

## SEDIMENT–WATER INTERACTIONS IN AN ERODED AND HEAVY METAL CONTAMINATED PEATLAND CATCHMENT, SOUTHERN PENNINES, UK

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**Abstract.** Atmospherically deposited lead in the upper layer of the heavily eroded peatlands of the Peak District, southern Pennines, UK, reaches concentrations in excess of  $1,000 \text{ mg kg}^{-1}$ . Erosion of the upper peat layer in this region is releasing lead, associated with eroded peat particles, into the fluvial system. Understanding the process mechanisms that control dissolved lead concentrations in contaminated peatland streams is vital for understanding lead cycling and transport in peatland streams. Many headwater streams of the southern Pennines recharge drinking water reservoirs. Measurements in the Upper North Grain (UNG) study catchment show that mean sediment-associated and dissolved lead concentrations are  $102 \pm 39.4 \text{ mg kg}^{-1}$  and  $5.73 \pm 2.16 \text{ } \mu\text{g l}^{-1}$ , respectively. Experimental evidence demonstrates that lead can desorb from suspended sediments, composed of contaminated peat, into stream waters. In-stream processing could therefore account for the elevated dissolved lead concentrations in the fluvial system of UNG.

**Keywords:** peat erosion, lead, acidic water, desorption, in-stream processing

### 1. Introduction

Ombrotrophic peat bogs receive all their inputs from the atmosphere (Clymo et al., 1990). The nature of ombrotrophic peat, and the ability of peat to effectively sorb heavy metals, makes such environments excellent archives of atmospheric lead deposition. There is great spatial variability in lead concentrations in peatland environments around the globe (Table I). Peatland environments located near urban centres or close to industrial sites can be highly contaminated with lead. The peatlands of the Peak District, southern Pennines, UK, are situated in the heartland of the nineteenth century English Industrial Revolution, between the cities of Sheffield and Manchester. Consequently, very high concentrations of lead are stored in the upper peat layer in this region (e.g., Jones & Hao, 1993; Livett, Lee, & Tallis, 1979; Rothwell, Robinson, Evans, Yang, & Allott, 2005).

The peatlands of the southern Pennines are also the most severely eroded in the UK (Tallis, 1997), with approximately three quarters of the peatlands eroded or subjected to degradation (Anderson & Tallis, 1981). Erosion of contaminated land and subsequent transport of contaminated sediment to fluvial systems is

TABLE I  
Maximum lead concentration in a selection of peatland environments

Location	Maximum Pb concentration (mg kg <sup>-1</sup> )	Reference
Gola di Lago, Switzerland	1,528	Shotyk (2002)
Upper North Grain, Derbyshire, UK	1,148	Rothwell et al. (2005)
Grassington Moor, North Yorkshire, UK	800	Livett et al. (1979)
Boží Dar, Czech Republic	479	Vile, Wieder, and Novak (2000)
Etang de la Gruère, Canton Jura, Switzerland	83	Shotyk (2002)

common in a variety of environmental contexts, and the role of suspended sediment as a vector for contaminants is widely recognised (e.g., Blake et al., 2003).

Pore water concentrations of heavy metals in peatlands are controlled by heavy metal loading, pH, the affinity of heavy metals for organic matter and dissolved organic carbon, and competition between heavy metals for binding sites (Lawlor & Tipping, 2003). Dissolved lead concentrations in upland peatland streams have been explained by leaching of dissolved heavy metals from catchments peats, as groundwater moves through contaminated layers of the peat into the fluvial system (e.g., Lawlor & Tipping, 2003; Vinogradoff et al., 2005). However, sediment-associated heavy metals in fluvial systems are subject to adsorption and desorption processes, where heavy metals can move between particulate and dissolved phases (Foster & Charlesworth, 1996). Chemical, physical, and biological conditions of stream waters control interactions of heavy metals between sediment and water (Kersten, 2002). Streams draining peatland catchments are often highly acidic, as organic acids and industrially-derived acid species are flushed out of the peats during stormflow (Evans, Jenkins, & Wright, 2000). Under such conditions, sediment-associated heavy metals in peatland streams may be desorbed from contaminated sediment into the water column.

The aims of this study are to assess the degree of lead contamination of the fluvial system at UNG, and to test empirically whether sediment-associated lead in streams draining contaminated peatlands is susceptible to desorption into the water column.

## 2. Materials and Methods

### 2.1. STUDY AREA

Upper North Grain (UNG) is a small headwater stream that drains a peat-covered catchment in the Peak District, southern Pennines, UK (Figure 1). UNG joins the

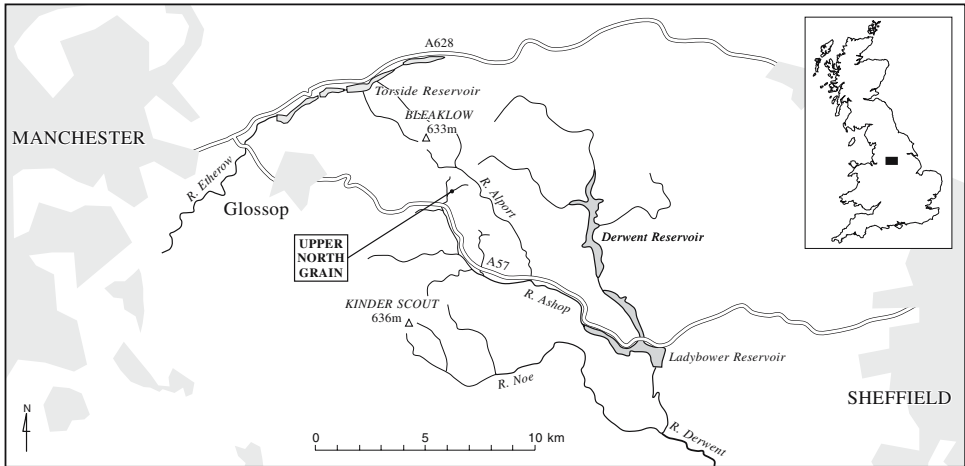


Figure 1. Location of study area.

River Ashop, which feeds Ladybower Reservoir in the Upper Derwent Valley. Ladybower Reservoir is one of ~200 drinking water supply reservoirs in the southern Pennines. The catchment has a drainage area of 0.38 km<sup>2</sup> and rises to an altitude of 520 m OD. The peats of the catchment are severely eroded.

## 2.2. CORING

During October 2002, eight peat cores were collected from intact peat areas within the UNG catchment. All cores were extracted with a 50 cm Russian corer, and subsequently wrapped in cling film. Seven of the peat cores were sliced at contiguous 1 cm intervals, disaggregated, dried at 105°C for 24 h, and then prepared for lead analysis as described below.

## 2.3. STORM WATER SAMPLES

Between June 2002 and November 2004, 205 stream samples were collected from UNG during 12 storm events. Stream water samples were taken at 15 min intervals from UNG by a Sigma 900 water sampler, triggered automatically by a rise in stage. 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<sub>3</sub> (Analar, BDH), and then rinsed with distilled water. All storm water samples were filtered through pre-weighed glass microfibre filter paper circles (Whatman GF/C), in order to retain the suspended sediment fraction. Filter papers were then oven-dried at 105°C for 24 h, and the dry weight recorded.

## 2.4. SOLID PHASE LEAD

Peat samples and suspended sediments (including filter papers) were digested on a hot-plate at  $\sim 100^{\circ}\text{C}$  for 4 h using 5 ml of 15.6 M  $\text{HNO}_3$  (Analar, BDH). After digestion, all samples were made up to 25 ml with distilled water, filtered through Whatman GF/C filter paper, and stored at  $\sim 4^{\circ}\text{C}$  in polythene tubes prior to lead analysis. Lead concentrations in peat and suspended sediment samples were determined using AAS (Thermo Unicam S11), wavelength 217 nm. Lead standard solutions (Spectrosol, BDH), ranging from 7.5 to 15  $\text{mg l}^{-1}$ , were used to calibrate the AAS. The sensitivity of the AAS was 0.1 ppm for lead. Certified Reference Material LGC6139 River Sediment (LGC Promochem) was digested and analysed along with the sediment samples, and a recovery of 105% was obtained for lead. A series of blank samples (digested, unused filter papers) were also analysed and were below the detection limit of the AAS.

## 2.5. DISSOLVED LEAD

Of the 12 storm events sampled, seven sets of storm water samples were filtered through 0.45  $\mu\text{m}$  cellulose nitrate membrane filters (Whatman), acidified with 2% (v/v)  $\text{HNO}_3$  (Ultrapur, BDH), and analysed for dissolved lead using ICP-MS (VG Elemental Plasmaquad 2 STE TM - Williamson Research Centre for Molecular Environmental Science, School of Earth, Atmospheric and Environmental Sciences, The University of Manchester). The ICP-MS is operated in a class 1,000 cleanroom. In sequential mode, the ICP-MS has a quantitation range of 1,000 ppb to 50 ppt. Duplicate measurements for all samples were undertaken, and analytical uncertainty was  $<2\%$ . Duplicate blanks and standards were used during analysis to ensure accuracy and precision.

## 2.6. MIXING EXPERIMENT

On 1 October 2003,  $\sim 2$  l of stream water was collected during a storm at UNG. The stream water was filtered through a 0.45  $\mu\text{m}$  cellulose nitrate membrane filter (Whatman), and measured for pH using a Jenway 3320 pH meter (pH 3.68). The top 10 cm of the un-sliced peat core was homogenised whilst still moist. A sub-sample was dried at  $105^{\circ}\text{C}$  and analysed for lead content ( $694 \text{ mg kg}^{-1}$ ). A sub-sample of the homogenised moist peat (equivalent to  $\sim 6$  g dry weight) was placed into a large polyethylene bottle with the filtered stream water. The approximate suspended sediment concentration (SSC) was  $3 \text{ g l}^{-1}$ , a SSC typical of large storm events at UNG (Rothwell et al., 2005). The bottle containing peat and water was mixed using a Stuart flask shaker for 20 min, 40 min, 1 h, 3 h, 6 h and 24 h. After each time period had elapsed, 10 ml of water was extracted, using a modified pipette. Five replicates were taken for each time interval, and all samples were

filtered through 0.45  $\mu\text{m}$  cellulose nitrate membrane filters, and analysed for lead using ICP-MS as described above.

### 3. Results and Discussion

The upper layer in the peat catchment of UNG is severely contaminated with lead. In a previous study at UNG by Rothwell et al. (2005), a maximum lead concentration of 1,148  $\text{mg kg}^{-1}$  was recorded in the near-surface peat. In this study, a maximum lead concentration of 1,614  $\text{mg kg}^{-1}$  was recorded in one of the peat cores analysed (Table II). The seven down-core lead profiles were similar to the downcore lead profile described by Rothwell et al., each with significant lead concentrations in the near-surface, with a lead peak at  $\sim 5$  cm. Compared to other blanket peats from around the globe, the peatland catchment of UNG in the Peak District, southern Pennines, is amongst the most severely contaminated in the world (Table I).

Suspended sediment concentrations (SSC) for peatland catchments characterised by severe erosion are usually high, especially when there is good slope–channel linkage (Evans & Warburton, 2005). High SSC during storm events at UNG (Table II) are consistent with the severe erosion seen in the catchment. There are no established guidelines for the quality of sediment in UK rivers. However, in Canada, there are Sediment Quality Guidelines (CSeQGs) for the protection of aquatic life in the fluvial environment (CCME, 2002). For sediment-associated lead, there is a ‘probable effect level’ (PEL) to aquatic life of 91.3  $\text{mg kg}^{-1}$  (CCME, 2002). The mean sediment-associated lead concentration of  $102 \pm 39.4$   $\text{mg kg}^{-1}$  at UNG exceeds this PEL.

Dissolved lead concentrations in streams draining upland peatland catchments can be spatio-temporally variable. In a study of surface waters in the English Lake District by Lawlor and Tipping (2003), mean lead concentrations in three

TABLE II  
Lead concentrations in system components at UNG

	Mean $\pm$ SD	Range
<sup>a</sup> , <sup>c</sup> Peat	1121 $\pm$ 312	713–1614
<sup>b</sup> , <sup>d</sup> SSC	163 $\pm$ 435	2.89–4620
<sup>c</sup> Sediment-associated Pb	102 $\pm$ 39.4	4.43–395
<sup>e</sup> Dissolved Pb	5.73 $\pm$ 2.16	2.26–11.3

<sup>a</sup>Maximum lead concentration recorded for each peat core

<sup>b</sup>Suspended sediment concentration

<sup>c</sup> $\text{mg kg}^{-1}$

<sup>d</sup> $\text{mg l}^{-1}$

<sup>e</sup> $\mu\text{g l}^{-1}$

tributaries of the River Duddon, were  $0.42$ ,  $0.23$  and  $0.70 \mu\text{g l}^{-1}$ . Vinogradoff et al. (2005) measured dissolved lead concentrations over a two-year period at an upland stream at Glensauigh, NE Scotland. Dissolved lead concentrations ranged from  $0.08$  to  $7.53 \mu\text{g l}^{-1}$ , with a mean of  $0.60 \pm 0.71 \mu\text{g l}^{-1}$ . At UNG the dissolved lead concentrations vary from  $2.26$  to  $11.3 \mu\text{g l}^{-1}$ , with a mean of  $5.73 \pm 2.16 \mu\text{g l}^{-1}$  (Table II). When compared to dissolved lead levels reported by Lawlor and Tipping and Vinogradoff et al., dissolved lead concentrations are higher at UNG.

Results of the mixing experiment reveal that under laboratory conditions, lead bound to suspended sediment, which is composed of contaminated peat, can desorb from the sediment into stream water (Figure 2). The dissolved lead concentration in the stream water at the start of the experiment, prior to any addition of contaminated peat, was  $5.63 \pm 0.14 \mu\text{g l}^{-1}$ . However, after only 20 min of mixing the dissolved lead concentration rose to  $8.67 \pm 0.20 \mu\text{g l}^{-1}$  and after 24 h the concentration was  $12.75 \pm 0.44 \mu\text{g l}^{-1}$ . Dissolved lead values from the mixing experiment are very similar to the range of values measured during storm events at UNG (Table II). Dissolved lead levels in upland peatland streams have often been explained by the leaching of lead from catchment peats (e.g., Lawlor & Tipping, 2003; Vinogradoff et al., 2005). Although the mixing experiment was conducted under a worst-case scenario basis, where a large sample of contaminated peat was mixed with acidic stream water, the study establishes empirically that in-stream processing may be important in controlling dissolved lead levels in peatland streams, and can potentially account for the elevated stream water lead concentrations in these systems. However, this would need to be validated in a field context. A thorough

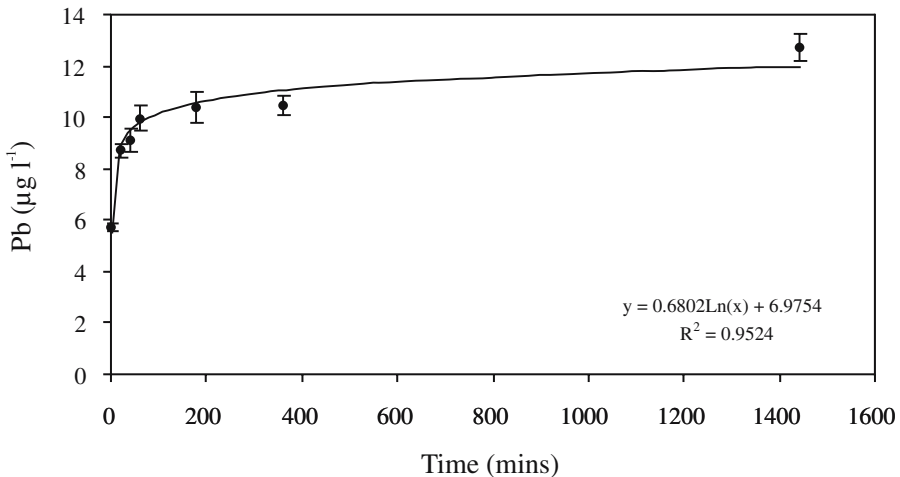


Figure 2. Dissolved lead as a function of time, measured in acidic stream water (pH 3.68) mixed with  $3 \text{ g l}^{-1}$  of peat contaminated with lead ( $694 \text{ mg kg}^{-1}$ ).

investigation of the relative importance of in-stream processing and leaching of lead from catchments peats in governing lead concentrations in peatland streams is therefore required.

#### 4. Conclusion

Erosion of the upper peat layer at UNG is releasing large quantities of sediment-associated lead into the fluvial system and dissolved lead concentrations in the stream at UNG are higher than those of other upland peatland environments in the UK. An experimental approach demonstrates that the interaction of contaminated sediment and acidic stream water in peatland streams potentially explains elevated dissolved lead levels in such fluvial environments, but validation of the relative importance of this process is required. Erosion of contaminated peatlands in the southern Pennines, and elsewhere, may not only influence particulate heavy metal levels in streams, but sediment-associated lead may interact in a deleterious way with the water column.

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