

2021-04-15

# Spatial distribution of sediment phosphorus in a Ramsar wetland

Crocker, R

<http://hdl.handle.net/10026.1/17435>

---

10.1016/j.scitotenv.2020.142749

Science of The Total Environment

Elsevier BV

---

*All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.*

1 ACCEPTED COPY OF MANUSCRIPT

2 AVAILABLE AT:

3 Science of The Total Environment 765:142749-142749 Article number 142749 Apr 2021

4 Spatial distribution of sediment  
5 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>

7 <sup>a</sup> School of Geography, Earth and Environmental Sciences, University of Plymouth, Plymouth, Devon  
8 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  
16 treatment works) and diffuse (largely agricultural runoff) sources, is currently the central reason for  
17 failure in the majority of surface water bodies in England to meet required water quality guidelines.  
18 This study assesses phosphorus storage in the ditch systems at West Sedgemoor, a designated site of  
19 special scientific interest. Elevated phosphorus concentrations in sediment was observed across the  
20 Moor up to 4,220 mg Kg<sup>-1</sup>, almost 10 times that which may be expected from background levels. The  
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

27    Eutrophication; Managed floodplain; Drainage ditch; Surface sediment geochemistry; Non-point  
28    source 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  
33    benefit water supply; agriculture; fisheries and recreational fishing; tourism; and wetland products  
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  
48    vegetation to algae or duckweed dominance, leading to shading and potentially anoxic conditions and  
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  
64 stopovers have forced intensified use of the surviving habitat. These large bird populations, relative  
65 to the size and/or volume of the waterbody, can have a significant fraction of the internal P load cycling  
66 through their diet. Waterfowl have the potential to affect wetland P cycling by altering the form of P  
67 and by inputting and/or exporting P to and/or from external areas to the wetland (Adhurya et al.,  
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 ( $>0.1 \text{ mg-P l}^{-1}$  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.

89 Ditch sediment samples were collected from a range of locations, corresponding with different land  
90 uses, from agricultural to Royal Society for the Protection of Birds (RSPB) nature reserve areas. In order

91 to assess potential factors of P loading in sediments, sediments were also analysed for a range of major  
92 and minor element constituents and particle size. Multivariate principle component analysis was used  
93 to determine whether land use impacts ditch surface sediment geochemistry.

## 94 2 Material and methods

### 95 2.1 Study area

96 West Sedgemoor SSSI (51°01'40.8"N 2°54'45.2"W) is an area of the Somerset Levels and Moors  
97 Ramsar site and a Special Protection Area (SPA) site in Somerset, England; Fig. 1. This inland wetland  
98 has a total area of 10.16 km<sup>2</sup> and consists of many small, low lying fields and meadows separated by  
99 narrow water-filled ditches, locally called rhyne. 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  
113 the moor, swiftly followed by the addition of the North Drove Rhyne which was dug parallel to the  
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).

117 Runoff provides one of the main sources of water to West Sedgemoor, from a relatively small  
118 catchment (roughly 41 km<sup>2</sup>). Widness Rhyne in the west contributes most of the runoff water entering  
119 the moor. Other runoff water sources include the North Curry and Stoke St Gregory ridge, draining  
120 directly to both Sedgemoor Old Rhyne and West Sedgemoor Main Drain, and Wick Moor (fed also by  
121 the River Parrett; nontidal) and Curry Rivel ridge, draining to Wickmoor Rhyne. During the summer, a  
122 culvert allows the moor to be supplied with water direct from the River Parrett (nontidal) via the Oath

123 Farm Inlet. Although the area is still often flooded, water levels are lowered in the winter to reduce  
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  
129 changing from drainage to irrigation, barring high flood risk conditions (e.g. heavy rainfall). During the  
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  
135 Wigeon (*Anas penelope*), Teal (*Anas crecca*) and Lapwing (*Vanellus vanellus*). The moor also supports  
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 Sedgemoor 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 erythrophthalmus*),  
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

151 Surface sediment samples were collected in March 2018. 59 sampling sites (Fig 2.) were chosen based  
152 upon (1) coverage of IDB viewed rhynes and potential inputs (2) site accessibility/access permission  
153 (3) minimal disturbance to nature conservation efforts of the RSPB. Samples were collected using a  
154 Van Veen Grab sampler and transferred into hydrochloric acid (10% - Fisher Scientific Primar Plus) and

155 Ultra high purity water (>18 Mohm.cm) soaked HDPE 500 ml Nalgene bottles, and stored frozen at -  
156 18°C in the dark until further analysis.

157 Once thawed, samples were centrifuged at 4000 rpm for 10 minutes, and the majority of the pore  
158 water was poured off. At this stage samples were individually mixed and had subsamples taken for  
159 particle size analysis. Roots and other large plant material were either not present or removed from  
160 samples manually. These subsamples of sediment were pushed through a stainless steel mesh sieve  
161 with a 1.00 mm aperture, and then pretreated with H<sub>2</sub>O<sub>2</sub> to remove organic constituents. Particle size  
162 analysis was measured using a Malvern Mastersizer 2000. Particle size analysis data was analysed  
163 using GRADISTAT (Blott S.J. and Pye K., 2001).

164 The remaining sediment was frozen, freeze-dried, disaggregated and sieved to the <63 µm fraction.  
165 Subsamples were then taken, milled and pressed into pellets for analysis using a PANalytical  
166 Wavelength Dispersive X-Ray Fluorescence Spectrometer (WD-XRF) (Axios Max); the concentrations  
167 of a range of major and minor element constituents (F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co,  
168 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  
169 (Blake et al., 2013). Sites 12, 46 & 50 were unable to be analysed by WD-XRF due to an insufficient  
170 amount of <63 µm fraction available.

## 171 2.3 Principle Component analysis

172 Principal component analysis (PCA) of the WD-XRF and particle size analysis data was conducted using  
173 Minitab 17. No outliers were observed from examining the Mahalanobis distances plotted in Fig. A1  
174 of the Electronic Supplementary information (ESI) (Brereton, 2015). The grouping of the sites was  
175 visualized with a scatterplot of the scores of the second principal component versus the scores of the  
176 first principal component. The variables responsible for the grouping of sites were identified by  
177 plotting the coefficients of each variable for the first component versus the coefficients for the second  
178 component.

## 179 3 Results and discussion

### 180 3.1 Spatial phosphorus distribution in sediment

181 The spatial distribution of total phosphorus (TP) in sediments is shown in Fig. 3. The highest TP content  
182 of 4220 mg kg<sup>-1</sup>, around 10 times that which may be expected from background levels (Owens and  
183 Walling, 2002), was recorded at site 53 located on the section of Wickmoor Rhyne that intersects  
184 Eastern Rhyne, south of the Oath Supply Ditch. Site 30, on the southern end of the Middle Rhyne, had  
185 the lowest observed TP concentration of 957 mg kg<sup>-1</sup>, while the mean concentration for the whole site  
186 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  
188 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  
189 mg kg<sup>-1</sup>. Lower TP concentrations were generally observed around winter roost sites with a mean  
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>-1</sup>  
199 <sup>1</sup>, across 28 sites, with a highest concentration of 3020 mg kg<sup>-1</sup> (Baxa et al., 2019). Although the  
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

204 The correlation coefficients between P, Fe, S, Al, Ca and % mud (<63 µm) particle size, for West  
205 Sedgemoor SSSI, are shown in Table 2. Sediment P was not correlated with Fe (r = 0.169), Al (r = 0.261),  
206 Ca (r = -0.051) or % mud (r = -0.066). This varies from data reported for other rivers in England for  
207 example where a stronger correlation was observed (Burns et al., 2015) between P and Ca. The  
208 reasons for a lack of correlation potentially reflects the varying sources and magnitudes of the  
209 elements across the wetland site including agricultural runoff, inflows from the main river, including  
210 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  
215 have the capability to keep iron in its oxidised form, their decline can cause redox-sensitive release of  
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  
219 a large supply of biodegradable organic matter, enables dissimilatory sulphate reduction



220 (desulphurication) and sulphide-mediated chemical iron reduction. This sulphide precipitation  
221 depletes the amount of Fe available for P binding, influencing both short- and long-term P retention  
222 in sediments (Søndergaard et al., 2003; Wu et al., 2019; Zhao et al., 2019). A weak negative correlation  
223 was observed between P and S ( $r = -0.400$ ), suggesting a possible S interference in iron-phosphorus  
224 cycling by sulphide-mediated chemical iron reduction. However, there is a general lack of significant  
225 correlations observed, for the site as a whole, from which to draw conclusions.

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

248 Surface sediments of sites surrounded by land that is not RSPB nature reserve showed less significant  
249 correlations than in RSPB surrounded sites. P concentrations were not correlated to Fe ( $r = -0.120$ ), Al  
250 ( $r = -0.012$ ), Ca ( $r = 0.174$ ) or % mud ( $r = -0.263$ ). A weak negative correlation was observed between  
251 P and S ( $r = -0.400$ ) and a moderate positive correlation between Fe and S ( $r = 0.659$ ) suggest that  
252 sulphide interference of iron-phosphorus cycling is occurring (Fig. A8 and A9 of the ESI). A potentially

253 high input of organic matter, such as cow manure from pasture or leaf-fall from arable land withy  
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  
259 and/or species with lower radical oxygen rates than the marsh and wet hay meadow managed RSPB  
260 land. However, it is unclear what mechanisms affect P storage for sites that don't boarder RSPB land.

261 Surface sediments of sites adjacent to both land that is RSPB nature reserve and land that is not RSPB  
262 nature reserve showed less significant correlations than in RSPB surrounded sites and sites that don't  
263 boarder RSPB land. Therefore, the sites bordering both types of land are relatively more different from  
264 each other geochemically, which suggests that the dominate land management influence varies for  
265 these sites. P showed a significant moderate positive correlation with Fe ( $r = 0.635$ ) (Fig. A10 of the  
266 ESI). P concentrations were not correlated to S ( $r = -0.009$ ), Al ( $r = 0.124$ ), Ca ( $r = -0.007$ ) or % mud ( $r =$   
267  $0.213$ ). This suggests P at these sites is primarily stored in the sediment bound to Fe, not Al or Ca.

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

274 The lack of significant correlations observed for % mud ( $< 63 \mu\text{m}$ ) 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  
278 four sites being classified as silty sand. Of the silty sand sites, 46 and 50 were unable to be analysed  
279 by WD-XRF due to an insufficient amount of  $<63 \mu\text{m}$  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.

297 The principal component analysis score plot of West Sedgemoor SSSI surface sediment sample sites  
298 (Fig. 5a) is shown based on chemical and physical differences illustrated in the accompanying 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  
316 enriched in the group B sites due to soil runoff. Although correlation coefficient analysis indicated that  
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

319 be slightly higher outside of the RSPB nature reserve (Fig. 5b). This suggests that higher P  
320 concentrations at group B sites is due to higher P input from the surrounding agricultural land.  
321 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:

- 324 • The analysis of total phosphorus (TP) in sediments show that all the sites have elevated  
325 concentrations, with sites in the north of the moor, near key inlets and the outlet generally  
326 showing the highest concentrations. Mean TP concentration in the north of the site (sites 1-  
327 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  
330 Society of the Protection of Birds (RSPB) nature reserve and privately owned land. Correlations  
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  
333 land. As opposed to sites surrounded by land that is not RSPB nature reserve that had no  
334 significant positive correlations between P and the selected parameters. Also, the lack of  
335 significant correlations observed for % mud (< 63 µm) in the correlation coefficient analysis,  
336 is most likely due to the lack of variance in particle size of the sediments.
- 337 • Principal component analysis showed clear distinction between sites surrounded by RSPB  
338 nature reserve land and sites surrounded by land that is not RSPB nature reserve, based upon  
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)  
343 nature reserve and privately owned (e.g. agricultural) land influences ditch surface sediment  
344 geochemistry, which could have the potential to affect P storage in sediments. P has a weak  
345 negative loading on the first component suggesting that P concentrations tend to be slightly  
346 higher outside of the RSPB nature reserve.

## 347 Acknowledgements

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

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

## 356 References

- 357 Adhurya, S., Das, S., Ray, S., 2020. Guantrophication by Waterbirds in Freshwater Lakes: A Review  
358 on Ecosystem Perspective, in: Springer Proceedings in Mathematics and Statistics. Springer, pp.  
359 253–269. [https://doi.org/10.1007/978-981-15-0422-8\\_22](https://doi.org/10.1007/978-981-15-0422-8_22)
- 360 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  
362 nutrients and organic matter recycling in agricultural landscapes. *Ecol. Eng.* 127, 151–159.  
363 <https://doi.org/10.1016/j.ecoleng.2018.11.009>
- 364 Blake, W., Comber, S., Burns, E.E., Goddard, R., Dougal, M., Taylor, A., Couldrick, L., 2013. Spatial and  
365 geochemical distribution of particulate P in river sediments impacted by DWPA and urban and  
366 industrial effluent., University of Plymouth Catchment and River Science (CARiS) research group  
367 report for Westcountry Rivers Trust.
- 368 Blott S.J., Pye K., 2001. GRADISTAT: a grain size distribution and statistics package for the analysis of  
369 unconsolidated sediments. *Earth Surf. Process. Landforms* 26, 1237–1248.
- 370 Brereton, R.G., 2015. The Mahalanobis distance and its relationship to principal component scores. *J.*  
371 *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.,  
376 2020. Influence of flow on phosphorus-dynamics and particle size in agricultural drainage ditch  
377 sediments. *PLoS One* 15, e0227489. <https://doi.org/10.1371/journal.pone.0227489>
- 378 Carpenter, S.R., Bennett, E.M., 2011. Reconsideration of the planetary boundary for phosphorus.  
379 *Environ. Res. Lett.* 6, 014009.
- 380 Chen, Y., Shen, L., Huang, T., Chu, Z., Xie, Z., 2020. Transformation of sulfur species in lake sediments

381 at Ardley Island and Fildes Peninsula, King George Island, Antarctic Peninsula. *Sci. Total Environ.*  
382 703. <https://doi.org/10.1016/j.scitotenv.2019.135591>

383 Collins, A.L., McGonigle, D.F., 2008. Monitoring and modelling diffuse pollution from agriculture for  
384 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  
386 of phosphorus in wastewater effluent from a variety of treatment processes. *J. Environ. Chem.*  
387 *Eng.* 3, 2924–2930.

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

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

393 Drake, C.M., Stewart, N.F., Palmer, M.A., Kindemba, V.L., 2010. The ecological status of ditch  
394 systems: an investigation into the current status of the aquatic invertebrate and plant  
395 communities of grazing marsh ditch systems in England and Wales Technical Report.  
396 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.

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

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

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

408 Hughes, J.M.R., Heathwaite, A.L., 1995. Introduction, in: Hughes, J.M.R., Heathwaite, A.L. (Eds.),  
409 *Hydrology and Hydrochemistry of British Wetlands*. John Wiley & Sons, Inc., Chinchester, UK,  
410 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.

414 Jarvie, H.P., Jürgens, M.D., Williams, R.J., Neal, C., Davies, J.J.L., Barrett, C., White, J., 2005. Role of  
415 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-](https://doi.org/10.1111/j.1747-0765.2010.00489.x)  
429 [0765.2010.00489.x](https://doi.org/10.1111/j.1747-0765.2010.00489.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  
433 the lowland Havel River, Germany, by agricultural fertilization and effluents of sewage  
434 treatment plants. *Appl. Geochemistry* 41, 62–72.

435 Mora, M.A., Taylor, R.J., Brattin, B.L., 2007. Potential ecotoxicological significance of elevated  
436 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.

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

442 Environ. Manage. 135, 54–62.

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

445 Owens, P.N., Walling, D.E., 2002. The phosphorus content of fluvial sediment in rural and  
446 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., Viridis, T.,  
448 Buscarinu, P., Lugliè, A., 2017. Consequences of eutrophication in the management of water  
449 resources in Mediterranean reservoirs: A case study of Lake Cedrino (Sardinia, Italy). *Glob. Ecol.*  
450 *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 Petkuvienė, 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.,  
467 2018. Small Water Bodies in Great Britain and Ireland: Ecosystem function, human-generated  
468 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.

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

476 Schnug, E., Jacobs, F., Stöven, K., 2018. Guano: The White Gold of the Seabirds, in: Mikkola, H. (Ed.),  
477 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](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).

487 Van der Perk, M., Owens, P.N., Deeks, L.K., Rawlins, B.G., Haygarth, P.M., Beven, K.J., 2007. Controls  
488 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.

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

500 Zhang, W., Zhu, X., Jin, X., Meng, X., Tang, W., Shan, B., 2017. Evidence for organic phosphorus  
501 activation and transformation at the sediment–water interface during plant debris

502 decomposition. *Sci. Total Environ.* 583, 458–465.

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

506