	Spring TP	Summer TP	Autumn TP	Winter TP	Spring TSP	Summer TSP	Autumn TSP	Winter TSP	Spring TRP	Summer TRP	Autumn TRP	Winter TRP	Spring SRP	Summer SRP	Autumn SRP
Summer TP	-0.543														
Autumn TP	-0.047	-0.25													
Winter TP	0.117	0.064	-0.565												
Spring TSP	0.991	-0.495	-0.028	0.093											
Summer TSP	-0.542	0.98	-0.349	0.073	-0.494										
Autumn TSP	-0.031	-0.277	0.971	-0.479	-0.011	-0.37									
Winter TSP	0.299	0.071	-0.522	0.956	0.294	0.076	-0.413								
Spring TRP	0.992	-0.553	-0.076	0.176	0.991	-0.539	-0.057	0.357							
Summer TRP	-0.542	0.99	-0.549	0.045	-0.513	0.996	-0.52	0.028	-0.496						
Autumn TRP	-0.204	0.115	0.868	-0.364	-0.181	-0.028	0.867	-0.336	-0.252	-0.543					
Winter TRP	-0.002	0.045	-0.665	0.954	-0.042	0.08	-0.575	0.897	0.066	0.205	-0.517				
Spring SRP	0.986	-0.486	-0.05	0.102	0.996	-0.475	-0.04	0.305	0.993	-0.467	-0.22	-0.017			
Summer SRP	-0.495	0.992	-0.317	0.082	-0.449	0.993	-0.338	0.09	-0.502	0.996	0.037	0.066	-0.436		
Autumn SRP	0.029	-0.372	0.956	-0.478	0.047	-0.443	0.985	-0.407	0.016	-0.493	0.787	-0.552	0.027	-0.424	
Winter SRP	0.169	0.034	-0.582	0.953	0.152	0.074	-0.472	0.965	0.245	0.178	-0.461	0.96	0.179	0.063	-0.439

p value	<0.05	<0.01

1

0

-1

Appendix Table C.2: Correlation matrix of Pearson's correlation coefficients between total phosphorus (TP), total soluble phosphorus (TSP), total reactive phosphorus (TRP) and soluble reactive phosphorus (SRP) for each of the seasons: spring, summer, autumn, and winter, Parrett Internal Drainage Board (IDB) hydrological block 3 surface water samples at West Sedgemoor SSSI.

	Spring TP	Summer TP	Autumn TP	Winter TP	Spring TSP	Summer TSP	Autumn TSP	Winter TSP	Spring TRP	Summer TRP	Autumn TRP	Winter TRP	Spring SRP	Summer SRP	Autumn SRP
Summer TP	-0.546														
Autumn TP	0.586	-0.608													
Winter TP	-0.149	0.617	0.241												
Spring TSP	0.952	-0.51	0.431	-0.268											
Summer TSP	-0.277	0.949	-0.545	0.63	-0.234										
Autumn TSP	0.4	-0.736	0.912	0.076	0.329	-0.739									
Winter TSP	-0.203	0.583	0.245	0.995	-0.344	0.569	0.092								
Spring TRP	0.991	-0.53	0.509	-0.22	0.983	-0.255	0.352	-0.284							
Summer TRP	-0.41	0.974	-0.611	0.664	-0.394	0.981	-0.796	0.625	-0.399						
Autumn TRP	0.551	-0.589	0.998	0.235	0.398	-0.54	0.918	0.239	0.474	-0.604					
Winter TRP	-0.27	0.552	0.231	0.977	-0.428	0.508	0.093	0.994	-0.358	0.588	0.226				
Spring SRP	0.944	-0.535	0.399	-0.335	0.998	-0.263	0.311	-0.409	0.978	-0.418	0.366	-0.49			
Summer SRP	-0.368	0.978	-0.554	0.672	-0.348	0.99	-0.747	0.622	-0.356	0.993	-0.544	0.572	-0.376		
Autumn SRP	0.571	-0.707	0.983	0.054	0.438	-0.667	0.948	0.062	0.505	-0.728	0.984	0.055	0.416	-0.672	
Winter SRP	-0.248	0.552	0.244	0.982	-0.405	0.516	0.102	0.996	-0.336	0.59	0.238	1	-0.468	0.577	0.067

p value	<0.05	<0.01

1

0

-1

Appendix Table C.3: Correlation matrix of Pearson's correlation coefficients between total phosphorus (TP), total soluble phosphorus (TSP), total reactive phosphorus (TRP) and soluble reactive phosphorus (SRP) for each of the seasons: spring, summer, autumn, and winter, in surface water samples, and TP in surface sediment samples for West Sedgemoor SSSI (Crocker et al., 2021). Water sites 5, 6, 8, 9, 12, 13, 14, 18, 19, 20, 21, 22, 3 ,2, and 4, included and compared against sediment sites 1, 2, 3, 5, 13, 15, 18, 26, 28, 32, 33, 34, 51, 52, and 54 respectively.

	Sediment TP	Spring TP	Summer TP	Autumn TP	Winter TP	Spring TSP	Summer TSP	Autumn TSP	Winter TSP	Spring TRP	Summer TRP	Autumn TRP	Winter TRP	Spring SRP	Summer SRP	Autumn SRP
Spring TP	0.158															
Summer TP	-0.16	-0.285														
Autumn TP	0.14	0.627	-0.318													
Winter TP	0.148	0.292	0.279	0.598												
Spring TSP	0.072	0.885	-0.112	0.628	0.337											
Summer TSP	-0.107	-0.142	0.971	-0.154	0.402	0.073										
Autumn TSP	0.063	0.53	-0.407	0.833	0.528	0.581	-0.267									
Winter TSP	0.092	0.327	0.285	0.567	0.983	0.357	0.398	0.516								
Spring TRP	0.162	0.978	-0.2	0.623	0.296	0.957	-0.04	0.542	0.326							
Summer TRP	-0.17	-0.204	0.995	-0.253	0.319	-0.028	0.98	-0.351	0.335	-0.117						
Autumn TRP	0.026	0.568	-0.39	0.837	0.539	0.57	-0.272	0.887	0.504	0.566	-0.337					
Winter TRP	0.046	0.189	0.346	0.588	0.976	0.249	0.45	0.502	0.959	0.198	0.383	0.509				
Spring SRP	0.062	0.864	-0.082	0.602	0.294	0.995	0.102	0.54	0.315	0.946	0.002	0.522	0.216			
Summer SRP	-0.146	-0.138	0.971	-0.147	0.42	0.075	0.994	-0.248	0.431	-0.038	0.984	-0.25	0.472	0.103		
Autumn SRP	0.012	0.681	-0.279	0.9	0.554	0.733	-0.122	0.913	0.576	0.704	-0.196	0.834	0.537	0.705	-0.094	
Winter SRP	0.063	0.266	0.345	0.58	0.977	0.319	0.46	0.51	0.985	0.274	0.393	0.477	0.984	0.286	0.489	0.576

p value	<0.05	<0.01

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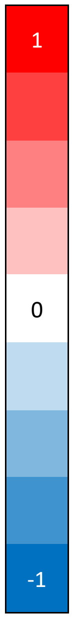
Appendix Table C.4: Eigenvalues, explained variance and cumulative variance of the data from principal component analysis of West Sedgemoor SSSI surface water samples.

Order of Components	Eigenvalue	Explained variance /%	Cumulative variance /%
1	6.50	40.7	40.7
2	5.45	34.1	74.7
3	2.34	14.6	89.4
4	1.44	9.0	98.3
5	0.09	0.6	98.9
6	0.05	0.3	99.3
7	0.04	0.3	99.5

Appendix Table C.5: Correlation matrix of Pearson's correlation coefficients between total phosphorus (TP), total soluble phosphorus (TSP), total reactive phosphorus (TRP) and soluble reactive phosphorus (SRP) for each of the seasons: spring, summer, autumn, and winter, in surface water samples, and TP (g kg^{-1}) in surface water biomass samples and mass of surface water biomass samples at West Sedgemoor SSSI.

	Spring Mass	Summer Mass	Autumn Mass	Winter Mass	Spring g kg^{-1}	Summer g kg^{-1}	Autumn g kg^{-1}	Winter g kg^{-1}
Summer Mass	-0.048							
Autumn Mass	-0.173	-0.234						
Winter Mass	0.366	0.103	0.126					
Spring g kg^{-1}	0.036	0.152	-0.524	-0.171				
Summer g kg^{-1}	-0.256	0.245	0.117	0.066	0.38			
Autumn g kg^{-1}	0.03	-0.231	0.492	0.429	-0.291	0.354		
Winter g kg^{-1}	0.874	0.998	-0.973	0.993	0.719	-0.755	0.736	
Spring TP	-0.037	-0.196	-0.234	-0.125	0.709	0.023	-0.474	0.773
Summer TP	-0.326	-0.104	0.545	0.308	-0.628	0.154	0.45	-0.984
Autumn TP	0.399	0.099	-0.165	0.181	0.441	-0.162	-0.098	0.977
Winter TP	-0.446	-0.091	0.212	0.026	0.341	0.546	0.029	-0.971
Spring TSP	-0.066	-0.099	-0.158	-0.144	0.657	0.133	-0.513	0.572
Summer TSP	-0.352	-0.14	0.615	0.334	-0.608	0.149	0.418	-0.979
Autumn TSP	0.36	0.115	-0.219	0.157	0.482	-0.101	0.031	0.861
Winter TSP	-0.457	-0.131	0.091	-0.08	0.507	0.593	-0.159	-0.919
Spring TRP	-0.074	-0.188	-0.195	-0.148	0.676	0.072	-0.505	0.601
Summer TRP	-0.364	-0.129	0.541	0.286	-0.64	0.156	0.388	-0.98
Autumn TRP	0.398	0.101	-0.24	0.183	0.456	-0.156	-0.104	0.938
Winter TRP	-0.44	-0.077	0.31	0.111	0.188	0.589	0.15	-0.921
Spring SRP	-0.079	-0.102	-0.122	-0.131	0.641	0.161	-0.525	0.484
Summer SRP	-0.362	-0.142	0.595	0.312	-0.602	0.155	0.375	-0.974
Autumn SRP	0.332	0.069	-0.203	0.099	0.482	-0.117	-0.105	0.844
Winter SRP	-0.478	-0.107	0.218	0.022	0.344	0.592	0.011	-0.988



p value | <0.05 | <0.01