

Examination of cadmium sorption characteristics for a boreal soil near Fairbanks, Alaska

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Abstract

The objective of this research was to better understand cadmium (Cd) mobility in an organic-rich, boreal soil. Cadmium was selected for the study because of its tendency to be more mobile in soils than other heavy metals, such as lead or mercury. The release of metals from soil is a concern for northern regions where soils are gradually warming, resulting in an increased rate of natural organic matter (NOM) decomposition and soil erosion. Soil samples were collected from three principle soil horizons at a research site in the Caribou–Poker Creeks Research Watershed (CPCRW), near Fairbanks, Alaska. A dilute Cd solution was added to the soil and the soil solution was allowed to mix for 72 h. The soil solution was then passed through a 75 μm sieve and a 0.3 μm filter. Particulate samples retained on the sieve and filter were analyzed by atomic absorption (AA) to determine how much Cd was bound to the different size particles. The NOM in each particle size fraction was analyzed by pyrolysis-gas chromatography/mass spectrometry (py-GC/MS) to determine the nature of the NOM present. Our results showed that the concentration of Cd was almost equal for the different particle sizes in each horizon. That is, the amount of Cd associated with particles larger than 75 μm was nearly the same, on a per mass basis, as the amount of Cd associated with particles ranging in size between 0.3 and 75 μm . Since the mass ratio of Cd to solids normally increases as particle size decreases, this result suggested unusual sorption behavior. Based on the Cd distribution among the particles and the percentage of NOM in each particle size range, it is believed that NOM is a primary factor influencing the sorption behavior of Cd in the boreal soil tested.

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1. Introduction

1.1. Health risks of cadmium

The soil concentration of many metals, especially Nickel (Ni), Chromium (Cr), and Cadmium (Cd), has increased in the United States over the last 60 years [1,2]. The increase can be attributed to the use of pesticides and fertilizers, mining, electroplating and other industrial operations [1]. The environmental hazards and health concerns associated with certain heavy metals, such as Cd are well known [3,4]. For example, consuming water with high levels of Cd severely irritates the stomach, leading to vomiting and diarrhea [5].

Long-term exposure to lower levels of Cd in air, food, or water leads to a chronic accumulation of Cd in the kidneys, and ultimately, kidney failure [5]. Other potential long-term effects of Cd exposure are lung damage and fragile bones [2].

1.2. Sources

Cadmium enters the environment as a result of both natural and anthropogenic activities. It is believed that Cd found in central Alaskan soil is derived mainly from natural sources, such as parent rock decay, dust storms, volcanic eruptions, and forest fires. Volcanic dust recently deposited in the Fairbanks area is primarily derived from the 1912 and 1989 eruptions of Mt. Katmai and Mt. Redoubt, respectively [6]. There are approximately 40 major dust layers deposited from volcanic eruption in the loess around Fairbanks, some as thick as 20–30 cm [6]. Most of these layers

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are more than 100,000 years old, and so lie at depths of several meters or more. However, depending on local erosion and redeposition, the volcanic dust can be a modern source of Cd in air and water.

1.3. Cadmium sorption behavior

The equilibrium between Cd in the soil solution and that sorbed on the solid phase of soil depends on the pH, the stability of Cd complexes, the binding affinity of organic and inorganic ligands, the presence of competing ions and the ionic strength of the soil solution [7]. For Cd, binding with organic and inorganic ligands is an important control on Cd solubility [8,9]. The many negatively charged functional groups on humic substances serve as binding sites for positively charged metals, such as Cd [10]. Inorganic ligands, such as chloride (Cl) also affect the solubility of Cd [9]. It is the soil pH, however, that is the primary governing variable in controlling Cd mobility because soil pH influences the availability of ligands in solution. The parameter K_d is used to describe partitioning of metals between the solid and liquid phases of soil. K_d is defined as the total metal in the soil divided by the amount of the metal in the soil solution. In a summary study of 830 soil solution experiments, the linear dependence of K_d on pH for Cd was defined by the equation, $\log_{10} K_d = 0.49 \pm 0.02, \text{pH } 0.6 \pm 0.49$ [8]. This equation was fit with an R^2 of 0.467 [8]. Since an increasing value of K_d corresponds to a decreasing solubility of Cd, the equation shows that a negative relationship exists between pH and Cd solubility.

In a summary of 37 different studies, Sauve et al., [8] found that K_d values for Cd ranged from 0.44 to 192,000 l/kg for soil pH values ranging from 3 to 9. For a pH of 7, the K_d for Cd ranged from 5 to 50,000, four orders of magnitude. This suggests that the interaction of the organic matter, the soil minerals, and the Cd for any given pH can result in dramatically different sorption behaviors. The fact that individual characteristics of natural organic matter (NOM) play an important role in mobilizing Cd is well known [10,11]. Predicting how NOM from different soils will affect Cd mobility, however, is not well understood. For instance, if Cd binds to insoluble organic matter, or soluble organic matter that is bound to soil minerals, the Cd is immobilized. However, if Cd is bound to NOM that can be leached from the soil, NOM can serve to mobilize Cd. Unfortunately, it is extremely difficult to separate the effects of the soil minerals on metal solubility from the effects of NOM. This separation is particularly difficult in the natural environment where soil pH can vary within the soil horizon. Soil pH affects not only the mineral and NOM ligand availability, but NOM solubility, as well as oxide and carbonate speciation [8].

1.4. Cadmium mobility

Cadmium associated with NOM is immobile as long as the organic matter itself is immobile. However, if the NOM

complexed with Cd is decomposed, the metal may be released to the environment. In the past 30 years, the earth's northern climate has warmed appreciably. Mounting evidence suggests that climate warming is being amplified at the earth's polar regions [12]. A warmer northern climate could lead to the gradual loss of circumpolar permafrost. Northern soils are estimated to contain 25–33% of the world's soil carbon, much of which is frozen in permafrost as poorly decomposed plant remains. Continued warming of the earth's climate would lead to the decomposition of this NOM. If NOM is a controlling factor in Cd immobilization in boreal soils, climate change could trigger a net release of Cd from these soils.

2. Materials and methods

2.1. Field sampling

The soil used in this study was collected from the Caribou Poker Creeks Research Watershed (CPCRW), 31 miles Northeast of Fairbanks, Alaska at 65°10'N, 147°30'W. The CPCRW is an important component of the Bonanza Creek Long Term Ecological Research (LTER) Program. Research conducted at the LTER is aimed at collecting and publishing scientific measurements for use by scientists worldwide. In addition, process studies on the interactions between contaminants, permafrost, hydrology, and meteorology are being conducted.

The CPCRW is underlain by discontinuous permafrost and has bedrock of highly fractured schist [13]. The CPCRW is entirely within the Yukon–Tanana metamorphic complex [14]. Chapman et al. [15] described the complex in the watershed as a greenschist facies metapelite, dominated by chloritic and quartz–mica schists, with some micaceous quartzites, garnet–mica schists, phyllites, and possible greenstone or impure marble.

Soil samples were collected from an open black spruce forest, 200 m North of the confluence of Caribou Creek and Poker Creek. The vegetation at the sampling site was classified as coniferous woodland [16] and is typical of the open black spruce stands that develop in poorly drained soils overlying shallow permafrost. The forest floor vegetation was dominated by Sphagnum moss and sparse, low growing shrubs. The soils were classified as a Saulich silt loam, characteristic of foot slopes throughout the region [17]. The Saulich formation is described as a loamy, mixed, nonacid histic pergelic cryaquept inceptisol [17]. In this area, permafrost is normally encountered less than 50 cm below the surface. The full depth of seasonal thaw, however, is not reached until late August. The samples for this study were collected in June, 2000 when the thaw depth was approximately 10 cm. Samples were collected from a soil pit dug to a depth of approximately 25 cm. The materials collected represented an O1 horizon with a thickness of approximately 12 cm, an O2 horizon with a thickness of approximately 8 cm

and an A1 horizon collected from a depth between 20 and 25 cm. The O1 horizon consisted of undecomposed Sphagnum moss, the O2 horizon consisted of dark reddish brown finely divided peat with roots, and the A1 horizon consisted of very dark grayish brown silt loam. Very few peat fragments were present in the A1 horizon. Soil horizons were separated in the field and transported to the laboratory in 20 l coolers.

2.2. Analytical procedures

2.2.1. Determination of the natural abundance of Cd

Subsamples of each of the soil horizons were homogenized, dried, ground and analyzed by the University of Alaska Fairbanks, Agricultural and Forestry Experiment Station using ICP on an Optima 3000 XL. All analyses were run in duplicate.

2.2.2. Determination of K_d

An experiment was conducted to determine the K_d of the soil/Cd solution. Soil samples from the O1, O2 and A1 horizons were analyzed separately. All samples were homogenized, air-dried and sieved through 1 mm mesh screen. A 500 mg sample of dry soil was then added to 20 ml of an aqueous solution of cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$) containing 10, 20, 50, 100, 250, 500, or 1000 $\mu\text{g/l}$ of Cd. The pH of all the samples was set to 7 ± 0.1 by adding either 0.1 Molar (M) sodium hydroxide (NaOH) or 0.1 M nitric acid (HNO_3). A soil pH of 7 was chosen to establish a basis for comparison. The solutions were agitated for 72 h on a Eberbach shaking table at 120 revolutions per minute (rpm), in a room held at $20 \pm 1^\circ\text{C}$ to reach equilibrium. Following the equilibrium period, the soil was separated from the solution by filtering the soil solution through a 0.45 μm glass fiber filter. The Cd concentration in the soil samples was determined by atomic adsorption (AA) as described below. K_d was calculated as the total Cd in the system, including natural abundance Cd, divided by the Cd in solution.

2.2.3. Determination of cadmium distribution among particle sizes

For each of the three soil horizons, 50 g of wet soil was added to 2 l of an aqueous solution containing 50 $\mu\text{g/l}$ of Cd. The soil solutions were adjusted to a pH of 7 ± 0.1 by adding either 0.1 M NaOH or 0.1 M HNO_3 . The soil solutions were then agitated for 72 h on an Eberbach shaking table at 120 rpm, in a room held at $20 \pm 1^\circ\text{C}$. Sorption of Cd to soil is normally rapid, with more than 90% occurring within the first 10 min [18]. After 72 h of mixing, the samples were passed through a 75 μm sieve and a 0.3 μm glass fiber filter in series. Sub-samples of the solids remaining on the 75 μm sieve and the 0.3 μm glass fiber filter were collected, as was the liquid passing the 0.3 μm filter. The NOM in all samples was analyzed by py-GC/MS and loss on ignition (LOI). The Cd in all samples was analyzed by AA.

2.3. Cadmium analysis

Except for the analysis of the natural abundance of Cd, all Cd analyses were conducted as follows.

2.3.1. Sample digestion

Solid or liquid samples were transferred to an Erlenmeyer flask and acidified to $\text{pH} < 2$ using 10 ml of 15 M HNO_3 . The total volume was increased to 100 ml with deionized (DI) water. The samples were then heated on hot plates to reduce the volume to 20 ml. The concentrate was filtered through a 0.45 μm glass fiber filter into a 100 ml volumetric flask and diluted to 100 ml. The concentration of Cd was then determined by AA.

2.3.2. Atomic absorption

A Perkin–Elmer 300 HGA 850 graphite furnace AA (GFAA) was used to determine the Cd content for each sample. A total of 2 ml of concentrated acid from the soil/water digestion was pipetted into the GFAA auto sampler. The sample was then introduced into an electrically heated graphite tube. The electro-thermal vaporization atomized the entire sample and retained the atomized sample in the light path at wavelength of 228.8 nm. The instrument was operated with a linear standard curve ranging between 1 and 20 ppb Cd. A new standard curve was prepared each time the instrument was run.

2.4. Py-GC/MS of soil and water samples

Solid samples collected for py-GC/MS analysis were oven-dried at 60°C , ground, homogenized, and stored in a desiccator until analyzed. For the liquid samples passing the 0.3 μm filter, 1 liter of sample was reduced to a volume of approximately 20 ml in a Buchi RE111 Rotovap vacuum evaporator at 40°C . This concentrate was poured into a 4 oz jar and oven dried at 60°C until the sample dried completely. The duration of the drying phase lasted between 2 and 3 days, depending on the concentrate volume. When dried, the residue was scraped free from the jar, ground to a fine powder, homogenized, and stored in a desiccator until analyzed by py-GC/MS.

Py-GC/MS was conducted with a CDS Pyroprobe 2000 pyrolyzer with AS2500 autosampler mounted on an HP 6890 gas chromatograph with a Restek Rtx35-MS column, $30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$. Pulsed splitless injection was used, with pulse pressure at 25 psi. The pyrolysis interface and GC injection port were kept at 280°C . Before pyrolysis, the sample was held in the 280°C chamber for 15 s while the chamber was purged with helium carrier gas. The pyrolyzer was then switched online to the GC and pyrolysis began. The pyrolyzer temperature was ramped at 10°C/ms to 700°C and held constant for 10 s. After 1 min, the pyrolyzer was switched off-line and the column head pressure was reduced to provide a constant flow of helium at 2.0 ml/min. The GC temperature program was 40°C for 30 min, then ramped at

Table 1
Compounds identified in chromatograms from py-GC/MS

Compound	Likely origin
Dimethyl benzene	Aromatic hydrocarbon precursors (AHP)
Furfural	Primary polysaccharides (Ps)
Trimethylbenzene	AHP
2-Furancarboxaldehyde, 5-methyl	Ps or secondary polysaccharide
Phenol	Protein (Pr) or phenol precursors (PP)
3-Methylhydantoin	Unknown
Methyl indene	AHP
Larixinic acid	Unknown
2-Methyl naphthalene	Unknown
4-Vinyl 2-methoxy phenol	Lignin
di-Isohexyl ethylene	Lipids

1 °C/min to 120 °C ramp at 2 °C/min to 220 °C, with a final ramp at 10 °C/min to 280 °C and held for 10 min to clean out the column in preparation for the next sample. The GC was plumbed directly to an HP 5973 Mass Selective Detector on electron impact (EI) mode. The MS scanned mass units 45–350. All mass spectra were compared to the Wiley 275 spectral library.

A total of 11 compounds were identified by py-GC/MS as dominant compounds in the soil and water pyrolyzates (see Table 1). These 11 compounds were further referred to as “index” compounds. The chromatographic areas of all 11 index compounds were summed in each chromatogram to find the total index area for each chromatogram. For every sample, the “fraction of index” for each of the 11 compounds was calculated. The fraction of index for each compound was used to determine if any one compound or group of compounds could help explain the distribution of Cd in the different soil horizons and particle sizes. This method was used previously to better understand the role of organic matter on soil formation processes [19,20].

2.5. Loss on ignition (LOI)

Samples of dry solids were collected for LOI. The LOI test was conducted by determining the mass lost following sample combustion in a Sybron Thermolyne Furnatrol muffle furnace at 550 °C for 4 h. The LOI was used to approximate the percent NOM of the samples.

3. Results and discussion

3.1. Natural abundance of cadmium

The natural abundance of Cd for the O1, O2 and A1 horizons was 8.27, 10.57, and 8.87 mg/kg, respectively. These values are higher than the 0.01–7 mg/kg range of Cd normally found in non-agricultural soils [21]. This may be the result of the thin layers of volcanic dust that occur throughout the soil profile. The results suggest that the boreal soil

either had a high proportion of fixed Cd (i.e., Cd in mineral complexes), or the soil had a high complexation capacity for Cd, or both.

3.2. K_d for Cadmium in O1, O2 and A1 horizons

The K_d for the O1, O2 and A1 horizons was 45 ± 1.5 , 44 ± 1.2 and 43 ± 0.81 /kg, respectively, where “ \pm ” values represent 95% confidence intervals. In comparison to the study by Sauve et al. [8], these soils are near the low end of the range of K_d values. A low K_d means that a large proportion of the total Cd is in the soil solution, or bound to colloidal material smaller than 0.45 μm . This result suggests that a large percentage of the Cd in these boreal soils can be mobilized in the soil solution under the appropriate conditions. Using the data collected to calculate K_d , Langmuir isotherms were plotted, revealing a “ q_{max} ”, of 1.7, 1.6, and 2.0 mg/kg for the O1, O2 and A1 horizons, respectively. This result shows that at pH 7, the maximum amount of Cd associated with the soil solids was well below the natural abundance. This result suggests that when suspended during the experiment, much of the Cd originally present in the soil was liberated to the soil solution, most likely in colloidal complexes.

3.3. Cadmium distribution in the particulate samples

Fig. 1 represents the percent of Cd associated with the different particle size ranges for each soil horizon. The results showed that less than 7% of the Cd was dissolved or associated with particles smaller than 0.3 μm for all three horizons. This result was compared to results of testing done to determine the K_d values for the same soil/Cd solution concentration. In the determination of K_d , Cd passing a 0.45 μm

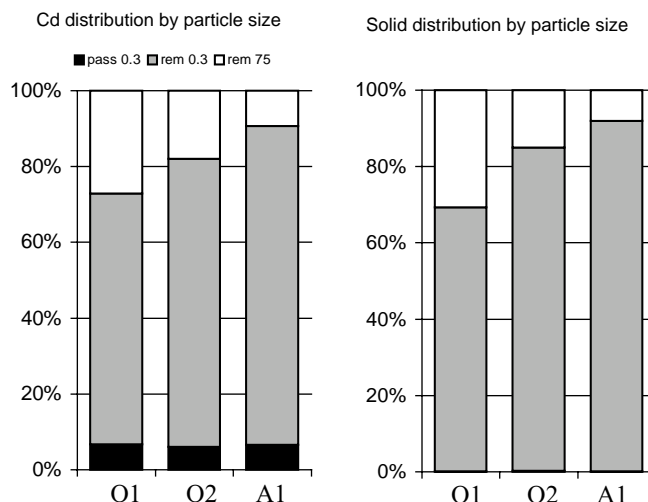


Fig. 1. Cadmium and solids abundance as a function of particle size. The legend is the same for both panels. In the legend, “pass 0.3”, material passing a 0.3 μm filter; “rem 0.3”, solids retained on a 0.3 μm filter and “rem 75”, solids retained on a 75 μm sieve.

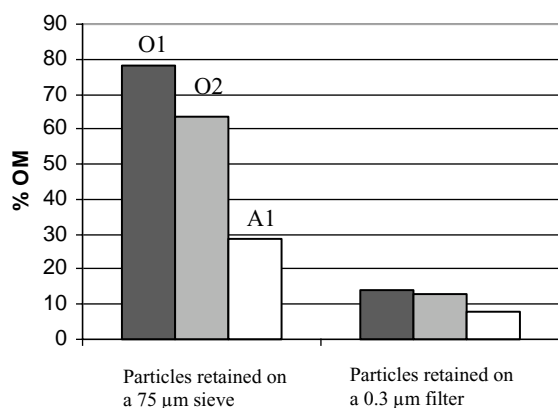


Fig. 2. Percent organic matter in the particle size range for the O1, O2 and A1 soil horizons. On the vertical axes, OM, organic matter was defined by loss on ignition.

filter represented 83, 86, and 90% of the Cd for the O1, O2 and A1 horizons, respectively. However, only 6.8, 6.1 and 6.8% of the Cd in the O1, O2 and A1 horizons, respectively, passed a 0.3 µm filter. This result suggests that the Cd was mostly associated with the colloidal matter smaller than 0.45 µm but larger than 0.3 µm. The abundance of the Cd associated with particles greater than 0.3 µm was in direct proportion to the abundance of particles in each size range for all horizons (see Fig. 1).

A mass balance for this experiment accounted for 82, 81 and 84% of the Cd for the O1, O2 and A1 horizons, respectively. This included both the natural abundance Cd and the Cd added. It is believed that the Cd not accounted for was associated with particles trapped in the filters or lost on glassware.

Since sorption is a surface phenomenon, we expected to find the highest concentration of Cd associated with the smaller particles [22,23]. In the O1 horizon, approximately 10 mg/kg Cd were found on particles larger than 75 µm and 10 mg/kg Cd were found on particles in the size range 0.3–75 µm. This result suggests that the smaller particles did not preferentially sorb Cd on a per mass basis. In the O2 horizon, 12 mg/kg of Cd was associated with particles larger than 75 µm whereas only 9 mg/kg were found on particles

in the 0.3–75 µm size range. The same pattern was observed for the A1 horizon, where 11 mg/kg Cd were found on the particles larger than 75 µm and only 9 mg/kg Cd were found on the particles in the 0.3–75 µm size range. The fact that the same or greater mass fraction of Cd was found on the larger particles was attributed to the higher mass fraction of NOM in the largest particle size fraction. Approximately 80% of the NOM in all horizons was present as particles larger than 75 µm (Fig. 2). In all three horizons, the mass of particles present in the size range smaller than 0.3 µm represented less than 0.2% of the total solids in the soil. While approximately 6% of the Cd was associated with the solution passing the 0.3 µm filter, it was not determined what fraction of the Cd was colloidal and what fraction was dissolved.

3.4. Relationship between NOM and cadmium

Py-GC/MS was conducted on particulate and water samples in an attempt to understand the possible relationship between NOM speciation and Cd distribution. The relative abundance of a group of compounds, including aromatics, phenolics, indenenes, and furfurals were considered. Of particular interest were the polysaccharides, since Zakaria [24] found that polysaccharides associated with bacteria sorbed large amounts of Cd. Furfurals and furans are known pyrolysis products of polysaccharides. As shown in Fig. 3, the polysaccharides (i.e., furfural and 5-methyl-2-furancarboxaldehyde) were in approximately the same relative abundance in the O1, O2 and A1 soil horizons even though the organic matter percentage ranged from 8 to 78%. Since bacteria preferentially degrade polysaccharides, one normally expects them to be depleted in the well-decomposed NOM normally found in an A1 horizon [25,26].

These results suggest that organic matter may be equally effective at complexing Cd whether it is in the undecomposed O1 horizon, or the more humified A1 horizon. The percentage of NOM in each particle size fraction could also help explain why the particles larger than 75 µm sorbed a greater mass fraction of Cd than the particles in the size range 0.3–75 µm. Since organic matter appears to be an important

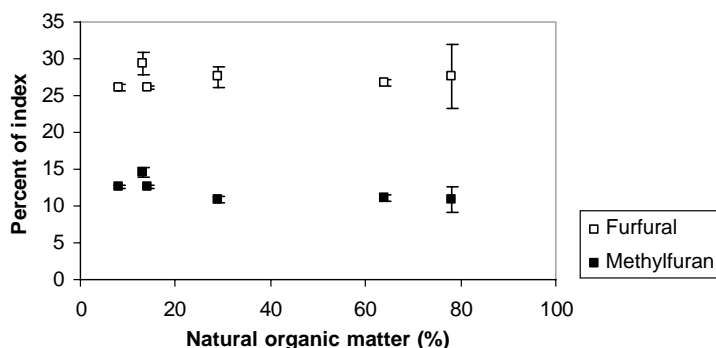


Fig. 3. Graph shows percent NOM vs. percent of index for polysaccharides in the O1, O2 and A1 horizons. In the graph, data represents solids retained on a 0.3 µm filter and solids retained on a 75 µm sieve. Error bars represent 95% confidence intervals. In the legend, "Methylfuran" represents 5-methyl-2-furancarboxaldehyde.

factor in binding Cd in boreal soil, decomposition of the organic matter, particularly polysaccharide compounds, could result in Cd liberation to the soil solution. Organic matter decomposition is a significant concern in boreal soils where permafrost is slowly thawing, exposing greater amounts of NOM to decomposition [12].

4. Conclusion

The objective of this research was to better understand the mobility of Cd in organic rich, boreal soil. This study was motivated by the relatively high concentrations of Cd found in the soils tested, and the fact that Cd sorption to soils is highly site specific. Results showed that while the soils had a comparatively high natural abundance of Cd, the K_d for these soils was relatively low. One would normally expect soils with a high natural abundance to have a high K_d . The low K_d in this case was attributed to the fact that a large proportion of the Cd in the soils tested was associated with fine particles smaller than $0.45 \mu\text{m}$.

Our results suggested that Cd was mainly associated with particulates greater than $0.3 \mu\text{m}$ but smaller than $0.45 \mu\text{m}$. Based on this data, the Cd seems to be trapped in the soil in the very fine particulate, or colloidal matter. Due to its high natural abundance, this Cd seems to be stable in the soil. However, due to its apparent small particle size, colloidal Cd could be transported long distances if released into water courses by erosion or other surface disturbance.

Since particles ranging in size between 0.3 and $75 \mu\text{m}$ were most abundant in the three soil horizons analyzed, most Cd was associated with these particles. On a per mass basis, however, more Cd was associated with particles greater in size than $75 \mu\text{m}$ than on particles in the 0.3 – $75 \mu\text{m}$ size range. The higher mass fraction of Cd associated with the larger particles was attributed to the high percentage of organic matter in this fraction. It is believed that this fraction of Cd could be liberated as the organic matter decomposes into humus. The release of metals from organic matter is a concern for northern soils that are gradually warming and being exposed to greater decomposition. This study showed that the boreal soil tested may be a source of Cd that could be quite mobile in a colloidal phase if liberated from the soil environment through leaching, erosion, or other soil disturbance.

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