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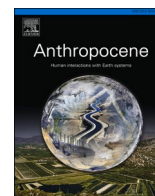
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Research article

Chemical speciation of sediment phosphorus in a Ramsar wetland



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ABSTRACT

Phosphorus (P) is an essential nutrient, which at excessive concentrations can cause eutrophication of aquatic ecosystems. In freshwater wetlands, water quality deteriorates under these conditions, often succumbing to algal or duckweed dominance, over the biodiversity of other aquatic vegetation. Freshwater sediment may act as an internal source of legacy bound P that can induce production of algal and duckweed blooms beyond what may be expected from external loading of P alone. This study assesses the mobility, bioavailability, and origin of phosphorus in wetland ditch systems at the designated site of special scientific interest, West Sedgemoor. Based upon associations with different P species, using principal component analysis, a clear distinction was observed between sites outside and within the West Sedgemoor Nature Reserve (managed by the Royal Society of the Protection of Birds). Sites outside the nature reserve, typically wet and damp grassland used for arable use and grazing, were generally correlated to higher percentages (median 58.5 %) of non-apatite inorganic P (associated with iron and aluminium mineralogy) and higher total P levels (average 1277 mg/kg), associated with algal and duckweed blooms, in comparison to areas within the nature reserve (median non-apatite inorganic P; 49.9 % (average total phosphorus; 936.9 mg/kg).

1. Introduction

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

However, not all P species contribute towards eutrophication due to differences in sediment release mobility and bioavailability. Hence, the ability of a sediment to store or release P is dependant not only on the amount of P, but also the proportions of different P species present. Consequently, it is crucial to determine P fractionation, not just total P

content, in the planning of water management and restoration of water bodies (González Medeiros et al., 2005; Ruban et al., 2001a).

Environmental studies often use sequential extraction schemes to quantify discrete chemical fractions and assess the mobility and bioavailability of P (Hupfer et al., 2020; Martin et al., 1987; Psenner and Puckso, 1988; Ruban et al., 2001a; Wang et al., 2013). These methods can also allow for the assessment of P in the sediment. Despite many developed extraction schemes for P speciation, there is no widely acceptable standardised method, largely due to its variety and changeability in sediments. Data comparability is possible based on standardised procedures, but it requires collaborative verification by group(s) of researchers (González Medeiros et al., 2005; Ruban et al., 2001a; Wang et al., 2013). Therefore, a proposed harmonised sequential extraction scheme for P in freshwater sediments was produced by the European Commission through the Standards, Measurements and Testing (SMT) Programme. Referred to as the SMT method, it has the added advantage of an associated certified reference material (CRM), BCR 684, for quality control (González Medeiros et al., 2005; Ruban et al., 2001b; Wang et al., 2013). Table 1 summarises and compares the SMT method to several other sediment P sequential extraction procedures. Both the Golterman (1996) and sequential extraction method (SEDEX) (Ruttenberg, 1992) methods have the benefit of separating out

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more specific P fractions. However, both of these schemes are difficult to perform. Alternately, the Hietjes and Lijklema (1980) method is simple and practical, but it is limited as it only determines three separate fractions directly, none of which are organic P (OP). Organic P can still be calculated as the difference between total P (TP) and inorganic P (IP). The extraction scheme of Williams et al. (1976) as modified by Burrus et al. (1990) is simple and practical, involving two independent procedures, which determine NaOH-P (non-apatite IP, NAIP), HCl-P (apatite inorganic phosphorus, AP), OP, and TP. As a modified version of the Burrus et al. (1990) scheme, the SMT extraction method builds upon its predecessor, adding a third independent procedure and yielding an IP fraction in addition to NAIP, AP, OP, and TP. The SMT method was therefore chosen for this study owing to its simplicity, practicality, and how it allows laboratories to generate reproducible and comparable results using its associated CRM (Ruban et al., 2001a,b; Wang et al., 2013).

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

2. Material and methods

2.1. Study area

West Sedgemoor SSSI (51°01'40.8"N 2°54'45.2"W) is an area of the Somerset Levels and Moors Ramsar site and a Special Protection Area (SPA) site in Somerset, England; Fig. 1. It has a total area of 10.16 km², typically 5 m above sea level, consisting of low-lying fields and meadows separated by narrow water-filled ditches locally referred to as rhyes. The Parrett Internal Drainage Board (IDB) manages water levels and flow circulation, while the Environmental Agency (EA) operates the only outlet from the site, West Sedgemoor Pumping Station, which drains into the River Parrett (tidal).

Runoff provides one of the main sources of water to West Sedgemoor, from a relatively small catchment (roughly 41 km²). Most of the runoff water entering the moor is provided by Widness Rhyne, located south-west of the site. North Curry and Stoke St Gregory ridge drain runoff directly to both Sedgemoor Old Rhyne and West Sedgemoor Main Drain. Runoff water is also provided by Wick Moor (fed also by the River Parrett; nontidal) and Curry Rivel ridge, draining to Wickmoor Rhyne. The moor can also be supplied with water direct from the River Parrett (nontidal) via a culvert, during the summer. Water levels are lowered in the winter to reduce flood risk, although, a raised water level area is maintained year-round in the interest of nature conservation efforts (Parrett, 2009). The moor hosts England's largest breeding population of wading birds such as lapwing (*Vanellus vanellus*), snipe (*Gallinago gallinago*) and curlew (*Numenius arquata*), making the site internationally important for supporting wintering waterfowl populations (Natural England, 2019). Rare and scarce invertebrate fauna are also abundant, particularly water beetles (*Hydaticus transversalis*, *Dytiscus dimidiatus*, *Hydrophilus piceus*), in part justifying the Somerset Levels' Ramsar status

Table 1
Sediment phosphorus sequential extraction schemes for the determination of fractional composition.

Method	Extraction Procedure	Proposed fraction	Advantages	Disadvantages
(Burrus et al., 1990; Williams et al., 1976)	a. NaOH 1 M (Extract + 3.5 M HCl)	Non-apatite P	Simple, practical	Partial resorption of NaOH extracted P on CaCO ₃
	a. 1 M HCl	Apatite P		
	a. Calcination + HCl 3.5 M	Total P		
	a. Calcination + HCl 1 M	Organic P		
SMT (Ruban et al., 2001a,b)	a. NaOH 1 M (Extract + 3.5 M HCl)	Non-apatite inorganic P	Simple, practical	Partial resorption of NaOH extracted P on CaCO ₃
	a. 1 M HCl (a. residue)	Apatite P		
	a. Calcination + HCl 3.5 M	Total P		
	a. 1 M HCl	Inorganic P		
(Hietjes and Lijklema, 1980)	a. Calcination + HCl 1 M (d. residue)	Organic P	Simple, practical	Dissolution of small amounts of Fe-P and Al-P by NH ₄ Cl; hydrolysis of organic P; no relation with bioavailability
	a. NH ₄ Cl 1 M pH 7	Labile P		
	a. NaOH 0.1 M	Fe- and Al-bound P		
	a. HCl 0.5 M	Ca-bound P		
(Golterman, 1996)	a. H ₂ O	Labile P bioavailable	Extracts specific compounds; permits extraction of organic P fractions; provides information on bioavailable fractions	Not practical; EDTA interferes with P determination; complicated solution preparation; in some sediments, extraction must be repeated
	a. Ca-EDTA 0.05 M + dithionite	Fe-P bioavailable		
	a. Na ₂ -EDTA 0.1 M	Ca-P nonavailable		
	a. H ₂ SO ₄ 0.25 M	Acid-soluble Organic P bioavailable		
SEDEX (Ruttenberg, 1992)	a. NaOH 2 M reductant	Organic P non-available	Separating between different apatite forms; no redistribution of P on to residual solid surfaces	Long; not practical; difficult to achieve butanol extraction
	a. MgCl ₂ 1 M	Loosely sorbed P		
	a. Na ₃ -citrate 0.3 M + NaHCO ₃ 1 M	Ferric Fe-bound P		
	a. Na-acetate 1 M	Authigenic apatite, Ca-bound P, biogenic apatite		
	a. HCl 1 M	Detrital apatite P		
	a. Calcination + HCl 1 M	Organic P		

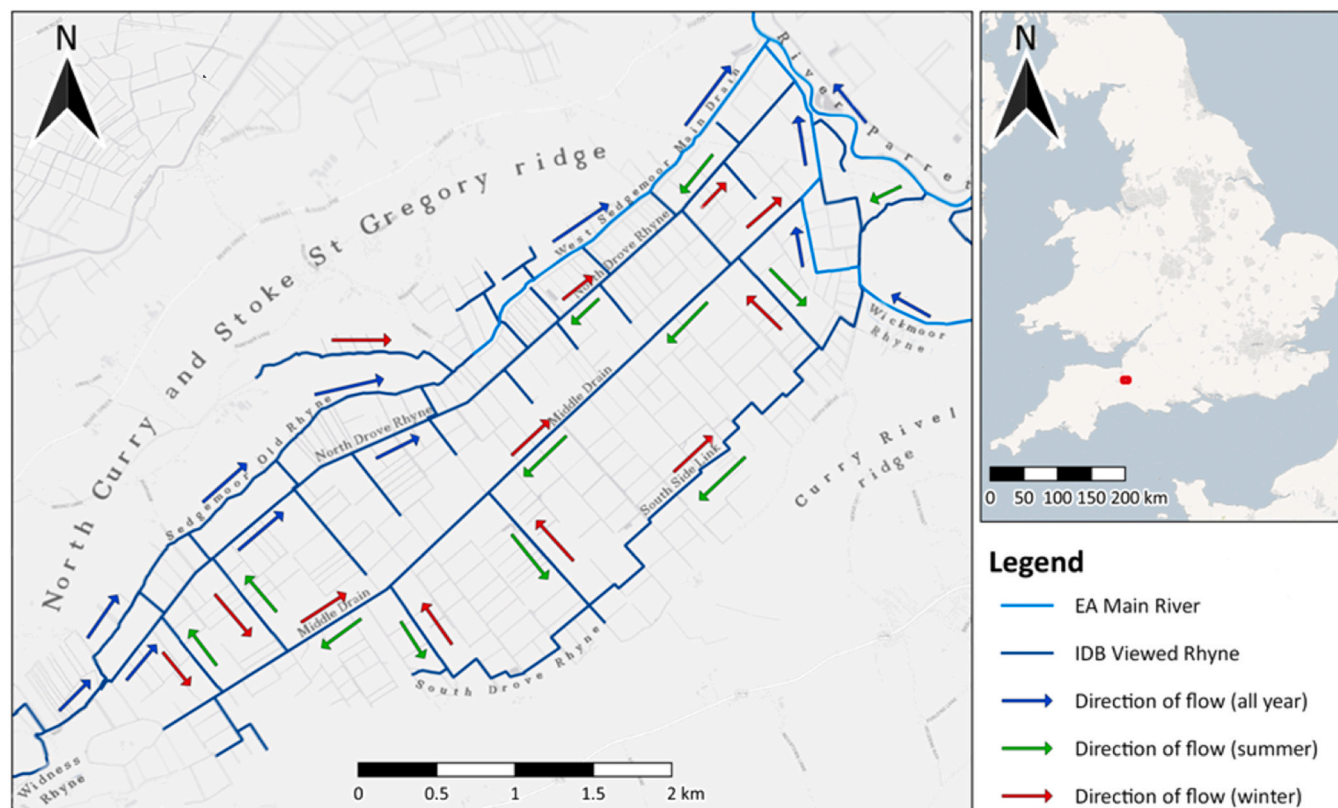


Fig. 1. Location and controlled water flows of West Sedgemoor SSSI. Upper right inset shows the study area within Southwest England (red box). Left panel shows seasonal dependant water flow directions, indicated by coloured arrows (blue, all year; green, summer; red, winter). Reproduced from Crocker et al. (2021).

under Ramsar criterion 2 (Drake et al., 2010).

2.2. Sampling and chemical analyses

Surface sediment samples were collected using a Van Veen grab sampler (maximum 10 cm depth) in March 2018 at 59 sampling sites covering areas both within and outside of the RSPB nature reserve (Fig. 2). Sites were chosen based upon (1) coverage of IDB viewed rhyne; (2) accessibility/access permission; and (3) minimal disturbance to RSPB nature conservation efforts. Samples were collected in HDPE 500 ml Nalgene bottles pre-soaked in hydrochloric acid (10 % - Fisher Scientific Primar Plus) and Ultra high purity water ($>18 \text{ Mohm.cm}^{-1}$), and stored frozen at $-18 \text{ }^\circ\text{C}$ in the dark. Unwanted material (e.g., fragments of vegetation) was removed from the sediment grab samples prior to collection.

Total elemental concentrations were determined according to methods described in Crocker et al. (2021), using a Wavelength Dispersive X-Ray Fluorescence spectrometer (WD-XRF) (PANalytical Axios Max) for a range of major and minor element constituents (F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Br, Rb, Sr, Y, Zr, Nb, Ba, Ce, Pb, As, Au, Bi, Ge, Ir, Mo, Nd, Pr, Se, Tl and V) and by particle size analysis (Malvern Mastersizer 2000).

For sequential extraction analysis, post-thawing, samples were centrifuged at 4000 rpm for 10 min, and pore water was discarded, prior to refreezing and subsequent freeze-drying. After this, samples were homogenised and subsequently sieved to the $<63 \mu\text{m}$ fraction. Sub-samples of sediment (0.2 g) were then taken and were sequentially extracted using the SMT method (Fig. 3). NAIP is the fraction associated with Fe, Al and Mn oxides and hydroxides (typically bioavailable), while the AP fraction is associated with Ca-bound P (typically non available) (Pardo et al., 1999; Ruban et al., 2001b; Wang et al., 2013). All P determination was made by either inductively coupled plasma - optical

emission spectrometry (ICP-OES; Thermo Scientific ICAP 7400 Series) or inductively coupled plasma mass spectrometry (ICP-MS; Thermo Scientific X 199 Series 2).

2.3. Data analysis

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

Principal component analysis (PCA) of the sequential extraction data and previously determined WD-XRF and particle size analysis data was conducted using Minitab 19 (Crocker et al., 2021). No outliers were observed from examining the Mahalanobis distances plotted in Fig. A1 of the ESI (Brereton, 2015). Grouping of the sites was visualised with a scatterplot of the scores of the second principal component versus the scores of the first principal component. Sites were defined by surrounding land management (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), where surrounding refers to the associated land on the banks of each ditch sampling site. Variables responsible for the grouping of sites were identified by plotting coefficients of each variable for the first component versus coefficients for the second component.

3. Results and discussion

3.1. Reliability of the sequential extraction

Modified Z-scores identified potential outliers in 13 of the 59 sites

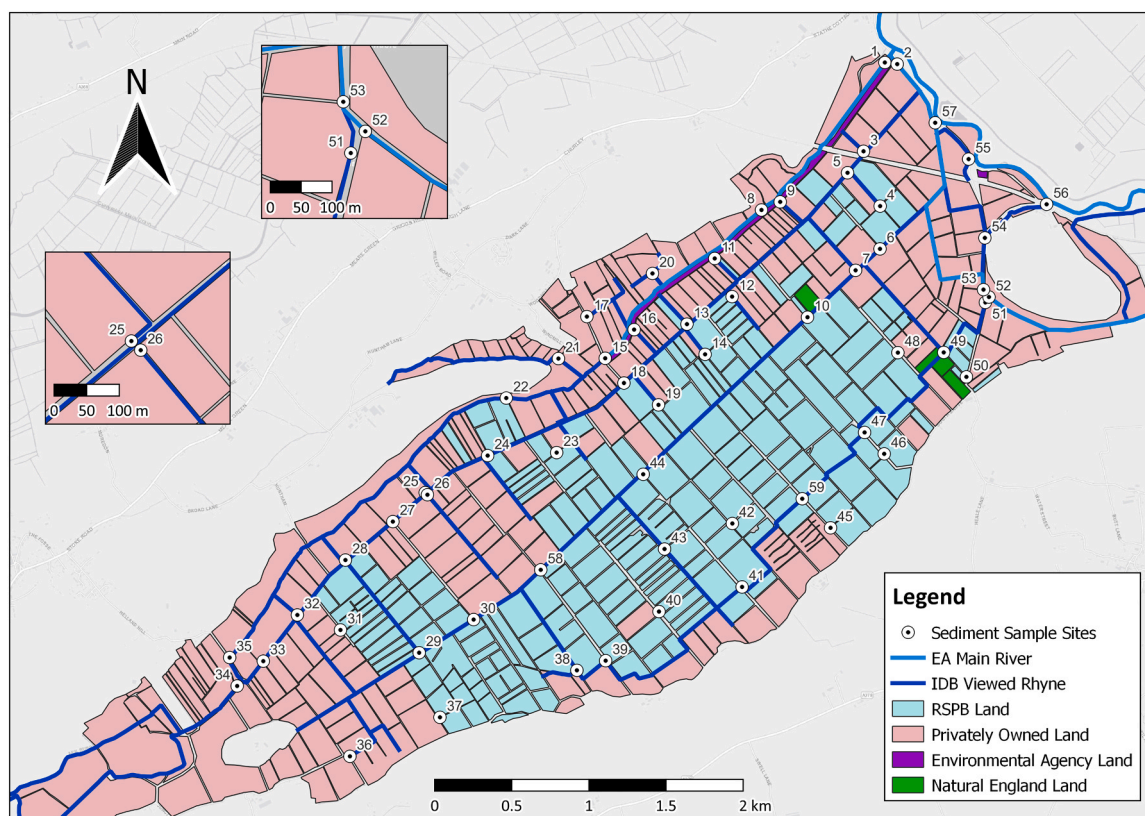


Fig. 2. Sediment sampling sites and land ownership on West Sedgemoor SSSI. Site numbering begins in the upper right corner and proceeds generally in an anticlockwise fashion. Insets present a magnified highlight of sites that otherwise appear to overlap at the scale of the main map. Reproduced from (Crocker et al., 2021).

sampled: sites 2, 6, 8, 10, 26, 28, 30, 34, 40, 42, 43, 46 and 50 were removed from the data set. Comparing values of TP from the sequential extraction with the corresponding WD-XRF TP value revealed the sequential extraction procedure extracted on average 40 % less TP than what was observed using WD-XRF, despite previous studies observing high correlation between the two techniques (Pardo et al., 2003). WD-XRF was previously shown to be a reliable technique for P analysis (Blake et al., 2013).

In spite of the development of many procedures, P extraction has no standardised method in part because of the variation in sediment compositions (calcareous, siliceous, organic rich, etc.). Hence, extraction procedures are designed for specific sediment types. The SMT method is most suited to siliceous sediments, although it has been shown to be satisfactory in the analysis of various sediment types (Pardo et al., 2003; Wang et al., 2013). Advantages of the SMT method include being more economical and simpler than other methods, as well as having an associated certified reference material (CRM), BCR 684, which was used in this study with acceptable recoveries (Table. A1 of the Electronic Supplementary information) (Pardo et al., 2003, 1999; Wang et al., 2013). A representative subsample of 10 sites (sites 5, 18, 20, 29, 35, 39, 44, 52, 55 & 59) analysed for organic matter by loss on ignition (LOI) showed 53.1–92.1 % combustion (average 71.1 %, median 69.2 %; Table. A2 of the Electronic Supplementary information), indicating that the sediment at West Sedgemoor is organic rich. This is unsurprising as the area is a fen peat environment; and the majority of the sediment is classified as sandy silt (Crocker et al., 2021; Ross and Heathwaite, 1984). To assess the possibility that high organic matter content of the West Sedgemoor sediments caused low recoveries of TP by the siliceous sediment suited SMT method, the correlation between percent recovery (between SMT and WD-XRF) and organic matter content (% LOI) was analysed. A strong positive correlation of $R = 0.904$ with a p-value significance level of < 0.01 was observed between percent recovery and

% LOI showing that SMT extraction TP values were closer to the corresponding WD-XRF TP value in sediments with higher organic matter content. Alternatively, P mineralisation could be the cause of low TP recoveries. One of the known shortcomings of the SMT method is the partial resorption of P extracted by NaOH on CaCO_3 , a common problem with sequential extraction methods for sediment P (Wang et al., 2013). A weaker correlation was observed between percent recovery and Ca concentration ($R = -0.593$, p-value = 0.071), and given that Ca concentrations (29,600–99,500 mg/kg) were well in excess of P concentrations, a degree of resorption of P could not be discounted. Both Cl and Pb were observed to have strong negative correlations with percent recovery (Cl; $R = -0.888$, p-value < 0.01) (Pb; $R = -0.703$, p-value < 0.05). This suggests the presence of pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$), a highly insoluble lead phosphate mineral that is chemically and biologically and forms in surface soil environments (Tai et al., 2013). It's likely that sequential extraction techniques would have difficulty extracting P from minerals such as pyromorphite. Conversely, XRF techniques have been demonstrated effective at analysing phosphate rock (Amar et al., 2022; Hasikova et al., 2014; Safi et al., 2006) This could also explain the large number of outliers observed through modified Z-scores. While sequential extraction data cannot be considered reliably quantitative, sites with acceptable modified Z-scores (for the sum of the determined values of component fractions as a percentage of the determined value of their sum fraction) can still be observed qualitatively and a comparison of relative values across sites remains valid. Only in comparison with other data reported using the same methodology, should caution be used in interpretation.

3.2. Qualitative analysis of sediment phosphorus fractions

The spatial distribution between sum fractions NAIP & AP (Fig. 4a) and IP & OP (Fig. 4b), are shown in Fig. 4. The spatial distribution of the

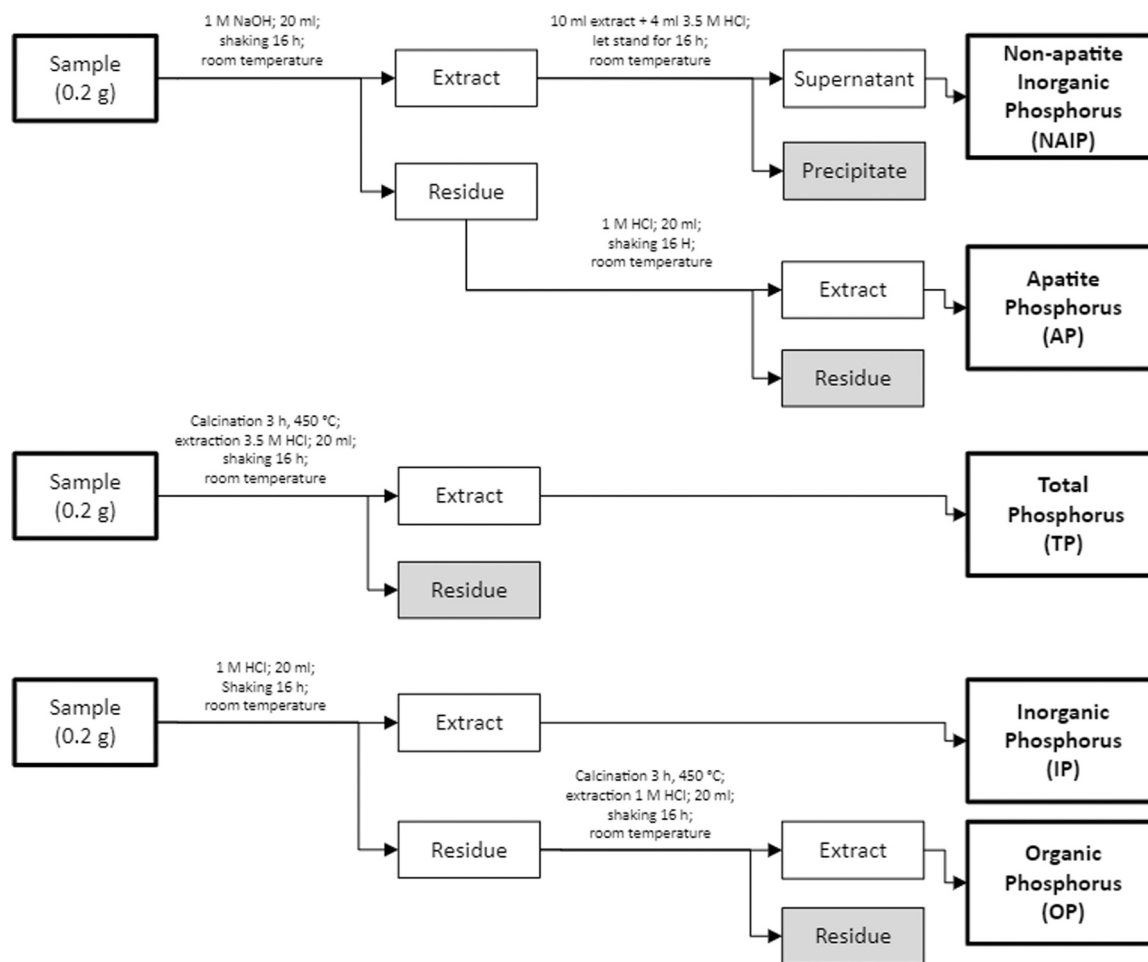


Fig. 3. Standards Measurements and Testing Programme of the European Commission (SMT) extraction method protocol flow chart.

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

The principal component analysis score plot of West Sedgemoor SSSI surface sediment sample sites observed in this study (Fig. 5a) is shown based on chemical and physical differences illustrated in the accompanying loading plot (Fig. 5b), using previously published XRF and particle size analysis data (Crocker et al., 2021) and sequential extraction data from this study. The first principal component explains 34.7 % of the variation (eigenvalue = 12.146) and is mainly based on Al, Si, S, Cl, Ti, Br, Sr, Y and Zr (factor loadings = 0.257, 0.278, -0.267, -0.251, 0.279, -0.246, -0.245, 0.228 and 0.219, respectively). The second principal component explains 11.6% of the variation (eigenvalue = 4.056) and is mainly based on NAIP, AP, TP, IP, XRF TP, Mg, K, Cr, Rb and Ba (factor loadings = 0.257, 0.285, 0.297, 0.293, 0.329, -0.313, -0.324, 0.235, -0.287 and -0.222, respectively). Eigenvalues

explained variance, and cumulative variance of subsequent principal components is provided in Table A3 of the ESI. Between sites surrounded by RSPB nature reserve land (group A) and sites surrounded by land that is not RSPB nature reserve (group B), a clear distinction can be observed based on separation along the first principal component axis (Crocker et al., 2021). Sites of group A are generally negatively correlated along the first principal component, characterised by relatively higher concentrations of S, Br, Cl and Sr, with site 37 considered an outlier in this case. This is likely due to avian inputs on RSPB nature reserve land (Crocker et al., 2021), with S and Cl being associated with avian guano input (Chen et al., 2020; Schnug et al., 2018), and Sr being observed to bioaccumulate in eggshells (Kitowski et al., 2014; Mora et al., 2007). Sites of group B are generally positively correlated along the first principal component, characterised by relatively higher concentrations of Si, Ti, Al, and Y. This is likely due to agricultural soil runoff inputs (Crocker et al., 2021), with Si, Ti and Al being associated to terrigenous watershed input (Sabatier et al., 2014), and Y being associated with diffuse pollution of agricultural fertilisers (Möller et al., 2014; Otero et al., 2005). Of the P variables, OP is the only one to not have a strong positive PC2 eigenvector (factor loading = -0.031) and to have a negative PC1 eigenvector (factor loading = -0.159). This suggests that sites surrounded by RSPB nature reserve land are more associated with higher OP levels while sites surrounded by land that is not RSPB nature reserve are generally correlated with higher IP and TP levels.

Land surrounding group B sites is typically wet and damp grassland suitable for arable use and grazing. Much of this land is used for grazing dairy cattle, together with a limited amount of beef cattle farming and crop farming (typically associated with willow production). In

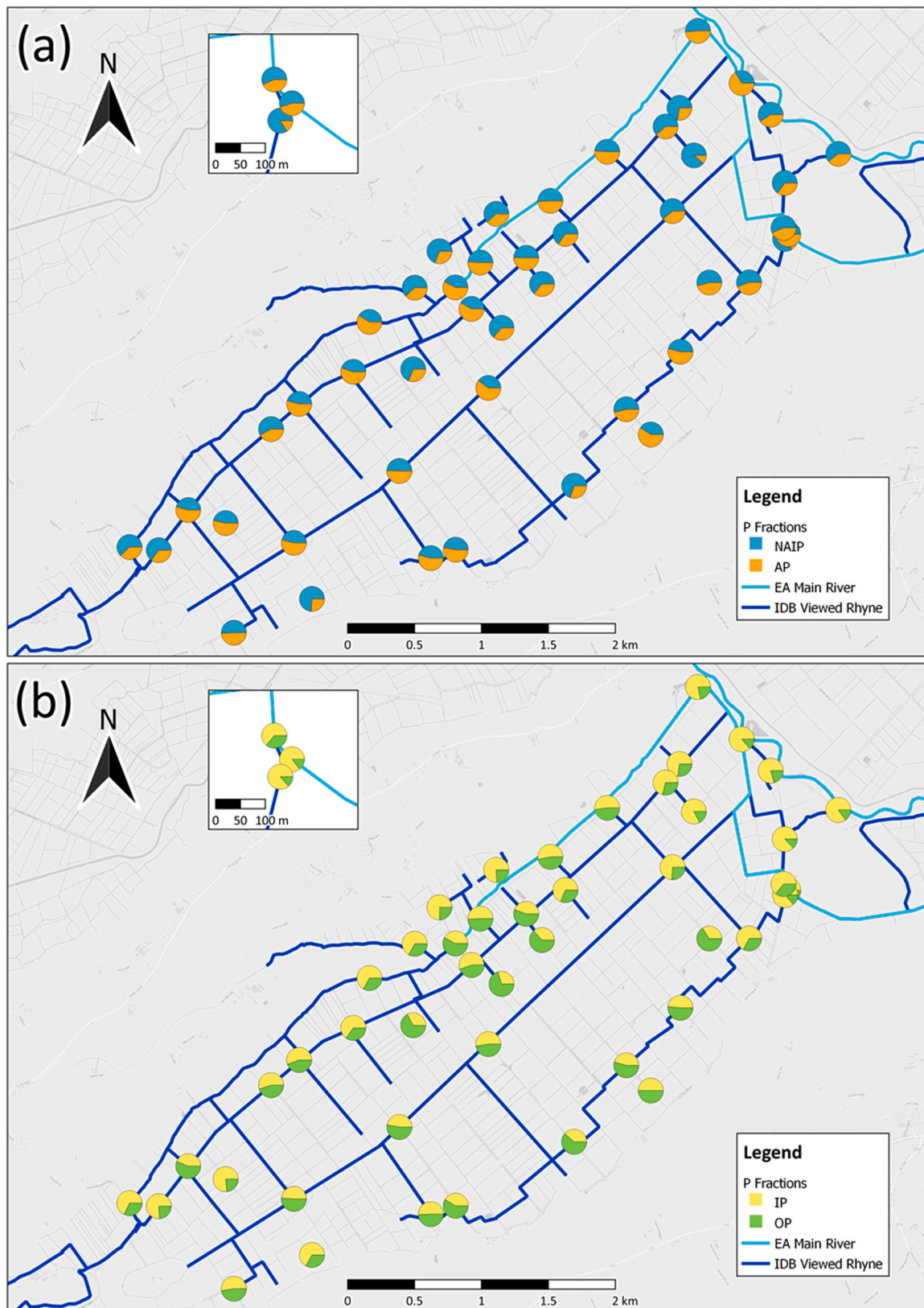


Fig. 4. (a) distribution of the partitioning between sum fractions non-apatite inorganic phosphorus (NAIP) & apatite inorganic phosphorus (AP) at West Sedgemoor SSSI; (b) distribution of the partitioning between sum fractions inorganic phosphorus (IP) and organic phosphorus (OP) at West Sedgemoor SSSI. Insets present a magnified highlight of sites that otherwise appear to overlap at the scale of the main map.

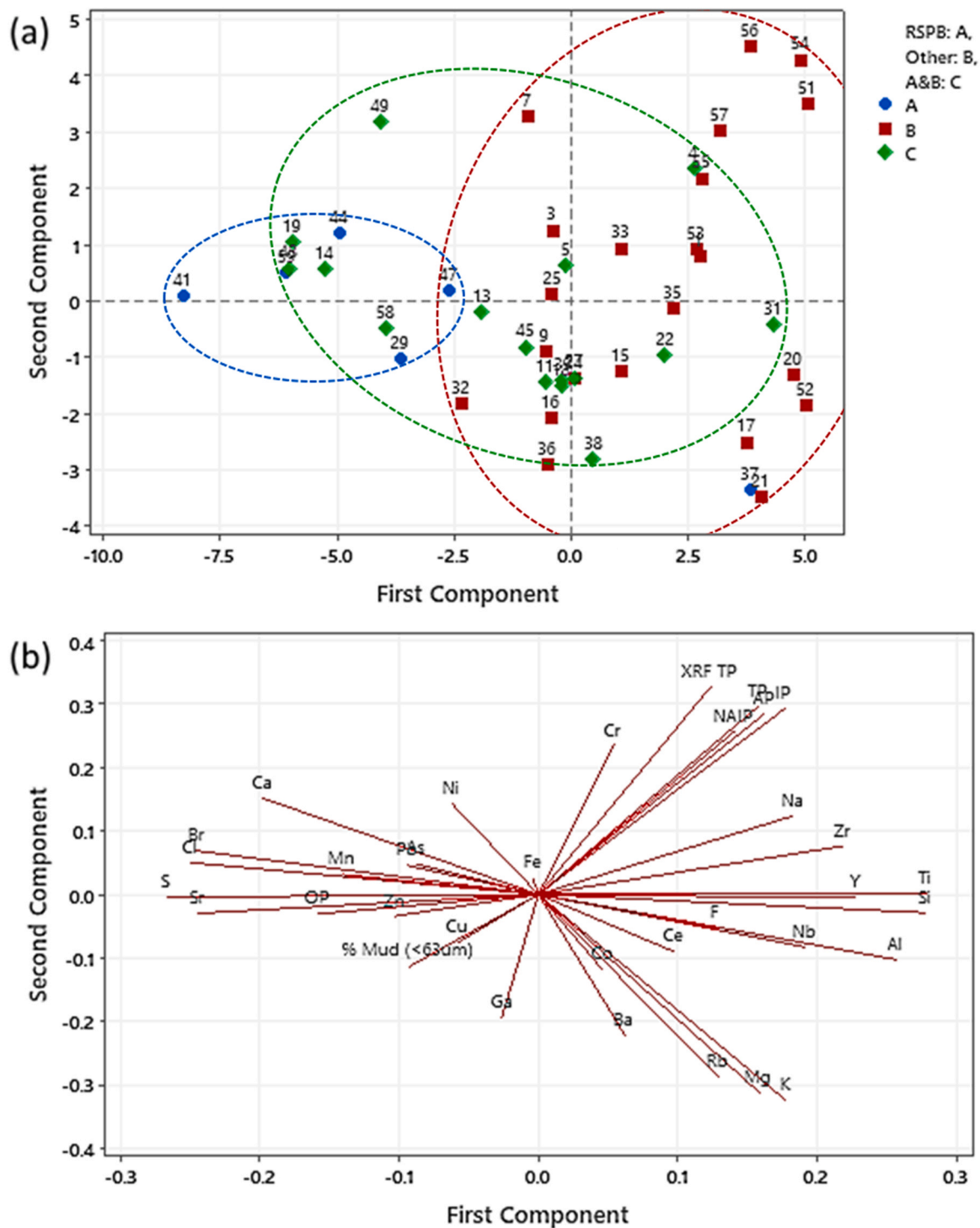


Fig. 5. (a) principal component analysis score plot of West Sedgemoor SSSI surface sediment sample sites based on chemical and physical differences. Scores for the first two principal components are plotted. The first principal component explains 34.7 % of the variation (eigenvalue = 12.146). The second principal component explains 11.6 % of the variation (eigenvalue = 4.056). Sites are defined by surrounding land management (sites surrounded by RSPB nature reserve land, A; sites surrounded by land that is not RSPB nature reserve, B; and sites adjacent to both land that is RSPB nature reserve and land that is not RSPB nature reserve, C). (b) principal component analysis loading plot of West Sedgemoor SSSI surface sediment chemical and physical properties. The coefficients of each variable for the first component versus the coefficients for the second component are plotted.

agricultural soils, the major input of IP are P fertilisers, with approximately 70–80 % of P being IP in cultivated soils (Foth, 1990). Within hours of application, fertiliser P is converted into water-soluble IP as orthophosphate ions H_2PO_4 and HPO_4^{2-} (Schute and Kelling, 1996). Available moisture in the soil dissolves fertiliser particles, increasing IP concentrations in solution. Relatively insoluble complexes are then

formed between negatively charged IP and positively charged Fe, Al and Ca ions (Bhattacharya, 2019). Runoff water can then carry this IP adsorbed to particles of soil or manure into nearby water bodies such as wetland ditches. This is likely to cause IP enrichment of ditch sediments on West Sedgemoor, at sites surrounded by agricultural land and at inlet sites allowing water in from intensely farmed catchment areas. Manure

and urine from large numbers of livestock kept in small areas can also result in excess P (both organic and inorganic) leaching into the surrounding environment when not managed efficiently (Barnett, 1994; Department for Environment Food and Rural Affairs, 2006).

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

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

4. Conclusions

The main findings of the research are as follows:

- The Standards Measurements and Testing Programme of the European Commission (SMT) sequential extraction method was poorly suited for the quantitative analysis of the sediments found on West Sedgemoor. Data were therefore examined qualitatively after removing identified outliers using modified Z-scores.
- Principal component analysis showed clear distinction between sites surrounded by differing land management, based upon their associations with different P species. Sites surrounded by land not RSPB nature reserve were generally correlated to higher IP and TP levels, while sites surrounded by RSPB nature reserve land were more associated with higher OP levels. This suggests P storage in sediments was directly affected by surrounding land management influences.
- The difference in IP enrichment between ditch sites could be caused by land management differences regarding P fertiliser application. Artificial fertilisers were not applied on the RSPB nature reserve land, where IP concentration in surrounding ditch sediments was relatively lower. Agricultural cultivated soils are typically IP enriched with fertiliser use, where surrounding ditch sediments were higher in IP concentration.
- Sites surrounded by land that is not RSPB nature reserve were generally correlated with higher NAIP and TP sediment levels and are more likely to facilitate eutrophic algal blooms than sites surrounded by RSPB nature reserve land.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ancene.2023.100398.

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