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Transport of lead and diesel fuel through a peat soil near Juneau, AK: a pilot study

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Abstract

A set of peat column experiments was used to determine the transport potential of lead (Pb) and diesel range organics (DRO) in palustrine slope wetlands near Juneau, AK. This project is important to southeast Alaskan communities because limited land resources are forcing development of regional wetlands. This study was instigated by concerns that proposed modifications to a nearby rifle range using DRO-contaminated soil posed a potential risk to an anadromous fish-bearing stream 250 m from the site. Three pairs of peat columns were extracted from the rifle range for analysis, one pair along and two pairs across the natural bedding planes of the soil. One column in each pair was spiked with Pb and DRO and the other was used as a control. Approximately 1-year worth of water (171 cm) was passed through each column and leachate was collected at regular intervals. The results showed that substantial DRO transport only occurred along the bedding planes. Leads was surprisingly mobile, both along and across the bedding planes with estimated soil–water partition coefficients several orders of magnitude lower than commonly published values, probably because the peat was heavily Pb-loaded by lead from bullets and because the peat's acidic, organic-rich environment enhanced Pb mobility. The chemical outflow behavior agreed with a simple macropore transport model. These results underscore the need for caution when developing regional wetlands. © 2004 Elsevier B.V. All rights reserved.

Keywords: Peat; Contaminant transport; Lead (Pb); Diesel range organic (DRO); Macropore; Rifle range; Wetland

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1. Introduction

Although, research on the physical properties of peat soils with respect to structure and hydrological character spans several decades (e.g., Lauren and Mannerkoski, 2001; Nordén et al., 1992; Levesque and Dinel, 1982; Boelter, 1964, 1965, 1969, 1974), predicting how chemicals will move through peat systems remains difficult (e.g., Ours et al., 1997). In southeast Alaska, abundant rainfall, steep hillslopes, and slowly permeable substrates in the heavily glaciated region have combined to develop a mosaic of well-drained soils. The rainfall and slow decomposition rates result in the formation of mineral soils (Spodosols) and deep, saturated organic soils (Histosols) (Alexander and Ford, 1990). These organic soils form part of the wetlands that comprise 29% of the land area and can be found at high elevations as well as in the valleys. These organic soils are poorly drained and can be quite deep depending upon age. The degree of decomposition and physical make-up of the peat in the organic soils varies with depth, age, and plant community (Swanson and Grigal, 1989; Schoephroster and Furbush, 1974). The transport of contaminants through these and similar peat system is complicated and remains poorly understood, especially with respect to metals (e.g., Dumontet et al., 1990) and organic pollutants (e.g., Zynter et al., 1989). Some research shows how peat structure (e.g., Hoag and Price, 1997) and adsorption potential (e.g., Viraraghavan and Ayyaswami, 1989) work to retard contaminant movement while other studies show the potential for very rapid transport through peat (e.g., Jordan et al., 1997; Ours et al., 1997). Despite regional ubiquity, there is relatively little research with regard to the peat environments in and around Juneau and the rest of southeast Alaska, especially with respect their potential for chemical transport. To date, most of the soil hydrological research has concentrated on steep, sloping terrain related to landslides (Swanston, 1967; Sidle, 1984) or roads (Kahklen, 1999; McGee, 2000). The main regional peatland/wetland studies are limited to a preliminary a recharge–discharge and geochemical investigation in the Juneau area (Siegel, 1988a,b). Therefore, additional information on the physical and hydrological characteristics of peatland systems is critical in evaluating the use and management of these systems adjacent to urbanized areas in southeast Alaska.

The objective of this study was to test lead (Pb) and diesel range organic (DRO) transport potential through peat soil near Juneau, AK. This study was prompted by U.S. Army Corps of Engineer Section 404 permit application to use diesel-contaminated soil for modifications to a local rifle range that sits on a wetland near an anadromonous salmonid-bearing stream, Montana Creek. Lead transport was included in the investigation because of concerns that the large quantity of bullets in the rifle range might be a source of lead contamination in the creek. Both Pb and DRO are potentially lethal to aquatic ecosystem and local planners and environmental agencies are uncertain about how the rifle range may impact Montana Creek, an important local stream for sport fishing containing *Oncorhynchus kisutch* (Coho salmon), *Oncorhynchus mykiss* (Steelhead) and *Oncorhynchus clarki* (Cutthroat trout). The rifle range is approximately 250 meters north of main Montana Creek channel and was developed on a peat wetland that is bordered and transected by several small tributaries (Fig. 1). Initial on-site tracer studies to look at potential contaminant movement through the peat were inconclusive because the dyes used as tracers were highly absorbed to the peat. In an attempt at more controlled experiments, this study extracted
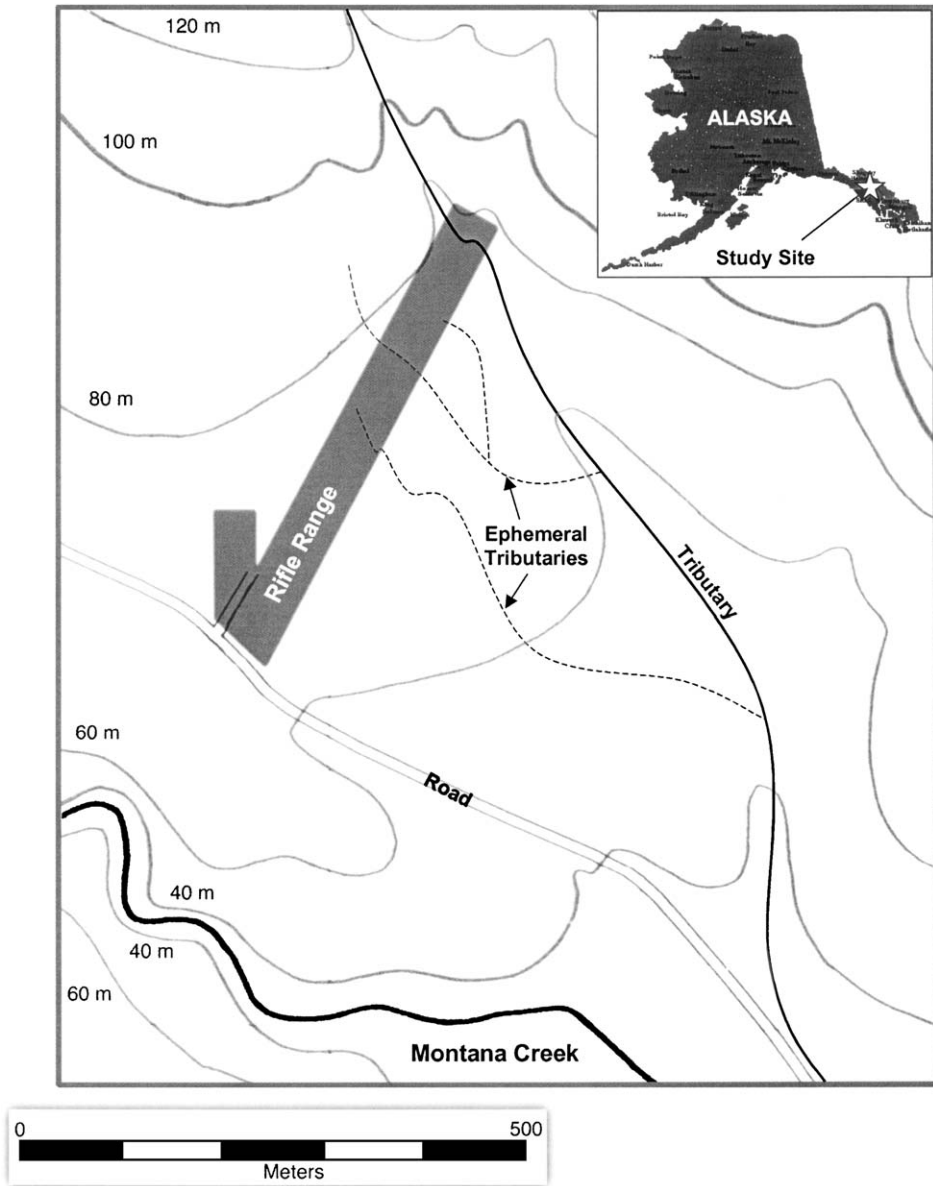
Fig. 1. Topographic map showing the location of the rifle range and Montana Creek; insert shows location of study site relative to Alaska.

several undisturbed peat columns from the rifle range and experiments were run using controlled water flow and known contaminant additions. We anticipated that this simple exploratory study will help the Southeast Alaska Research Team identify future research question with regards to transport mechanisms and relevant hydrological processes.

With respect to toxicity to animals, lead is often grouped with such lethal elements as mercury and cadmium (McBride, 1994). Decades of research from agricultural systems has resulted in the commonly held dogma that metals, especially lead and copper, are essentially immobile in the environment (e.g., McBride, 1994). In fact, lead is considered so immobile that it is often used as a depositional tracer over thousands of years, especially in areas dominated by highly organic soils like peat (e.g., Shotyk et al., 1998; Vile et al., 1999). New research challenges the ''immobile metal'' dogma particularly where lead and other metals have been applied in high concentrations (e.g., Richards et al., 2000; McBride et al., 1999; Camobreco et al., 1996) and suggests that the behavior of metals in the environment is more complicated than previously thought, even potentially linked to biological activity (Qureshi et al., 2003). Recent research has shown that shooting ranges can contribute a substantial quantity of lead into the soil (Cao et al., 2003a,b; Chen et al., 2002; Astrup et al., 1999; Murray et al., 1997); none of these studies looked at shooting ranges on peatlands.

Diesel fuel is similarly dangerous to aquatic organisms, specifically the poly-aromatic hydrocarbon (PAH) fraction (Barron et al., 1999). Copious research has shown that hydrophobic organic compounds (HOC) in general are sorbed to carbonaceous material (e.g., Petruzzeli et al., 2002; Karapanagioti et al., 2000; Rügner et al., 1999; Kleineidam et al., 1999) and that sorbtion kinetics can be complicated and depend on specific properties of the carbonaceous material (e.g., Allen-King et al., 2002). Interestingly, much of this work has focused on organic matter in aquifer matrices, aquitards, and sediments (e.g., Karapanagioti et al., 2000; Xia and Ball, 1999; Allen-King et al., 1997), although sorbtion to organic matter is identified as the primary inhibitor of HOCs movement in soils as well (e.g., Pignatello, 1998; Grathwohl, 1990). Although little, if any, research has been done on HOC transport in peat soils, by extrapolation of the previous work, we expect DRO to be highly sorbed to our peat soil.

2. Methods

Three sets of paired column experiments were run to compare transport differences due to bedding direction and pre-saturation. The peat used in this study was from the Hank–Harmon rifle range located near Juneau, AK (Fig. 1). The bedding structure of the peat was horizontal and the matrix density and homogeneity increased with depth. Root density and pores sizes decrease with depth. Throughout the length of the horizontal columns, the soil layers were of uniform composition and there was an abundance of roots ranging in size from root hairs to ~ 3 mm diameter.

The study site is a peatland that can be most accurately characterized as a sloping bog. All of the samples taken for this study came from surface soils (0–30 cm) that are very acidic with pH of 3.0–4.0 and an ombrotrophic, shrub–scrub vegetation community (NWI mapping). Although no detailed hydrologic studies have been completed on this part of the peatland, observations of several flowpaths that cross the peatland indicate that water flows laterally across the surface giving the peatland fen characteristics. However, this water flow is limited and the dominant water source for the peat is rainfall. The soils have a slightly decomposed (fibric) surface horizon (0–15 cm) that

changes to a more moderately decomposed (hemic) subsurface horizon (15–30 cm). The soil is classified as a Dysic typic cryohemist (Soil Survey Staff, 1999) closely associated with the Kina soil series (USDA-NRCS, 2003). This site has been used as a rifle range for the past three decades. The saturated hydraulic conductivity (K_s) of the peat is highly variable and generally decreases with depth; average K_s in the top 15 cm is 0.03 cm s^{-1} (S.D. = 0.04 cm s^{-1}) and over the top 30 cm K_s = 0.0003 cm s^{-1} (S.D. = 0.0003 cm s^{-1}). Bulk density (ρ_b) of the top 15 cm was 0.12 cm^{-3} (S.D. = 0.017 cm^{-3}) and for 15–30 cm depth (ρ_b = 0.20 g cm^{-3} (S.D. = 0.082 g cm^{-3}). These values are similar to published bulk densities (D'Amore and Lynn, 2002). Assuming the density of organic peat "particles" is ρ_p = 1.0 g cm^{-3} (e.g., Boelter and Blake, 1964 Boelter, 1969), the average porosities, $n = 1 - \rho_b/\rho_p$, for the horizontal and vertical columns were 80% and 88%, respectively.

Four columns were extracted vertically, i.e., across the bedding layers, and two were extracted horizontally, i.e., along the bedding (Fig. 2). Each column pair was extracted within a few centimeters of each other to minimize heterogeneity in peat structure within an experimental set of paired columns. All the columns were extracted from the same general area, within a few meters of each other. One column in each column pair was spiked with contaminants and the other was a blank control column. Table 1 summarizes the column experiments. Columns were constructed of 25 cm long, 10.2 cm I.D. copper pipe. These copper columns were used to extract the peat in the field by simultaneously
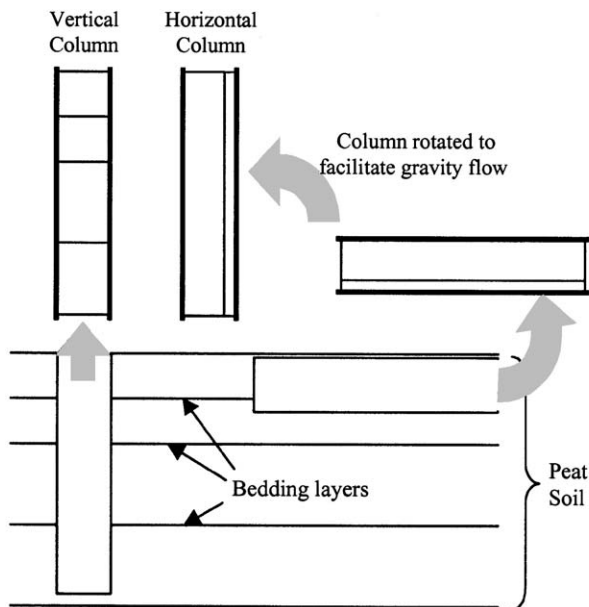

Fig. 2. Schematic diagram illustrating how the soil columns were extracted. The terms "vertical" and "horizontal" refer to bedding orientation and both columns were oriented upright during the leaching part of the experiments. Note that the columns were open at both ends.

Table 1
Summary of the experimental design for the column experimental sets

Column ID	Set 1		Set 2		Set 3	
	1S[a]	1C[b]	2S[a]	2C[b]	3S[a]	3C[b]
Bedding direction	Vertical	Vertical	Vertical	Vertical	Horizontal	Horizontal
Initial moisture condition	Pre-saturated	Pre-saturated	Field condition	Field condition	Pre-saturated	Pre-saturated
Contaminant addition	Yes	No	Yes	No	Yes	No

[a] "S" indicates the column was "spiked" with contaminant, i.e., DRO and Pb.
[b] "C" indicates the column was a control.

inserting into the ground and cutting the peat to ensure a tight fit while minimizing compaction. All columns were oriented in an upright position in the laboratory and each column top was capped. The caps contained a port where the contaminant spikes and water were introduced. The column bottoms were secured with copper screen to ensure the soil would not slide out during the experiments (Fig. 3a). Although the peat appeared wet, one set of vertical columns was pre-saturated by inverting the columns into a bucket of water for several days (Fig. 3b). Comparisons between the pre-saturated columns and the "field condition" columns were used to see if any contaminants were lost due to the "wetting-up" in the early stages of the unsaturated column experiments. After the experimental runs, the spiked columns were divided into slices and layers were selectively quantitatively analyzed for DRO and to determine if there had been any preferential flow along the column edges.

All column experiments were run simultaneously. Water was introduced through the column port at a constant pressure head of 0.02 m using a Marriott bottle. Contaminant spikes, consisting of 2.0 ml of 1000 ppm Pb and 1.0 ml neat DRO (877.0 mg), were added to all spiked columns before the experiments began; in set 2, we only added 1.0 ml of the Pb
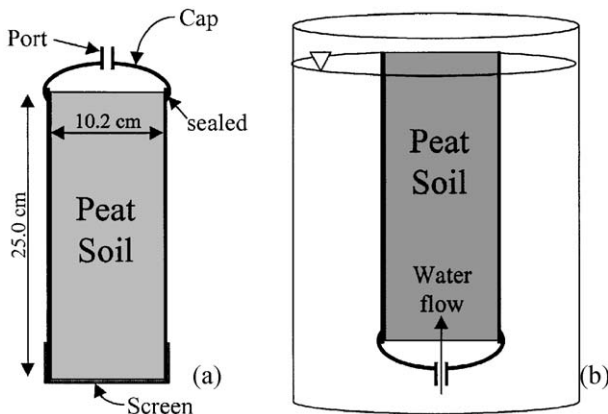

Fig. 3. Schematic diagrams of the column set-up (a) and the method used to saturate the column (b).

Table 2
Summary of experimental results

Column ID	Set 1			Set 2			Set 3		
	1S	1C	Avg.	2S	2C	Avg.	3S	3C	Avg.
Average flow rate (ml min^{-1}) [S.D.]	14.2 [5.7]	102.2 [6.1]	58.2	65.7 [1.8]	65.1 [1.7]	65.4	100.0 [7.5]	101.4 [5.6]	100.7
Total DRO leached (mg)	0.00	0.00	0.00	0.01	0.00	–	9.76	0.00	–
Total Pb recovered (mg)	0.79	0.48	0.64	1.80	1.59	1.70	2.84	0.82	1.83
k_{Pb} (l g^{-1})	–	1.56	–	–	1.13	–	1.21	1.44	1.31
Background Pb in columns, M_0 (g cm^{-2})	–	18.1	–	–	5.2	–	–	8.8	–
Mixing depth^a L_m (cm)	–	–	–	–	–	–	2×10^{-8}; 7×10^{-6}	–	–

^{a} The top mixing depth is based on Pb data and the lower based on DRO.

solution. The pH of the Pb spike was adjusted using NaOH prior to injection into the column so that the pH of the Pb spikes was similar to the pore-water pH. Effluent was collected from both the control and spiked columns in 14 1-l samples. Each sample was analyzed for Pb and DRO. A total of 14 l of double-distilled water passed through the columns which is equivalent to slightly more than one year of average Juneau precipitation; airport is ~ 150 cm. Fourteen corresponds to 8.6 and 7.8 pore-volumes for the vertical and horizontal soil columns, respectively. The pH of the water added to the column, was ~ 6, which is similar within the range of reported rainwater pH (5.1, Bormann et al., 1989 to 6.5, Stednick, 1981). From each 1-l sample, 10 ml was removed for Pb analysis. Lead was analyzed on a graphite furnace atomic absorption (AA), and DRO was analyzed with gas-chromatograph mass spectroscopy (GC/MS). The methods used were modified EPA procedures SW846 3510C (Pb) and SW46 3050B (DRO) and the associated detection limits are 0.28 µg l^{-1} and 0.01 mg l^{-1}, respectively.
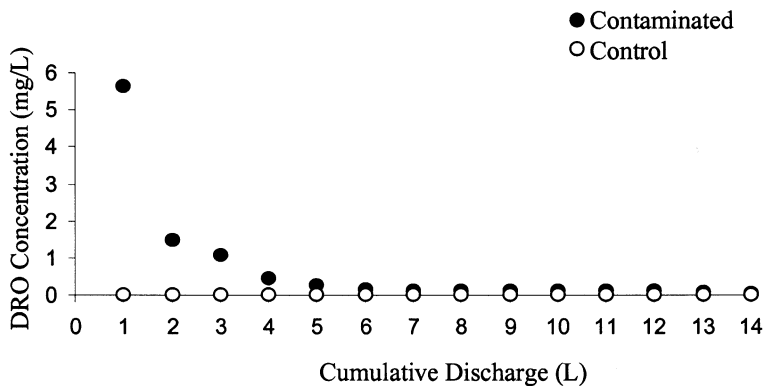

Fig. 4. DRO concentration vs. cumulative discharge for the horizontal column experiments. Solid symbols represent values from spiked columns and open symbols represent control or blank columns. Note that no appreciable DRO leached from the vertical columns.

3. Results

The flow rates for the experiments showed good repeatability and small temporal variability ($< 6\%$) for experimental sets 2 and 3, but set 1 showed greater variability with generally an order of magnitude difference in the flow rates between columns 1S and 1C (Table 2). However, the magnitudes and relative difference in average flow rates for vertical and horizontal columns are consistent with expected hydraulic conductivities. In addition, earlier literature has shown that the complicated subsurface structure of peat-lands and bogs routinely results in orders-of-magnitude differences in flow rates over small spatial distances (e.g., Glaser and Janssens, 1986; Ingram, 1983). Horizontal flow rates in peat can be 10 times greater than vertical flow rates due to different decompo-sition levels of the peat substrate (Boelter, 1969). A relatively thin, horizontal bed of low permeability material can substantially decrease vertical flow rates but has little impact on
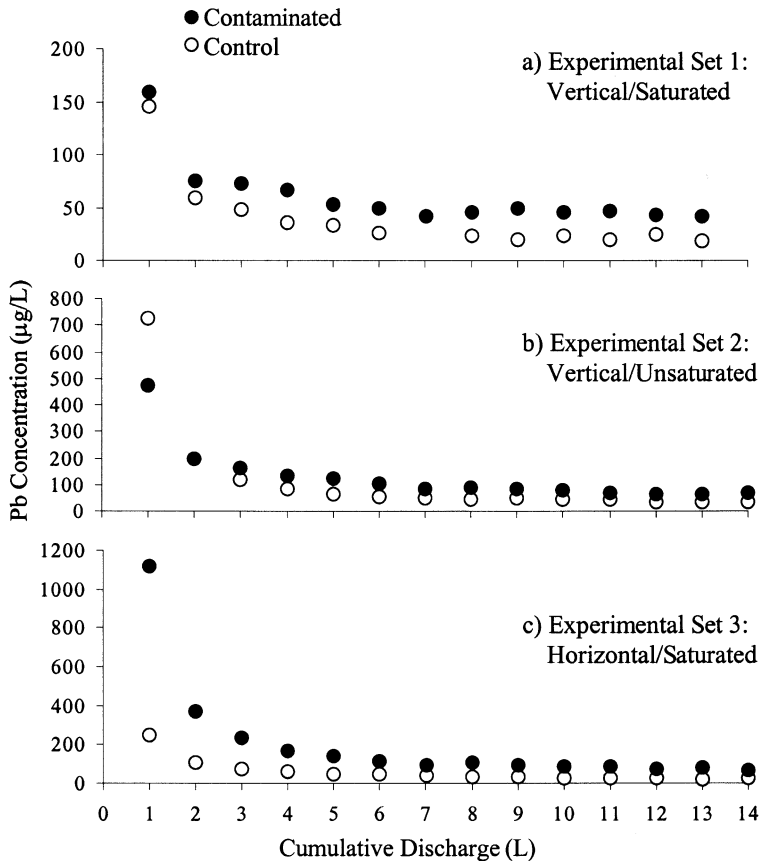

Fig. 5. Pb concentration vs. cumulative discharge for all experiments. Solid symbols represent values from spiked columns and open symbols represent control or blank columns.
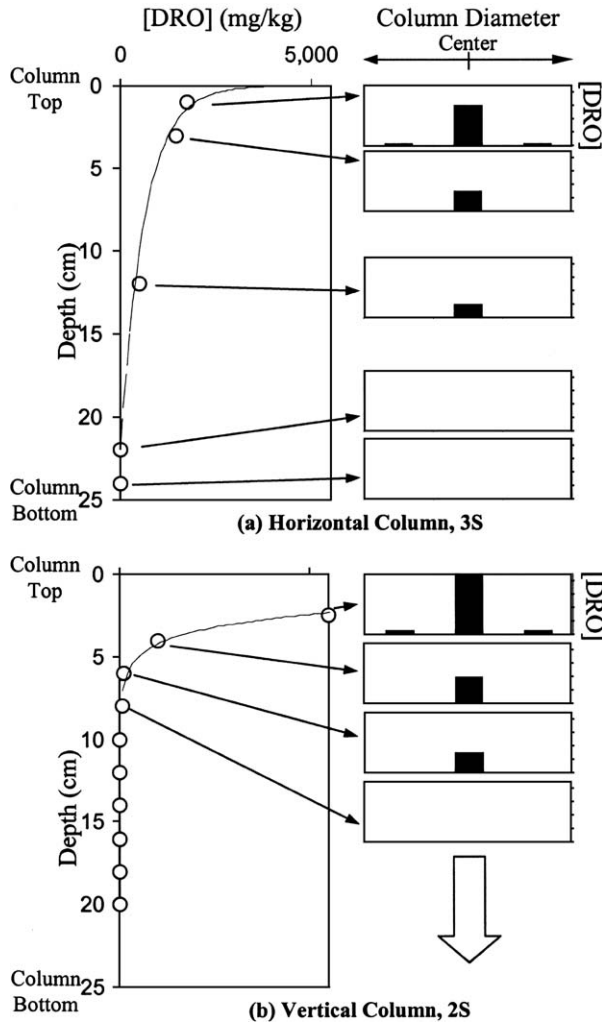
Fig. 6. Distribution of [DRO] in columns 3S (a) and 2S (b) after the experiments. The circles represent measurements of average concentration over a 2-cm-thick slice of peat and the lines show the interpolated trends in concentration. The bars represent the pattern of concentration through the column cross-section for each "slice". The scale of the bar charts is $0–9000$ mg l^{-1}.

horizontal flow rates and the presence of a such a layer in 1S may explain its uniquely low flow rate or, conversely, perhaps the other vertical columns contained more macropore flow paths than 1S; such flow paths are not easy to consistently capture in small column experiments like these. The conductivities of the soil columns were between 0.002 and 0.02 cm s^{-1}, which is within the range of field measurements of K_s. Comparing the columns in sets 1 and 2 showed no evidence that pre-saturating the columns had any systematic impact on their hydraulics.
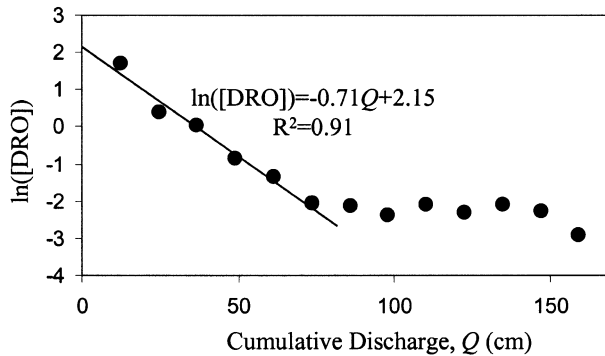
Fig. 7. Modeled (line) and observed (symbol) ln([DRO]) vs. cumulative discharge, Q (cm) for the horizontal spiked column, 3S, i.e., the only column to leach DRO. The model only predicts for the macropore-flow period.

Figs. 4 and 5 show the concentrations of DRO and Pb vs. cumulative discharge, respectively, and Table 1 shows the total mass recoveries of the contaminants for each experiment. Surprisingly, Pb consistently moved more readily through the peat than DRO. Essentially no DRO leached from the vertical columns and, thus, no figures are shown; the second sample from column 2S was the only non-zero concentration, 0.01 mg l^{-1}. The horizontal spiked column, 3S, leached the most Pb and DRO. All of the spiked columns had higher total Pb removal than their associated controls, which suggests that some of the Pb removed from the spiked columns were indeed from the contaminant spike. However, Pb removal from the control columns was also substantial. In fact, the total Pb recovered from the control columns was, on average, 50% of the spike quantity, although they received no contaminant spike (Table 2). Note also that column 2S leached more than 100% of the spiked amount. The high background Pb contamination in the peat soils should perhaps have been expected because the soil was extracted from the rifle range, and, therefore, contained a relatively high concentration of lead from bullets.

Fig. 6a and b shows the distribution of DRO remaining in the horizontal spiked column, 3S, and vertical spiked column, 2S, after the experiments. The DRO detected in the columns accounted for about 80% and 88% of the total spiked for the horizontal, 3S, and vertical, 2S, columns, respectively. In vertical the column, DRO accumulated in the top few centimeters of peat and there was no detection of contamination in the lower 4/5ths of the column. Although the residual DRO is spread throughout a deeper profile in the horizontal column, 3S, than in vertical, 2S, no DRO was found in the bottom few centimeters of peat. To ensure that no material was moving along the column walls, the center (5 cm diameter) and outer-ring of each slice were tested independently. These results are plotted in the bar graphs in Fig. 6 and show that the highest concentrations were consistently in the center suggesting that the flow was not preferentially moving along the walls. The total mass of DRO recovered in these experiments, i.e., in the leachate and in the peat, accounted for 82% and 88% of the total spike. The missing fraction, 12–18%, is possibly explained by imprecision in separating the DRO signal from background organic compounds or adsorption to various experimental or lab equipment. Because of the high background levels of Pb, no mass balance was attempted.

4. Discussion

The movement of both dissolved Pb and DRO through peat is complicated because both the controlling hydraulic and biogeochemical systems are complicated and inseparable in these experiments. Both Pb and DRO have a potential affinity for peat's organic matter (Zynter et al., 1989; Viraraghavan and Ayyaswami, 1989) and can therefore bind with and release from the peat in ways that can be difficult to predict. Additionally, dissolved contaminants may diffuse out of flowing water and into isolated, static pores or visa versa (Hoag and Price, 1997).

The relatively high Pb mobility in our experiments was surprising, even alarming considering the ubiquitous dogma of immobility that is associated with heavy metals in general and Pb in particular. Note however that this site is much more heavily contaminated with Pb than others that have been extensively studied, especially where ^{210}Pb isotopes have been used to date peat and sediment cores (e.g., Shotyk et al., 1998). Some recent studies have suggested that metals may be more mobile than expected in areas where metal loading is high (e.g., Richards et al., 2000; McBride et al., 1999; Harrison et al., 1999; Camobreco et al., 1996).

In addition to the high contaminant-loading, Pb's enhanced-mobility was likely facilitated by the presence of organic compounds (e.g., Karathanasis, 2000; Jordan et al., 1997; Camobreco et al., 1996), high acidity, and perhaps some iron in the soils (e.g., McBride, 1994). Although we did not measure carbon compounds in our effluent, leachate from all columns was markedly colored, which is consistent with substantial amounts of organic matter. In fact, highly colored streamwater in southeast Alaska is an indicator of positively charged organic acids leaching from soils (Stednick, 1984). DOC concentration from a peatland upstream of ours was measured at 28 mg l^{-1} in the pore water and 18 mg l^{-1} in adjacent streamwater. In systems that contain both colloidal organics and iron compounds, with which Southeast Alaska's geology is very rich, there exists a set of interactions that can change the way that Pb exists in the system such that Pb mobility increases in aging peat systems (Martínez and McBride, 1999; Cameron and Liss, 1982). Generally, the soluble complexes are sorbed to mineral soil once the concentration of organic matter is reduced. Therefore, if the Pb is in acidic, organic-rich environment, like our site, it may remain mobile for longer periods of time. In addition, competition from aluminum in acid soils can lead to increased lead solubility (Pinheiro et al., 2000). Aging peat has a low mineral fraction and a high organic fraction (D'Amore and Lynn, 2002; Levesque and Dinel, 1982) although some iron and aluminum may enter our system via lateral upslope flows. In acid soils with high extractable Pb concentrations, the solubility and bioavailability of Pb is elevated (Turpeinen et al., 2000).

Lead has been observed at very high (toxic) concentrations in soils at shooting ranges, but remained immobile in where the soils were well-drained (e.g., Astrup et al., 1999). However, Pb is sometimes more mobile in saturated peat (Mackenzie et al., 1998). Interestingly, MacKenzie et al. (1998) contrasted unsaturated, ombrotrophic peat with saturated iminerotrophic environment peat and found that Pb was immobile in the unsaturated, ombrotrophic environment, but mobile in the saturated, minerotrophic environment. The Juneau rifle range is most likely saturated and ombrotrophic, although the specific characteristics of the peatland have yet to be well defined.

In addition to the chemical enhancement of Pb mobility, our experiments suggest that macropore or similar preferential pathways played important roles in the observed pollutant transport. For example, the lack of detected residual DRO in the bottom portions of the peat columns (Fig. 6) despite the fact that some DRO clearly traveled the entire length of at least one column (Fig. 4 and Table 2) is consistent with rapid macropore flow. The very rapid appearance of pollutants in the leachate is also consistent with similar observations of pesticides in groundwater attributed to preferential flow (e.g., Kladivko et al., 1991; Gish et al., 1991; Smith et al., 1990). The temporal trends in concentration, despite very constant discharge rates, appear to be very similar to those observed in both field (e.g., Steenhuis et al., 1994) and column (e.g., Edwards et al., 1992) experiments of macropore flow of adsorbed chemicals. Due to peat's complicated physical structure, which includes pore sizes that span many orders of magnitude, highly variable conductivity, and many macropore pathways (Holden et al., 2001; Baird, 1997; Glaser and Janssens, 1986), hydraulic flow paths through peat will be very non-uniform.

To test the hypothesis that macropore-like-flow was a substantial transport mechanism, we used the simple model proposed by Shalit and Steenhuis (1996) to gain insights into the soil–water–chemical interactions in our columns. This model is based on the assumptions that the system can be described as having two primary flow regimes, one rapid flow regime via macropores, and a slower flow regime via matrix flow and that a simple adsorption–desorption partition coefficient, k, can be used to describe the interactions between dissolved chemicals and the soil particles. Using these assumptions, Shalit and Steenhuis (1996) showed that the contaminant concentration from macropore flow can be estimated with:

$$C = \frac{M_0}{(n + \rho_b k)L_m} \exp\left(-\frac{Q}{(n + \rho_b k)L}\right) \tag{1}$$

where C is the chemical concentration in the discharge [M L^{-3}], M_0, is the initial mass of contaminant in the soil [M L^{-2}], n is the soil porosity, ρ_b is the soil bulk density [M L^{-3}], L is the length of soil columns for these experiments [L], Q is the cumulative discharge [L], and L_m is the depth to which the contaminant was initially incorporated [L]. Log-transforming Eq. (1) results in the following linear equation with respect to cumulative discharge:

$$\ln(C) = \ln\left(\frac{M_0}{(n + \rho_b k)L_m}\right) - \left(\frac{1}{(n + \rho_b k)L}\right)Q \tag{2}$$

To apply the model of Pb in the control columns, we assumed that lead was initially well distributed throughout the column by the process of bullets being shot into the substrate over several decades, i.e., $L_m = L = 25$ cm. We then fit the model to the data with k and M_0. We tried to isolate the "spike" contributions for the Pb spike columns by subtracting the control column concentrations from the spiked-column concentration within each pair. We fit the model to the spike Pb column and DRO data with k and L_m. All other parameters were independently measured.

Figs. 7 and 8 show modeled and observed ln([DRO]) vs. Q and ln([Pb] vs. Q, respectively, for these experiments and Table 2 summarizes the model fitting parameters.
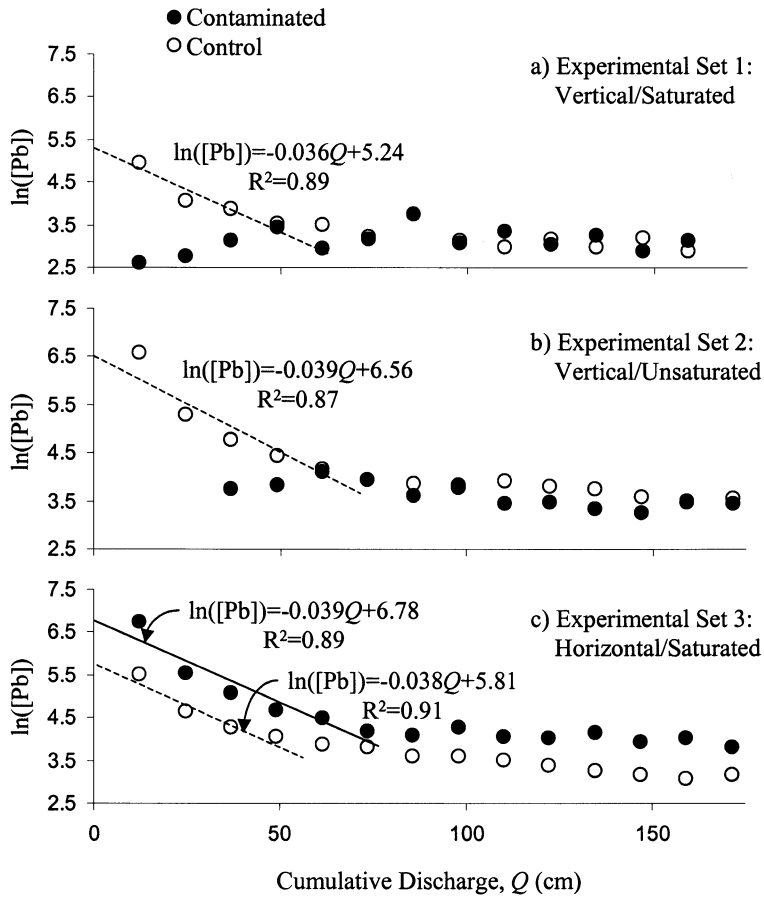
Fig. 8. Modeled (line) and observed (symbol) ln([Pb]) vs. cumulative discharge, Q, for all three experimental sets. The model only predicts for the macropore-flow period. Open symbols are data from the control columns and the solid symbols are for the contaminated columns after subtracting the background, i.e., control concentration data. In (a) and (b), there is no evidence of a macropore-flow period for the contaminated columns after subtracting the background concentrations and thus, no regression lines for these data.

Notice that all the plots have a characteristically steep, early section, that the macropore model fits, and a much flatter late section. These two regimes have been observed in other experiments and interpreted as an early regime in which macropore transport dominates and a late regime in which matrix transport, or some other slower transport flow path, dominates (Shalit and Steenhuis, 1996; Steenhuis et al., 1994). Our data do not indicate any preferential flow for the spiked, vertical columns, thus the model was not fit to these data and the following discussion implicitly excludes these experiments. It is interesting that even though the total flow rate was very constant, Figs. 7 and 8 clearly suggest that the DRO and Pb moved initially through preferential flow paths and later primarily via a slower flow path. Presumably macropore transport of Pb and DRO is substantially diminished once the matrix region draining into the macropores becomes flushed of

contaminant. An alternative explanation for the "slow transport" regime is that transport is controlled by diffusion out of "dead" pores as suggested by mobile–immobile models and similar concepts (e.g., VanGenuchten and Wierenga, 1976; Sposito et al., 1986). In general, our observations of macropore transport agree with observations and conclusions by Ours et al. (1997). It is also interesting that, for the horizontal columns, both DRO and Pb appears to transition from macropore transport to transport via a slower process at about 3 pore-volumes. The complete significance of this observation is unclear, although it suggests that this characteristic is a property of the soil rather than the contaminant. Also note that we chose not to fit our data to a more complicated model, of which there are many, because more complex models require more parameter calibration, which diminishes our confidence that the primary controls have been identified. Steenhuis et al. (1999) convincingly showed that model complexity does not translate into improved understanding of the controlling processes.

For the control columns, the background Pb loading, M_0, ranged from 5 to 18 g cm^{-2}, which is much higher than the spike loading, 2×10^{-5} g cm^{-2} and is consistent with our inability to isolate the spike for two of the three columns. Presumably, the background mass is mostly in the form of Pb dust. The mixing depths, L_m, for both the spiked Pb and DRO models were very shallow $< 10^{-5}$ cm, which is consistent with the topical application method.

The fitted adsorption–desorption partition coefficient for DRO, k_{DRO}, was ~ 1000 l g^{-1} and the average adsorption–desorption partition coefficient for Pb, k_{Pb}, was 1.33 l g^{-1} (standard deviation = 0.20 l g^{-1}). The k_{Pb}'s for each experiment are shown in Table 2. There is no obvious systematic trend in the k_{Pb}'s relative to different experimental conditions and all the values were similar (Table 2). The k_{DRO} was typical for strongly adsorbed pollutants like DDT (Bailey et al., 1974), Paraquat (Smith et al., 1978), and Toxaphene (Helling et al., 1971), and was similar to published values of sorption characteristics for organic compounds in soil (e.g., Karapanagioti et al., 2000). Note that hydrophobic organic compounds, like DRO, typically have very nonlinear adsorption isotherms unlike our crude linear approximation. The nearly complete absence of DRO leaching from the vertical columns is consistent with a high adsorption constant. The k_{Pb}, on the other hand, was similar to published values for moderately mobile substances like Atrazine, Dichlobenil, (Smith et al., 1978), and 2,4-D (Walter et al., 1979) and was orders of magnitude lower than most published adsorption constants for heavy metals, especially Pb (e.g., Morera et al., 2001). The low adsorption coefficient is consistent with our speculation that something about the highly Pb-loaded, acidic, organic-rich environment potentially facilitates a dynamic exchange of Pb into solution although the exact mechanism is not yet clear; certainly not clear enough for precise mechanistic modeling.

5. Conclusions

The most surprising, and perhaps significant finding in this pilot study was the unusually high mobility of Pb. We speculated that this unique observation is due heavy Pb-loading at the site as a result of its being a rifle range, which has resulted in a large portion of the Pb adsorbing sites in the peat being occupied. The background Pb

accounted for the dominant fraction of the Pb leached from the columns. This pilot study also suggests that contaminant transport risks in peatlands may be more pronounced for lateral flow (along the bedding planes) than for vertical flow (across the bedding planes), especially with respect to DRO. To more fully support this conclusion, further work is needed to quantify the in situ hydraulic gradients controlling flow in each of these directions, but, because our site is on the side of a mountain, it is probable that lateral hydraulic gradients will be substantial. Macropore transport appeared to be an important pathway for both DRO and Pb leaching, especially for lateral flow, and this hypothesis was corroborated with a macropore model, which agreed well with the data. Estimates of the soil adsorption–desorption coefficients for Pb were similar for all the experiments, ~ 1.33 l mg^{-1}, which was several orders of magnitude lower than most published values and indicated moderate mobility, probably facilitated by organic complexing. For DRO, the adsorption–desorption coefficient was ~ 1000 l mg^{-1}, indicating low mobility, consistent with previously published work. These results underscore the need for caution when developing in southeast Alaska's sensitive wetland environments.

Acknowledgements

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