## 1 ACCEPTED COPY OF MANUSCRIPT

# <sup>2</sup> AVAILABLE AT:

- 3 Science of The Total Environment 765:142749-142749 Article number 142749 Apr 2021
- <sup>4</sup> Spatial distribution of sediment

## <sup>5</sup> phosphorus in a Ramsar wetland

6 Ry Crocker<sup>a</sup>, William H. Blake<sup>a</sup>, Thomas H. Hutchinson<sup>a</sup>, Sean Comber<sup>a\*</sup>

- <sup>a</sup> School of Geography, Earth and Environmental Sciences, University of Plymouth, Plymouth, Devon
  PL4 8AA, UK.
- 9 \* Corresponding author: sean.comber@plymouth.ac.uk
- 10

## 11 Abstract

12 Eutrophication is a significant threat to surface water biodiversity worldwide, with excessive 13 phosphorus concentrations being among the most common causes. Wetland ditches under these 14 conditions shift from primarily submerged aquatic vegetation to algae or duckweed dominance, 15 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 16 17 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 18 19 special scientific interest. Elevated phosphorus concentrations in sediment was observed across the Moor up to 4,220 mg Kg<sup>-1</sup>, almost 10 times that which may be expected from background levels. The 20 21 highest concentrations were generally observed at the more intensively farmed sites in the north of 22 the moor, near key inlets and the outlet. Based upon their chemical and physical properties, clear 23 distinction was observed between sites outside and within the Royal Society of the Protection of Birds 24 nature reserve, using principal component analysis.

#### 26 Keywords

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

#### 29 1 Introduction

30 Wetland ecosystems are important worldwide, providing numerous valuable ecological services for 31 people and wildlife. They are biologically diverse habitats serving hydrological functions, including 32 water storage; storm protection and flood mitigation; and water purification. Economically, wetlands benefit water supply; agriculture; fisheries and recreational fishing; tourism; and wetland products 33 34 such as herbal medicines (Hughes and Heathwaite, 1995; Ramsar Convention Secretariat, 2016). 35 However, wetlands are one of the most threatened ecosystems due to loss and degradation, with 87% 36 lost globally in the last 300 years, and 54% since 1900 (IPBES, 2018). Human activities are the main 37 driver of wetland degradation. Intensified agriculture has seen considerably increased crop and 38 livestock yields across the world, but when managed inappropriately, can cause soil erosion, and 39 eutrophication of aquatic systems via diffuse pollution (IPBES, 2018; Ockenden et al., 2014). Objectives 40 of the European Habitats Directive (Council of the European Communities, 1992) and the Water 41 Framework Directive (WFD) (Council of the European Communities, 2000) demand action to restore 42 waterbodies that are either not meeting good status, WFD, or need to meet favourable conservation 43 status, Habitats Directive. Wetland areas are also protected under the Ramsar Convention (Ramsar 44 Convention, 1994).

45 Eutrophication of surface water is a significant threat to biodiversity worldwide, with excessive 46 phosphorus (P) concentrations being among the most common causes (Comber et al., 2015; Zhang et 47 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 48 49 therefore deterioration of aquatic ecosystems (Zhang et al., 2017). Heavy shading via surface 50 coverage, and bacterial degradation of excessive amounts of organic matter, produced by algal and 51 duckweed blooms, causes depletion of oxygen in the water column, bringing about fish kills and 52 development of bad odours (Padedda et al., 2017; Riley et al., 2018; Zhang et al., 2017).

53 Significant improvements have been made to reduce the amount of P input from point source 54 discharges to water courses, such as wastewater treatment Works (WwTW), and land management 55 policy is encouraging farming best management practices to reduce biogeochemical flows (Ockenden 56 et al., 2014). Specifically, the linear biogeochemical flow of P from mineral reserves to agriculture and 57 then into catchments and oceans is considered to be exceeding the planetary boundary, thence

58 leading to eutrophication (Carpenter and Bennett, 2011; Ockenden et al., 2014). In arable catchment, 59 surface runoff is an important driver of erosion damage and of fertilizer P export to waterbodies. P 60 contributions from pasture catchment include dissolution of cow manure from overland flow or from 61 subsurface flow (Verheyen et al., 2015). However, wetland managed as waterfowl nature reserve can 62 potentially cause P loading through bird droppings (guanotrophication). Sadly, the degradation and 63 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 64 to the size and/or volume of the waterbody, can have a significant fraction of the internal P load cycling 65 through their diet. Waterfowl have the potential to affect wetland P cycling by altering the form of P 66 and by inputting and/or exporting P to and/or from external areas to the wetland (Adhurya et al., 67 68 2020; Scherer et al., 1995).

69 However, measures put in place to reduce P loads discharged to a catchment could be negated as 70 legacy P bound in sediment has the potential to act as a secondary source of P to the water column, 71 following disturbance (Collins and McGonigle, 2008; Van der Perk et al., 2007) or in response to 72 changes in condition of overlying waters (Jarvie et al., 2005; Reynolds, 1992). This ability of sediment 73 to release stored P to the water column could significantly delay the recovery and compliance with 74 water column-based standards, and give rise to algal and duckweed bloom production in excess of 75 what may be expected from external loading alone (Heaney et al., 1992). Therefore, it is crucial to 76 generate data on particulate P storage in sediments in systems that are failing to meet WFD 77 requirements.

78 In this study, the spatial distribution of surface sediment P is examined across West Sedgemoor, a Site 79 of Special Scientific Interest (SSSI) and part of the Somerset Levels and Moors, Ramsar site no. 914. 80 Water quality across a number of sites on the moor has already been shown to exceed the Common 81 Standards Monitoring Guidance for phosphorus (>0.1 mg-P |<sup>-1</sup> as total P) set as part of the Natura 2000 82 series of which include Special Protection Areas (SPAs), designated under the European Birds 83 Directive, and Special Areas of Conservation (SACs), designated under the European Habitats Directive 84 (Council of the European Communities, 1992; European parliament and the council of the European 85 Union, 2009; Taylor et al., 2016). This eutrophication necessitates the requirement to identify the 86 sources of contamination and to put in measures to remediate the situation. Understanding the 87 potential sediment contribution to this overlying water exceedance is crucial and so for the first time 88 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.

### 94 2 Material and methods

#### 95 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 96 97 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<sup>2</sup> and consists of many small, low lying fields and meadows separated by 98 99 narrow water-filled ditches, locally called rhynes. Water levels and the circulation of water flow on the 100 moor is managed by the Parrett Internal Drainage Board (IDB), although the only water outlet is via 101 West Sedgemoor Pumping Station, discharging to the River Parrett (tidal), which is operated by the 102 Environmental Agency (EA). The site is of a maritime temperate climate, typically 5 m above sea level 103 with the average monthly temperature ranging from 8.3 °C (January) to 21.8 °C (July) with an annual 104 mean temperature of approximately 14.6 °C. The area receives a mean annual precipitation of 708.5 105 mm (Met Office, 2019).

106 Lowland wet grassland in the UK usually consists of reclaimed floodplain land managed as grazing 107 marshes with some being cut for hay or silage (Jefferson and Grice, 1998; Williams, 1970). West 108 Sedgemoor was drained in 1816, making it one of the last moorland reclamations of the Somerset 109 Levels. The surrounding higher ground gave limitations to how the area could be dealt with, this gave 110 a certain unity to the drainage scheme, which other areas in the Levels lacked. Also, the relatively late 111 reclamation meant experience from previous drainage schemes across the Levels could be applied. 112 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 113 114 Middle Rhyne (Williams, 1970). This arterial ditch system is still in operation today; however the 115 pumping station was not constructed until 1944, allowing for stricter control over water levels (Parkin 116 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<sup>2</sup>). 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 123 124 flood risk by allowing better drainage. However, most watercourses retain low pen level in the interest 125 of conservation efforts and in order to reduce frost damage and bank erosion. Winter target water 126 levels in Raised Water Level Area (RWLA) blocks range from 4.65 m to 5.15 m ODN (Ordnance Datum 127 Newlyn). Outside of RWLAs, winter target water levels range from 4.20 m to ~4.70 m ODN, barring 128 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 129 130 period of early April to late November, water levels are allowed to rise in rhynes and ditches. Summer 131 target water levels range from 4.65 m to 5.30 m ODN. These higher levels provide 'wet fences' around 132 fields to contain livestock, maintain the groundwater table for the growing period and continue the 133 watercourse conservation interest (Parrett IDB, 2009).

134 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 135 136 England's largest breeding population of waders such as Lapwing (Vanellus vanellus), Snipe (Gallinago 137 gallinago) and Curlew (Numenius arquata) (Natural England, 2019). Additionally, Fivehead Woods and 138 Meadow on the southern edge of the moor has one of the largest heronries in the UK with more than 139 100 breeding pairs of Grey Heron (Ardea cinerea) (Drewitt et al., 2008). West Sedgemoor is also the 140 location for the Great Crane Project aimed to secure the future for the Crane (Grus grus) in the UK, 141 after a five year reintroduction was completed in 2015 (The Great Crane Project, 2014). West 142 Sedgmoor Drain, Stathe, to the north of the moor is a recreational fishing site managed by the Taunton 143 Angling Association (TAA). Fish species present include Common Bream (Abramis brama), Tench 144 (Tinca tinca), European Perch (Perca fluviatilis), Common Roach (Rutilus rutilus), Northern Pike (Esox 145 Lucius), Common Carp (Cyprinus carpio), Gudgeon (Gobio gobio), Rudd (Scardinius erythrophalmus), 146 Sunbleak (Leucaspius delineatus), Stone Loach (Barbatula barbatula), 3-Spined Stickleback 147 (Gasterosteus aculeatus), 10-Spined Stickleback (Pungitius pungitius) and Eels (Anguilla anguilla) 148 (Environment Agency, 2020). Finally, the site is also rich in rare and scarce invertebrate fauna, 149 particularly water beetles (Drake et al., 2010).

#### **150** 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<sub>2</sub>O<sub>2</sub> 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.</p>
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.</p>

171 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.

### 179 3 Results and discussion

180 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<sup>-1</sup>, 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<sup>-1</sup>, while the mean concentration for the whole site was 1870 mg kg<sup>-1</sup>. Higher TP concentrations were generally observed in the north of the moor, near 187 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<sup>-1</sup>, in the south (sites 23-47, 58 & 59) It was 1560 188 mg kg<sup>-1</sup>. Lower TP concentrations were generally observed around winter roost sites with a mean 189 190 concentration of 1460 mg kg<sup>-1</sup>, compared to 1960 mg kg<sup>-1</sup> for the rest of the site. However, most of 191 these winter roost samples are taken from the ditches that outline the boarder of the winter roost 192 sites (Fig A2 of the ESI); this was done to cause minimal disturbance to the roosting birds and the 193 nature conservation efforts of the RSPB. Table 1 compares the TP concentration range, in ditch 194 sediment, of this study to other literature data for similar rural ditch environments. West Sedgemoor 195 had the highest single observed TP sediment concentration, of all the compared sites TP ranges, and 196 the second highest low-end concentration. Even compared to other man-made managed aquatic 197 ecosystems, West Sedgemoor can be considered to have exceedingly high TP concentrations; a study 198 of fishponds in the Czech Republic observed an average sediment TP concentration of 1113.2 mg kg<sup>-</sup> <sup>1</sup>, across 28 sites, with a highest concentration of 3020 mg kg<sup>-1</sup> (Baxa et al., 2019). Although the 199 200 analytical method of this study differs from that of the other literature data, previous studies have 201 shown that the methods are equivalent (Blake et al., 2013; Matsunami et al., 2010).

#### 202 3.2 Main factors affecting phosphorus storage in sediment

**203** 3.2.1 Correlation coefficient analysis

The correlation coefficients between P, Fe, S, Al, Ca and % mud (<63  $\mu$ m) 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.

211 Seasonal increases in temperature and biological activity influences internal loading, retention 212 capacity and release mechanisms. Increasing temperatures stimulate mineralisation of organic matter 213 and the release of soluble inorganic phosphate. Increased sediment respiration during mineralization 214 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 215 216 P. Under oxic conditions, P is bound to Fe(III) compounds; under anoxic conditions, both P and Fe are 217 released to the water column as insoluble Fe(III) compounds are reduced to soluble Fe(II) 218 (Søndergaard et al., 2003). Additionally, low nitrate and high sulphate concentrations, combined with a large supply of biodegradable organic matter, enables dissimilatory sulphate reduction 219

(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).

231 In surface sediments of sites surrounded by RSPB nature reserve land, P showed significant positive 232 correlations with Fe (r = 0.682) and Al (r = 0.764) and significant negative correlations with S (r = -0.905) 233 and Ca (r = -0.758). This suggests P at these sites is primarily stored in the sediment bound to Fe and 234 Al, not Ca. The moderate P-Fe positive correlation along with significant negative correlations between 235 S-P (r = -0.905) and S-Fe (r = -0.894) suggest that sulphide interference of iron-phosphorus cycling is 236 happening, but Fe concentration is high enough that, in RSPB surrounded sites, Fe storage of P is still 237 a primary pathway (Fig. A3-A7 of the ESI). P retention from coprecipitation with Fe oxides may be 238 more prevalent in RSPB surrounded sites due to a larger influence of rooted macrophyte radial oxygen 239 loss (ROL) induced oxidised chemical conditions in the sediment rhizosphere. Most macrophytes 240 shield against harmful Fe sulphide precipitates via the ROL process, in which the roots release oxygen 241 into the rhizosphere forming protective plaques of Fe oxides (LaFond-Hudson et al., 2018; Smith and 242 Luna, 2013). These Fe oxides would then be available for coprecipitation with P (Petkuviene et al., 243 2019). This larger influence of ROL in RSPB surrounded sites may be due to higher S concentrations at 244 these sites and/or the RSPB land management as marsh and wet hay meadow, as this could be 245 supporting a larger amount of macrophytes and/or macrophytes species with higher radial oxygen 246 rates (Smith and Luna, 2013). Many of the plant species at West Sedgemoor are described in Table A1 247 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 253 254 (willow) beds, could be increasing mineralisation, decreasing oxygen and nitrate sediment penetration 255 depth and subsequently enabling sulphide-mediated chemical iron reduction, at these sites. Sulphide 256 interference of P retention from coprecipitation with Fe oxides may be more prevalent in sites 257 surrounded by land that is not RSPB nature reserve due to less rooted macrophyte ROL. As this land 258 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 259 260 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.

274 The lack of significant correlations observed for % mud (< 63  $\mu$ m) in the correlation coefficient analysis, 275 is most likely due to the lack of variance in particle size of the sediments. Fig. 4 is a sand, silt and clay 276 trigon (SSC trigon) showing sediment classification schemes based on the relative percentages of sand, 277 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 278 279 by WD-XRF due to an insufficient amount of <63  $\mu$ m fraction available; sites 31 and 57 are located at 280 opposite ends of the West Sedgemoor, so it's unlikely their increased particle size is linked. Localised 281 bank collapses could be a possible explanation for these sites having coarser sediment. A relatively 282 consistent particle size distribution suggests that variance in the P concentrations across the site 283 cannot be attributed to a bias towards higher concentrations being associated with finer sediment 284 (Capasso et al., 2020; Xiao et al., 2013).

#### **285** 3.2.2 Principal components analysis

286 A principal component analysis was conducted to determine whether the three designations of 287 sample sites (sites surrounded by RSPB nature reserve land, A; sites surrounded by land that is not 288 RSPB nature reserve, B; and sites adjacent to both land that is RSPB nature reserve and land that is 289 not RSPB nature reserve, C) could be distinguished from each other using their chemical and physical 290 properties. The first principal component explains 28.3% of the variation (Eigenvalue = 11.309) and is 291 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, 292 -0.284, 0.262, 0.246, -0.248 and -0.226, respectively). The second principal component explains 8.5% 293 of the variation and is mainly based on Na, Mg, K, Ca, Fe, Co, Cu, Ga, Rb, Ge and Ir (factor loadings = 294 -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 295 values, explained variance and cumulative variance of subsequent principal components is provided 296 in Table A2 of the ESI.

The principal component analysis score plot of West Sedgemoor SSSI surface sediment sample sites 297 298 (Fig. 5a) is shown bassed on chemical and physical differences illustrated in the occompaning loading 299 plot (Fig. 5b). A clear distinction can be seen between sites surrounded by RSPB nature reserve land 300 and sites surrounded by land that is not RSPB nature reserve, based on separation along the first 301 principal component axis. Sites of group A are generally positively correlated with the first principal 302 component, although site 37 appears to be an outlier in this case. Sites of group B are generally 303 negatively correlated with the first principal component. This suggests that land management 304 influences ditch surface sediment geochemistry, which could have the potential to affect P storage in 305 sediments. However, sites of group C are spread relatively evenly across the first principle component 306 axis, most likely owing to the groups varying land management influences. This shows that some group 307 C sites are more similar to group A sites than others, suggesting that certain sites are less influenced 308 by land that is not RSPB nature reserve than others, and vice versa. Group A sites were characterised 309 by relatively higher concentrations of S, Br, Cl and Sr, whereas the group B sites had higher Si, Ti, Al 310 and Y (Fig. 5b). Of these, S and Cl are likely associated with avian guano input on RSPB nature reserve 311 land (Chen et al., 2020; Schnug et al., 2018), while Sr has been reported to accumulate in egg shells 312 which suggests an input from migratory breeding (Kitowski et al., 2014; Mora et al., 2007). Si, Ti and 313 Al are related to terrigenous watershed input (Sabatier et al., 2014), whereas Y is present in 314 agricultural fertilisers which can cause diffuse pollution of rare earth elements in runoff and surface 315 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 316 317 group B sites have a lower chemical ability to bound P in the sediment, compared to groups A and C, 318 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).

#### 322 4 Conclusions

323 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<sup>-1</sup>, in the south (sites 23-47, 58 & 59) it was 1560 mg kg<sup>-1</sup>.
- 328 Based on correlation coefficient analysis, sediments phosphorus storage mechanisms vary 329 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 330 331 between P and Fe, indicating P bound to Fe(III) compounds and a greater chemical ability to 332 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 333 significant positive correlations between P and the selected parameters. Also, the lack of 334 significant correlations observed for % mud (< 63  $\mu$ m) in the correlation coefficient analysis, 335 336 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 337 nature reserve land and sites surrounded by land that is not RSPB nature reserve, based upon 338 339 their chemical and physical properties. RSPB nature reserve land surrounded sites were 340 characterised by relatively higher concentrations of S, Br, Cl and Sr, whereas sites surrounded 341 by land that is not RSPB nature reserve had higher Si, Ti, Al and Y concentrations. This suggests 342 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 343 geochemistry, which could have the potential to affect P storage in sediments. P has a weak 344 negative loading on the first component suggesting that P concentrations tend to be slightly 345 346 higher outside of the RSPB nature reserve.

## 347 Acknowledgements

This study was financially supported by a PhD studentship funded by the University of Plymouth, UK;
Natural England, UK; and Wessex Water, UK. The authors gratefully acknowledge; co-sponsor contacts
Mark Taylor (Natural England), Chris Tattersall and John Bagnall (Wessex Water); Harry Paget-Wilkes

at the Royal Society for the Protection of Birds for allowing access to the nature reserve at West Sedgemoor SSSI and sharing expert knowledge of the site; Phil Brewin at the Somerset Drainage Boards Consortium for sharing expert knowledge of the site; Alex Taylor at the University of Plymouth Consolidated Radio-isotope Facility (CORIF) for analytical expertise. The authors declare that there is no conflict of interest.

## 356 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
- Baxa, M., Šulcová, J., Kröpfelová, L., Pokorný, J., Potužák, J., 2019. The quality of sediment in shallow
- 361 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.
- 363 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
- 372 Burns, E.E., Comber, S., Blake, W., Goddard, R., Couldrick, L., 2015. Determining riverine sediment

373 storage mechanisms of biologically reactive phosphorus in situ using DGT. Environ. Sci. Pollut.

- 374 Res. 22, 9816–9828. https://doi.org/10.1007/s11356-015-4109-3
- 375 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.

380 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.
- 385 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.
- 397 Drewitt, A., Evans, T., Grice, P., 2008. Natural England Research Report NERR015 A review of the
   398 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.
- 404 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
- 407 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.

- 411 IPBES, 2018. Summary for policymakers of the thematic assessment report on land degradation and
- 412 restoration of the Intergovernmental Science-Policy Platform on Biodiversity and Ecosystem
  413 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
- 416 basins: The Hampshire Avon and Herefordshire Wye. J. Hydrol. 304, 51–74.
- 417 Jefferson, R.G., Grice, P. V., 1998. The conservation of lowland wet grassland in England, in: Joyce,
- 418 C.B., Wade, P.M. (Eds.), European Wet Grasslands: Biodiversity, Management and Restoration.
  419 John Wiley & Sons, Chichester, pp. 31–48.
- 420 Kitowski, I., Sujak, A., Wiącek, D., Strobel, W., Rymarz, M., 2014. Trace element residues in eggshells
  421 of Grey Heron (Ardea cinerea) from colonies of East Poland. J. Zool. 10, 346–354.
- 422 LaFond-Hudson, S., Johnson, N.W., Pastor, J., Dewey, B., 2018. Iron sulfide formation on root
- 423 surfaces controlled by the life cycle of wild rice (Zizania palustris). Biogeochemistry 141, 95–
  424 106. https://doi.org/10.1007/s10533-018-0491-5
- 425 Matsunami, H., Matsuda, K., Yamasaki, S., Kimura, K., Ogawa, Y., Miura, Y., Yamaji, I., Tsuchiya, N.,
- 426 2010. Rapid simultaneous multi-element determination of soils and environmental samples
- 427 with polarizing energy dispersive X-ray fluorescence (EDXRF) spectrometry using pressed
- 428 powder pellets. Soil Sci. Plant Nutr. 56, 530–540. https://doi.org/10.1111/j.1747-
- 429 0765.2010.00489.x
- 430 Met Office, 2019. Yeovilton climate information Met Office [WWW Document]. URL
- 431 https://www.metoffice.gov.uk/public/weather/climate/gcn45vme7 (accessed 3.5.19).
- 432 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.
- 437 Natural England, 2019. European Site Conservation Objectives: Supplementary advice on conserving
  438 and restoring site features Somerset Levels and Moors Special Protection Area (SPA) Site Code:
  439 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.

442 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.
- 447 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.
- 451 Parkin, G., Birkinshaw, S., Benyon, P., Humphries, N., Bentley, M., Gilman, K., 2004. Water availability
  452 and budgets for wetland restoration and recreation sites BD1316. DEFRA.
- 453 Parrett IDB, 2009. West Sedgemoor and Wick Moor Water Level Management Plan. Parrett Internal
  454 Drainage Board.
- 455 Petkuviene, J., Vaiciute, D., Katarzyte, M., Gecaite, I., Rossato, G., Vybernaite-Lubiene, I., Bartoli, M.,
  456 2019. Feces from Piscivorous and Herbivorous Birds Stimulate Differentially Phytoplankton
  457 Growth. Water 11, 2567. https://doi.org/10.3390/w11122567

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

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

460 Ramsar Convention Secretariat, Gland, Switzerland.

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

464 Riley, W.D., Potter, E.C.E., Biggs, J., Collins, A.L., Jarvie, H.P., Jones, J.I., Kelly-Quinn, M., Ormerod,

- 465 S.J., Sear, D.A., Wilby, R.L., Broadmeadow, S., Brown, C.D., Chanin, P., Copp, G.H., Cowx, I.G.,
- 466 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.
- 469 Sabatier, P., Poulenard, J., Fangeta, B., Reyss, J.L., Develle, A.L., Wilhelm, B., Ployon, E., Pignol, C.,
- 470 Naffrechoux, E., Dorioz, J.M., Montuelle, B., Arnaud, F., 2014. Long-term relationships among
- 471 pesticide applications, mobility, and soil erosion in a vineyard watershed. Proc. Natl. Acad. Sci.

- 472 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.

475 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.
- 478 Smith, K.E., Luna, T.O., 2013. Radial oxygen loss in wetland plants: Potential impacts on remediation
- 479 of contaminated sediments. J. Environ. Eng. (United States) 139, 496–501.
- 480 https://doi.org/10.1061/(ASCE)EE.1943-7870.0000631
- 481 Søndergaard, M., Jensen, J.P., Jeppesen, E., 2003. Role of sediment and internal loading of

482 phosphorus in shallow lakes. Hydrobiologia 506–509, 135–145.

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

486 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.
- 489 Environ. Qual. 36, 694–708.
- 490 Verheyen, D., Van Gaelen, N., Ronchi, B., Batelaan, O., Struyf, E., Govers, G., Merckx, R., Diels, J.,
- 491 2015. Dissolved phosphorus transport from soil to surface water in catchments with different
- 492 land use. Ambio 44, 228–240. https://doi.org/10.1007/s13280-014-0617-5

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

- 494 Wu, S., Zhao, Y., Chen, Y., Dong, X., Wang, M., Wang, G., 2019. Sulfur cycling in freshwater
- 495 sediments: A cryptic driving force of iron deposition and phosphorus mobilization. Sci. Total
  496 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

- 502 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.