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Lead contamination of fluvial sediments in an eroding blanket peat catchment

J.J. Rothwell *, M.G. Evans, T.E.H. Allott

Upland Environments Research Unit, School of Environment and Development, The University of Manchester, Manchester, M13 9PL, UK

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Abstract

Over the last few years there has been growing concern over the mobilisation of anthropogenically derived, atmospherically deposited Pb from upland blanket peat soils to receiving surface waters. The near-surface layer of blanket peat soils of the Peak District, southern Pennines, UK, is severely contaminated with high concentrations of Pb. Erosion of peat soils in this upland area may be releasing large quantities of previously deposited Pb into the fluvial system. Samples of fluvial sediments (suspended, floodplain, streamside fan, trash-line and channel bed) were collected from a severely eroding blanket peat catchment in the Peak District in order to investigate Pb contamination of fluvial sediments, to determine the mechanism for fluvial Pb transport and to determine if erosion of contaminated peat soils in the catchment is releasing Pb into the fluvial system. Concentrations of Pb associated with fluvial sediments are considerably higher than those in the catchment geology, but not as high as those in peat soils in the catchment. Intra- and inter-storm variability in the Pb content of suspended sediments can be explained by differences in organic matter content of these sediments and differences in erosion processes operating within the catchment. High Pb concentrations are associated with suspended sediments that have a high organic matter content. The results of this study suggest that organic matter is the principle vector for sediment-associated Pb in the fluvial system. Erosion of contaminated peat soils in the Peak District is releasing Pb into the fluvial system. The extent to which this is a problem in other peatland environments is an area requiring further research.

1. Introduction

Organic matter has a high affinity for heavy metals, and in peat soils metal uptake occurs by cation exchange at acidic sites where ions sorb to functional chemical groups (Ringqvist and Öborn, 2002; Tipping et al., 2003a; Turetsky et al., 2004). Lead (Pb) deposited from the atmosphere, as either wet or dry deposition, is stored within blanket peat soils and can be used to reconstruct temporal trends in Pb deposition (e.g. Livett et al., 1979; Clymo et al., 1990; Bindler et al., 2004; Farmer et al., 2005). This is because this heavy metal is not susceptible to post-depositional mobility within blanket

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[*] Corresponding author. Present address: Department of Environmental and Geographical Sciences, Manchester Metropolitan University, Manchester M1 5GD, UK. Fax: +44 161 247 6318.

E-mail address: j.j.rothwell@mmu.ac.uk (J.J. Rothwell).

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peat soils (Vile et al., 1999). As blanket peat soils receive their inputs from the atmosphere, peatlands in close proximity to industrial or urban areas can be highly contaminated with potentially toxic heavy metals (e.g. Livett et al., 1979; Mighall et al., 2002; Smith et al., 2005; Rothwell et al., 2007).

In recent years there has been growing interest in the mobilisation and delivery of heavy metals stored in upland blanket peats to freshwater ecosystems. Much of the work has focused upon heavy metal pollutants in dissolved form (e.g. Lawlor and Tipping, 2003; Tipping et al., 2003b; Vinogradoff et al., 2005). Blanket peat covers approximately 8% of the land surface of the UK (Evans and Warburton, 2001), but over 10% of blanket peats in the UK may be in an eroded state (Tallis, 1997). Once peat has been eroded, particles are transferred to, and transported in, streams draining eroding peatland areas. Over the last few decades many workers have measured suspended sediment fluxes in rivers draining catchments dominated by eroding blanket peat (e.g. Crisp, 1966; Burt and Gardiner, 1984; Francis, 1990; Labadz et al., 1991; Evans and Warburton, 2005). Erosion of soils and sediments has long been recognised as a mechanism for the release of heavy metals into the fluvial system (e.g. Macklin and Klimek, 1992; Merrington and Alloway, 1994; Salomons, 1995; Collins and Walling, 2002; Blake et al., 2003; Hudson-Edwards, 2003; De Carlo et al., 2004). In a study by Rothwell et al. (2005) it was demonstrated that erosion of atmospherically contaminated blanket peats in the southern Pennines, UK, is potentially releasing large quantities of Pb into the fluvial system. Shotbolt et al. (2006) reveal that sediments in reservoirs of the uplands of the southern Pennines are contaminated with Pb and have suggested that erosion processes operating in the peat-dominated reservoir catchments are releasing previously deposited Pb into these reservoirs. Although the physical process of erosion has been alluded to as a mechanism for the release of Pb into peatland fluvial systems in the southern Pennines, there is very little known about the dynamics of sediment-associated Pb transport in upland fluvial systems draining contaminated and eroding peatland catchments. In order to fully understanding sediment-associated heavy metal dynamics in river systems, suspended sediment, overbank sediment and channel bed sediment must be investigated, as each of these are important components of the sediment system in fluvial environments (Owens et al., 2001).

This paper describes an investigation into the Pb contamination of fluvial sediment (suspended, floodplain, streamside fan, trash-line and channel bed) in a severely eroding peatland catchment in the southern Pennines, UK. The main objectives of the study were:

1. To determine the Pb content of peat soils and underlying geology.
2. To examine temporal patterns in the Pb content of stormflow suspended sediments.
3. To examine the relationship between the Pb content of suspended sediments and suspended sediment concentration and the Pb content of suspended sediments and discharge.
4. To examine the relationship between the Pb content of fluvial sediments and the organic matter content of these sediments.
5. To determine the mechanism for Pb transport.
6. To evaluate if peat erosion is releasing Pb into the fluvial system.

Overall, this study will provide information on the cycling of sediment-associated Pb in a peat dominated catchment in upland Britain and add to the understanding of the fate of atmospherically deposited heavy metals in upland blanket peat environments. Understanding the sources, transport and behaviour of sediment-associated heavy metals in sensitive upland fluvial systems is needed as detrimental effects are often associated with the release of heavy metal contaminants into aquatic systems (Salomons and Forstner, 1984).

2. Study area

The Peak District in the southern Pennines, UK, is characterised by extensive blanket peat soils. High concentrations of Pb are stored in the near-surface layer of the blanket peat soils of this region due to the close proximity of this area to the industrial cities of Manchester and Sheffield (e.g. Livett et al., 1979; Jones, 1987; Markert and Thornton, 1990; Jones and Hao, 1993; Rothwell et al., 2007). The Peak District is also an area that is particularly affected by peat erosion (Tallis, 1997; Evans et al., 2006). Upper North Grain is a small headwater stream that drains a blanket peat-covered catchment (0.38 km^2) in the Peak District (Fig. 1). Geologically, this area of the Peak District is dominated by interbedded sandstones and shales of the Millstone Grit Series (Wolverson-Cope, 1976). At Upper North Grain there are

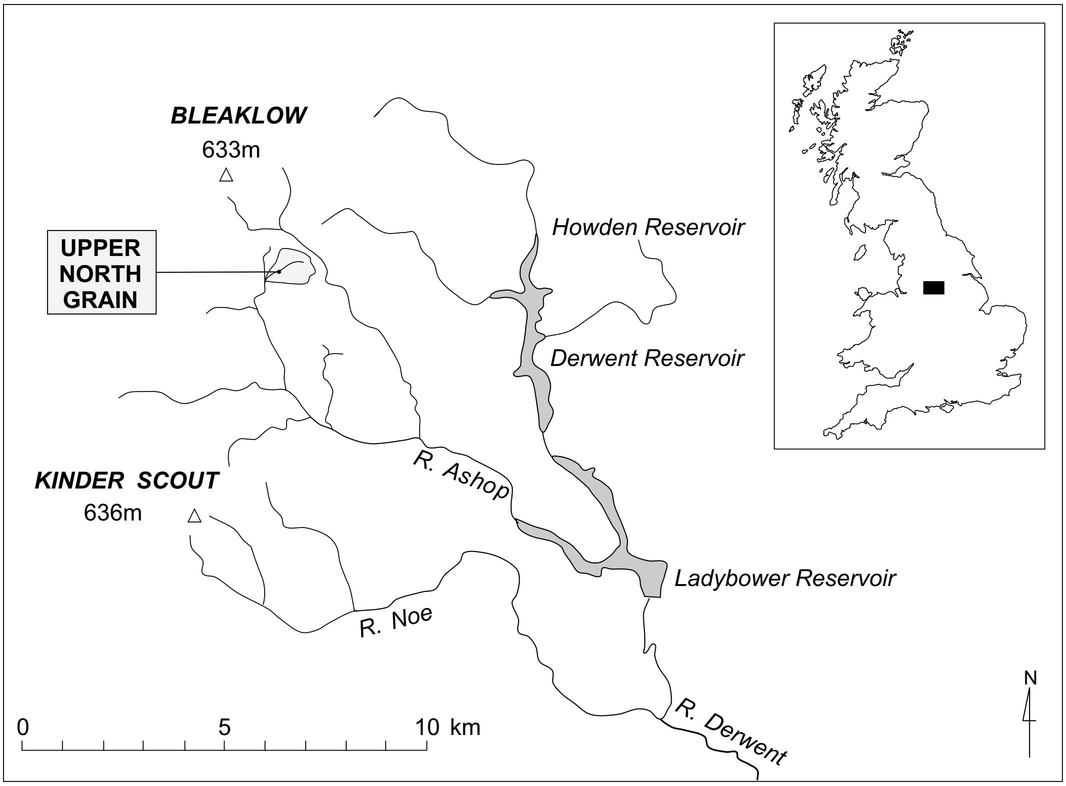

Fig. 1. Study location. The catchment area is shaded in grey.

some small exposures of shales but coarse-grained sandstone is dominant. Some of the bedrock of the catchment is overlain by periglacial head deposits, which are derived from weathered sandstones and shales. No Pb mineralisation is present within the catchment. Peat soils in the catchment vary in thickness, but maximum depths do not exceed 4 m. The peat soils in the catchment are severely gullied and in some locations the underlying geology is exposed. Land use in the catchment is dominated by rough grazing by sheep.

3. Methodology

3.1. Sampling

3.1.1. Peat soils and catchment geology

During October 2002, six peat cores were collected from intact peat areas within the catchment. Coring sites were based on a random stratified sampling strategy. A 50 cm stainless steel Russian corer (internal diameter 5 cm) was used to extract the peat cores. Each core was wrapped in cling film, labelled, transported back to the laboratory in half drainpipe sections and stored horizontally at 4 °C prior to analysis. During March 2004, 10 samples from each of the catchment geologies (Millstone Grit sandstone, shales and periglacial head deposits) were sampled using a small plastic shovel (periglacial head deposits) and a stainless steel hammer (sandstones and shales). These samples were collected from the base of exposures in eroding gullies and a random stratified sampling strategy was used in sample collection. All samples were bagged, labelled and returned to the laboratory.

3.1.2. Fluvial sediments

Between June 2002 and November 2004, 205 stream samples were collected automatically from the main stream channel in the catchment during high flow by a SIGMA 900 water sampler. The water sampler was programmed to abstract 24 water samples of approximately 500 mL at pre-determined intervals (usually every 15 min) triggered by a rise in stage. Water samples were returned to the laboratory within a few days of collection, refrigerated at 4 °C and analysed for sediment-associated Pb within two days as described below.

Between July 2003 and December 2004, sediment samples were collected from a small floodplain area and streamside fan within the catchment. Samples were collected using an array of fixed Astroturf mats. This technique has been routinely used to collect overbank sediments due to the efficient capture and retention of sediment on Astroturf mats (e.g. Lambert and Walling, 1987; Owens et al., 2001; Walling et al., 2003; Evans et al., 2006). Five mats (23 by 23 cm) were installed in a grid across the floodplain area in the upper catchment and five identical mats on a vegetated streamside fan at the outlet of a large eroding gully in the lower part of the catchment. The mats were fixed into position using stainless steel pins. All mats were located within 10 m of the river channel. The mats were emptied 10 times over the 18 month period. Sediment on each mat was removed using a stainless steel spatula (cf. Walling et al. (2003)). All samples were bagged, labelled and returned to the laboratory. The material collected on the mats is likely to represent sediment that was active in the stream channel during high flow conditions.

After a series of large storm events in February 2004, trash-line sediments were sampled from areas adjacent to the main stream channel in the catchment. A total of 22 trash-line sediments were collected by hand at approximately every 20 m down the full length of the main channel. All trash-line debris adjacent to the main stream channel appeared to be organic-rich and these sediments were deposited at the maximum water level during the February storm events.

During March 2004, channel bed sediments were collected from the catchment during baseflow conditions. A channel bed sediment sample was collected from the base of eight eroding peat gullies in the catchment. The ephemeral nature of flow in these gullies meant that channel bed sediments could be collected easily by hand. Fifteen channel bed sediment samples were also collected along the 400 m length of the main stream channel of the catchment. Samples were collected at approximately every 25 m. Since the water depth was <30 cm, channel bed sediments could be collected by hand using a 500 mL water bottle.

3.2. Flow measurements

Measurement of stage on a rated stream section at Upper North Grain between June 2002 and December 2004 was obtained using an Intelisys pressure transducer and data logger. A stage-discharge relationship was established from a series of flow measurements using a SENSA-RC2 electromagnetic flow meter.

3.3. Laboratory techniques

Prior to use, all field and laboratory equipment was soaked in 10% Decon 90 detergent solution overnight, rinsed with distilled water (ELGA PURELAB Option R7), soaked overnight in 2 M HNO_3 (Analar, BDH), and then rinsed again with distilled water. All peat cores were sliced at contiguous 1 cm intervals for the top 30 cm and disaggregated. In order to retain the suspended sediment fraction of the storm water samples, all water samples were filtered through pre-weighed glass microfibre filter paper circles (Whatman GF/C). Channel bed sediments from the main stream channel were settled-out over a one week period and the sediment recovered by centrifugation. Peat core samples, filtered suspended sediments and channel bed sediments from the main stream channel were then oven-dried at 105 °C for 24 h. Geological samples and the remaining fluvial sediments were also dried in the same manner. After drying, the organic matter content of sub-samples of the top centimetre of the peat cores and sub samples of all geological, fan, trash-line and channel bed sediments was determined by loss-on-ignition (5 h at 550 °C). The organic matter content of 25 floodplain sediments was also calculated in the same way. The method for the determination of organic matter content for suspended sediments is described below. All suspended sediments (including filter paper) were digested on a hot-plate at approximately 100 °C for 4 h using 5 mL of 15.6 M HNO_3 (Analar, BDH). The method used was adapted from Cook et al. (1997). After digestion, all samples were allowed to cool and made up to 25 mL with distilled water. Fifty randomly selected digested suspended sediment samples were then vacuum filtered through pre-weighed Whatman GF/C filter paper into new sterile polythene tubes and stored at 4 °C prior to Pb analysis. The mineral residue retained on the filter papers was then dried at 105 °C for 24 h and weighed. To calculate the organic matter content of these suspended sediments the weight of the mineral residue was subtracted from the original suspended sediment weight. The remaining digested suspended sediment samples were filtered in the same manner, but the mineral component was not calculated. Due to the consolidated nature of the sandstone and shales, these samples were homogenised for 10 min using a ball mill with carbide cartridge and balls prior to sample digestion. Sub samples of these catchment materials and the remaining fluvial sediments were weighed and then prepared for Pb analysis as described above. Pb concentrations were determined using AAS (Thermo Unicam S11). Pb standard solutions (Spectrosol, BDH) were used to calibrate the AAS. The sensitivity of the AAS was 0.1 ppm for Pb. With each batch of sediment samples, a blank sample (unused digested filter paper) and Certified Reference Material (CRM) LGC6187 River Sediment (LGC Promochem) were also digested using the same procedure as the sediment samples. Blank samples were below the detection limit of the AAS and the recovery of the CRM was always within 12%. Machine drift for each sample batch was recorded and sample results corrected accordingly.

4. Results

4.1. Peat soils and catchment geology

Although there is within-site variability in Pb pollution records at Upper North Grain, all down-core Pb profiles reveal that there are much higher Pb concentrations in the near-surface peat layer than in the lower depths of the cores (Fig. 2). Maximum Pb concentrations in cores UNG1 – UNG6 are 1148, 1097, 1370, 1614, 1122 and 873 mg kg^{-1}, respectively. Mean Pb concentrations for the sandstone, shale and periglacial head deposits are signif-

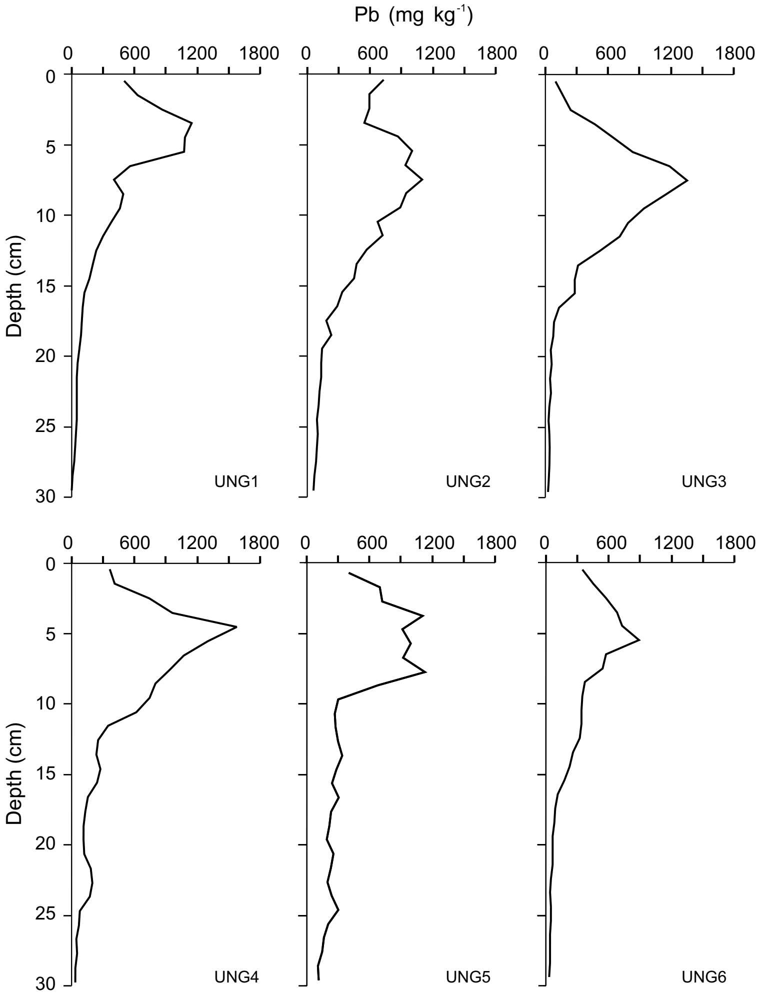

Fig. 2. Down-core Pb profiles for six peat cores collected from Upper North Grain.

icantly lower than Pb concentrations in the near-surface layer of the catchment peats (Table 1). The sandstone, shale and periglacial head deposit are also characterised by a low organic matter content (Table 1).

4.2. Fluvial sediments

4.2.1. Suspended sediments

Fig. 3 shows the temporal pattern in suspended sediment concentration (SSC), discharge (Q) and the Pb content of suspended sediments for storm water samples collected during 12 individual storm events over the 29 month sampling period. The storm events sampled were the 8/6/02, 14/6/02, 9/9/02, 1/11/02, 7/3/03, 8/3/03, 12/11/03, 24/2/04, 18/4/04, 21/4/04, 4/11/04 and 16/11/04. Intra-storm trends in SSC, Q and sediment-associated Pb concentrations are markedly different for each storm. Sediment-associated Pb concentrations range from 4.43 mg kg^{-1} (8/3/03) to 395 mg kg^{-1} (1/11/02). Lower sediment-associated Pb concentrations are associated with the three largest storms collected during the sampling period (8/6/02, 9/9/02 and 8/3/03). Peak sediment-associated Pb concentrations for individual storm events range from 96.3 mg kg^{-1} (8/3/03) to 395 mg kg^{-1} (1/11/02). The peak in stormflow sediment-associated Pb concentration occurs before, at, or proceeding the peak in SSC and Q. The peak in sediment-associated Pb occurs before the peak in SSC and Q during the 9/9/02, 1/11/02, 24/2/04, 4/11/04 and 6/11/04 storm events. The peak in sediment-associated Pb occurs after the peak in SSC and Q during the 8/6/02, 14/6/02, 7/3/03, 12/11/03 and 21/4/04 storm events. During the 8/3/03 storm event, the sediment-associated Pb peak occurs simultaneously with the peak in Q. During the 18/4/04 storm event the sediment-associated Pb peak occurs simultaneously with both the peak in SSC and the peak in Q. For all storm events there is no relationship between storm magnitude or SSC and the position or size of the Pb peak.

In peatland fluvial systems, positive hysteresis between SSC and Q is usually observed (e.g. Labadz et al., 1991; Evans et al., 2006). In the present study positive hysteresis between SSC and Q is observed in most of the storm events collected from the catchment (Fig. 3). There is a good positive relationship between SSC and Q at Upper North Grain ($\mathrm{SSC} = 20.0e^{11.7Q}$, $R^2 = 0.44$, $p < 0.001$), although this relationship would be improved by closing the hysteresis loop.

Fig. 4a shows the relationship between Pb content of suspended sediments and SSC for all storm events and Fig. 4b shows the relationship between the Pb content of suspended sediments and Q for all storm events. There is a very weak, but significant, negative relationship between sediment-associated

Table 1
Summary statistics for the Pb content and organic matter content of peat soils, geology and fluvial sediments at Upper North Grain

	Soils and geology				Fluvial sediments					
					Suspended	Overbank			Channel bed	
	Peat[a]	Sandstone	Shale	Head		Floodplain	Fan	Trash-line	Gully	Main
Pb content[b]										
Mean	1204	9.32	15.7	21.8	102	66.1	40.2	43.5	89.8	53.8
SD	104	14.1	3.85	15.4	39.4	51.0	26.1	20.0	25.5	34.4
Minimum	873	2.38	9.46	7.14	4.43	7.69	9.92	19.2	38.7	22.5
Maximum	1614	49.0	21.7	101	395	341	99.7	91.4	112	139
n	6	10	10	10	205	41	26	22	8	15
CL (95%)	268	10.1	2.75	11.9	5.42	16.1	10.5	8.88	21.3	19.1
Organic content[c]										
Mean	97.6	0.50	4.12	2.44	58.9	27.1	39.9	89.6	94.3	46.4
SD	1.15	0.29	0.16	1.18	18.6	28.5	35.5	6.95	2.08	30.7
Minimum	95.7	0.28	3.94	1.52	9.03	2.81	5.22	68.1	91.2	2.16
Maximum	98.9	0.82	4.24	3.78	77.0	86.4	96.8	98.2	97.9	95.3
n	6	10	10	10	50	25	26	22	8	15
CL (95%)	1.21	0.71	0.40	2.94	5.23	9.63	14.3	3.08	1.67	17.0

[a] Maximum Pb concentration in near-surface peat.

[b] mg kg^{-1}.

[c] Organic matter content expressed as a percentage.

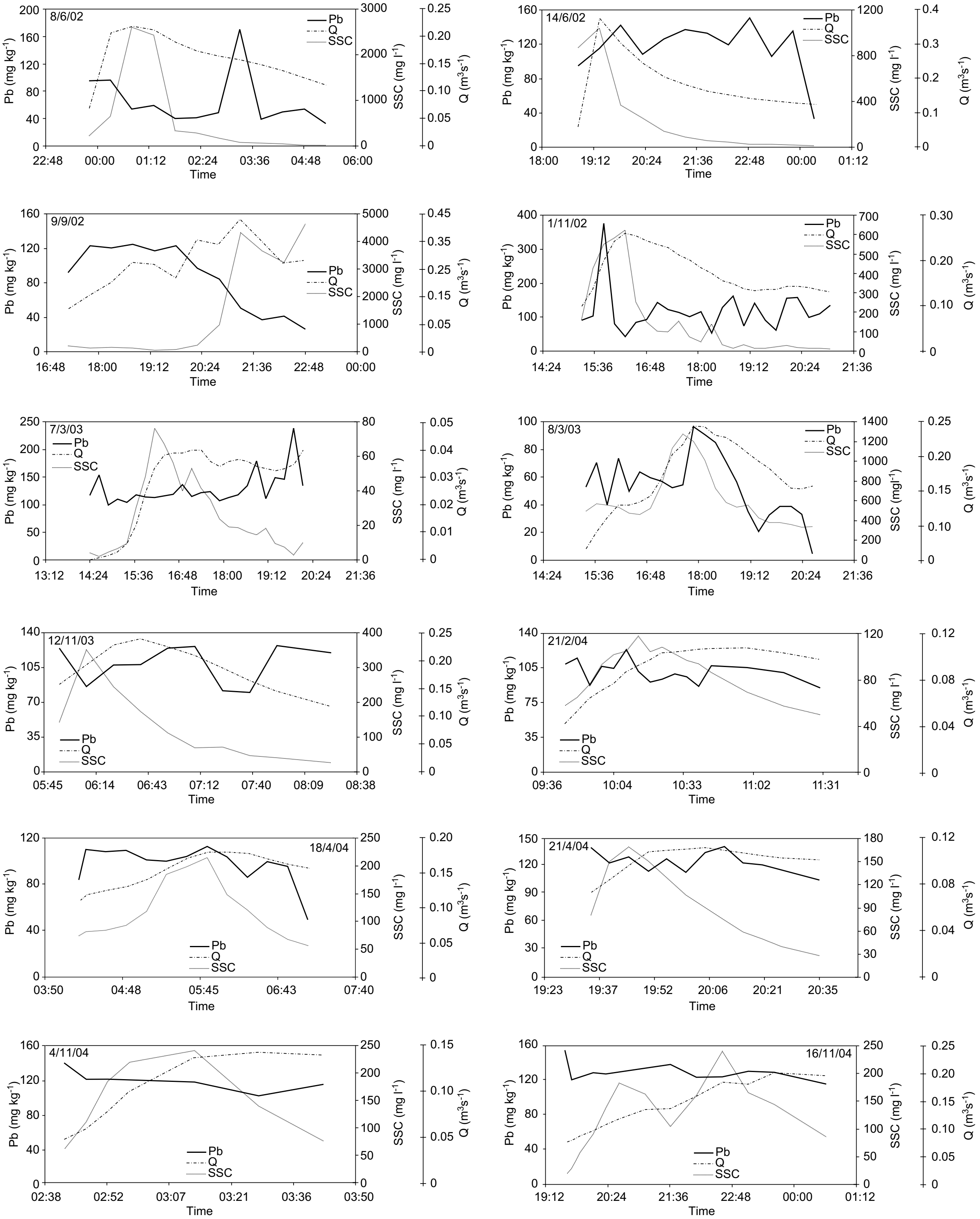

Fig. 3. Sediment-associated Pb concentrations for suspended sediments, suspended sediment concentration (SSC) and discharge (Q) for storm events collected from Upper North Grain. Note the different scales.

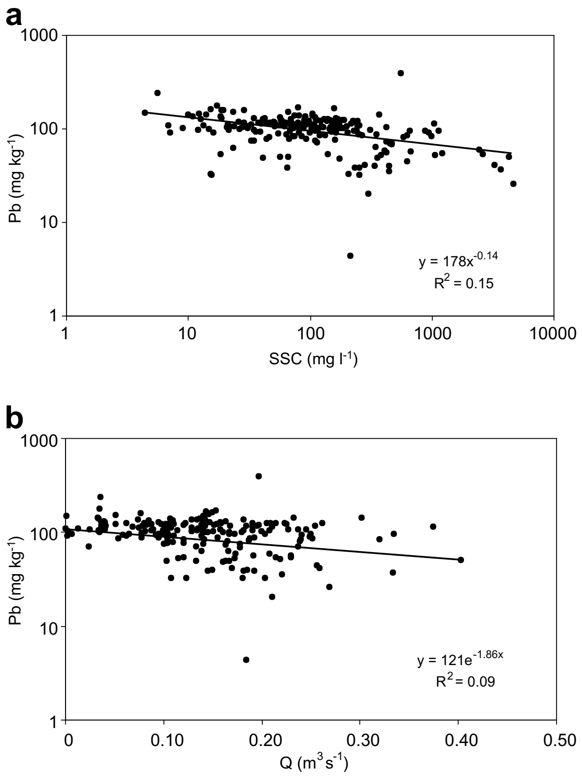

Fig. 4. The relationship between the Pb content of suspended sediments collected from Upper North Grain and suspended sediment concentration (SSC) (a) and discharge (*Q*) (b). Note the different scales.

Pb concentration and SSC ($R^2 = 0.15$, $p < 0.001$). As SSC values increase, the Pb content of suspended sediment decreases. However, there is no statistically significant relationship between the Pb content of suspended sediments and *Q* (Fig. 4b).

The relationship between the Pb content of 50 suspended sediment samples and the organic matter content of these sediments is shown in Fig. 5. There is a good positive relationship between the Pb content and organic matter content of suspended sediments ($R^2 = 0.62$, $p < 0.001$). Suspended sediments with high organic matter contents have a high Pb content. Based on the 50 suspended sediment samples analysed for organic matter content, the mean organic matter content of suspended sediments is approximately 60% (Table 1).

Flow-weighted mean concentrations for sediment-associated Pb concentrations and SSC for each storm event are shown in Table 2 together with mean *Q* for each storm event. There is no seasonal or annual trend in sediment-associated Pb, SSC or *Q*. Histogram analysis revealed that the sediment-associated Pb concentrations for suspended sediment at Upper North Grain were normally distributed. Although there is variability in sediment-associated Pb concentrations, especially for the first six storm events (Fig. 3), the error for the mean Pb content of all suspended sediments is small (102 ± 5.42 mg kg^{-1} – Table 1). The mean Pb content of all suspended sediment samples is lower than the mean peak Pb concentration recorded for the peat soils of the catchment, but is much higher than the mean Pb content for sandstones, shales and periglacial head deposits within the catchment.

4.2.2. Overbank and channel bed sediments

Table 1 shows summary statistics for the Pb content and organic matter content of floodplain, streamside fan, trash-line and channel bed sediments. The mean Pb contents of these fluvial sediments are lower than the mean Pb content of suspended sediments. However, the maximum Pb content of one of the floodplain sediments is 341 mg kg^{-1} (Table 1). This value is comparable to the maximum Pb concentration recorded for one of the suspended sediments (Table 1).

Trash-line sediments and channel bed sediments collected from the gullies within the catchment are characterised by high organic matter contents. Floodplain, fan and channel bed sediments from the main stream channel are more minerogenic (Table 1). The relationship between the Pb content of floodplain, streamside fan, trash-line and channel bed sediments and the organic matter content of these sediments is shown in Fig. 5. For the floodplain and streamside fan sediments and the channel bed sediments from the main stream channel, there is a good positive relationship between the Pb content and organic matter content of these sediments (R^2 values are all approximately 0.60). High organic matter contents in these sediments are associated with high Pb contents. For trash-line sediments and channel bed sediments collected from the gullies within the catchment there is no statistically significant relationship between the Pb content of these sediments and the organic matter content (Fig. 5).

5. Discussion

The Pb profiles in the top 30 cm of the peat soils of Upper North Grain (Fig. 2) most likely reflect temporal variations in the atmospheric deposition of Pb to this upland site in the Peak District. The peak Pb concentration in the near-surface peat layer

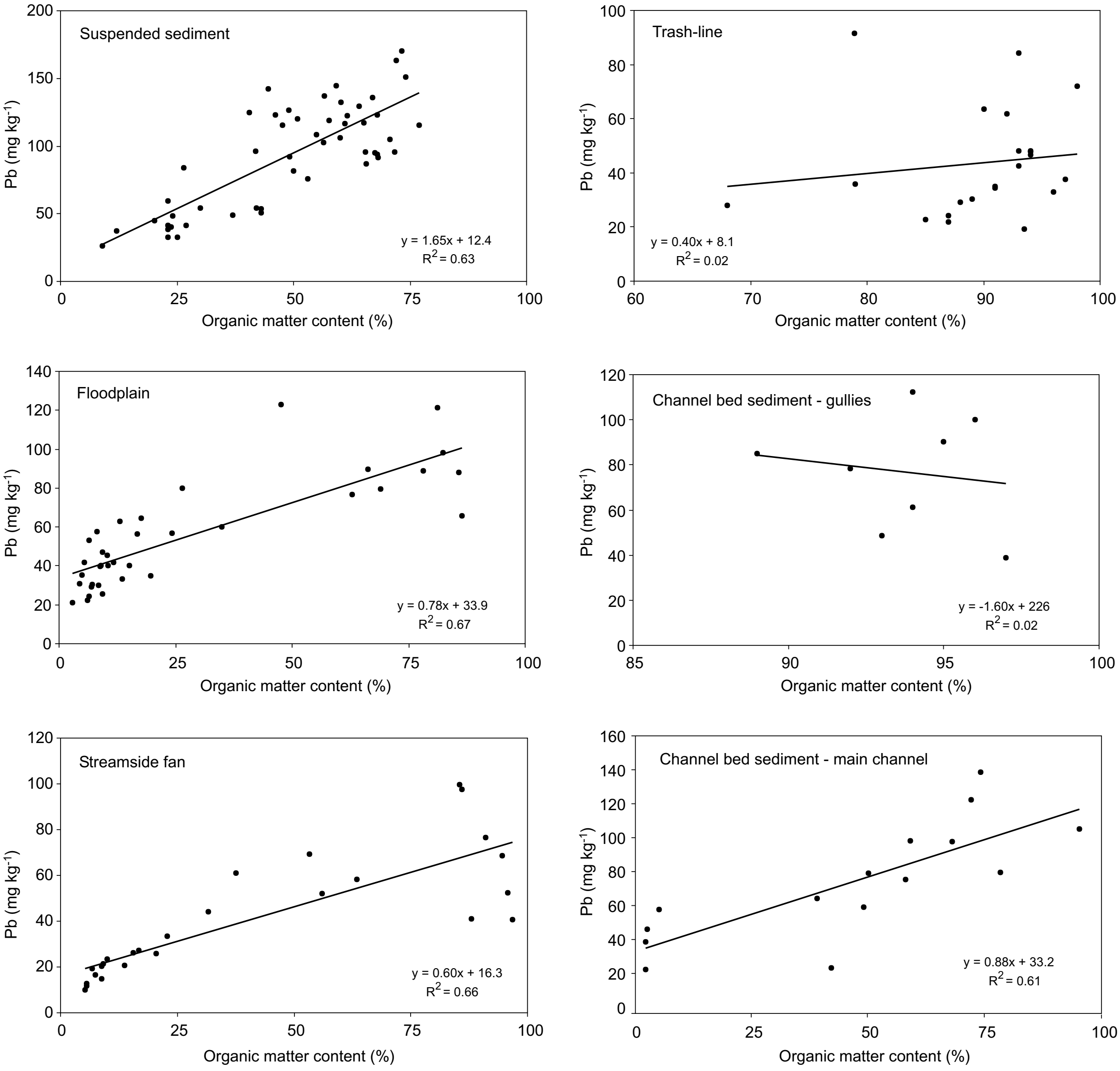

Fig. 5. The relationship between the Pb content of fluvial sediments at Upper North Grain and the organic matter content of these sediments. Note the different scales.

is likely to date to the early to mid 1800s when the English Industrial Revolution was at its peak and high levels of Pb were being emitted into the atmosphere during fossil fuel combustion and Pb smelting activities (Livett et al., 1979). The maximum Pb content of the near-surface peat is two orders-of-magnitude greater than that of the sandstones, shales and periglacial head deposits that underlay the peat soils of the catchment (Table 1). Therefore, the near-surface layer of the peat soils of Upper North Grain is contaminated with high concentrations of Pb. Maximum Pb concentrations recorded in the peat soils at Upper North Grain are comparable to those of other contaminated peatland sites around the world (cf. Mackay and Tallis, 1996; Zhulidov et al., 1997; Shotyk et al., 2000).

The results of this study show that fluvial sediments in the Upper North Grain catchment are also contaminated with Pb, although Pb concentrations in these sediments are not as high as the peak Pb values recorded for peat soils in the catchment (Table 1). This study demonstrates that there is variability in the Pb content of fluvial sediments in the catchment (Table 1). A number of physical and chemical characteristics influence the concentration of heavy metals in fluvial sediments (Horowitz,

Table 2
Mean sediment-associated Pb concentration, suspended sediment concentration (SSC) and discharge (*Q*) for suspended sediments for 12 storm events collected from Upper North Grain

Storm	Pb[a]	SSC[b]	*Q*[c]
08/06/02	64.5	741	0.16
14/06/02	120	310	0.18
09/09/02	80.7	1793	0.26
01/11/02	120	176	0.18
07/03/03	126	33.3	0.03
08/03/03	54.7	540	0.19
12/11/03	109	137	0.19
24/02/04	106	93.1	0.09
18/04/04	98.7	122	0.16
21/04/04	122	93.4	0.10
04/11/04	120	159	0.10
16/11/04	123	131	0.14

[a] Flow-weighted mean Pb concentration (mg kg^{-1}).

[b] Flow-weighted mean suspended sediment concentration (mg L^{-1}).

[c] Discharge (m^3 s^{-1}).

1991). The grain size characteristics and composition of fluvial sediments are important physical controls. In fluvial systems heavy metals are not evenly distributed over the various grain size fractions. Heavy metals are usually associated with the fine-grained sediment fractions, which generally consist of organic matter, clays and feldspars. Coarse-grained sediments usually consist of quartz and are therefore characterised by lower heavy metal concentrations (Horowitz, 1991; Salomons and Forstner, 1984; Walling et al., 2000). This is because quartz grains have a small specific surface area and a low cation exchange capacity (Horowitz, 1991). Suspended sediments at Upper North Grain are generally organic-rich, but there is variability in the organic matter content of the suspended sediment (Table 1, Fig. 5). Suspended sediment samples characterised by a high organic matter content are also characterised by a high Pb content (Fig. 5). Therefore, it is very likely that variation in the organic matter content of the suspended sediment explains the intra- and inter-storm variability in Pb content of suspended sediments at Upper North Grain. Numerous studies have demonstrated that as discharge increases there is a concomitant decrease in sediment-associated heavy metal concentrations (e.g. Bradley and Lewin, 1982; Dawson and Macklin, 1998). This is because as discharge increases, the percentage of sand-sized particles usually increases as coarse-grained particles are suspended at high flow (Horowitz, 1991). Although there is no significant relationship between the Pb content of suspended sediments and *Q* at Upper North Grain, and there is only a weak relationship between the Pb content of suspended sediments and SSC (Fig. 4), the three storm events with the lowest mean sediment-associated Pb concentration are associated with high *Q* and high SSC (Table 2). During these events it is possible that coarse quartz-rich sandstone grains, low in Pb content (Table 1), were entrained into the water column. These sandstone grains would physically dilute the Pb content of suspended sediments at the periods of high discharge. At Upper North Grain high SSC values occur during spring and summer months (Table 2). In southern Pennine blanket peat catchments organic sediment production on eroding peat gully walls is at a maximum during spring and summer months (Yang, 2005). High organic sediment production on peat gully walls at Upper North during spring and summer, coupled with convective thunderstorms may explain the higher SSC during storm events in spring and summer. Variability in the SSC concentrations between storm events is due to differences in the supply and transport of material to and within the stream channel. These are related to antecedent weather conditions and storm magnitude (Yang, 2005).

Although variability in the composition and grain size characteristics of suspended sediment appear to explain the differences in the Pb content of suspended sediment at Upper North, other physical controls may also explain some of the variability in the Pb content of suspended sediments. During the 1/11/02 storm event the sediment-associated Pb concentration reaches a maximum of 395 mg kg^{-1} (Fig. 3). This high sediment-associated Pb concentration is not seen in any other storm event sampled, even though the discharge characteristics of this storm event are fairly typical for the study site (Table 2). Although gully erosion is the dominant peat erosion mechanism in the catchment, some surface erosion on bare peat flats is evident at the head of some peat gullies. Erosion and mobilisation of peat from the near-surface peat into the fluvial system may explain the occurrence of the very high Pb content of a suspended sediment sample in the catchment. Therefore, differences in erosion processes operating in the catchment may also explain some of the variability in the Pb content of suspended sediments. The 1/11/02 storm event is discussed in more detail by Rothwell et al. (2005).

Streams draining organic-rich upland catchments are acidic due to the flushing of organic and industrially derived acid species from peat soils during rainfall events (Tipping et al., 2003b; Worrall et al., 2003). The pH of surface waters can strongly influence the partitioning of heavy metals between particulate and aqueous phases (Foster and Charlesworth, 1996). Rothwell et al. (2006) demonstrate through laboratory experiments that sediment-associated Pb in peatland streams can desorb from contaminated sediment into acidic stream water. Therefore, some of the variability in the Pb content of suspended sediment at Upper North Grain may be explained by differences in the desorption of Pb. However, the relative importance of this process in a field context needs further investigation.

Variability in the Pb content of floodplain sediments, streamside fan sediments and channel bed sediments from the main stream channel (Table 1) can also be explained by differences in organic matter content. The empirical data suggests that organic matter is the principle vector for Pb in these sediments (Fig. 5). Although the results of this study reveal that there is deposition of sediment-associated Pb in overbank sediments, this contaminated sediment is not removed from the fluvial system, since this contaminated sediment may be remobilised and re-introduced into the fluvial system by channel bank erosion and channel migration (Walling et al., 2003). At Upper North Grain the mean Pb concentration associated with suspended sediments is higher than equivalent values for the other fluvial sediments (Table 1). This is due to differences in the organic matter content of these sediment types (Table 1), but it may also be due to differences in the particle size composition of the different fluvial sediment types. Suspended sediment is finer than floodplain or channel bed sediment due to the effect of hydraulic sorting by grain size (Owens et al., 2001). Suspended sediments are therefore more likely to be characterised by higher heavy metal concentrations. This is reflected in the results of this study. The occurrence of the very high sediment-associated Pb concentration for one of the floodplain samples (Table 1) may also be due to the nature and grain size composition of this sample. It is likely that this sample was fine-grained and highly organic.

The mean sediment-associated Pb concentration for suspended sediments provides a realistic assessment of pollution of fluvial systems, because large deviations from this mean can be short-lived. This has clearly been demonstrated in the present study. The flow-weighted mean Pb concentration for stormflow suspended sediment for the entire Upper North Grain dataset is 96.8 mg kg^{-1}. Table 3 shows published data for the mean Pb concentration for suspended sediments in some river systems around the world, including some agricultural catchments. Although the catchment area of Upper North Grain is much smaller than those listed in Table 3, the mean Pb content of suspended sediments at Upper North Grain is higher than those characterised by agriculture and is comparable to the mean Pb content of suspended sediments in some fluvial systems draining urban areas.

Erosion of contaminated peatlands of the Peak District is releasing previously deposited Pb into the fluvial system. Even with continued reductions in atmospheric Pb emissions to the UK atmosphere

Table 3
Mean Pb content of suspended sediments for a selection of rivers

Location	Context	Mean Pb concentration[a]	Reference
Puyango River, southern Ecuador	Mining	2372	Tarras-Whalberg and Lane (2003)
Columbia River at Northport, USA	Urban	230	Horowitz et al. (2001)
Dordogne River, France	Agricultural/urban	142	Schafer and Blanc (2002)
River Rhine, Netherlands	Urban	109	Qu and Kelderman (2001)
Upper North Grain, Derbyshire, UK	Agricultural	96.8[b]	This study
Ala Wai Canal, Oahu, Hawaii	Urban	93	De Carlo et al. (2004)
Lower Po River, Italy	Agricultural/urban	75	Pettine et al. (1994)
Chesterville Branch, Chesapeake Bay, USA	Agricultural	39	Miller et al. (2003)
River Danube (Germany to Romania)	Agricultural/urban	34.6	Woitke et al. (2003)
Milwaukee River, Wisconsin, USA	Agricultural	21.5	Shafer et al. (1997)
Wolf River, Wisconsin, USA	Forested	16.3	Shafer et al. (1997)
Batsto River, New Jersey, USA	Agricultural	1.60	Sherrell and Ross (1999)

[a] mg kg^{-1}.

[b] Flow-weighted mean Pb concentration.

(Dore et al., 2003), the fluvial system of this upland area will continue to be affected by the erosion of contaminated peat. Peat erosion is not confined to the southern Pennines. Many upland areas that are characterised by peat soils exhibit some degree of erosion. If these peat soils are contaminated with previously deposited Pb, the physical process of peat erosion could be releasing Pb into other upland fluvial systems. This is an area of research requiring further assessment. Contaminated sediment in the fluvial system is known to have deleterious effects upon aquatic organisms, especially sediment dwelling species (e.g. Naimo, 1995). The ecological impact of heavy metal contaminated sediments in upland surface waters draining eroding and contaminated peat soils is also an area requiring further research.

6. Conclusions

This detailed investigation of Pb contamination of fluvial sediments in an eroding blanket peat catchment in the southern Pennines has shown that:

1. The near-surface layer of peat soils is severely contaminated with Pb.
2. Suspended, floodplain, streamside fan, trash-line and channel bed sediments are also contaminated with Pb, but Pb concentrations in these sediments are an order-of-magnitude less than peak Pb concentrations in the peat soils.
3. It is likely that variability in the Pb content of fluvial sediments is due to differences in the organic matter content of these sediments and differences in catchment erosion processes.
4. Organic matter is the main vector for Pb transport in the fluvial system.
5. Erosion of the contaminated near-surface layer of peat soils is releasing Pb into the fluvial system.
6. The Pb content of suspended sediments at Upper North Grain is high when compared to other rivers draining agricultural catchments, but is similar to catchments that drain urban areas.

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