

CHEMICAL CHARACTERISTICS OF LEACHATE FROM PULP AND PAPER MILL RESIDUALS USED TO RECLAIM A SANDY SOIL

C. E. CATRICALA^{1,*}, W. B. BOWDEN², C. T. SMITH^{2,**} and W. H. MCDOWELL²

¹ Dept. of Earth Sciences, University of New Hampshire Durham, NH 03824; ² Dept. of Natural Resources, University of New Hampshire Durham, NH 03824

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Abstract. Primary sludge, secondary sludge, and wood ash from a pulp and paper mill were combined with sand to create a synthetic topsoil (C:N ratio of 18:1) to restore an abandoned gravel pit. Synthetic topsoil was applied to field microcosms at rates equivalent to 0, 2170, 4341, or 6511 kg N/ha; each was seeded with grass. Fifteen chemical constituents in leachate were measured during two field seasons. Cadmium, Ni and Zn were mobilized rapidly by soil disturbance. Chloride and SO₄-S eluted rapidly from the sludge along with Na. Nitrate leached with Ca late in each field season when sludge N-mineralization and nitrification exceeded plant uptake and microbial immobilization. Ammonium elution was negligible. Dissolved organic carbon (DOC) was mobilized by decomposition of organic matter in the sludge, as were Mg and K. Copper eluted with DOC, probably as an organic ligand. Lead and ortho-P were below our detection limits. We concluded that a synthetic topsoil with a 30:1 C:N ratio applied at a rate of 2100-4300 kg N/ha should provide adequate plant nutrition while minimizing water quality hazards.

Key words: Pulp and paper mill sludge, nitrogen, DOC, heavy metals, water quality.

1. Introduction

Each year the pulp and paper industry in Maine produces roughly 1 million tons of waste (Jordan Co., 1984). Disposal of this waste is increasingly expensive and as a consequence the industry has sought alternative uses for these residual materials. Alternatives include incorporation of primary sludge into landfill capping materials (McKeown, 1982), conversion of secondary sludge into an animal feed protein supplement (Rogers, 1982), use as a fuel (Rock and Beyer, 1982; Sell and McIntosh, 1988), and recycling by land application.

Land application of pulp and paper mill residuals, properly mixed and incorporated at acceptable loading rates, could provide substantial benefits to soils that have low levels of nutrients and organic matter, and might benefit vegetation growth without adverse effects on groundwater quality. For example, direct application of pulp and paper mill sludge to forested sites may enhance growth of existing stands (Bockheim *et al.*, 1988; Eck, 1986; Henry, 1991) and improve levels of Ca, N, and pH in forest soils (Shimek *et al.*, 1988).

Pulp and paper mills produce three residual materials that might be used for land reclamation. Primary sludge consists largely of fibrous, solid sediments that

* Current address is The Ecosystems Center, Marine Biological Laboratory, Woods Hole, MA 02543; ** Current address is New Zealand Forest Research Institute, Rotorua, NZ.

increase soil water holding capacity and decrease bulk density (Khaleel *et al.*, 1981). This promotes root establishment and plant growth, and provides an immediate carbon (C) source for soil microbes. Secondary sludge is much lower in fibrous content than primary sludge, but richer in nutrients and is an excellent organic fertilizer. Wood ash from boilers is low in carbon, contains little nitrogen, has high pH and contains high concentrations of nonvolatile elements such as base cations in forms readily available to plants (oxides and hydroxides).

Individually, none of these materials is always ideal for good soil conditioning or plant growth, particularly in disturbed areas. For example, primary paper mill sludge has a high C:N ratio, while secondary sludge generally has a low C:N ratio. A high C:N (>30:1) results in immobilization of N and limits vegetative production, while a low C:N (<20:1) results in excessive nitrate production and leaching (Cole *et al.*, 1986; Devoe, 1990; Henry, 1991). An appropriate combination of ash, primary and secondary sludges, and existing soil (base material) mixed to achieve a C:N ratio between 20:1 and 30:1 should produce a synthetic topsoil that can provide a balanced mix of nutrients at an appropriate rate for plant uptake.

Nevertheless, the potential for groundwater contamination from land application of pulp and paper mill residuals is an important concern. Previous studies on the behavior and mobility of elements in pulp and paper residuals and sludge-amended soils have shown the possibilities of toxicity in plants due to high Na, and NO₃-N leaching to groundwater (Brockway, 1983; Dolar *et al.*, 1972; Bockheim *et al.*, 1988).

The primary goal of this study was to determine whether a synthetic topsoil created from pulp and paper mill residuals could be used to promote revegetation of sand and gravel mines, with minimal adverse effects on surface or groundwater quality. Specifically, the objectives of this study were (1) to determine the mobility of nutrients and heavy metals from a topsoil created by blending sand with primary sludge, secondary sludge and boiler ash, and (2) to identify relationships between the mobility of nutrients, dissolved organic carbon (DOC), and heavy metals derived from the sludge mixture, and (3) to determine acceptable loading rates that enhance vegetative growth while minimizing water quality degradation.

2. Methods and Materials

2.1. MICROCOSM EXPERIMENT

Soil-water leachate was collected quantitatively from field microcosms (zero-tension lysimeters) constructed from 55 gal plastic juice drums (Figure 1; Catricala, 1993). A drain was placed in the bottom of each microcosm, near the outside edge, to which polyethylene tubing was attached. The tubing drained into a 20 L collection vessel.

Twelve microcosms and a central collection area for the carboys were installed in an abandoned sand and gravel pit near Bingham, Maine. The site, known locally

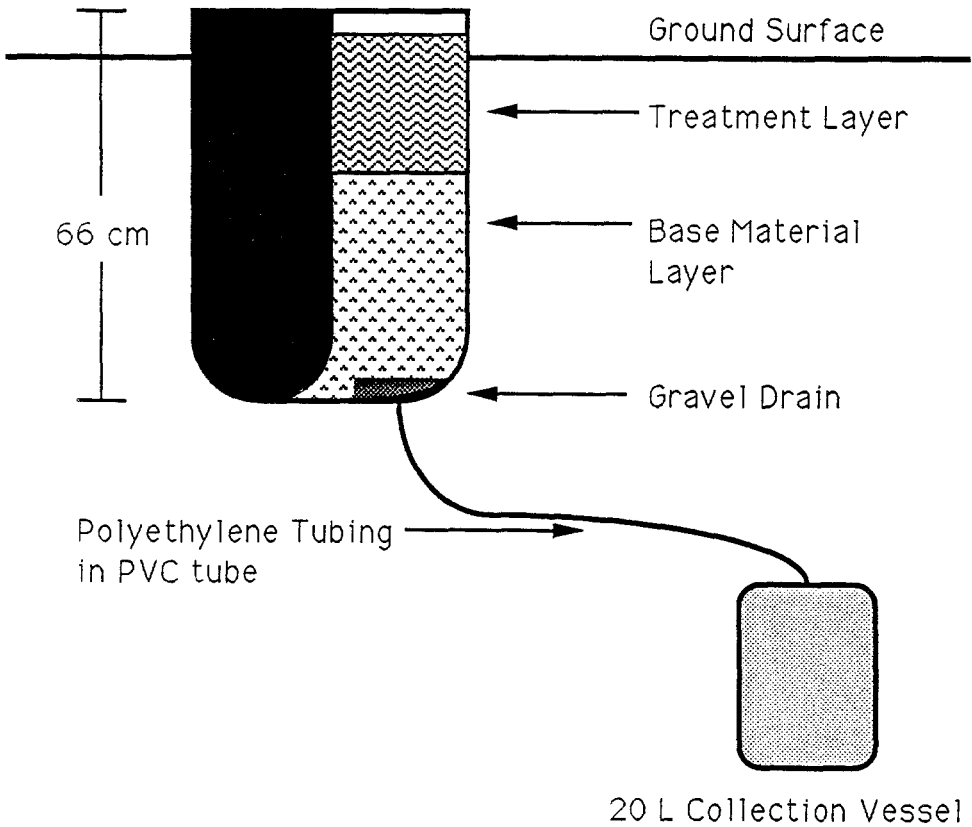


Fig. 1. Schematic of microcosm design and construction.

as Deadwater Pit, was mined about 40 years previously and was still unvegetated at the time of this study. Organic horizons and approximately 1-2 m of sand had been removed, leaving the C horizon exposed.

The existing sand was excavated and sieved (12.7 mm mesh) to remove large stones. Each microcosm was packed with sieved sand to the measured field bulk density of 1.68 gm/cm^3 (excavation method, Blake 1965). The microcosms were set in place at a slight angle, to facilitate flow of leachate to the drain.

2.2. SLUDGE-SAND MIX

The residual materials used in this study consisted of (1) RWT, a primary sludge which contained up to 20% secondary sludge, produced by a partially integrated recycled fiber pulp and paper mill, (2) SS, a secondary sludge obtained from an integrated Kraft pulp and paper mill, and (3) an ash composite containing equal parts (dry wt.) from two cyclones and two scrubbers on boilers that burn approximately 94% wood, 2% oil, and 4% primary paper sludge.

The RWT was first mixed with the boiler ash composite (30:1 ratio dry wt basis). This RWT sludge-ash mixture was then combined 2:1 (dry weight) with the SS. Finally, the sludge mixture was combined 1:2 (by volume) with sand from the site. The sludge mix was applied at three loading rates (112 dry Mg/ha = low rate; 224 Mg/ha = medium rate; and 336 dry Mg/ha = high rate) to determine a dose-response relationship between constituent loading rate and elemental mass flux. These rates were chosen on the basis of the expected total nitrogen release from these materials (USEPA, 1983).

The sludges for each replicate were mixed in the lab and transported to the site in individual bags. On 6 August 1990 the sludge mix was combined with the sieved sand in the field, mixed by hand to break up large clumps, and packed firmly into the microcosms. Each microcosm contained the same total volume of sand to simulate an operational sludge application in which different amounts of sludge would be mechanically tilled into the surface of the sand, and to monitor water quality at a fixed depth relative to the original soil surface level. All microcosms were seeded on 13 August 1990 with Agway Conservation seed mix at the recommended rate of 122 kg/ha.

Pore volume (P.V.) in each microcosm was calculated as follows, using estimated values of particle densities from Brady (1974):

$$\text{One P.V.} = V_s * P_s + V_t * P_t \quad (1)$$

where V_s = volume of sand-only layer (cm^3), P_s = porosity of sand, V_t = volume of the synthetic topsoil layer (cm^3), and P_t = porosity of the synthetic topsoil. Pore volumes were approximately 58.4 L for the high treatment, 51.5 L for the medium treatment, 55.0 L for the low treatment, and 48.6 L for the control microcosms.

2.3. SAMPLING PROTOCOL AND ANALYTICAL METHODS

The site was visited weekly from 6 August 1990 to 19 November 1990, and from 13 April 1991 to 4 December 1991. Each week precipitation was measured to the nearest 0.01 inch and the volume of leachate collected in each of the twelve, 20-L jugs was recorded. Samples for chemical analyses were collected every other week from the 20-L jugs, transferred into 1-L high density polyethylene (HDPE) bottles, and placed in a cooler for transport to the lab (3 hr). Collections on alternate weeks were discarded once volume had been recorded.

In the lab, pH was determined on an aliquot of each sample, then the remaining sample was filtered through a 0.4 μm Nuclepore polycarbonate filter into a clean, dry, 250 mL HDPE sample bottle reserved for nutrient and anion analyses. Calcium and Mg were determined by flame atomic absorption spectrophotometry (AAS) on filtered, unacidified samples to which LaCl_3 (20% by wt.) was added; Na and K were determined by flame emission spectrophotometry. Ortho-P and $\text{NH}_4\text{-N}$ were determined colorimetrically on filtered, unacidified samples (Technicon, 1983). Leachate samples were analyzed for $\text{NO}_3\text{-N}$, $\text{SO}_4\text{-S}$ and Cl by single column,

non-suppressed, ion chromatography after a second filtration (0.2 μm Acrodisc) and pretreatment with a Millipore Millitrap membrane cartridge to remove matrix interferences (alkali metals, alkaline cations) which disrupt the baseline (Waters, 1989).

Once a month, a second subsample was filtered (0.4 μm polycarbonate) into a separate 125 mL HDPE sample bottle and acidified to $\text{pH} \leq 2$ with 1 *N* nitric acid. Graphite furnace AAS was used to determine Cu, Cd, Ni and Pb on filtered, acidified samples; flame AAS was used to determine Zn concentrations. Persulfate digestion (McDowell *et al.*, 1987) was used to analyze dissolved organic carbon in these aliquots. All filtered samples were refrigerated at 4 °C until analyzed.

Physical analyses of the solid materials (sludge mix, sand) included moisture content (oven-dried at 105 °C), loss on ignition (combustion at 500 °C for 6 hr), and soil texture (Bouyucous method, Blake, 1965). Total Kjeldhal nitrogen (TKN) and total phosphorus (TP) were determined by colorimetric analyses of acid digests ($\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2\text{-HgO}$; Technicon, 1975). Exchangeable $\text{NH}_4\text{-N}$ was determined colorimetrically following extraction of solid samples for 48 hr with 1*N* KCl (Kenney and Nelson, 1982). $\text{NO}_3\text{-N}$, $\text{SO}_4\text{-S}$ and Cl were determined by ion chromatography (IC) on distilled, deionized water extracts (Waters, 1989). A gel-filled combination electrode was used to determine pH of slurries (1:1 wt:vol) made with distilled deionized water (McLean, 1982). Base cations (Ca, Mg, K and Na) and heavy metals (Cu, Cd, Ni, Pb, and Zn) were determined by inductively coupled plasma (ICP) emission spectroscopy. For the sludge mix, total base cation quantities were obtained by acid digestion ($\text{HNO}_3\text{-HCl}$). For the sand, exchangeable base cations were obtained by extraction with 1*N* ammonium acetate at pH 4.8 (Thomas, 1982), and metals were extracted with DTPA (Baker and Amacher, 1982).

2.4. STATISTICAL

Analysis of variance (ANOVA), Duncan's multiple range test, and t-tests were used to interpret the annual total chemical flux data (Little and Hills, 1972). Sample years were kept separate for ANOVA since they could not be considered statistically independent. Equations from Bethea *et al.* (1985) were used to estimate a t-statistic and appropriate degrees of freedom, to correct for unequal variances.

For all of these tests, $p \leq 0.10$ was chosen over $p \leq 0.05$ to favor a Type I error (reject H_0 when it is true). When dealing with critical water quality parameters, such as nitrates and metals, a conservative approach is preferable. With the larger Type I error (larger p value and area of rejection) the Type II error (failure to reject a false H_0) is smaller, so truly significant differences are more likely to be clearly identified at the expense of including some differences that may actually be insignificant.

For each of the thirteen constituents, annual elemental flux from each replicate microcosm was calculated by multiplying weekly leachate volume (L) times con-

TABLE I
Properties of sludge mix and base material (as mg/kg dry wt)

Parameter	Sludge mix ^a	Base material ^b	Max. perm. level ^c	Range of soil values ^d
TKN	19400 ^e	485	–	–
TP	2250 ^f	526	–	–
Nitrate (-N)	0.83	0.56	–	–
Ammonium (-N)	1500	1.3	–	–
Chloride	1040	2.96	–	–
Sulfate (-S)	450	0.95	–	–
pH	7.35	4.95	–	–
% LOI	62.4%	1.3%	–	–
% Moisture	74% ^g	na	–	–
Calcium	29000	4.1	–	–
Magnesium	1600	0.8	–	–
Potassium	2200	5.6	–	–
Sodium	2800	2.9	–	–
Cadmium	1.8	0.07	10	0.01-2
Copper	54	0.002	1000	0.6-495
Lead	15	0.093	700	7.5-135
Nickel	13	0.012	200	0.7-269
Zinc	500	0.04	2000	3-264
Aluminum	16000	58.6	–	–
Iron	1500	2.0	–	–

^a Sludge mix analyzed for total cations.

^b Sand analyzed for exchangeable cations.

^c Maximum permissible level. Maine DEP 1986; lifetime loading limit for agricultural land application.

^d Alloway, 1995; Uncontaminated agricultural soils.

^e Weighted average for total nitrogen using RWT 2537 mg/kg dry wt., and SS Q53050 mg/kg dry wt.

^f Weighted average for total phosphorous using RWT 612 mg/kg dry wt., and SS 5517 mg/kg dry wt.

^g Weighted average using RWT 69%, and SS 83%.

centration (mg/L or $\mu\text{g/L}$). Total volumes of leachate were calculated on an annual basis, by replicate.

Estimation of net negative charge on DOC was based on an empirical relationship whereby 1 mg C/L is approximately equal to 10 $\mu\text{eq/L}$ (Oliver *et al.*, 1983). Regressions of ion concentration relationships were determined using a linear model (DOC-Cu) or a polynomial (x^2) model (Nitrate-N).

3. Results

3.1. PHYSICAL AND CHEMICAL CHARACTERISTICS OF BASE MATERIAL AND SLUDGE

Base material from the site, used in the microcosms, was 99.85% sand, 0.11% silt and 0.04% clay. The sludge mix (2 RWT:1 SS) contained much more organic matter, total N and P, and base cations than the base material on a mg/kg dry wt. basis (Table I). Metal concentrations in the sludge mix were also higher than those found in the sand. However, all metal concentrations were within the range of values commonly found in uncontaminated agricultural soils, except for Zn (Alloway, 1995), and all were well below the maximum permissible levels (Maine DEP, 1986). The C:N ratio of the synthetic topsoil (2 base material:1 sludge mix) ranged from 15:1 to 18:1.

3.2. PRECIPITATION DURING THE STUDY PERIOD

During the 1990 field season (6 August to 19 November), precipitation was adequate to produce leachate during each bimonthly sampling interval, and the grass cover became well established. Grass re-established rapidly during the second field season (20 April to 4 December 1991). However, below-normal rainfall from mid-May to mid-August 1991 (27.5 cm rainfall versus a normal of 35 cm) resulted in no leachate, and the grass became stressed and wilted. This dry period was followed by a major precipitation event (approximately 10 cm of rainfall over a 48-hr period) which flushed all of the microcosms.

3.3. CONSTITUENT FLUX PATTERNS

Cadmium, nickel and zinc eluted quickly in the first year (Figure 2; LLD=limit of detection, WQS=water quality standard), peaking near one pore volume and quickly returning to values at or below detection limits for all microcosms. Concentrations eluted were not significantly different among the treated and untreated groups in either year (Table II). Only Cd concentrations, in the early October 1990 sampling, briefly exceeded Maine water quality standards (Maine DHS 1983).

Chloride, sulfate-S, and sodium also moved through the system quickly (less than one pore volume) during the first season; only small amounts eluted in the second season (Figure 3). Unlike the metals, Cl, SO₄-S and Na concentrations in leachate did exhibit significant differences among sludge loading rates. Over 90% of the Cl added with the sludge was leached in the first year from all groups, including the control (Table II). The combined chloride and sulfate-S flux was balanced quantitatively by sodium loss [moles(+) Na = moles(-) Cl + moles(-) SO₄-S]. Only about 60% of the sodium added with the sludge was required to balance the chloride and sulfate-S export; the rest of the sodium from the sludge remained in the microcosms. Nevertheless, during 1990 Na concentrations

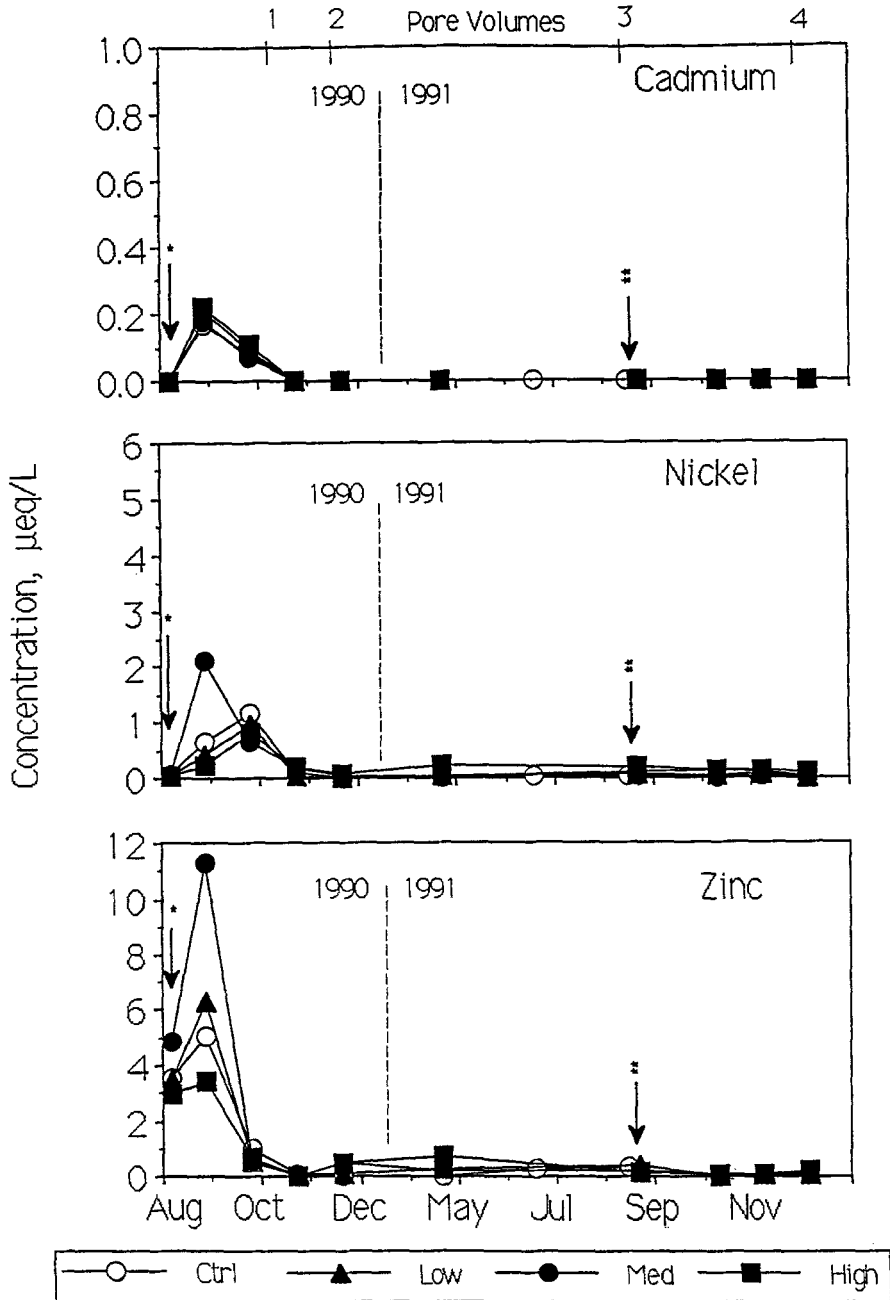


Fig. 2. Mean cadmium (top), nickel (middle), and zinc (bottom) concentrations in leachate for August 1990 through December 1991. * denotes sludge applied, ** denotes hurricane. Pore volumes estimated by Equation (1). Standard error by loading rate averaged over all dates, for cadmium: C = 0.02, L = 0.03, M = 0.01, H = 0.02; for nickel: C, L, and M = 0.21, H = 0.13; for zinc: C = 0.33, L = 0.71, M = 0.50, H = 0.36. LLD-Cd = 0.04, WQS-Cd = 0.18; LLD-Ni = 0.04, WQS-Ni = 0.46; LLD-Zn = 0.14, WQS-Zn = 150.0; all in µeq/L.

TABLE II

Amount of constituent present in sand or in sludge mix, as added by treatment rate, and amounts leached per year by treatment rate

Parameter	Control		Low (112 Mg/ha)		Medium (224 Mg/ha)		High (336 Mg/ha)		MDEP max.		NADP (4)	
	kg/ha present in sand (1)		kg/ha in sludge (2)		kg/ha in sludge (2)		kg/ha in sludge (2)		permissible loading rate (3)		precipitation	
	1990	1991	1990	1991	1990	1991	1990	1991	1990	1991	1990	1991
TP, OP (5)	4483	0.0	0.0	0.0	503	0.0	0.0	0.0	755	0.0	0.0	-
TKN	4134	na	na	na	4341	na	na	na	6511	na	na	-
Nitrate-N	4.76	3.87	3.15	0.09	0.18	5.86	47.1	0.28	39.7	119	5.13	4.92
Ammonium-N	11.1	0.16	0.16	168	336	0.15	0.48	504	13.2	13.2	20.0	0.83
Sulfate-S	8.08	11.0	3.77	54.7	109	83.6	12.7	164	162	162	20.0	7.57
Chloride	25.2	24.4	18.6	115	229	134	8.78	344	343	343	21.6	0.76
Calcium	35.1	6.91	10.0	3248	6497	14.7	64.7	9745	192	310	-	0.26
Magnesium	6.49	2.24	2.54	179	358	7.48	9.98	538	54.2	24.9	-	0.06
Potassium	47.5	2.62	2.00	246	493	5.04	2.09	739	59.3	42.2	-	0.08
Sodium	25.0	21.0	2.82	314	627	189	10.4	941	622	26.0	-	0.31
Copper	0.02	0.01	0.00	6.05	12.1	0.02	0.02	18.1	0.06	0.03	125	-
Cadmium	0.60	0.01	0.00	0.20	0.40	0.01	0.00	0.60	0.01	0.00	2.5	-
Zinc	0.34	0.07	0.01	56.0	112	0.11	0.01	168	0.11	0.02	250.0	-
Nickel	0.10	0.04	0.00	1.46	2.91	0.04	0.00	4.37	0.04	0.01	50.0	-
Lead	0.79	0.00	0.00	1.68	3.36	0.00	0.00	5.04	0.00	0.00	500.0	-

(1) All quantities from sand, excluding TKN and TP are extractable.

(2) All quantities from sludge and leachate are total.

(3) Maine Department of Environmental Protection (1988).

(4) Source: National Acid Deposition Program; Data compiled from Greenville, Me. Station for 27 June to 25 December 1990, and 25 December 1990 to 31 December 1991.

(5) Phosphate measured as total phosphate (TP) in sand and sludge, and as ortho-phosphate (OP) in leachate.

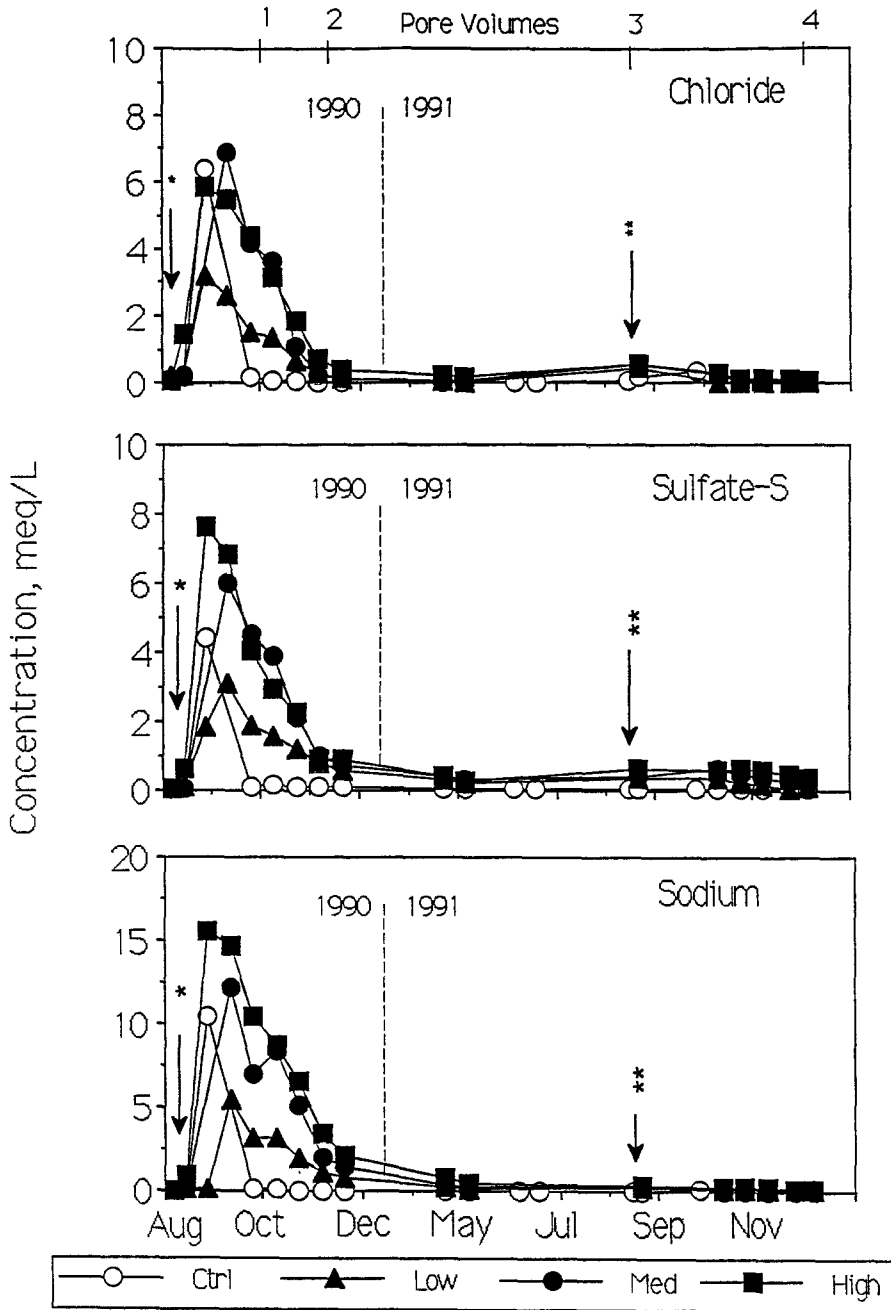


Fig. 3. Mean chloride (top), sulfate-S (middle), and sodium (bottom) concentrations in leachate for August 1990 through December 1991. * denotes sludge applied, ** denotes hurricane. Pore volumes estimated by Equation (1). Standard error by loading rate averaged over all dates, for chloride: C = 0.02, L = 0.06, M = 0.13, H = 0.17; for sulfate-S: C = 0.01, L = 0.10, M = 0.08, K = 0.23; for sodium: C = 0.01, L = 0.10, M = 0.25, H = 0.32; WQS-C1 = 7.06, WQS-sulfate = 15.63, WQS-sodium = 0.87, all in meq/L.

exceeded water quality standards by up to 18 times that allowed (Maine DHS, 1983), a potential health concern with respect to hypertension (NRC, 1977).

In general, concentrations of dissolved organic carbon (DOC) in leachate increased as sludge loading rates increased (Figure 4a). Except for the early Oct. 1990 collection, very little DOC leached from control microcosms. Copper followed an elution pattern similar to DOC (Figure 4b). Both DOC and Cu differed significantly in response to loading rate in both years. DOC and Cu ion concentrations were linearly related (Figure 4c, $R^2 = 0.78$).

Amounts of nitrate-N produced and eluted increased with increasing sludge loading rate (Figure 5a); calcium eluted in a pattern similar to nitrate-N (Figure 5b). Both nitrate-N and Ca increased slightly in late fall 1990 and 1991, and increased markedly in late 1991 further exacerbated by the drought/hurricane events. Calcium flux differed significantly in response to treatment rate in both years. However, despite high Ca loading rates (up to 300 times the amount existing in the base material) only 2-5% of the total Ca added was eluted (Table II). For most of 1991, calcium loss was balanced quantitatively by nitrate-N loss. Magnesium and potassium concentrations (Figure 6) increased late in the 1990 field season, as did nitrate and calcium. A significant relationship ($R^2 = 0.66$) existed between the nitrate-N ion concentration and the sum of the Ca+Mg+K concentrations (Figure 5c). Ammonium-N was rarely observed in leachate from any of the microcosms (Figure 7a), except for late fall of the first year.

Values for pH in 1990 were much more variable within loading rates than was the case in 1991 (Figure 7b). The 1991 results, obtained with a new probe, were more consistent and hence the 1990 pH values should be used with caution. The pH of leachate from the treated microcosms was consistently higher than the control group leachate in 1991.

Both ortho-phosphate (PO_4) and lead (Pb) concentrations were consistently at or below the limits of detection (PO_4 : 0.04 mg P/L, Pb : 2.0 $\mu\text{g/L}$) over the two year study (Table II).

4. Discussion

Mobilities of the measured constituents were controlled by four different factors: disturbance, salt/counter ion effect, sludge mineralization, and physical sorption/plant uptake.

Cadmium, nickel and zinc were mobilized by a short-lived disturbance effect (August through September 1990) associated with construction of the microcosms. Disruption of the sand and exposure of new surfaces apparently mobilized these ions until a new soil solution equilibrium could be reached. The timing of their elutions in 1990 and the fact that eluted concentrations were not significantly different among all treatments strongly suggests that the sand, not the sludge, was the source of these metals eluting in 1990. The total masses of these metals

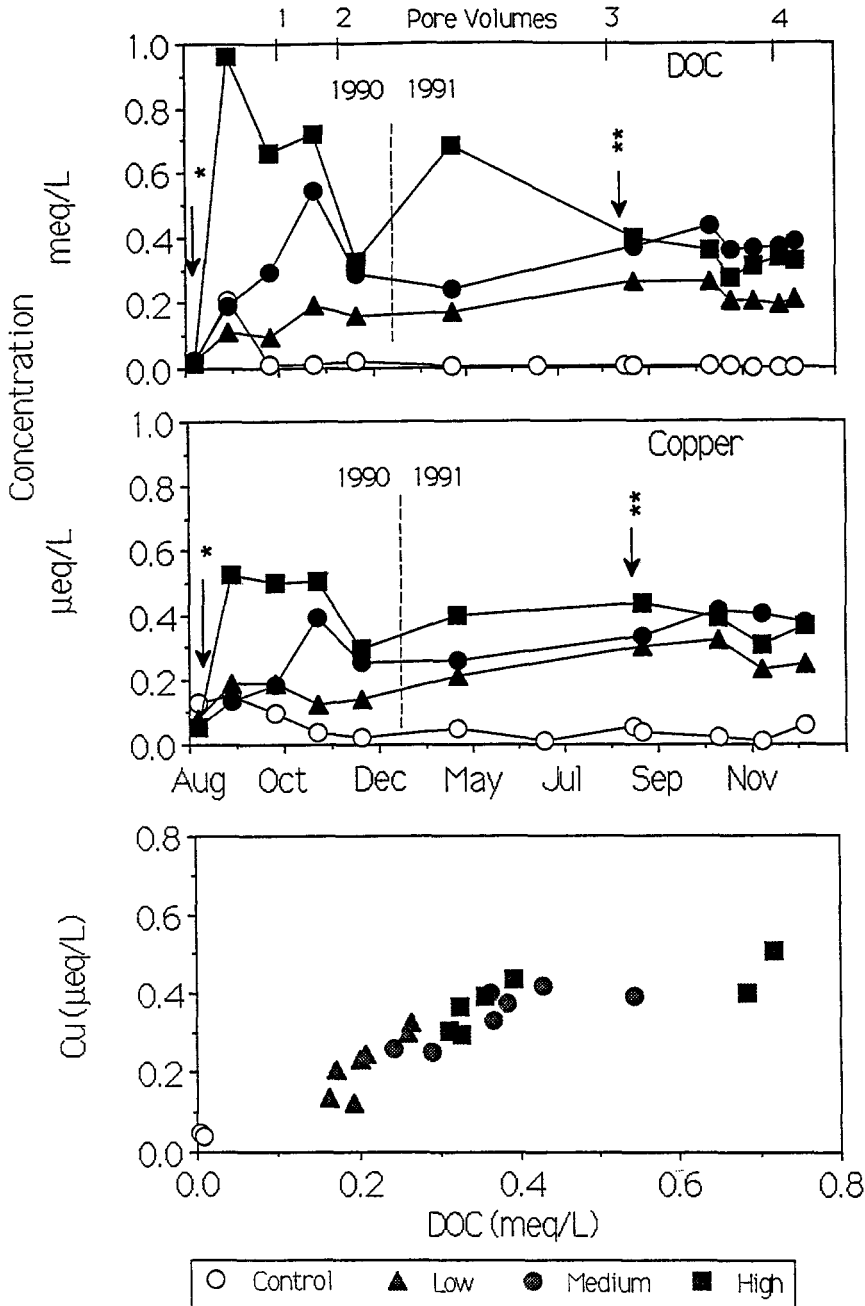


Fig. 4. Mean DOC (top) and copper (middle) concentrations in leachate for August 1990 through December 1991, and DOC vs Cu concentrations (bottom) for October 1990 through December 1991. * denotes sludge applied, ** denotes hurricane. Pore volumes estimated by Equation (1). Standard error by loading rate averaged over all dates, for DOC: C < 0.01, L = 0.02, M = 0.03, H = 0.05 all in meq/L; for copper: C = 0.03, L = 0.04, M = 0.03, H = 0.06. LLD-Cu = 0.03, WQS-Cu = 30.0, all in µeq/L.

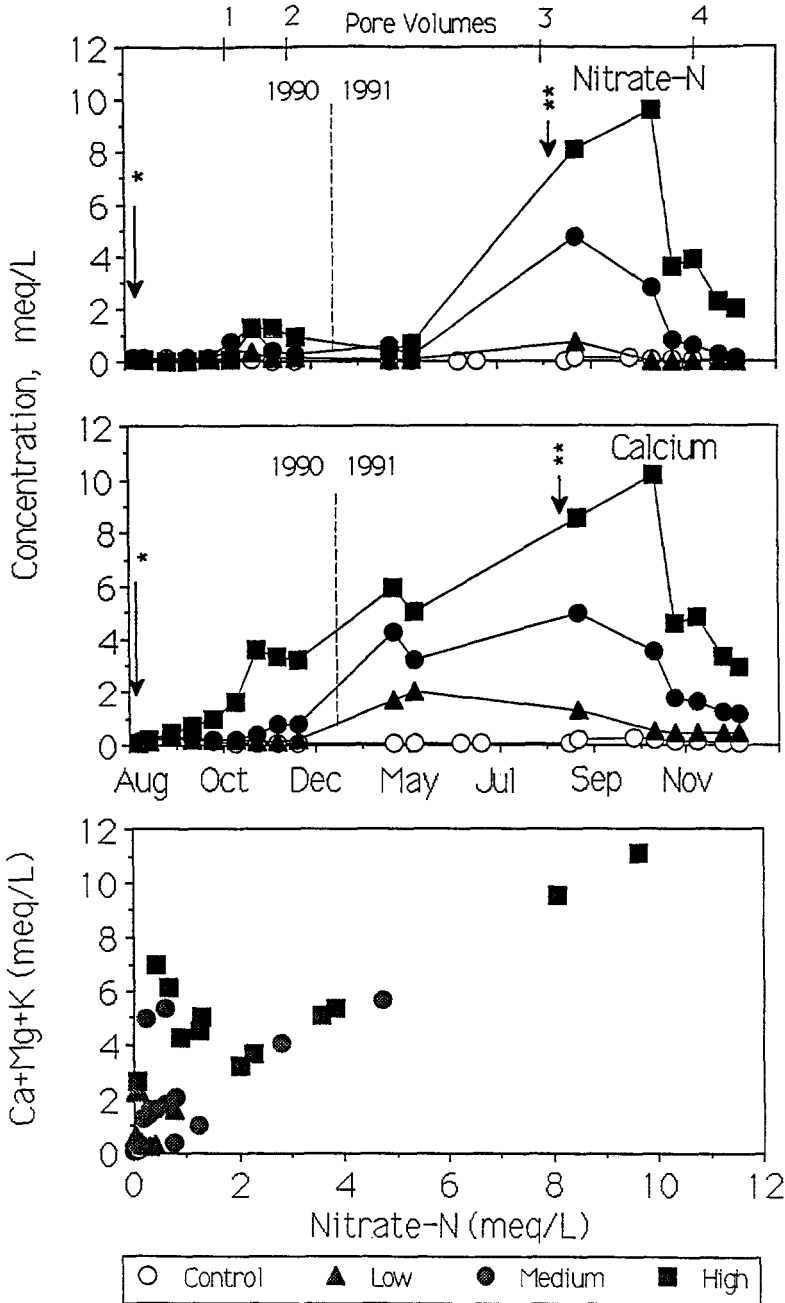


Fig. 5. Mean nitrate-N (top) and calcium (middle) concentrations in leachate for August 1990 through December 1991, and nitrate-N vs Ca+Mg+K concentration (bottom) for October 1990 through December 1991. * denotes sludge applied, ** denotes hurricane. Pore volumes estimated by Equation (1). Standard error by loading rate averaged over all dates, for nitrate-N: C = 0.01, L = 0.05, M = 0.29, H = 1.07; for calcium: C = 0.01, L = 0.08, M = 0.28, H = 1.04, all in meq/L. WQS-nitrate = 0.71 meq/L.

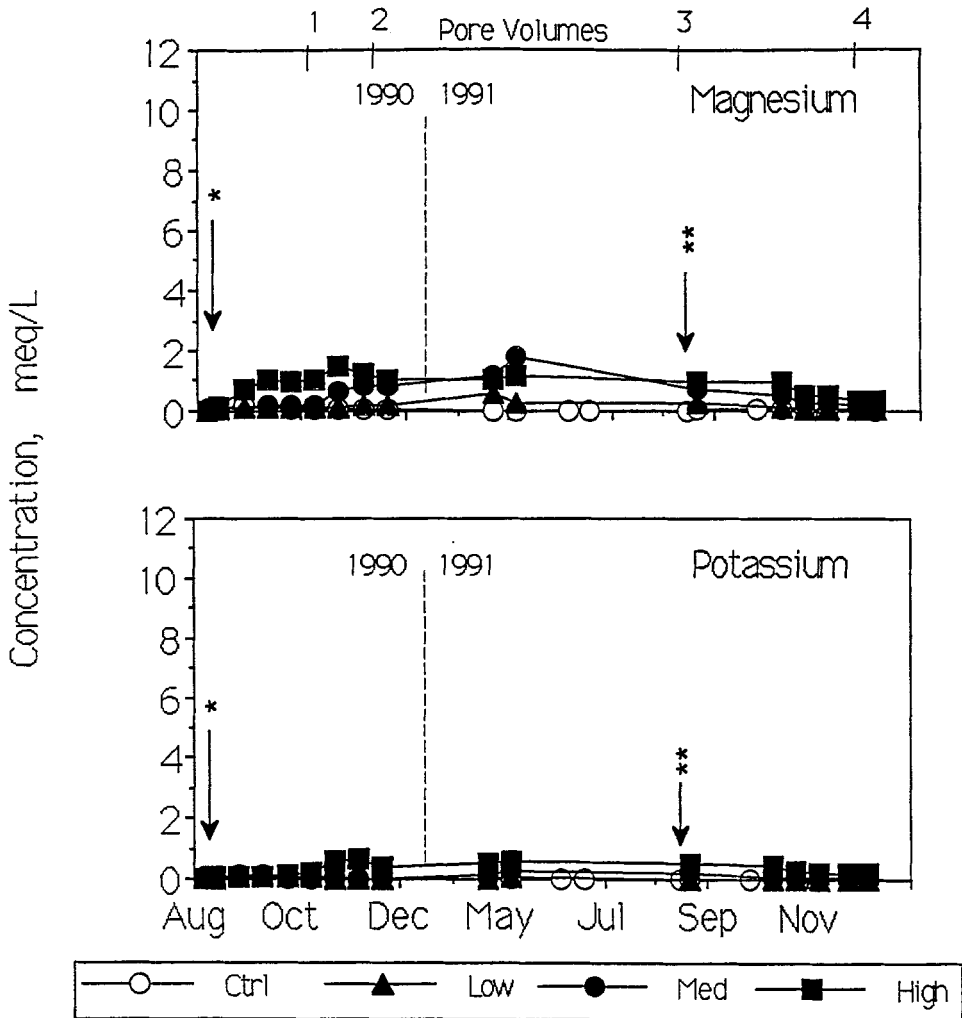


Fig. 6. Mean magnesium (top) and potassium (bottom) concentrations in leachate for August 1990 through December 1991. * denotes sludge applied, ** denotes hurricane. Pore volumes estimated by Equation (1). Standard error by loading rate averaged over all dates, for magnesium: C < 0.01, L = 0.05, M = 0.08, H = 0.26; for potassium: C, L < 0.01, M = 0.01, H = 0.12, all in meq/L.

mobilized by the disturbance were small despite the fact that, especially at the high treatment rates, the total amounts of each metal added with the synthetic topsoil were greater than that in the subsurface sand (Table II).

Chloride, sulfate-S and sodium were mobilized quickly in the first year due to a salt (counter ion) effect; i.e. cations leach with available, excess anions to maintain electrochemical neutrality (Johnson and Cole, 1980). Non-reactive elements like chloride can elute from these microcosms in less than one pore volume because the soil is typically unsaturated, and because of anion exclusion (James and Rubin,

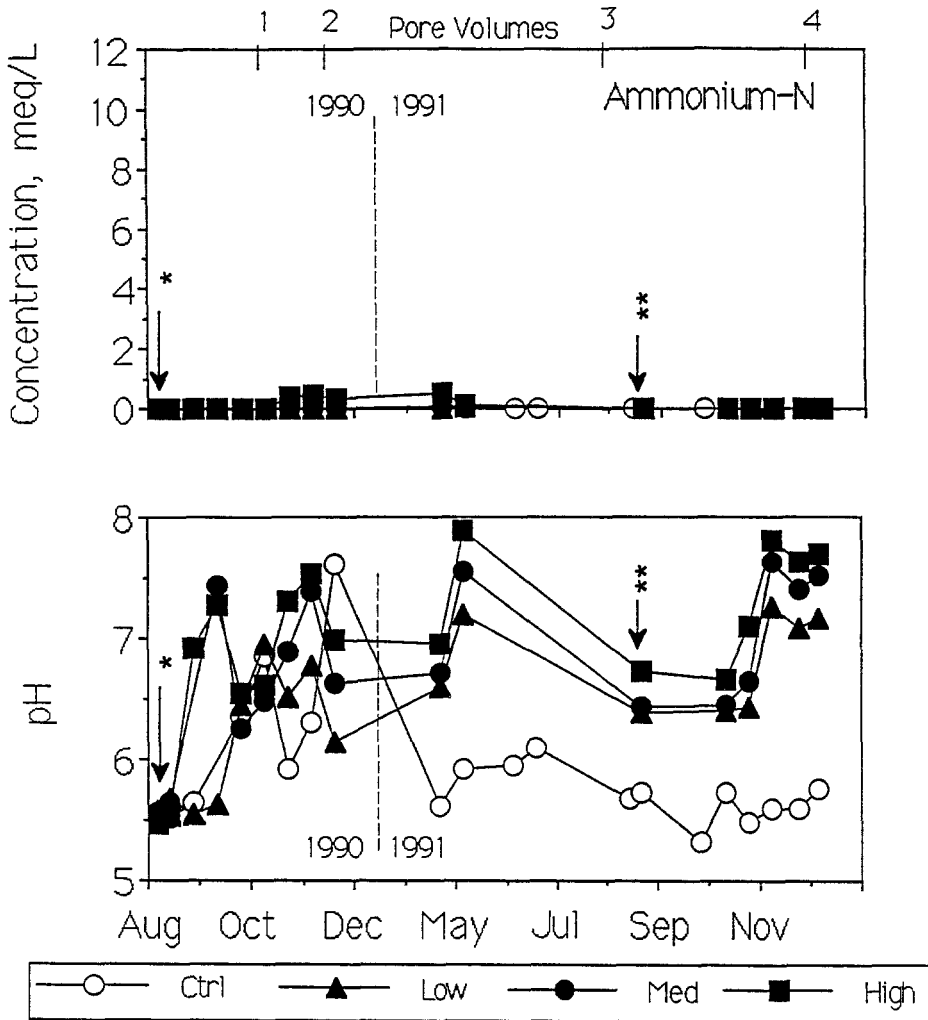


Fig. 7. Mean ammonium-N concentrations in (top) and pH (bottom) of leachate for August 1990 through December 1991. * denotes sludge applied, ** denotes hurricane. Pore volumes estimated by Equation (1). Standard error by loading rate averaged over all dates for ammonium-N: C, L and M < 0.01, H = 0.06, all in meq/L.

1986). Since large amounts of these three ions were added with the sludge mixture (Table II), the excess was flushed from the system as sodium salts. Release of SO_4 , Cl, and Na from the control microcosms in 1990 (Figure 2) does suggest that there was some disturbance effect for these ions. However, sludge must have been the primary source of these three ions because the concentrations eluted showed statistically significant differences with loading rates, and total efflux was much greater than quantities initially present in the sand (Table II). A similar release of

Na and SO_4 was also documented when papermill sludge was added to forest soils (Kraske and Fernandez, 1993).

Mineralization of sludge was the major factor influencing ion mobility once the disturbance and salt effects had ceased. The total amount of sulfate-S efflux over the two seasons was slightly greater than the total amount loaded with sludge plus that added in precipitation (Table II). The excess sulfate-S was likely mineralized from organic-S in the sludge.

Mineralization of the organic matter (OM) added with the sludge apparently supported significant effluxes of dissolved organic C (DOC) from all treated microcosms (Figure 3a). DOC plays a major role in the transport of metals in natural water systems (Drever, 1988) and is believed to contribute to the downward migration of metals in soils (Khanna and Stevenson, 1962). Initially, both DOC and Cu were affected by the disturbance, i.e. concentrations in the control group peaked near one pore volume and returned to values near zero. The similarity of their subsequent elution patterns suggests a constant release or decomposition of OM once the immediately soluble carbon fractions had eluted. DOC and Cu ion concentrations were linearly related for the treated groups clearly (Figure 4c, $R^2 = 0.78$). Close correspondence between DOC and Cu elution patterns at high concentrations suggests that Cu was produced from sludge mineralization and may have been transported as an organic ligand. A strong relationship between concentrations of Cu and DOC has been shown in other studies (Domergue and Vedy, 1992; Sposito *et al.*, 1982; Dudley *et al.*, 1986). For our data, this relationship is unclear at the lower DOC and Cu concentrations (control microcosms), since for most samples the DOC and Cu concentrations were at or near the limit of detection expected for the analytical methods (0.25 mg C/L and 1.0 μg Cu/L, respectively).

Initially there was more immediately available nitrate-N present in the base material than in the sludge. As mineralization and nitrification of organic-N in the sludge mix occurred, far more NO_3 -N leached from the microcosms than was added in sand or sludge.

Nitrate export is governed by interactions among several factors, the most important of which are uptake by vegetation, microbial immobilization, nitrification, denitrification, and water for export (Vitousek *et al.*, 1979). Nitrate-N concentrations for the 1990 season were highest from mid-October through early November, when plant uptake was low and the potentials for nitrification and hydrologic flushing were high. During the growing season, plant uptake was high, and nitrification and hydrologic flushing were low, therefore NO_3 -N loss was low.

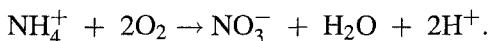
Nitrate-N concentrations in leachate from the high and medium rate treatments were highest from late August through early October 1991. These high values occurred after a large precipitation event which was preceded by a period of severe moisture stress. During this dry period, mineralization of organic nitrogen and subsequent nitrification probably continued. However, the water-stressed grasses could not assimilate the mineralized nitrogen, and without sufficient water to transport the mobile nitrate anions, it is likely that the NO_3 -N produced accumulated

in the microcosms. When water became available, a large amount of $\text{NO}_3\text{-N}$ was flushed out of the microcosms before it could be utilized by vegetation. A similar increase in $\text{NO}_3\text{-N}$ concentration following a dry period was also observed by Reynolds *et al.* (1992) and by Medalie *et al.* (1994).

Although there was a relatively large amount of total N in the base material (roughly 4000 kg/ha, Table II), this material alone did not support significant $\text{NO}_3\text{-N}$ leaching (controls, Figure 5a), probably because this N was old, refractory organic N that was resistant to mineralization. In contrast, N in the sludge was concentrated and readily mineralizable, and supported extensive leaching of nitrate-N.

The amounts of nitrate-N eluted in 1991 were in excess of Maine water quality standards by 10 times (MDHS 1983). However, in field operations $\text{NO}_3\text{-N}$ concentrations would probably be lower for two reasons. First, the microcosm design, which eliminated dilution by lateral flow, caused the grasses to become more water stressed, which led to lower assimilation rates and increased $\text{NO}_3\text{-N}$ leaching. In contrast, concentrations of elements measured in leachate from the microcosms used in this study may have been lower if lateral hydrologic inputs were allowed. Dilution of the vadose zone water with less concentrated phreatic water would likely lead to a substantial reduction in concentration. Second, the final C:N ratio of the synthetic topsoil used in this study (15:1 to 18:1) strongly favored net mineralization. A wider C:N (25:1 to 40:1) would moderate excess $\text{NO}_3\text{-N}$ production (Bowden *et al.*, 1993). In contrast to the increased $\text{NO}_3\text{-N}$ levels seen in the second year of this study, $\text{NO}_3\text{-N}$ concentrations returned to earlier levels after an initial flush in a similar study done on forest soil (Kraske and Fernandez, 1993). Differences in soil and vegetation type most likely accounts for this difference.

Nitrification provides a mobile anion, NO_3^- , and hydrogen ions which, behaving as trivalent ions, can displace cations from the soil-sludge complex (Bohn *et al.*, 1979); nitrification:



As nitrification proceeded and plant uptake decreased in the microcosms in 1991, the hydrogen ions produced by nitrification apparently desorbed Ca, and to a lesser extent Mg and K; the H^+ likely remained on the exchange sites as evidenced by only a mild decrease in pH. These three cations were then mobilized by the available nitrate. A significant ($p \leq 0.05$) relationship was found between nitrate-N ion concentration and the sum of the cation (Ca+Mg+K) concentrations (Figure 5c). Strong $\text{NO}_3\text{-Ca}$ relationships have been noted previously (Devoe, 1990; Hornbeck and Kropelin, 1982; Martin and Pierce, 1980; Medalie *et al.*, 1994). Furthermore, inspection of Figures 5a and b shows that calcium loss was balanced quantitatively by the $\text{NO}_3\text{-N}$ loss for most of 1991, although in the spring of 1991 Ca was eluted in excess of nitrate-N.

Magnesium and potassium did not appear to be affected by the initial construction disturbance (Figure 6). However in 1991, Mg and K concentrations exhibited a pattern of constant release which coincided with the DOC elution pattern, suggest-

ing a gradual loss due to sludge decomposition and mineralization. Overall, Mg and K losses were low, compared to the amounts added via the sludge (Table II), and only potassium efflux appeared to be dependent on loading rate.

Concentrations of Mg and K were also correlated with nitrate-N ion concentrations (Figure 5c). The H^+ ions produced by nitrification desorbed K and Mg, as well as Ca, but at an order of magnitude lower than Ca. This difference in the amount of each cation eluted is probably due in part to the differences in relative abundances of the cations as added with the sludge ($Ca \gg Mg \approx K$; Table II), and the ease of replacement on exchange complexes ($Ca > Mg > K$; Sposito, 1989). Potassium was applied at much lower levels than Ca and Mg, and was probably outcompeted by both.

Ammonium-N flux was apparently not affected by the disturbance or the salt effect. Soil sorption, nitrification, and plant uptake (and perhaps volatilization from the unvegetated controls), probably prevented substantial ammonium-N mobility and export. Small amounts of NH_4 -N, produced in excess of nitrification and plant uptake, were released at the end of the first year, primarily from the high loading rate. In early 1991, NH_4 -N concentrations were high initially, again from the high treatment group, but fell quickly, most likely in response to plant uptake and nitrification. Ammonium-N flux exhibited no significant differences among treatment rates in either year, and no significant differences between years for each rate. While large amounts of NH_4 -N were added with the sludge (roughly 15-50 times that added with the base material), <1% of the total added was leached in all groups, including controls (Table II).

Lead was most likely immobilized by strong organic binding with the soil-sludge complex and was therefore not detected in leachate from any group, (Elliott *et al.*, 1986; Hertz *et al.*, 1990). Ortho-phosphate, also undetected, was probably immobilized despite high P loadings (over 4000 kg/ha) due to a combination of sorption on the soil-sludge complex and plant uptake. This anion is strongly adsorbed by soils, in the order of $HPO_4^{=}$ > $SO_4^{=}$ > $NO_3^- \approx Cl^-$, and is also known to form precipitates with aluminum (Johnson and Cole, 1980), which was plentiful in both the base material and the sludge (Table I).

Finally, unmeasured ions may help to further explain the pattern of elemental mobility. The most important missing cations were probably Al and Fe, based on their quantities in the sludge (Table I). Treated groups tended to show a deficit of anions once decomposition began. In Aug. and Sept. 1990, the average cation:anion ratio for treated groups was 1:1.2, while by May 1991 the average C:A ratio for treated groups was 10:1. The high pH after sludge addition suggests that HCO_3^- and $CO_3^{=}$ probably provided most of the missing negative charge. In early spring of 1991, for example, when nitrate-N production was still low relative to Ca, Mg, and K concentrations (Figures 5b and 6), a coincident increase in pH suggests that bicarbonate may have provided the necessary mobile anion.

5. Conclusions

The use of pulp and paper mill residuals to create a synthetic topsoil for revegetation of sandy soils appears feasible. The four mechanisms of ion mobility identified in this study were disturbance, salt/counter ion effect, sludge decomposition/mineralization, and physical sorption/plant uptake. Only cadmium, nitrate-N and sodium exceeded Maine DHS (1983) drinking water quality standards in this study; however the Cd mobilized here apparently originated in the soil, not the sludge. All other measured constituents were within acceptable limits. Concentrations of any soluble constituent are likely to be highest in the unsaturated zone of the soil, which was the zone simulated with the microcosms. However, concentrations of elements measured in leachate from the microcosms used in this study may have been lower if lateral hydrologic inputs were allowed. Finally, a slightly higher total C:N ratio of the synthetic topsoil (perhaps 30:1) or a lower maximum loading rate of 2100-4300 dry kg/ha would also help limit excess nitrate-N production after periods of extended water stress, without sacrificing the fertilizer value of the synthetic topsoil.

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