PULLEY, S., FOSTER, I. D. L. and ANTUNES, A. P. M. (2015) The dynamics of sediment-associated contaminants over a transition from drought to multiple flood events in a lowland UK catchment. *Hydrological Processes.* 0885-6087.

Abstract:

Fine sediment in suspended form, recently deposited overbank and in temporary storage on or in channel beds was collected in the Nene basin during a period of drought through to a period of four high flows. The sediment was analysed for arsenic, copper, lead, phosphorus and zinc concentrations with the aim of investigating their sources, movement, temporary storage and potential for environmental harm.

Copper, lead and zinc probably originated from urban street dusts, phosphorus (originally in dissolved form) from sewage effluent and arsenic from natural soils developed over ironstone. There was little difference in the metal or arsenic concentrations in the sediment under different flow conditions; instead proximity to pollutant sources appeared to control their concentrations. Phosphorus in tributary sub-catchments probably adsorbed to sediment during periods of low flow but these sediments were flushed away during high flows and replaced by sediment with lower concentrations. However, concentrations of all pollutants in overbank sediments along the Nene's main channel were not reduced in successive flood events, suggesting no first flush effect. Only phosphorus accumulated on sediment at concentrations exceeding those of its catchment – based sources (e.g. street dusts, channel banks, catchment soils). This scavenging of aqueous phosphate by sediment explained the difference in behaviour between phosphorus, arsenic and heavy metals. The surface area and organic matter content were shown to have a small effect on contaminant concentrations.

Street dust contaminants only exceeded predicted effect levels (PELs) in close proximity to urban areas, suggesting a small potential for harm to the aquatic environment. Arsenic concentrations exceeded PELs in most sediment samples. However, it has been shown to be largely non-bioavailable in previously published research on the Nene, limiting its potential for significant environmental harm. Phosphorus concentrations in river sediments are high in comparison to the soils in the catchment and in comparison with sediment-P concentrations in other published lowland catchment studies, indicating a large potential for eutrophication should the Phosphorus be, or become, bioavailable.

Keywords: Sediment-associated contaminants, Heavy metals, Arsenic, Phosphorus, Pollutant dynamics.

Introduction

The European Union Water Framework Directive (2000/60/EC) requires National Governments to achieve good chemical and ecological status of water bodies, and recognises the importance of sediment-associated contaminants when complying with environmental quality guidelines. Heavy metals and metalloids (subsequently referred to here as trace elements) such as arsenic have commonly been considered to be major pollutants in urbanised river catchments and have been shown to have toxic, genotoxic, mutagenic and carcinogenic effects (e.g. Mouvet, 1984; Von Burg and Liu, 1993; Gurrieri, 1998). Unlike a variety of other pollutants, trace elements are generally not degraded by natural processes or decomposed by bacteria, making them persistent in the environment over historical time scales (Wang *et al*., 2012).

Primary production in aquatic ecosystems in the UK is primarily limited by bioavailable phosphate (Jarvie, *et al*., 1998). As a result, excess phosphate inputs to rivers and lakes will lead to an increase in algae and macrophyte growth, which is symptomatic of the eutrophication of rivers and lakes. Eutrophication causes a loss of biodiversity and a reduction in water appearance and chemical quality (Carpenter *et al*., 1998). For these reasons phosphorus and heavy metal inputs to surface waters have become a focus attention for both researchers and catchment managers.

Nutrients and trace elements have been shown to originate from a variety of sources, such as the natural diffuse weathering of bedrock and the erosion of soils and river channel banks (Wragg *et al*., 2007; Charlesworth *et al*., 2010). They may come from a variety of diffuse anthropogenic sources, such as urban street dusts and run-off from agricultural land, as well as point source inputs such as sewage and industrial effluent discharges (Foster and Charlesworth, 1996; Charlesworth *et al*., 2010).

After entering fluvial environments trace elements and nutrients have been shown to be primarily transported in particulate form, in association with fine sediment and organic matter

(Gibbs, 1973; Salomons and Förstner, 1984; Horowitz and Elrick, 1987; Horowitz, 1991; Walsh and O'Halloran, 1996; Foster and Charlesworth, 1996; Ernstberger *et al*., 2004; Macklin *et al*., 2006). Within the fluvial environment sediment and its associated contaminants can be considered to be in transport in suspended form or in temporary channel bed storage. Walling *et al*. (1998) and Owens *et al*. (1999) calculated that between 4 and 10% of the annual suspended sediment load of the rivers Ouse, Wharfe and Tweed, UK resided in temporary channel bed storage. However, it has been shown by Walling *et al*. (2003) that only <3% of the total annual contaminant flux of the rivers Aire, Calder and Swale resided in temporary channel bed storage. Contaminants stored on channel beds are, however, considered to be important for benthic habitat quality (Poulton *et al*., 2011). Concentrations of pollutants in suspended and / or temporarily stored sediment have been shown to be controlled by proximity to sediment sources (Foster and Charlesworth, 1996; Walling *et al*., 2003). For example, phosphate pollution in the Warwickshire Avon, UK has been shown to primarily originate from point source sewage effluent inputs and highest concentrations have been found close to the point of sewage effluent discharge (Bowes *et al*. 2005). Once within the fluvial environment, inputs from such point pollution sources have been shown to be dispersed and diluted downstream of initial inputs (Wolfenden and Lewin, 1978; Macklin and Dowsett, 1989). However, in contrast, downstream enrichment in pollutants has been shown to occur in some catchments due to the selective transport of the finer particle sizes where trace metal concentrations are usually highest (Walling *et al*., 2000).

Flow has also been shown to be a key control on contaminant concentrations and fluxes. For example phosphate inputs from point sources are considered most important during dry summer months when flows and dilution potential are at their lowest (Jarvie *et al*., 2006). During high flows there may be either the dilution of sediment-associated contaminant concentrations by 'clean' sediment inputs or the mobilisation of stored contaminated sediment, resulting in either an increase or decrease in concentrations (Carton *et al*., 2000; Davide *et al.*, 2003). Seasonal relationships between flow and contaminant concentrations have also been observed, with a 'first flush effect' causing a peak in contaminant runoff in the first high flow event after sustained periods of little or no rainfall, where pollutants accumulate on street surfaces or within combined sewer systems (Geiger 1987; Buffleben *et al.,* 2002).

The dynamics of fine sediment and pollutants have been shown to be highly variable in different catchments (Walling *et al*., 2007), therefore there is a need to investigate pollutant dynamics in individual catchments. At present the dynamics of sediment-associated contaminants have been investigated in highly urbanised catchments (e.g. Walling *et al*., 1998; Owens *et al*., 1999) and mineralised areas (e.g. Macklin *et al*., 1997) as well as in permeable lowland agricultural catchments (e.g. Collins *et al*., 2005). However, a paucity of information exists in many other catchment types.

The aim of this paper is to investigate the dynamics of arsenic, copper, lead, phosphorus and zinc during the transition from a period of drought through to a period characterised by multiple successive high flows. Pollutant inputs, movement, temporary storage and the potential for environmental damage are investigated using the following three objectives.

1: To describe the movement and storage of the pollutants from different sources during the period of drought through to the high flow events.

2: To determine the major controlling factors on sediment-associated pollutant concentrations.

3: To assess the potential for the pollutants to cause environmental harm by comparing concentrations found in a range of sediment compartments with published sediment - associated quality guidelines.

Study catchment

The Nene river basin is located in the East Midlands region of the UK and has a catchment area of 1,634 km^2. It is a lowland agricultural catchment with a low sediment yield calculated at between 6 t km^{-2} yr^{-1} and 18 t km^{-2} yr^{-1} (Wilmott and Collins 1981; Walling *et al*., 2007; Pulley, 2014). It has a maximum elevation of 226m above Ordnance Datum. The river channel is heavily modified and flood defences are found extensively along the main channel, and locks downstream of Northampton produce a navigable stretch of river.

A variety of potential pollutant sources exist within the Nene basin. The 2007 UK Land Cover Map indicates that land utilisation in the catchment at the time was 56% cultivated land, 22% improved grassland and 9% urban, with the remainder of the catchment covered by

woodland, rough grassland and surface water bodies (Morton *et al*., 2011). There therefore exists potential for an input of trace metals and nutrients associated with different land utilisation, including urban surface water runoff and a range of industrial and manufacturing point source discharges to the river. There is also potential for phosphorus inputs from the erosion of agricultural land as well as from sewage effluent inputs from major treatment plants in urban areas and septic tanks in rural environments. High phosphorus concentrations have been measured in the fluvial sediments of the Nene, and have been attributed to the combination of diffuse agricultural inputs and sewage treatment inputs (Tye *et al*., 2013). The Environment Agency Anglian river region basin management plan highlights inputs of phosphorus-rich sewage effluent to the Nene to be one of the major influences on water quality (Environment Agency, 2009). The primary sewage treatment facilities in the basin include tertiary effluent treatment to comply with the requirements of the Urban Wastewater Directive (91/271/EEC) (River Nene Regional Park, 2013).

Arsenic is a pollutant which is regionally important in the UK. In former mining regions, such as Devon and Cornwall, high arsenic concentrations have been found in soils, river and estuarine sediments (e.g. Garelick *et al*., 2008). In addition to these regions of the UK Wragg *et al*. (2007) havefound arsenic concentrations of between 20 and 100 mg kg^{-1} in soils around the town of Wellingborough in the Nene basin. The arsenic within the Nene basin is primarily associated with Middle Jurassic oolitic ironstones and their overlying soils (Cave *et al*., 2003). The iron oxide minerals associated with the ironstone have been shown to have a high affinity for arsenic and molecularly similar phosphorus, resulting in the high concentrations which have been found within the basin (Palumbo-Roe *et al*., 2005).

Figure 1 shows the locations of potential contaminant sources present in the Nene basin. Ironstone bedrock is primarily located in the in the centre, north eastern and south western parts of the basin. These ironstone deposits are capped by glacial diamicton at high altitude. The major towns of Daventry, Kettering, Wellingborough and Rushden, as well as many small villages and the road network, represent potential sources of urban street dust pollutants present in the basin. Sewage treatment facilities are located throughout the Nene basin, the large facility at Billing processes a large proportion of sewage from Northampton and the surrounding area.

The basin has a mean annual rainfall of 638mm (standard deviation of 67mm) and mean monthly rainfall of 53.1mm measured at Althorp over the previous 140 years. Little rain fell

during the initial part of the study period from January 2011 to April 2012 (a mean of 23.7mm per month; measured at the Northampton, Moulton Park climatological station) (Figure 2). The period from April 2012 to December 2013 was then characterised by high rainfall (a mean of 88.7mm per month), therefore the study period represents a transition from a period of drought to a period of successive high flows, with major overbank flows occurring during April, July, October, November and December 2012. Rainfall in the monitoring period was therefore a-typical when compared to historical averages.

Methods

Fine sediment sampling was conducted in the upper and middle Nene basin between the source of the Nene, south of Daventry, to downstream of Wellingborough and Rushden **Error! Reference source not found.**. Samples of suspended sediment were collected using time-integrated suspended sediment traps based on the design of Philips *et al*. (2000). The traps were deployed at 8 locations in the major tributaries of the Nene at 0.6 of the water depth at the time of trap installation **Error! Reference source not found.**. The traps were emptied at monthly intervals between September 2011 and March 2013.

Overbank sediment was collected from the leaves of riparian vegetation (Comfrey; *Symphytum officinale* and Stinging Nettle; *Urtica dioica*) following the methods of Walling et al. (1997) immediately after water levels had receded after each of four overbank events in April, July, October and November 2012. The vegetation was washed using native river water into a 5l plastic container before the sediment and water were transported to the laboratory for analysis.

Sediment stored on channel beds was sampled using the re-suspension method developed by Lambert and Walling (1988). A plastic tube of ~0.4m diameter was pushed into the river bed to create a seal and prevent sediment escaping during the experiment. The water and channel bed were then disturbed to an approximate depth of 5 cm using a wooden pole before a 1l sample of the contained water and re-suspended sediment were collected for analysis. The depth of water inside the cylinder and mass of recovered sediment was also recorded so that the mass of sediment stored on the bed could be determined. Sampling was repeated three times at each ~50m river reach and the sediment was amalgamated prior to trace metal and

nutrient extraction and analysis. Sampling was performed quarterly for six repetitions in June 2011, September 2011, January 2012, June 2012, September 2012 and February 2013.

Samples of potential sediment sources were recovered from the upper and middle Nene basin. Sediment sources were classified as surface agricultural land, channel banks and urban street dusts. In total 247 samples were collected from the top 2cm of agricultural land of which 39 were from the ironstone lithology. Sixty five samples were collected from areas of visibly eroding channel banks and 21 samples were collected from the dusts deposited at the sides of major streets and roads within the catchment. Samples of agricultural topsoils and channel banks were retrieved using a non-metallic trowel. Road dust samples were collected using a dustpan and brush.

In the laboratory all samples were oven dried at 40°C before being manually disaggregated using a pestle and mortar. Sediment source samples were sieved to <63um to produce a particle size distribution comparable to that of the fine sediment transported or deposited by the Nene. Concentrations of arsenic (As), copper (Cu), lead (Pb), phosphorus (P) and zinc (Zn) were measured using a Thermo Scientific iCAP 6500 Duo View inductively coupled plasma optical emission spectrometer. Around 0.8g sub-samples of sediment were digested in 10ml of Aqua Regia at 180°C for 20 minutes in a CEM Mars 6 microwave digestion unit. The percentage of each element recovered by the analysis was determined using Canadian Stream Sediment Reference Material STSD-1 (Table 1). The results presented were not corrected for extraction efficiency.

Sediment particle size was quantified as specific surface area which was measured using a Malvern instruments mastersizer 2000 laser granulometer. Prior to analysis, organic matter was removed using hydrogen peroxide pre-treatment for 24 hours, followed by 4 hours of heating at 80°C (Gray *et al.*, 2010). The sediment was then disperesed with sodium hexametaphosphate and 2 minutes of ultrasonic dispersal in a Malvern 2000 MU wet sample dispersal unit.Sediment particle size was quantified as specific surface area (SSA) calculated on the assumption that the sediment particles were roughly spherical.

Organic matter content was determined using loss on ignition at 450°C. Approximately 1-2g of soil or sediment was placed into a Carbolite muffle furnace and LOI was calculated using the pre combustion dry sample mass and the post combustion sample mass (Grimshaw *et al.* (1989).

The concentrations of the pollutants found in the sediment were compared to the Environment Agency draft sediment quality guidelines sediment quality criteria for England and Wales predicted effect levels (PELs). The PELs determine the potential of the pollutants to cause adverse environmental impacts. The PELs determine the potential of the pollutants to cause adverse environmental impacts. The PELs, are specified as As 17 mg kg^{-1}, Cu 197 mg kg^{-1}, Pb 91 mg kg^{-1} and Zn 315 mg kg^{-1} (Hudson-Edwards *et al*., 2008). The PEL represents the lower limit of the range of concentrations associated with adverse biological effects.

Results

The results are structured into four sections, the first examines the pollutant concentrations in the sediment source samples. The dynamics of sediment associated pollutants originating from urban street dusts, sewage effluent and natural geological inputs are then investigated in the subsequent three sections. In each section the spatial locations of the highest pollutant concentrations were examined before the changes in concentration between the period of drought and high flow were identified. The relationships between sediment particle size, organic matter and pollutant concentration were then examined. The concentrations of the pollutants found in the sediment were finally compared to the Environment Agency draft sediment quality guidelines sediment quality criteria for England and Wales predicted effect levels (PELs).

Pollutant sources and concentration distributions

An examination of the concentrations of the six trace metals and nutrients in the potential sources of fine sediment identified in Figure 1 show that high As and P concentrations are predominantly associated with Ironstone soils (Table 2). Cu, Pb, and Zn have high concentrations in urban street dusts. No sample of sewage effluent could be obtained from within the Nene basin, however, Edwards and Withers (2008) estimate dissolved P (PO_4) concentrations in sewage effluent in the UK to be typically 2.90 mg l^{-1} with an upper limit of 13.1 mg l^{-1}. Foster et al. (1997) showed dissolved P concentrations in the nearby River Avon

(Warwickshire) did not exceed 10 mg l^{-1} over a one year period (1995) prior to the implementation of the Urban Waste Water Treatment Directive. A major decrease in PO_4 in the water of the Nene was recorded after 1998, where concentrations were reduced from 2 - 3 mg l^{-1} to 0.1 - 0.2 mg l^{-1} (Tye et al., 2013).While discharges are primarily in dissolved form as opposed to particulate form, P has been shown to adsorb to particulate sediment from solution (Fox et al., 1989).

The concentrations of Cu, Pb and Zn in the sediment are most similar to the non-ironstone topsoils and channel banks within the basin (Figure 3), higher concentrations are however present in some sediment samples. The range of As concentrations in the sediment are comparable to those found in the non-ironstone topsoils and channel banks. Phosphorus concentrations in the sediment follow a distribution comparable to the ironstone topsoils, however, some concentrations exceed those found in these soils. There is little difference between the range of contaminant concentrations found in the channel bank sediment and found in the suspended sediment.

Urban street dust pollutants

In this section analysis will focus on Pb concentrations as Pb behaves in a very similar way to Cu and Zn as all three appear to be closely associated with street dust inputs. Pb concentrations in channel bed sediment were highest close to Northampton (Figure 4; Figure 6), supporting the suggestion in Table 2 that urban street dusts are the primary source of these pollutants. Likewise, in overbank sediment, concentrations were low in the sampling sites upstream of Northampton and reached their peak in the centre of the town (Figure 5). The concentrations in overbank sediment then reduced with increasing distance downstream of the town.

The changes in sediment-associated Pb concentration over the study period were examined in more detail in the channel bed T10 and T11 samples and suspended sediment at the Northampton and Wellingborough sites, where they were highest (Figure 4 site locations are marked in **Error! Reference source not found.**). Concentrations in channel bed sediment

and at the Wellingborough suspended sediment sampling site did not show a clear difference between the periods of drought (before April 2012) and high flows (after April 2012) (Figure 6). In contrast, Pb concentrations in the Northampton suspended sediment sampling site declined consistently throughout the study period. The result suggests that the stores of contaminants present in street dusts within the almost entirely urbanised T10, T11 and Wellingborough catchments are not being depleted by the successive periods of heavy rainfall and high flows, with the possible exception of the T11 sampling site in February 2013. There was no significant reduction in mean Pb, Cu or Zn concentrations in the overbank sediment deposited in the four overbank events (Kruskal Wallis $p > 0.05$) (Figure 10).

Lead, copper and zinc concentrations are significantly correlated ($p < 0.05$) with LOI and SSA upstream of Northampton (see online supplementary material), but with low r^2 values (15% and 29% respectively). LOI and SSA are not significantly correlated downstream of Northampton, where high pollutant concentrations were found or in the urban street dust source samples. Therefore the LOI and SSA of the sediment appears to have little impact on urban street dust concentrations.

Natural Arsenic inputs

Arsenic concentrations appear to originate from natural diffuse inputs and concentrations in channel bed sediment in June 2011 were the highest in the two sampling sites at T10 and T11 (Figure 4, site locations are given in **Error! Reference source not found.**), which are catchments with lithologies dominated by ironstone (Figure 1). In overbank sediment As concentrations remained fairly constant throughout the entire catchment and are generally lower than concentrations found in the ironstone soils.

Arsenic concentrations in the temporarily stored channel bed sediment, suspended sediment and overbank sediment remained fairly consistent throughout the study period (Figure 8; Figure 10), and concentrations were not significantly correlated with either LOI or SSA (see online supplementary material).

Sewage effluent discharges

Phosphorus concentrations in the June 2011 channel bed sediment are highest in the sampling locations close to Dodford and Heyford (Figure 4site locations are given in **Error! Reference source not found.**). The Heyford site is in close proximity and downstream of a sewage treatment plant, and Dodford includes the large town of Daventry in its upstream catchment (Figure 1).. Low As / P ratios were found in this sediment (0.0025) compared to those in the ironstone soil (0.0230), agricultural soils (0.0167) or channel bank sediments (0.0245) suggesting that inputs from soils were not the primary source of the P. Phosphorus concentrations in overbank sediment are also low upstream of Northampton and increase within the town (Figure 6). However, unlike Pb, concentrations of P continued to increase downstream of the town, suggesting large inputs of dissolved phosphorous from around the vicinity of Billing sewage treatment works.

The sampling locations at Dodford and Heyford had the highest P concentrations and were selected for further investigation. Prior to the April 2012 flood very high concentrations of P was found in sediment stored in the channel beds (Figure 7). After the first high flow in April 2011, P concentrations in channel bed sediments at both sites were reduced by ~30-40%. At Heyford concentrations continued to gradually reduce during the subsequent high flows between July 2012 and February 2013 while at Dodford concentrations remained relatively constant. The concentrations in suspended sediment follow a comparable trend to the channel bed sediment. Concentrations are elevated prior to the high flow in April 2012 before being reduced by ~30 % to 50% after the event. Like channel bed sediment, concentrations remained fairly consistant in the months of sampling prior to the April 2012 flood and the period after the April 2012 flood. P concentrations in the overbank sediment do not significantly decrease over the four flood events (Kruskal Wallis $p > 0.05$; Figure 10)

Phosphorus concentrations are significantly correlated ($p < 0.05$) with LOI and SSA upstream and downstream of Northampton. However, R^2 values are fairly low (upstream 25% and 21% respectively) (downstream 23% and 23% respectively).

Comparisons with predicted effect levels

Concentrations of the urban street dust pollutants were below the draft predicted effect levels (PEL) in 96.25% (Pb), 92% (Zn) and 100% (Cu) of sediment samples. The Pb and Zn PELs

were exceeded in sampling sites close to urban areas (Northampton and Wellingborough suspended sediment and T10 channel bed and St Georges and Bridge street sampling sites.

Arsenic concentrations exceed the PEL (of 17 mg kg^{-1}) in 60% of sediment samples. However, the average concentration of 24.95 mg kg^{-1} found in channel banks is only exceeded in 13.5% of overbank, suspended and channel bed sediment samples, indicating inputs are mostly below concentrations found in sediment sources which are not associated with the Ironstone geology. Flow had no observable effect on when As PELs were exceeded (Figure 7).

Sediment quality guidelines are not available for P, however P concentrations could be compared to the soil and channel bank samples to determine if in-stream enrichment in P is taking place through the adsorption of dissolved P that probably derives from sewage effluent discharges. For sediment stored on the channel beds the median P concentration of 1354 mg kg^{-1} in surface agricultural soils was exceeded in 91% of samples in June 2011, 84% in June 2011, 91% Jan 2011, 66% in June 2012, 25% in September 2012 and 28% in February 2013. The reduction in exceedances over the study period represents the previously shown flushing and dilution of P during high flows. The concentration of phosphorous in sediment also exceeded the concentration found in soils in 55 of the 58 overbank sediment samples collected. In suspended sediment, P concentrations exceed those found in agricultural soils in almost all cases. Exceptions are the Wellingborough sampling site where 46% of samples are below the median concentration found in soils and the Knuston site where concentrations are lower in 25% of samples. The Wellingborough site is the only sampling location with no sewage treatment works present in its upstream catchment, and probably explains the lower concentrations of sediment P. The mean concentration of P in all sediment samples was 2308 mg kg^{-1} (standard deviation of 1408 mg kg^{-1}) with a maximum concentration of 9819 mg kg^{-1}.

Discussion

The concentrations of all contaminants appeared to be primarily controlled by proximity to their source; which is a finding that has previously been identified in other catchments such as in the Rivers Aire and Calder by Walling *et al*. (2003) and in the Warwickshire Avon UK by Bowes *et al*. (2005). The concentrations of urban heavy metals and As were shown to decrease with increasing distance from pollutant inputs. In contrast a slight downstream increase in sediment-associated P concentration was found, which is a finding also described

by Owens and Walling, (2002) in the river Swale and by Owens *et al*. (2001) in the rivers Aire and Calder.

There were different trends in the contaminant concentrations during different flow conditions. Sediment-associated heavy metal contaminants have previously been shown to accumulate on urban channel beds during periods of low flow (Foster and Charlesworth, 1996; Ballantine *et al*., 2006). Within the Nene during the period of drought in June 2011, P had accumulated to concentrations well in excess of those in soils and channel banks or in effluent discharges. In contrast As and the urban road dust pollutants showed no evidence of having accumulated to concentrations in any of the river sediment samples to levels higher than their potential sources. None of the contaminant concentrations were significantly higher in the first April flood that occurred after the period of drought, than in the subsequent floods taking place during a sustained period of high flows (Kruskal Wallis $p > 0.05$) (Figure 10). The 'first flush' effect is based upon the likelihood of a greater supply of pollutants being available for transport after a period of drought (Lee *et al*., 2002) and is often used to explain the well documented hysteresis effect in urban rivers (Lawler et al., 2006). The findings observed for overbank sediment in the Nene therefore suggest that there was no 'first flush' effect. Likewise, examination of Pb and As concentrations in suspended and channel bed sediment showed that there was no significant difference in concentration in suspended and channel bed sediment under different flow conditions. The exception is Pb in the Northampton suspended sediment sampling site where a reduction in concentration was found in higher flows which may be a result of the dilution of urban inputs by cleaner sediments from the rest of the catchment. The potentially unlimited As stores available in the channel banks and surface agricultural soils provide a potential explanation as to why there was little variability in its concentration through time and under any flow condition. The lack of temporal variability also suggests that inputs from As-rich ironstone soils, or changes in sediment sources, are not causing changes in sediment- associated As concentration. Low connectivity is therefore suggested between the ironstone soils of the basin and the river channel. There was no clear reduction in P concentration over the study period in the overbank sediment collected from the Nene's main channel; however there was a clear reduction in the suspended and channel bed sediments in the Nene's tributaries. A possible explaination for this pattern is that either the stores of channel bed sediment trapped between the locks along the main channel are not depleted during sucessive floods, or that fresh sewage effluent discharges are replenishing P stores in the Nene's main channel between or

during flood events. The absence of locks in the Nene's tributaries likely mean that stored P can be more readily flushed from channel beds than in the main channel with the presence of extensive locks installed to aid navigation. The wash load paradigm (Garcia, 2007) ignores sediment storage and assumes that sediment moves directly with flow. However, it has been shown that a sediment particle is at any given time is more likely to be in storage than in active transport (Meade, 2007). A downstream reduction in sediment-associated reduced mercury inventories in the South River, Virginia, USA, indicated that sediment typically moves 10 km (95% confidence interval: 5–25 km) before entering storage (Pizzuto, 2014). The downstream reduction in Cu, Pb and Zn concentrations observed in the Nene suggests that sediment may be entering storage shortly downstream of Northampton. The implication of this finding is that where catchment management seeks to reduce suspended pollutant loads, the long-term storage of pollutants on channel beds or off-channel may require the re-evaluation of the best management practices (Pizzuto et al., 2014).

Contaminant concentrations have previously been shown to be positively correlated with decreasing sediment particle size, or increasing specific surface area (Horowitz 1991; German and Svensson, 2002). Therefore, selective transport processes can often cause different particle sizes to be transported and therefore different pollutant concentrations to be observed in different parts of a catchment (Owens *et al*., 2001). Within the Nene, sediment SSA was shown to have little impact on any of the pollutant concentrations. Horowitz and Elrick (1987) showed that pollutants such as Pb and Zn are often associated more with larger particles within the <63µm fraction of urban dusts, providing a possible explanation for this lack of effect. A second explanation is that only a small proportion of Pb transported to oceans (<1%) has been shown to be in soluble form (Meybeck and Helmer, 1989). The lack of dissolved Pb inputs, which can bind to the surface river sediments (Horowitz 1991), likely is the reason that concentrations were not shown to increase in sediments to concentrations in excess of the street dust sources. Similarly, As has been shown to primarily be associated with the iron oxide fraction of soils within the Nene basin (Cave *et al*., 2003) and therefore is bound within the mineral structure of transported sediments. Therefore, As also has little opportunity to adsorb to the surface of sediment particles, explaining its lack of correlation with SSA. Palumbo-Roe *et al*. (2005) showed that the iron oxide minerals in the soils and sediments of the Nene basin have a high chemical affinity for P. The scavenging of the dissolved P in discharged effluent by sediment is a likely explanation for the very high concentrations of P found in the river sediment in comparison to the potential sediment

sources. It also explains the different dynamics observed between P and other pollutants. Particle size had only a small impact on P concentrations and the chemical affinity of the sediment for P shown by Palumbo-Roe *et al*. (2005) therefore appears to be of greater importance than its surface area alone.

It has been previously demonstrated that Cu, Pb, and Zn can be enriched by up to three orders of magnitude within the organic fraction of sediments (Hirner *et al.,* 1990) and have also been shown to be associated with the organic fraction of urban street dusts (Robertson *et al.*, 2003). Relationships between As and Pb and LOI are very weak in the Nene (R^2 0.0055 - 0.02) (see online supplementary material). Therefore, the association of pollutants with the organic fraction of the sediment is probably not an important control on these contaminant concentrations within the Nene basin. LOI was shown to be more strongly related to sediment P concentration. This relationship may be the result of the association of P with organic matter or the scavenging of P by aquatic organisms.

The urban contaminants were below the PELs in the majority of sediment samples, except for those samples collected from close proximity to urban areas. Therefore, these contaminants are unlikely to have a large detrimental effect on environmental quality extensively throughout the Nene catchment. Cave *et al*. (2003) showed that only ~ 2 to 9% of As in the ironstone soils close to Wellingborough is bioavailable. Therefore, there is a reduced potential for environmental harm from As pollution than its high concentrations suggest. The P concentrations of up to 9000 mg kg^{-1} in the Nene's sediments are very high in comparison to previously investigated lowland agricultural catchments. For example concentrations of 783 to 1355 mg kg^{-1} were found in the Pang and Frome catchments by Collins *et al*. (2005).

Concentrations of P were shown to be fairly constant before and after the April 2012 flood suggesting that an equilibrium may have been reached between P discharges and the capacity of the sediment so adsorb it. Research in the River Swale in Yorkshire has indicated in the mass balance of a 55 km river section that up to 50% of the soluble reactive phosphorus (SRP) load was lost from the water column (House and Warwick, 1998). Therefore, given the high chemical affinity of the Nene's sediment for P (Palumbo-Roe *et al*., 2005) it would be expected that P would rapidly associate with the sediment. In the Anglian District River Basin Management Plan it was determined that phosphate is a leading cause of environmental degradation in the river Nene (Environment Agency 2009). This study has shown that the sediment is scavenging very high concentrations of phosphorus in the Nene. The role of this

accumulation on environmental quality was explored by Tye et al. (2013) who determined that sediment is acting to decrease soluble reactive phosphorus (SRP) concentration in the river water. However, it was identified that there was potential for sediment to act as a source of SRP if its concentration in river water falls. Further research is therefore required to determine if sediment is likely to act as a P source when sediment with a very high phosphorus concentrations (up to 9819 mg kg^{-1}) is flushed from channel beds during high flow events. Additionally, it should be identified if the sediment within the Nene is able to become fully saturated by P during periods of extreme drought, removing its ability to act as a P sink.

Conclusions

It was found that proximity to sediment source was the dominant factor controlling sediment-associated As, Cu, Pb, and Zn concentrations in the Nene catchment. Phosphorus concentrations were also heavily controlled by proximity to source, however, concentrations did not decrease with increasing distance downstream of the source. Concentrations of As, Cu, Pb, and Zn were not significantly higher during periods of low flow than during periods of high flow and did not decrease over successive flood events. Phosphorus concentrations accumulated to very high concentrations in tributary bed sediment during periods of low flow, before the contaminated sediment was flushed away during high flows. There was, however, no reduction in P concentration in the Nene's main channel over successive flood events. The accumulation of P to very high concentrations was explained by the discharge of dissolved sewage effluent into the river and the scavenging of P by the sediment. The other pollutants originated primarily in particulate form so were limited in concentration by that of their original sources. Sediment particle size and organic matter content were suggested to be more minor controls on sediment-associated contaminant concentrations than proximity to sediment source, or flow. The lack of a reduction in sediment concentration over successive flood events suggests that the stores of pollutants in the catchment were not depleted by multiple floods or that they were replenished between flood events.

Concentrations of Cu, Pb and Zn were indicated to be predominantly below PELs and pose little risk of environmental damage in the Nene basin. Whilst concentrations of As were found to be very high; previously published research has shown that the majority of the As is not bioavailable and therefore poses little risk. Sediment associated P was found in very high

concentrations and poses a significant environmental risk if the P is or should become bioavailable.

Acknowledgements

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Figures and tables

Figure 1: The Nene basin showing potential sources of pollutants (A) and the suspended sediment, recently deposited overbank and channel bed sediment sampling locations (B).

Figure 2: Total monthly rainfall and the highest daily total rainfall per month throughout the monitoring period. The historical average total monthly rainfall measured at Althorp over the previous 140 years is also plotted for comparison.

Figure 3: Distributions of the contaminants in pollutant sources, suspended sediment (including overbank deposits) and channel bed sediment.

Figure 4: Concentrations of arsenic, lead and phosphorus in channel bed sediment in June 2011 (mg kg^{-1}).

Figure 5: Concentrations of arsenic, lead and phosphorus in recently deposited overbank sediment (mg kg^{-1}).

Figure 6: The relationships between distance from Northampton and As, Pb and P concentration in overbank deposited sediment, negative values are upstream of Northampton, based upon the methodology used by Pizzuto (2014).

Figure 7: Sediment-associated lead concentrations in channel bed sediment at the T10 and T11 sampling sites (A) and suspended sediment of the Northampton and Wellingborough sampling sites (B and C).

Figure 8: Phosphorus concentrations and storage in channel bed sediment (A) and suspended sediment (B and C) of the Dodford and Heyford sampling sites.

Figure 9: Arsenic concentrations and storage in channel bed sediment (A) and suspended sediment (B and C) of the Weedon 2 and Northampton sampling sites.

Figure 10: Mean concentrations of trace elements in sediments deposited overbank after the April, July, October and November high flow events, with standard deviation.

Table 1: The amount of sediment element concentration recovered by the microwave digestion and ICP analysis procedure, determined using a certified reference material analysed for three repetitions (a certified concentration for phosphorus was not available).

Element (mg kg^{-1})	Measured concentration		Certified concentration	Percentage recovered
	Average	Standard deviation		
As	17.50	0.12	23	76.17
Cu	19.51	1.41	36	54.19
Pb	28.75	0.35	35	82.14
Zn	126.32	3.09	178	70.97

Table 2: Median and median absolute deviation (MAD) concentrations of trace metals and nutrients present in potential sediment sources in the Nene basin.

Source property (mg kg^{-1})	Surface agricultural soils (n = 247)		Channel banks (n= 65)		Ironstone soils (n = 39)		Urban street dusts (n = 21)	
	Median	MAD	Median	MAD	Median	MAD	Median	MAD
As	22.62	9.23	24.95	9.44	56.83	12.3	17.68	1.64
Cu	21.62	4.2	20.75	4.52	20.36	4.68	222.47	49.74
P	1354	374	1018	249	2431	519	1319	160
Pb	30.98	7.83	26.47	7.18	42.9	9.77	107.45	17.62
Zn	85.27	23.06	85.82	12.68	127.18	19.85	853.82	290.51

Online Supplementary material

Table 3: Spearman rank significance and correlation coefficients for pollutants, SSA and LOI upstream and downstream of Northampton.

Upstream of Northampton

Pollutant	LOI		SSA	
	p	r^2	p	r^2
As	.087	0.018	.615	0.002
Cu	**.000**	**0.109**	**.000**	**0.126**
P	**.000**	**0.250**	**.000**	**0.211**
Pb	**.000**	**0.149**	**.000**	**0.288**
Zn	**.000**	**0.113**	**.000**	**0.206**

Downstream of Northampton

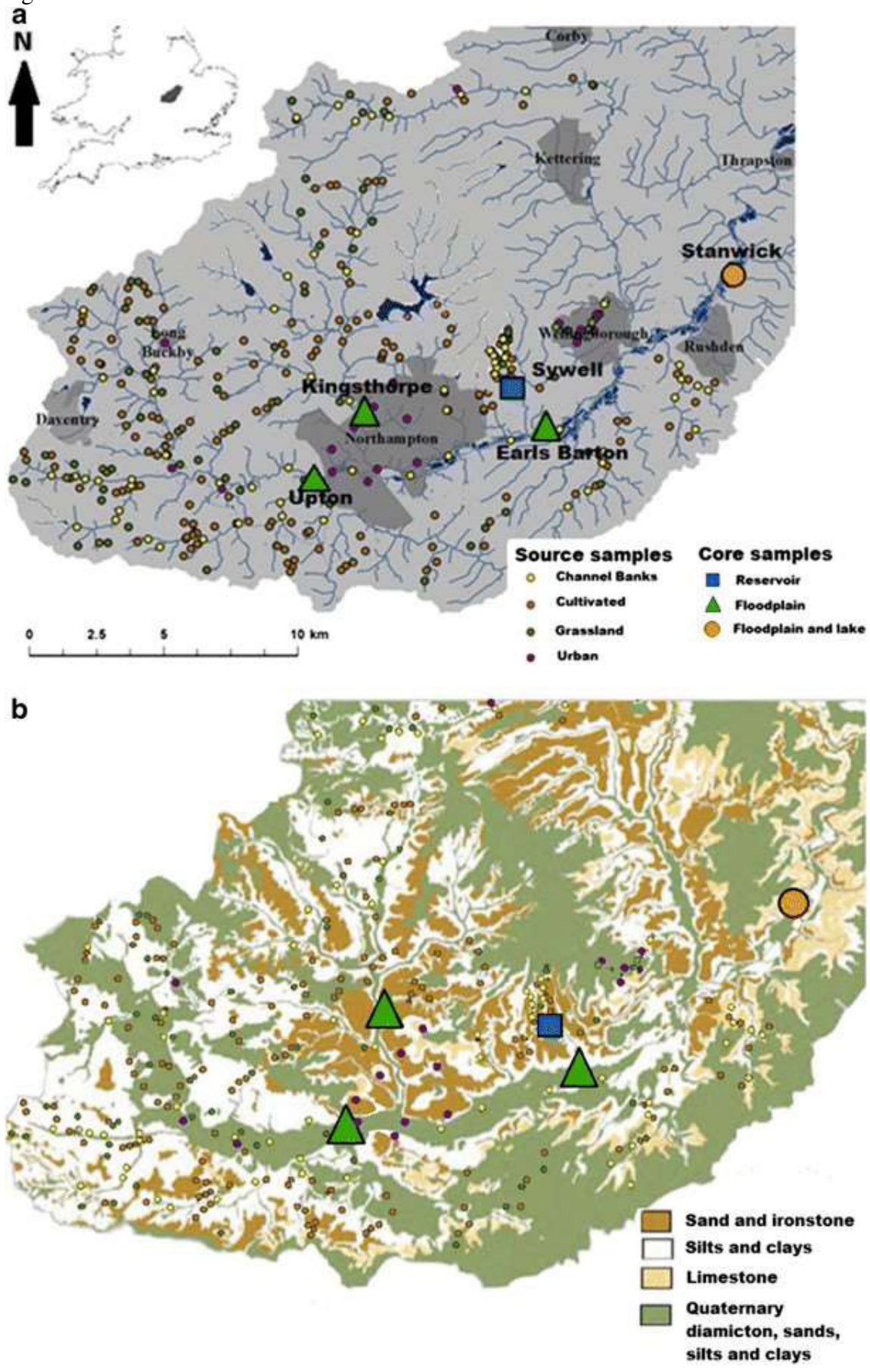
Pollutant	LOI		SSA	
	p	r^2	p	r^2
As	.354	0.012	.979	0.000
Cu	**.000**	**0.262**	.136	0.030
P	**.000**	**0.234**	**.000**	**0.235**
Pb	.091	0.039	.510	0.006
Zn	**.003**	**0.112**	.410	0.009

Figure S1: Relationships between Lead, LOI and SSA in sediment samples upstream and downstream of Northampton.

Figure S2: Relationships between Arsenic, LOI and SSA in sediment samples upstream and downstream of Northampton.

Figure S3: Relationships between Phosphorus, LOI and SSA in sediment samples upstream and downstream of Northampton.

Figure 1


a
N
Corby
Kettering
Thrapston
Stanwick
Wellingborough
Rushden
Sywell
Kingsthorpe
Northampton
Earls Barton
Upton
Daventry
0
2.5
5
10 km
Source samples
Channel Banks
Cultivated
Grassland
Urban
Core samples
Reservoir
Floodplain
Floodplain and lake
b
Sand and ironstone
Silts and clays
Limestone
Quaternary diamicton, sands, silts and clays

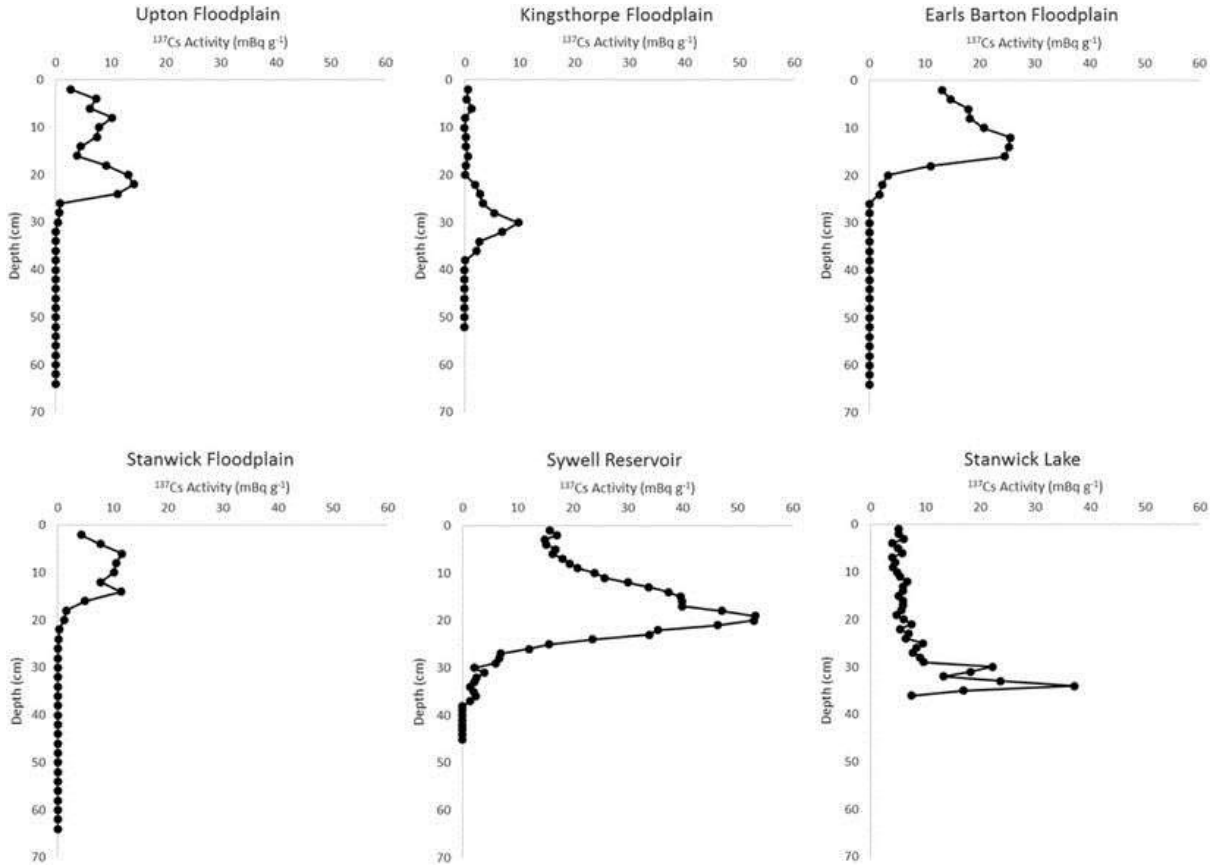

Upton Floodplain
Kingsthorpe Floodplain
Earls Barton Floodplain
Stanwick Floodplain
Sywell Reservoir
Stanwick Lake
137Cs Activity (mBq g-1)
Depth (cm)

Figure 2

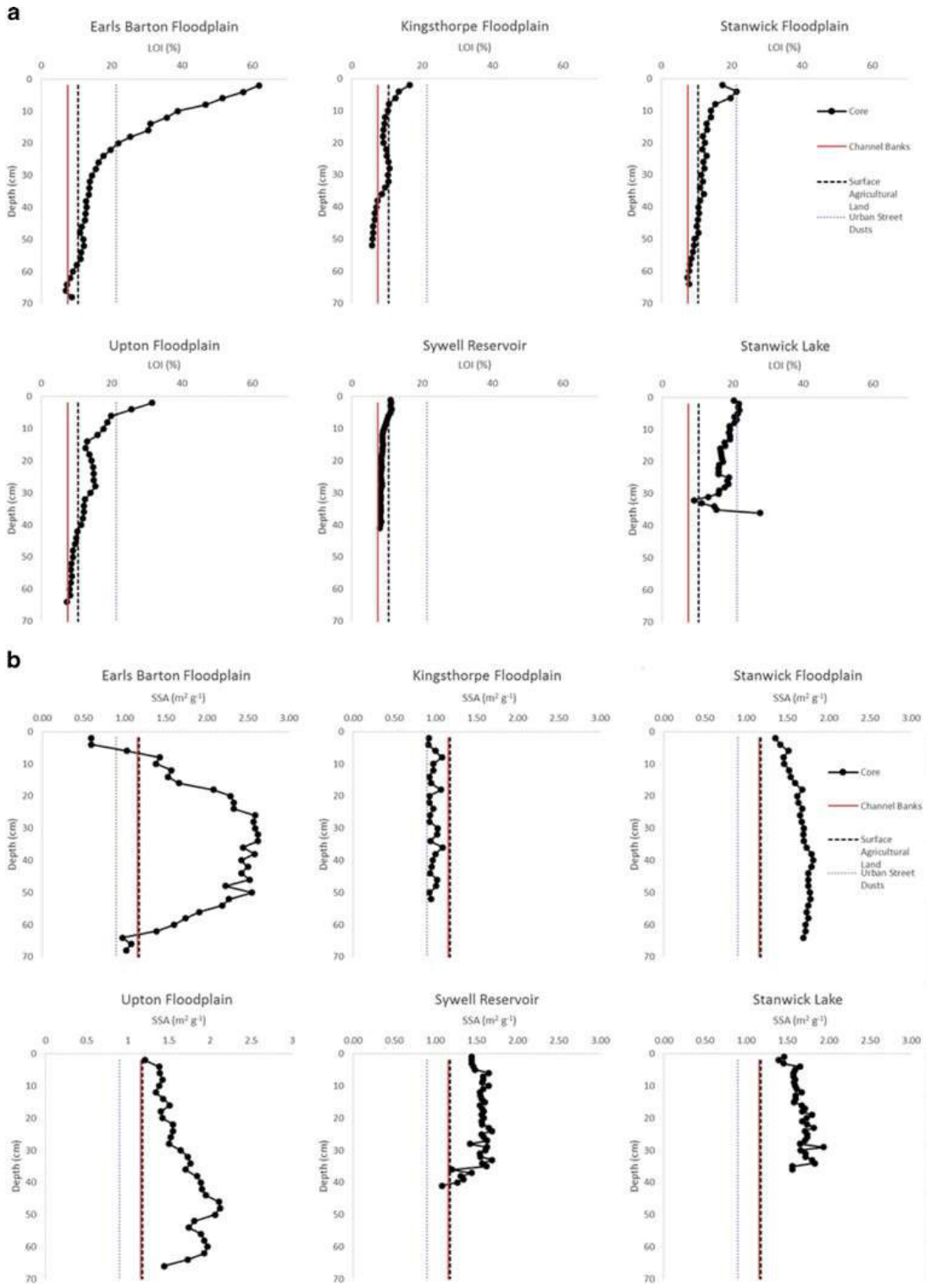

a
Earls Barton Floodplain
Kingsthorpe Floodplain
Stanwick Floodplain
Upton Floodplain
Sywell Reservoir
Stanwick Lake
LOI (%)
Depth (cm)
Core
Channel Banks
Surface Agricultural Land
Urban Street Dusts
b
Earls Barton Floodplain
Kingsthorpe Floodplain
Stanwick Floodplain
Upton Floodplain
Sywell Reservoir
Stanwick Lake
SSA (m² g⁻¹)
Depth (cm)
Core
Channel Banks
Surface Agricultural Land
Urban Street Dusts

Figure 3

Figure 4

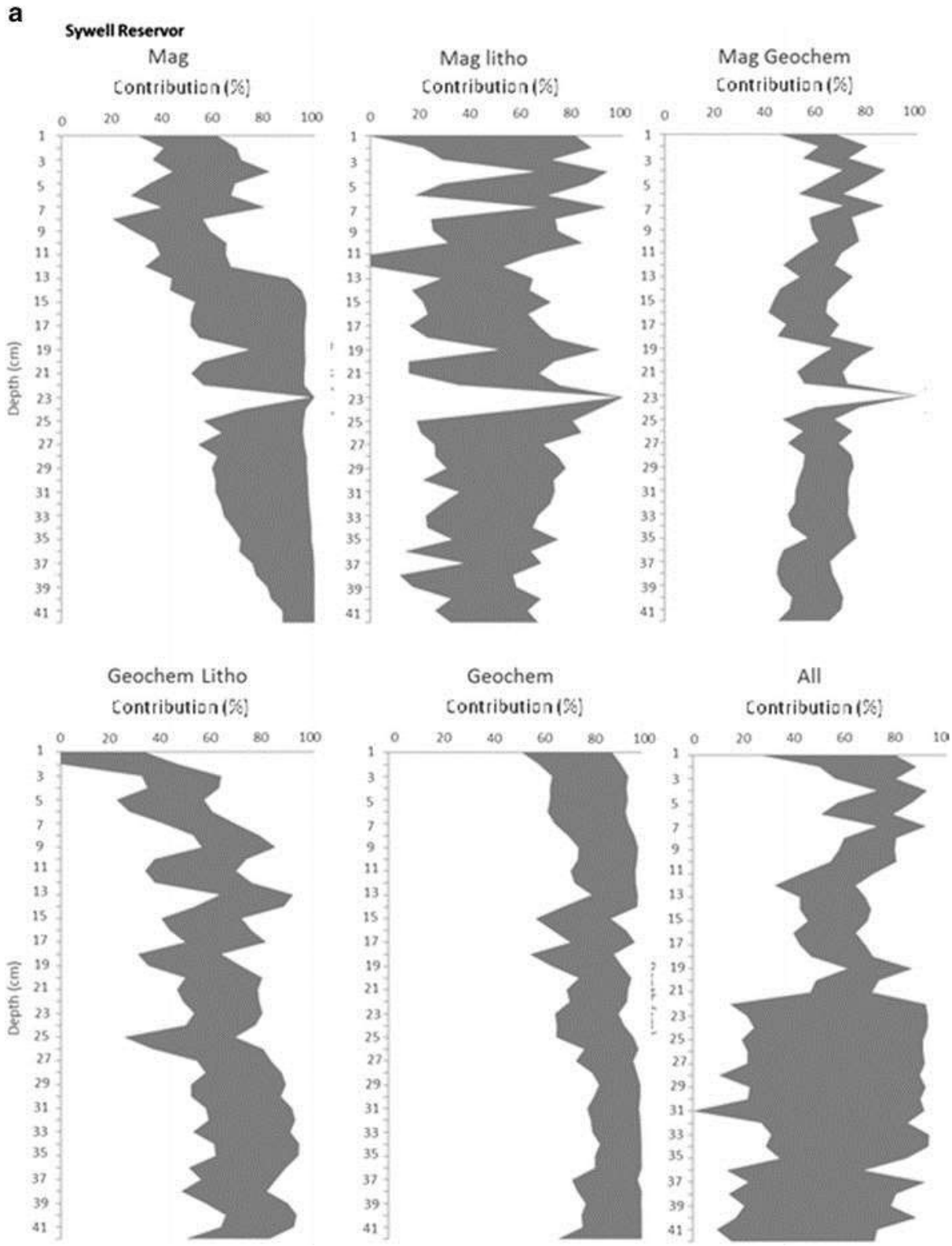
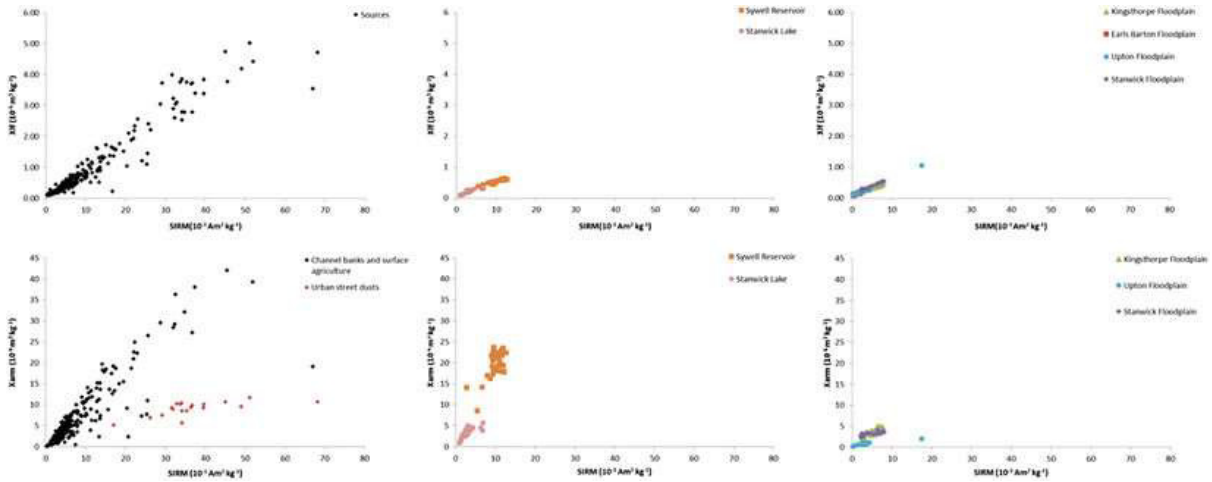

a
Sywell Reservor
Mag
Contribution (%)
Mag litho
Contribution (%)
Mag Geochem
Contribution (%)
Geochem Litho
Contribution (%)
Geochem
Contribution (%)
All
Contribution (%)
Depth (cm)

Figure 5


Sources
Sywell Reservoir
Stanwick Lake
Kingsthorpe Floodplain
Earls Barton Floodplain
Upton Floodplain
Stanwick Floodplain
Channel banks and surface agriculture
Urban street dusts
SIRM(10⁻³ Am² kg⁻¹)
Xfd (10⁻⁸ m³ kg⁻¹)
Xarm (10⁻⁸ m³ kg⁻¹)