

Leachate Chemistry of Field-Weathered Spent Mushroom Substrate

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ABSTRACT

Passive leaching by rainfall and snowmelt is a popular method to treat piles of spent mushroom substrate (SMS) before its reuse. During this field weathering process, leachate percolates into the underlying soils. A field study was conducted to examine the chemistry of SMS leachate and effects of infiltration. Two SMS piles were deposited (90 and 150 cm in height) over a Typic Hapludult and weathered for 24 mo. Leachate was collected biweekly using passive capillary samplers. The SMS leachate contained high concentrations of dissolved organic carbon (DOC; 0.8–11.0 g L⁻¹), dissolved organic nitrogen (DON; 0.1–2 g L⁻¹), and inorganic salts. The pH, electrical conductivity, and acid neutralizing capacity were 6.6 to 9.0, 21 to 66 ds m⁻¹, and 10 to 75 mmol L⁻¹, respectively. Inorganic chemistry of the leachate was dominated by K⁺, Cl⁻, and SO₄²⁻. Leachate DOC was predominantly low molecular weight (<1000 Da) organic acids. During 2 yr of weathering, the 90-cm SMS pile released (per cubic meter of SMS) 3.0 kg of DOC, 1.6 kg of dissolved N, and 26.6 kg of inorganic salts. The 150-cm pile released (per cubic meter of SMS) 2.8 kg of DOC, 0.7 kg of dissolved N, and 13.6 kg of inorganic salts. The 150-cm pile retained more water and exhibited lower net nitrification compared with the 90-cm pile. The top 90 cm of soil retained 20 to 89% of the leachate solutes. Weathering of SMS in piles of 90 cm depth or greater may adversely affect ground water quality.

SPENT mushroom substrate (SMS) is an organic waste resulting from commercial mushroom production. In the USA, production of the white button mushroom *Agaricus bisporus* results in the generation of more than 10⁶ m³ of SMS annually, with half of the material being generated in Pennsylvania alone (Chong and Hamersma, 1997). The major ingredients of SMS are composted straw, hay, peat, horse manure, poultry manure, and gypsum. In addition to these bulk components, SMS may also contain some nutrient additives, such as potassium salts, ammonium nitrate, super phosphate, etc. (Gerrits, 1988). On average, fresh SMS is approximately 60% water (by mass) (Levanon and Danai, 1995), whereas approximately 65% of the dry matter is organic (Gerrits, 1994; Beyer, 1999).

Spent mushroom substrate is regarded favorably as a soil amendment in production agriculture and ecosystem restoration (Chong et al., 1991; Steffen et al., 1994; Stark and Williams, 1994; Wuest et al., 1995). However, a high salt content limits its suitability as a medium for plant growth (Chong and Rinker, 1994; Ciavatta et al., 1993). For this reason, Pennsylvania state law requires that SMS be weathered in the field for 2 yr prior to reuse (Pennsylvania Department of Environmental Protection, 1997).

During the weathering process, SMS is leached of soluble constituents by rainwater and snowmelt. Al-

though field studies are lacking, laboratory studies have shown that water extracts of SMS contain high concentrations of organic carbon, K, Ca, Mg, Cl, and SO₄ (Chong and Rinker, 1994). Maher (1994) found that leaching an SMS–peat column with distilled water at 10-d intervals over a 60-d period resulted in leaching of about 94% of total K, 33% of total P, and 15% of total N. The leachate percolates into soil and associated solutes may be transported to ground water. When 170 m³ ha⁻¹ of SMS were mixed with the top 8 cm of soil, after 210 d of field weathering, 80% of S, 3% of K, 16% of Ca, and 37% of Mg in the applied SMS were recovered in soil leachate collected at 24 cm depth (Stewart et al., 2000). The chemical composition and transport of SMS leachate in field soil environments are not known, despite the fact that they probably affect the quality of receiving waters. In the interest of protecting ground water resources, the chemical properties of SMS leachate, as affected by interaction with soil, warrant further study.

When applied to the field at low rates, SMS appears to be beneficial to soil fertility and it does not pose a threat to water quality. For example, when SMS was spread 2.5 cm thick over a corn field three times per year, ground water quality was not influenced (Kaplan et al., 1995). Wuest et al. (1995) reported that when fresh SMS was applied to a corn field at a thickness of 10 cm, soil cation exchange capacity (CEC), Mg, K, Ca, and P levels were improved, whereas solute loss with runoff and leaching to depth were negligible. If applied to the field at high rates, SMS may pollute ground water. Kaplan et al. (1995) monitored soil water (100 cm depth) and ground water quality under 50-cm piles of weathering SMS over 1 yr. They measured DOC in soil water up to 880 mg L⁻¹, and concentrations of K⁺, Ca²⁺, Cl⁻, and SO₄²⁻ were more than 1000 mg L⁻¹. Ground water concentrations of DOC, K⁺, Na⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻ were 5 to 20 times higher than background values. However, their method of sampling does not permit a quantitative evaluation of solute flux. Also, the conditions employed in that study do not accurately depict the current practice employed by producers, which involves stacking SMS piles to 90 cm height for 2 yr of weathering.

Currently, the Pennsylvania Department of Environmental Protection regulates stacking of SMS piles at or

Abbreviations: ANC, acid neutralizing capacity; DOC, dissolved organic carbon; DOM, dissolved organic matter; DON, dissolved organic nitrogen; EC, electrical conductivity; HMW, high molecular weight; IC, ion chromatography; LMW, low molecular weight; LMWOA, low molecular weight organic acid; PL3, leachate collected directly from the 90-cm spent mushroom substrate pile; PL5, leachate collected directly from the 150-cm spent mushroom substrate pile; SL3, soil leachate collected underneath the 90-cm pile at 90 cm soil depth; SL5, soil leachate collected underneath the 150-cm pile at 90 cm soil depth; SC, control soil leachate collected in an adjacent corn field at 90 cm soil depth; SMS, spent mushroom substrate.

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Table 1. Description of the soil profile underneath the spent mushroom substrate piles.

Genetic horizons	Depth	pH [†]	Texture [‡]	Color	Structure	Moist consistence
	cm					
Ap1	0–13	7.03	silt loam	7.5YR 3/3	strong, granular	very firm
Ap2	13–27	7.32	silt loam	7.5YR 4/4	strong, blocky	firm
AB	27–40	7.60	sandy loam	7.5YR 4/3	weak, blocky	firm
Bt1	40–58	7.67	sandy loam	7.5YR 4/6	moderate, blocky	firm
Bt2	58–86	7.69	sandy loam	7.5YR 5/6	moderate, blocky	firm
Bt3	86–112	7.71	sandy loam	10YR 5/6	moderate, blocky	firm
BC	112–125	7.09	loam	10YR 5/8	weak, blocky	firm
C1	125–141	7.41	loam	7.5YR 5/6	massive	very firm
C2	141–200+	7.38	loam	2.5YR 4/6	massive	very firm

[†] Determined by pH electrode in a 1:1 (by mass) soil–water paste.

[‡] Measured using the hydrometer method.

below a height of 90 cm (3 ft) after settling in fields with seasonal ground water tables more than 50 cm from the surface. No information is available about the leachate chemistry of SMS weathered in piles at 90 cm height. The extent to which underlying soils retain leachate solutes produced from such a load remains unclear. Faced with the large quantity of SMS produced each year in Pennsylvania, a recent proposal suggests increasing the allowable height of SMS weathering piles to 150 cm (5 ft). However, little is known about the effect of this practice on soil and ground water quality. Therefore, the objectives of this study were to characterize changes in the chemistry of SMS leachate over the full course of weathering, estimate the amount of associated solute release and subsequent retention by the soil, and evaluate the proposed increase in height of SMS weathering piles.

MATERIALS AND METHODS

Field Trial

A field experiment was carried out in Chester County, PA. Two SMS piles were deposited in a fallow agricultural field dominated by grasses. The piles were formed into two rows (20 × 6 m) to be 90 cm (3 ft) and 150 cm (5 ft) in height after settling. The SMS employed in the field experiment was obtained from Elite Mushroom Co., Avondale, PA and was composed mainly of composted horse manure, straw, poultry manure, waste brewer's grains, and gypsum. The experiment site has a mean annual precipitation of 1160 mm, a mean annual temperature of 11.9°C, a slope of 5%, and a very deep, well drained, moderately permeable soil formed in residuum weathered from micaceous schist (fine-loamy, mixed, semiactive, mesic Typic Hapludult). Table 1 contains soil profile descriptions of the study site. Selected chemical properties of the SMS are listed in Table 2.

Six glass-fiber wick samplers were constructed and pre-treated as described in Goyné et al. (2000) prior to installation beneath each pile. Prior field and laboratory studies have shown this type of sampler to exhibit ca. 100% collection efficiency as a result of its high conductivity and the constant tension applied at the soil–sampler interface (Brown et al., 1986; Boll et al., 1992). Three replicate samplers were installed at the soil surface to collect SMS leachate, and three replicates were installed at 90 cm depth in the soil to sample soil leachate as influenced by SMS weathering. Surface area of each sampler was 900 cm², and the hanging wick water column provided 0.5 m of tension at soil contact. For comparison, three additional samplers were placed at 90 cm depth in an adjacent corn (*Zea*

mays L. subsp. *mays*) field that received N fertilization at the recommended rate, in addition to shallower-depth SMS applications more than 12 yr prior to this study.

The field weathering experiment lasted for 2 yr, from July 1997 to July 1999. During weathering, the piles were undisturbed. The SMS and soil leachate samples were collected every 1 or 2 wk, depending on the amount of precipitation. For convenience, leachates from the 90- and 150-cm SMS piles are referred to hereafter as PL3 and PL5, respectively. Soil leachate, collected at 90 cm soil depth underneath the 90- and 150-cm SMS piles and in the corn field, are referred to as SL3, SL5, and SC, respectively.

Analytical Methods

After collection, the samples were centrifuged at 10 200 × g for 15 min and then passed through a 0.5-μm glass fiber filter to remove particulate matter. The filtrates were stored at 4°C prior to analysis. The pH values of leachate samples were measured using a Beckman Φ310 pH meter (Beckman Coulter, Fullerton, CA) with an Orion ROSS 81-02 combination pH electrode (Thermo Orion, Beverly, MA). Electrical conductivity (EC) was analyzed by an Accumet Model 50 pH/ion/conductivity meter (Fisher Scientific, Pittsburgh, PA) with a YSI 3403 conductance cell (cell constant = 1.0 cm⁻¹) equipped with an ATC probe to normalize the reading to 25°C. Dissolved organic carbon (DOC) content was determined with a Shimadzu TOC-5000A total organic carbon analyzer and an ASI-5000A auto sampler (Shimadzu, Kyoto, Japan). Acid neutralizing capacity (ANC) was measured using the Gran-titration method (Morel and Hering, 1993). Inorganic anions and low molecular weight organic acids (LMWOAs) were measured by ion chromatography (IC) (Dionex Series 4000I with an AS40 automated sampler, an IonPac AS11 ion exchange column, and a CD20 conductivity detector; Dionex Corp., Sunnyvale, CA). The flow rate was 1 mL min⁻¹ and run time was 30 min per sample. A gradient mobile phase comprising water and 0.05 M NaOH was employed. Inorganic cations were determined using a Video 22 AA/AE spectrophotometer (Instrumentation Laboratories, Lexington, MA) and Technicon (Franklin, MA) autoanalyzer for NH₄⁺. Total organic N concentrations in leachates were calculated by subtracting NH₄⁺ concentrations from total Kjeldahl N concentrations. Kjeldahl digestion of organic N to NH₄⁺ was performed using standard methods (Clesceri et al., 1998) and NH₄⁺ was measured using a Technicon autoanalyzer.

Allocation of dissolved organic matter (DOM) into low (<1000 Da) and high (>1000 Da) molecular weight fractions was achieved by ultrafiltration and dialysis with an Amicon (Beverly, MA) CH2 ultrafiltration system equipped with an Amicon S1Y1 spiral-wound membrane filter cartridge (re-

Table 2. Selected chemical components of fresh spent mushroom substrate (SMS; oven-dry basis).

Compound	Contents
	g kg ⁻¹
Organic matter	675
Organic carbon	330
Organic nitrogen	26.4
Ash content	325
Water-extractable components†	
DOC‡	42.4
NH ₄ ⁺	ND§
NO ₃ ⁻	0.2
Cl ⁻	6.3
SO ₄ ²⁻	31.1
PO ₄ ³⁻	2.7
K ⁺	11.9
Na ⁺	2.1
Ca ²⁺	9.4
Mg ²⁺	2.3

† Extract at a 1:19 SMS–water ratio for 24 h.

‡ Dissolved organic carbon.

§ Nondetectable.

generated cellulose, 1000-Da molecular weight cutoff). The percent of DOC in each molecular weight fraction was determined. Molar absorptivity was determined using UV spectroscopy (Shimadzu 3101PC UV-Vis-NIR spectrometer) with absorbance at 280 nm normalized by DOC concentration.

Data Analysis

Data are expressed as monthly means of triplicate values weighted by sample volume. Volume weighted mean (VWM) concentrations of all constituents were calculated as follows:

$$\text{VWM}_a = \frac{\sum_{i=1}^n C_{ai} V_i}{\sum_{i=1}^n V_i} \quad [1]$$

where C_{ai} is the concentration of species a in sample i , V_i is the volume of leachate sample i , and n is the number of samples collected in a given month from the set of triplicate samplers.

The mass flux of each solute (i) released from the SMS pile and (ii) leached through the 90-cm soil depth were calculated from the product of volume weighted mean data and associated water fluxes over the 24-mo period. Retention of leachate solutes in the top 90 cm of soil was calculated by the difference between (i) and (ii).

RESULTS AND DISCUSSION

Leachate Flux Pattern

Leachate water fluxes exhibited time dependencies that were similar to those of the precipitation regime (Fig. 1). In the first 4 mo, only a small volume of SMS leachate was collected as most of the precipitation was absorbed by the SMS material. Breakthrough of water from the 150-cm pile proceeded 30 d after it was observed for the 90-cm pile. In the 2-yr field experiment, approximately 51 and 40% of the precipitation passed through the 90- and 150-cm SMS piles, respectively, and percolated to 90 cm depth in the soil.

Leachate pH and Electrical Conductivity

The pH values of SMS and soil leachates fluctuated between pH 6.5 and 9.0 (Fig. 2). The results are consis-

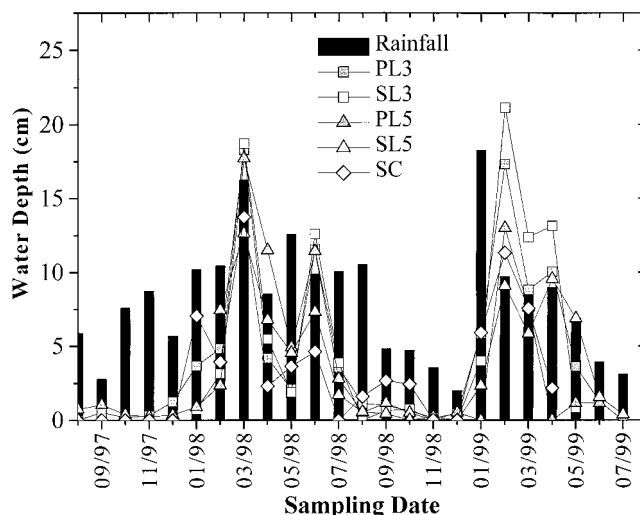


Fig. 1. Rainfall and water flux time series measured under spent mushroom substrate (SMS) piles (PL3 and PL5), at 0.9 m depth in soil under SMS piles (SL3, SL5), and in an adjacent corn field (SC).

tent with previously reported values for SMS leachate and water extracts (Szmidski and Chong, 1995; Kaplan et al., 1995). Most pH values fall between 7.5 and 8.5. Interaction with the top 90 cm of soil had little influence on leachate pH. Soil leachate collected underneath the SMS piles had pH values of 7.7 to 8.4, which were close to the pH level of the control soil solution (7.6 to 8.1). The initial high pH of SMS leachates was probably due to the production of ammonia from deamination of amino acids and proteins during composting (Zibilske, 1998). The fact that PL3 reached a maximum pH (August 1997) earlier than PL5 (November 1997) is suggestive of greater microbial activity in the 90-cm pile at early times.

Electrical conductivity (EC) values provide an index of the total dissolved electrolyte concentrations. The

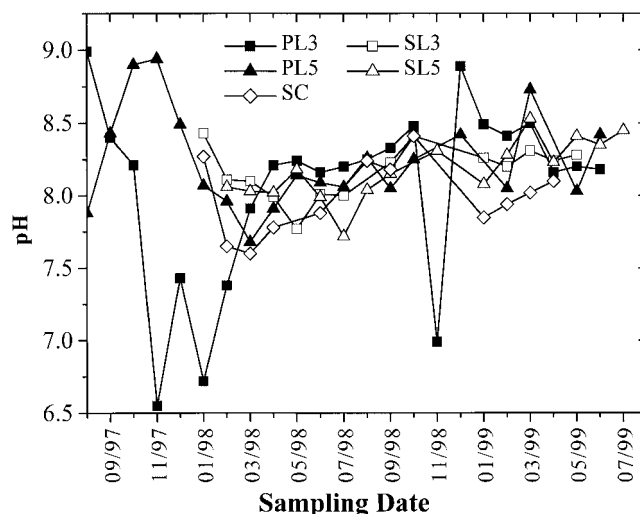


Fig. 2. pH of the spent mushroom substrate (SMS) leachate (PL3 and PL5) and soil leachate (SL3 and SL5) under SMS piles and in an adjacent corn field (SC). Symbols indicate monthly volume weighted means of triplicates by sampling date.

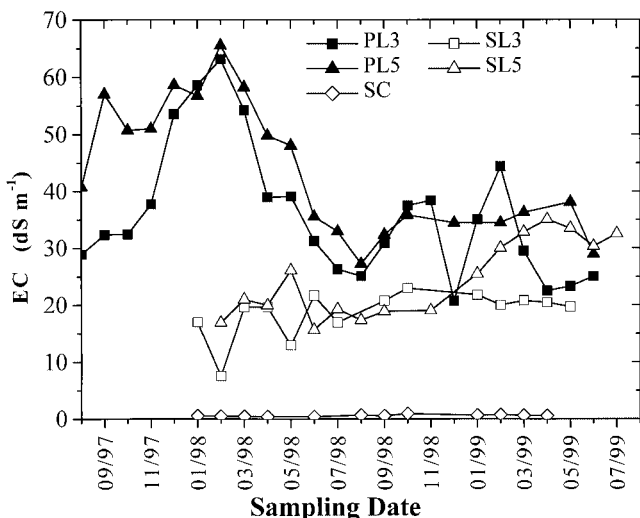


Fig. 3. Electrical conductivity (EC) of the spent mushroom substrate (SMS) leachate (PL3 and PL5) and soil leachate (SL3 and SL5) under SMS piles and in an adjacent corn field (SC). Symbols indicate monthly volume weighted means of triplicates by sampling date.

EC values of SMS and soil leachates were very high initially and decreased with time, but remained elevated relative to the control for the duration of the study (Fig. 3). There was no effect of pile height on EC; PL3 and PL5 EC values ranged from 21 to 63 dS m⁻¹ and 29 to 66 dS m⁻¹, respectively. Prior studies have shown that soil solution EC values in excess of 4 dS m⁻¹ can hinder plant growth as a result of osmotic stress (Plaster, 1992). A large decrease in EC was observed in soil leachates collected at depth (Fig. 3), indicating that the top 90 cm of mineral soil retained a significant fraction of SMS derived salts. Even so, compared with the EC of the control soil leachate (0.5 dS m⁻¹), soil waters affected by SMS were quite saline.

The EC values of leachates from both SMS piles showed similar time trends: a gradual increase for the first 6 mo, a maximum value after 7 mo of weathering, and then a slow decrease thereafter. After 2 yr, PL3 and PL5 had EC values of 25 and 29 dS m⁻¹, respectively. The ECs of soil leachates under the SMS piles were relatively stable, but that of SL5 began to increase after 18 mo of weathering, and finally exceeded that of PL5.

Inorganic Cations in Spent Mushroom Substrate Leachate

The major inorganic cations in SMS leachate were K⁺, Na⁺, Ca²⁺, and Mg²⁺ with concentrations ranging from 72 to 316, 21 to 76, 2 to 116, and 27 to 86 mmol_c L⁻¹, respectively (Fig. 4). Concentrations of total Fe, Al, and Mn in the leachates were always less than 0.5 mmol L⁻¹, and Cu, Zn, and Pb were less than 6 μmol L⁻¹. The time trends in cation concentrations track the EC values (Fig. 3), increasing gradually at early weathering times, reaching a maximum after 6 or 7 mo, and then decreasing slowly. PL5 had higher concentrations of K⁺ and Na⁺ than PL3, but concentrations of Ca²⁺

and Mg²⁺ were similar for PL3 and PL5. Ammonium, which was present in Year 1, later became undetectable (Fig. 4). Since fresh SMS contains little NH₄⁺ (Table 2), leachate NH₄⁺ was a product of either ammonification of amino acids and proteins in SMS, or dissimilatory nitrate reduction. Field weathering of SMS is a passive composting process (Pennsylvania Department of Environmental Protection, 1997) that begins with a fast breakdown of sugars, amino acids, and other easily degradable substances (Finstein and Morris, 1975; Chefetz et al., 2000). The fact that maximum pH and NH₄⁺ coincided for both PL3 and PL5 strongly suggests that the high pH derives from ammonification (Fig. 2 and 4). It is also interesting to note that these maxima arrived 5 mo earlier in the weathering process for PL3 relative to PL5 (Fig. 4a,b). This suggests that the composting process proceeds more rapidly in the 90-cm pile than the 150-cm pile. With increased weathering, NH₄⁺ decreased and eventually was undetectable in SMS leachates. This is probably a result of nitrification.

Soil leachate under the SMS piles had the same major cations and relative predominance, but much lower concentrations, than SMS leachate. However, these concentrations were still 10 to 150 times higher than the SC values (Fig. 4c). Similar results were reported by Kaplan et al. (1995), who found that soil water collected at 1 m depth by vacuum lysimeters contained elevated concentrations of K⁺, Na⁺, Ca²⁺, and Mg²⁺, and ground water concentrations of these cations were increased 10 to 30 times. The concentrations of these cations in soil water were increased 2 to 200 times even when SMS was applied at 3 cm depth.

Weathering of SMS altered the relative predominance of cations in soil leachate relative to the control; in SC the predominant cation was Ca²⁺ (Fig. 4c) whereas K⁺ was dominant in SL3 and SL5 (Fig. 4a,b). Throughout the weathering process, the major cations in SL3 had relatively stable concentrations (Fig. 4a). But in SL5, after 18 mo, K⁺ concentration increased and finally reached the same level as PL5 (Fig. 4b). The increase in K⁺ is evidently responsible for the concurrent increase in EC (Fig. 3).

Inorganic Anions in Spent Mushroom Substrate Leachate

Chloride, SO₄²⁻, and NO₃⁻ were dominant inorganic anions in SMS leachate with concentrations ranging from 27 to 196, 79 to 324, and 0.03 to 118 mmol_c L⁻¹, respectively (Fig. 4). Phosphate concentration was consistently less than 2.5 mmol L⁻¹. As with the cations, concentrations of all three major inorganic anions peaked at the fifth or sixth month of weathering, and then stabilized after 12 mo. Therefore, in terms of salt release, most of the weathering occurs in the first year.

Despite the higher mass of N in overlying SMS, NO₃⁻ concentrations were lower in PL5 than in PL3 (Fig. 4a,b). Leachate NO₃⁻ is a product of ammonium oxidation. Prior work has shown that ammonification is predominant in early phases of composting and the resulting high pH inhibits nitrification (Myrold, 1998).

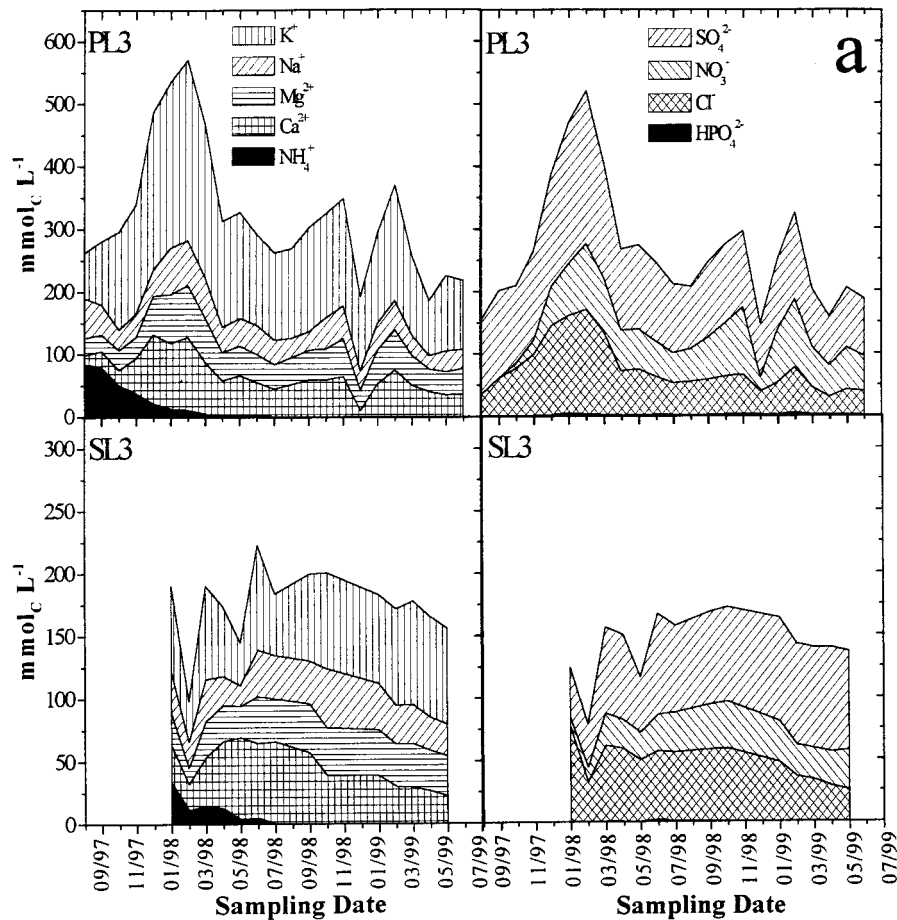


Fig. 4. (a) Cation and anion concentrations of the spent mushroom substrate (SMS) leachate (PL3) and soil leachate (SL3) under SMS piles. Symbols indicate monthly volume weighted means of triplicates by sampling date.

As a result, the SMS leachates contained little NO_3^- at early weathering times (Fig. 4a,b). Accumulation of NH_4^+ under oxic conditions stimulates the growth of NH_4^+ oxidizing bacteria and increases leachate NO_3^- concentrations. This was observed for PL3, where oxic conditions appeared prevalent enough to generate high NO_3^- concentrations and NH_4^+ concentrations were subsequently diminished (Fig. 4a). The low concentration of NO_3^- in PL5 is suggestive of the predominance of anoxia in the deeper pile (i.e., nitrification was inhibited by a lack of O_2 or denitrification occurred in the lower wet portion of the pile). The prevalence of anoxic conditions in the 150-cm pile was also evident from structural data on organic matter diagenesis (Chefetz et al., 2000) and the fact that upon removal of the SMS piles, the bottom of the 150-cm pile was relatively wet and enriched in noxious sulfide odors. This suggests that increasing SMS pile height from 90 to 150 cm slows the SMS weathering process by decreasing the extent of aerobic composting. Reduced rates of microbial activity with increased pile depth are consistent with the observation that PL5 showed a maximum NH_4^+ concentration 5 mo later than PL3 (Fig. 4a,b).

The top 90 cm of soil retained a large quantity of SMS-derived inorganic anions (Guo et al., 2001) and

concentrations of the three major anions were significantly reduced in soil leachate. Anion retention at $\text{pH} > 7$ (Table 1) is counterintuitive because the density of positive charged sites on soil particles is expected to be small. However, the high ionic strength of SMS leachate would increase the charge density on Al or Fe oxides and hydroxides that are below their point of zero charge at ambient pH (Chan et al., 1980). Soil retention of anions may also occur through adsorption of ion pairs or via inner-sphere complexation reactions on soil (hydr)oxides (Thomas and Swoboda, 1970; Sposito, 1989). Indeed, retardation of anion transport relative to bulk water has been observed in variable-charge soils at circumneutral pH (Kinjo and Pratt, 1971; Chan et al., 1980).

Despite reductions in the soil, NO_3^- concentrations in SL3 and SL5 ranged from 7 to 38 mmol L^{-1} and 1 to 24 mmol L^{-1} , respectively. These concentrations greatly exceed the USEPA drinking water standard of 0.73 mmol L^{-1} NO_3^- . After the SMS piles were removed, continuous monitoring of NO_3^- in SL3 and SL5 over the following year revealed concentrations ranging from 2 to 32 mmol L^{-1} (data not shown), implying that both 90- and 150-cm SMS piles have the potential to pollute ground water with nitrate.

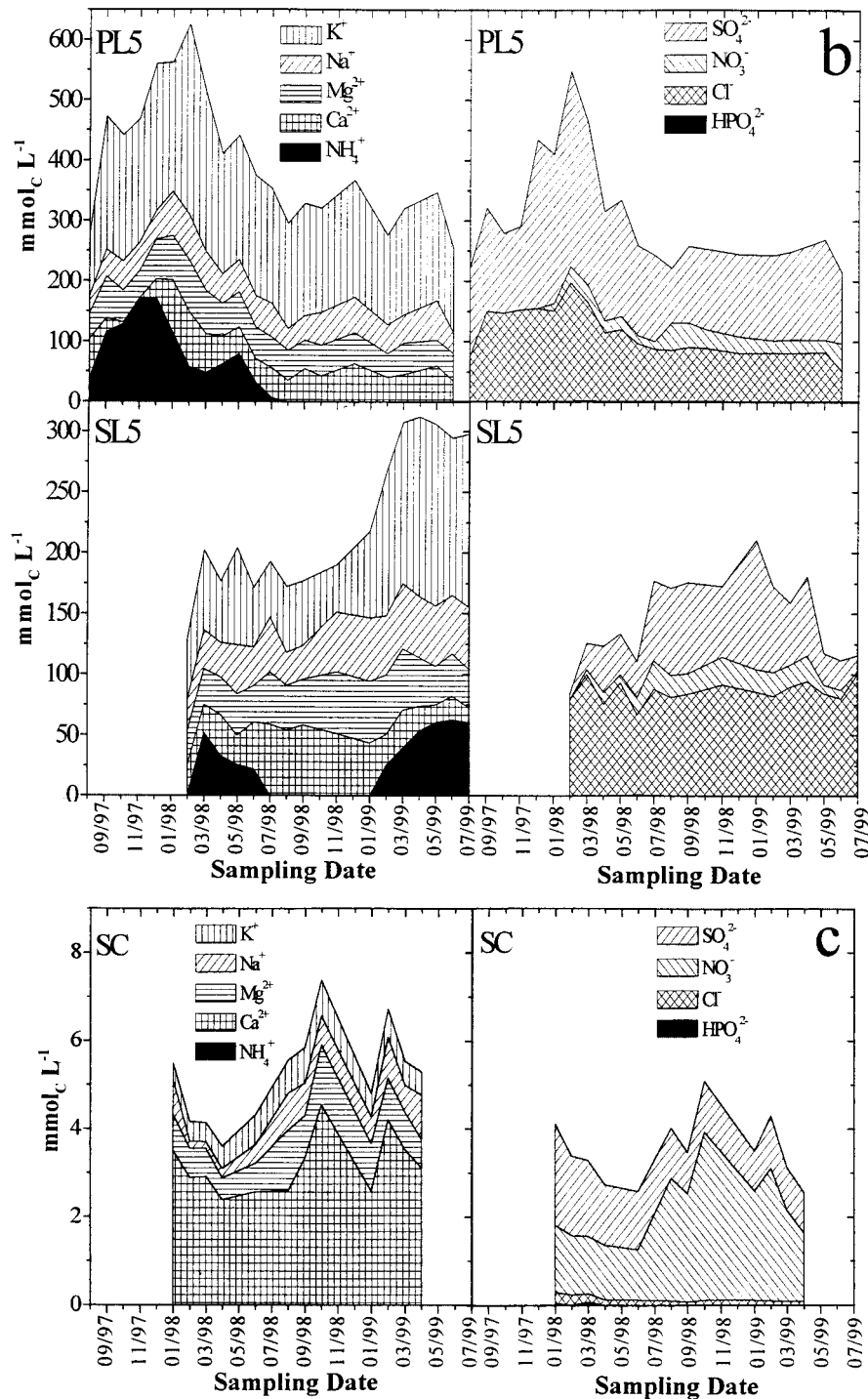


Fig. 4. (b) Cation and anion concentrations of the spent mushroom substrate (SMS) leachate (PL5) and soil leachate (SL5) under SMS piles and (c) in an adjacent corn field (SC). Symbols indicate monthly volume weighted means of triplicates by sampling date.

In addition to increased concentrations, weathering of SMS altered the anion composition of soil leachate relative to the corn field control. In SC, the predominant anion was NO_3^- , but in SL3 and SL5, Cl^- was dominant. After 18 mo of weathering, the concentrations of Cl^- in SL5 exceeded that in PL5, indicating breakthrough of retarded anions. This corresponds to the rise of EC

and K^+ concentration in SL5 at the same time (Fig. 3 and 4b).

Dissolved Organic Carbon and Nitrogen

The DOC concentrations of PL3 and PL5 ranged from 800 to 7900 and 1500 to 11 100 mg L^{-1} , respectively

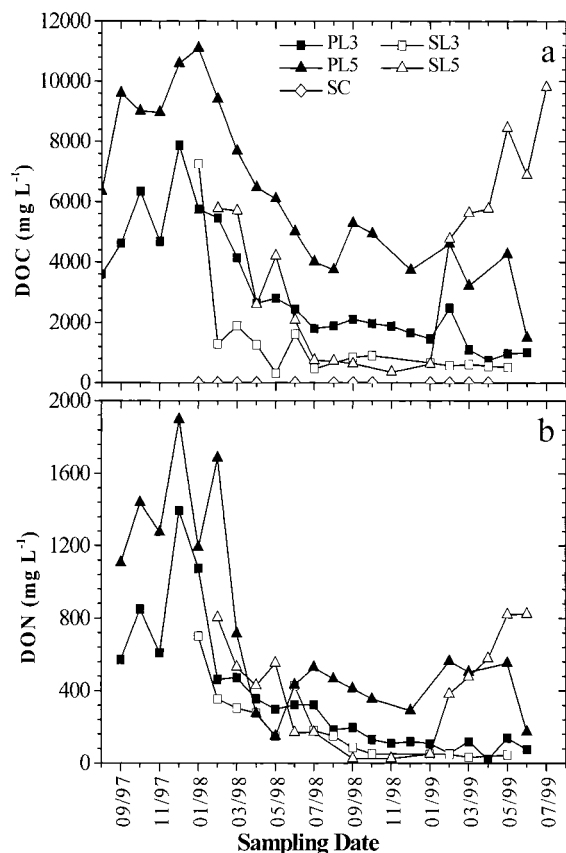


Fig. 5. (a) Dissolved organic carbon (DOC) and (b) organic nitrogen (DON) concentrations of the spent mushroom substrate (SMS) leachate (PL3 and PL5) and soil leachate (SL3 and SL5) under SMS piles and in an adjacent corn field (SC). Symbols indicate monthly volume weighted means of triplicates by sampling date.

(Fig. 5a). These SMS leachates contain much higher DOC concentrations than natural waters. Leachate from organic horizons of forest soils, which generate some of the highest DOC concentrations in natural ecosystems, contain 10 to 100 mg L⁻¹ of DOC (Currie et al., 1996). For both SMS piles, DOC increased gradually at the beginning, reached a maximum after 5 or 6 mo of weathering, and then decreased slowly. This trend is consistent with patterns for EC, and major ions (Fig. 3 and 4), and supports the contention that weathering of SMS mainly occurs in the first year. Reduced concentrations of DOC in soil leachate indicates that a large quantity of DOC was removed in the top 90 cm of soil, either via adsorption or biodegradation (Fig. 5a). However, compared with the control (ca. 8.5 mg L⁻¹), soil leachate under the SMS piles was still 40 to 200 times higher in DOC.

The DON concentrations of PL3 and PL5 ranged from 70 to 1400 and 150 to 1900 mg L⁻¹, respectively (Fig. 5b). As expected, DON in the SMS leachate correlated with DOC. The DON in the soil leachates decreased after passing through the top 90 cm of soil. The molar C to N ratio of leachate DOM is 8 to 15 depending on sampling date, and is not a clear function of weathering time. This ratio is comparable with that of municipal solid waste reported by Chefetz et al. (1998) to be 8.6

to 10.8. The SMS and soil leachates did not show obvious differences in their C to N ratio. In SL5, a large increase in DOC and DON was observed between January and July 1999 (Fig. 5a). The concurrent increases in EC (Fig. 3) and K⁺ (Fig. 4b) suggest that K⁺ was co-eluted with the DOM, whereas other ions were largely unaffected (Fig. 4 and 5). The molecular weight and aromaticity of the DOM was found to increase significantly in SL5 during the same period (discussed below).

Acid Neutralizing Capacity of Spent Mushroom Substrate Leachate

Acid neutralizing capacity (ANC) is the equivalent sum of all the bases that can be titrated with a strong acid to an equivalence point. It is a useful parameter for measuring the environmental effect of SMS leachate and its potential utility in remediation of acid soils and other acid-affected sites (Stark and Williams, 1994; Buswell, 1994). It indicates the net deficiency of protons in an aqueous solution (Stumm and Morgan, 1996) and the capacity of the solution to buffer additional proton inputs against changes in pH. In these leachate-affected solutions, ANC is likely to be dominated by weakly acidic organic anions.

Leachates from the 90- and 150-cm SMS piles had ANC values ranging from 10 to 45 and 25 to 74 mmol_c L⁻¹, respectively (Fig. 6). These values are much higher than those measured for the SC because the leachates and SMS-affected soil solutions contain high concentrations of DOM. In general, ANC values tracked DOC concentrations quite closely (Fig. 6), indicating the importance of organic anions to the buffering of proton inputs in these systems. For example, the sudden increase in ANC of SL5 after 18 mo is a result of the increase in DOC discussed above. Subtle differences between ANC and DOC indicate that the ANC of DOM is not constant with time, but changes over the course of organic matter diagenesis that accompanies SMS weathering. In particular, changes in the relative predominance and total concentrations of carboxylic and phenolic functional groups will affect the C-normalized values of ANC (Sposito, 1989).

Molar Absorptivity of Leachate Dissolved Organic Matter

Molar absorptivities (ϵ) of leachate and soil solution DOM were measured using UV spectroscopy (absorbance at 280 nm normalized by DOC concentration). The results are presented in Fig. 7. Molar absorptivity is an index of DOM aromaticity. Chin et al. (1994) observed a strong correlation between the aromaticity of aquatic fulvic acids (measured by NMR spectroscopy) and ϵ at 280 nm. Measured values of ϵ for all of our samples varied from 200 to 600 L mol_c⁻¹ cm⁻¹, which is within the range reported for DOM from a diversity of sources (Chin et al., 1994; Chorover and Amistadi, 2001). Molar absorptivity of leachate DOM was not a function of weathering time, and it did not exhibit any clear trends during the 2 yr field experiment. The regression equa-

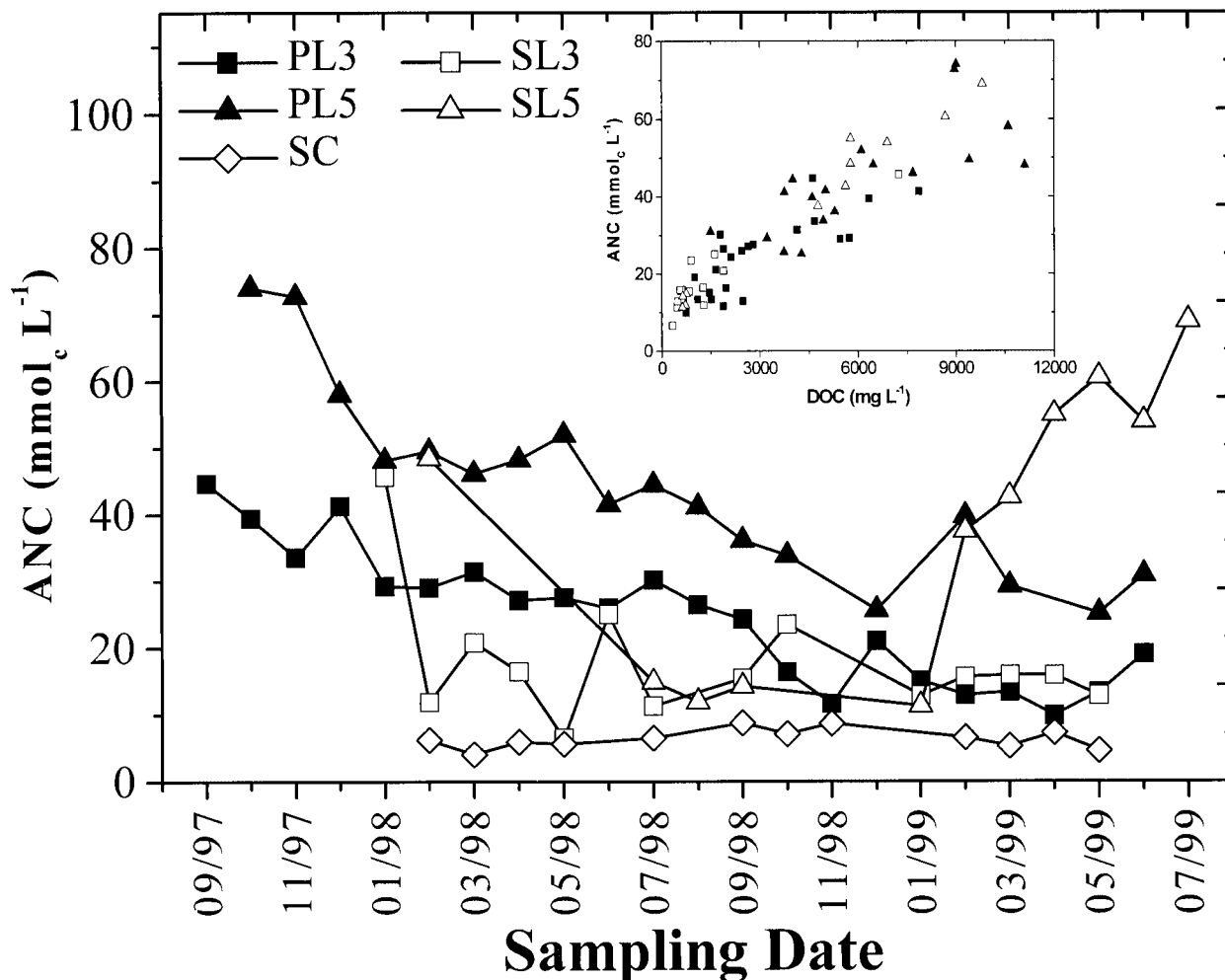


Fig. 6. Acid neutralizing capacity (ANC) of the spent mushroom substrate (SMS) leachate (PL3 and PL5) and soil leachate (SL3 and SL5) under SMS piles and in an adjacent corn field. Symbols indicate monthly volume weighted means of triplicates by sampling.

tion of Chin et al. (1994) predicts that SMS leachate DOM comprised 22 to 36% aromatic C.

For most of the experiment, interaction with the top 90 cm of soil resulted in a reduction in molar absorptivity of DOM (Fig. 7). Aromatic DOM is generally less hydrophilic than aliphatic constituents (Malcolm, 1993). Therefore, these data suggest preferential retention of hydrophobic constituents in the soil. Laboratory studies have shown that aromatic organic compounds are preferentially sorbed by soil minerals (McKnight et al., 1992; Gu et al., 1995; Chorover and Amistadi, 2001).

Molecular Size Distribution of Leachate Dissolved Organic Matter

Leachate and soil solution DOM were separated into low molecular weight (LMW) and high molecular weight (HMW) fractions by ultrafiltration through a membrane with a nominal molecular weight cutoff of 1000 Da. This cutoff is derived from calibration with globular proteins, so it may not represent the true molecular mass of DOM molecules. However, ultrafiltration provides a means for comparing DOM molecular size across treatments and through time. The percentage of DOM that is HMW

is shown in Fig. 8. Evidently, leachate DOM was composed mainly of LMW constituents. High molecular weight DOM constituted 4 to 26% and 7 to 50% of the total DOC in PL3 and PL5, respectively. Investigations of DOM from other composting environments indicate similar results. Harmsen (1983) showed that 33% of leachate DOC from a methanogenic landfill was HMW, whereas Russo et al. (1986) found that more than 56% of landfill leachate DOC passed through a 500-Da filter. In general, LMW constituents are dominant components of soluble OM in a wide range of environments, while macromolecules are less prevalent (Peuravuori and Pihlaja, 1997).

Passage through the top 90 cm of soil did not affect the relative proportion of HMW DOM (Fig. 8). Laboratory studies have shown that larger organic molecules are preferentially adsorbed to some mineral surfaces (Wang et al., 1997; Meier et al., 1999; Chorover and Amistadi, 2001) and, therefore, soil leachate might be expected to contain a higher fraction of LMW constituents than SMS leachate. However, LMW DOM is also readily biodegradable (Russo et al., 1986) and it is possible that selective degradation of LMW components limits their relative accumulation in solution despite preferential

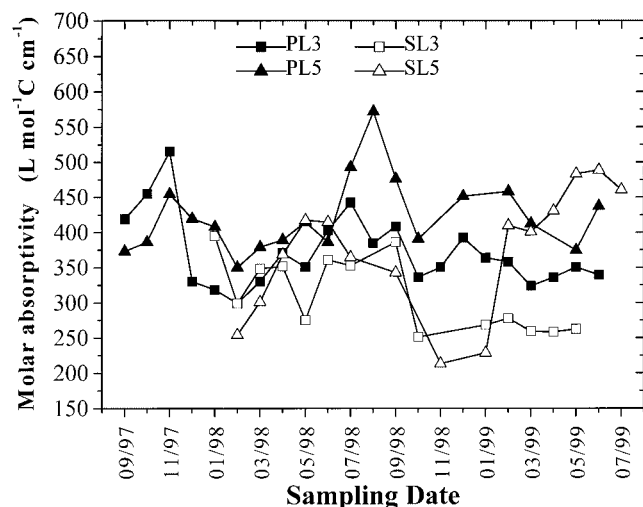


Fig. 7. Molar absorptivity at 280 nm of dissolved organic matter in the spent mushroom substrate (SMS) leachate (PL3 and PL5) and soil leachate (SL3 and SL5). Symbols indicate monthly volume weighted means of triplicates by sampling date.

adsorption of HMW components. It is interesting to note that the breakthrough of DOM observed in SL5 after 18 mo of weathering (Fig. 5) is composed of relatively large (Fig. 8), aromatic (Fig. 7) molecules. As discussed earlier, weathering-induced transformations of organic matter in the deep pile occurred in an anoxic environment, where genesis of aromatic compounds was favored (Chefetz et al., 2000). In the case of SL5, the structure of DOM transported to depth after 18 mo appears to have been influenced by the anoxic diagenetic environment.

In an attempt to elucidate the composition of the LMW DOM, SMS and soil leachate solutions were analyzed for six common aliphatic low molecular weight organic acids (LMWOAs: formic, acetic, malonic, oxalic, phthalic, and citric) using ion chromatography (IC). These acids were present in DOM solution at very low concentrations, mostly 0.02 to 0.4 mmol L⁻¹, and never in excess of 3 mmol L⁻¹ (data not shown). Formic acid was the most prevalent of those measured and it was always present in SMS leachate. At the onset of weathering, SMS leachate contained relatively higher concentrations of these identifiable acids but, as the weathering progressed, their concentrations were reduced. After Month 12, only formic acid was detectable. Evidently, these acids were consumed during transport through the soil and they were rarely detected in soil leachate samples after the first few months. None of the LMWOAs was detected in the SC samples.

Release of Leachate Solutes from Spent Mushroom Substrate Weathering and Their Retention in Soil

The flux of solutes from SMS piles to soils was calculated from water flux and solute concentration data. Release of leachate solutes from SMS piles and their retention in the top 90 cm of soil are listed in Table 3. Over the 2-yr weathering duration, solute efflux from

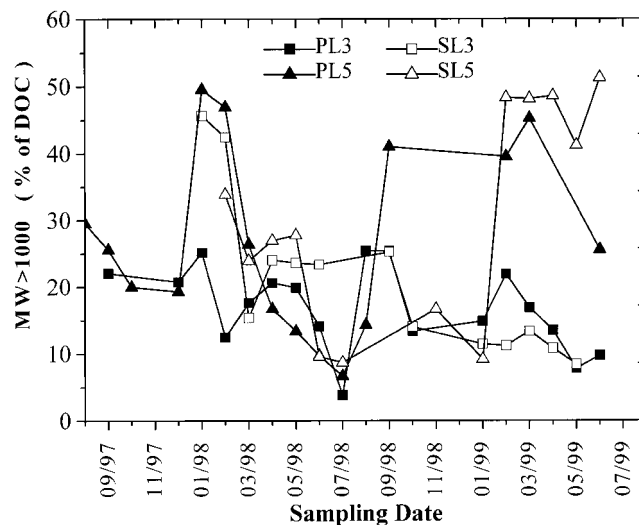


Fig. 8. Percentage of total leachate dissolved organic carbon (DOC) that did not pass through a 1000-Da molecular weight cutoff ultrafiltration membrane. The terms PL3 and PL5 refer to pile leachate solutions. The terms SL3 and SL5 refer to soil leachate solutions. Symbols indicate monthly volume weighted means of triplicates by sampling date.

the 90- and 150-cm piles included 27.3 (PL3) and 43.4 (PL5) Mg ha⁻¹ of DOC, 3.0 and 4.3 Mg ha⁻¹ of DON, and 242 (PL3) and 206 (PL5) Mg ha⁻¹ of inorganic salts. Total effluxes of Cl⁻, SO₄²⁻, and NH₄⁺ were higher for the 150-cm pile (32.2 vs. 28.1, 71.6 vs. 66.1, 5.2 vs. 1.0 Mg ha⁻¹, respectively, for PL5 vs. PL3) but releases of Na⁺, K⁺, Ca²⁺, Mg²⁺, and NO₃⁻ were lower (9.9 vs. 10.6, 63.8 vs. 68.2, 7.9 vs. 13.0, 5.3 vs. 6.73, 10.7 vs. 47.2 Mg ha⁻¹, respectively), especially when normalized to SMS volume as in Table 3. Despite higher leachate solute concentrations, the flux of water from the 150-cm pile was only 80% of that released from the 90-cm pile (Table 3). In other words, the 150-cm pile retained much more water, as was reflected in the greater predominance of anoxic conditions. Greater anoxia in the 150-cm pile probably contributed to the fact that it released only 23% of the NO₃⁻ that was generated during weathering of the 90-cm pile. Given that NH₄⁺ and DON efflux was higher for the 150-cm pile, we infer that nitrification was inhibited and greater denitrification occurred there, although gas efflux was not measured directly. Given the concern regarding nitrate contamination of ground water, SMS release of this mobile contaminant is critical to assessing the risk of SMS weathering (USEPA, 1996).

The top 90 cm of soil under the SMS piles retained 20 to 89% of the leachate solutes, and 11 to 80% of the solute mass penetrated to greater depth. Monovalent ions Na⁺, K⁺, Cl⁻, and NO₃⁻ were retained to a similar extent as polyvalent ions Ca²⁺, Mg²⁺, and SO₄²⁻. Although they had much lower leachate concentrations than Na⁺ and K⁺, Ca²⁺ and Mg²⁺ were still retained in the soil. Prior work shows that anion adsorption affinity is in the order phosphate > sulfate > chloride > nitrate (Parfitt, 1977; Katou et al., 1996), and adsorption of lower-affinity anions decreases linearly with increasing concentration of competing anions (Kinjo and Pratt, 1971). Dissolved organic matter competes with inor-

Table 3. Release of leachate solutes and their retention in the top 90 cm of soil during the 2 yr of field weathering of spent mushroom substrate (SMS).†

	90-cm SMS pile			150-cm SMS pile		
	Released from SMS	Through 90 cm soil	Percent retained	Released from SMS	Through 90 cm soil	Percent retained
	cm	cm	%	cm	cm	%
Water	100.7	99.2	–	80.0	77.2	–
	kg m ⁻³			kg m ⁻³		
DOC‡	2.96	1.16	60.8	2.85	1.69	40.7
DON§	0.33	0.14	57.6	0.28	0.18	35.7
Cl ⁻	3.09	1.80	41.7	2.11	1.41	33.2
NO ₃ ⁻	5.19	1.78	65.7	0.70	0.34	51.4
SO ₄ ²⁻	7.27	4.18	42.5	4.70	1.06	77.4
HPO ₄ ²⁻	0.12	0.01	89.0	0.04	0.01	83
Na ⁺	1.17	0.72	38.5	0.65	0.42	35.4
K ⁺	7.49	2.94	60.7	4.19	1.59	62.1
Ca ²⁺	1.43	0.81	43.4	0.52	0.26	49.4
Mg ²⁺	0.74	0.43	41.9	0.35	0.20	42.6
NH ₄ ⁺	0.11	0.09	20.0	0.34	0.25	26.5
TDN¶	1.59	0.61	61.6	0.70	0.45	35.7

† To convert solute release values to Mg ha⁻¹, multiply values by 9.1 for the 90-cm pile and by 15.24 for the 150-cm pile.

‡ Dissolved organic carbon.

§ Dissolved organic nitrogen.

¶ Total dissolved nitrogen.

ganic anions for adsorption sites and facilitates cation transport to depth (Camobreco et al., 1996; Berggren et al., 1990). The penetration of 11 to 80% of DOM and inorganic salts to a depth greater than 90 cm indicates that field weathering of SMS in 90- or 150-cm piles may affect ground water quality in systems with a high seasonal water table. In addition, the long-term release pattern of soil-sorbed constituents is not known.

CONCLUSIONS

Leachate from SMS field weathering contains high concentrations of DOM and inorganic salts. The major cations in the leachate are K⁺, Na⁺, Ca²⁺, and Mg²⁺, and major anions are DOM, Cl⁻, SO₄²⁻, and NO₃⁻. Potassium and Cl⁻ are the predominant inorganic ions. Leachate DOM is mainly composed of low molecular weight (<1000 Da) organic acids and it has molar absorptivities of 200 to 600 L mol⁻¹ C cm⁻¹.

In 2 yr of weathering the 90- and 150-cm SMS piles generated 100 and 80 cm of leachate, respectively. In the 90-cm pile, a cubic meter of SMS released about 3.0 kg of DOC and 26.6 kg of inorganic salts. In the 150-cm pile, 2.8 and 13.6 kg m⁻³ of DOC and inorganic salts were released. The top 90 cm of soil retained 20 to 89% of the leachate solutes against leaching during the 2-yr weathering cycle. Although the larger pile released a smaller flux of nitrate into ground waters, the total fluxes (in Mg ha⁻¹) of DON and NH₄⁺ were higher. Mineralization of DON in the underlying soil and subsequent nitrification is likely. For both pile heights, high flux rates of dissolved N, DOM, and inorganic solutes certainly alter the quality of ground water with high seasonal water tables (ca. 1 m depth) and probably affect deeper systems as well.

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