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Colloid-facilitated Pb transport in two shooting-range soils in Florida

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ABSTRACT

Shooting range soils with elevated Pb contents are of environmental concern due to their adverse impacts on human and animals. In Florida, the problem merits special attention because of Florida's sandy soil, high rainfall, and shallow groundwater level, which tend to favor Pb migration. This study used large intact soil column to examine colloid-facilitated Pb transport in two Florida shooting-range soils with different physicochemical properties (e.g., organic carbon content, pH, and clay content). Simulated rainwater (SRW) was pumped through the intact soil columns under different ionic strengths (0.07 and 5 mmol L^{-1}) and flow rates (2.67, 5.30 and 10.6 cm h^{-1}) to mobilize Pb and soil colloids. Our results showed that colloids dominated Pb transport in both soils and there was a significant correlation between colloids and Pb in the leachates. Decreases in ionic strength and increases in flow rate enhanced the release of both colloids and Pb in the soils. Size fraction analyses showed that in OCR soils (sandy soils with low organic carbon), most of the Pb (87%) was associated with coarse colloid fraction (0.45–8 μm). However, high Pb level (66%) was found in the dissolved and nano-sized colloid fraction (<0.1 μm) in the MPR soils (sandy soils with high organic carbon). This suggests that soil properties are important to Pb migration in soils and groundwater. Our study indicated that colloids play an important role in facilitating Pb transport in shooting range soils.

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1. Introduction

Lead (Pb) is a toxic heavy metal, which has received much attention because of its adverse environmental and health impacts [1]. The amount of Pb consumed as munitions in hunting and recreation shooting in the United States exceeded 3 million metric tons in the 20th century [2]. With large amounts of bullets being discarded in shooting ranges, Pb is ubiquitous in shooting range soils. For example, Pb content in the surface soils was as high as 7.5% in a 30-year-old shooting range [3] and 4.8% in a 16-year-old shooting range [4]. High Pb concentrations were detected even at 100 cm below the surface in shooting range soils, indicating its downwards movement in soils [5]. If Pb is leached from the shooting range soils into groundwater underneath and enters drinking water aquifers, it will impose potential risks to the ecosystem and the public health. It is therefore important to understand Pb mobility in shooting range soils.

Lead is often thought to be immobile in soils because of its low solubility and a strong affinity to soil particles [6]. However, several studies suggested that mobile colloids in pore water can enhance Pb mobility in soils [7–9]. The term colloid generally applies to suspended particles of 1 nm to 10 μm, which include many soil fractions such as clay minerals, metal oxides, and humic substances [10]. With large specific surface area and abundant surface functional groups, soil colloids have a strong ability to adsorb various chemical species including heavy metals [10–12]. Colloid-facilitated transport of heavy metals in soils has been reported [11,13]. It has been recognized as one of the most important mechanisms governing the mobility of heavy metals in soils, and thus has attracted much attention [14,15].

The mechanisms governing colloid-facilitated transport of heavy metals in soils have been investigated [16–18]. Based on batch desorption and column leaching experiments in laboratory settings, perturbations in solution and flow conditions play important roles in controlling the release of colloid-borne heavy metals [19–21]. For example, physicochemical perturbations such as reduction in ionic strength (IS), increase in solution pH, and increase in flow velocity may favor the release of colloids and colloid-borne metals in soils [14,19,22].

The dependency of colloid-borne metal release in soils on IS can be predicted using the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [23,24]. Experimental data of metal leaching from soil columns under different IS indicated that colloid-borne metals increased as solution IS increased due to reduced electrostatic repulsive forces (electro double layer—EDL forces) [22]. When solution IS is reduced, it reduces the EDL forces, therefore remobilizing

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the initially deposited colloidal metals in soil [25–27]. The mobility of colloid-borne metals in soils may also increase with increasing pH and flow rates [22,28]. In batch experiments with shooting range soils, Klitzke et al. [29] found that increases in solution pH enhanced release of both colloidal and dissolved Pb. At low pH, they found that the release of organic colloids may dominate the Pb transport in soils. However, few studies examined colloid mobilization by hydrodynamic shear detachment [19,30]. As such, to what degree do perturbations in flow rates mobilize colloids in soils needs further examination.

This study used large intact soil columns from two shooting ranges in Florida to investigate the role of colloids in Pb mobilization under simulated natural perturbations. The role of colloid-facilitated Pb migration in these soils was assessed with synthetic rainwater (SRW) (pH 4.9) at different IS (high IS corresponding to typical soil, and low IS corresponding to typical rain), and flow rates (high flow rate corresponding to irrigation, and low flow rate corresponding to natural drainage).

Our overall objective was to investigate colloid-facilitated Pb transport in shooting range soils. Specifically, we were to: (1) evaluate the importance of colloid-facilitated Pb transport in shooting range soils; (2) determine the effects of IS and flow rate on colloid-facilitated Pb transport in shooting range soils; (3) examine Pb distribution in colloids of different size fractions in leachates; and (4) investigate the role of soil property on colloid-facilitated Pb transport in shooting range soils.

2. Materials and methods

2.1. Intact columns

Large intact soil columns were taken from two shooting ranges in Florida, which have been in operation since 1986 [31]. They were taken approximately 2 m in front of the berm at both locations. Transparent polyvinyl chloride pipe (4.25 cm internal diameter and 116 cm long) was inserted into a steel sleeve fitted with a bottom cutting edge and forced into the soil using Geoprobe Model 5410 hydraulic soil probe [31]. The intact soil cores were then removed using the hydraulic probe, and sealed before transporting back to the laboratory.

The two shooting range soils were designated as OCR and MPR. Three OCR and two MPR intact soil cores were collected. While one intact soil column from each soil was sacrificed for characterization, the other three columns (OCR-1, OCR-2, and MPR) were used for leaching experiments. The OCR soil was a typical sandy Florida soil whereas the MPR soil was disturbed with a plastic liner at 90 cm below the surface. To make it comparable, only the top 80 cm soil was used for all three soil columns. The bulk density of OCR and MPR soils was 1.53 and 1.35 $g\,cm^{-3}$, and their porosity was 0.42 and 0.49 [31].

2.2. Soil characterization

The soil columns were divided into 10-cm sections. The soil samples were ground to pass through a 2-mm sieve, and digested by adding 10 ml of 1:1 water:HNO_3 to 0.5 g of soil in a digestion vial and heating to 105 °C for digestion (USEPA 3050a). Quality control samples including a standard reference material for soils were included (2709 San Joaquin soil and 2710 Montana soil; National Institute of Standards and Technology, Gaithersburg, MD 20899). Satisfactory precision and accuracy within ±20% were obtained. Total Ca, Fe, Al and Pb in the digests were measured with flame atomic absorption spectrophotometry (FAAS; Varian 220 FS with SIPS, Walnut Creek, CA). Soil pH was measured with a 1:1 ratio of solid to water after 1 h. Soil organic carbon [32] and soil texture [33] were also determined.

Water-dispersible colloid in soil was determined by placing 5 g of soil to 100 mL of water [19]. The mixture was placed on a reciprocating shaker for 1 h and centrifuged at 750 rpm for 3.5 min. Colloid concentration was determined gravimetrically by drying 100 mL aliquots at 100 °C for 24 h.

Due to the high Ca concentrations in the MPR soil (Table 1), X-ray diffraction (XRD) was used to determine the presence of $CaCO_3$. The MPR soil was sectioned into 20-cm segments and was analyzed from 2 to 60° 2θ using Cu Kα radiation on a computer-controlled diffractometer (Philips Electronic Instruments, Inc., Mahwah, NJ) equipped with stepping motor and graphite crystal monochromator [34]. Selected physicochemical properties of the two soils are presented in Table 1.

2.3. Leaching experiment

Simulated rainwater (SRW) was prepared based on the data from the National Atmospheric Deposition Program, which consisted of the average seasonal precipitation weighted mean concentrations from 1990 to 2000 from two sites in Florida located near sampling sites [31]. The SRW was adjusted to pH of 4.9 of two different IS (0.07 and 5 $mmol\,L^{-1}$) by adding NaCl, NaOH, or HCl for the leaching experiment.

Leaching experiments were performed with large intact soil columns (4.3 cm × 80 cm). A glass wool with 8 μm pore size and a rubber stopper were used to seal the soils in the columns. Two polyvinyl chloride tubes (diameter of 3.2 mm) were inserted into the stopper on each side, which were used to connect column to tubing. Vacuum pump (Gilson 302, Gilson, France) was used to control the flow rate.

The columns were oriented vertically and saturated from the bottom at a flow rate of 0.76 $cm\,h^{-1}$ with 1 pore volume (PV) of deionized water to remove air pockets followed by stabilization for 28 h before leaching. After the intact soil columns (two OCR and one MPR) were saturated with water, the leaching experiments were initiated by pumping SRW through the column at constant flow rate. The leaching was performed at different stages using SRW of different IS and flow rate (Table 2).

A two-stage leaching was performed using column OCR-1 to determine the effect of IS perturbation on Pb transport in the soil. The column was first flushed with high IS-SRW (5 $mmol\,L^{-1}$) for ∼8 PV followed with low IS-SRW (0.07 $mmol\,L^{-1}$) for additional 7 PV. In both stages, the solution pH was 4.9 and flow rate was 2.67 $cm\,h^{-1}$. A three-stage leaching was performed using column OCR-2 to determine the effects of flow rate perturbations on Pb transport in the soil. The flow rate in the ORC-2 column was increased from 2.67 $cm\,h^{-1}$ (stage-1) to 5.3 $cm\,h^{-1}$ (stage-2), and to 10.6 $cm\,h^{-1}$ (stage-3), while keeping the IS (0.07 $mmol\,L^{-1}$) and pH (4.9) constant during the experiment. The leaching study of MPR column was only performed for one stage at IS of 0.07 $mmol\,L^{-1}$, pH of 4.9, and flow rate of 1.35 $cm\,h^{-1}$. A lower flow rate was used for MPR column because the soil had a lower hydraulic conductivity than OCR soil (Table 1).

2.4. Effluent analysis

A fraction collector was used to collect the effluent every 40 ml in 50 ml plastic bottles. Total Pb was measured with graphite furnace atomic absorption spectrophotometry (GFAAS; AA240Z, Varian Inc., CA). Because soil leachates contained different inorganic and organic colloids, it is difficult to quantify their actual concentrations. In a water-quality protocol developed by the U.S. Geological Survey, light attenuation methods based on sample turbidity are listed as standard methods to estimate colloid concentrations in natural water samples [35]. In this study, turbidities of the effluents were determined with a UV spectrophotometer (Shimadzu, Japan)

Table 1
Properties of the two Florida shooting range soils.

Soil	Depth (cm)	OC content[a] ($g\,kg^{-1}$)	pH[a]	Total Pb[a] ($mg\,kg^{-1}$)	Total Ca[a] ($mg\,kg^{-1}$)	Total Al[a] ($mg\,kg^{-1}$)	Total Fe[a] ($mg\,kg^{-1}$)	Clay (%)	Silt (%)	Sand (%)
OCR	10	5.79 ± 0.41	6.98 ± 0.04	5284 ± 2734	230 ± 1.10	1751 ± 23.9	1200 ± 115	1.72	17.7	80.6
	20	6.77 ± 0.57	6.56 ± 0.02	3252 ± 748	122 ± 4.90	1822 ± 0.37	1206 ± 202			
	30	15.86 ± 0.51	6.26 ± 0.02	2096 ± 750	175 ± 10.2	2561 ± 104	1283 ± 102	5.39	0.65	94.0
	40	6.34 ± 1.35	6.14 ± 0.31	1339 ± 1167	156 ± 28.9	8150 ± 3379	4049 ± 1546			
	50	7.75 ± 0.40	5.96 ± 0.48	1118 ± 1118	160 ± 41.9	2796 ± 853	1704 ± 514	1.73	0.61	97.7
	60	5.08 ± 1.24	5.62 ± 0.63	25.8 ± 25.8	74.4 ± 36.0	2694 ± 677	1825 ± 191			
	70	4.91 ± 1.32	5.33 ± 0.34	5.71 ± 5.71	88.0 ± 51.4	2256 ± 320	1594 ± 376	1.63	0.53	97.8
	80	4.11 ± 0.74	5.60 ± 0.10	22.3 ± 22.3	52.6 ± 12.2	2478 ± 631	1700 ± 337			
MPR	10	39.8 ± 3.55	7.67 ± 0.21	29892 ± 16295	63354 ± 8100	2157 ± 1254	1473 ± 308	8.53	9.68	81.8
	20	21.1 ± 0.69	7.83 ± 0.06	12838 ± 930	81009 ± 7689	3152 ± 891	1750 ± 318			
	30	21.8 ± 0.10	7.85 ± 0.19	13080 ± 8348	98675 ± 11263	4403 ± 513	2066 ± 281	9.50	7.91	82.6
	40	21.1 ± 2.00	8.06 ± 0.13	4323 ± 1203	94184 ± 9422	5166 ± 279	2157 ± 108			
	50	19.8 ± 4.77	8.05 ± 0.09	4548 ± 1183	111106 ± 14841	4420 ± 864	1980 ± 294	9.35	7.94	82.7
	60	18.2 ± 2.33	7.87 ± 0.07	4193 ± 1148	105566 ± 17591	3879 ± 810	2169 ± 36.3			
	70	19.9 ± 2.33	7.86 ± 0.01	2510 ± 520	122133 ± 13782	4624 ± 175	2357 ± 174	11.6	11.4	76.9
	80	10.64 ± 4.65	8.03 ± 0.20	685 ± 400	226112 ± 55506	3024 ± 818	1626 ± 26.4			

[a] Mean value of three measurements followed by standard deviation.

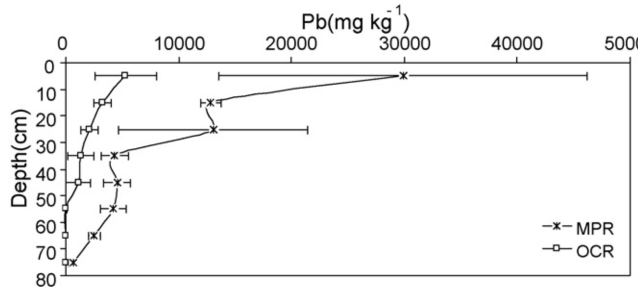

Fig. 1. Pb distributions in the two soil columns used in the study.

at 350 nm and were expressed as AU (Attenuation Unit). Colloid concentrations in the leachates were assumed to be proportional to AU [35].

2.5. Size fraction

Effluent samples collected from OCR-2 (stage-2 and -3) and MPR columns were filtered to determine Pb content in colloids of different size fractions. The colloids in these samples were smaller than 8 μm after passing through the glass wool filter. Filters with pore sizes of 0.45 and 0.1 μm were used to separate the sample into different size fractions: soluble and nano-sized (PbS) (<0.1 μm), fine colloid (PbF) (0.1–0.45 μm) and coarse colloid (PbC) (0.45–8 μm) [36–38]. After successively filtered through the two filters, the leachates of PbS and PbF fractions were digested following USEPA Method 3050a. The Pb concentrations in the digests were determined with GFAAS to determine PbS and PbF concentrations. The PbC concentrations were calculated by subtracting PbS and PbF from total Pb (PbT).

2.6. Statistical analysis

Only simple statistical analyses were conducted. The correlation among AU (colloid concentration) and total Pb concentration (PbT) were statistically tested for significance by analyses of variance according to the Generalized Linear Model procedure of the Statistical Analysis System [39].

3. Results and discussion

3.1. Properties of the two shooting range soils

Although the two shooting range soils were both sandy (>77% sand), they had different properties. The OCR soil was characterized with low pH (5.3–7.0), low organic carbon (OC) content (2.4–9.2 $g\,kg^{-1}$), and low clay content (1.6–5.4%; Table 1). The MPR soil, on the other hand, had alkaline pH of 7.7–8.0, high OC content of 6.2–23.1 $g\,kg^{-1}$, and high clay content (8.5–11.6%; Table 1). The alkaline pH coupled with high Ca concentrations in the MPR soil clearly indicated the presence of calcium carbonate, which was confirmed with XRD (data not shown). In addition, the water-dispersible colloid concentrations in the MPR soil (6.4–27.4 $mg\,kg^{-1}$) were much higher than those in the OCR (3.7–11.7 $mg\,kg^{-1}$) (Data not shown).

Both ranges have been in operation for over 20 years [31], high Pb concentrations were therefore detected throughout the soil profiles (Fig. 1). The Pb concentrations in the MPR soil were substantially higher than those in the OCR soil. The Pb concentrations in the top 30-cm in the MPR soil ranged from 13.1 to 29.9 $g\,kg^{-1}$, while those in the OCR soil ranged from 2096 to 5284 $mg\,kg^{-1}$. Similar trend was observed in the subsurface (60–80 cm), with the total Pb concentrations being <26 $mg\,kg^{-1}$ in the OCR soil compared to

Table 2
Leaching experimental procedures and conditions.

Column	Stage-1			Stage-2			Stage-3		
	Ionic strength (mmol L^{-1})	pH	Flow rate (cm h^{-1})	Ionic strength (mmol L^{-1})	pH	Flow rate (cm h^{-1})	Ionic strength (mmol L^{-1})	pH	Flow rate (cm h^{-1})
OCR-1	5	4.9	2.67	0.07	4.9	2.67	–	–	–
OCR-2	0.07	4.9	2.67	0.07	4.9	5.29	0.07	4.9	10.6
MPR	0.07	4.9	1.35	–	–	–	–	–	–

685–4193 mg kg^{-1} in the MPR soil (Table 1). In a study to determine the background concentrations of trace metals in Florida soils, Chen et al. [40] reported total Pb concentrations ranged from 0.18 to 290 mg kg^{-1} in 450 representative soil samples in Florida. Based on this information, it is obvious that substantial Pb migration from top soil to subsurface soil had occurred in the MPR soil. A dramatic decreasing of Pb concentrations in the OCR soils at 60 cm below the surface was observed. It might be because of the low Pb holding capacity of the soil attributing to its low clay and OC content (Table 1).

3.2. Strong correlation between Pb and colloid concentrations in the leachates

Statistical analysis was performed to identify the role of colloids in Pb transport in the two soils. Significant correlation between the total Pb concentrations and the turbidities (colloid concentrations) of the effluents were found for both soils. The correlation coefficients were 0.86 and 0.95 for the OCR (n = 210) and MPR (n = 23) soils, respectively (p < 0.001; data not shown). For all effluent samples, total Pb (PbT) concentrations showed a linear relationship with turbidity (R^2 > 0.74) (Fig. 2). The strong linear correlation between Pb and colloid concentrations suggest that colloids may play an important role in Pb transport in shooting range soils.

3.3. Effects of ionic strength on Pb and colloid transport in the OCR soil

Only small amounts of Pb and colloids were leached from the OCR soil column (OCR-1) at IS of 5 mmol L^{-1} at stage-1 (Fig. 3). Total Pb and colloid concentrations in the leachates were correlated excluding one outlier (R = 0.62, p = 0.001). Both colloids and Pb concentrations increased dramatically when IS in SRW was reduced from 5 to 0.07 mmol L^{-1} at stage-2 (Fig. 3). The peak concentrations were detected at ~9 PV with values as high as 70 AU colloids and 80 μg L^{-1} Pb. The concentrations were then gradually reduced to 13 AU and 20 μg L^{-1} towards the end. Similarly the Pb and colloid concentrations were highly correlated in the leachates of the low IS (R = 0.95, p < 0.0001) (data not shown).

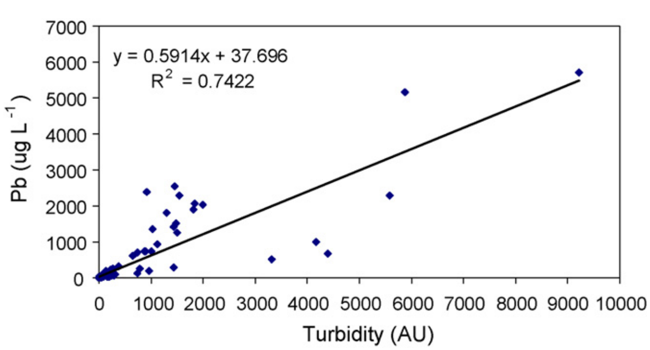

Fig. 2. Correlation between total Pb concentrations and turbidity in the leachates of OCR-2 column.

Our data based on large intact columns are consistent with the literature. For example, Ryan and Gschwend [41] examined the release of colloidal hematite from hematite-coated sand columns under different IS. They found that colloid release rate increases as IS decreases. Increased Pb mobility under reduced IS further confirmed that colloids may play an important role in enhancing Pb mobility in the OCR soils.

At stage-2 when low IS-SRW was applied to the column, most of the Pb concentrations in the leachates (82%) were notably higher than the EPA drinking water standard of 15 μg L^{-1}. This suggests that if low-IS flow (e.g., rain) is applied to the OCR shooting range soil, it may impose Pb contamination risks to the groundwater underneath.

3.4. Effects of flow rate on Pb and colloid transport in OCR soil

Similar to the IS perturbation experiment, only small amounts of Pb and colloids were leached from the OCR soil column (OCR-2) at stage-1 when low flow rate (2.67 cm h^{-1}) was applied (Fig. 4). Substantial increases in Pb and colloid concentrations were observed when the flow rate was increased from 2.67 to 5.29 cm h^{-1} at stage-2. The Pb concentrations and the turbidity detected in stage-2 were several orders higher than those in stage-1 (Fig. 4). Several studies suggested that increased flow rate in porous media (including soils) may generate extra hydrodynamic shear stresses on the solid matrix, therefore mobilizing colloids from grain surfaces [30,42]. The results from the two-stage flow experiment indicate that flow rate may play an important role in governing colloid and Pb transport in shooting range soils.

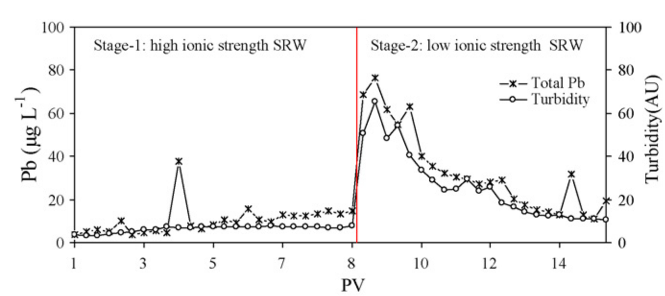

Fig. 3. Effect of ionic strength perturbation on colloid and Pb leaching in OCR-1 column.

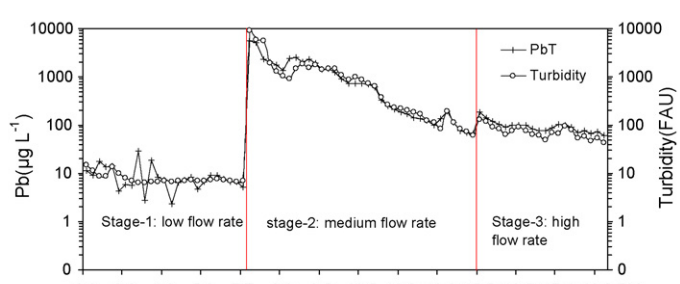

Fig. 4. Effect of flow perturbations on colloid and Pb leaching in OCR-2 column.

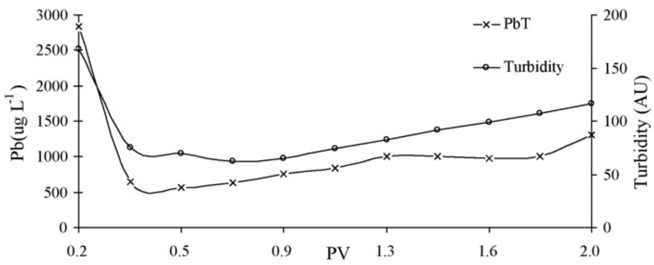

Fig. 5. Leaching of Pb and colloids in MPR column.

Further increase in flow rate from 5.29 to 10.6 cm h^{-1} in stage-3, however, showed little effect on the leaching pattern of both colloids and Pb in the OCR-2 column. This may be because flow rate was already above a certain critical value to mobilize colloids in the soils. Both colloid concentrations and turbidity in the leachates in stage-2 and stage-3 were high during the experiment, confirming that both high (10.6 cm h^{-1}) and medium (5.29 cm h^{-1}) flow can mobilize colloids and Pb in the column. In addition, the turbidity and Pb concentrations in the effluents were stabilized at around 70 AU and 70 μg L^{-1}, which were much higher than the stabilized concentrations detected in column OCR-1 in the IS experiment (20 μg L^{-1}; Fig. 3). The results suggest that increases in infiltration/irrigation at shooting range soils could impose potential risks in Pb contamination to the groundwater.

In the flow rate perturbation experiment, the Pb and colloid concentrations were also highly correlated for all three stages (R = 0.92, p < 0.0001), indicating the dominance of colloids in Pb transport in shooting range soils.

3.5. Pb and colloid transport in the MPR soil

Compared to the OCR soil, much greater Pb concentrations were detected in the leachate from the MPR column, with the initial concentration being as high as 3 mg L^{-1} (600–3000 μg L^{-1} vs. 60–200 μg L^{-1}). Within the first PV, the Pb concentrations dropped sharply to ~800 μg L^{-1}, and then increased gradually to ~1 mg L^{-1} at 2 PV (Fig. 5). The colloid concentrations showed a similar pattern, the turbidity dropped from 170 AU to 70 AU in the first PV, and then slightly increased to 120 AU at 2 PV. The greater Pb concentrations in the MPR soil may result from the high Pb content in the surface MPR soil, which was 2–14 times higher than that in OCR soil (Table 1). The high Pb content coupled with its high OC and alkaline pH may have caused higher leaching of Pb in the MPR soil. This indicates that soil property also played important roles in affecting Pb leaching in shooting range soils.

Similar to the OCR soil, the Pb and colloid concentrations leached from the MPR column were also highly correlated (R = 0.95, p < 0.0001) indicating the dominance of colloids in Pb transport in MPR soils.

3.6. Pb concentrations in colloids of different size fractions

To better understand the Pb distribution in colloids of different size fractions in shooting range soils, the Pb concentrations in the coarse colloids (PbC: 0.45–8 μM), fine colloids (PbF: 0.1–0.45 μM) and soluble and nano-sized fraction (PbS: <0.1 μM) were determined for both soils (Fig. 6). In the MPR soil, the contributions from PbC, PbF and PbS to the total Pb concentration were 19%, 15%, and 66% in the leachates (Fig. 6a). In contrast, in the OCR soil, they were 87%, 1%, and 12%, respectively (Fig. 6b).

Clearly coarse colloids played a significant role in Pb transport in the OCR soil whereas nano-sized colloids were in the MPR soil. This may attribute to the different properties of the two soils (Table 1).

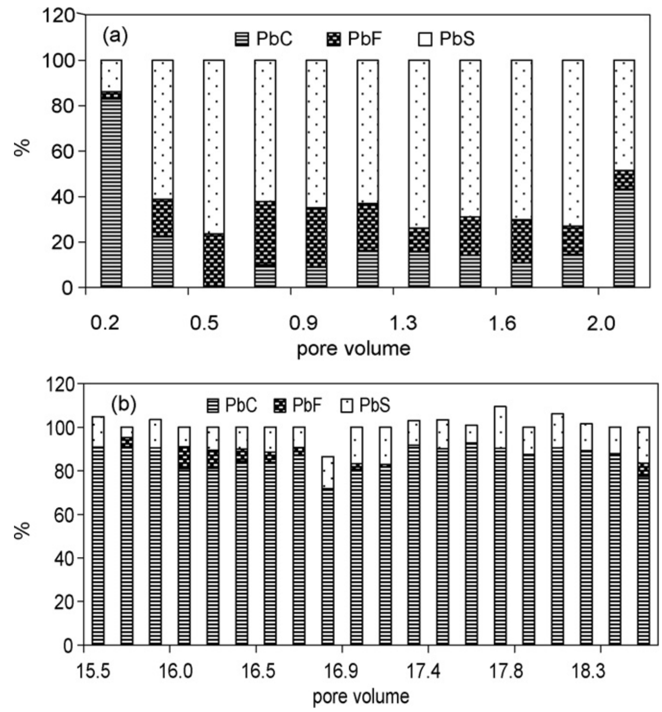

Fig. 6. Lead distributions in colloids of different size fractions in the leachates in MPR (a) and OCR-2 (b) columns. PbC = coarse colloid (0.45–8 μm), PbF = fine colloid (0.1–0.45 μm), and PbS = soluble and nano-sized (<0.1 μm).

The high soluble and nano-sized Pb in the MPR soil may results from its high OC, which is nano-sized colloids and is reactive to Pb. In the leachates from the MPR column, high levels of dissolved organic carbon (DOC) were detected with an average concentration of 92 mg L^{-1} (data not shown). On the other hand, there was little DOC in the leachates from the OCR soil columns (~8 mg L^{-1}). So for the OCR soil, most of the Pb transport was probably associated with coarse colloids.

4. Conclusions

For the first time, large intact soil columns (4.3 cm × 80 cm) from two Florida shooting ranges were used to explore the role of colloids in Pb migration under various physicochemical conditions. Our results indicate that: (1) colloids may dominate Pb transport in shooting range soils; (2) decreases in solution IS and increases in flow rate enhanced the transport of colloids and Pb in shooting range soils; and (3) when released, Pb may associate with colloids of different size fractions depending on soil properties.

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