

Effect of Deicing Salts on Metal and Organic Matter Mobilization in Roadside Soils

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■ Roadside soils were sampled from areas that receive heavy traffic and deicing salts. These soils were leached in columns at 6 °C with solutions of NaCl, calcium magnesium acetate (CMA), or deionized water to simulate the runoff of salty water from a roadway followed by snowmelt or rainwater. In the salt solution leachates, the concentrations of Cr, Pb, Ni, Fe, Cd, and Cu tended to increase with increasing salt concentration, suggesting that ligand complexation and competitive exchange affected mobilization. In the soils leached initially with NaCl, followed by deionized water, extensive mobilization of organic matter and elevated concentrations of Cr, Pb, Ni, Fe, and Cu were observed. The dominant mechanism controlling metal mobilization was dispersion of organic matter under conditions of high exchangeable Na and low electrolyte concentration.

Introduction

The widespread use of NaCl for snow and ice removal from roads has resulted in environmental impacts in many areas. Some of the problems associated with the use of NaCl are the corrosion of bridges, road surfaces, and vehicles and damage to roadside vegetation and aquatic systems that receive water from deiced roads (1). Contamination of drinking water supplies is a serious side effect from road salt use. Several states in the northeast United States and Canada have measured Na from road salt in well waters at concentrations that are 2–140 times the recommended limit for individuals on salt-restricted diets (2, 3). The state of Michigan has considered a bill to ban the use of NaCl as a deicer. In California, the Lake Tahoe and Mammoth Lakes areas and Donner Pass are environmentally sensitive regions that have been adversely impacted by the use of NaCl as a deicer (4). Average Cl⁻ concentration in runoff water in these areas is 8 mmol L⁻¹ and a maximum of 58 mmol L⁻¹ has been measured (4).

As an alternative to NaCl, calcium magnesium acetate (CMA) is gaining popularity in several areas around the United States and Europe. CMA at a Ca:Mg ratio of 3:7 has been found to be the most effective deicer (5) and is less toxic to fish, zooplankton, and phytoplankton and less corrosive than chloride salts (6). There are, however, potential indirect consequences of CMA application such as the possibility of trace-element mobilization.

Emissions from vehicles have resulted in high levels of trace metals in roadside soils (7, 8). Tetraethyllead in gasoline is the major source of Pb in roadside soils, while diesel oil (Cd), tire attrition (Zn, Cd), steel parts attrition (Ni, Cr, V, W, Mo) and the wear of bearings and bushings (Cu) all contribute trace metals to roadside soils. Because acetic acid, sodium acetate, and ammonium acetate have been used for metal extractions in soils (9–11), there is concern that CMA may increase the concentration of metals in soil solutions and ultimately lead to increased metals in groundwaters and surface waters (6). Ca and Mg are better competitors than Na for cation-exchange sites and may displace trace metals from cation-exchange sites to a greater extent than Na. This may be an important mechanism by which Cd is mobilized because studies have reported between 20 and 26% of the Cd in soils and road

dusts is readily exchangeable (12, 13). Cation-exchange reactions are expected to be less important for Pb mobilization because Pb is more strongly associated with organic matter. It has been reported that less than 1.5% of the Pb in road dust and roadside soils is exchangeable with 1.0 M MgCl₂ (12, 14). In addition, acetate forms stronger metal-acetate ion pairs than Cl, potentially increasing the trace-metal concentration in solution. It has been found that high concentrations of NaCl (0.1 and 0.5 M) leached 1.1–4 times more Ni, Cu, and Cd from a soil than an equal concentration of NaClO₄ (15). The increased trace-metal mobility in soils leached with NaCl was attributed to the metal-Cl complexes.

A field study showed that a shallow groundwater in southern Ontario, Canada, had elevated Na, Cl, Ca, and Mg concentrations due to road salt use (3). However, there was no difference in Zn, Cd, Ni, Pb, or Cr concentrations in water below urban roadside soils and in water below fallow fields. These findings suggest that runoff waters may not be solubilizing trace metals even though Na and Cl are reaching groundwater.

In this paper, we report the effect of road salts (NaCl and CMA) on trace-metal and organic matter mobility in roadside soils at salt concentrations that are typical for runoff waters. Because CMA is proposed as an alternative to NaCl, the mobility of metals in CMA-treated soils was compared with NaCl treatments at equal concentrations and with distilled water (snowmelt). This was done to determine the degree to which CMA might contribute to trace-metal contamination of groundwater.

Experimental Section

Materials. Roadside soil samples were collected from Donner Pass, CA; Albany and Buffalo, NY; and Cape Cod, MA. The Donner Pass, CA, soil was collected off of Interstate 80 eastbound between Kingvale and Soda Springs. The Albany, NY, soil was collected off of Interstate 487 north of Interstate 87. The Buffalo, NY, soil was collected at the intersection of Interstate 209 and Interstate 190. The Cape Cod, MA, soil was collected at the southern end of Interstate 495. The soil classifications are given in Table I. The Albany, Buffalo, and Donner soils were chosen for their long-term, high salt use and heavy traffic. The soil collected at Cape Cod, MA, was next to a new road that had not yet received NaCl but had received one winter's use of CMA. All soils were collected within 3 m of the road at a point where snow and water would accumulate or where snow was dumped from the road. Each soil was sampled at three depths; a surface sample (0–5 cm) was collected and then the remaining A horizon (generally 5–15 cm), and a deeper sample (often the B horizon, as determined by a change in structure or clay content). In addition, a sample of road dust/sand was swept from the road's shoulder within 0.5 m of the road and adjacent to the soil sampling site. The soils were sampled in early November, prior to snowfall, and were air-dried and crushed to pass a 2-mm sieve.

These samples were analyzed for total trace-metal concentration (Cu, Fe, Ni, Cd, Cr, Pb), cation-exchange capacity (CEC), exchangeable Na, soluble salts, texture, pH, CaCO₃ and organic matter content. Total trace metals

Table I. Characterization of the Roadside Soils^a

depth sampled, cm	texture			saturatn water content, L kg ⁻¹	electr conductiv sat ext (25 °C), dS m ⁻¹	sat paste pH	Na ⁺ sat ext, mM	CaCO ₃ , %	CEC, mol _c kg ⁻¹	exchangeable sodium percentage ESP ^c	% organic C
	sand, %	silt, %	clay, %								
Cape Cod Soil											
shoulder	89	7	4	0.28	1.12	5.5	1.6	<0.1	0.14	1.7	3.3
1-5	74	19	7	0.21	0.70	5.5	1.3	0.1	0.11	1.4	4.1
5-15	78	15	7	0.19	0.59	5.4	2.4	<0.1	0.13	1.5	1.3
>15	65	26	9	0.26	0.41	5.1	2.0	<0.1	0.14	1.3	1.7
Albany Soil											
shoulder	77	16	7	0.24	1.53	7.3	2.1	5.6	0.10	2.2	1.8
0-5	60	30	10	0.38	0.80	7.3	0.5	1.0	0.17	1.3	1.9
5-20	67	21	10	0.28	0.64	7.5	0.8	1.2	0.13	1.7	1.1
>20	46	39	15	0.31	0.50	7.7	1.7	1.3	0.16	1.4	1.0
Donner Soil											
shoulder	89	7	4	0.19	2.54	7.6	20	0.2	0.078	8.4	1.0
0-5	89	8	3	0.20	8.83	6.4	75	<0.1	0.089	18	0.80
0-15	78	17	5	0.21	1.84	6.4	16	<0.1	0.10	13	0.73
>15	67	29	4	0.18	1.46	6.5	12	<0.1	0.11	11	0.43
Buffalo Soil											
shoulder	83	13	4	0.23	1.12	7.8	3.4	17.8	0.096	3.4	5.3
0-5	31	48	21	0.72	1.66	7.5	6.4	6.6	0.31	2.9	7.4
5-18	23	54	23	0.53	1.77	7.6	10.2	5.4	0.31	4.4	5.5
>18	16	58	25	0.54	1.90	7.5	11.8	5.8	0.26	6.1	4.1

^a Cape Cod: Carver series; mesic, uncoated Typic Quartzipsamment. Albany: Genesee series; fine-loamy, mixed, nonacid, mesic Typic Udifluent. Donner: Tallac series or Bucking variant; sandy mixed frigid Entic Xerumbrupt. Buffalo: Odessa series; fine, illitic, mesic Aeric Ochraqualf. ^bCEC, cation exchange capacity. ^cESP, exchangeable sodium percentage.

were determined using a hot HNO₃/HClO₄ digest (9) and atomic absorption spectrophotometry as described below. The procedures for CEC, exchangeable Na, soluble salts, texture, pH, and CaCO₃ content were from ref 16. Organic matter content in the soils was determined by solid combustion on a Dohrmann carbon analyzer and the CaCO₃ content subtracted from this value.

Trace metals (Pb, Cd, Cr, Ni, Cu) were analyzed by graphite furnace atomic absorption spectrometry with Zeeman background correction using the method of standard additions and either palladium + citric acid or Mg(NO₃)₂ as a matrix modifier. Iron was analyzed by flame atomic absorption spectroscopy. All metal standards were prepared in reagent-grade salt backgrounds as well as distilled H₂O to check for possible interferences due to high salt concentrations. Metal analyses were periodically checked with National Institute for Standards and Technology quality control standards.

The deicing salts used were mined NaCl from the state of Kansas and CMA from the Chevron Chemical Co. The CMA had a reported composition of 91% (minimum) Ca_{0.3}Mg_{0.7}(C₂H₃O₂)₂, 5% H₂O (maximum), and 4% insoluble material (maximum). Analysis of the actual CMA found 95.1% Ca_{0.29}Mg_{0.71}(C₂H₃O₂)₂, 3.4% water, and 1.4% insoluble material. This insoluble fraction consisted of calcite (85%); amorphous iron, aluminum, and manganese oxyhydroxides (3.5, 2.4, and 0.4%, respectively); 1.1% organic C (not acetate); and traces of quartz and talc. Trace contaminants were determined by X-ray diffraction; acid dissolution and atomic absorption analysis for Fe, Al, and Mn; and total C analysis by furnace combustion at 950 °C and infrared detection of CO₂ before and after carbonate removal (Dohrmann carbon analyzer). Carbonates were determined by acid reaction and manometry.

Methods. Soil column leaching experiments were conducted to evaluate the mobility of metals and organic matter through reconstructed soil profiles.

The soils were packed into 50-mL plastic syringes in 7.5-g layers. The depth of each layer in the column did

not necessarily correspond to the actual horizon depth measured in the field. To simulate trace-metal pickup from road runoff, 7.5 g of road dust was added to the surface of the soil column. The columns contained a total of 30 g of soil + road dust. The soils were leached at a constant rate using a mechanical vacuum extractor (Centurion International, Model 24; see ref 17 for a schematic diagram) at 6 °C in a constant-temperature cold room.

Two leaching experiments were carried out. In the first experiment, 175 mL of salt solution was drawn through the Cape Cod soil, followed by 105 mL of distilled water (DW; snowmelt). The rate of leaching was 35 mL through each column over a 12-h period. The pore volume of the column was 7.1 mL. The salt solutions used were 10 and 100 mmol_c L⁻¹ NaCl and 10 and 100 mmol_c L⁻¹ CMA. In the second experiment, the Albany, Buffalo, and Donner soils were leached in 30-mL increments, first with 90 mL of salt solution and then 90 mL of distilled water. The rate of leaching was 30 mL through each column over a 12-h period. The pore volumes for the Albany and Buffalo soils were 9.1 and 15.2 mL, respectively. The salt solutions used were 10 and 100 mmol_c L⁻¹ CMA; 10, 50, and 100 mmol_c L⁻¹ NaCl; and distilled water. These experiments were designed to simulate an input of salty runoff water to a soil followed by rainfall or snowmelt. The 10 mmol_c L⁻¹ solution is representative of an average salt concentration for runoff waters and the 100 mmol_c L⁻¹ solution represents a worst case situation.

The pH of each of the leachates was measured at 6 °C at the time of sampling and the solutions were filtered through 0.45-µm membrane filter. The first 1-2 mL of filtrate was discarded to rinse the filter and reduce adsorption of organic carbon by the filter. The filtrate was analyzed promptly for dissolved organic carbon (DOC) on a Dohrmann carbon analyzer. The absorbance at 254-nm wavelength was measured on the leachates to quantify the concentration of humic and fulvic acids in solution (refs 18 and 19 and references therein). Absorbance at 254 nm is a good measure of native soil organic matter in solution

Table II. Total Metal Concentrations

depth, cm	concn, mg kg ⁻¹					
	Cu	Cd	Ni	Pb	Cr	Fe
Cape Code Soil						
shoulder	16	0.31	5.5	14	23	11 600
1-5	4.5	0.82	3.0	6.9	15	9 800
5-15	4.0	0.040	3.0	5.4	14	9 200
>15	4.0	0.036	4.0	6.6	47	10 500
Albany Soil						
shoulder	186	3.1	47	939	187	38 600
1-5	34	0.39	28	53	64	25 500
5-15	32	0.30	28	30	54	27 900
>15	40	0.51	53	65	23	25 500
Donner Soil						
shoulder	16	0.43	11	94	36	16 200
1-5	20	0.25	8.0	62	37	22 500
5-15	24	0.19	5.5	97	34	28 500
>15	25	0.14	4.0	38	28	26 800
Buffalo Soil						
shoulder	191	5.3	41	505	96	59 500
1-5	47	1.5	29	167	62	26 000
5-15	38	1.2	29	134	65	30 300
>15	27	0.49	27	51	55	29 300

without the interference of acetate. Absorbance of a 0.1 M acetate solution was equal to distilled water.

The solutions were then acidified to pH 2 with Baker Instra-Analyzed HNO₃. Cd, Cr, Pb, Ni, Fe, and Cu were determined on the leachates as mentioned earlier.

The water infiltration rates of the soils were determined following the leachings. Water was ponded to a depth of 5 cm on the soil and the columns were allowed to drain by gravity. The head was maintained near-constant by periodic additions of water and the volume of leachate used to calculate a flux.

Results

Total trace-metal concentrations in the roadside soils (Table II) are comparable to reported concentrations in urban roadside soils (7, 12, 13, 20). The concentrations of trace metal in samples swept from the shoulder were generally higher than the soil, and metal concentration decreased with soil depth. The Cape Cod soil, collected adjacent to a new road, had metal concentrations comparable to an uncontaminated soil. The physical and chemical compositions of these soils are given in Table I. The Buffalo soil had the finest texture and highest organic matter (OM) content. Both the Donner and Cape Cod soils were coarse textured and leached readily. These two soils were slightly acid and the Albany and Buffalo soils were calcareous.

The concentrations of Cd in the leachates from the Cape Cod soil are given in Figure 1 and show that, initially, the high-salt solutions mobilized more Cd than the low-concentration salt solutions. This supports the hypotheses mentioned earlier that Cd may be mobilized through a cation-exchange process and/or complexation by Cl and acetate. Upon addition of the deionized water, no further Cd was mobilized. The data for the mobilization of Cr from the Cape Cod soil are presented in Figure 2 and show that, initially, the CMA solutions solubilized more Cr than did the NaCl solutions. Upon addition of the deionized water, elevated concentrations of Cr were measured in the solutions from the columns initially leached with NaCl. Associated with the elevated Cr concentration was dissolved organic matter (Figure 3). We suspected this because the deionized water leachates were slightly yellow-brown in color. The concentration of these fulvic and

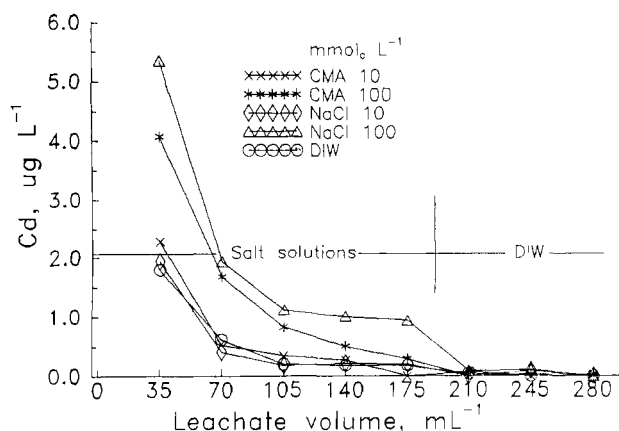


Figure 1. Leachate volume vs Cd concentration for the Cape Cod soil leached with CMA and NaCl solutions.

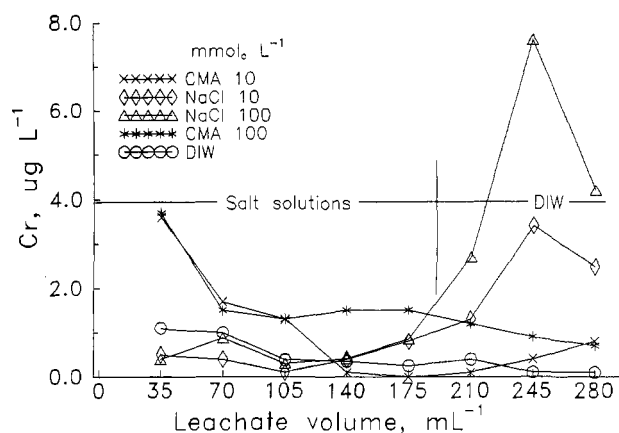


Figure 2. Leachate volume vs Cr concentration for the Cape Cod soil leached with CMA and NaCl solutions.

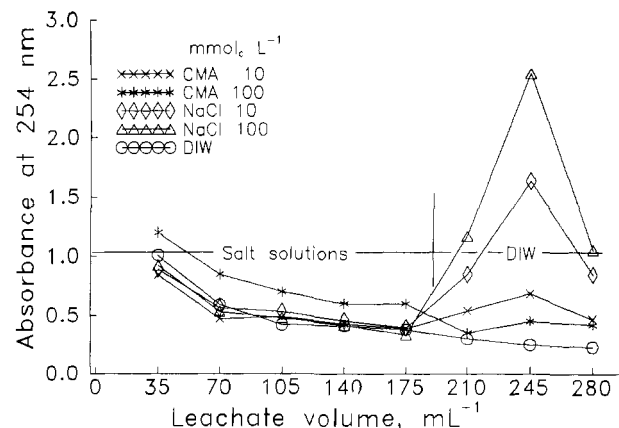


Figure 3. Leachate volume vs organic matter concentration (as measured by absorbance at 254 nm) for the Cape Cod soil leached with CMA and NaCl solutions.

humic acids (as measured by absorbance at 254 nm) is given in Figure 3. Figure 4 shows a good linear relationship ($r^2 = 0.75$) between the Cr concentration in the leachate and the dissolved organic matter concentration, suggesting that the mobilization of OM also mobilized the Cr.

A further test of this observation was pursued in the second set of leachings using the Buffalo, Albany, and Donner soils. The effect of OM on trace-metal mobilization could be focused on because these soils had a wide range of organic matter contents.

The concentrations of soluble fulvic and humic acids in the leachates from the Buffalo, Albany, and Donner soils are presented in Figure 5. In the Buffalo and Albany soils, the columns leached initially with NaCl had the highest

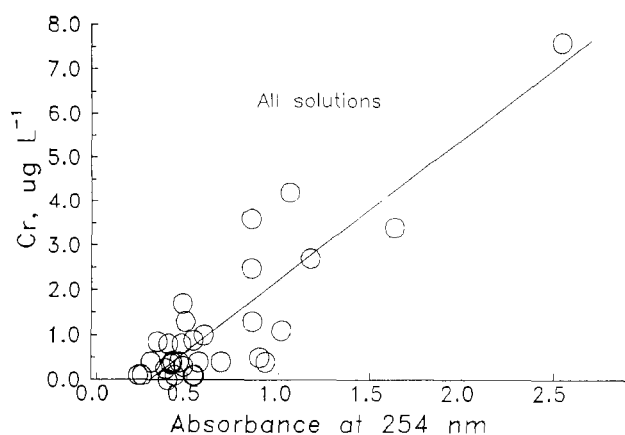


Figure 4. Linear relationship between organic matter concentration and Cr concentration for the Cape Cod soil leached with distilled water and CMA and NaCl solutions.

Table III. Linear Regression Correlation Coefficient (*r*) of Trace-Metal Concentration vs Absorbance at 254 nm (All Solutions)

metal	soil		
	Albany	Donner	Buffalo
Pb	0.67	0.32	0.85
Cd	0.042	0.084	0.63
Cu	0.98	0.97	1.00
Cr	0.91	0.54	0.98
Ni	0.78	0.42	0.87
Fe	0.91	0.12	0.58

amount of OM mobilized. In the Donner soil, the deionized water leached columns mobilized the highest amount of OM. This is attributed to the high exchangeable Na percentage of the Donner soil (Table I). These results support the commonly observed phenomenon that humic and fulvic acids are mobilized under the conditions of high exchangeable Na and low electrolyte concentration. The total amount of OM solubilized was proportional to the organic matter content of the soils (compare the ordinates in Figure 5 with the percent organic carbon in Table I).

Figure 6 shows the relationship between dissolved organic carbon (DOC, as measured by wet oxidation) and the absorbance at 254 nm for the leachates from the Albany, Buffalo, and Donner soils. The CMA-leached soils are not included in this figure because acetate dominates the DOC measurement in these solutions. There is a very good correlation between DOC and 254-nm absorbance, except for the first leachate solutions. Apparently, when the soils were dried, the death of microbes, fungi, and roots released a large pool of water-soluble organic carbon that was not fulvic or humic in structure (that is, it does not have aromatic ring structures which absorb the UV light).

Associated with this UV-absorbing dissolved organic matter were several trace metals, particularly Cu, Pb, Cr, Ni, and Fe. Plotted in Figures 7 and 8 are the relationships between Cu and Pb concentration and dissolved OM, as measured by absorbance at 254 nm, in the Buffalo soil leachates. Table III summarizes this relationship for all the metals analyzed. These data show that the primary factor controlling the concentration of Cu, Pb, Cr, Ni, and Fe in these leachate solutions was the solution concentration of native organic matter. Qualitatively, if organic matter dispersion was an important mechanism controlling metal mobilization, there was a high correlation coefficient (Table III). Cadmium did not follow this trend because Cd is only weakly associated with OM and its Ca-like nature makes competitive exchange and Cl complexation

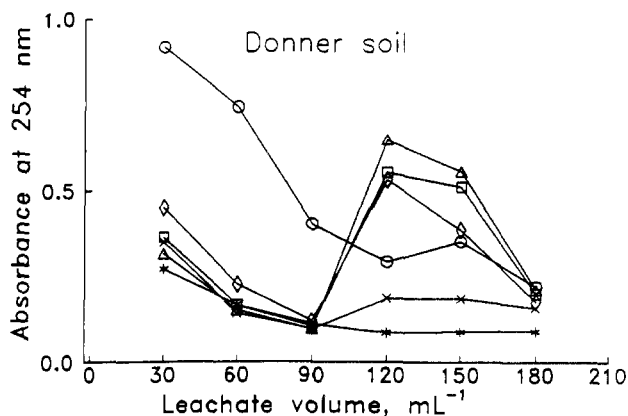
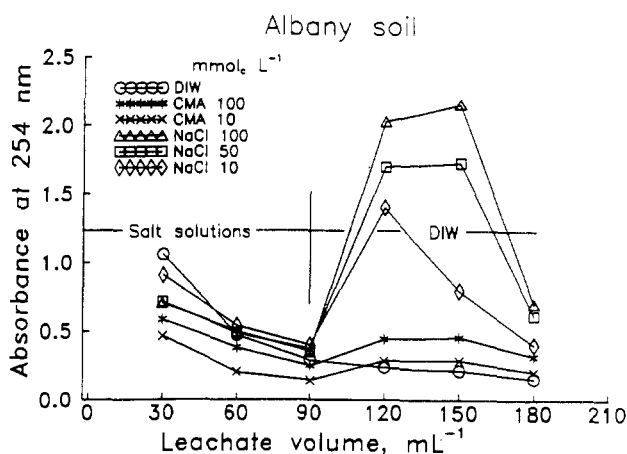
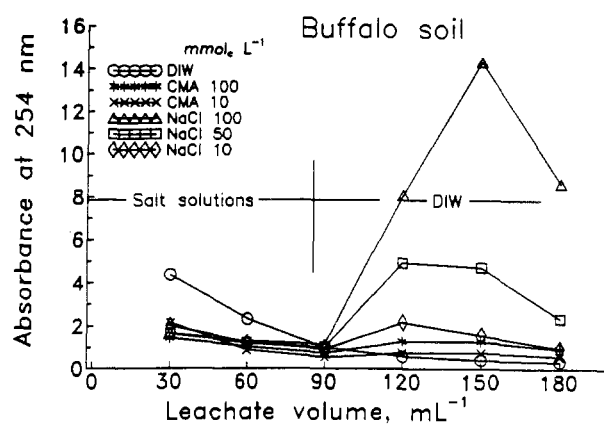


Figure 5. Concentration of soluble organic matter (as measured by absorbance at 254 nm) vs leachate volume as a function of road salt type and concentration for the Buffalo, Albany, and Donner soils.

more important factors in its mobilization.

Table IV summarizes the total mass of trace metals removed in the six leachates from the Albany, Buffalo, and Donner soils as compared to the total mass of metals in the soil. Only a small fraction of the total metals were leached, demonstrating the enormous capacity that soils have for retaining metals. In general, the concentrations of metals in the distilled water and NaCl leachings were controlled by OM mobilization. In the CMA-leached soils, the 100 mmol_c L⁻¹ CMA solution mobilized more metals than the lower concentration solution. In three cases, the 100 mmol_c L⁻¹ CMA solution mobilized more metals than the 100 mmol_c L⁻¹ NaCl solution (Albany, Pb; Donner, Pb and Cr).

Discussion

Water Quality. In all the soils leached with deionized water, NaCl, or CMA, the concentrations of Pb, Cr, Ni, Cd, and Cu in the leachates were always less than the

Table IV. Total Metals Leached from 30 g of Soil (Reconstructed Soil Profile and Road Dust)^a

init solutn, mol _e L ⁻¹	amount, μg					
	Pb	Cd	Cu	Cr	Ni	Fe
Albany Soil						
DW	0.44	0.040	3.1	0.22	0.67	48
0.10 CMA	2.2	0.093	2.6	0.48	0.42	15
0.01 CMA	0.21	0.038	1.9	0.16	0.17	3.0
0.1 NaCl	0.92	0.095	9.1	1.04	1.1	168
0.05 NaCl	0.58	0.044	7.7	0.69	0.99	105
0.01 NaCl	0.17	0.037	5.6	0.36	0.71	34
total in 30 g of soil	8150	32.4	2190	2460	1170	8.8 × 10 ⁵
Donner Soil						
DW	1.17	0.028	2.00	0.15	1.3	75
0.10 CMA	1.51	0.30	0.38	0.12	0.51	4.9
0.01 CMA	0.20	0.10	0.76	0.025	0.23	4.5
0.1 NaCl	0.65	0.45	1.39	0.094	0.91	28
0.05 NaCl	0.47	0.31	1.54	0.080	1.3	20
0.01 NaCl	0.28	0.042	1.28	0.056	0.77	11
total in 30 g of soil	2180	7.58	638	1020	214	7.0 × 10 ⁵
Buffalo Soil						
DW	0.339	0.040	5.5	0.38	1.3	77
0.10 CMA	1.2	0.097	3.8	0.26	0.60	13
0.01 CMA	1.6	0.046	3.3	10	0.68	3.5
0.1 NaCl	2.2	0.20	24	1.90	4.9	509
0.05 NaCl	0.57	0.080	10	0.74	2.5	87
0.01 NaCl	0.24	0.055	5.4	0.23	0.83	19
total in 30 g of soil	6430	63.7	2270	2090	945	10.9 × 10 ⁵

^aLeachate: 180 ml (90 mL initial solution followed by 90 mL of DW).

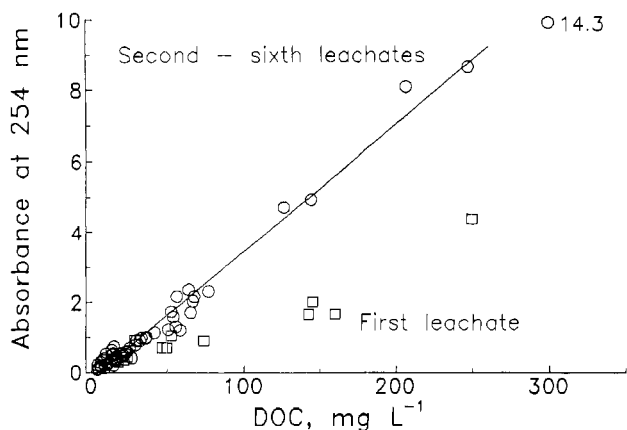


Figure 6. Relationship between dissolved organic carbon (DOC) as measured by wet oxidation to CO₂ and measurement of the evolved CO₂, vs absorbance at 254 nm.

drinking water criteria, which are 50, 50, 632, 10, and 1000 μg L⁻¹, respectively (21). The concentrations of Cd, Pb, and Cr were generally well within the water quality criteria for aquatic life. However, the Cu criterion of 6.5 μg L⁻¹ for freshwater species in soft water was exceeded in 78% of the samples and exceeded the 4-day average value for hard water (21 μg L⁻¹) in 36% of the samples. Thus, Cu mobility appears to be a possible problem if leachate water enters a stream or lake. However, nearly all of this mobilized copper was complexed by native OM and its toxicity is greatly reduced as a result of complexation (22).

The Ni criterion for aquatic life in softwater of 56 μg L⁻¹, at a hardness of 50 mg L⁻¹ as CaCO₃, was exceeded in 29% of the samples. Most of these values were associated with the first increment of leachate or soluble organic matter.

The Fe criterion of 300 μg L⁻¹ for drinking water was exceeded in 23% of the samples and exceeded the 1000 μg L⁻¹ level established for aquatic life 9% of the time. However, these high levels of Fe were never associated with CMA-leached soils and it is noted in the EPA criteria (21)

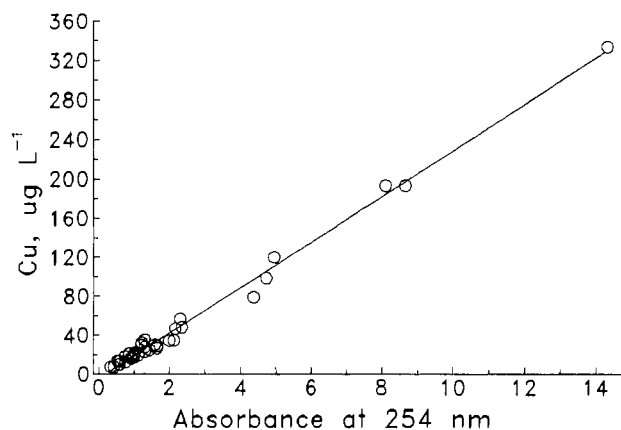


Figure 7. Relationship between soluble organic matter (absorbance at 254 nm) and Cu concentration for the Buffalo soil in column leaching experiment.

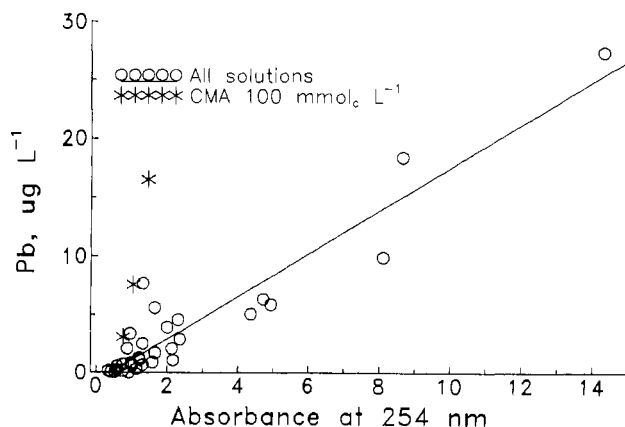


Figure 8. Relationship between soluble organic matter (absorbance at 254 nm) and Pb concentration for the Buffalo soil in column leaching experiment.

that the iron found in "black or brown swamp waters", often at concentrations of several milligrams per liter, "has

little effect on aquatic life". Once again, this suggests that organic matter complexation greatly reduces metal toxicity.

There have been other reports of OM-metal complexes controlling the movement of trace metals. In water samples from a subalpine watershed in Colorado, a linear regression correlation coefficient (r) of 0.96 between Al and DOC was reported (23). The DOC in the water samples ranged from 1 to 4.9 mg L⁻¹, which is very low when compared to a soil solution leachate (Figure 6) and suggests the strong, specific complexation that OM can have for trace metals. In simulated acid rainfall studies on podzolized spruce forest soil, Bergkvist (24, 25) found that the fluxes of Fe, Al, Cu, and Pb were regulated mainly by the formation of water-soluble organic compounds rather than pH, whereas the movement of Na, Ca, Mg, Mn, Cd, and Zn increased with increasing solution acidity.

Modeling. Our attempts to model the effect of OM on trace-metal concentration were not successful for several reasons. First, the concentration of OM in solution was not controlled by any solubility relationship. The reactions that solubilize OM are dispersion and deflocculation reactions, which are strongly affected by the exchangeable sodium percentage (ESP) of the soil and the total electrolyte concentration.

Second, the amount of OM in solution was a good predictor of metal concentration, but only for a particular soil. The relationships between metal concentration vs OM concentration were different for the different soils and these relationships were not related in any simple way to the total OM or metal content of the soils.

Third, the metal-OM stability constants for naturally occurring fulvic and humic acids are quite variable or unavailable. The reported values are inconsistent due to variations in the composition of OM from different sources (marine, peat, coal, soil, aquatic), and variations in the background electrolyte, pH, and the presence of competing metals. In addition, metal-OM stability constants vary as a function of metal concentration. There is evidence that, at very low concentrations of trace metals, stability constants are much larger than typically measured due to site heterogeneity on the OM, with a few sites exhibiting a very strong specific binding for certain trace metals (28). Stability constants are most often determined at metal concentrations of $>10^{-6}$ M (>200 μ g L⁻¹ Pb or >60 μ g L⁻¹ Cu) and may not be representative of actual metal-OM concentration ratios (27-30).

Effects on Soil Structure. The conditions of high exchangeable Na and low electrolyte concentration that result in the mobilization of organic matter also cause clay dispersion and soil swelling. Under these conditions, the hydraulic conductivity of the soil can be greatly reduced. One major benefit of CMA is its effect on roadside soil permeability. The steady-state infiltration rate of the Buffalo soil was 2.8 mm h⁻¹ when leached with 100 mmol_c L⁻¹ CMA. The final infiltration rates measured on the Buffalo soil, initially leached with 100 mmol_c L⁻¹ CMA and NaCl, followed by deionized water, were 2.7 and 0.04 mm h⁻¹, respectively (average of six replicates). The NaCl-leached soil had a final hydraulic conductivity that was on the average 88 times lower than the CMA-treated soil. As a point of reference, an infiltration rate less than 1 mm h⁻¹ makes a soil unsuitable for agriculture (16). Increases in soil permeability allow more of the roadway runoff to infiltrate the soil, reducing erosion and providing the opportunity for immobilization of the metals washed from the road surface. It has been reported that the major input of heavy metals to a stream receiving runoff from a salt-treated road was associated with the sediment and de-

creasing the sediment load and runoff volume decreased the heavy metals in the stream (31).

Conclusions

The mobilization of Cu, Ni, Cr, Pb, and Fe from roadside soils was mostly controlled by organic matter mobilization. Organic matter mobilization occurred in soils with high exchangeable Na and low electrolyte concentration. This situation could occur in roadside soils receiving salty runoff from deicing operations followed by snowmelt or rainwater. Slightly more Ni, Cr, Cd, Pb, and Fe were leached in the high-concentration CMA solutions, suggesting some effects of ligand complexation (Cl vs acetate) and competitive exchange on metal mobilization. The solubilization of Cd was largely controlled by competitive cation exchange as well as complexation by Cl and acetate. High concentrations of CMA leached more Cd than high concentrations of NaCl and more than dilute salt solutions.

The concentrations of potentially toxic trace elements (Pb, Cr, Ni, Cd, and Cu) in the leachate solutions never exceeded the drinking water criteria. The concentrations of Cu, Ni, and Fe often exceeded the criteria established to protect freshwater aquatic life; however, the extensive complexation of these metals with organic matter should greatly reduce their toxicity.

It appears that the effect of calcium magnesium acetate on trace-metal mobility in roadside soils should have less of an impact when compared to NaCl. The Ca and Mg ions are beneficial to soil permeability and soil structure and reduce the dispersion of organic matter and clays. Sodium tends to destroy soil structure and increase organic matter mobility, thereby increasing the chances of metal mobilization as complexes with native organic matter and via colloid-assisted transport.

Registry No. Cu, 7440-50-8; Cd, 7440-43-9; Ni, 7440-02-0; Pb, 7439-92-1; Cr, 7440-47-3; Fe, 7439-89-6; NaCl, 7647-14-5; CaMg, 76123-46-1; water, 7732-18-5.

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Design and Evaluation of a Long-Term Soil Gas Flux Sampler

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■ The development and evaluation of a device for measuring soil-air fluxes of organic contaminants is presented. The sampler is deployed at the ground surface and measures fluxes coming to the surface by using a passive sampling element. A computer model is used to aid the design and calibration of the sampler. Laboratory tests of prototype samplers are used to verify the model and to determine the accuracy and precision of measurements. Several field demonstrations are conducted in which results are compared to conventional measurement approaches. Measurements were obtained at fuel-contaminated soils near a leaking underground storage tank and at a land treatment unit for refinery wastes. Long-term fluxes estimated using the passive sampler closely matched results obtained by a series of emission isolation flux chamber measurements. The passive sampler offers several advantages as compared to other measurement approaches. It is considerably simpler to use and more cost-effective than active samplers, yet may offer comparable performance in many environments.

Introduction

Measurements of fluxes of contaminants from the ground to the atmosphere are used to monitor and evaluate air emissions and ambient impacts occurring at waste sites. Flux measurements provide a direct method of obtaining the source term for dispersion models which predict ambient concentrations (1). Such measurements also can help assess the extent of subsurface contamination by delineating subsurface plumes (2, 3). For sites undergoing corrective actions, monitoring can aid in the selection of remedial actions and help ensure that cleanup activities do not form a pollution source for the nearby public. Finally, flux measurements can monitor the effectiveness

of the selected remedy to determine, for example, whether a containment barrier is intact. A significant need of personnel involved in any of these tasks is a flexible and low-cost method for determining soil-air fluxes.

Existing measurement approaches include the emission isolation flux chamber, vent sampling, concentration profiles, and transect techniques (1). On the basis of studies at several sites, the flux chamber is the preferred method. The flux chamber obtains short-term (5-15 min) samples released from soils over a 0.1-0.3-m² area. Contaminants are collected onto a sorbent in the continuously purged chamber. Later, laboratory analysis of the sorbent is performed. This approach has been found to provide accurate and precise measurements. However, the flux chamber has several disadvantages, including disturbance of soil, short-term measurements, and the need for intensive and careful field work (e.g., precise flow balancing). The design is somewhat costly, and electrical power and gas cylinders are required. Since fluxes are measured from a small area, data obtained from large and heterogeneous sites may not be representative (1, 4); thus this technique is not applicable to large areas and operating facilities. While the other flux measurement approaches may be useful in special studies, their use is limited by several general disadvantages. The transect and concentration profile sampling approaches utilize considerable instrumentation, are labor intensive, require favorable meteorological conditions, and depend on the site configuration. Vent sampling is straightforward, but such emissions may be intermittent and may not provide representative measurements.

Several factors reduce the accuracy of soil-air flux measurements, no matter which monitoring approach is used. Sampling in the field is subject to both temporal and areal nonuniformities or heterogeneities in emission rates. This variation can be large. Consequently, to reliably characterize emissions, a large number of monitoring locations may be needed, and sampling periods should be long. However, field measurements of low-level contam-

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