

Leachate migration from spent mushroom substrate through intact and repacked subsurface soil columns

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Abstract

Field weathering of spent mushroom substrate (SMS) produces soluble compost leachate that percolates into underlying soils and may adversely impact groundwater. Laboratory experiments were conducted to investigate movement and retention of SMS leachate solutes in subsurface soil columns. Spent mushroom substrate leachate with high concentrations of dissolved organic matter (DOM) and inorganic salts was passively loaded to intact and repacked columns of Bt1 soil (fine-loamy, mixed, semiactive, mesic Typic Hapludults) and effluents were monitored for changes in chemical composition. Transport of SMS leachate in undisturbed soil cores was mainly via preferential flow, whereas matrix flow was predominant in repacked soil columns. Leachate DOM and phosphate were sorbed by soil minerals while Cl^- , SO_4^{2-} , Na^+ and NH_4^+ were eluted. Leachate K^+ displaced exchangeable native cations and was retained. Biodegradation of leachate DOM resulted in reduction and elution of soil Mn and Fe, especially in repacked columns. Persistent anoxia also inhibited nitrification. Precipitation of gypsum and CaCO_3 blocked preferential flow channels, and movement of SMS leachate was subsequently reduced. The results demonstrate that SMS leachate migrates via rapid preferential flow initially, followed by matrix flow at a lower rate. Leachate solutes may transport to depth in soil profiles through preferential channels. To protect water resources, weathering of deep SMS piles should be conducted on compact surfaces or in fields with a condensed soil layer (no structural cracks) above the groundwater table, and measures controlling leachate runoff be imposed.

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1. Introduction

Mushroom growers use formulated compost as growth media to produce the white button mushroom *Agaricus bisporus*. The compost is made from wheat straw, field hay, corn cobs, cotton seed hulls, horse manure, chicken litter and gypsum. In addition to these bulk ingredients, it also contains some nutrient additives such as potash, urea and super phosphate (PADEP, 1997). In the mushroom industry, this compost is known as “mushroom substrate”. After several mushroom harvesting cycles, the productivity of the substrate decreases such that the substrate is declared “spent”. Spent mushroom substrate

(SMS) is discarded as a waste, but also may be used as a soil amendment or potting material in agriculture, horticulture and environmental amelioration.

In the US, mushroom production results in the generation of over 10^6 m^3 of SMS annually, with half of the material being generated in Pennsylvania (Wuest et al., 1995). The volume greatly exceeds the amount that is used in commercial applications. The surplus material is commonly stacked in fields to undergo two years of “weathering” (passive composting) to reduce volume and excessive inorganic salts. Leachate resulting from SMS field-weathering percolates into soils and the potential environmental impacts are of great concern because mushroom production is highly concentrated in particular localities. Field studies show that SMS leachate contains high concentrations of dissolved organic

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carbon (DOC, 0.8–11.0 g l⁻¹), dissolved organic nitrogen (DON, 0.1–2.0 g l⁻¹) and inorganic salts (250–620 mmol_c l⁻¹) (Guo et al., 2001a). In soils influenced by SMS weathering, water-soluble organic carbon and inorganic ions NO₃⁻, Cl⁻, SO₄²⁻, Na⁺, K⁺, Ca²⁺, and Mg²⁺ are significantly elevated (Guo et al., 2001b).

Field weathering of SMS poses a risk of groundwater pollution. When SMS was spread at 50 cm pile height over a landscape with fine loam soil for one year, DOC in soil water collected at 100 cm reached 880 mg l⁻¹, and concentrations of K⁺, Ca²⁺, Cl⁻ and SO₄²⁻ were over 1000 mg l⁻¹. In the underlying groundwater (250 cm depth), concentrations of DOC, K⁺, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻ were 5–20 times higher than background values (Kaplan et al., 1995). Currently the Pennsylvania Department of Environmental Protection (PADEP) in the USA regulates weathering of SMS at or below a pile height of 90 cm (3 ft) after settling in fields with seasonal groundwater tables more than 50 cm from the surface (PADEP, 1997). It is unlikely that the 50 cm of topsoil can retain all leachate solutes. When SMS was stacked in the field at 90 cm pile height for 2 years, approximately 40% of DOC and 11% to 80% of inorganic salts released from the piles were recovered in soil leachate collected at 90 cm depth (Guo et al., 2001a). Chemical examination of the underlying soils indicated that leachate solutes had migrated more than 200 cm in soil profiles, and significant retention had occurred in the subsoil (Guo et al., 2001b). Our results suggested that SMS leachate migrates through the organic-rich surface soils mainly by preferential flow because of structural cracks, wormholes and root channels, which limits the retention of solute, particularly DOM. However, the subsurface soils behaved as more reactive adsorbents because of their lower organic matter content and fewer structural channels. We hypothesize that, in the subsoil, movement of SMS leachate is dominated by matrix flow, and reactive solutes should be more effectively retained. Thus, weathering of SMS on compact surfaces or in fields with a deep groundwater tables should be environmentally benign from the perspective of groundwater resource protection. The objectives of this study were: (i) to measure the migration and sorptive retention of SMS leachate solutes in subsoils representative of SMS impacted sites, and (ii) to assess the importance of subsoil structure in solute transport behavior. The research utilized both intact and repacked soil column experimental techniques.

2. Materials and methods

2.1. SMS leachate collection

Spent mushroom substrate leachate was obtained from laboratory-controlled SMS weathering (Guo and

Chorover, 2004). Briefly, 23.6 kg of fresh SMS was packed into a 150 cm high × 20 cm i.d. acrylic column and leached with deionized water at 2.5 ml min⁻¹ for 28 consecutive hours every 10 days to simulate the wet-dry cycle in the field. Leachate collected in the first 90 d of the 180 d weathering process was mixed and stored at 4 °C prior to use. The leachate was chemically similar to that collected during SMS field weathering (Guo et al., 2001a). Selected chemical properties of the leachate are listed in Table 1.

2.2. Preparation of intact and repacked soil columns

Triplicate intact soil columns were obtained from a fallow field in West Grove, Pennsylvania, adjacent to an area where SMS field weathering is conducted routinely. Since our prior work indicated the importance of subsurface horizons in SMS solute retention (Guo et al., 2001a,b), the top 45 cm of soil was removed and PVC pipes (15 cm long × 7.6 cm i.d.) were driven into the Bt1 soil horizon (Glenelg fine-loamy, mixed, semiactive, mesic Typic Hapludult) to 10 cm depth (for soil profile description, see Table 1 in Guo et al., 2001a). Choosing 10 cm as the column height was based on preliminary tests with 30 cm long soil columns showing that more than 30 days were required to collect 50 ml of effluent, impractical to carry out the experiments. Intact soil columns were carefully removed, immediately covered with plastic films at both ends, and stored at 4 °C prior to use. For the effluent collection, a PVC pipe-reducer (7.6 cm i.d. → 3.8 cm i.d.) connected to a custom-made polyethylene funnel was installed at the bottom of each soil column. Between the reducer and the column bottom, a perforated polyethylene plate and a layer of glass fiber (1 mm on compaction) were employed to provide column support.

Table 1
Chemical properties of the input spent mushroom substrate leachate^a

Properties	Values
pH	8.20 (0.04)
EC (dS m ⁻¹)	23.03 (0.01)
DOC (mg L ⁻¹)	3420 (8.5)
Ca ²⁺ (mmol L ⁻¹)	24.20 (0.63)
Mg ²⁺ (mmol L ⁻¹)	17.07 (0.37)
Na ⁺ (mmol L ⁻¹)	12.61 (0.33)
K ⁺ (mmol L ⁻¹)	117.77 (0.34)
NH ₄ ⁺ (mmol L ⁻¹)	17.00 (0.24)
Cl ⁻ (mmol L ⁻¹)	36.73 (0.12)
SO ₄ ²⁻ (mmol L ⁻¹)	47.24 (0.73)
NO ₃ ⁻ (mmol L ⁻¹)	n.d. ^b
HPO ₄ ²⁻ (mmol L ⁻¹)	0.16 (0.02)

EC, electrical conductivity; DOC, dissolved organic carbon.

^a Data are means of triplicate measurements, and values in parentheses are standard errors.

^b Non-detectable.

Triplicate repacked soil columns were obtained by gentle grinding, sieving (<2 mm), and repacking soil from the same site (45–55 cm depth) to 10 cm depth to give a mean bulk density equivalent to that of the intact soil columns. Selected physical and chemical properties of the intact and repacked soil columns are listed in Table 2.

2.3. Leachate loading

The intact and repacked soil columns were pre-equilibrated by passing through 3 pore volumes of a DOC-free solution (0.2 mM K₂SO₄, 0.2 mM CaCl₂, 0.2 mM NaCl, 0.2 mM MgSO₄, pH 7.3) prepared to match clo-

sely the chemistry of 1:1 soil/water extracts. Spent mushroom substrate leachate was centrifuged at 12,000g for 15 min, passed through a 0.5 μm glass fiber filter, and passively loaded to the soil columns to keep a constant 2 cm head of leachate on the top of the column. Effluents from the soil columns were collected in 50 ml increments (~0.24 pore volumes) with aluminum foil-covered volumetric flasks, and the time elapsed for each sample was recorded. The column experiments were conducted at 24 ± 1 °C.

2.4. Chemical analysis of effluents

The soil column effluents were centrifuged at 12,000g for 15 min and filtered with 0.5 μm glass-fiber filters prior to analysis. Dissolved organic carbon (DOC) content of the samples was determined with a Shimadzu TOC-5000A total organic carbon analyzer with an ASI-5000A auto sampler (Shimadzu, Kyoto, Japan). Inorganic anions Cl⁻, NO₃⁻, SO₄²⁻ and HPO₄²⁻ were measured by ion chromatography (IC) (Dionex series 4000I with an AS40 automated sampler, an IonPac AS11 ion exchange column, and an ED40 conductivity detector, Dionex Corp., Sunnyvale, CA). A gradient mobile phase comprising water and 0.05 M NaOH was employed. Inorganic cations K⁺, Na⁺, Ca²⁺ and Mg²⁺ were measured using a Video 22 AA/AE spectrophotometer (Instrumentation Laboratories, Lexington, Massachusetts).

3. Results and discussion

3.1. Effluent solution flux

Effluent solution fluxes from the intact and repacked soil columns are presented in Fig. 1 (*x*-axis of all figures is pore volumes of effluent collected). Initially the intact soil columns had much greater water flow rates than the repacked columns, indicating higher hydraulic conductivities and larger pore sizes (i.e., preferential flow channels) in the field soil. Preferential flow has been observed in field soils or intact soil columns by many researchers (Camobreco et al., 1996). In the soil sampling site, structural cracks, root channels and wormholes were observed from the surface to 1.2 m in the soil profile, which explains why leachate solutes with an affinity for sorption migrated more than 200 cm depth in the underlying soils in 2 years (Guo et al., 2001b). The water flow rates decreased with time and converged at low levels for the two types of columns at long times (Fig. 1), suggesting that soil macropores were blocked and leachate was then transported in both types of the soil columns via matrix flow. Based on results from our previous studies (Guo et al., 2001a,b), it is inferred that sulfate and carbonate precipitates, formed during SMS

Table 2
Selected properties of the intact and repacked soil columns^a

Properties	Values
<i>Column</i>	
Dimension (cm)	10 long × 7.6 i.d.
Bulk density (ρ_b , g cm ⁻³)	1.45 (0.03)
Porosity (ϕ)	0.47 (0.01)
Pore volume (cm ³)	215 (4.8)
<i>Soil</i>	
Taxonomic name	Fine loamy, mixed, semiactive, mesic Typic Hapludults
Mineralogy	Quartz, muscovite, smectite, kaolinite and hematite
Particle density ^b (g cm ⁻³)	2.71 (0.01)
Texture ^c (g kg ⁻¹)	Clay 87 (1); Silt 329 (3); Sand 584 (1)
pH (soil:H ₂ O = 1:1)	7.33 (0.03)
TOC (g kg ⁻¹)	2.13 (0.06)
CEC ^d (mmol _c kg ⁻¹ soil)	69.10 (0.36)
Exchangeable Ca ²⁺	58.48 (0.62)
Exchangeable Mg ²⁺	5.92 (0.09)
Exchangeable Na ⁺	0.22 (0.01)
Exchangeable K ⁺	2.90 (0.03)
<i>Water extractable^e</i>	
Organic C (g kg ⁻¹ soil)	0.067 (0.003)
Ca ²⁺ (mmol _c kg ⁻¹ soil)	n.d. ^f
Mg ²⁺ (mmol _c kg ⁻¹ soil)	0.031 (0.015)
Na ⁺ (mmol _c kg ⁻¹ soil)	0.104 (0.008)
K ⁺ (mmol _c kg ⁻¹ soil)	0.060 (0.002)
Cl ⁻ (mmol _c kg ⁻¹ soil)	0.102 (0.010)
SO ₄ ²⁻ (mmol _c kg ⁻¹ soil)	0.530 (0.002)
NO ₃ ⁻ (mmol _c kg ⁻¹ soil)	0.051 (0.008)
HPO ₄ ²⁻ (mmol _c kg ⁻¹ soil)	n.d. ^f
CBD extractable Fe ^g (g kg ⁻¹)	36.69 (1.30)
CBD extractable Mn ^g (g kg ⁻¹)	0.25 (0.04)

TOC, total organic carbon; CEC, cation exchange capacity.

^a Data are means of triplicate measurements, and values in parentheses are standard errors.

^b Measured by pycnometer method.

^c Measured by hydrometer method.

^d 1 M NH₄OAc exchangeable.

^e Extracted at 1:5 soil/water ratio for 60 min.

^f Non-detectable.

^g Extracted with CBD reagent (0.3 M sodium citrate + 0.1 M sodium bicarbonate + sodium dithionite) (Loeppert and Inskeep, 1996).

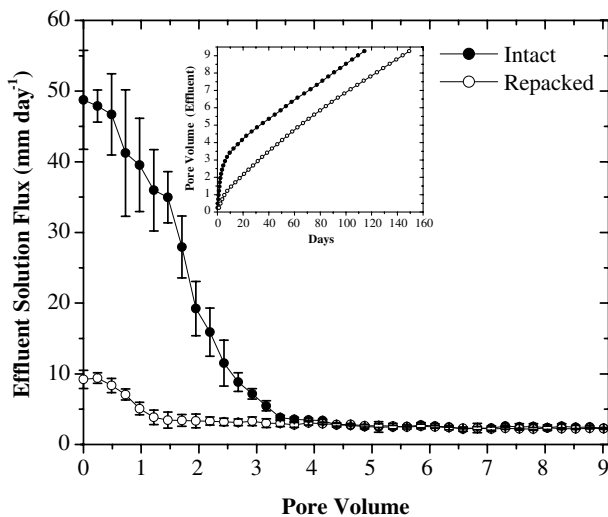


Fig. 1. Effluent solution fluxes from the intact and repacked soil columns. Error bars represent standard deviation of triplicate measurements.

leachate transport in the columns, were deposited in the pore spaces. Additionally, accumulation of microbial biomass may have contributed to the reduced macroporosity (biofilling). The comparison of the two water flux patterns suggests that leachate moved in the repacked soil columns primarily by matrix flow, while in the intact soil columns preferential flow predominated at the beginning, and then shifted to matrix flow with time. Evidently, transport via matrix flow greatly diminished SMS leachate movement in soils with a bulk density of 1.45 g cm^{-3} . In deep finely-textured soils with few structural channels, movement of SMS leachate is expected to be fairly slow.

3.2. Movement of leachate DOM

Breakthrough curves for leachate DOC in the soil columns are shown in Fig. 2. Due to the preferential flow effect, early effluents from the intact columns had higher DOC concentrations than those from the repacked columns. The first plateau on the effluent DOC concentration curves of intact soil columns ($2300\text{--}2500 \text{ mg l}^{-1}$, Fig. 2) results from movement through macropores for an effluent flux less than one pore volume. Mixing of the macropore and matrix (low DOC) solutions results in effluent DOC values 65–75% of input values. The subsequent decrease reflects the blocking of macropores and confinement of leachate transport to the soil matrix. The second increase of the intact column curves suggests that the soil matrix became increasingly saturated with organic matter and the sorption was subsequently decreased (Fig. 2). The effluent DOC concentrations in the repacked soils increased consistently, and reached a stable level after 5 pore volumes. Clearly, some fraction of DOM was retained in the soils such

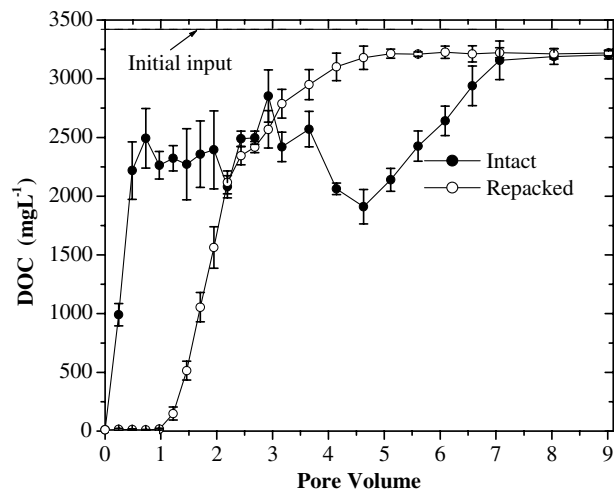


Fig. 2. Dissolved organic carbon (DOC) contents of effluents from the intact and repacked soil columns. Error bars represent standard deviation of triplicate measurements.

that effluents had lower DOC levels than input. Adsorption of DOM by soil minerals is well documented (Dosskey and Bertsch, 1997; Guo and Chorover, 2003). Even at the plateau value lasting to the end, DOC in the column effluents was approximately 200 mg l^{-1} lower than the input value, implying either continued solid-phase retention or that a portion of DOC was degraded by microorganisms during its transport in the columns. Given the stable maximum achieved, the latter explanation seems more plausible.

Biodegradation is further supported by the Mn and Fe release data shown in Fig. 3. These results suggest that the introduction of concentrated, labile DOM solutions gave rise to anoxic conditions in the repacked columns, which led to reductive dissolution of soil Mn and Fe (hydr)oxides. In contrast, for macroporous intact soil columns, Fe and Mn releases were much smaller. After 5–6 pore volumes, when micropore flow became predominant, significant increases in Mn and Fe release were observed for intact soils (Fig. 3). Under the experimental conditions, microorganisms consumed approximately 6% of the input DOC (predicted by the difference in DOC between the final column effluent and the input leachate). Thus, biotic consumption is not sufficient to significantly deplete DOM inputs from SMS leachate in field soils.

3.3. Movement of leachate Cl^- and SO_4^{2-}

Chloride is a weakly sorbed anion that is commonly used as a tracer in solute transport studies. Movement of SMS leachate Cl^- in the soil columns is shown in Fig. 4(a). In the repacked soil columns, Cl^- breakthrough was consistent with matrix flow (Camobreco et al., 1996), indicating that macropore flow was insignificant. Input Cl^- concentrations in effluent (i.e.,

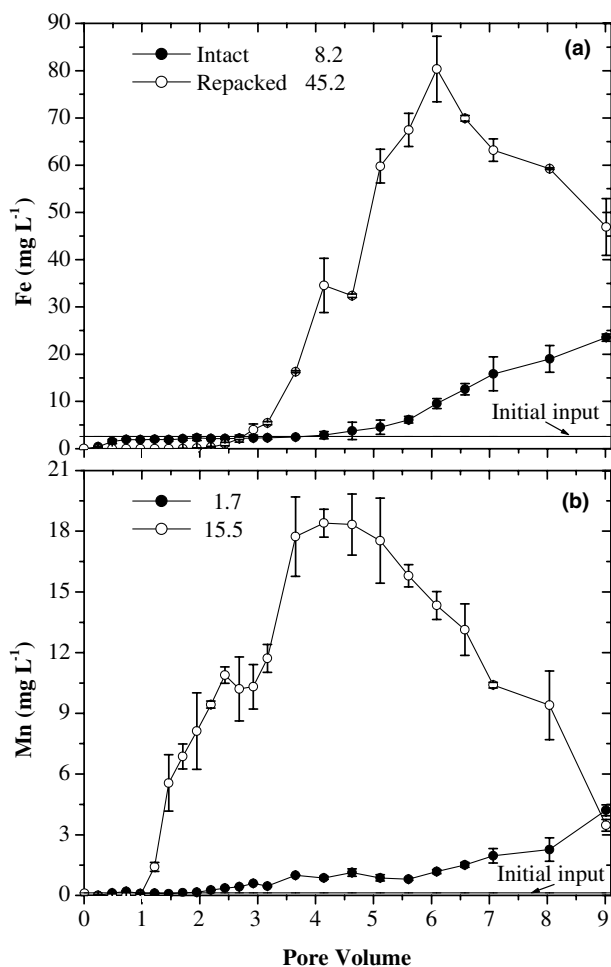


Fig. 3. Dissolution and release of (a) Fe and (b) Mn as coupled to biodegradation of leachate DOM in the intact and repacked soil columns. Error bars represent standard deviation of triplicate measurements. The numbers shown in the legends correspond to the cumulative total Fe and Mn released from the soil (in mg kg^{-1}) over the duration of the experiment. The totals can be compared to the extractable Mn and Fe values given in Table 2.

$C/C_0 = 1$) were reached at approximately 1.9 pore volumes. Dunnivant et al. (1992) found that 1.7 pore volumes of wash solution were required to flush pore water Cl^- in soil columns. It may be inferred that at about 1.9 pore volumes the original soil water in the columns was completely displaced by the loaded SMS leachate. It is evident that little Cl^- was retained during its transport in soil columns. Prior to 1.0 pore volume, the intact columns released much higher concentrations of Cl^- than the repacked columns, confirming the importance of preferential flow in the intact columns. Consistent with the DOC data, it appears that the first Cl^- plateau of the intact column curves (26–28 mmol l^{-1} , Fig. 4(a)) is contributed by mixing of macropore solution (with $[\text{Cl}^-] = C_0$) and soil matrix solution (with $[\text{Cl}^-] \approx 0.6 \text{ mmol l}^{-1}$). The second increase in the Cl^- concentration is associated with the breakthrough of soil matrix Cl^- . After 5 pore

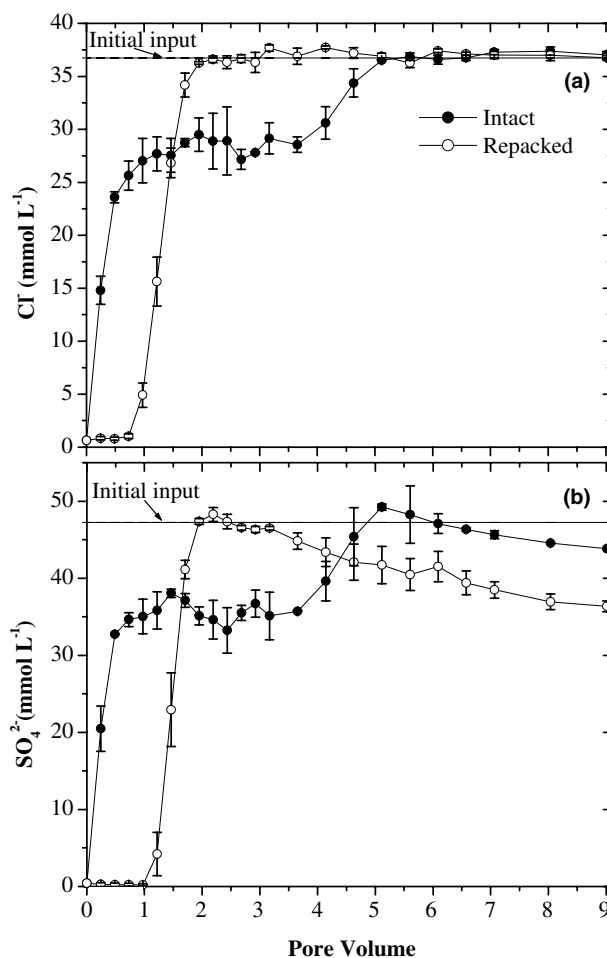


Fig. 4. (a) Chloride and (b) sulfate concentrations of effluents from the intact and repacked soil columns. Error bars represent standard deviation of triplicate measurements.

volumes, concentrations of Cl^- in effluents from the intact soil columns reached the input value (Fig. 4(a)). Evidently, little leachate Cl^- was retained during its transport in soil columns.

Movement of SO_4^{2-} was similar to that of Cl^- except for a tailing decrease in the effluent concentrations at long times (pore volumes > 3 , Fig. 4(b)). The intact soil columns had a slightly higher concentration of SO_4^{2-} at 2 pore volumes, relative to initial input, suggesting soil indigenous SO_4^{2-} (Table 2) was displaced into the effluent solution. Dissolved organic matter competes effectively with SO_4^{2-} for soil adsorption sites (Gu et al., 1995; Chorover and Amistadi, 2001). At high DOC concentrations (3420 mg l^{-1} , Table 1), little SO_4^{2-} is likely retained by the soils (Kaiser and Zech, 1997). The SO_4^{2-} concentrations in the effluents decreased after column breakthrough and remained lower than input values (Fig. 4(b)), suggesting column retention of SO_4^{2-} by mechanisms other than adsorption. A simultaneous decrease in effluent Ca^{2+} concentrations (Fig. 5(c)) suggests precipitation and deposition of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

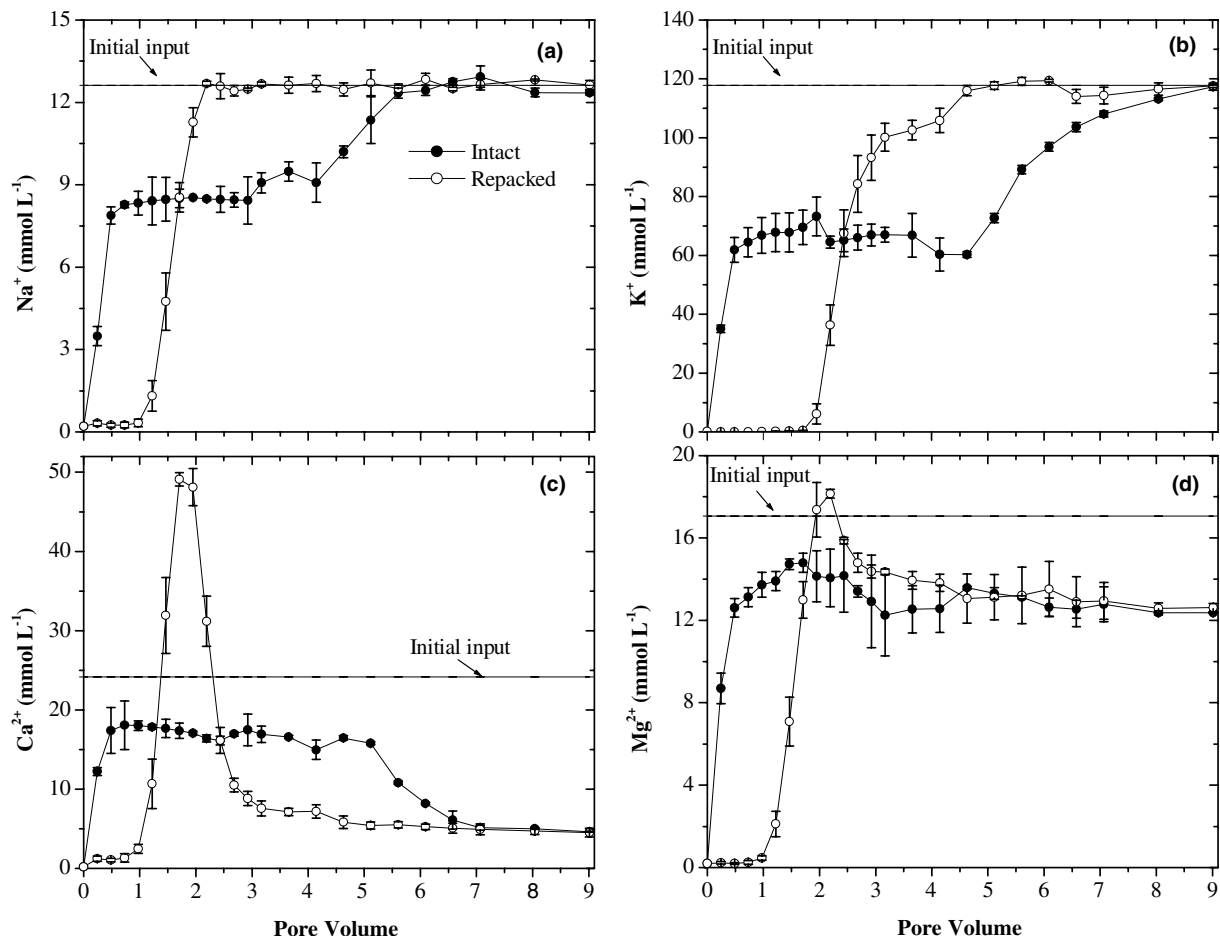


Fig. 5. (a) Sodium, (b) potassium, (c) calcium, and (d) magnesium concentrations of effluents from the intact and repacked soil columns. Error bars represent standard deviation of triplicate measurements.

H_2O , $K_{\text{SP}} = 2.4 \times 10^{-5}$ at 25°C , Langmuir, 1997). Formation of gypsum precipitates was also observed in field studies (Guo et al., 2001b) and during leachate sample storage in the laboratory. Therefore, gypsum precipitation is also likely responsible for the time-dependent reduction in hydraulic conductivities shown in Fig. 1.

3.4. Movement of leachate Na^+ , K^+ , Ca^{2+} and Mg^{2+}

Movement of leachate Na^+ (Fig. 5(a)) was similar to Cl^- (Fig. 4(a)). The lower sorptive reactivity of Na^+ may be attributed to the high concentration of K^+ in the SMS leachate ($117.77 \text{ mmol}_c \text{ l}^{-1}$, Table 1); little Na^+ was adsorbed because of the “swamping” effect of K^+ and its higher affinity for soil particles (Varadachari et al., 1991).

Breakthrough of K^+ was retarded relative to Na^+ . As shown in Fig. 5(b), effluent K^+ reached input values only after 5 pore volumes of leachate had passed through the repacked soil columns. For Cl^- , SO_4^{2-} (Fig. 4) and Na^+ (Fig. 5(a)), $C/C_0 = 1$ occurred at 1.9 pore volumes. Clearly, leachate K^+ was preferentially adsorbed. The

K^+ concentration curves are quite similar to those of DOC (Fig. 2).

Breakthrough behavior of the bivalent cations Ca^{2+} and Mg^{2+} was unique. As illustrated in Fig. 5(c), $C/C_0 = 1$ for Ca^{2+} occurred at ~ 1.25 pore volumes for repacked columns. Effluent concentrations were double that of input values by 1.9 pore volumes. Elevated effluent Ca^{2+} concentrations apparently result from displacement of soil indigenous exchangeable Ca^{2+} ($29.2 \text{ mmol kg}^{-1}$, Table 2) by leachate K^+ . This “pulse” of displaced Ca^{2+} was followed by a dramatic reduction to effluent values that were $< 1/3$ of input values (Fig. 5(c)), demonstrating soil retention of leachate Ca^{2+} by mechanisms other than adsorption. In addition to the precipitation of gypsum reflected in sulfate losses (Fig. 4(b)), leachate Ca^{2+} may have also precipitated with CO_3^{2-} present in the input solution and resulting from DOM oxidation (Fig. 2) during leachate transport.

Speciation of the input solution (Table 1) in equilibrium with atmospheric $P \text{ CO}_2$ using MINTEQA2 (Allison et al., 1990), including consideration of DOM complex formation (Allison and Perdue, 1994), indi-

cated supersaturation with respect to aragonite, calcite, gypsum, magnesite and hydroxyapatite. This was despite the fact that ca. 45% of the Ca and 8% of the Mg speciated into DOM complexes. The CaCO_3 and gypsum precipitates blocked the soil pores and decreased the leachate flow rate (Fig. 1). Deposition of CaCO_3 particles in the effluent collectors was also observed. The precipitate dissolved instantly and produced gas bubbles upon addition of dilute HCl, indicative of carbonate solids. A measured increase in soil inorganic carbon content from 0 to 1.5 g kg^{-1} after the experiments were completed also indicates that CaCO_3 had precipitated. Leachate Ca^{2+} moved in the intact soil columns in patterns similar to the repacked columns, except for the initial preferential flow effect and a lower total displacement of indigenous Ca^{2+} . Replacement of soil exchangeable Ca^{2+} with leachate K^+ resulted in a broad plateau of effluent Ca^{2+} in the intact columns. Lower effluent Ca^{2+} concentrations relative to input at long times is consistent with formation of CaCO_3 . The effluent never exceeded input Ca^{2+} concentrations, suggesting that displaced Ca^{2+} was largely retained in carbonate and sulfate solids.

The high concentration of leachate K^+ also displaced soil adsorbed Mg^{2+} and promoted a peak in effluent Mg^{2+} concentration in excess of input values for the repacked columns (Fig. 5(d)). For Mg^{2+} , $C/C_0 = 1$ occurred in repacked columns at 1.9 pore volume, suggesting that adsorptive retardation of Mg^{2+} was negligible. Concentrations of effluent Mg^{2+} were diminished progressively after the peak, suggesting precipitation of Mg^{2+} in mixed carbonate and sulfate solids (e.g., $\text{Ca}_x\text{Mg}_{1-x}\text{SO}_4$, $\text{Ca}_x\text{Mg}_{1-x}\text{CO}_3$). Accumulation of Ca^{2+} and Mg^{2+} precipitates was also found to occur in field soils subjected to SMS weathering (Guo et al., 2001b).

3.5. Movement of leachate HPO_4^{2-} , NO_3^- and NH_4^+

Although the input solution had a phosphate concentration at 0.16 mmol l^{-1} (Table 1), no HPO_4^{2-} was detected in any of the column effluents, implying that all HPO_4^{2-} had been adsorbed by soil minerals and/or precipitated as hydroxyapatite. Phosphate has a high affinity for hydroxylated surfaces and can form inner-sphere complexes with Fe/Al hydroxides (Hiradate and Inoue, 1998). The test soil contained a significant amount of CBD-extractable Fe (Table 2). Field studies also showed that 2 years of weathering released 1.1 and 0.6 Mg ha^{-1} of HPO_4^{2-} into underlying soils from 90 to 150 cm high SMS piles, respectively, but it was not detected after interaction with 90 cm of soil (Guo et al., 2001a), and no water extractable HPO_4^{2-} was detected in the affected soils (Guo et al., 2001b).

The input solution contained no NO_3^- (Table 1), and little NO_3^- was detected in effluents, indicating that net

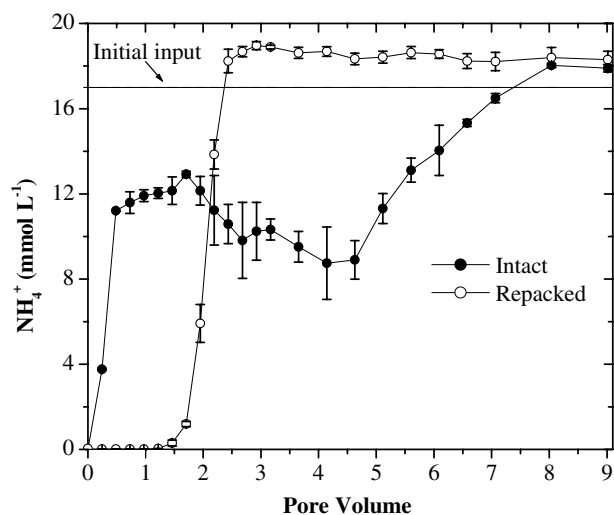


Fig. 6. Ammonium concentrations of effluents from the intact and repacked soil columns. Error bars represent standard deviation of triplicate measurements.

nitrification did not occur during leachate transport in the soil columns. This is despite the fact that input solutions contained 17 mmol l^{-1} of NH_4^+ (Table 1). Presumably, nitrification was inhibited by the anoxic conditions predominant in the water-saturated, organic-rich columns.

The NH_4^+ breakthrough curve is illustrated in Fig. 6. Breakthrough of NH_4^+ in the repacked columns occurred at 1.9 pore volumes, similar to Cl^- . No NH_4^+ was retained by the soil, probably because of the high concentration of competing K^+ ions ($118 \text{ mmol}_c \text{ l}^{-1}$, Table 1). Further, N mineralization (ammonification) and/or desorption of indigenous NH_4^+ (if there are any) resulted in concentrations of NH_4^+ $1\text{--}2 \text{ mmol l}^{-1}$ higher in the effluent (both intact and repacked) than the input solutions (Fig. 6). The N mineralization corroborates our contention that biodegradation of DOM occurred during SMS leachate transport in the soil columns (Fig. 2).

4. Conclusions

Movement of SMS leachate in repacked soil columns was mainly through matrix flow, whereas preferential flow predominated in early transport through intact soil columns. Solution chemistry was significantly altered during leachate movement in soil. Leachate DOM and phosphate were retained by soil minerals while Cl^- , SO_4^{2-} , Na^+ and NH_4^+ were excluded. High concentrations of leachate K^+ were adsorbed and soil indigenous exchangeable cations were displaced. Bio-decomposition of DOM was coupled with reductive dissolution of Fe and Mn (hydr)oxides, particularly in repacked soil columns, and N mineralization increased effluent NH_4^+

over input values. Nitrification was inhibited due to a lack of O_2 (g). Soil retention of leachate Ca^{2+} and Mg^{2+} was facilitated through formation of SO_4^{2-} and CO_3^{2-} precipitates, concentrations of the latter being augmented by DOM oxidation. As a result of carbonate and sulfate precipitation, preferential flow channels in the intact soil columns were blocked and SMS leachate moved dominantly via matrix flow in the late stage. The precipitates appeared to also diminish microporosity; matrix flow rates in all soil columns decreased greatly. The results suggest that the rapid movement of SMS solutes in field soils is mainly via preferential flow. In deep subsurface soils with few preferential channels, leachate solutes may be completely retained. The results herein and those in Guo et al. (2001a,b) indicate that groundwater may be adversely impacted if weathering of SMS is carried out in fields with shallow water table (i.e. <3 m) or coarse subsoil. It should be safe with respect to groundwater quality if weathering of SMS is conducted on compact surfaces or in fields with a condensed soil layer (no structural channels) above the groundwater table. However, SMS leachate may scatter via runoff and cause surface water contamination if impeded on compact surfaces without a trench or barrier around. Necessary is that SMS weathering sites be adequately distant from rivers and streams. Conservatively, all leachate from SMS field weathering should be collected and disposed of properly.

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