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Erosion and physical transport via overland flow of arsenic and lead bound to silt-sized particles

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Abstract

Understanding of the transport mechanisms of contaminated soils and sediment is essential for the sustainable management of contaminated lands. In New England and elsewhere, vast areas of agricultural lands are contaminated by the historical application of lead-arsenate pesticides. Left undisturbed the physical and chemical mobility of As and Pb in these soils is limited due to their strong affinity for adsorption onto solid phases. However, soil disturbance promotes erosion and overland flow during intense rainstorms. Here we investigate the event-scale transport of disturbed As and Pb contaminated soils through measurement of concentrations of As and Pb in suspended sediment and changes in Pb isotopic ratios in overland flow. Investigation of several rain events shows that where land disturbance has occurred, physical transport of silt-sized particles and aggregates is the primary transport vector of As and Pb derived from pesticide-contaminated soil. Although both As and Pb are associated with similarly-sized particles, we find that solid-phase As is more effectively mobilized and transported than Pb. Our results demonstrate that anthropogenic land disturbance of historical lands contaminated with lead-arsenate pesticides may redistribute, through physical transport, significant amounts of As, and lesser amounts of Pb, to riparian and stream sediments, where they are potentially more bioavailable.

Keywords

Overland flow; Erosion; Contaminant transport

1. Introduction

Arsenical pesticides were widely used in the United States during the first half of the 20th century until they were largely replaced by dichloro-diphenyl-trichloroethane (DDT)

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beginning in the late 1940s (Hood, 2006). It is well documented that arsenic (As) and lead (Pb) have limited chemical mobility in most surface soils due to their strong retention on soil particles, particularly amorphous oxides, under oxidizing and circumneutral pH conditions (Elfving et al., 1994; Morin et al., 1999; Cances et al., 2005; He et al., 2005). For example, As, which is slightly more mobile than Pb, particularly in the presence of phosphate (Peryea and Kammereck, 1997), is rarely found deeper than approximately 30 cm below the soil surface even decades after its application (Jones and Hatch, 1937; Peryea and Creger, 1994; Renshaw et al., 2006). Despite this limited chemical mobility, arsenical pesticide contamination is documented to extend well beyond historical orchard land boundaries. For example, in New England a correlation exists between areas with a high density of agriculture and elevated levels of As in streambed sediments (Robinson and Ayuso, 2004). In some cases the contamination of stream sediments is associated with disturbance of contaminated orchard lands (Renshaw et al., 2006). Given the strong chemical retention of As and Pb on soil particles, their mobilization due to land disturbance is likely mediated by physical erosion.

Erosion of soils with elevated concentrations of As and Pb in historic agricultural lands represents a potential health concern, particularly when contaminated farmland is developed into residential areas. In the United States, over 2500 km² of former agricultural lands have been developed during the first part of this decade alone (USDA, 2003). Increased human exposure to As and Pb has been directly linked to occupancy of residences built on lead-arsenate contaminated soil (Wolz et al., 2003). Furthermore, erosion of contaminated soils into adjacent riparian and wetland environments may extend their environmental impact (Hernández et al., 1999; Galicki et al., 2008). Knowledge concerning mechanisms controlling the fate and transport of these eroded contaminants is crucial for understanding potential trace metal exposure in and adjacent to former agricultural lands.

Solid phase transport of heavy metals adsorbed to colloids has been studied both in the vadose zone (Ranville et al., 2005) and in overland flow (Cooper and Gillespie, 2001; Wu et al., 2004; Ranville et al., 2005). However, little work has focused specifically on the mobilization of As and Pb contaminated particles via overland flow. This lack of previous work may partly reflect the relative rarity of overland flow in forested landscapes where former orchard lands are common (Wolman, 1967; Renshaw et al., 2003). However, localized land disturbance such as tilling or development can promote erosion and subsequent overland flow (Wolman and Schick, 1967; Kleinman and Sharpley, 2003), potentially resulting in the mobilization of As and Pb contaminated soil particles, as has been observed in tilled soil, contaminated with P (Daverede et al., 2003).

This study seeks to answer the following questions concerning the mobility of As and Pb derived from soils contaminated with lead-arsenate pesticides: 1) Is suspended sediment transport in overland flow a significant transport mechanism for As and Pb from contaminated soils? 2) If so, what size particles are the primary transport vectors of As and Pb in the solid phase? 3) Are As and Pb transported equally during overland flow events? We provide insights into each of these questions by measuring the As and Pb solid phase and dissolved concentrations, Pb isotopic compositions, and particle sizes of suspended sediment in overland flow collected from a site contaminated with lead-arsenate pesticides that was under development over the course of this study.

2. Site description

The site for this study, McQuade Brook watershed in Bedford, NH (Fig. 1), was selected from a subset of streams analyzed in a regional survey that contained streambed As concentrations exceeding the U.S. Environmental Protection Agency's probable effects

concentration (33 mg kg^{-1}) (Robinson and Ayuso, 2004). From this set of streams, McQuade Brook was chosen for further study based on the availability of well-documented evidence for historical orchard lands within this watershed and its recent and extensive residential development. Orchard lands, both current and historical, were identified by reviewing current and historical USGS topographic maps, USGS aerial photos, USDA soil survey aerial photographs, and New Hampshire White Pine Blister Rust Survey Maps (USGS, 1900–1960; New Hampshire Division of Archives and Record Management, 1930; USDA, 2001).

Records of application rates of lead-arsenate pesticides in Bedford, NH are not available due to the lack of state or federal regulations requiring pesticide application documentation (D'Angelo et al., 1996); however, in an orchard approximately 20 miles south in Hudson, NH an application rate of $0.4 \text{ g m}^{-2} \text{ yr}^{-1}$ was estimated based on local records of seven years of application (1965–1972) (Chorman, 1985). At a second nearby orchard established in the 1920s, Renshaw et al. (2003) measured total lead-arsenate masses of 120 g m^{-2} . Assuming lead-arsenate use was phased out in the 1950s and 1960s as the use of DDT became more prevalent, this gives an average application rate of $3\text{--}4 \text{ g m}^{-2} \text{ yr}^{-1}$. It is likely that the lead-arsenate application rate was similar at our site on the order of $1 \text{ g m}^{-2} \text{ yr}^{-1}$.

At the furthest downstream sampling site, McQuade Brook has a watershed area of ca. 10 km^2 . Within the study reach the stream has a typical gradient of 0.03 and the dominant surficial streambed sediment ranges in size from silt to large cobbles. Water is generally circumneutral (pH 6.8) and, typical of most New England streams, low in suspended sediment due to the granitic terrain and abundant young till (Rainwater, 1962).

This study primarily focuses on soils and sediment within and near the largest area of former orchard land adjacent to McQuade Brook. Soils within the historical orchard area (and its control site) are classified as Paxton fine sandy loam, a coarse-loamy, mixed, active, mesic Oxyaquic Dystrudepts (USDA, 2001) with a pH of 5.5. Most of this former orchard is now a housing development, but at the start of this study one portion of the orchard was undisturbed with several remaining orchard trees. This intact site was ultimately developed during this study.

3. Methods

3.1. Soils

Soil samples were collected from in and around historical orchard lands undergoing residential development (Fig. 1). Samples were collected from soil pits dug with a steel shovel down to approximately 60 cm. We dug orchard soil pits under the drip line of three remaining apple trees where the arsenical pesticide residue is likely to be the highest (Veneman et al., 1983; Renshaw et al., 2006). We dug three control soil pits approximately 500 m outside of the known orchard area. Soil was collected from the upper and lower half of each soil horizon with an acid clean plastic shovel. A total of 20 samples were collected from the contaminated area (eight within the O and A horizon) and from the uncontaminated area (12, five within the O and A horizon).

3.2. Stream sediment

Stream sediment was collected in riffles where sediment is generally neither eroding nor aggrading and thus best represents stream average sediment concentrations (Ladd et al., 1998). We collected streambed samples along a 1 km long reach immediately downstream of the junction with an ephemeral tributary (identified during a storm event) where runoff from the orchard drains into McQuade Brook (Fig. 1). Sediment samples were collected by placing half of a 55-gallon metal drum open on both ends in the middle of a riffle to slow the

flow of water and thereby minimize the loss of fine particles during sample collection. We removed the upper armor layer composed of cobbles greater than 7 cm diameter from inside the barrel and then sampled the top 5 cm of sediment with an acid-cleaned plastic shovel. An additional three sediment samples were collected using the same procedure approximately 3.4 km upstream of the orchard lands to provide information on background sediment As and Pb concentrations.

3.3. Suspended sediment

Suspended sediment and water samples were collected from five runoff events during intense ($>1 \text{ cm hr}^{-1}$) rain events on June 16, June 22, July 20, July 24 and November 25, 2008. We collected a complete set of suspended sediment samples along the overland flow path on July 24, 2008 during an intense summer rainstorm (1.1 cm hr^{-1} for 20 min at the peak of the storm). Samples were collected with an acid clean bucket, funnel, and 5-gallon carboys.

3.4. Analytical methods

Soil and sediment samples were oven dried at 80°C , sieved to $<2 \text{ mm}$, and then leached with trace metal grade aqua regia; aqua regia leaches were conducted similarly to those used by Papacostas et al. (2008). Subsequent measurements show for a series of six reference materials the recovery of As and Pb was 95–100% for five and 85% for the sixth. A matrix-matched analytical standard using high-purity salts was analyzed between every 10 samples to control for detector drift. Aliquots of the water and overland flow samples were filtered through a $0.2 \text{ }\mu\text{m}$ filter; the remainder of each suspended sediment sample was then oven dried at 80°C prior to leaching with trace metal grade aqua regia as described above. All samples were analyzed for As and Pb on a Thermo Iris Intrepid II (radial view) inductively coupled plasma–optical emissions spectrometer (ICP–OES). Final concentrations reflect subtraction of acid-extraction blanks. This method provided detection limits of 0.2 and 0.35 mg kg^{-1} for As and Pb, with typical analytical uncertainties of 3–4%. Lead isotopes were analyzed on a Thermo Scientific Element 2 high-resolution inductively coupled plasma–mass spectrometer (ICP–MS) with analytical precision of 0.35–1.2% (relative standard deviation). An LS230 Coulter counter was used to determine the particle size distribution, and still-water settling columns were used to size-fractionate suspended sediment samples into fractions between 0.2 and $250 \text{ }\mu\text{m}$; methods are similar to those of Lovell and Rose (1988).

An FEI Company, XL-30 environmental scanning electron microscope (ESEM) equipped with a field emission gun was used to image suspended sediment grains. Particles bearing Pb were indicated by back-scattered electron images (BSE). Potential composition of Pb bearing grains determined by energy dispersive spectroscopy (EDS) with a Si(Li) detector. The EDS spectra of each lead location was compared to a sample of pyromorphite to indicate its potential presence (Cotter-Howells, 1996; Cao et al., 2003).

4. Results and discussion

4.1. Site characterization

Lead-arsenate pesticide has not been applied to the sampled orchard lands for approximately 50 years, but the soil still contains levels of As ($81 \pm 16 \text{ mg kg}^{-1}$; mean $\pm$ standard error (SE), $n = 6$), and Pb ($431 \pm 70 \text{ mg kg}^{-1}$, $n = 6$) in the O and A horizons which are elevated well above average background levels of As ($4 \pm 1 \text{ mg kg}^{-1}$, $n = 6$) and Pb ($20 \pm 2 \text{ mg kg}^{-1}$, $n = 6$) found in these same horizons of soils not associated with orchard use (Fig. 2). The elevated concentrations and the maximum depth of contamination (ca. 30 cm) in the pesticide-contaminated soils are similar to those observed in other soils where lead-arsenate

was applied (Peryea and Creger, 1994; Renshaw et al., 2006). The limited depth of highly elevated concentrations is consistent with the mixing depth of tilling, and indicates that neither As nor Pb are significantly redistributed by downward solute or colloid transport. These coarse, cobbled soils are slightly acidic ($\text{pH} = 5.5$), moderately sloped (12%), and stay oxidized (+480 mV) even during major storm events. Under circumneutral to slightly acidic pH and oxidized conditions, As and Pb are expected to be strongly bound to mineral phases in the soil (Cances et al., 2005; He et al., 2005) with little potential for solute transport. The measured low dissolved concentrations of As and Pb in overland flow ($<1 \mu\text{g L}^{-1}$), even during rain events, are consistent with its strong retention to soil minerals. The limited vertical redistribution of the As and Pb and their retention in the solid phase on soil particles implies that physical erosion leading to overland flow may be a primary transport vector for these contaminants (Renshaw et al., 2006).

4.2. Transport of solid phase As and Pb via erosion and overland flow

Overland flow was observed along an ephemeral tributary (Figs. 1 and 3A) on several occasions and was studied in detail on July 24th, 2008. Overland flow is typically rare in the forested landscapes of New England due to high infiltration rates and, at this site, moderate slopes (Wolman, 1967; Renshaw et al., 2003). However, we observed that rainstorms with intensities $>1 \text{ cm hr}^{-1}$ were adequate to exceed the infiltration capacity of these soils (possibly due to recent land development) and produce overland flow along the ephemeral tributary. Measured suspended sediment concentrations along overland flow paths on July 24, 2008 (Fig. 3B) were 1–4 orders of magnitude larger than the suspended sediment concentration of McQuade Brook on the same date (0.9 mg L^{-1}), and the regional average of $16 \pm 70 \text{ mg L}^{-1}$ (mean $\pm \sigma$) for eight small rivers in New England with average annual discharges $<20 \text{ m}^3 \text{ s}^{-1}$ (USGS, 2009).

The sediment flux into McQuade Brook from overland flow carries significant amounts of adsorbed As and Pb (Fig. 3C); suspended sediments entering McQuade Brook on July 24th, 2008 contained $53 \pm 2 \text{ mg kg}^{-1}$ As and $52 \pm 9 \text{ mg kg}^{-1}$ Pb ($n = 4$). Although soil concentrations of Pb are much higher than As in contaminated soils, the concentrations of Pb and As in overland flow reaching the stream are nearly equal. Similar solid phase concentrations of As and Pb in overland flow were observed during all studied storm events in which the rainfall rate exceeded 1 cm hr^{-1} . At the same time, dissolved concentration of As and Pb in overland flow and stream water at multiple locations along the overland flow path and in McQuade Brook were consistently $<1 \mu\text{g L}^{-1}$, confirming that As and Pb are transported primarily in the solid phase. The measured pH of the overland flow samples is slightly acidic (5.1 ± 0.2), which is also consistent with the As and Pb remaining predominantly bound to the solid phase (Cances et al., 2005; He et al., 2005).

Lead isotopic ratios further elucidate that the source of lead transported in overland flow is derived from lead-arsenate pesticides. Three statistically distinct end member Pb isotopic ratios of $^{207}\text{Pb}/^{206}\text{Pb}$ are observed in the study site (Fig. 3D): the highest ratios (0.865 ± 0.0011 (mean $\pm \text{SE}$), $n = 7$) are observed in highly-contaminated O and A horizons of lead-arsenate contaminated soils and primarily represent the isotopic signature of lead-arsenate pesticide (Ayuso et al., 2004); the intermediate ratios observed in the O horizons of soils uncontaminated with lead-arsenate pesticides (0.823 ± 0.0025 , $n = 3$) are similar to those attributed to low-level contamination from atmospheric fallout associated with the use of leaded gasoline (Kaste et al., 2006); the lowest ratios are consistently observed in stream sediment at the headwaters (0.810 ± 0.006 , $n = 4$) and the lowest horizons of the soil profile (0.807 ± 0.0019 , $n = 22$) which both contain low (background) Pb concentrations. These low isotopic ratios presumably represent the geogenic isotopic signature of local bedrock sources. Similar to the Pb concentrations, along the overland flow path, the $^{207}\text{Pb}/^{206}\text{Pb}$ isotopic ratios monotonically decrease from the high ratios of the pesticide contaminated O

and A horizons to the low ratios of the stream sediment, although even at the end of the overland flow path almost half of the Pb is pesticide-derived. If the decrease in isotopic ratio were due to dilution with leaded gasoline-contaminated soil horizons, or soils with geogenic Pb, then the metal concentrations in the overland flow should all plot near the mixing region defined by these three end members (Fig. 4). Instead, the concentration of Pb in suspended sediment is depleted relative to what would be expected by linear mixing of the pesticide contaminated soil and the geogenic soil and sediment. Further, field observations do not support dilution due to sediment from other sources as the only location along the overland flow path visibly eroding was the small area of residential construction at the headwaters of the overland flow path (Fig. 1). Instead, the coincident decreases in isotopic ratio and concentration along the overland flow path indicate the preferential depletion of pesticide-derived Pb (i.e., high $^{207}\text{Pb}/^{206}\text{Pb}$) during transport.

The lines of evidence, discussed in detail above, indicate that arsenical pesticides are the source of the high concentration of As and Pb in the overland flow suspended sediment. These lines of evidence are summarized as: 1) the direct observation of erosion of pesticide-contaminated soils during intense rain events, 2) the monotonically decreasing metal concentrations in overland flow downstream of the contaminated soils (Fig. 3C), and 3) measured Pb isotopic ratios.

What causes the more rapid depletion of pesticide-derived Pb relative to As? Much of the depletion in both Pb and As occurs within the first 100 m of transport (Fig. 3); however, the corresponding losses in As and total suspended sediment concentration within this region are more modest, indicating that the mechanism of loss is selective to Pb. Further, as noted above, the significant decrease in the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio in the suspended sediment indicates the selective loss of pesticide-derived Pb.

One possibility is that particle-bound Pb is more exchangeable than As. As a result, Pb preferentially desorbs from suspended particles and becomes bound to immobile soil ligands. Such a release could be facilitated by a decrease in pH caused by acidic precipitation; lower pH tends to drive Pb desorption and As retention while higher pH tends to favor As desorption (Smedley and Kinniburgh, 2002) and Pb retention (Basta and Tabatabai, 1992; Strawn et al., 1998; Sukreeyapongse et al., 2002). However, the measured pH of overland flow (5.1 ± 0.2) is only slightly more acidic than the measured soil pH (5.5) while pH values lower than ca. 4 appear to be needed for significant desorption of Pb from sediments with iron and manganese oxides (Sharma et al., 2009); desorption kinetics of Pb from iron oxides are much slower than for adsorption (Glover et al., 2002; Garman et al., 2007) and may not be sufficiently fast for significant desorption during the less than ca. 5 minutes required for the suspended sediment to travel the first 100 m of the overland flow pathway. Finally, we note that dissolved concentrations of Pb in overland flow remain very low ($<1 \mu\text{g L}^{-1}$), consistent with the strong retention of Pb in the sorbed phase. Therefore, within the geochemical conditions measured during these rain events As and Pb likely remain in the solid phase.

As an alternative to chemical exchange, we suggest that the observed rapid loss in As and Pb concentrations is due to the settling of As and Pb-bearing particles in overland flow. Moreover, the preferential decrease in pesticide-derived Pb along the overland flow path might be due to Pb-bearing particles preferentially settling out of the overland flow. The rate of particles settling from overland flow is a function of particle size, density, fluid viscosity, and fluid density. Thus knowing particle size and density is crucial for predicting transport distances and may provide insight into the mechanisms of transport.

4.3. Particle size distribution of As and Pb bearing particles

Results from the particle size analyses show that both Pb and As are primarily associated with the finer fractions of the soil and suspended sediment; the largest fraction of suspended sediment in the overland flow and in the O soil horizon is within the 20–30 μm diameter range (solid lines, Fig. 5), while the largest mass fractions of As and Pb transported in overland flow are associated with particles with diameters in the 1–5 μm (points, Fig. 5). Very little Pb or As is transported with particles $<1 \mu\text{m}$. The median and geometric mean diameters of particles bearing As (22 and 24 μm respectively) and Pb (29 and 30 μm) are larger than their respective modes, but indicate that silt size particles are the primary transport vector of As and Pb in this disturbed environment. Given the relatively large (i.e., non-colloidal) size of As- and Pb-bearing particles, As and Pb are likely associated with the surface of these particles. Indeed, the correlation of the suspended sediment surface area (estimated assuming spherical particle geometries; dashed line, Fig. 5) with As and Pb concentrations supports the idea that As and Pb are primarily associated with particle surfaces.

4.4. Differential Transport of As and Pb bearing particles

Given the similar size distribution of particles transporting As and Pb (Fig. 5) it is noteworthy that fully 65% of the initial concentration of As is transported into the stream compared to only 12% of the initial Pb concentration (Fig. 3). Furthermore, in the streambed sediment As concentrations are elevated above background levels at least 600 m downstream of the confluence of the overland flow and McQuade Brook whereas Pb concentrations stay elevated only 200 m downstream (Fig. 6). Both of these observations suggest that solid-phase As is more mobile than Pb. Given similar sizes of As and Pb bearing particles, if the different transport properties of As or Pb are due to preferential settling, then As and Pb would need to be associated with particles of different densities. This density contrast could result from their association with different mineral phases; Pb may be less mobile due to the formation of dense mineral phases like pyromorphite $\text{Pb}_5(\text{PO}_4)_3(\text{Cl},\text{OH})$ (density = 7.04 g cm^{-3}), which form in other Pb contaminated soils (Cotter-Howells et al., 1994; Cotter-Howells, 1996; Cao et al., 2003).

In a suspended sediment sample collected during the July 24, 2008 rain-storm a ca. 4 μm diameter grain of pyromorphite was identified through an SEM-BSE image coupled with an EDS spectrum. The normalized peak intensities of the EDS spectrum of the grain with a high Pb content are comparable to the Pb and P peaks of a pyromorphite sample (Fig. 7). Furthermore, the ratio of the Pb and P peaks are similar between the pyromorphite standard and the Pb bearing grain. Bulk mineralogy studies remain to be completed on these samples in order to determine the fraction of pyromorphite in these sediments and thus their relative importance in impeding the transport distance of Pb.

5. Conclusions

Streams and rivers in New England have some of the lowest average suspended sediment concentrations in the U.S. (Rainwater, 1962; Dunne and Leopold, 1978). The mobilization of fine sediment via erosion and overland flow, particularly in regions of land disturbance, represents one of the primary vectors of sediment transport to streams in this region. Increased erosion due to land disturbance is of particular concern when contaminants are adsorbed to the eroded sediments. The transport of heavy metals adsorbed to colloids has been widely observed in many systems (Ranville et al., 2005; Slowey et al., 2007). However, in the transient overland flow events facilitated by land disturbance that we observed, it is the larger clay to silt-sized particles that appear to transport significant amounts of trace metals from soils where lead-arsenate pesticides were applied, consistent

with studies of P mobilization (Heathwaite, 1997). These large particles settle rapidly, limiting their mobility via physical erosion. Further, the apparent preferential settling of slightly larger and potentially denser particles associated with Pb further limits the mobility of Pb relative to As.

Understanding the differential redistribution of As and Pb via overland flow from the soil to the riparian environment is important to long-term environmental management as As and Pb are potentially more chemically mobile in riparian environments due to the potential for the reductive dissolution of the minerals to which the As and Pb are often adsorbed (Galicki et al., 2008). Thus, physical erosion of disturbed larger clay to silt-sized soil particles during transient overland flow events is the primary transport vector that redistributes heavy metals from soil into adjacent streams as opposed to colloidal or solute transport. Therefore erosion and overland flow spread these soil contaminants to a larger area and to the ecologically more sensitive riparian and fluvial environments where they may be more bioavailable and toxic.

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Fig. 1. Map of the study site and sample locations within the McQuade Brook watershed in Bedford, NH, USA. Roman numerals indicate the locations of the collected overland flow samples. Location of Bedford in the state of NH is shown in the lower right.

Fig. 2. Mean As and Pb concentrations in three soil pits dug under the drip line of the three remaining apple trees located on our study site. Error bars represent the standard error between the three soil pits.

Fig. 3. Topographic profile, suspended sediment concentration, As and Pb solid phase concentration, and Pb isotope composition along the overland flow path during an intense summer rain storm on July 24, 2008. Standard error bars of four replicate measurements of total As and Pb concentration are smaller than the data points. Square symbols represent soil samples, circles represent overland flow suspended sediment, and diamonds represent streambed sediment. Roman numerals indicate locations of samples as indicated in Fig. 1.

Fig. 4. Concentrations of As and Pb in suspended sediment, pesticide contaminated soil horizons, and uncontaminated soils and sediment.

Fig. 5. The particle size distribution of soil and the suspended sediment eroding from the soil (solid lines) compared to the particle sizes associated with As and Pb (circles). Dashed line indicates surface area distribution of suspended sediment, assuming spherical particles.

Fig. 6. Arsenic and Pb concentrations in streambed sediment as a function of the distance from the mouth of the ephemeral tributary carrying suspended sediment from the study site.

Fig. 7. SEM image and EDS spectrum of a ca. 4 µm in diameter particle of pyromorphite within the suspended sediment eroding from the McQuade Brook orchard on July 24, 2008 compared to the EDS spectrum of a pyromorphite standard.