

Solute Release from Weathering of Spent Mushroom Substrate under Controlled Conditions

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Weathering of piled material in the field is a popular method to treat spent mushroom substrate (SMS) before reuse. During the weathering process, rainfall and snowmelt pass through SMS piles and a large amount of solutes is released in the leachate. To investigate solute release patterns, the field weathering process was simulated under controlled conditions in the laboratory. Fresh SMS was packed in an acrylic column (20 cm i.d.) to 150 cm height and leached intermittently with a cumulative total of 230 cm of deionized water over 180 days. Leachate was collected and analyzed for dissolved organic carbon (DOC), dissolved organic nitrogen (DON), electrical conductivity (EC), and inorganic salts. Solute release patterns were described using first order models, and total released solutes were calculated. The SMS leachate had DOC, DON and EC values ranging from 450 to 15,500 mg L⁻¹, 50 to 1,700 mg L⁻¹, and 3 to 50 dS m⁻¹, respectively. The major inorganic cations were K⁺, Na⁺, Ca²⁺, Mg²⁺ and NH₄⁺, and anions were Cl⁻ and SO₄²⁻. Release of DOC, DON, and bivalent cations Ca²⁺ and Mg²⁺ were described by a first order Exponential Rise to Maximum model, while releases of monovalent ions Cl⁻, K⁺, Na⁺ and NH₄⁺ were described as a first order Sigmoidal Logistic process, and SO₄²⁻ release was best modeled by a Sigmoidal Chapman equation. Following six months and 230 cm applied water, 3.1 kg of DOC, 0.58 kg of dissolved N, and 8.6 kg of inorganic salts were leached per cubic meter of bulk SMS (220 kg oven dry mass). Weathering of SMS involves a significant removal of nutrients from the composted material, which can contribute to pollution of soil and groundwater.

Introduction

Pennsylvania generates over 50,000 m³ of spent mushroom substrate (SMS) annually due to production of the white button mushroom *Agaricus bisporus* (Chong and Hamersma 1997). Improper disposal of this volume of organic waste may cause environmental problems such as air, water and soil pollution. Considering that its major ingredients include incompletely composted straw, hay, manure, gypsum and potash, SMS may be reused as potting soil, topsoil or soil amendments in agriculture, horticulture and ecosystem restoration (Stark and Williams 1994; Wuest *et al.* 1995). However, a high salt content limits its suitability as a plant growth medium without dilution (Ciavatta *et al.* 1993; Chong and Rinker 1994), and fresh SMS is usually stacked in the field for two years of weathering or "passive composting" to remove soluble salts prior to land application.

During the weathering process, rainwater and snowmelt percolate through SMS piles and a large amount of solutes is leached out. Field studies with lysimeter sampling showed that SMS leachate from 90 cm and 150 cm high piles contained high concentrations of dissolved organic carbon (DOC) and inorganic

salts. The DOC concentrations ranged from 800-11,100 mg L⁻¹, and K⁺, Ca²⁺, Cl⁻ and SO₄²⁻ concentrations ranged from 72-316, 2-116, 27-196 and 79-324 mmol L⁻¹, respectively. In two years, 90 cm piles released (per cubic meter of SMS) 3.0 kg of DOC and 26.6 kg of inorganic salts. Piles of 150 cm height released (per cubic meter of SMS) 2.8 kg of DOC and 13.6 kg of inorganic salts (Guo *et al.* 2001a).

Solute release from organic composting including SMS weathering determines the pretreatment efficiency and related environmental impacts. As labile components in organic wastes are decomposed and leached out, the composting product becomes mature. Meanwhile, released solutes may enter into surface water with runoff or migrate into groundwater by percolation. For example, Holcomb *et al.* (2000) found that leaching each pot of SMS with three volumes of irrigation water for 15 minutes removed excessive salts and the leached SMS was then an effective growth medium for most ornamental plants. The solutes released during SMS field weathering of 90-cm and 150-cm piles migrated to at least 200 cm depth in soil profiles in two years, posing a threat to groundwater with high water tables (Guo *et al.* 2001b). Kaplan *et al.* (1995) observed that groundwater concentrations of DOC,

K^+ , Ca^{2+} , Mg^{2+} , Cl^- and SO_4^{2-} were 5 to 20 times higher than background values in fields with weathering SMS at 50 cm pile depth. Composting tree leaves in piles of 180-cm depth in the field for 9 months resulted in significantly elevated BOD (Biochemical Oxygen Demand), COD (Chemical Oxygen Demand), K, NH_4^+ , and phenols in subsurface soil waters (Richard and Chadsey 1990). Even mature compost can release significant amounts of solutes under conditions favoring leaching. In a 2.5-year lysimeter study, Christensen (1983, 1984) reported that leachate from 15-50 cm piles of municipal compost (aged 3-12 months) contained DOC, Kjeldahl-N, ammonia-N, nitrate-N, Na, K, Ca, Mg, Mn, Fe, Cl, SO_4 , and P with concentrations exceeding the drinking water standards several to hundreds of times, especially in the first year of the leaching process.

To better understand the SMS weathering process and to control its adverse environmental impacts, knowledge of solute release kinetics is essential. Stewart *et al.* (1998a) incubated fresh SMS amended soil (20, 40, 80 t ha⁻¹) in columns at 25°C for 16 weeks and leached the tubes with 100 mL of deionized water every 2 weeks. The inorganic-N leaching from SMS applied soils followed a zero order model $N_t = k_0 t + c$, where t is the time since the start of the incubation period and c is a constant. The authors also found that in SMS amended soils, release of SO_4^{2-} -S from the applied SMS was rapid and followed a first or mixed order (first/zero) exponential equation, while release of K^+ , Ca^{2+} and Mg^{2+} was initially rapid (first order) and then declined to a constant rate (zero order) (Stewart *et al.* 1998b, 2000). To date, there are no published data on solute release patterns representative of those to be expected during 2 years of SMS field storage. The objectives of this study were 1) to investigate concentration profiles of solutes in SMS leachate; 2) to determine release kinetics of leachate solutes; and 3) to estimate release potential of various solutes from SMS piles by simulating the field weathering process in the laboratory.

Materials and Methods

Simulation of SMS weathering

An SMS weathering simulation system was constructed in the laboratory. It consisted of a water container (4.2 L bottle), a peristaltic pump (Technicon Instruments Corp., Tarrytown, New York), a water distribution reservoir (a 10 cm high × 20 cm i.d. acrylic cylinder with a perforated bottom and a custom-made glass fiber pad on the bottom), a Teflon sheeting lined acrylic column (175 cm high × 20 cm i.d.), a leachate collector (2 L glass beaker), and a wooden support stand.

Spent mushroom substrate, containing a composition representative of Pennsylvania mushroom farms, was obtained from the Penn State Mushroom Test Demonstration Facility (University Park, PA). Selected chemical properties of the SMS are listed in Table 1. A total of 23.6 kg of fresh SMS (10.9 kg oven dry mass) were packed into the column to 150 cm height with slight compaction. Currently, Pennsylvania mushroom farmers are required to limit SMS piles to 90 cm (3 feet) high in the field, but it has been proposed that the allowable height be increased to 150 cm (5 feet).

Deionized water was pumped from the container to the reservoir at a rate of 4.6 mm hr⁻¹ (equivalent 2.5 mL min⁻¹), and then was distributed evenly to the SMS column through the whole cross-section. The water-loading rate is equal to a moderate rainfall intensity of 2.5-7.6 mm hr⁻¹. To simulate wet-dry cycles that occur in the field, 129 mm (4180 mL) of water was fed through the column consecutively for 28 hours each time with a dry interval of 10 days between each "rain" event. Given that the average annual precipitation where most PA SMS weathering occurs (i.e., Chester County, Pennsylvania) is approximately 1160 mm and that we wanted to simulate the two-year weathering process in 180 days, a total of 2320 mm of water was loaded to the column in 18 "rain" events.

The weathering process lasted for six months at a room temperature of 23-25°C. Typical SMS weathering sites (Chester County, Pennsylvania) have mean annual temperatures of 16°C, and the year-round temperature ranges from -5°C to 35°C. The precipitation is relatively

TABLE 1.
Selected chemical components of fresh spent mushroom substrate

| Components | Content kg m ⁻³ |
|-------------------------------|-------------------------------|
| Organic matter | 162.42 |
| Organic carbon | 88.32 |
| Organic nitrogen | 5.02 |
| Ash content | 61.58 |
| Water extractable components† | 0.00 |
| DOC | 8.36 |
| NH_4^+ | 0.06 |
| NO_3^- | n.d.‡ |
| Cl^- | 1.37 |
| SO_4^{2-} | 5.08 |
| PO_4^{3-} | 0.47 |
| K^+ | 4.14 |
| Na^+ | 0.29 |
| Ca^{2+} | 1.16 |
| Mg^{2+} | 0.44 |

¶ Bulk volume of SMS. Multiply 4.46 to convert the values to g kg⁻¹ of oven dry SMS. † Extract freeze-dried and finely ground SMS at 1:10 solid/water ratio for 24 hours. ‡ Nondetectable.

evenly distributed, with 75-125 mm per month. Though the temperature and the rain pattern of SMS weathering were different in the laboratory and in the field, solute release kinetics should be comparable under both conditions. Separate leachate samples were collected on the 1st, 2nd and 3rd day of each 10-day water-loading interval. A combined sample was collected for the remaining days. Solution samples were centrifuged at 10,000 rpm for 15 minutes, passed through a 0.5 mm glass fiber filter to remove any particulate matter, and then stored at 4°C prior to chemical analysis.

Analytical Methods

The pH values of leachate samples were measured using a Beckman Φ310 pH Meter with an Ag/AgCl Sure-Flow pH electrode (ORION PerpHect, model 9272). Electrical conductivity (EC) was analyzed with an Accumet Model 50 pH/Ion/Conductivity Meter with an 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 (Toyok, Japan). Inorganic anions Cl⁻, NO₃⁻, SO₄²⁻ and HPO₄²⁻ were measured by ion chromatography⁴ (IC) using a Dionex series 4000I with an AS40 automated sampler, an IonPac AS11 ion exchange column, and an ED40 electrochemical detector (Dionex Corp., Sunnyvale, California). Inorganic cations Ca²⁺, Mg²⁺, Na⁺ and K⁺ were determined using a Video 22 AA/AE spectrophotometer (Instrumentation Laboratories, Lexington, Massachusetts). Ammonium (NH₄⁺), NO₂⁻ and NO₃⁻ were measured with a Technicon auto-analyzer (Franklin, Massachusetts). Total dissolved nitrogen (TDN) contents were measured by persulfate digestion and second-derivative UV spectroscopy at 224 nm (APHA 1995; Crumpton *et al.* 1991). Dissolved organic nitrogen (DON) concentrations were calculated by subtracting NH₄⁺-N, NO₃⁻-N and NO₂⁻-N from TDN.

Data Analysis

Mass release of leachate solutes in each 10-day interval was calculated as follows:

$$M_a = \sum_{i=1}^n C_{ai} V_i \dots\dots\dots (1)$$

where M_a is the total mass of solute a released in a 10-day water-loading event, C_{ai} is the concentration of species a in sample i , V_i is the volume of sample i , and n is the number of samples collected in a 10-day water-loading interval ($n = 4$).

The cumulative release of solutes from the SMS column was calculated by summing the mass of released solutes in each water-loading interval from the initiation of the experiment as follows:

$$CR_{aj} = (\sum_{j=1}^j M_{aj}) / V \dots\dots\dots (2)$$

where CR_{aj} is the cumulatively released mass of solute species a per unit volume of bulk SMS from the onset of the experiment to after the j^{th} water-loading event, M_{aj} is the amount of released solute a in j^{th} water-loading event, j is the number of water-loading events ($j = 1, 2, \dots, 18$), and V is the volume of the SMS column ($V = 0.0486 \text{ m}^3$).

Solute release kinetics were described by fitting the cumulative solute release data against depth of loaded water using computational models (SigmaPlot 2000, Jandel Scientific, San Rafael, California), employing the Marquardt-Levenberg algorithm in an iterative process. The best fit of kinetic models was determined using paired t tests (Kirchner and Lauenroth 1987), r^2 values and the standard errors (SEs) of model parameters.

Results and Discussion

Water Flux Pattern

A total of 232 cm of water were applied to the SMS column, and 202 cm were collected as leachate. The difference was either retained by the SMS material (~ 25 cm) or lost to evaporation (~ 5 cm). The SMS exhibited a high water holding capacity (1.93 g g⁻¹, oven dry basis), and the water loaded during the first 10-day interval was completely retained within the column (Figure 1). The SMS became thoroughly water-soaked by the 7th water-loading event, and thereafter 96%-100% of added water mass percolated through the column.

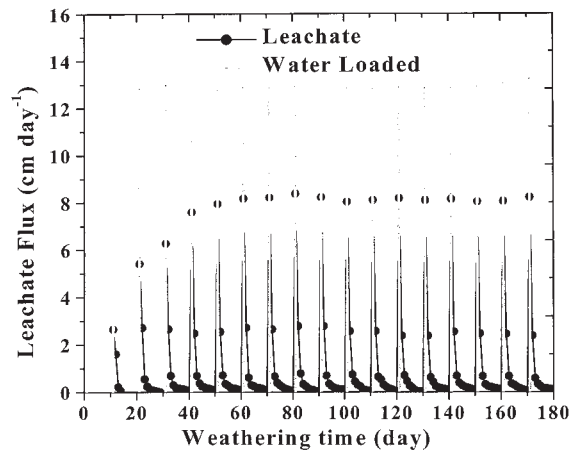


FIGURE 1. Leachate flux from the 150 cm SMS column.

Water was conducted through the column at a high rate (no surface accumulation occurred), and more than 90% of the leachate was collected in the first three days of each 10-day water-loading interval (Figure 1). Even so, a small amount of leachate was collected on the 10th day of all water-loading intervals except during the first two events (Figure 1). This implies anaerobic conditions developed inside the SMS column due to water saturation, especially in the middle and lower sections of the column. In the field weathering process, only 40% (78 cm) of the precipitation (195 cm in two years) percolated through the 150-cm SMS pile and was collected as leachate (Guo *et al.* 2001a), and approximately 95 cm was evaporated into the atmosphere (predicted by the average evaporation rate). Because of the less frequent rain events and high evaporation, the interior of SMS piles in the field were mostly aerobic. The redox differences inside SMS piles in the field and laboratory weathering conditions would cause leaching variations of biodegradation-related solutes such as organic C, organic N, ammonia-N and nitrate-N, but would not influence the leaching of inorganic salts.

Leachate Chemistry

The pH of leachate from the simulated weathering process was 7.4-8.6, which is comparable to that of leachate from field weathering in the 150 cm pile (7.8-8.9, Guo *et al.* 2001a). Leachate alkalinity may be attributed to bicarbonate ions generated during decomposition of DOC. Electrical conductivity (EC) of SMS leachate falls between 3 and 50 dS m⁻¹, decreasing with weathering time (data not shown). The final EC value of 3 dS m⁻¹ is below the threshold value of 4 dS m⁻¹ above which plant growth is inhibited (Plaster 1992), demonstrating the appreciable weathering efficiency.

The leachate contained high concentrations of DOC. Initially the DOC content was 15,500 mg L⁻¹. It decreased quickly to 5,800 mg L⁻¹ in the first 30 days, then gradually to 1,100 mg L⁻¹ in the next 60 days, and slowly to 450 mg L⁻¹ in the last phase of the study (Figure 2a). Although the temperature inside the column was not measured, we postulated that a typical composting process comprising mesophilic phase, thermophilic phase and curing phase (Golueke 1972) had occurred, and the DOC trend may correspond to the three stages. In the initial mesophilic phase, sugars, amino acids and other easily degradable substances were broken down by mesophilic bacteria (Finstein and Morris 1975), resulting in high leachate DOC concentrations. As readily biodegradable constituents in SMS declined, thermophilic microorganisms became dominant. In the second thermophilic

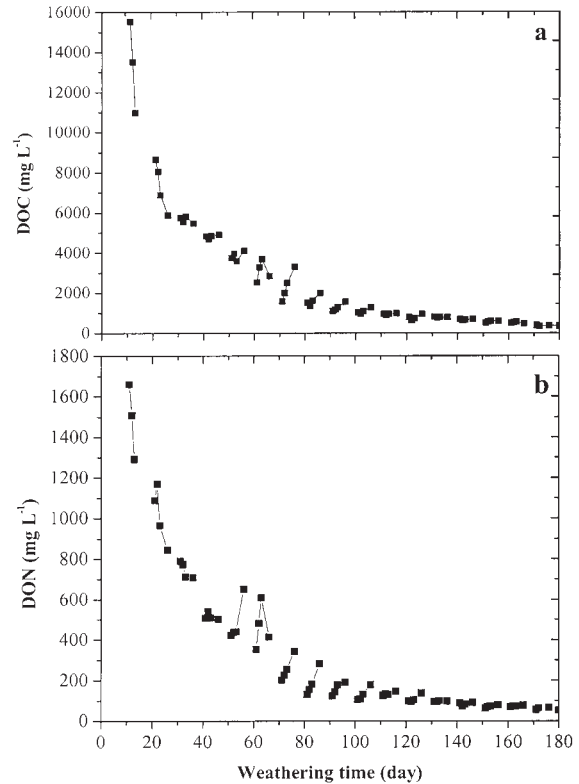


FIGURE 2. (a) Dissolved organic carbon (DOC) and (b) nitrogen (DON) concentrations of the SMS leachate.

phase, cellulose and some lignins were broken down (Finstein and Morris 1975), and leachate DOC concentrations decreased gradually. In the last curing stage, the main remains in SMS were lignins and humic substances were formed. Microbial activities decreased as easily degradable ingredients were less available, and the leachate DOC remained at low levels. The DON concentration of SMS leachate tracked the DOC content, with a range of 50 to 1,700 mg L⁻¹ (Figure 2b). The molar C/N ratio of leachate dissolved organic matter (DOM) fluctuated between 8 and 12, and was not significantly altered with weathering time.

Major cations in SMS leachate were K⁺, Ca²⁺, Mg²⁺, NH₄⁺ and Na⁺ with concentrations ranging respectively from 8-223, 8-150, 7-86, 0.5-47, and 1-26 mmol L⁻¹ (Figure 3a). Ammonium had an initial concentration of 26 mmol L⁻¹. It increased gradually with time, reached a maximum at 48 mmol L⁻¹ after 30 days of weathering, and then decreased slowly to about 0.5 mmol L⁻¹ by the end of the study. Fresh SMS contains a small amount of NH₄⁺ (Table 1), and leachate NH₄⁺ (Figure 3a, Table 3) was principally a product of microbial ammonification. Leachate DON decreased with time (Figure 2b) while NH₄⁺ peaked 30 days later, demonstrating that microbial activities were highest after one month. Accompanying the high micro-

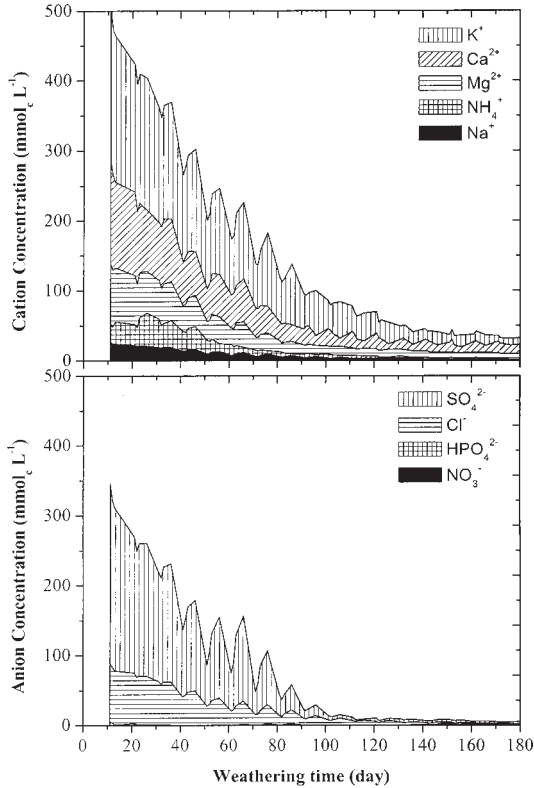


FIGURE 3. (a) Cation and (b) anion concentrations of the SMS leachate.

bial activities and ammonium release, leachate DOC content decreased quickly (Figure 2a) and pH increased from 7.4 to 8.2. It is a characteristic of organic composting that microbial activities reach highest levels after a certain amount of time concurrent with a maximum in ammonia production (Goluke 1972). As nitrogen became less available to microbes, NH_4^+ concentrations in the leachate decreased. Meanwhile, oxygen diffused into the SMS column as solutes were leached, and part of the NH_4^+ was oxidized to NO_3^- . As a result, NO_3^- was present in the leachate in the late weathering stage.

The dominant inorganic anions in the SMS leachate were SO_4^{2-} and Cl^- with concentrations ranging from 2-287 and 1-85 mmol L^{-1} , respectively (Figure 3b). Phosphate was consistently present in the leachate, but its concentration was less than 2.5 mmol L^{-1} , and mostly remained around 0.3 mmol L^{-1} . No nitrate was detected in the first 60 days of weathering, and afterward it appeared in the leachate with a concentration less than 4 mmol L^{-1} .

Solute Release Kinetics

Since the amount of water applied is the key parameter governing SMS solute release, input water

depth is used instead of weathering time as the independent variable in plots of solute release patterns [A total of 12.9 cm of water was loaded in a 10-day water loading event. To convert from water depth (cm) to weathering time (days), values may be divided by 1.29]. Release of DOC from the SMS column is described by a first order exponential rise to maximum (ERM) equation as follows:

$$CR_h = CR_0 + CR_p(1 - e^{-k_1h}) \dots \dots \dots (3)$$

where CR_h is the cumulative mass of DOC released from the SMS column after h cm of water is loaded, CR_0 is the DOC that is resident initially in the column, CR_p is the mass of DOC that is potentially leached from the column, k_1 is a first order rate constant, and h is cumulative loaded water (cm). The fitted curve accurately describes cumulatively released DOC as a function of loaded water depth, and it has a coefficient of determination r^2 of 0.998 (Figure 4a). Parameters CR_0 , CR_p , and k_1 for Equation 3 are given in Table 2. The negative sign of CR_0 denotes the column retention of DOC. The model predicts that under the described conditions, 4.05 kg of DOC are potentially be released per cubic meter of SMS in 150 cm SMS piles, which accounts for approximately 5% of the total organic carbon (88.3 kg m^{-3} , Table 1) and 48% of the water extractable organic carbon initially in the column (8.36 kg m^{-3} , Table 1). SMS has a high water holding capacity (1.93 g g^{-1}), and the water loaded in the first 10-day interval was completely retained (Figure 1). Approximately 64 cm of water (25 cm of applied water plus 39 cm of water deriving from the fresh SMS) maintained the column at saturation, and 0.79 kg m^{-3} of DOC was initially retained. The DOC release rate varied with the leachable DOC remaining in the SMS, and the rate constant k_1 (0.015 cm^{-1}) indicates that 1.5% of leachable OC is removed in solution per cm of applied water.

Weathering of SMS is a passive composting process (PADEP 1997) driven by microbial activity, which follows a first-order exponential model if substrate is unlimited (Maier 2000). The DOC release is associated with organic matter decomposition, which can be described as a first-order reaction (Boyle and Paul 1989; Paul and Clark 1996). The CENTURY model simulates soil organic matter mineralization from three pools (active, slow and passive) by first order exponential kinetics (Metherell *et al.* 1993), each pool with its own rate constant. In contrast, our results suggest DOC leaching from SMS weathering results principally from degradation of one pool, probably the active pool (Equation 3). Environmental factors such as temperature, moisture and aeration influence microbial activities, and it is expected that the DOC

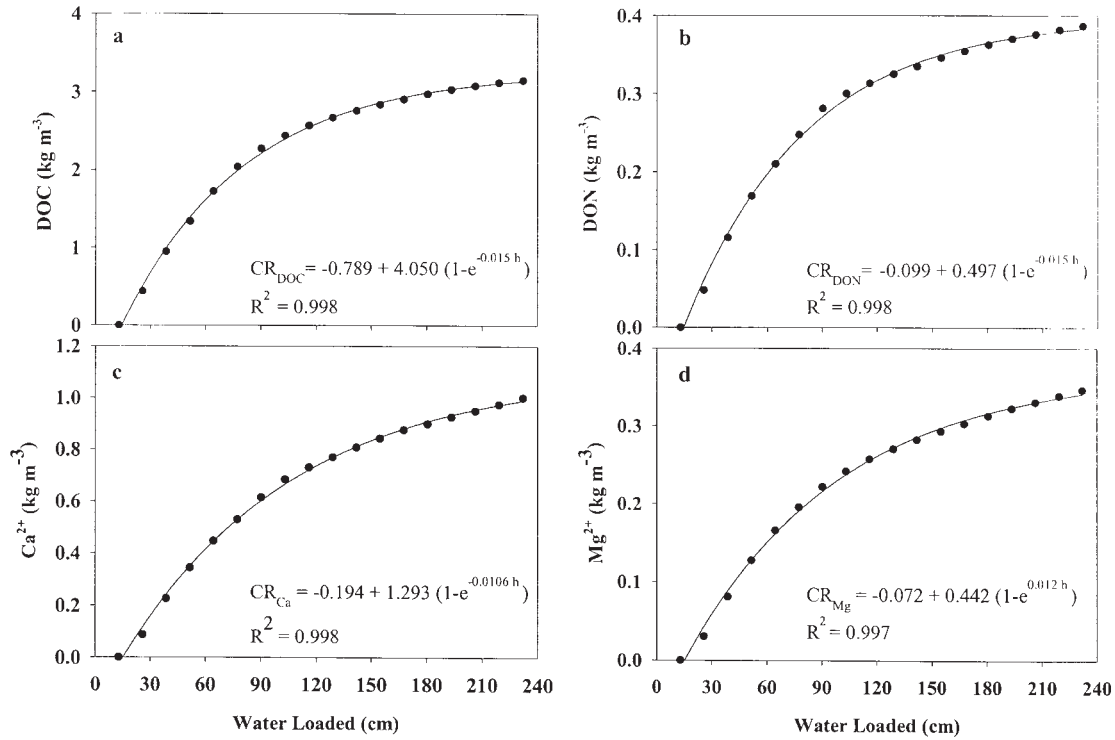


FIGURE 4. Cumulative release kinetics of (a) DOC, (b) DON, (c) Ca²⁺ and (d) Mg²⁺ in the SMS weathering process.

TABLE 2
Solute release model parameters, standard errors, P-values from paired t test and r² values of spent mushroom substrate weathering in 150 cm pile height

| Model | r ² | Coefficient | Std. Error | t-test | P | |
|-------------------------------|----------------|------------------|------------|--------|--------|---------|
| DOC | 0.9983 | CR ₀ | -0.7891 | 0.0548 | 14.40 | <0.0001 |
| | | CR _p | 4.0500 | 0.0461 | 87.88 | <0.0001 |
| | | k ₁ | 0.0150 | 0.0005 | 33.03 | <0.0001 |
| DON | 0.9975 | CR ₀ | -0.0992 | 0.0820 | 12.12 | <0.0001 |
| | | CR _p | 0.4968 | 0.0069 | 72.06 | <0.0001 |
| | | k ₁ | 0.0152 | 0.0006 | 27.37 | <0.0001 |
| Ca | 0.9983 | CR ₀ | -0.1936 | 0.0156 | 12.40 | <0.0001 |
| | | CR _p | 1.2930 | 0.0144 | 89.75 | <0.0001 |
| | | k ₁ | 0.0106 | 0.0004 | 25.63 | <0.0001 |
| Mg | 0.9974 | CR ₀ | -0.0716 | 0.0068 | 10.53 | <0.0001 |
| | | CR _p | 0.4422 | 0.0058 | 75.72 | <0.0001 |
| | | k ₁ | 0.0116 | 0.0005 | 22.41 | <0.0001 |
| Na | 0.9985 | CR _m | 0.2205 | 0.0030 | 73.43 | <0.0001 |
| | | h _{1/2} | 70.04 | 1.3066 | 53.60 | <0.0001 |
| | | k | -2.1495 | 0.0748 | 28.75 | <0.0001 |
| K | 0.9993 | CR _m | 3.6130 | 0.0362 | 99.72 | <0.0001 |
| | | h _{1/2} | 75.08 | 0.9893 | 75.90 | <0.0001 |
| | | k | -2.1960 | 0.0531 | 41.34 | <0.0001 |
| NH ₄ ⁺ | 0.9973 | CR _m | 0.2551 | 0.0033 | 78.31 | <0.0001 |
| | | h _{1/2} | 64.07 | 1.1452 | 55.95 | <0.0001 |
| | | k | -2.6306 | 0.1187 | 22.16 | <0.0001 |
| Cl ⁻ | 0.9992 | CR _m | 0.9037 | 0.0057 | 158.87 | <0.0001 |
| | | h _{1/2} | 58.32 | 0.5552 | 105.04 | <0.0001 |
| | | k | -2.4967 | 0.0580 | 43.02 | <0.0001 |
| SO ₄ ²⁻ | 0.9983 | CR _p | 2.8354 | 0.0100 | 283.58 | <0.0001 |
| | | k ₁ | 0.0350 | 0.0009 | 40.92 | <0.0001 |
| | | k ₂ | 3.8571 | 0.1788 | 21.57 | <0.0001 |
| NO ₃ ⁻ | 0.936 | c | 0.0005 | 0.0008 | 0.63 | 0.5358 |
| | | a | 0.0001 | 0.0000 | 1.41 | 0.1803 |
| | | k ₁ | 0.0273 | 0.0031 | 8.74 | <0.0001 |

release rate constant k_1 will vary with variables that affect aeration, such as water loading rate, frequency and SMS pile depth.

Nitrogen was leached out dominantly as organic-N. Release of DON, which followed a pattern similar to that for DOC, can be described as (Figure 4b). Based on the model, the potential release of N in organic form amounts to 0.50 kg m^{-3} (10% of the organic N in fresh SMS).

Release of Ca^{2+} (Figure 4c) and Mg^{2+} (Figure 4d) can also be described by models similar to that for DOC release. Values for potentially leachable Ca^{2+} and Mg^{2+} were 1.29 and 0.44 kg m^{-3} , respectively (Table 2). The release rates for these two cations were nearly equivalent, and both were apparently associated with DOM anions and SO_4^{2-} , as release of these anions followed similar patterns to the bivalent cations. The ion activity product of Ca^{2+} and SO_4^{2-} in the leachate greatly exceeded the solubility constant of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), strengthening the contention that a large portion of Ca^{2+} was bound into soluble complexes. The predicted maximum leachable Ca^{2+} and Mg^{2+} are 111% and 100% of the water extractable amounts (Table 2), respectively. In SMS amended soil, releases of Ca^{2+} and Mg^{2+} were also simulated with SigmaPlot software as a first order exponential model (Stewart *et al.* 1998b, 2000), but coefficients of determination for the fitted curves were lower than those reported here.

The patterns of release for monovalent Na^+ , K^+ and NH_4^+ (Figure 5a, b and c) differed from bivalent Ca^{2+} and Mg^{2+} ; cumulative releases of these ions was best described by a first order sigmoidal logistic equation:

$$CR_h = \frac{CR_m}{1 + \left(\frac{h}{h_{1/2}}\right)^k} \dots \dots \dots (4)$$

where CR_m is the maximum amount of leachable monoionic solutes in the SMS column, h is depth of the loaded water, $h_{1/2}$ is the amount of water required to leach $0.5 CR_m$, and k is the release rate constant. The maximum leachable Na^+ (CR_m) was 0.22 kg m^{-3} , which is equal to the amount of water extractable Na^+ in the SMS (Table 1). When 70 cm of water were loaded to the SMS column, half of the leachable Na^+ was released. The potentially leachable K^+ in the 150-cm SMS column was 3.61 kg m^{-3} , which accounts for 87% of the water extractable form (Table 1). It is notable that K^+ and Na^+ release had similar $h_{1/2}$ and k values (Table 2), indicating similar leaching efficiencies. The maximum releasable NH_4^+ is 0.26 kg m^{-3} , which is 430% of water extractable NH_4^+ or 5.1% of total N in fresh SMS (Table 1). Evidently, leachate NH_4^+ was dominantly a product of organic N mineralization, which proceeded over the course of the study.

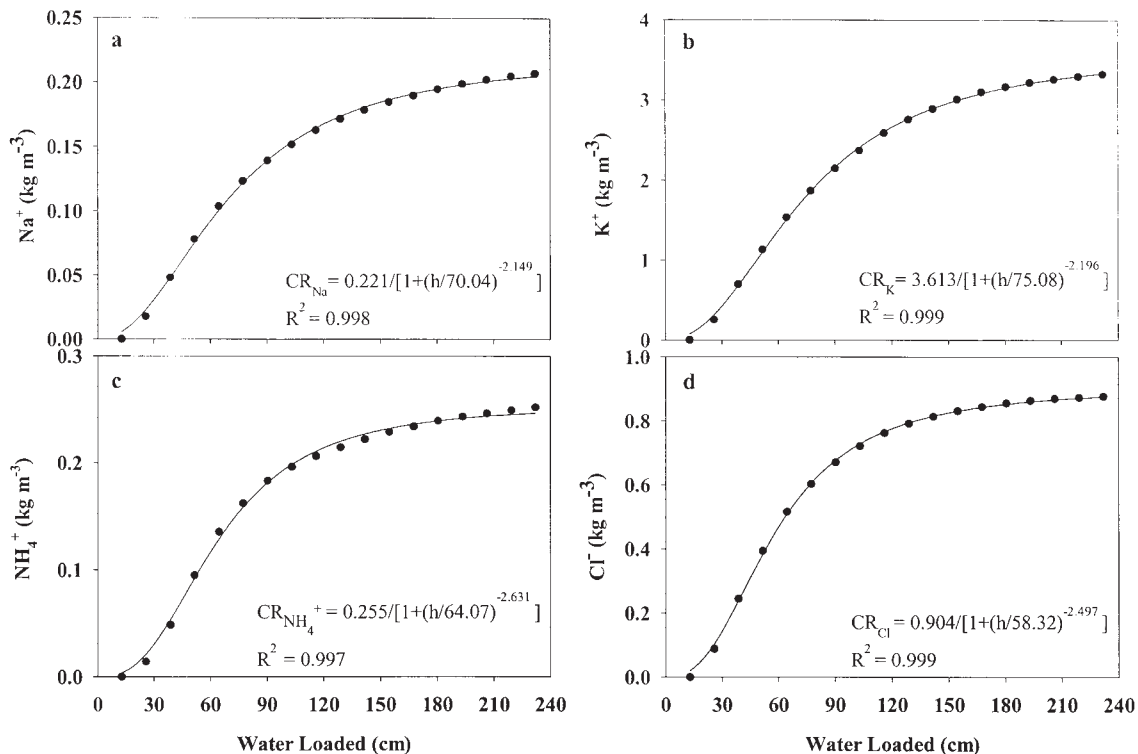


FIGURE 5. Cumulative release kinetics of (a) Na^+ , (b) K^+ , (c) NH_4^+ and (d) Cl^- in the SMS weathering process.

Like the monovalent cations, release of Cl⁻ from SMS weathering followed the sigmoidal logistic model (Figure 5d). There was a total of 0.90 kg m⁻³ of leachable Cl⁻ in the SMS column (equivalent 66% of water extractable Cl⁻, Table 1), and 58.32 cm of water was required to leach out half of the total leachable pool. The chloride anion is water-soluble and mobile in porous media. Release of Cl⁻ is a physical process, controlled mainly by water dissolution dynamics and transport of chloride-containing constituents (Jury *et al.* 1991). Few studies reported release or leaching of Cl⁻ from chloride containing fertilizers or minerals. Transport of Cl⁻ in soil obeys a transitional model (Jury and Pratt 1980). Under water saturated conditions, Cl⁻ transports through porous media principally via convection and dispersion, and drainage breakthrough curves of Cl⁻ in soil with diffusion coefficients of 1-4 are close to the sigmoidal logistic shape (Jury *et al.* 1991). The release curves for Cl⁻ had a lower $h_{1/2}$ and a higher k than K⁺ and Na⁺ (Table 2), demonstrating Cl⁻ moves faster through the column, likely due to its negative charge. The similar release patterns for K⁺, Na⁺ and Cl⁻ imply that K⁺ and Na⁺ may exist in chloride forms in the solid SMS.

Sulfate release is described by a sigmoidal Chapman model:

$$CR_h = CR_p (1 - e^{-k_1 h})^{k_2} \dots \dots \dots (5)$$

where CR_p is the mass of potentially leachable of SO₄²⁻ per cubic meter of SMS, and k_1 and k_2 are first order and second order release rate constants. The model fits the experimental data well ($r^2 = 0.998$, Figure 6a), and the values for CR_p , k_1 and k_2 are given in Table 2. According to this model, the mass of potentially leachable SO₄²⁻ from the SMS column was 2.84 kg m⁻³, which constitutes 56% of water extractable SO₄²⁻ in the SMS (Table 1). It is proposed here that the release pattern of SO₄²⁻ had two steps, the first step involves dissolution of sulfate containing constituents (gypsum, MgSO₄, etc.), which is described by a first order exponential equation with a rate constant k_1 of 0.035 cm⁻¹; the second step involves transport through the column, which obeys a power law with a rate constant k_2 of 3.86. Leaching of SO₄²⁻ and Cl⁻ reveals different release patterns, both because of the low solubility of CaSO₄ · 2H₂O and because of the stronger sorptive affinity of SO₄²⁻ than Cl⁻ for solids. Drainage breakthrough curves of SO₄²⁻ and Cl⁻ in soils are typically different (Jury *et al.* 1991). Stewart *et al.* (1998b, 2000) investigated the release of SO₄²⁻ from SMS amended soil under laboratory and field conditions and observed a first/zero mixed order exponential model for SO₄²⁻ release.

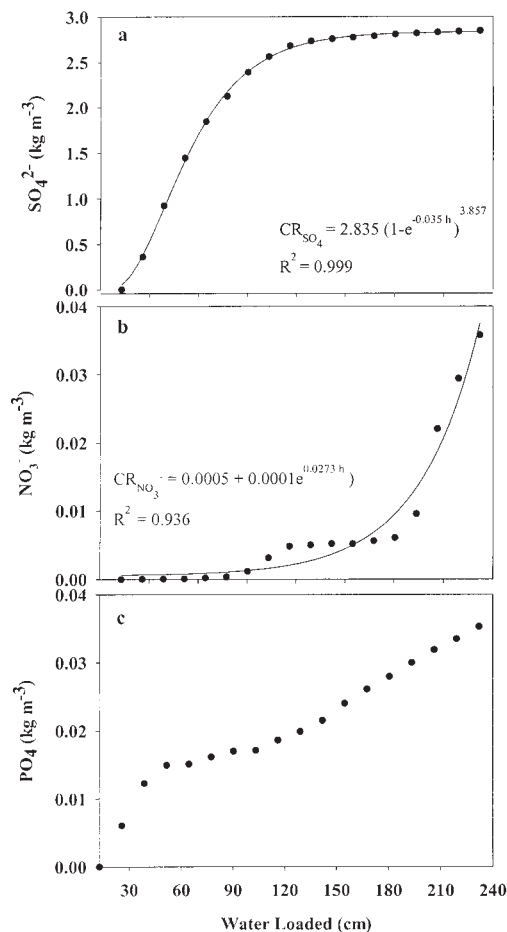


FIGURE 6. Cumulative release kinetics of (a) SO₄²⁻, (b) NO₃⁻, and (c) PO₄³⁻ in the SMS weathering process.

Release of NO₃⁻ showed a pattern quite distinct from other solutes (Figure 6b). Since fresh SMS contained little NO₃⁻ (Table 1), leachate NO₃⁻ was a product of oxidation of NH₄⁺ by nitrifying microbes. Due to initial anoxic conditions inside the SMS column, activities of nitrifying bacteria (requiring O₂ as an electron acceptor) were inhibited and little NH₄⁺ was oxidized until labile C concentrations were reduced and leached SMS developed a pore structure that permitted oxygen diffusion into the column at the late stage of the weathering process. The best model to describe the cumulative leached NO₃⁻-N is an exponential growth equation:

$$N_t = c + ae^{k_1 t} \dots \dots \dots (6)$$

where a and c are constants. The fitted curve, which has an r^2 of 0.936, suggests that if O₂ and NH₄⁺ are available, the activity (and presumably the biomass) of nitrifying bacteria increase initially exponentially with

time, resulting in an exponential increase in leached NO_3^- -N. Indeed, most of the net mineralized NH_4^+ from organic N decomposition will be nitrified if O_2 supply is adequate, resulting in little NH_4^+ in the leachate. In related work, we observed that leachate collected from SMS field weathering in 90 cm and 150 cm high piles initially had high concentrations of NH_4^+ and little or very low concentrations of NO_3^- (Guo *et al.* 2001a). During the field trial, the concentration of NH_4^+ decreased, while NO_3^- concentration increased. After one year, NH_4^+ was undetectable in the leachate and a high concentration of NO_3^- was observed (Guo *et al.* 2001a). It is expected that the exponential increase of cumulatively leached NO_3^- in the laboratory experiments would eventually shift to a first- or zero-order pattern as less NH_4^+ and more O_2 became available (the column interior becomes aerobic).

Although fresh SMS contained a small amount of water extractable phosphate (0.47 kg m^{-3} , Table 1), leaching of HPO_4^{2-} (the dominant form of orthophosphate at pH 7-8) from the SMS weathering was fairly slow and may be separated into two stages (Figure 6c). The first stage occurred in the initial weathering process. Soluble PO_4^{3-} in the fresh SMS was leached as water was applied, and thus release of phosphate dropped as this fraction ran out. The second stage began after 110 cm of water had been applied (or 90 days of weathering), at which time phosphate was leached at a low but steady rate. Approximately 1g of phosphate was released per cubic meter of SMS with the addition of each 10 cm of water. Apparently, this mass of phosphate derives from organic-P mineralization and dissolution of sparingly soluble phosphates.

Total Masses of Released Solutes

Masses of solutes released from SMS over the six month weathering period were calculated from water flux and solute concentration data and are reported in Table 3. Of the leached N, 65.4% was DON, and 33.2% was NH_4^+ -N, and 1.4% was NO_3^- -N. Although substantially less leachate was generated in a field weathering experiment (80 cm) than in this laboratory study (201 cm), 2 years of SMS weathering in the field released a similar amount of DOC and more inorganic salts (Guo *et al.* 2001a), indicating the field process was more complete. The higher weathering efficiency of the field process can be attributed to the longer processing duration (24 vs. 6 months) and aeration of the pile interior. Upon removal of the weathered SMS, the field product was a fine powder throughout the pile, while only the top 25 cm of the laboratory product had a fine structure and the rest had a coarse

TABLE 3
Solute masses released from weathering of SMS
in 150 cm pile height

| Solutes | Amount Released $\text{kg m}^{-3} \text{ SMS}^\dagger$ |
|--------------------|---|
| DOC | 3.10 |
| Cl^- | 0.86 |
| SO_4^{2-} | 2.80 |
| PO_4^{3-} | 0.04 |
| Na | 0.20 |
| K | 3.27 |
| Ca | 0.98 |
| Mg | 0.34 |
| TDN | 0.58 |
| DON | 0.38 |
| NH_4^+ -N | 0.19 |
| NO_3^- -N | 0.01 |
| NO_2^- -N | 0 |

[†] Multiple 15 to convert values to Mg ha^{-1} . DOC: dissolved organic carbon. TDN: total dissolved nitrogen. DON: dissolved organic nitrogen.

structure similar to fresh SMS. It is possible that anoxic conditions inside the column slowed the laboratory composting process (Walters 1993).

Conclusions

Weathering of SMS in the laboratory under controlled conditions produced a leachate with similar chemical compositions as leachate from field weathering (Guo *et al.* 2001a). The leachate has pH and EC values ranging from 7.4 to 8.6 and 3 to 50 dS m^{-1} , respectively, as well as high concentrations of DOM and inorganic salts. The DOC and DON contents are 450-15,500 mg L^{-1} , and 50-1,700 mg L^{-1} , respectively. The major cations are K^+ , Na^+ , Ca^{2+} , Mg^{2+} , and NH_4^+ , and major anions are DOM, Cl^- , and SO_4^{2-} . Due to the anaerobic conditions caused by water saturation, the lab-leachate contained much more NH_4^+ and less NO_3^- than field leachate.

Substantial masses of solutes were released during SMS weathering. In 6 months with 230 cm of water applied, released DOC, dissolved N, and inorganic salts per cubic meter of bulk SMS (220 kg oven dry mass) in the 150 cm SMS column were 3.1, 0.58, and 8.6 kg, respectively, and the potential solute release could be estimated by water extractable amounts. DON and NH_4^+ were the two major forms of leached N. The release pattern varied with different solutes. Release of DOC, DON, and bivalent cations Ca^{2+} and Mg^{2+} were described by a first order exponential rise to maximum model, while releases of monovalent ions Cl^- , K^+ , Na^+ and NH_4^+ were described as a first order sigmoidal logistic process. Sulfate release was best mod-

eled by a sigmoidal Chapman equation, and NO_3^- was modeled as a first order exponential growth equation. High dissolved N, DOM, Ca^{2+} , K^+ , Mg^{2+} , SO_4^{2-} and Cl^- fluxes from weathering of SMS illustrate a remarkable loss of plant nutrients and a potential source of contamination for soils and receiving waters. The related environmental implications should be considered, particularly in large SMS weathering operations.

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