Using $^{206/207}\text{Pb}$ isotope ratios to estimate phosphorus sources in historical sediments of a lowland river system

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Abstract

Purpose Engineering and dredging strategies to manage sediment, along with river-scouring, can reveal older sediments. These present a unique opportunity to assess past sources of phosphorus (P) inputs into river sediments. We used the sediment concentrations of P, lead (Pb) and $^{206/207}\text{Pb}$ isotopes to produce ‘first-order’ estimates of the source (diffuse agricultural or sewage treatment) of phosphorus.

Materials and methods Sediment cores ($n = 30$) were collected from the length of the non-tidal River Nene, a lowland river in eastern England. Cores were analysed for sediment elemental concentrations and Pb isotopes. Principal component analysis and linear regression modelling were used to assess the relationships between P, Pb and Pb isotopes. Monte-Carlo simulations and bootstrapping were undertaken to estimate, with 95% confidence intervals, the source of P in these sediments.

Results and discussion Analysis of the relationships between P_{Total} , Pb_{Total} and $^{206/207}\text{Pb}$ isotope ratios suggested that sediments were deposited largely prior to the phasing out of tetra-ethyl Pb (Pb_{BHT}) from petrol. Regression models showed positive correlations between P_{Total} and Pb_{Total} ($R^2 = 0.85$). Principal component analysis suggested a strong sewage treatment signal for Pb and P enrichment. In the rural upper three water bodies, little sewage treatment work (STW)-derived P was found in the sediment, a consequence of limited STW input and greater sediment transport. In the more urbanised water bodies 4–6, ‘first-order estimates’ of STW P suggest that median concentrations were 30–40% of P_{Total} .

Conclusions The strong relationships between Pb and P concentrations in river water provided the opportunity to use $^{206/207}\text{Pb}$ isotope ratios to calculate ‘first-order’ estimates of the proportion of P released from STWs in the historical sediment. Understanding the sources of historical sediment P can be used to assess the success of current sediment management strategies and to base further mitigation measures. Results suggest that whilst much recent sediment P is removed, the legacy sediment remains to contribute P to the water body. Thus, options regarding the practical removal of these sediments and the extent to which this would improve water P status need to be assessed and balanced against options such as further decreasing soil P or STW P stripping.

Keywords Phosphorus · Lead · $^{206/207}\text{Pb}$ isotope · Sediment

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1 Introduction

River sediment phosphorus has been identified as a major ‘legacy issue’ (Johnes et al. 2007; Sharpley et al. 2013; Environment Agency 2014), contributing as surface waters failing ‘Good Ecological Status’ in accordance with the EU Water Framework Directive (Directive EC 2000/60/EC). For example, recent modelling work by Powers et al. (2016) on the Thames catchment in the UK demonstrated that net P outputs still exceed net inputs. This suggests that sources of accumulated legacy P are still contributing to the catchment P balance, despite the

decrease in soluble reactive P in the Thames (Kinniburgh and Barnett 2010).

Sediment can be either a P sink or a P source depending on its characteristics and P concentration. When riverine P is fixed within oxide phases or P containing minerals such as octacalcium phosphate, calcium hydroxyapatite, tri-calcium phosphate (House and Denison 1997; House and Denison 2000), or vivianite under reducing conditions (Tye et al. 2016), they act as a P sink. Recent work has contributed towards a greater understanding of the interactions between sediment and P with respect to accumulation within river systems. Proximity to STWs has been identified as a cause of increased sediment P concentrations downstream (Dorizio et al. 1989; Howell 2010). Bowes et al. (2008) modelled the relative contribution of point and diffuse sources for Total P (TP) in waters from three UK rivers finding that point sources accounted for 0–93% of yearly TP load, depending on flow and proximity to STWs. Sediments will act as a P source when labile phosphate is desorbed and released to the water column, for instance when soluble reactive P concentrations, decline to concentrations below the equilibrium phosphate concentration (EPC₀) value (Froelich 1988). This may occur if P stripping in sewage treatment works (STWs) decreases soluble reactive P (SRP) in waters sufficiently. In addition, seasonal changes in EPC₀ concentrations have been found primarily through changes in sediment particle size (House and Denison 1997; House and Denison (2002).

Recent work has examined P in suspended particulate matter (SPM), which may potentially form riverine sediment deposits. For example, Cooper et al. (2015) examined three agricultural headwater catchments of the River Wensum, UK, and found that the source of SPM-P changed, with P having a greater association with Fe oxides under base flow conditions and particulate organic carbon (POC) under flood conditions. Ballantine et al. (2008) suggested geological controls on suspended sediment TP, as well as demonstrating that suspended sediment P was greater in areas of input associated with intensive agriculture.

Whilst these studies have identified interactions and processes affecting P concentrations in SPM, they do not identify the balance between sources (e.g. agriculture, STWs) of P in deposited sediment. A number of factors such as water velocity, sediment trapping by vegetation and resuspension during changing flow regimes will determine sediment deposition in natural systems. Prior to deposition suspended sediment is liable to in-channel processes of sorption and desorption of elements with river water. The concentration in the river water along with sediment properties, water pH and conductivity will all contribute towards the equilibrium between sediments and water. In heavily engineered rivers, with mediation strategies for sediment deposition which include dredging, the dynamics of sediment deposition, when combined with

natural processes such as scour, can have major effects on where and how long sediment deposits build.

Within the complexity of these processes, some sediments will become stabilised over time, leaving concentrations of ‘legacy P’, which may potentially interact with the river water, over a range of different time scales. However, key questions relating to ‘legacy sediment P’ remain unanswered. These include (i) understanding the residence time of sediment and its associated P within the river system; and (ii) the relative contribution of sediment P from diffuse (e.g. agriculture) or point sources (e.g. STWs) and their changes with distance from the headwaters. Increasing our understanding of these factors may inform the effectiveness of current and future P mitigation measures from STWs and agricultural land. This is of growing importance particularly as recent work by Ockenden et al. (2017) suggests that the influence of increased winter rainfall, as a result of a changing climate, may increase winter P loads by up to 30% by 2050, through increases in surface runoff and soil erosion.

One way of addressing these sediment P questions is through the use of geochemical tracers that demonstrate similar behaviour and pollution pathways to the major sources of phosphorus in sediments, and whose source can be identified. For example, one such technique may be the use of $\delta^{18}\text{O}$ in phosphates (e.g. Gooddy et al. 2018). The aims of this paper are to report on a ‘first-order’ basis the historical contributions of point and diffuse sources to sediment P stored within a lowland river in southern England. Sources of sediment P are estimated through the broad geochemical relationships found in the sediments combined with knowledge of their sources, and in particular through the relationship between P and the concentration of Pb and $^{206/207}\text{Pb}$ isotopes. The use of Pb and $^{206/207}\text{Pb}$ isotopes as a tracer for this purpose is unusual as large-scale Pb emittance to the environment ceased when tetra-ethyl Pb was no longer added to petrol. However, a combination of river engineering improvements, the use of buffer strips, dredging interventions within the river system and natural scour during flooding events have permitted older sediments to remain, allowing the use of $^{206/207}\text{Pb}$ isotope ratios as a tracer for this specific purpose. Understanding the historical source contributions of P in sediments may be used as evidence when assessing the success of current management interventions of sediment P to improve water quality.

2 Materials and methods

2.1 The Nene catchment

The River Nene rises in Northamptonshire, flowing in a northeasterly direction out to the sea via the town of Northampton and City of Peterborough (Fig. 1). It is the 10th longest river in the UK, being 161-km long with a total catchment area of

Fig. 1 Map of the study area and sampling locations in each of the water bodies of the River Nene. Sewage treatment works that discharge to the

Nene are shown. Coordinates show kilometres of the British National Grid

2270 km². This length of the non-tidal river is divided into six Water Framework Directive (WFD) water bodies by the Environment Agency and cores taken from each water body are identified in Fig. 1. The catchment for these upper six water bodies has an area of 1590 km². The source starts at ~160 m above ordnance datum (AOD) and falls to ~6 m AOD at Peterborough. The largest fall occurs in the first 9.5 km, with the channel lying at 80 m AOD at the end of water body 1 (Meadows 2007). The floodplain varies in width from a few hundred meters to ~2 km. The channel frequently bifurcates and in sections is heavily engineered (Williams and Fawthrop 1988; Meadows 2007). Major land use within the catchment is agriculture, mainly arable (cereals and oilseed rape) with areas of grassland. Several urban centres including Northampton and Peterborough are sited within the catchment. Further information on the Nene catchment including elevation, land

cover, precipitation and historical flow data can be accessed at the National River Flow Archive (<https://nrfa.ceh.ac.uk/data/station/spatial/32010>). Further information on the geology can be accessed from the British Geological Survey online viewer (<http://mapapps.bgs.ac.uk/geologyofbritain/home.html?>). Samples were collected from the non-tidal section of the River Nene, from its source close to Daventry to the west of Peterborough.

2.2 Catchment geology

The bedrock geology of the non-tidal River Nene catchment is dominated by mudstones of the Lias group (Early Jurassic). The Dyrham formation (interbedded siltstones and mudstones) is dominant for the catchment of water bodies 1–3, and the Whitby Mudstone formation is dominant in the

catchment associated with water bodies 4–6 (Cox et al. 1999). A small area of Charmouth mudstone exists within water bodies 1–3, but this is a minor geological component. In addition, Jurassic ironstones and marlstones that belong to the Great Oolite group are present within the catchment. The Nene catchment is beyond the southern ice limit of the Devensian stadial but some glacial outwash along with sands and gravels are found in the catchment. The sands and gravels (Milton Sand) represent earlier trunk rivers (Brown et al. 1994) and their extraction has left a range of adjacent wetland environments to some stretches of the river.

2.3 Sediment sources and dynamics

The River Nene is heavily engineered and has a history of interventions to remove sediment. It is recognised as a slow flowing river and has suffered from major siltation and macrophyte growth in the past. The River Nene Catchment Board was formed in 1930 to enable extensive dredging and improved sediment management (Meadows 2007). Engineering has led to bends being straightened to speed water flow thereby decreasing deposition. In addition, regular dredging has taken place. Recent dredging events have been undertaken in 2009, 2013 and 2017. These operations typically remove $\sim 10,000 \text{ m}^3$ of sediment from known areas of deposition. This is likely to reduce sediment availability within a system that already has low sediment input.

Recent work by Pulley and Foster (2017) in the Nene catchment suggests that annual sediment yields are of the order of $11.2 \text{ t km}^{-2} \text{ year}^{-1}$ pre-1963 and only $\sim 11.9 \text{ t km}^{-2} \text{ year}^{-1}$ post-1963 (typically sediment yields are between 28 and $51 \text{ t km}^{-2} \text{ year}^{-1}$ for similar UK catchments with high arable agricultural land usage). ^{137}Cs measurements suggest that almost 100% of the sediment yield originates from bank sediments in the Nene, a consequence of the high usage of buffer strips on arable land and riparian fencing on grassland adjacent to the river, preventing surface soil erosion. The soils are slow draining (as a result of the mudstones being the dominant parent material) and sediment input direct to the channel from under field drainage was identified during the sediment sampling program. However, the large volume of water flowing through the system when these high precipitation events occur mean that much of this sediment is likely to be transported straight into the tidal Nene. Common flooding events also induce scour. Significant large-scale sediment flushing has previously been recorded for the River Nene and this is a relatively common event (Brierley et al. 1989; Meadows 2007; EA 2008). These events combined are likely to mean that there may not be a typical geomorphological response with respect to sediment deposition in the river.

2.4 Site selection and sampling

The sampling strategy was originally designed to obtain robust estimates of sediment P concentrations in each of the six water bodies with a reasonable estimate of variability (Tye et al. 2016). Thus, five sediment cores were collected from each water body and each homogenised prior to analysis to give a total of 30 cores from the river. A sixth core (Core_D) was taken from each water body to allow P variations with depth to be examined in the initial study (Tye et al. 2016) but these cores (core numbers on Fig. 1: 2, 7, 15, 20, 28, 35) do not form part of the current work. Data on water sample quality (pH, electrical conductivity, temperature) at the time of sampling in each water body can be found in Tye et al. (2013). Locations of the cores collected from each water body are shown (Fig. 1). For water bodies 1 and 2 and several samples of water body 3, the cores were collected by wading in the river, whilst a boat was used to collect samples from water bodies 4, 5 and 6. Sampling positions in WB 4–6 were partially determined by the availability of boat launch sites and the travelling time between sites. Sampling was undertaken in the winter so little information regarding potential habitats of sediment sampled was available, although a tour of sampling sites in the summer revealed that they were mainly covered in macrophytes (e.g. *Iris pseudacorus*). Because the sampling design was established to examine the concentrations of phosphorus through the length of the non-tidal river, it is not of a fine enough resolution to specifically trace P and other contaminants declining downstream from STWs.

Sampling followed the very wet autumn/winter of 2012/13 in January and February 2013, a time of unusually long periods of flooding and high river flows. Extensive probing of the river channel suggested that a large sediment flushing event had occurred, with only well stabilised sediment deposits remaining. River flow was still above base-flow when the samples were collected. Cores were taken by pushing a length of polycarbonate tube (internal diameter = 58 mm) into the sediment until hard substrate was reached. Sediment was retained through the use of a core catcher, at the base of the tube. However, in the upper three water bodies, there was insufficient sediment at nine sites to collect a core sample. At these sites, a sample of the sediment was taken by hand. All core sections used in total sediment analysis were kept $< 4^\circ\text{C}$ after sampling and before drying. The total depth of hand sampled sediment and sediment cores taken was recorded.

2.5 Sediment sample characterisation

The homogenised core samples taken from each water body were air-dried ($< 30^\circ\text{C}$) before being sieved to $< 2 \text{ mm}$. The depth of core was recorded and the mass of air-dry sediment from each of the cores in each water body was weighed. Total elemental and Pb isotope analyses of the sediment were

undertaken on dried and homogenised sediment subsamples (~30 g). These were ground in an agate mill to <150 µm. Milled samples were digested by weighing 0.25 g of soil into a Savillex™ vial and adding 2.5 mL HF, 3 mL 50 % HNO₃ and 1 mL HClO₄ concentrated and analytical grade acids, with a subsequent stepped heating program up to 170 °C overnight, to digest silicate and oxide phases. The dry residue was re-constituted after warming with Milli-Q water, HNO₃ and H₂O₂, to 25 mL of 5% v/v HNO₃ and stored in HDPE bottles. Reference materials (SRM2711 Montana Soil (mean 108% Pb recovery) and MES4 marine sediment (mean 105% Pb recovery)), duplicated samples and blanks were all prepared in a similar manner to check accuracy of the analytical and digestion method. The labs operate under ISO17025:2017 Quality Management for Laboratories accreditation.

The Pb isotope ratios in the sediment samples were determined using an Agilent 7500 quadrupole ICP-MS. Preparation of the instrument for isotope ratio determinations involved the plateauing of the detector voltage, cross-calibration of the pulse counting-analogue modes and updating of the dead-time correction factors. Isotope ratio determinations consisted of 10 replicate integrations of 30 s; each integration being 1000 peak jumps (1 point per peak) across the isotopes ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb. Mass bias was addressed by using the isotope ratio for the reference material NIST SRM981, whilst correction factors were interpolated with reference to the accepted isotope ratios (Thirlwall 2002). All samples were diluted to produce best counting statistics within the linear range of the pulse counting detector (<8000 k cps). Quality control for Pb isotope ratios was performed using an in-house solution produced from a naturally occurring UK galena—‘Glendenning’ with long-term (6 years) precision being 0.09% for ²⁰⁶Pb/²⁰⁷Pb and 0.11% for ²⁰⁸Pb/²⁰⁷Pb ratios. Individual sample errors in Pb isotope ratios were calculated by propagating the precision of individual sample measurements and the uncertainty in the measurements of the SRM981 sample. Typical sample uncertainties estimated are as follows: 2SD [²⁰⁶Pb/²⁰⁷Pb] = 0.009; 2SD [²⁰⁸Pb/²⁰⁷Pb] = 0.015.

2.6 Potential sources of tracer elements within the Nene catchment

In this paper, the source of P and Pb is of particular interest. Elevated concentrations of other elements, in particular Zn, Cd, Sb, can also act as additional confirmatory tracers as they exhibit similar pathways. Sources of ‘diffuse’ P are generally related to agricultural practice including that from soil erosion (including erosion via under field drainage), run off from manure or concrete in farmyards and potentially from leaking septic tanks. The extent of the latter is not known for this catchment. Point sources of P are those from STWs with sources including (i) as a by-product of human waste and (ii)

P injected into drinking water by water companies to limit the solubilisation of Pb from domestic water systems (Ascott et al. 2016).

Sources of ‘diffuse’ Pb will be largely associated with soils. From the BGS G-BASE survey, concentrations of soil Pb are typically <50 mg kg⁻¹. Information regarding collection of samples and analysis can be found in Johnson et al. (2005). There is no coal mining or Pb mining within the catchment. In urban parts of the catchment, soils are likely to have accumulated greater additional Pb from petrol than rural soils, with greater Pb isotope changes in soils in close proximity to roads. In agricultural fields, diffuse Pb pollution will be mixed when soils are ploughed and cultivated. Izquierdo et al. (2012) examined changes in Pb isotope ratios along the River Trent in the English Midlands and found that elevated Pb concentrations in floodplain soils were found close to urban areas. However, only where samples were taken within range of road drainage or downstream of STWs were changes in Pb ratios indicative of greater deposition of petrol Pb.

A survey of Nene catchment soil Pb concentrations and ²⁰⁶/²⁰⁷Pb isotope ratios was undertaken to assess potential ‘geological Pb’ end members (Table 1). Deep soil ²⁰⁶/²⁰⁷Pb (~50 cm) ratios for the Dyrham and Whitby mudstones which would be representative of river bank values were 1.1925 and 1.2001. A third, and much smaller parent material in the catchment, is the glacio-fluvial sand and gravels had a ²⁰⁶/²⁰⁷Pb ratio of 1.1812. Pb isotope data for an urban soil developed over the Jurassic ironstone formations (BGS Guidance Material 102) in the neighbouring county of Lincolnshire gave a ²⁰⁶/²⁰⁷Pb ratio of 1.1766 and a ²⁰⁸/²⁰⁷Pb ratio of 2.4609, similar to Pb_{geo} ratios within the catchment (Table 1). P concentrations in soils and sediments derived from ironstones are typically <4500 mg kg⁻¹ P, with most values ~2000 mg kg⁻¹, but fertiliser sources need also to be considered (Breward 2007).

The local Pb isotope ratio from Leicestershire coal, a likely source of diffuse Pb deposition within the catchment, has a normal distribution with a mean of 1.182 and a standard deviation 0.008. This figure is similar to that reported for other coal samples from the East Midlands (Farmer et al. 1999). All soil samples collected from the Nene Catchment, with the exception of four flood plain samples from water body 6, had ²⁰⁶/²⁰⁷Pb values within the range of error associated with British coal and ore.

Historically, petrol Pb had a major ‘point’ source through STWs. The transfer of tetra-ethyl derived Pb to STWs is likely through the direct deposition of aerosols to the road surface from exhausts that were later washed from the road into the water treatment system during precipitation events. Biggins and Harrison (1980) identified PbSO₄·(NH₄)₂SO₄ as the dominant Pb-bearing species in atmospheric particulates collected next to a major road in Lancaster (UK). This is an intermediate compound

Table 1 $^{206/207}\text{Pb}$ isotope ratios from samples taken within the Nene catchment

Sample	Easting	Northing	Sample depth (cm)	Water body	Total Pb (mg kg ⁻¹)	$^{206/207}\text{Pb}$	$^{208/207}\text{Pb}$
1 Dyrham formation top soil	458210	259544	0–15	1	44.8	1.182	2.461
2 Dyrham formation sub soil	458210	259544	50–75	1	20.2	1.201	2.482
3 Dyrham formation Alluvium	457106	259282	0–15	1	43.3	1.180	2.460
4 Dyrham formation top soil	458067	259445	0–15	1	48.0	1.170	2.450
5 Dyrham formation Alluvium	458067	259445	0–15	1	24.3	1.193	2.475
6 Chamwood formation top soil	458813	258945	0–15	1	32.7	1.176	2.455
7 Chamwood formation sub soil	458813	258945	50–75	1	22.9	1.193	2.474
8 Whitby formation Alluvium	458722	259132	0–15	1	43.4	1.186	2.466
9 Whitby formation topsoil	458424	260167	0–15	1	35.5	1.179	2.463
10 Whitby formation subsoil	458424	260167	35–50	1	23.5	1.200	2.483
11 Milton S&G formation top soil	465617	259581	0–15	2	36.3	1.181	2.460
12 Alluvium	465617	259581	0–15	2	43.5	1.183	2.462
13 Alluvium	507029	292300	0–15	6	28.9	1.184	2.460
14 Alluvium	506694	292602	0–15	6	25.2	1.183	2.460
15 Alluvium	506477	292811	0–15	6	31.8	1.183	2.459
16 Alluvium	501641	283184	0–15	6	61.6	1.166	2.439
17 Alluvium	501633	283210	0–15	6	59.2	1.162	2.437
18 Alluvium	501821	283084	0–15	6	60.2	1.168	2.441

formed by the reaction of car exhaust-emitted halides (PbBrCl) with atmospheric ammonia and acid sulphates. The exposure and water leaching of $(\text{NH}_4)_2\text{SO}_4\cdot\text{PbSO}_4$ produce PbSO_4 , the main Pb compound in street dust and soils (Biggins and Harrison 1980; Cao et al. 2008). In addition, a range of other elements exist that are closely linked to the STW ‘point source’ of Pb derived from petrol. These include Zn and Cd from tyres and Sb from brake linings.

Within the UK, $^{206/207}\text{Pb}$ end-members used in sourcing studies (e.g. Chenery et al. 2012; Izquierdo et al. 2012) are from UK ore/coal sources (Farmer et al. 1999) and from tetra-ethyl Pb used as an ‘anti-knocking’ agent in petrol. Before its withdrawal in 2000, petrol-derived Pb in the UK consisted of a mixture of Australian (‘Broken Hill Type’) and British Columbian (Canada) ores depleted in ^{206}Pb in relation to UK Pb. Sugden et al. (1993) and Delves (1988) suggest that the $^{206/207}\text{Pb}$ signature for petrol-derived Pb in the UK is ~ 1.076 . Tetra-ethyl Pb used in petrol was withdrawn throughout the EU in 2000 (Council Directive 98/70/EC 1998), although its use started to decline from the mid-1980s. For sewage sludge, $^{206/207}\text{Pb}$ ratio values of between ~ 1.12 and 1.13 have been found in soil samples taken from a dedicated sewage disposal facility in the East Midlands of the UK (Atkinson et al. 2011). Therefore, the presence or absence of ‘BHT type’ Pb (Pb_{BHT}) can be used as an indicator of sediment residence time and sediment movement.

2.7 Statistical analysis and the estimation of STW sourced P in historic sediments

Multiple linear regression by ordinary least squares was used to determine the relationships between P_{Total} , Pb_{Total} and $^{206/207}\text{Pb}$. For each model, the residuals were examined to ensure that they approximated a normal distribution. To obtain a multi-variate signature for mapping processes through the river system, factor analysis was undertaken in MiniTab. The data were log normalised so that major elements did not dominate the analysis as many trace elements are naturally log normally distributed. The factor analysis started with a principle component analysis (PCA), with the number of factors used selected from the scree plot. The data were then varimax rotated to highlight elements most associated with each factor. Elemental loadings were plotted to observe the significance of element associations with individual factors, whilst factor analysis scores were plotted along the river course to identify where different multi-variate signatures were most significant.

The use of $^{206/207}\text{Pb}$ isotope ratios as a tracer in determining STW P concentrations is dependent on two factors. Firstly, that the sediment has at least two identifiable Pb isotope end-members along with an understanding of the potential sources of intermediate background $^{206/207}\text{Pb}$ isotope signatures. Secondly, that the behaviour between the sediment and the STW released P and Pb is reasonably consistent overtime. In particular, this relates to (i) in-stream sorption of P and Pb and (ii) that no major changes in deposited sediment

concentrations occur over sediment storage periods, although mineral phases may change (e.g. mobilisation of P through redox processes and its re-mineralisation as Vivianite). If these conditions can be satisfied, then ‘first-order’ calculations describing the contributions of STWs to sediment P can be made with associated uncertainty estimates.

The ‘first-order’ estimation of the amount of sediment P derived from STWs is calculated in two stages. Firstly, the concentration of Pb_{BHT} is calculated from the Pb isotope ratios of the samples, the isotope ratios of the local geogenic or soil Pb (Pb_{geo}) and the chosen isotope ratios of Pb_{BHT} using Eq. 1.

$$Pb_{BHT}(\%) = \left[\frac{\frac{^{206}Pb_{geo} - ^{206}/^{207}Pb_{sample}}{^{206}/^{207}Pb_{geo} - ^{206}/^{207}Pb_{BHT}}}{1} \right] \times 100 \quad (1)$$

Secondly, the linear regression model developed with Pb_{Total} as the predictor variable and P_{Total} as the dependant variable is used with the median Pb_{BHT} concentrations calculated from step 1 to predict STW P concentrations ($mg\ kg^{-1}$).

For step one, the major uncertainties are in the Pb isotope ratios chosen to represent Pb_{BHT} and the Pb_{geo} . The uncertainty in the proportion of Pb_{BHT} was calculated using a Monte-Carlo approach where a probability density function describing the uncertainty in the Pb isotope ratios for the end members is produced. The $^{206}/^{207}Pb$ isotope ratio used for UK Pb_{BHT} was from 1.055 to 1.100 (Izquierdo et al. 2012) and can be described as a uniform distribution with high and low values equal to this range. The local geogenic Pb (Pb_{geo}) isotope data collected from the soil samples has a normal distribution with a mean of 1.1849 and a standard deviation 0.00849. Thus, Pb_{geo} in the model was allowed to vary between the mean and 2SD (1.1679 and 1.2018). These soil values also approximate the $^{206}/^{207}Pb$ range of UK coal and Galena (Farmer et al. 1999). Using these two distributions, random selection of values for Pb_{geo} and Pb_{BHT} was used in Eq. 1 to estimate the proportion of Pb_{BHT} in each sediment sample. Random samples ($n = 10,000$) were drawn to produce a representative distribution of Pb_{BHT} values for each sediment sample.

In the second stage, the uncertainty on the linear regression model with total sediment Pb as the predictor variable and total P as the dependant variable was calculated using bootstrap resampling (Draper and Smith 1998) of the original total P and Pb sediment pairs. A bootstrap resampled model was produced for each of the Monte-Carlo estimates of anthropogenic Pb and used to predict STW P. This gave rise to 10,000 estimates of STW P for each sediment location. The median value of the 10,000 estimates was used as a measure of central tendency and uncertainty represented by the 95th percentile range of each estimate group (2.5th percentile to the 97.5th percentile).

3 Results

3.1 Distribution of Pb and P in the river system

Both P_{Total} and Pb_{Total} follow a similar pattern along the length of the river with low concentrations dominating in the rural upper three water bodies and subsequent increases in concentrations in water bodies 4–6 (Fig. 2). The increase in P_{Total} and Pb_{Total} in water bodies 4–6 is accompanied by a general decrease in $^{206}/^{207}Pb$ isotope ratio's to values of around 1.13–1.14 (Fig. 2).

Soil concentrations of both P and Pb within the catchment were assessed as eroded soil is a likely source of both and may influence element concentrations as soil parent material changes down the catchment. Using data from the British Geological Surveys Baseline Geochemical Survey (G-BASE), box plots were constructed for soil P_{Total} and Pb_{Total} concentrations from the catchment areas where the Dyrham ($n = 45$; WB 1–3) and Whitby ($n = 200$; WB 4–6) mudstone formations are the dominant soil parent materials (Fig. 3). Median Pb_{Total} values for the Dyrham formation (water bodies 1–3) and Whitby formations (WB 4–6) are 30.6 and 31.8 $mg\ kg^{-1}$ respectively (Fig. 3b). Until the 75th percentile in the Whitby formation, the distribution of concentrations for soils formed in these parent materials was very similar. Increases in soil Pb_{Total} concentrations above the 75th percentile in the Whitby formation are likely because of the impact of peri-urban soils included within the G-BASE survey. In the Nene sediments, median values of Pb_{Total} for WB 1–3 and WB4–6 are 30.1 and 53.3 $mg\ kg^{-1}$ respectively, indicating an increase in sediment concentrations compared to those of the soil in the lower part of the catchment. A similar pattern of response was found for concentrations of P_{Total} (Fig. 3a).

3.2 Sediment depth and particle size changes

Sediment depth increased after WB 2 and had a mean value of ~60 cm in the four lower water bodies (Fig. 4). There is a general decrease in particle size as distance from the headwaters increases (Fig. 5). With a few exceptions, the particle size distribution (PSD) of the soils is generally finer than those of the sediments found in the lower water bodies (WB 5 and 6). This information indicates increases in Pb_{Total} and P_{Total} are not a function of sediment with a larger fine fraction, which typically provides additional surface area for sorption and fixation

3.3 Identifying geochemical associations within the sediment

A PCA analysis was undertaken using the geochemistry of the 30 cores. The three major PCA components accounted for ~80% of the variance (See Figs. 1 and 2 Supplementary

Fig. 2 Graphs showing Total P (a), Total Pb (b) and $^{206/207}\text{Pb}$ isotope ratios (IR) (c) in sediment cores taken down the length of the non-tidal River Nene

Information). Group 1 accounted for ~44% of the variance and can be described as ‘lithogenic elements’ (Ti, Al, Zr, Mg, Th, K, Rb and U, along with LOI). These elements are

associated with clay minerals and heavy minerals. The LOI concentration is likely linked to the clay mineralogy contained within this group. This assumption was checked by plotting

Fig. 3 Box and whisker plots showing distributions of P (a) and Pb (b) concentrations in soils developed from different parent materials found in the catchment of the River Nene. In addition, the P and Pb sediment concentrations found in stretches of the river channel that lie adjacent to these soil parent material domains are shown

Fig. 4 Variations in sediment depth of the six water bodies of the non-tidal River Nene

FA score-1 values against % clay concentrations where a R^2 value of 0.80 was produced (see Supplementary Information Fig. 3a).

The elements in group 2 consist of trace elements, with the addition of P, and accounted for ~21% of the variance (Fig. 2b; Supplementary Information). This group of elements is typical of elements found as waste water outputs from STWs and includes Cd, P, Sb, Cu, Pb, Zn and Cr, and suggests that P concentration increases along with the concentration of the trace element assemble, particularly those associated with road wash-off. In particular, the presence of Sb is a key indicator of STW source as the major likely source is from road dust where it is a component of brake disc linings (Patinha et al. 2015). It was found that $^{206/207}\text{Pb}$ isotope ratios had a strong negative correlation to this group of elements

Fig. 5 Particle size distributions of homogenised sediments ($n = 30$) from the River Nene channel and soils derived from major soil parent materials from the catchment. Sediments are marked as black circle for water body 1, triangle for water body 2, plus sign for water body 3, multiplication sign for water body 4, black square for water body 5 and diamond for water body 6. Particle size of the soils derived from the parent materials that make up the Nene catchment is marked as ALL, alluvial soils; D, Dyrham formation; CM, Charnmouth mudstone; and WM, Whitby mudstone formation

(Supplementary Information Fig. 2b). This is because the source of the Pb in samples with higher Pb concentrations is most likely ‘BHT’ Pb which has a lower isotope ratio end-member compared to the Nene soils and UK coal/ore Pb end-member (see Section 2.6). There was a R^2 value of 0.77 when $^{206/207}\text{Pb}$ isotopes (as a representative STW output) were plotted against the Factor scores (Supplementary Information Fig. 3b). Pulley et al. (2016) examined suspended sediments, overbank sediments and sediment temporarily stored on the channel bed in the River Nene. They also suggested that Cu, Pb and Zn probably originated from street dusts (i.e. traffic related) and P from sewage effluent.

Factor analysis group 3 include those elements typically associated with binding to Fe (oxyhydr)-oxides, particularly at the time of deposition in aerobic environments consisting of Fe, Co, As, Ni, V, Mn and Be (Supplementary Information Fig. 2c) and accounting for ~16% of the variance. Plotting the FA score-3 values against Fe_{Total} produced an $R^2 = 0.89$, indicating that this assumption was likely correct (see Supplementary Information Fig. 3c). Interestingly many of these elements are redox sensitive, so these results suggest that if the mineral phase has changed post-deposition, the mass of elements has largely been conserved within the sediment. In Supplementary Information Fig. 4, the factor analysis scores are plotted with distance from the headwaters to demonstrate their relative importance in various parts of the river system.

3.4 Relationships between Pb and Pb isotope ratios

In general, increases in Pb_{Total} reflect decreases in $^{206/207}\text{Pb}$ isotope ratios (Fig. 6). Where $1/\text{Pb}_{\text{Total}}$ is largest, (i.e. where Pb_{Total} is smallest (e.g. 50-cm soil samples)), the $^{206/207}\text{Pb}$ ratio likely represents close to the background geogenic value. The Nene soil samples and sediment samples from water bodies 1–3 suggest a range of background geogenic (Pb_{Ore}) $^{206/207}\text{Pb}$ values between ~1.18 and 1.200. There is considerable scatter in the points reflecting the range of potential Pb_{geo} sources. A second feature of the graph is how the majority of sediment samples from water bodies 4–6 have $^{206/207}\text{Pb}$ ratios between 1.12 and 1.16 and exist on a relatively tightly constrained line, suggesting a dominant source of Pb exists in these samples. Those samples with highest Pb concentrations (WB 4–6) have $^{206/207}\text{Pb}$ ratio values close to those quoted for East Midlands sewage sludge (Atkinson et al. 2011) and road dust.

Pb isotope ratios ($^{206/207}\text{Pb}$ v $^{208/207}\text{Pb}$) all fit on a mixing line between BHT Pb and the ore and coal Pb common to the UK (Fig. 7). As stated previously, the majority of Nene soil samples, with the exception of 4 samples from water body 6, all fall within the range of UK ore and coal samples. Included in Fig. 7 are other Pb isotope ratios from sources within the UK.

Fig. 6 The relationship between Pb_{Total} (expressed as $1/Pb_{Total}$) and $^{206}/^{207}Pb$ isotope ratio for homogenised sediment cores taken from the River Nene

3.5 Relationships between P, Pb_{Total} and the $^{206}/^{207}Pb$ isotope ratio

The strong relationships identified in the PCA between Pb_{Total} , the $^{206}/^{207}Pb$ ratio and P_{Total} suggest that the $^{206}/^{207}Pb$ isotope ratio is a suitable tracer for assessing the behaviour and source of P in the Nene sediment sampled. A model was produced using least squares regression to predict P_{Total} from Pb_{Total} (Table 2; Fig. 5 Supplementary Information) and had an adjusted R^2 of 0.85. In addition, the correlation coefficient between P_{Total} and $^{206}/^{207}Pb$ was $r_s = -0.77$, indicating the strong association between the STW source of P_{Total} and Pb_{Total} .

There is significant evidence in the presented data that a strong correlation exists in P and Pb enrichment along the river course and that changes in the $^{206}/^{207}Pb$ isotope ratios suggest an increasing STW influence. The strong correlations between Pb and P are likely to be lost if the proportions of

each element coming from different sources changed significantly. Noticeable changes in the relationship between $^{206}/^{207}Pb$ isotope ratios and P_{Total} would result if sediment started accumulating without Pb_{BHT} input over the last 20 years. However, this was not found in the current work and the most likely explanation is that the sediments analysed are historical sediments (> 20 years old as evidenced by their $^{206}/^{207}Pb$ isotope ratios) that have stabilised, with new sediment prevented from accumulating due to scour events, increased by engineering of the river system.

3.6 Calculating contributions of Pb_{BHT} and P sources in sediments

Within water bodies 1–3, there is very little Pb_{BHT} present in the sediment (Fig. 8a). The median values from the Monte-Carlo simulation suggest < 10% Pb_{BHT} is present but when the 95th percentile confidence range of values is considered,

Fig. 7 Isotope mixing line for Pb isotopes found in homogenised sediment samples of the River Nene. End members include UK coal and Galena values and UK petrol Pb (Pb_{BHT}). The Galena end member sits behind the Coal end member. Other Pb isotope values for Nene catchment soils and UK aerosols, sewage farms and road dust are reported

Table 2 Output from linear regression model where P_{Total} is predicted from Pb_{Total}

	Estimate	Std. Error	<i>t</i> value	<i>p</i>
Intercept	29.361	283.438	0.104	0.918
Pb_{Total}	52.697	4.267	12.350	< 0.001

Residual standard error: 751.8 on 27 degrees of freedom

Multiple *R*-squared: 0.8496, adjusted *R*-squared: 0.844

F-statistic: 152.5 on 1 and 27 DF; *p* value: < 0.001

values are likely to be between 0 and 20%. However, considering that there are no significant point sources such as STWs (Fig. 1) within this part of the catchment, and sediment appears effectively transported downstream, the contribution of Pb_{BHT} is likely to be towards the lower estimates. In water bodies 4–6, the median value of Pb_{BHT} was ~40% with the 95th percentile confidence range reported as being between 0 and 60%. The highest concentration of Pb_{BHT} was found in Core 20 (water body 4 core 2), which had a median value of ~60%. Results can be seen in Fig. 8b along with the 95th percentile confidence range obtained from the bootstrapping procedure outlined in Section 2.9. The calculations show that only in water bodies 4–6 are there reasonable quantities of STW-derived P, which for most cores are likely to have a median value of ~1000–2000 mg kg⁻¹. This suggests that between 30 and 40% of the sediment P was derived from STWs (Fig. 8c).

4 Discussion

The sources of P in the river sediment change as the river flows downstream. In water bodies 1–3, the P was largely of river bank or agricultural origin (median value > 80%), and despite the number of large STWs associated with increasing urbanisation within the catchment and discharging into water bodies 4–6, diffuse (largely agricultural) sources still contributed a large component of sediment P within the system (~50%). This reflects (i) an increase in arable agriculture in the lower three water bodies, (ii) greater under-field drainage discharging and increasing the hydraulic connectivity between the land and river or (iii) the continuous down river sediment transport from further up the catchment. These results also provide evidence as to the behaviour and residence time of sediment and sediment P within an engineered and managed (dredged) river system. The evidence suggests that the presence of Pb_{BHT} in sediments, 20 years after it was phased out, is indicative of stabilised river sediments being present for long periods. Thus, the sediment P still present appears to be largely legacy P deposited prior to 2000 and the phasing out of Pb_{BHT} . This suggests that sediment management within the catchment (e.g. dredging, buffer strips,

riparian fencing) is achieving aims of reducing recent sediment P, but with longer term legacy P remaining.

The spatial distributions of P, Pb and ^{206/207}Pb isotope ratios represent concentrations of these elements on a broad basis down the river. However, this does not exclude the fact that more localised patterns of P and Pb may exist, such as those often found downstream of STWs (e.g. Pulley et al. 2016). However, to capture these specific patterns, more focused sampling strategies would be required. The results from the survey of sediments at sampling time and geochemical analysis suggest that sampled sediments are older. More recent sediments would appear to be (i) more mobile due to the engineering of the channel and are likely partially removed by scour during periods of high flow and that (ii) dredging from areas of known sediment accumulation causes a significant reduction in sediment supply (see Section 2.4). In addition, Pulley and Foster (2017) have suggested that the main source of sediment is via bank erosion which would have the background ‘geogenic’ ^{206/207}Pb signature.

Sediment particle size analysis showed the expected trend of general fining with distance travelled from the headwaters. However, sediment did not generally become finer than the catchment soils. Thus, strong relationships between Pb, ^{206/207}Pb isotope ratios and P (along with other STW elements such as Zn, Cd and Sb) suggest that the core samples must represent largely historical inputs of Pb and P into the river system, rather than a result of enrichment due to the fining of sediment. The strong correlations between these three variables would not be expected in more recent sediments, because ‘BHT-type’ Pb was phased out nearly 20 years ago. This was demonstrated by Pulley et al. (2016) who examined recent suspended sediments in the River Nene. They noted that flushing of sediment occurred during high river flow events, and there were no correlations between Pb and P concentrations.

The factors determining the geochemical relationships in the sediment has allowed the use of ^{206/207}Pb isotope ratios to produce ‘first-order’ estimates of the spatial distribution of P released from STWs or soil/agricultural sources at the time of sediment deposition. A key factor in these geochemical associations is that both concentrations of P and Pb in the river water were much higher in the Nene in the recent past. Supplementary information Fig. 6a shows the decline in P in rivers of the English Midlands and Fig. 6b shows the decline in river water Pb across nearly 200 rivers in the UK since 1985 (<https://data.gov.uk/dataset/c6ad19a1-360d-4e62-9fd3-26f9e3ac39dd/river-water-quality-annual-average-concentrations-of-selected-determinands>). The decline in river Pb is similar to the decline in the atmospheric emissions of Pb across the UK which were largely (> 99.9%) from transport (e.g. Pb_{BHT}) and shown in Fig. 6c (http://naei.beis.gov.uk/overview/pollutants?pollutant_id=17). These graphs illustrate the potential for the existence of the

Fig. 8 Graph showing ‘first-order estimates’ of % Pb derived from STW in cores taken from River Nene based on the proportion of Pb_{BHT} obtained from Eq. 1 with associated uncertainty calculated using a Monte-Carlo simulation to form a probability density function (a); the

concentration of P obtained using the regression model predicting P_{Total} from Pb_{Total} (Table 2) with uncertainty calculated using a bootstrapping procedure (b); the percentage of sediment P this equates to with error (c)

pathway described in Section 2.6 between tetra-ethyl Pb used in petrol and its eventual discharge from STWs to rivers.

It is also notable that after deposition, in situ processes did not appear to change these geochemical associations significantly. For example, there did not appear to be a significant imbalance in the uptake of P and Pb by macrophytes (e.g. *Iris pseudacorus*) or to other biotic sinks (e.g. algae). This may have been a consequence of the continued elevated concentrations of P in the river water. Whilst rooted aquatic plants (e.g. *Iris pseudacorus*) have the potential to derive almost all their P requirements from bio-available sediment P reserves (Mainstone and Parr 2002), the relative contribution of root uptake to macrophyte P demand has been found to vary with soluble reactive phosphate (SRP) concentrations in the

overlying water column (Pelton et al. 1998). In conditions where SRP concentrations are high, the P demands of biota are likely to be satisfied from SRP in the water. Concentrations of SRP in the Nene are currently of the order of $\sim 6.45 \mu\text{M P L}^{-1}$ (0.2 mg P L^{-1}), having decreased from historical concentrations (2 to 3 mg L^{-1} in 1998) through the introduction of P-stripping in STWs (Environment Agency data: Tye et al. 2016). Therefore, P requirements for macrophytes and algae are likely to be satisfied from SRP in the water column. In addition, under elevated SRP concentrations, P sorption to sediment is the dominant mechanism, whereas under low SRP concentrations, biotic uptake may exceed sorption (Meyer 1979). The equilibrium time between SRP and sediment can be rapid, as demonstrated in EPC₀

kinetic equilibrium experiments (Tye et al. 2016). There also did not appear to be a loss of P through redox processes, although a change in mineral phase may have occurred such as the precipitation of vivianite where Pb was found to exist as an impurity (see Supplementary Information 2 in Tye et al. 2016).

5 Conclusions

This work demonstrates the use of $^{206/207}\text{Pb}$ ratios in determining the proportion of historically STW released P in stable river sediments. This analysis has been enabled due to a specific set of circumstances arising from natural processes, along with sediment management within the catchment. Identifying the existence of these relationships in the Nene has helped the understanding of current processes involving sediment P. These would include the apparent small amount of recent sediment being deposited in the channel because of dredging and natural scour. Thus, the work provides an evidence base to understand whether current sediment management decisions are achieving their aims. However, the continued existence of legacy P in the remaining older sediments will likely continue influencing the P status of the river water. Thus, options regarding the practical removal of these sediments and the extent to which this would improve water P status need to be assessed. Further work may involve assessing whether the methodology could be used in other lowland rivers that have similar flow characteristics to the Nene such as the Witham and Welland in the east of England.

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