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Spatial distribution of sediment phosphorus in a Ramsar wetland

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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 was observed across 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.

Keywords

Eutrophication; Managed floodplain; Drainage ditch; Surface sediment geochemistry; Non-point source pollution; Somerset Levels

1 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 Convention, 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., 2015; 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. P 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 phosphorus (>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 principle component analysis was used to determine whether land use impacts ditch surface sediment geochemistry.

2 Material and methods

2.1 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. 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 Environmental 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).

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).

2.2 Sampling and chemical analyses

Surface sediment samples were collected in March 2018. 59 sampling sites (Fig 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.

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 was 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). Sites 12, 46 & 50 were unable to be analysed by WD-XRF due to an insufficient amount of <63 µm fraction available.

2.3 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. A1 of the Electronic Supplementary information (ESI) (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 Results and discussion

3.1 Spatial phosphorus distribution in sediment

The spatial distribution of total phosphorus (TP) in sediments is shown in Fig. 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 A2 of the ESI); this was done to cause minimal disturbance to the roosting birds and the nature conservation efforts of the RSPB. Table 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).

3.2 Main factors affecting phosphorus storage in sediment

3.2.1 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 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.

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 mineralization 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).

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. A3-A7 of the ESI). P retention from coprecipitation 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 coprecipitation 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 A1 of the ESI.

Surface sediments of sites surrounded by land that is not RSPB nature reserve showed less significant correlations than in RSPB surrounded sites. P 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. A8 and A9 of the ESI). 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. P showed a significant moderate positive correlation with Fe ($r = 0.635$) (Fig. A10 of the ESI). P 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. 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).

3.2.2 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 A2 of the ESI.

The principal component analysis score plot of West Sedgemoor SSSI surface sediment sample sites (Fig. 5a) is shown bassed on chemical and physical differences illustrated in the occompaning loading plot (Fig. 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 principle 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. 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. 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 A4, ESI).

4 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, 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 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 of 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. P has a weak negative loading on the first component suggesting that P concentrations tend to be slightly higher outside of the RSPB nature reserve.

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References

Adhurya, S., Das, S., Ray, S., 2020. Guanotrophication by Waterbirds in Freshwater Lakes: A Review on Ecosystem Perspective, in: Springer Proceedings in Mathematics and Statistics. Springer, pp. 253–269. https://doi.org/10.1007/978-981-15-0422-8_22

Baxa, M., Šulcová, J., Kröpfelová, L., Pokorný, J., Potužák, J., 2019. The quality of sediment in shallow water bodies – Long-term screening of sediment in Czech Republic. A new perspective of nutrients and organic matter recycling in agricultural landscapes. Ecol. Eng. 127, 151–159. https://doi.org/10.1016/j.ecoleng.2018.11.009

Blake, W., Comber, S., Burns, E.E., Goddard, R., Dougal, M., Taylor, A., Couldrick, L., 2013. Spatial and geochemical distribution of particulate P in river sediments impacted by DWPA and urban and industrial effluent., University of Plymouth Catchment and River Science (CARiS) research group report for Westcountry Rivers Trust.

Blott S.J., Pye K., 2001. GRADISTAT: a grain size distribution and statistics package for the analysis of unconsolidated sediments. Earth Surf. Process. Landforms 26, 1237–1248.

Brereton, R.G., 2015. The Mahalanobis distance and its relationship to principal component scores. J. Chemom. 29, 143–145. https://doi.org/10.1002/cem.2692

Burns, E.E., Comber, S., Blake, W., Goddard, R., Couldrick, L., 2015. Determining riverine sediment storage mechanisms of biologically reactive phosphorus in situ using DGT. Environ. Sci. Pollut. Res. 22, 9816–9828. https://doi.org/10.1007/s11356-015-4109-3

Capasso, J., Bhadha, J.H., Bacon, A., Vardanyan, L., Khatiwada, R., Pachon, J., Clark, M., Lang, T., 2020. Influence of flow on phosphorus-dynamics and particle size in agricultural drainage ditch sediments. PLoS One 15, e0227489. https://doi.org/10.1371/journal.pone.0227489

Carpenter, S.R., Bennett, E.M., 2011. Reconsideration of the planetary boundary for phosphorus. Environ. Res. Lett. 6, 014009.

Chen, Y., Shen, L., Huang, T., Chu, Z., Xie, Z., 2020. Transformation of sulfur species in lake sediments at Ardley Island and Fildes Peninsula, King George Island, Antarctic Peninsula. Sci. Total Environ. 703. https://doi.org/10.1016/j.scitotenv.2019.135591

Collins, A.L., McGonigle, D.F., 2008. Monitoring and modelling diffuse pollution from agriculture for policy support : UK and European experience. Environ. Sci. Policy 11, 97–101.

Comber, S., Gardner, M., Darmovzalova, J., Ellor, B., 2015. Determination of the forms and stability of phosphorus in wastewater effluent from a variety of treatment processes. J. Environ. Chem. Eng. 3, 2924–2930.

Council of the European Communities, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Off. J. Eur. Communities 43, 1–73.

Council of the European Communities, 1992. Council Directive 92/43/EEC of 21 May 1992 on the conservation of natural habitats and of wild fauna and flora. Off. J. Eur. Communities 35, 7–50.

Drake, C.M., Stewart, N.F., Palmer, M.A., Kindemba, V.L., 2010. The ecological status of ditch systems: an investigation into the current status of the aquatic invertebrate and plant communities of grazing marsh ditch systems in England and Wales Technical Report. Peterborough.

Drewitt, A., Evans, T., Grice, P., 2008. Natural England Research Report NERR015 A review of the ornithological interest of SSSIs in England. Sheffield, UK.

Environment Agency, 2020. Ecology & Fish Data Explorer [WWW Document]. NFPD (National Fish Popul. Database). URL https://environment.data.gov.uk/ecology-fish/ (accessed 8.5.20).

European parliament and the council of the European Union, 2009. Directive 2009/147/EC of the European Parliament and of the Council of 30 November 2009 on the conservation of wild birds 7–25.

Heaney, S.I., Corry, J.E., Lishman, J.P., 1992. Changes of water quality and sediment phosphorus of a small productive lake following decreased phosphorus loading, in: Sutcliffe, D.W., Jones, J.G. (Eds.), Eutrophication: Research and Application to Water Supply. Freshwater Biological Association, pp. 119–131.

Hughes, J.M.R., Heathwaite, A.L., 1995. Introduction, in: Hughes, J.M.R., Heathwaite, A.L. (Eds.), Hydrology and Hydrochemistry of British Wetlands. John Wiley & Sons, Inc., Chinchester, UK, pp. 1–8.

IPBES, 2018. Summary for policymakers of the thematic assessment report on land degradation and restoration of the Intergovernmental Science-Policy Platform on Biodiversity and Ecosystem Services. IPBES secretariat, Bonn, Germany.

Jarvie, H.P., Jürgens, M.D., Williams, R.J., Neal, C., Davies, J.J.L., Barrett, C., White, J., 2005. Role of river bed sediments as sources and sinks of phosphorus across two major eutrophic UK river basins: The Hampshire Avon and Herefordshire Wye. J. Hydrol. 304, 51–74.

Jefferson, R.G., Grice, P. V., 1998. The conservation of lowland wet grassland in England, in: Joyce, C.B., Wade, P.M. (Eds.), European Wet Grasslands: Biodiversity, Management and Restoration. John Wiley & Sons, Chichester, pp. 31–48.

Kitowski, I., Sujak, A., Wiącek, D., Strobel, W., Rymarz, M., 2014. Trace element residues in eggshells of Grey Heron (Ardea cinerea) from colonies of East Poland. J. Zool. 10, 346–354.

LaFond-Hudson, S., Johnson, N.W., Pastor, J., Dewey, B., 2018. Iron sulfide formation on root surfaces controlled by the life cycle of wild rice (Zizania palustris). Biogeochemistry 141, 95–106. https://doi.org/10.1007/s10533-018-0491-5

Matsunami, H., Matsuda, K., Yamasaki, S., Kimura, K., Ogawa, Y., Miura, Y., Yamaji, I., Tsuchiya, N., 2010. Rapid simultaneous multi-element determination of soils and environmental samples with polarizing energy dispersive X-ray fluorescence (EDXRF) spectrometry using pressed powder pellets. Soil Sci. Plant Nutr. 56, 530–540. https://doi.org/10.1111/j.1747-0765.2010.00489.x

Met Office, 2019. Yeovilton climate information - Met Office [WWW Document]. URL https://www.metoffice.gov.uk/public/weather/climate/gcn45vme7 (accessed 3.5.19).

Möller, P., Knappe, A., Dulski, P., 2014. Seasonal variations of rare earths and yttrium distribution in the lowland Havel River, Germany, by agricultural fertilization and effluents of sewage treatment plants. Appl. Geochemistry 41, 62–72.

Mora, M.A., Taylor, R.J., Brattin, B.L., 2007. Potential ecotoxicological significance of elevated concentrations of strontium in eggshells of passerine birds. Condor 109, 199–205.

Natural England, 2019. European Site Conservation Objectives: Supplementary advice on conserving and restoring site features Somerset Levels and Moors Special Protection Area (SPA) Site Code: UK9010031.

Ockenden, M.C., Deasy, C., Quinton, J.N., Surridge, B., Stoate, C., 2014. Keeping agricultural soil out of rivers: Evidence of sediment and nutrient accumulation within field wetlands in the UK. J.

Environ. Manage. 135, 54–62.

Otero, N., Vitòria, L., Soler, A., Canals, A., 2005. Fertiliser characterisation: Major, trace and rare earth elements. Appl. Geochemistry 20, 1473–1488.

Owens, P.N., Walling, D.E., 2002. The phosphorus content of fluvial sediment in rural and industrialized river basins. Water Res. 36, 685–701.

Padedda, B.M., Sechi, N., Lai, G.G., Mariani, M.A., Pulina, S., Sarria, M., Satta, C.T., Virdis, T., Buscarinu, P., Lugliè, A., 2017. Consequences of eutrophication in the management of water resources in Mediterranean reservoirs: A case study of Lake Cedrino (Sardinia, Italy). Glob. Ecol. Conserv. 12, 21–35.

Parkin, G., Birkinshaw, S., Benyon, P., Humphries, N., Bentley, M., Gilman, K., 2004. Water availability and budgets for wetland restoration and recreation sites - BD1316. DEFRA.

Parrett IDB, 2009. West Sedgemoor and Wick Moor Water Level Management Plan. Parrett Internal Drainage Board.

Petkuviene, J., Vaiciute, D., Katarzyte, M., Gecaite, I., Rossato, G., Vybernaite-Lubiene, I., Bartoli, M., 2019. Feces from Piscivorous and Herbivorous Birds Stimulate Differentially Phytoplankton Growth. Water 11, 2567. https://doi.org/10.3390/w11122567

Ramsar Convention, 1994. Present text of the Convention on Wetlands.

Ramsar Convention Secretariat, 2016. An Introduction to the Convention on Wetlands, 7th ed. Ramsar Convention Secretariat, Gland, Switzerland.

Reynolds, C.S., 1992. Eutrophication and the management of planktonic algae: what Vollenweider couldn’t tell us, in: Sutcliffe, D.W., Jones, J.G. (Eds.), Eutrophication: Research and Application to Water Supply. Freshwater Biological Association, pp. 4–29.

Riley, W.D., Potter, E.C.E., Biggs, J., Collins, A.L., Jarvie, H.P., Jones, J.I., Kelly-Quinn, M., Ormerod, S.J., Sear, D.A., Wilby, R.L., Broadmeadow, S., Brown, C.D., Chanin, P., Copp, G.H., Cowx, I.G., Grogan, A., Hornby, D.D., Huggett, D., Kelly, M.G., Naura, M., Newman, J.R., Siriwardena, G.M., 2018. Small Water Bodies in Great Britain and Ireland: Ecosystem function, human-generated degradation, and options for restorative action. Sci. Total Environ. 645, 1598–1616.

Sabatier, P., Poulenard, J., Fangeta, B., Reyss, J.L., Develle, A.L., Wilhelm, B., Ployon, E., Pignol, C., Naffrechoux, E., Dorioz, J.M., Montuelle, B., Arnaud, F., 2014. Long-term relationships among pesticide applications,mobility, and soil erosion in a vineyard watershed. Proc. Natl. Acad. Sci.

U. S. A. 111, 15647–15652.

Scherer, N.M., Gibbons, H.L., Stoops, K.B., Muller, M., 1995. Phosphorus loading of an urban lake by bird droppings. Lake Reserv. Manag. 11, 317–327. https://doi.org/10.1080/07438149509354213

Schnug, E., Jacobs, F., Stöven, K., 2018. Guano: The White Gold of the Seabirds, in: Mikkola, H. (Ed.), Seabirds. InTechOpen, pp. 79–100.

Smith, K.E., Luna, T.O., 2013. Radial oxygen loss in wetland plants: Potential impacts on remediation of contaminated sediments. J. Environ. Eng. (United States) 139, 496–501. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000631

Søndergaard, M., Jensen, J.P., Jeppesen, E., 2003. Role of sediment and internal loading of phosphorus in shallow lakes. Hydrobiologia 506–509, 135–145.

Taylor, A., Comber, S., Blake, W., 2016. An investigation into the temporal and spatial patterns of phosphorus concentrations across the ditch system of West Sedgemoor SSSI, University of Plymouth Catchment and River Science (CARiS) research group report for Natural England.

The Great Crane Project, 2014. Annual Report 2014 Release Year (Year 5 of 5).

Van der Perk, M., Owens, P.N., Deeks, L.K., Rawlins, B.G., Haygarth, P.M., Beven, K.J., 2007. Controls on catchment-scale patterns of phosphorus in soil, streambed sediment, and stream water. J. Environ. Qual. 36, 694–708.

Verheyen, D., Van Gaelen, N., Ronchi, B., Batelaan, O., Struyf, E., Govers, G., Merckx, R., Diels, J., 2015. Dissolved phosphorus transport from soil to surface water in catchments with different land use. Ambio 44, 228–240. https://doi.org/10.1007/s13280-014-0617-5

Williams, M., 1970. The Draining of the Somerset Levels. Cambridge University Press, Cambridge, UK.

Wu, S., Zhao, Y., Chen, Y., Dong, X., Wang, M., Wang, G., 2019. Sulfur cycling in freshwater sediments: A cryptic driving force of iron deposition and phosphorus mobilization. Sci. Total Environ. 657, 1294–1303.

Xiao, Y., Zhu, X.L., Cheng, H.K., Li, K.J., Lu, Q., Liang, D.F., 2013. Characteristics of phosphorus adsorption by sediment mineral matrices with different particle sizes. Water Sci. Eng. 6, 262–271. https://doi.org/10.3882/j.issn.1674-2370.2013.03.003

Zhang, W., Zhu, X., Jin, X., Meng, X., Tang, W., Shan, B., 2017. Evidence for organic phosphorus activation and transformation at the sediment–water interface during plant debris decomposition. Sci. Total Environ. 583, 458–465.

Zhao, Y., Zhang, Z., Wang, G., Li, X., Ma, J., Chen, S., Deng, H., Annalisa, O.-H., 2019. High sulfide production induced by algae decomposition and its potential stimulation to phosphorus mobility in sediment. Sci. Total Environ. 650, 163–172.