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**ARSENIC AND HEAVY METAL LEACHING POTENTIAL FROM TURKEY
LITTER STOCKPILED ON BARE SOIL**

By

Sanjay B. Shah¹

Garry L. Grabow¹

Rodney L. Huffman¹

Dean L. Hesterberg²

David H. Hardy³

Kim J. Hutchison²

James Parsons⁴

¹Department of Biological and Agricultural Engineering

²Department of Soil Science

College of Agriculture and Life Sciences

North Carolina State University

Raleigh, NC 27695

³North Carolina Department of Agriculture and Consumer Services

Agronomic Division, Soil Testing Section

Raleigh, NC 27699-1040

⁴North Carolina Cooperative Extension

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ABSTRACT

Roxarsone, an organic arsenic (As) formulation is fed to turkey for therapeutic purposes. Nearly all of the roxarsone is excreted and is then broken down into more toxic and mobile As species such as arsenate (As(V)) and arsenite (As(III)) by microbes in the litter and soil. This study was used to evaluate the transformation of As and other turkey litter constituent species during stockpiling and monitor movement of As and other species from stockpiles into the soil below. During an 11-mo. study, four turkey litter stockpiles were monitored during the summer and four more during winter. Turkey litter samples collected prior to and at the end of stockpiling were analyzed for various constituents. Soil samples were collected down to 610 mm depth both beneath stockpiles and beyond the stockpile footprints. Temperature and moisture conditions inside the stockpiles as well as in the soil below the stockpiles were favorable for biochemical transformation and movement of litter constituents. Arsenate was the dominant water soluble (WSE) As specie recovered in the litter at the end of stockpiling and some WSE-As was lost from the stockpiles. While roxarsone was completely degraded in the winter stockpiles, summer stockpiling increased roxarsone concentrations. Stockpiling resulted in highly mobile constituents (e.g., nitrate) impacting the entire sampled depth while less mobile species (e.g., WSE-As) mainly impacted the top 305-mm depth though there was some leaching into the deeper layer. The predominant WSE-As species in the soil was As(V) and high WSE-phosphorus levels in the soil could increase WSE-As leaching due to competitive sorption-desorption. Since the literature mentions litter with much higher As concentrations than measured in this study, leaching from litter stockpiles with higher As concentrations would likely increase the risk of As contamination of groundwater. There was also evidence of Cu leaching into the entire sampling depth.

(Keywords: Roxarsone, Arsenate, Phosphorus, Water quality, Nitrate, XANES)

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SUMMARY AND CONCLUSIONS

Since arsenic (As) is a carcinogen and can also cause other diseases, the EPA has established a maximum contaminant level of 0.01 mg/L for As in drinking water. However, As is fed to turkey (also broiler and swine) mostly as roxarsone for controlling coccidial intestinal parasites, blackhead disease in turkey, and as a growth promotant. Since roxarsone is largely excreted, microbes in litter and soil can mineralize roxarsone into more toxic and mobile species, such as, arsenate (As(V)) and arsenite (As(III)). When litter is removed from the turkey house, it may be land applied immediately or stockpiled to be applied later. When litter is stockpiled on bare ground without cover, as is common practice in North Carolina, warm and moist conditions inside the stockpile combined with rainfall can result in transformation of litter constituents, including As into more mobile and toxic species that may then leach into the soil. Over time, depending on soil properties and water table depth, As from turkey litter could contaminate the ground water. Turkey litter also contains many other constituents such as nitrate-nitrogen (NO_3^- -N), ammonium-N (NH_4^+ -N), phosphorus (P), and heavy metals that while useful as plant nutrients, can cause water quality problems if they contaminate ground or surface waters.

While researchers have evaluated the mobility of litter constituents in land-applied litter, no literature on mobility of As and other constituents from stockpiled poultry litter is available. The objectives of this study were (i) to evaluate transformation of As and other constituent species during stockpiling; (ii) to monitor movement of As and other species beneath the stockpile; and (iii) to correlate Mehlich 3 P and heavy metal concentrations with total concentrations. Four turkey litter stockpiles (~4.1 Mg ea.) were established in Orangeburg loamy sand soil in Clinton, NC, during May to November 2004 for 161 d (summer stockpiles). Two stockpiles received simulated rainfall (under rainfall deficit conditions). Two stockpiles were instrumented for measuring temperature and moisture content. Turkey litter samples were collected prior to and at the end of stockpiling. Soil samples were collected down to 610 mm depth both beneath stockpiles (center, half diameter, and diameter) as well as beyond the stockpile footprints. After removing the summer stockpiles and leaving the site bare for 13 d, four winter stockpiles (November 2004 to April 2005) were established for 162 d. The winter stockpiles were treated the same as the summer stockpiles but were not instrumented. The study ran from May 2004 to April 2005. Twenty-four turkey litter samples and 96 soil samples were analyzed for moisture content, pH, electrical conductivity (EC), total carbon (C), dissolved organic C (DOC), total N, NH_4^+ -N, NO_3^- -N, total P, water soluble extract (WSE)-P, total As, WSE-As, total copper (Cu), total zinc (Zn), and total manganese (Mn). Solid phase and water soluble As speciation were also performed on the turkey litter and soil samples. Some important conclusions are summarized below.

- High temperature ($>20^\circ\text{C}$ higher than ambient temperature) and moist conditions in the stockpiles during summer stockpiling provided favorable conditions for biochemical activity in the stockpiles.
- Increase in total concentrations of most species (except C, N, and As) during stockpiling were attributed to large losses of C (only winter) and N.
- During summer stockpiling, pH and concentrations of water soluble constituents (except NO_3^- -N) were higher in the core due to leaching from the skin (0-150 mm) into the core. However, during winter stockpiling, concentrations of all water soluble constituents decreased in the core as well, possibly, due to leaching into the soil below.
- Reduced WSE-As concentrations in both the skin and core in the winter stockpiles indicated that WSE-As leached into the soil below.
- Roxarsone completely degraded during winter stockpiling. However, roxarsone concentrations were higher at the end of summer stockpiling (vs. the initial samples) due to reasons that were unclear.
- Both solid-phase and water-soluble phase As speciation indicated that As(V) was the dominant As specie in the litter at the end of stockpiling (both summer and winter).

- Application of simulated rainfall to the stockpiles generally did not increase leaching losses (vs. natural rainfall only) probably due to the small depths of application (48.8 mm in summer and 32.0 mm in winter) and generally deficit rainfall conditions.
- Soil beneath the stockpile stayed warmer and wetter than the soil outside the stockpile footprints indicating that constituents leached into the soil from the stockpiles would have more favorable conditions for biochemical transformations and movement.
- Beneath the stockpiles, generally, the highest concentrations of most litter constituents in the soil were at the half diameter followed by the center. Greatest changes in pH were observed at the center and greater NO_3^- -N leaching occurred at the diameter location.
- Highly mobile constituents (e.g., NO_3^- -N) and pH impacted the entire 610 mm depth of soil; less mobile species (e.g., WSE-As and WSE-P) impacted mainly the top 305-mm depth though there was some evidence of leaching into the deeper layer.
- Concentrations of highly reactive and mobile species (e.g., NO_3^- -N) were generally lower throughout the soil profile at the end of the study than after summer stockpiling probably due to transformation within and leaching below the sampling depth. However, concentration of less reactive species (e.g., WSE-As) were higher in the soil at the end of the study.
- Solid phase As speciation analyses indicated that As in the soil was mainly in the As(V) form, consistent with the findings in the turkey litter after stockpiling.
- Total soil As concentrations beneath stockpiles were always <5 mg/kg, comparable to background soil As concentrations in the 305-610 mm depth. However, stockpiling resulted in elevated WSE-As concentrations throughout the sampling depth even though no background WSE-As had been detected.
- High WSE-P concentrations in the litter and the underlying soil can induce arsenate leaching by competitive sorption-desorption. Arsenic leaching would be of greater concern in poultry litter containing higher As concentrations. Sims and Wolf (1994) reported total As concentrations up to 77 mg/kg while the highest concentration in this study was <16 mg/kg.
- There was evidence of Cu leaching down into the soil profile from the stockpiles.
- Based on analyses in the top 76 mm of Orangeburg loamy sand soil and based on coefficient of determination (r^2), Mehlich 3 analysis provided the best index of total concentration estimate for Zn, followed by P, Cu, and finally, Mn.

RECOMMENDATIONS

1. Poultry producers should be persuaded not to stockpile litter in the open on bare ground. Ideally, litter should be stored in a covered shed with a concrete floor; however, a less expensive solution would be to store the litter on a tarpaulin and cover it with a tarpaulin as well. A proper storage system will not only reduce the potential for groundwater contamination but also runoff and volatilization losses of litter constituents.
2. There is need to evaluate movement of litter pollutants through the soil on poultry farms where litter is stockpiled on bare ground by monitoring soil, groundwater and well water samples. Monitoring of farms should be prioritized based on arsenic content in feed or litter, duration of stockpiling on bare soil, soil texture, water table depth, and drinking water source (humans or animals).
3. Currently there are no regulations governing poultry litter stockpiling in North Carolina. Neighboring states such as Georgia and South Carolina have litter stockpiling regulations. The NC Department of Environment and Natural Resources may need to investigate the need for such regulations to safeguard water quality.

INTRODUCTION

North Carolina ranks second behind Minnesota in turkey production, producing 39 million birds in 2004. After hatching, turkey poults are separated by sex and raised in brooder houses for 6-8 weeks. Thereafter, the birds are transferred to grow-out houses where the hens are kept for 13-14 weeks and the toms for 18-20 weeks. Typically, each batch of turkey poults is raised on fresh litter and after the brooding, the litter is deep-stacked to kill pathogens and then used in the grow-out houses. After each grow-out, the crust containing much of the excreta and feed is removed and may be replaced by fresh litter. Depending on the grower's management practices and the integrator's requirements, the litter in the grow-out house may be cleaned out annually or less often. Most litter (also broiler litter) is used as a nutrient source for crop production. If crop and environmental conditions are favorable, the poultry litter may be land-applied; otherwise, it is stockpiled until conditions are suitable for land application. In North Carolina, poultry (both turkey and broiler) litter is generally stockpiled over the winter months and then applied to corn ground in spring. While some producers apply litter to hayfields during summer, in the absence of disposal alternatives, others may stockpile litter for application to winter wheat in fall and spring.

Poultry litter contains many nutrients that while useful as plant nutrients, can cause water quality problems if they contaminate ground or surface waters. Constituents in turkey litter that are known to degrade water quality are nitrate-nitrogen (NO_3^- -N), ammoniacal-N (NH_4^+ -N+ NH_3 -N), phosphorus (P), pathogens, heavy metals [e.g., copper (Cu), manganese (Mn), and zinc (Zn)], and metalloids [arsenic (As)]. Organic As formulations, mostly as roxarsone (~28.5% As; 3-nitro-4-hydroxyphenylarsonic acid), are used for controlling coccidial intestinal parasites, blackhead disease in turkey, and as a growth promotant; they are also fed to broilers and swine. Between 1995 and 2000, >96% of feed mills blended roxarsone in concentrations ≥ 11 mg/kg-feed in broiler grower and starter feed with ~80% mills using 37-50 mg/kg (Chapman and Johnson 2000). Since roxarsone is largely excreted, microbes in litter and soil can mineralize roxarsone into more toxic and mobile species, such as, arsenate (As(V)) and arsenite (As(III)). Based on multiple sources, Sims and Wolf (1994) reported that poultry litter contained up to 77 mg-As/kg-dry weight (dw). Wershaw et al. (1999) estimated that 1,000 Mg of roxarsone and its degradation products were introduced into the environment annually through land-application of poultry litter.

Experts suggest that stockpiling poultry litter under cover (shed or tarpaulin) can reduce nutrient losses through runoff, leaching, or volatilization. Currently, there are no regulations on covering litter stockpiles in North Carolina; anecdotal evidence suggests that 70-95% of litter stockpiles are formed on bare ground with no cover (T. Cutts, NRCS, pers. com. 2005). In uncovered stockpiles, litter constituents may be transformed into more mobile and toxic species due to favorable litter [e.g., high dissolved organic carbon (C) and microbial concentrations] and environmental (e.g., high temperature and moisture content) conditions. Such soluble constituents of litter stockpiled on bare soil may be transported by rainfall into the soil beneath the stockpile. Since As in poultry litter is mostly in the water soluble form (Jackson and Miller 1999), there is potential for As to leach into the soil. The Coastal Plain of North Carolina supports a large poultry industry, has coarse-textured soils, high and fluctuating water tables (causing redox effects), and heavy rainfall (>1,270 mm, SERCC, 2003). Hence there is concern in this region that As in poultry litter may contaminate shallow groundwater. Shallow groundwater in the Coastal Plain is usually within 6 m of the soil surface and much higher during the wetter months and may also be used as drinking water. Arsenic is a carcinogen that can also cause gastrointestinal, neurological, dermal, hematological, cardiovascular, peripheral vascular, and immune system effects; additionally, it may also be a potent endocrine disruptor (Moplaisir et al. 2001). Given that most chronic As poisoning cases are due to inorganic As in drinking well water, the EPA has established a maximum contaminant level (MCL) of 0.01 mg/L for As in drinking water.

However, other pollutants such as NO_3^- -N, Cu, Mn, and Zn in poultry litter that can also impact drinking water quality. On a wet basis, turkey litter contains 2.75% total Kjeldahl-N (TKN) (NCCE 2005) which raises concerns about leaching of N species (NO_3^- -N and ammoniacal-N) into the soil. There is also concern about Cu, Mn, and Zn contaminations since concentrations of Cu, Mn, and Zn in poultry litter are reported as high as 1,003, 667, and 669 mg/kg (Sims and Wolf 1994). While NO_3^- -N can cause potentially fatal methemoglobinemia in infants, high Cu levels can cause gastrointestinal effects in the short term and kidney and liver damage in the longer term. Hence, the EPA established MCLs for Cu (1.3 mg/L) and NO_3^- -N (10 mg/L) as part of the primary drinking water standards. In addition to having low to moderate mammalian toxicity (McBride 1994), Mn and Zn impart undesirable taste, color or odor to drinking water. The EPA has established secondary standards for Mn (0.05 mg/L) and Zn (5 mg/L).

While there is considerable research on leaching of litter constituents from land-applied litter, no literature on leaching of As and heavy metals from stockpiled poultry litter could be located. Further, no published studies on the impact of stockpiling litter on the transformation of As species that could impact mobility and toxicity of these species are available. Hence, the overall goal of the proposed research was to evaluate the potential of constituents in turkey litter stockpiled on bare soil to contaminate groundwater. The specific research objectives were:

1. to evaluate transformations of As, N, and P species and changes in total C concentrations within the stockpiled turkey litter;
2. to monitor movement of As species, NO_3^- -N, ammoniacal-N, phosphate, Cu, Mn, and Zn beneath and outside the litter stockpile footprint; and
3. to correlate Mehlich 3 soil test P, Cu, Mn, and Zn concentrations with total concentrations.

LITERATURE REVIEW

This section includes a review of pertinent literature on transformation and mineralization of roxarsone, and possible mechanisms, interactions, and environmental conditions that could cause leaching of As and metals in soils. Also, past research on leaching of NO_3^- -N, As, and metals from turkey manure stockpiles, land application of litter, and use of organoarsenical pesticides are presented.

There is little information on the fate of roxarsone in the environment (Momplaisir et al. 2001). Building on the work of Wershaw et al. (1999), Momplaisir et al. (2001) proposed that while reduction of the nitro group resulted in the formation of 3-amino-4-hydroxyphenylarsonic acid and then 4-hydroxyphenylarsonic acid (due to subsequent deamination), cleavage of the C-As bond resulted in the formation of arsenite (inorganic As(III), mainly H_3AsO_3 and H_2AsO_3^-) (Fig. 1). Oxidation of arsenite results in the formation of arsenate, which can be reduced again to arsenite under anaerobic conditions (Momplaisir et al. 2001) (Fig. 1). Alternating methylation and reduction reactions resulted in the formation of arsonoalkyl acids (MMA(V), MMA(III), DMA(V), and DMA(III) in Fig. 1) as well as alkylarsines (TMAO(V) and TMA(III) in Fig. 1) (Momplaisir et al. 2001)

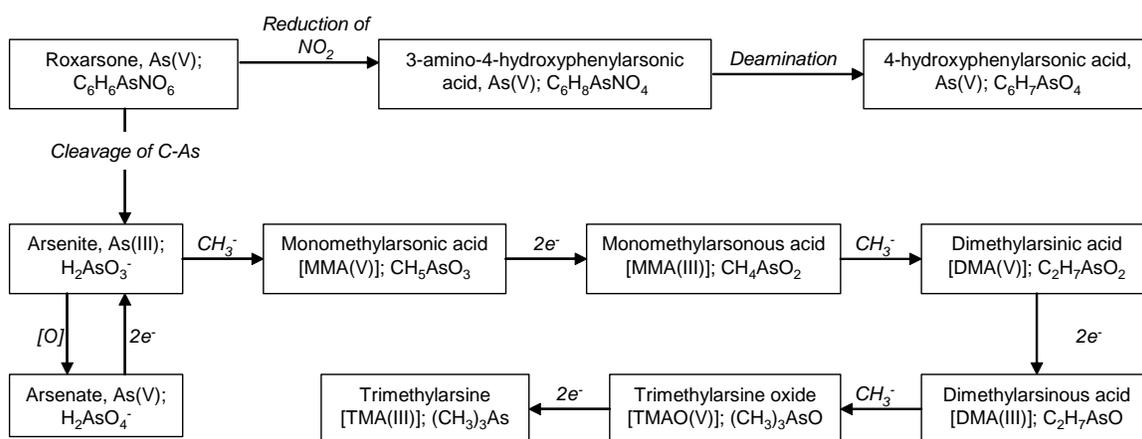


Figure 1. Proposed potential pathways for biotransformation of roxarsone (Adapted from Momplaisir et al. 2001)

Based on the work of Challenger and Higginbottom (1935), Wershaw et al. (1999) proposed that oxidative aromatic ring fission of roxarsone would result in the formation of arsonoalkyl acids. Wershaw et al. (2001) further proposed that while alkylarsines were stable under anaerobic conditions, they rapidly oxidized to arsenate (inorganic As(V), mainly H_2AsO_4^- and HAsO_4^{2-}) under aerobic conditions.

Hence, degradation of roxarsone results in the formation of multiple products and their fate will depend on environmental conditions. Their toxicity generally depends on their valence states and the trivalent (+3) As species are more toxic than the pentavalent (+5) species. While the toxicity of As species to humans depends on the route of delivery (e.g., ingestion vs. dermal absorption), ingestion of drinking water contaminated by roxarsone or its metabolites from poultry litter is the most likely means of entry. Among the pentavalent As species, roxarsone has an oral LD_{50} of 0.11 g/kg for chickens, and DMA(V) and MMA(V) have oral LD_{50} values of 1.2 and 1.8 g/kg, respectively, for mice (Momplaisir et al. 2001). The oral LD_{50} values for arsenate (Mg salt) and arsenite (Na salt) were 80 (rabbit) and 41 (rat) mg/kg, respectively (<http://ptel.chem.ox.ac.uk/MSDS/>). Citing recent research, Momplaisir et al. (2001) reported that MMA(III) and DMA(III) were more toxic than the inorganic species. Hence, contrary to what was

previously believed, some organic transformation products of roxarsone may be more toxic than inorganic As species.

In addition to specie-specific toxicity, the threat posed by As from poultry litter to groundwater depends on mobility, stability, and interaction of the various As species with other constituents in the litter and soil. More than 70% of As in poultry litter was found to be water soluble, with >90% of water-soluble As being in the As(V) form (Jackson and Miller 1999). Rutherford et al. (2003) also reported that 75% of As in poultry litter was readily soluble in water, with the first extraction accounting for 80% of the cumulative As extracted, compared with 13 consecutive water extractions. Hence, rainfall could leach a substantial amount of As from poultry litter stockpile. Beneath poultry litter stockpiles, where conditions are likely to be wet, anaerobic conditions may develop that favor the formation of the more toxic arsenite species (Momplaisir et al. 2001). While arsenate adsorbs strongly to many solids, arsenite is selective and binds strongly only to ferric (hydr)oxides (Fendorf et al. 2004); this may increase the mobility of arsenite (vs. arsenate) in most environmental systems (NRC 1999). Arsenate methylation is a metabolic process involving uptake by microorganisms (Cullen and Reimer 1989). Abundance of methyl ions in bacteria and fungi combined with reducing conditions beneath stockpiles may thus favor conversion of the less toxic organo-As(V) species into more toxic organo-As(III) species (Fig. 1). Cullen and Reimer (1989) did not give a clear relationship of methylation to redox, but most studies and occurrences of high methyl-arsenic compounds were on sediment porewaters. They mostly addressed differences in regard to differences in the microorganisms present. A review by Newman et al. (1998) echoed the Cullen and Reimer (1989) reference in that the organisms present were important, and no redox conditions favoring methylation of arsenate or arsenite to mono- or di-methyl arsenic or arsenous acids were cited. Masscheleyn et al. (1991) studied redox and pH effects on arsenic and selenium speciation in sediments and found no methylation of As occurring at any redox potential between 500 and -200 mV. However, Brannon and Patrick (1987) found organic As in some sediments incubated under anaerobic conditions, which was attributed to methylation of As(III). Overall, the literature indicated that methylation of As was more closely associated with the types of microorganisms present in the soil than its redox potential.

Research has shown that conditions in poultry litter stockpiles may enhance As mobility and toxicity. Garbarino et al. (2003) investigated the impact of composting temperature and moisture content on degradation of roxarsone in poultry litter in beakers. Degradation increased with temperature (15 to 40°C) and moisture content (range not reported); roxarsone completely degraded primarily to As(V) in about 30 d at 40°C and 50% moisture content (Garbarino et al. 2003). Hence, stockpiled litter exposed to rainfall could experience heating within the stockpile, enhancing degradation of the organic As to more mobile inorganic As species. However, in the absence of published research, it is difficult to comment on heating within stockpiles; while temperatures up to 60°C generally enhance microbial activity, higher temperatures (>65°C) can stop or reduce microbial activity. This is significant since roxarsone mineralization is a biotic process (Garbarino et al. 2003).

Other poultry litter constituents, namely, phosphates, soluble organic C compounds, and NO_3^- -N may affect the mobility and toxicity of As in poultry litter. Poultry litter contains relatively greater molar amounts of P than As. Arsenate ($\text{H}_2\text{AsO}_4^- + \text{HAsO}_4^{2-}$) and phosphate ($\text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-}$) have similar binding mechanisms in soils (Bohn et al. 1985). Although arsenate tends to have some binding preference over phosphate on soil constituents (Violante and Pigna 2002), the more abundant phosphate ions in poultry litter could displace As anions from the limited available sorption sites in sandy soils, thereby solubilizing arsenate and increasing the potential of As leaching. In leaching column studies with loam soil, application of phosphate fertilizers to arsenate-contaminated soil resulted in increased topsoil As depletion, enhanced As transport into and through the initially uncontaminated subsoil, and increased dissolved As concentrations (Peryea and Kammerick 1997). With 10 pore volume displacements, Peryea and Kammerick (1997) reported that 44% of the initial As was depleted from the topsoil with phosphate application vs. 5% without phosphate. Reynolds et al. (1999) evaluated As sorption in phosphate

amended soils during flooding and subsequent aeration. While dissolved As concentration was higher under flooded conditions, phosphate addition enhanced reduction of As(V) to the more mobile and toxic As(III) (Reynolds et al. 1999). In essence, phosphate contamination of groundwater is already a concern in intensive poultry-producing regions of North Carolina on sandy soils. If conditions are favorable for phosphate leaching, As leaching could also occur with a potentially increased fraction of it as arsenite due to the presence of phosphate.

Soluble organic C substances in poultry litter could increase mineralization of organic As and the mobility of inorganic As. Dissolved organic C compounds such as humic substances and simple organic acids (e.g., microbial degradation products) could reduce metal (and As) sorption and increase its concentration in soil solution in two ways: through competition for surface sites and through complexation. Grafe et al. (2001) reported that As(V) and As(III) sorption on mineral soil surfaces were reduced by humic and fulvic acids since the acids competed for surface sites with As species. Redman et al. (2002) reported that compared with As(V), As(III) was desorbed or prevented from sorbing to a greater extent, resulting in greater As(III) mobility. Aqueous complexation, involving organic acids in poultry litter can make metal cations more soluble (Snoeyink and Jenkins 1980). Metal cations can then provide a bridge to complex the As oxyanions with the anionic functional groups in organic compounds, reducing the tendencies of the As oxyanions to form solid-phase metal complexes (Redman et al. 2002). Unlike aqueous complexes, such solid-phase complexes could reduce metal and As mobility (Snoeyink and Jenkins, 1980). Organic matter may also catalyze redox reactions by serving as an electron shuttle between inert species and even between metals and microorganisms; this may result in As speciation thus affecting As mobility (Redman et al. 2002). Because arsenate, arsenite, and phosphate are oxyanions, they are expected to be less strongly bound to organic matter such as in poultry litter, unless considerable amounts of organically-bound ferric iron (or possibly trivalent Al) are present (Gerke and Hermann 1992; Gerke 1993; Violante and Pigna 2002).

Zhu and Schmidt (2000) investigated the impact of NO_3^- -N leaching from a turkey manure stockpile (age not reported) on a sandy loam soil in Minnesota. Nitrate-N concentrations at depths of 0.3, 0.6, 0.9, and 1.2 m were 47 ± 39 , 59 ± 29 , 57 ± 27 , and 60 ± 29 mg/L, far in excess of background soil levels of 2-3 mg/L (Zhu and Schmidt, 2000) and well in excess of the primary drinking water standard MCL of 10 mg/L. While NO_3^- -N leaching from animal waste stockpiles can by itself affect drinking water quality, it can also affect As mobility. Bednar et al. (2003) reported that roxarsone photolytic degradation to inorganic As species increased with NO_3^- -N and natural organic matter (as organic C) concentrations, with As(III) formation being observed at NO_3^- -N concentration of 15 mg/L. This could enhance mineralization and mobility of As, particularly on stockpile surfaces as well as in pooled liquids.

There is some evidence that poultry litter application over the long term can cause leaching of As and metals down to appreciable depths. Gupta and Charles (1999) sampled As, Cd, Cu, Mn, and Zn in 0.1-m decrements down to 0.6 m in manured vs. non-manured fields. Both types of fields were sandy clay loam and the manured fields had received poultry litter at 8.97 Mg/ha every alternate year for the previous 15-20 years. They found elevated levels of As, Cd, Cu, and Mn down to 0.6 m in the soil (0.5 m for Cd). Increased As levels deep in the soil were attributed to reduced sorption of arsenate due to competition by the phosphate ions, as well as due to redox transformations of methanoarsenates by microorganisms in the soil and litter. Leaching of other metals was attributed to leaching of soluble organic complexes (Gupta and Charles 1999).

There is evidence that As can leach deeper into the soil and even reach irrigation wells. Bednar et al. (2002) reported that use of organoarsenical herbicides had led to higher levels of As (mainly as arsenate and arsenite) compared with background levels. However, As concentrations in well water never exceeded the MCL of 10 $\mu\text{g/L}$ for primary drinking water standards (Bednar et al. 2002).

Hence, based on As chemistry and environmental conditions, As and other constituents in poultry litter could impact the quality of shallow groundwater. Producers may stockpile litter at the same location year after year for varying lengths of time. Compared to land application at agronomic rates where crops remove a portion of added metals, leaching losses of As and metals from stockpiled poultry litter could be higher given the greater localized concentrations, the longer duration of exposure to rainfall, and the absence of crop removal. While certain chemical characteristics (e.g., relative abundance of phosphate, organic C) of poultry litter could enhance mobility of As and metals, soil and environmental conditions in the Coastal Plains are especially favorable for As and metal movement into the soil profile. Compared with finer-textured soils, sandy soils in the Coastal Plain have lower capacity (fewer adsorption sites) to retain As, heavy metals, and phosphate in the surface horizons. Further, acidic soils (SCS 1985) combined with acidic rainfall in the region are likely to increase the solubility and mobility of metal cations. Reducing redox conditions promoted by water-saturation and the presence of metabolizable organic C compounds (e.g., from a litter stockpile) could enhance the dissolution of arsenic and phosphate. High annual rainfall (>1270 mm) (SERCC 2003) could further increase potential for leaching of soluble poultry litter constituents into the surficial aquifers in the region.

MATERIALS AND METHODS

The study was conducted at the Horticultural Crops Research Station (HCRS) at Clinton, NC during May 2004 through April 2005. The dates of important field operations are shown in Table 1.

Table 1. Dates of important field operations.

Date	Operation
24 May 2004	Obtained initial turkey litter samples and created stockpiles (summer batch)
28 Jul. 2004	Applied simulated rainfall to two of four stockpiles (48.8 mm)
1 Nov. 2004	Obtained final turkey litter samples from summer stockpiles prior to removal
2 Nov. 2004	Removed summer stockpiles
1-4 Nov. 2004	Obtained soil samples between stockpiles and beneath summer stockpiles
15 Nov. 2004	Obtained initial turkey litter samples and created stockpiles (winter batch)
31 Mar. 2005	Applied simulated rainfall to two of four stockpiles (32.0 mm)
25 Apr. 2005	Obtained final turkey litter samples from winter stockpiles prior to removal
26 Apr. 2005	Removed winter stockpiles
25-27 Apr. 2005	Obtained soil samples between stockpiles and beneath winter stockpiles

The study site (~24 × 60 m) was oriented NNE-SSW along the long axis (Fig. 2) and had Orangeburg loamy sand (fine-loamy, kalonitic, thermic Typic Kandiodult) on a slope of 3-5%. The site had been under sod and had never been fertilized. Soil sampling indicated that the top ~0.4 m was sandy while the soil below was sandy clay. Based on samples taken lengthwise along the site, soil properties are given in Table 2 (details on the methods used are discussed later).

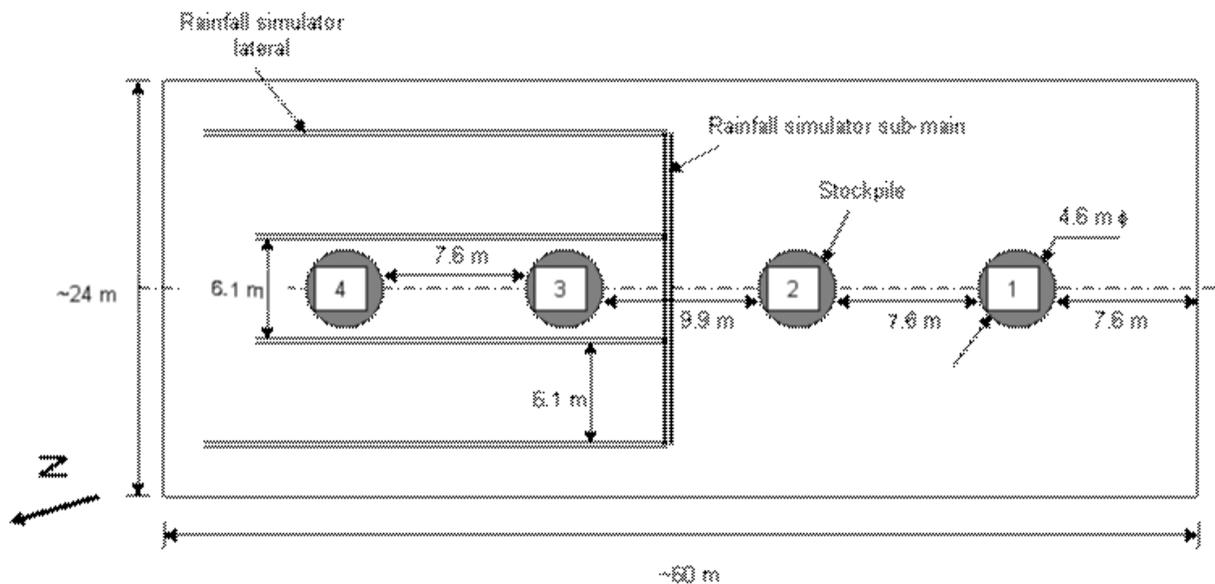


Figure 2. Layout of the research site. Stockpiles 2 and 3 were instrumented with moisture and temperature sensors during summer. Stockpiles 3 and 4 received simulated rainfall.

A weather station (Spectrum Watchdog) was installed at the site to measure and record hourly rainfall, air temperatures (dry bulb and wet bulb), wind speed, wind direction, and solar radiation. Missing weather data at the research site were complemented with data obtained from a weather station located ~1 km away that is maintained by the NC State Climate Office.

Table 2. Soil properties of Orangeburg loamy sand at the site.

Properties ^[a]	Depths, mm		
	0-76	76-305	305-610
Bulk density, g/cm ³	1.41 (0.02) ^[b]	1.59 (0.08)	1.43 (0.05)
pH, units	5.1 (0.1)	5.3 (0.1)	5.2 (0.2)
Electrical conductivity (EC), μ S/cm	39.2 (22.1)	24.4 (9.1)	21.0 (5.0)
Total C, g/kg	13.57 (0.50)	3.87 (0.10)	3.07 (0.13)
Dissolved organic C (DOC), mg/kg	38 (5)	17 (1)	16 (1)
Total N, g/kg	1.50 (0.06)	0.53 (0.04)	0.77 (0.00)
NH ₄ ⁺ -N, mg/kg	10.40 (0.17)	0.41 (0.11)	0.53 (0.30)
NO ₃ ⁻ -N, mg/kg	14.77 (1.17)	9.77 (0.30)	2.80 (0.43)
Total P, mg/kg	318 (10)	219 (7)	229 (6)
Water soluble P (WSE-P), mg/kg	4.32 (0.69)	2.10 (0.25)	0.01 (0.02)
Total As, mg/kg	0.93 (0.09)	0.85 (0.08)	3.30 (0.13)
Water soluble As (WSE-As), mg/kg	ND ^[c]		
Total Cu, mg/kg	2.53 (0.43)	1.83 (0.20)	4.80 (0.27)
Total Zn, mg/kg	9.63 (1.10)	10.10 (1.73)	12.50 (0.53)
Total Mn, mg/kg	28.13 (0.70)	22.20 (0.73)	28.43 (0.80)

^[a] Except for pH and EC, all other properties are reported on oven-dry basis

^[b] All Mean and SD values are based on three soil samples obtained along the length of the site; each soil sample was prepared by compositing multiple soil samples obtained along the width of the site

^[c] Not detected

SAMPLE HANDLING AND ANALYSES

Sample Handling

Twenty-four turkey litter (TL) and 96 soil samples were collected during the study (details are provided below). Turkey litter and soil samples were bagged into low-density polyethylene (LDPE) bags, transported on ice to the laboratory, and packed into 4 L glass jars to limit exposure to air. The samples were stored in the freezer (-14°C, TL) or the refrigerator (4°C, soil) to limit microbial activity. To help ensure that the samples remained close to field-redox conditions, all sample handling in the laboratory was done in a glove box under a N_{2(g)} atmosphere and a red-filtered safe light or low-intensity white light. The moist samples were sieved to <2 mm using a stainless steel sieve and homogenized by thoroughly mixing with a plastic spatula. The <2 mm fractions of TL and soil were sealed under N_{2(g)} into amber-colored borosilicate glass vials with crimp caps and teflon-coated rubber inserts, and stored at -14°C (TL) or 4°C (soil). The >2 mm TL fraction was oven-dried at 70° C and ground to <2 mm using a soil grinder and stored in LDPE bags at room temperature for subsequent analyses. All labware was washed or rinsed in sequence with detergent (Micro[®] solution, Cole Parmer, Vernon Hills, IL), tap water, either 7 M HNO₃ (acid digestions), 1 M HCl (nitrogen analyses), or 1 M HNO₃, and DI water.

Sample Analyses: Strong Acid Digestion

Soil and TL concentrations of Al, As, Cu, Fe, Mn, P, and Zn were determined by acid digestion using US-EPA Manual SW-846, methods 3050B and 6010C (US-EPA 1996). Randomly selected soil and TL samples were digested in duplicate or triplicate in batches of up to 24 samples, along with six quality control samples (NIST soil standard – 2710 Montana, and method blanks).

Strong-acid soluble metals were determined on field-moist soil, TL, and the NIST standard soil by weighing 2.0 g samples (on a dry-weight basis) into conical, borosilicate-glass beakers. Fifteen milliliters of a 1:1 solution of 15.8 M HNO₃ and DI water were added to each beaker and refluxed for 15 min. on a hot plate. After cooling, two separate additions of 7.5 mL of 15.8 M HNO₃ were added, and covered

samples (with watch glasses to prevent evaporation) were refluxed for 30 min. after each addition. After the third reflux, the uncovered samples were evaporated to 5 mL. After cooling, 2 mL of DI water and 3 mL of 30% H₂O₂ were added to each sample, and the covered samples were reheated until effervescence subsided. A total of 10 mL of 30% H₂O₂ were added in 1 mL aliquots, heated as described above, uncovered, and evaporated to 5 mL. The covered samples were then cooled and allowed to sit for 16 h. Next, 10 mL of 12 M HCl were added to each covered sample and refluxed for 30 minutes. Each cooled digestate sample was filtered through a 0.2 µm Isopore polycarbonate membrane (Millipore Corp., Bedford, MA), quantitatively transferred to a 50 mL volumetric flask, and brought to volume with DI water. These samples were stored in 125 mL HDPE sample bottles at 4°C. Digestates were analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES-Perkin Elmer-Optima 2000 DV) for As (λ =188.979, 197.197, and 228.812 nm) and P (λ =213.617 and 214.914 nm), or flame atomic absorption spectrometry (FAAS-Perkin Elmer-3100) for Al, Cu, Fe, Mn, and Zn (λ = 309.3, 324.7, 248.3, 279.5, and 213.9 nm, respectively). All instrumental analyses were done using secondary metal standards prepared by diluting primary standards (Fisher Scientific - Pittsburgh, PA or Spex Certiprep, Inc., New Jersey). The background of standards and samples were matched by addition of “trace metal” grade HCl or HNO₃ acid as needed.

Quality Control

For quality control, each acid digestion batch included triplicate samples of Standard Reference Material (SRM) 2710 (Montana Soil) from the NIST and reagent blanks. Digestions were performed using “trace metal” grade HCl and HNO₃ (Fisher Scientific). For ICP-OES and AAS analyses, standard curves and quality control checks were repeated every 10 and 15 samples, respectively. Limits of Quantitation (LOQ) were calculated for each analyte by measuring the concentration of 10 replicates of a low concentration standard, and multiplying the standard deviation by 10. Analyte recovery, when compared to “leachable” concentrations measured in SRM 2710, ranged from 91 to 105% (As), 83 to 106% (P), 93 to 104% (Cu), 100 to 122% (Zn), 90 to 123% (Mn), 99 to 133% (Fe), and 121 to 162% (Al) (Appendix C - Table C1) (US-EPA, 1996). Random duplicate TL and soil samples were spiked with As, P, Cu, Mn, and Zn to determine percent metal recovery for these matrices (Appendix C – Table C2) (US-EPA 1996). Metal recovery values of >120 % may have resulted from inaccuracy while adding the analyte.

Water-soluble Metals and Dissolved Organic Carbon (DOC), KCl, and Mehlich 3 Extractions

Water-soluble extractable (WSE) As, P, and DOC concentrations were measured using a 1:10 soil or TL to water ratio, respectively (Jackson et al. 2003). Extract solutions were shaken on a reciprocal floor shaker (220 cycles min⁻¹) for 2 h, centrifuged at 27,000G, and filtered through 0.2 µm Isopore polycarbonate membranes. Arsenic and P were analyzed by ICP-OES (described above) and DOC was measured on a Total Organic Carbon (TOC) analyzer (Shimadzu, TOC5050).

Ammoniacal nitrogen (NH₄-N) and nitrate nitrogen (NO₃-N) concentrations were measured using 1:10 soil to 1 M KCl or 1:60 TL to 1 M KCl ratios (Peters et al. 2003; Mulvaney 1996). Solutions were shaken for 1 h (soil) or 20 min. (TL), centrifuged, and filtered as described above. Filtrates were analyzed colorimetrically for NH₄-N (520 nm - QuickChem method 10-107-06-2-A) and NO₃-N (660 nm – QuickChem method 10-107-04-1-A) on a QuickChem 8000 Automated Ion Analyzer (Lachat Instruments, Milwaukee, WI) (Lachat 1995).

Mehlich 3 extractable (Mehlich 1984) Cu, Mn, Zn, and P were measured at the North Carolina Department of Agriculture (NCDA) Soil Testing lab using a 1:1 soil to Mehlich 3 extractant solution consisting of 0.25 N ammonium nitrate, 0.013 N nitric acid, 0.015 N ammonium fluoride, and 0.001 M EDTA. The methodology is described on-line at NCDA (2003). Concentrations of Cu (λ =324.753), Mn (λ =257.610), Zn (λ =213.856), and P (λ =214.914) were measured by use of a Thermo Elemental 61E ICP.

Total Carbon (C) and Nitrogen (N), pH and Electrical Conductivity

Moist TL and soil samples were freeze-dried and sieved or ground (TL - plant grinder) to <250 μm and analyzed by combustion (Nelson and Sommers 1996) for total C and N on a Perkin Elmer Series II CHNS/O analyzer. Soil and TL pH and electrical conductivity (EC) were measured using a 1:1 (or 1:2) soil (or TL) ratio (Peters et al. 2003; Thomas 1996). Moisture contents of the soil and TL were determined by drying triplicate samples for 24 h at 110°C (70°C for TL) and then weighing. Results of all chemical analyses were calculated on a dry mass basis. Data for sieved TL samples (<2 and >2 mm fractions) were reported on a whole sample basis (except water-soluble As speciation and As K-XANES) by calculating a weighted mean of the whole sample based on the % mass of each fraction as:

$$X_w = [(F_1 \times P_{MF1}) + (F_2 \times P_{MF2})] \quad [1]$$

where X_w is weighted mean of TL sample; F_1 and F_2 are measured analytical value of <2 and >2 mm fractions, respectively; and P_{MF1} and P_{MF2} are <2 and >2 mm fractions, respectively, of the whole litter (w/w). Standard errors of the weighted means were calculated using a pooled variance (Rao 1998).

Arsenic Speciation

Arsenic speciation analysis was performed at Savannah River Ecology Laboratory, Aiken, SC. Arsenic speciation was determined on extracts of 1:10 TL (<2 mm fraction):water after shaking for 2 h, filtering to < 0.22 μm , and running diluted (20-fold) extracts through a Dionex AS 16 column using a gradient elution of tetramethylammonium hydroxide and 2% methanol on a Perkin Elmer DRCplus IC-ICP-MS (Jackson and Bertsch 2001).

Synchrotron X-ray Absorption Near-edge Structure (XANES) Analysis

Arsenic K-XANES analyses were done at Beamline X-18B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), Upton, NY. This is a direct, non-destructive technique used to determine the oxidation state and solid-phase speciation of a given element in a complex matrix, such as turkey litter and soil. This technique can be used to investigate solid-phase components with reduced oxidation states, as samples that have been stored anoxically can be analyzed directly without changing the oxidation and solid-phase speciation that existed at field-conditions. Spectral data collected on prepared organic and inorganic standards that represent possible solid-phase species in the sample can be used in linear combination fitting (LCF) analysis to estimate the percentage of these components in a sample (Hutchison and Hesterberg 2001; Ravel and Newville 2006). The x-ray beamline is equipped with a computer-controlled Si(111) channel cut monochromator capable of analyzing at the x-ray absorption edge of As (also Cu, Zn, Mn, and Fe). In addition to ion chamber detectors, the beamline has a highly sensitive, solid-state, multielement detector capable of collecting XANES spectra on soil samples with As concentrations down to ~1 mg/kg.

Working in an inert atmosphere ($\text{N}_{2(g)}$), moist TL and soil solids (<2 mm fraction) were mounted in polyacrylic sample holders, covered with Kapton tape (Spex Certiprep, Inc.), wrapped in aluminum foil (to exclude light), and sealed in glass jars filled with $\text{N}_{2(g)}$ for transport to the NSLS for analysis. Inorganic and organic As standards were diluted in boron nitride and mounted in polyacrylic sample holders. Detailed procedures for XANES data collection are described in Hesterberg (2001). The energy scales of XANES spectra were normalized to the absorption edge of elemental As by subtracting 11,867 eV from all the data points after calibrating the monochromator. The data were baseline corrected and normalized over the energy ranges of -30 to -10 and 60 to 90 eV, respectively, using the EXAFS fitting program Athena (version 0.8.047; Ravel and Newville 2006). The energy of the absorption edge represents the binding energy required to eject a 1s electron from an As atom. As the oxidation state of an element increases [e.g., As(III) to As(V)], the 1s electron binding energy increases and the absorption edge shifts to a higher energy (Fendorf and Sparks 1996). This difference in edge positions is evident in the spectra of As(III) and As(V) standards in Fig. 12 (discussed below).

Granular Matrix Sensor Calibration

The granular matrix sensor (GMS, Watermark®), used to measure TL moisture content (indirectly), was calibrated in the laboratory during an 87-d study. Three PVC containers were fabricated by gluing a PVC sheet (with six 6.35 mm holes) as bottom to a PVC pipe (78 mm i.d; 153 mm high). The bottom was further lined with a double layer of cheesecloth. After pouring and packing ~220 g of moist TL into the container, a GMS that had been soaked for >24 h was pressed into the litter ensuring that there was proper sensor-litter contact. Prior to installing the sensor, the masses of the container and sensor were determined separately. At time intervals ranging from 1 to 12 d, the litter moisture tension (cbars) was read for each GMS using a Watermark® meter and each container was weighed and its mass loss determined for the time interval. The litter moisture tension varied across the entire measurement range of 0-199 cbars. However, since the measurement range of a GMS is in the 10-100 cbars (Scanlon et al. 2002), based on the average litter moisture tension readings of the three sensors, litter moisture characteristic curve developed (Fig. 3) was based on data obtained in the range of 12 to 95 cbars. Calibrating the GMS for TL moisture content may be less accurate than soils since the measured mass loss includes not just moisture, but also CO₂ and ammonia, and the three constituents cannot be separated.

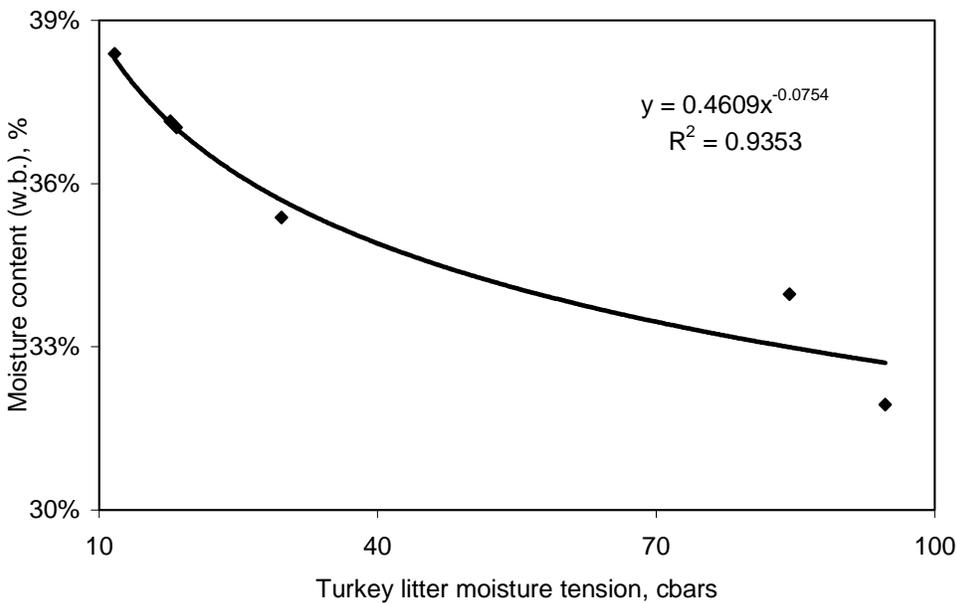


Figure 3. Moisture characteristic curve of turkey litter developed using granular moisture sensor.

FIELD WORK

Summer Stockpiling

About 20 Mg of whole house clean-out litter was obtained from a turkey house in May 2004. The litter was transported to the HCRS and stored close to the research site by piling over a tarpaulin sheet; to prevent runoff losses, the pile was covered with tarpaulin. After ~2 weeks, four stockpiles were created at the research site using the TL (Fig. 2). The stockpiles had a mean mass of ~4.1 Mg (CV=1.1%), footprint diameter of ~4.6 m and height of ~1.6 m. To ensure uniformity of size of the stockpiles, the mass of each load of litter was determined by weighing the tractor front end loader on wheel scales. Consecutive loads of litter were applied to different stockpiles to preclude systematic differences in TL characteristics among stockpiles. A composite TL sample was obtained for each stockpile by sampling each load of litter applied to that stockpile. The TL analyses (in triplicate) are presented in Table 3.

Table 3. Characteristics of the turkey litter used in the study.

Characteristics	Summer	Winter
Moisture content, %	33.7%	38.4%
pH, units	7.21 (0.25) ^[a]	6.87 (0.85)
EC, mS/cm ^[b]	10.4 (0.2)	11.6 (0.4)
Total C, g/kg	311 (3)	362 (6)
DOC, g/kg	77 (3)	76 (2)
Total N, g/kg	42.5 (0.5)	37.4 (0.5)
NH ₄ ⁺ -N, g/kg	15.0 (0.2)	9.9 (0.2)
NO ₃ ⁻ -N, mg/kg	66 (5)	176 (4)
Total P, g/kg	22.1 (0.6)	23.2 (0.6) ^[b]
WSE-P, g/kg	4.8 (0.1)	9.8 (0.1)
Total As, mg/kg	5.9 (0.1)	15.7 (0.4) ^[b]
Water soluble As (WSE-As), mg/kg	4.4 (0.6)	13.2 (0.2)
As (V) as roxarsone ^[b] , mg/kg	0.11 (0.08)	0.44 (0.33)
Total Cu, mg/kg	560 (10)	680 (10)
Total Zn, mg/kg	720 (10)	960 (30)
Total Mn, mg/kg	720 (20)	860 (20)
Total Fe, mg/kg	1620 (40)	1430 (30)
Total Al, mg/kg	1590 (70)	1210 (30)

^[a] Mean and SD of four values

^[b] Based on <2 mm fraction only

The veterinarian for the turkey grower had reported that roxarsone had been delivered to the birds through the drinking water at a concentration of 20 mg/L, following FDA recommendation. During summer stockpiling, only <2% of the roxarsone remained in the litter probably because prior to stockpiling the litter had been stored under a tarp where warm and humid conditions resulted in its breakdown. Garbarino et al. (2002) reported that roxarsone completely degraded (mainly to As(V)) in 3 to 4 weeks when litter was composted at 40°C with 50% w/w water. Higher roxarsone recovery (as percent of WSE-As) have been reported by Jackson et al. (2003) (35-80%), Jackson and Bertsch (2001) (61%), and Garbarino et al. (2003) (91%), in air-dried poultry litter freshly removed from grow-out houses. In the turkey litter used for summer stockpiling, water soluble As species accounted for 75% of the total As. This is consistent with the findings of Jackson and Miller (1999) and Rutherford et al. (2003) that >70% As in poultry litter was in the water soluble form.

Two stockpiles (#2 and #3) (Fig. 2) were instrumented to measure moisture content (indirectly using GMSs) and temperature beneath and in the stockpile. Prior to stockpiling litter, at the center of the footprint of stockpile, two pairs of sensors, each comprising of one GMS sensor coupled with one Type K thermocouple were installed at depths of 0.15 and 0.6 m (Fig. 4). Similarly, coupled moisture and temperature sensors were installed at the edge of the stockpiles at 0.15 and 0.6 m depths. Further, two pairs of sensors were buried some distance away from the stockpiles at 0.15 and 0.6 m depths. Thermocouples provided information, both for evaluating the impact of the stockpiles in modifying the thermal regime in the soil as well as for correcting the output of the GMS. The GMS provided mV outputs that were converted to soil moisture tension (cbars). Three pairs of sensors (GMS + Type K thermocouple) were installed at 0.25 (deep), 0.76 (mid-level), and 1.27 m (shallow) depths above the soil surface and at the center of the stockpiles (Fig. 4). Hourly data from all the sensors were recorded by a Campbell 10X data logger equipped with a multiplexer.

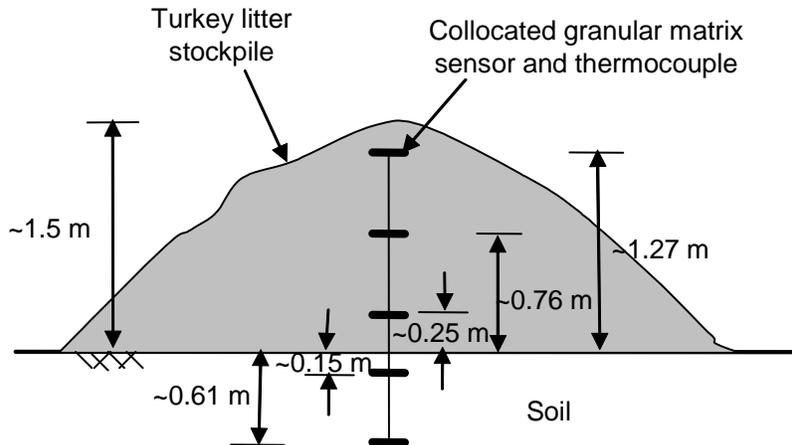


Figure 4. Location of GMS and thermocouples within and beneath stockpiles 2 and 3. The GMSs and thermocouples inserted 1.27 m, 0.76 m, and 0.25 m above the soil in the stockpile are referred to as shallow, mid-level, and deep sensors, respectively. The GMSs and thermocouples inserted 0.15 and 0.61 m, respectively, in the soil are referred to as shallow and deep sensors.

Within a month of stockpiling, all the stockpiles had shrunk in height by ~ 0.6 m; thereafter, decline in stockpile height was not noticeable. Shrinkage in stockpile heights resulted in shallow sensors in stockpiles 2 and 3 being exposed to the air; the mid-level sensors were probably ~ 0.15 m inside the litter. All of the GMS and thermocouples installed in the stockpiles and soil were removed when the summer stockpiles were removed in Nov. 2004.

As shown in Figure 2, a rainfall simulator was installed to cover stockpiles 3 and 4. The rainfall simulator was borrowed from Virginia Tech's Biological Systems Engineering Dept. and is described by Dillaha et al. (1987). Briefly, the submains and lateral spacings are both 6.1 m. The risers are 3.4 m high and carry Rainjet Model 78C full-circle pop-up sprinklers. At 0.19 MPa (28 psi) the sprinkler is designed to apply 34 L/min of rainfall with a diameter of coverage of 14.6 m; this results in an application rate of 50.8 mm/h of simulated rainfall (Dillaha et al. 1987). In this study, each riser was equipped with a 0.21 MPa (30 psi) pressure regulator rather than controlling the pressure of the pump connected to the hydrant.

It was decided that simulated rainfall would be applied to stockpiles 3 and 4 whenever the measured rainfall total at the site exceeded a deficit >25.4 mm vs. the 30-yr average for Clinton, beginning the day the stockpiles were established. Further, the deficit rainfall depth plus one SD (of the 30-year average for that period) but no more than 50.8 mm of rainfall would be applied at one time. Applying simulated rainfall only to stockpiles 3 and 4 allowed for comparison of leaching under 'average' rainfall conditions to 'actual' conditions. One rainfall event (48.8 mm) was applied to the summer stockpiles (Table 1; Fig. 5); the depth of application was determined based on collection in multiple rain gauges located between stockpiles 3 and 4. A total of 616 mm of natural rainfall was measured at the field site during the 162 d of stockpiling vs. 641 mm that would be expected based on 30-yr average monthly precipitation (Fig. 5). While total rainfall during summer stockpiling was within 4% of average for that period, monthly distribution showed considerable fluctuation from the 30-yr average (Fig. 5).

One day before removing the stockpiles in Nov. 2004, soil samples were obtained from a ~ 1.5 -m wide strip in between stockpiles 1 and 2 (location 1), stockpiles 2 and 3 (location 2), and stockpiles 3 and 4 (location 3). Soil samples were obtained from depth increments of 0-25, 25-76, 76-305, and 305-610 mm. While the two shallow cores were obtained with 25-mm soil probes, the deeper cores were obtained with a 51-mm Shelby tube driven into the soil with a drill rig. All core holes were plugged with bentonite. For each location, multiple soil cores (>20 for the two shallow depths and two for the other

depths) from a particular depth were composited to obtain a single sample per depth increment. The soil samples were transferred to plastic bags that were stored in air-tight glass jars (only the two surface samples). The two soil surface samples were sieved through a 2 mm sieve and the <2 mm fractions were analyzed, in triplicate, for constituents listed in Table 2 using the analytical methods described earlier. Additionally, the 0-25 and 25-76 soil samples from locations 2 and 3 were analyzed for As speciation XANES (discussed earlier). Comparing constituent concentrations in the soil between the stockpiles with those in the soil beneath the stockpiles (discussed below) allowed evaluation of the extent of constituent leaching from the stockpiles into the soil below.

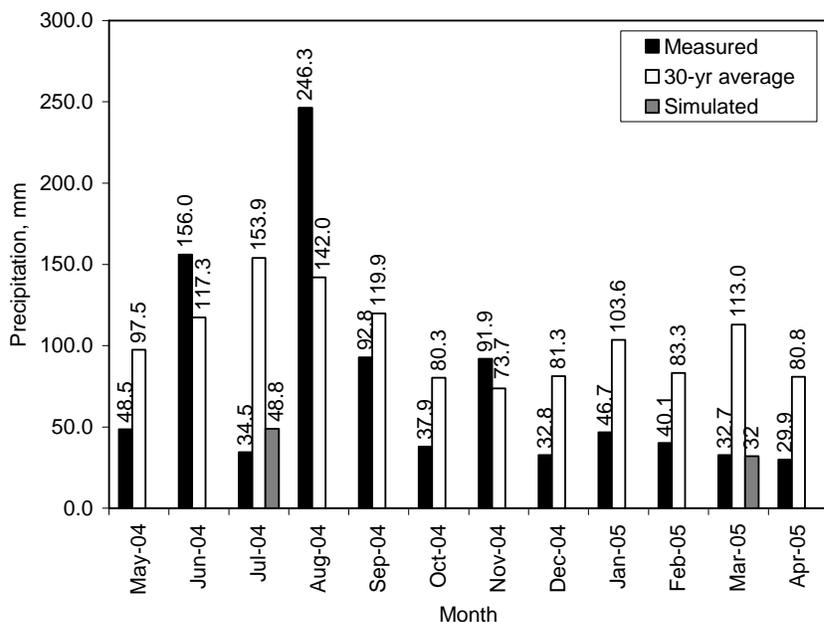


Figure 5. Measured precipitation, 30-year average monthly precipitation (Clinton, NC), and simulated rainfall at the site during May 2004 through April 2005. Measured precipitation for May 2004 is for 25-31 May and for April 2005 is for 1-25 April.

Just prior to removing the stockpiles, three skin (0~0.15 m) and three core (0.15~0.9 m) TL samples were obtained from each stockpile at about mid-height using a 76 mm auger type soil sampler inserted perpendicular to the stockpile slope. After compositing, one skin and one core sample from each stockpile were placed in plastic bags which were stored in airtight glass jars on ice. After transporting the samples to the lab, the samples were frozen if not immediately analyzed. The TL samples were analyzed in triplicate for constituents listed in Table 3. Comparing constituents in the TL before and after stockpiling allowed for evaluation of the impact of stockpiling TL uncovered and on bare ground, on transformations of litter constituents over time.

The stockpiles were removed using a tractor front end loader taking care to leave the soil below undisturbed. From the center of the stockpile two circles of half (2.3 m) and full (4.6) diameters were drawn. Soil samples from depth increments of 0-25, 25-76, 76-305, and 305-610 mm were obtained from the circumferences corresponding to the full diameter and half diameter as well as the center of the circle using soil sampling tools described earlier. Care was taken to carefully scrape away the TL remnants before taking soil samples. For the two shallow depths, >20 soil cores were obtained for each depth; for the full and half diameter circles, the samples were obtained from along the circumference at more or less equal spacing. For the deeper samples, four, three and two cores were obtained for the diameter, half diameter, and center, respectively. All core holes were plugged with bentonite. After compositing cores for the same location (e.g., full diameter) and depth, there were five samples each at the full diameter, half

diameter, and center for each stockpile; hence, the four stockpiles yielded a total of 60 samples. Sample extraction, handling, and analyses were identical to the soil samples obtained from between stockpiles in Nov. 2004. A total of eight out of 24 shallow surface samples from stockpiles 3 and 4 were analyzed for As speciation using XANES. The summer stockpiles were maintained for 161 d.

Winter Stockpiling

For the winter stockpiling, again ~20 Mg of TL was obtained from the same grower and was stockpiled the same way as in May 2004 for a total of 162 d, 2 weeks after removing the summer stockpiles. Unlike the summer stockpile, the litter for the winter stockpile was caked litter that had been removed from the turkey house 2.5 months earlier and stored outside at the turkey farm. The stockpiles were similar to one another and to the earlier stockpiles in size and mass (mean = 4.1 Mg; CV = 1.4%). However, no moisture and temperature measurements in the soil and stockpiles were taken as with the summer stockpiles. Between the times of removal of the summer stockpiles and creation of the winter stockpiles, a total of 41.7 mm of rainfall was measured at the Research Station.

In the winter batch, the total As and WSE-As concentrations were much higher than in the summer batch (Table 3) probably because the cake had a much higher proportion of As-rich feces than in the whole house clean-out litter used in summer. Arsenic as roxarsone was <3% of the total As (Table 3). Water soluble As accounted for >75% of the total As and was comparable to the summer batch.

The winter stockpiling period (162 d) was dry with measured precipitation of 228.2 mm vs. 485.4 mm based on the 30-yr monthly average (Fig. 5). Rainfall could not be applied during the winter because the pumping system had been winterized. In March 2005, one simulated rainfall event (32.0 mm) was applied to stockpiles 3 and 4. The stockpiles were removed in late-April 2005 (Table 1). Soil and TL were sampled, handled, and analyzed as had been done with the summer stockpiles except for slight differences in sample analyses. Instead of analyzing samples in triplicate as was done with the summer stockpiles, samples were only analyzed in duplicate if results varied by $\leq 10\%$; triplicate sample analyses were performed if variations were $>10\%$. Also, the soil samples were not analyzed for Fe and Al.

INTERPRETATION OF RESULTS

Changes in TL properties during stockpiling were evaluated based on comparing arithmetic means of TL properties before stockpiling and after stockpiling; comparisons were made separately for the stockpile skin (0~0.15 m) and core (~0.15~0.90 m). Changes in TL properties were also measured between stockpiles that received only natural rainfall (NR) with those that also received simulated rainfall (NR+SIM). Comparison of summer vs. winter stockpiles provided information on the impact of weather on transformation on TL constituents.

Soil properties outside the stockpiles (i.e., control) were compared with properties beneath the stockpiles at the same depth for a total of four depths, namely, 13, 51, 191, and 457 mm representing soil depth ranges of 0-25, 25-76, 76-305, and 305-610 mm, respectively. The control values were calculated based on samples from three locations between stockpiles one of which received simulated rainfall. For the outside samples, at each location, a sample was obtained by compositing ≥ 20 cores for the 0-25 and 25-76 mm depths while single cores were used for the two deeper samples. The data point beneath the stockpile was based on ≥ 20 cores for the 0-25 and 25-76 mm depths while for 76-305 and 305-610 mm depths, there were four, three, and two samples at the diameter, half diameter, and center, respectively. Comparison of outside soil properties were made separately for the NR versus NR+SIM stockpiles; combined data for all four stockpiles were also presented. The temporal effect of leaching was determined by comparing the November 2004 data with the April 2005 data. Sampling at three locations beneath the stockpile provided information on leaching as affected by the sampling location beneath the stockpiles.

RESULTS AND DISCUSSION

In this section, first, the impacts of turkey litter stockpiling on temperature and moisture contents in the stockpile and in the soil beneath the stockpile are discussed. Next, the impact of stockpiling on transformations of constituents within the stockpile is examined. Thereafter, leaching of litter constituents into the soil is examined. Finally, the correlation between Mehlich 3 P, Cu, Mn, and Zn and total concentrations are presented.

TEMPERATURE AND MOISTURE CONDITIONS IN THE STOCKPILES AND SOIL

Transformations of metal and nutrient species within the stockpiles are mostly biotic processes that are affected by environmental factors such as temperature and moisture content. Further, these soil factors will also affect the transformation and mobility of dissolved constituents in the soil. Precipitation and temperature (air, stockpile, and soil) during summer stockpiling are presented in Figure 6.

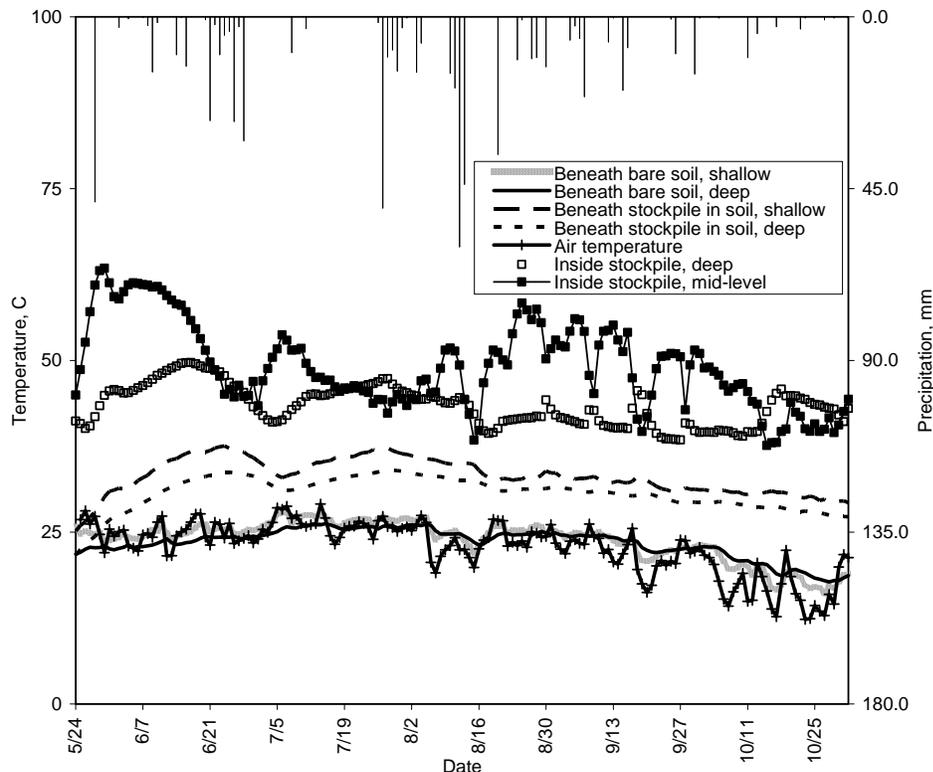


Figure 6. Total daily precipitation (including 48.8 mm of simulated rainfall on 28 July 2004) and average daily temperatures in the air, inside stockpiles 2 and 3 [deep (0.25 m above soil surface) and mid-level (0.76 m above soil surface)], beneath the stockpiles [deep (0.61 m below soil surface) and shallow (0.15 m below soil surface)], and away from stockpiles and in the soil [deep (0.61 m below soil surface) and shallow (0.15 m below soil surface)] during summer stockpiling. Inside stockpile temperatures are based on daily mean of stockpiles 2 and 3; however, the deep value is based on stockpile 2 only after 3 August and the shallow value is based on stockpile 2 after 9 October 2004. Both beneath stockpile temperature values are based on daily mean of stockpiles 2 and 3. All daily values are mean of 24 hourly values.

Temperatures inside the stockpile were higher than the ambient temperature (Fig. 6). Temperatures inside the stockpiles 0.25 m and 0.76 m above the soil were higher than the ambient temperature (22.8°C) by an average of 20.6 and 24.5°C, respectively. Temperature fluctuations inside the stockpile were likely affected by precipitation (heating/cooling and changed microbial activity), air temperature, and microbial

activity. There was some cooling within the stockpiles probably due to large precipitation events (Fig. 6). Temperatures inside the stockpile did not change monotonically with the ambient temperature changes (Fig. 6) probably because temperature in the stockpile was also a function of microbial activity. However, microbial activity is a complex function of temperature, moisture content, DOC, and other factors. Rapid increase followed by decline in temperature in the stockpiles at mid-level during the first month (Fig. 6) may have been due to shrinking of the pile resulting in greater cooling near the surface as well as precipitation. This study provided evidence that temperatures inside the stockpile were likely favorable for increased microbial activity; this could expedite the conversion of nutrient and metal species to more mobile and perhaps, more toxic species.

As expected, soil temperatures outside the stockpiles at 0.15 and 0.61 m mimicked air temperature quite closely (Fig. 6) with the shallow location showing greater fluctuations. On average, soil temperatures outside the stockpiles at 0.15 and 0.61 m depths were 1.1 and 0.6°C higher than the air temperature. Soil temperatures beneath the stockpiles at 0.15 and 0.61 m depths were on average higher than the air temperature by 10.4 and 7.9°C, respectively, and mimicked the temperature inside the stockpile at the deep location during the first three months (Fig. 6). Higher temperatures in the soil beneath the stockpiles would likely contribute to greater microbial activity as well as mobility of the pollutants.

Moisture content values within the stockpiles are shown in Figure 7. Due to malfunctioning of the GMS installed at 0.25 m above the soil surface within stockpile 2, data were unavailable for that stockpile at that depth. Since the moisture characteristic curve for turkey litter (Fig. 3) utilized the power equation and the GMS is not sensitive at very low tension values, low positive or negative (an electrical artifact) were converted to 12 cbars, the lowest tension value that was used in developing the curve. Hence, two of the sensors in Figure 6 appear to show constant moisture content values when in fact, the tension readings varied with time. The deep GMS was less sensitive to precipitation than the mid-level GMS (Fig. 7). The core of stockpile 3 remained wet for ~1.5 months even though the surface layer (as indicated by the mid-level GMS) showed considerable fluctuation in moisture content (Fig. 7). It is unclear why moisture content in the surface layer of stockpile 2 (no simulated rainfall) did not fluctuate.

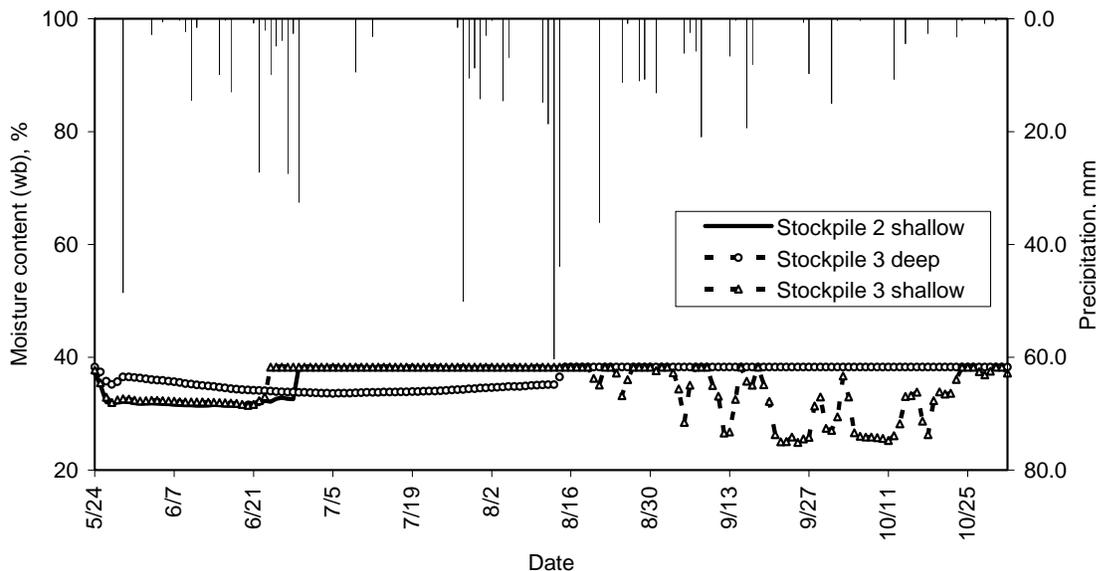


Figure 7. Total daily precipitation (including 48.8 mm of simulated rainfall on 28 July) and moisture content values in stockpiles 2 and 3 during May through October 2004. The shallow GMS was 0.76 m above the soil while the deep GMS was 0.25 m above the soil surface inside the stockpiles. All daily values are mean of 24 hourly values.

Soil moisture tension values measured in the soil beneath and beyond the stockpiles are shown in Figure 8. Except for a brief period in the beginning, the shallow sensor indicated saturated moisture conditions throughout; the deeper sensor, while showing some fluctuations, also remained quite moist (Fig. 8). By comparison, the soil moisture tension values in bare soil showed considerable fluctuations and were much drier than the sensors under the stockpiles (Fig. 8). Based on observations made while applying simulated rainfall and dismantling the stockpiles, it seemed likely that the stockpiles absorbed water (like a sponge); hence, as the core of the stockpile became saturated, the water containing dissolved solids leached into the soil below. Hence, the commonly held belief that a litter stockpile will shed water during rainfall events may not be true except when the stockpile, including the surface is thoroughly saturated.

High moisture conditions inside the stockpile may favor reducing conditions that are conducive to formation of inorganic As(III) and toxic arsanoalkyl acids containing methylated As(III) (Fig. 1). Further, the reducing conditions may also enhance the solubility of metals such as Fe by reducing the insoluble Fe^{3+} to soluble Fe^{2+} . While leaching of reduced metal cations can impact groundwater quality, loss of Fe^{3+} (due to conversion to more soluble Fe^{2+}) can increase the mobility of As(III) since As(III) has an affinity for Fe^{3+} (hydr)oxides (Fendorf et al. 2004). Higher temperatures inside the stockpiles (Fig. 6) can increase reaction rates and also increase solubility of constituents. Similarly, warmer and wetter soils can enhance reaction rates and mobility of constituents, and increase leaching losses.

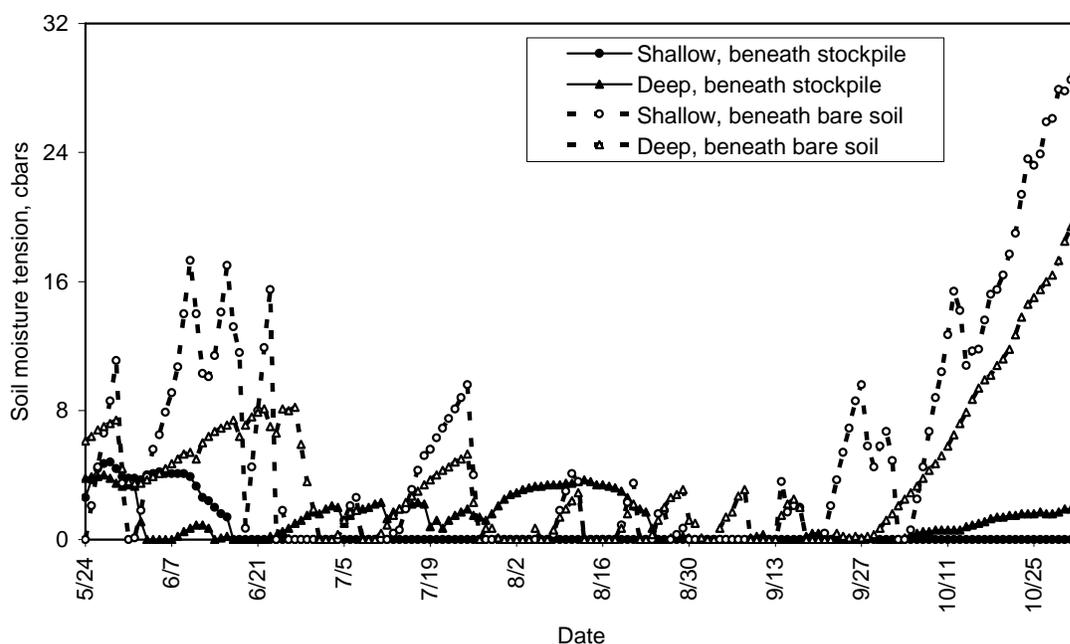


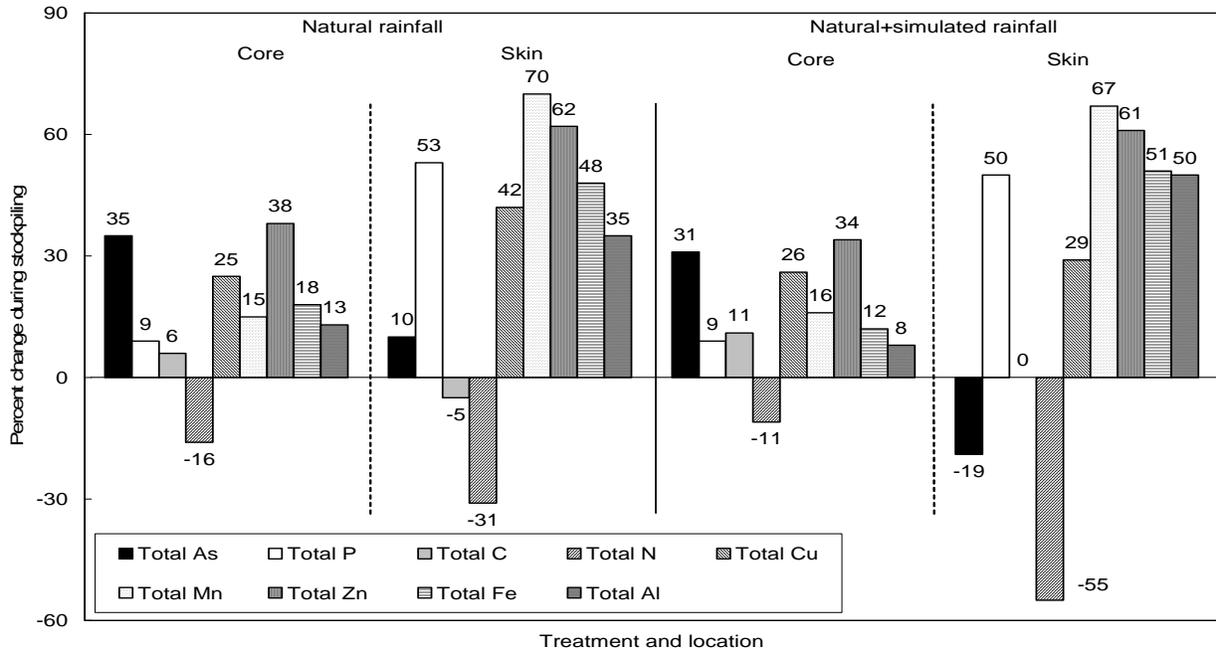
Figure 8. Soil moisture tension values beneath stockpiles 2 and 3 and beneath bare soil (single location) during summer stockpiling. The shallow GMS was 0.15 m below the soil while the deep GMS was 0.61 m below the soil. All daily values are mean of 24 hourly values.

TRANSFORMATIONS WITHIN STOCKPILES

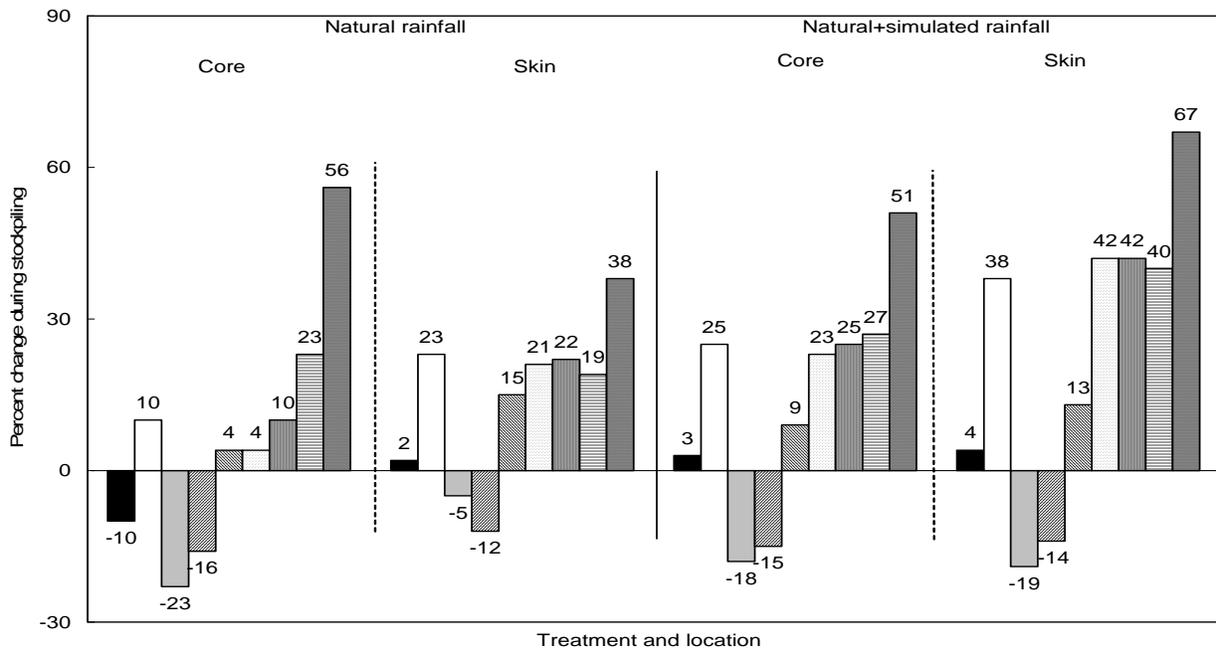
Changes in Concentrations of Total Nutrient, Metal/Metalloid Concentrations

Changes in total metal/metalloid and nutrient concentrations after stockpiling during the summer and winter periods are shown in Figure 9 ((a) and (b)). Overall, for the summer and winter stockpiles, concentrations of the constituents (except total N, C, and As) increased compared with initial litter concentrations (Table 3; Appendix A). Generally, increase in constituent (except total N, C, and As)

concentrations during both periods were greater in the skin samples than the core samples. The higher concentrations in the skin are likely due to greater mass losses on the surface of the stockpiles due to respiration (C) and gaseous N losses. Loss of the two most abundant species C (only winter) and N through aerial emissions (respiration and volatilization) and leaching likely resulted in the increase in concentrations of most of the conservative (non-reactive) constituents.



(a)



(b)

Figure 9. Changes in the total constituent concentrations in turkey litter after (a) summer and (b) winter stockpiling.

Decrease in total C concentrations in the winter stockpiles (Figure 9(b)) was expected due to loss of CO₂ through microbial respiration. Also expected was the greater C loss in the skin due to greater microbial activity resulting in increased respiration and hence, greater C consumption versus the core. However, the overall increase in C concentration during summer stockpiling was unexpected. While the 6% increase in total C in the core (vs. 5% decrease in the skin) in the NR stockpiles may partly be attributed to leaching of soluble C from the skin, in the NR+SIM stockpiles, 11% increase in total C in the core (vs. no increase in the skin) was difficult to explain (Figure 9(a)). Evidence of DOC leaching into the soil below (discussed later) further indicated that the fate of C in litter stockpiles was not clearly understood.

Percent change in concentration for total As showed no clear trends with regard to sampling location (core or skins) or treatment (NR and NR+SIM). Decreases in total As concentrations were observed only for skin samples in the summer stockpiles for the NR+SIM rainfall treatment (Figure 9(a); -21%) and for core samples in the winter stockpiles of the NR treatment (Figure 9(b); -10%). Arsenic was the only metal/metalloid that showed a decrease in concentration after stockpiling. Decrease in total As was likely due to leaching of WSE-As forms (see Speciation of Water-soluble Arsenic).

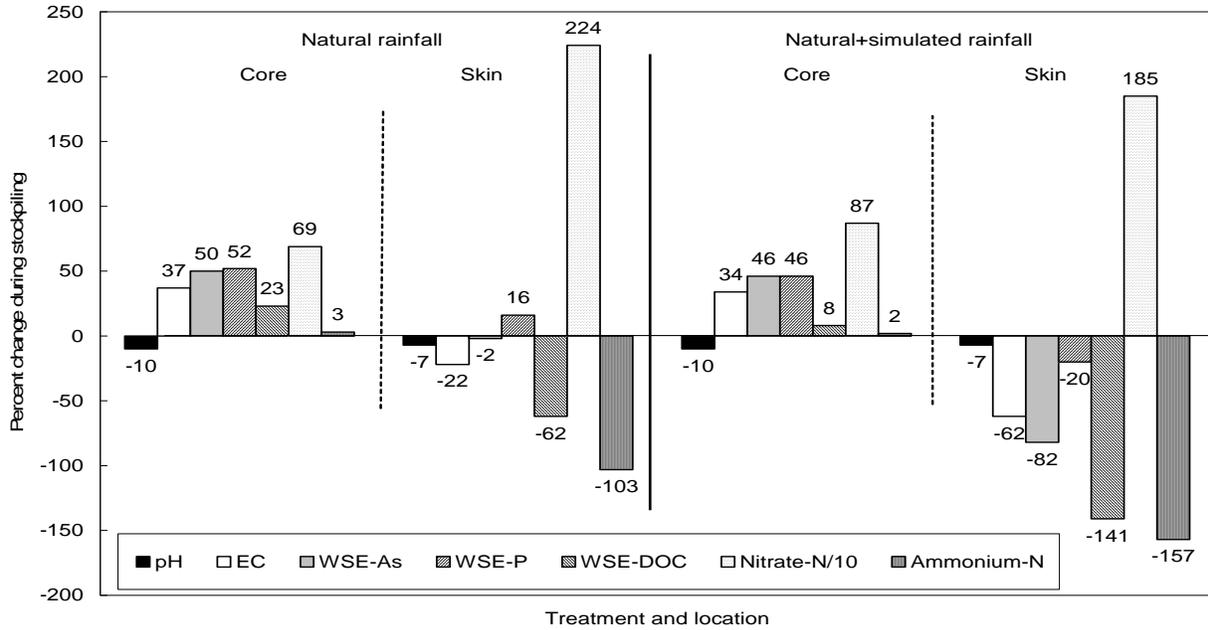
As expected, losses in total N concentration occurred in both the core and skin samples of the summer and winter stockpiles (Fig. 9). These losses were likely due to gaseous N losses, as well as leaching losses into the core of the stockpile and also the soil below. Greater N losses in the skin samples of the summer stockpiles (Fig. 9(a)) (vs. the winter stockpile, Fig. 9(b)) may have been due to greater gaseous N losses (primarily, ammonia volatilization) as well as nitrification (resulting in NO₃⁻ leaching) as the summer stockpile had ~50% more NH₄⁺-N than the winter stockpile (Table 3). Further, warmer conditions in summer (vs. winter) likely increased mineralization, volatilization, and denitrification, increasing total N losses.

Increases in percent total P concentrations were greater in the skin samples for both the summer and winter stockpiles (Fig. 9). Phosphorus is a conservative constituent and its concentrations were very high in the litter prior to stockpiling (Table 3); hence, mass losses of C (only winter) and N increased total P concentrations during stockpiling, particularly in the skin (vs. core) where C and N losses were higher.

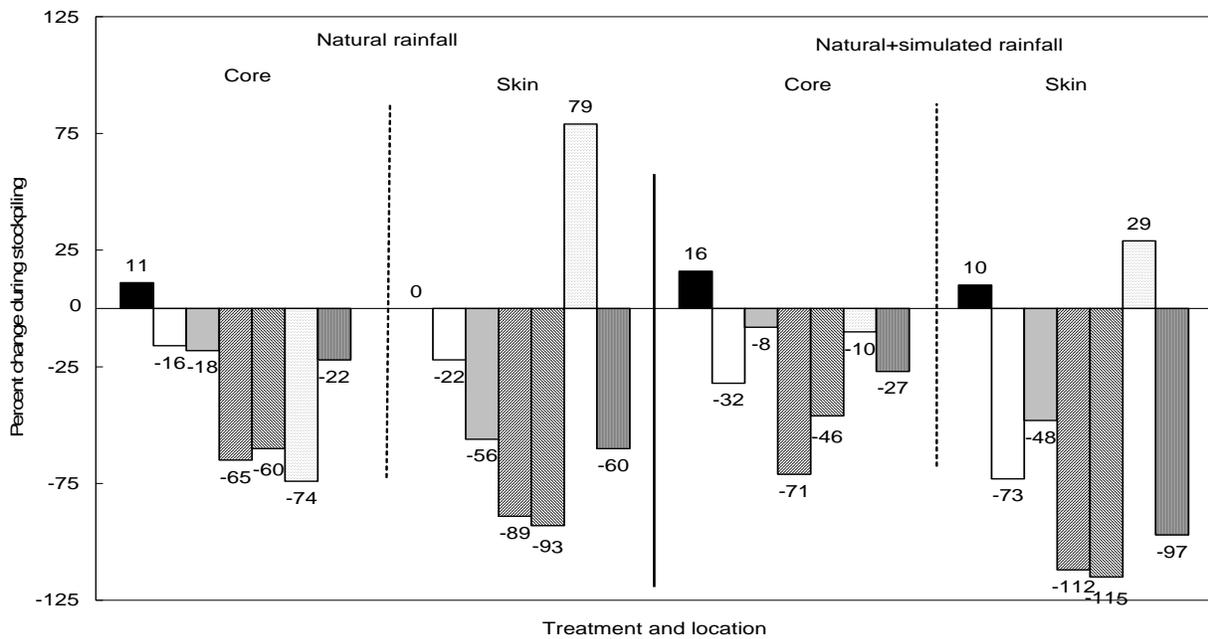
Concentrations of total Cu, Mn, Zn, Fe, and Al increased due to stockpiling, probably due to mass losses of C (only winter) and N. Generally, greater increase in total concentrations of these metals in the skin samples (vs. the core samples) was likely due to greater C and N losses in the aerobic skin of the stockpiles. However, the possibility of leaching of some of the metals from the stockpile cores into the soil below cannot be ruled out. For example, while some Fe could precipitate with other metals as oxyhydroxides in the aerobic skin layer, Fe³⁺ in the anaerobic core can be reduced to the relatively mobile Fe²⁺ under high pH conditions in the litter (Tables A2 and A3; Appendix A).

Changes in pH, EC, and Water-soluble Metal and Nutrient Concentrations

From a pollution perspective, it may be more insightful to look at changes in water soluble extract (WSE) concentrations than total concentrations. Figure 10 ((a) and (b)) shows the percent change in pH, EC, WSE-As, WSE-P, DOC, NO₃⁻-N and NH₄⁺-N, for core and skin samples with treatments of NR and NR+SIM, after the summer and winter stockpiling periods. Reduction in pH in the core and skin samples in the summer stockpiles were likely due to heavy nitrification (discussed later) which is an acid forming reaction. However, during winter stockpiling, pH increased or stayed the same; this could be due to lower nitrification (partly due to lower NH₄⁺-N concentration, Table 3) and also due to more reducing conditions. While there was more rainfall during the summer stockpiling period (Fig. 5), the initial moisture content was higher in the winter stockpiles (Table 3); such reducing conditions may have resulted in the consumption of protons by metal species undergoing reduction.



(a)



(b)

Figure 10. Changes in the properties and water-soluble constituent concentrations in turkey litter after (a) summer and (b) winter.

During summer stockpiling, decrease in EC in the skin and increase in EC in the core samples (Fig. 10(a)) was likely due to leaching of soluble salts from the skin to the core. The EC in both the skin and core samples in the winter stockpiles decreased (Fig. 10(b)). While reduction in EC in the skin was due to leaching into the core, reduction in EC in core samples may have been due to leaching into the soil below. This is supported by water soluble constituent concentrations in the surface soil (0-25 mm), particularly at the half diameter as shown in Appendix B (Tables B1 and B4).

In the summer stockpiles, WSE-As concentration decreased (only slightly in NR) in the skin and increased substantially in the core (Fig. 10(a)) indicating that there was inward movement of WSE-As within the stockpiles. However, in the winter stockpiles, decrease in WSE-As concentrations in both the skin and core (Fig. 10(b)) was likely due to leaching into the soil as was indicated by 5-6 times higher WSE-As concentrations in the surface soil (0-25 mm) at the half diameter (vs. the summer stockpiles) (Table B4; Appendix B). While the drier weather during winter stockpiling was less conducive to WSE-As leaching than the summer stockpiles, wetter initial litter (Table 3) and higher As (both total and WSE) concentrations in the winter stockpiles likely caused higher WSE-As leaching into the soil.

In the summer stockpiles, compared with initial concentrations, increased WSE-P levels in the core (Fig. 10(a)) was likely due to leaching from the skin layer. While increase in WSE-P in the skin layer in the NR stockpiles may have been due to mass losses of N, its decrease in the skin layer of the NR+SIM may have been due to wetter conditions increasing both mineralization of organic P and leaching of the WSE-P thus formed, into the core. Compared with initial values, WSE-P concentrations in the winter stockpiles decreased in both treatments (NR, NR+SIM) and both locations (skin and core) (Fig. 10(b)). The larger decrease in the NR+SIM stockpiles was probably because more water was available for leaching the WSE-P from the skin into the core and then from the core into the soil. While initial total-P values were comparable in between the summer and winter turkey litter batches, the winter batch had >2 times as much WSE-P vs. the summer batch (Table 3). Hence, despite cooler and lower rainfall (Fig. 5) conditions, there was more P available in the winter batch available to be leached through the stockpile and into the soil as was indicated by the higher WSE-P concentrations in the soil beneath winter vs. the summer stockpiles (Table B3 - Appendix B).

Compared with initial DOC concentrations, decrease in concentrations in the skin layer in both the summer and winter stockpiles (Fig. 10) were likely due to leaching from the skin into the core. In all summer stockpiles, DOC concentrations increased in the core with the smaller increase in the NR+SIM (vs. NR) indicating that DOC leaching into the soil below increased with depth of precipitation. Reduced DOC concentrations in both the skin and core layers in both treatments in the winter stockpiles indicated that DOC moved through the stockpile and then into the soil below. The soil data provided evidence of DOC leaching from the stockpiles in both seasons with heavier leaching in the NR+SIM vs. the NR stockpiles (Tables B3-B5 - Appendix B).

Compared with initial concentrations, decreasing NH_4^+ -N and increasing NO_3^- -N concentrations in the skin layer in both seasons were likely due to aerobic conditions resulting in increased nitrification (Figures 10). Skin samples of summer stockpiles showed greater nitrification than the winter stockpiles due to warmer and wetter (Fig. 5; Tables A2 and A3 - Appendix A) conditions. Decrease in NO_3^- -N concentrations in winter in the core samples was unexpected. Given that weather during winter stockpiling was drier than summer stockpiling (Fig. 5) and the summer stockpiles were wetter (Tables A2 and A3 - Appendix A), in the winter stockpiles, NO_3^- -N leaching and denitrification should have been lower, which should have increased NO_3^- -N concentrations in the core. Except at the edges of the stockpiles (due to aerobic conditions), possibly, substantial denitrification in the winter stockpile core likely reduced NO_3^- -N concentrations. High soil NO_3^- -N concentrations at the outer diameter of stockpiles (vs. half diameter and center) (Tables B3-B5 - Appendix B) provided indirect evidence of lower denitrification closer to the edges (vs. the center) of the winter stockpiles.

Change in turkey litter constituent concentrations during stockpiling, particularly the water soluble species indicated movement of As (and other constituents) from the skin of the stockpiles towards the core, and then, into the soil below. Since the toxicity and mobility of As will depend on the chemical specie [As(V) vs. As(III)] present in the turkey litter, aqueous and solid-phase speciation analyses were performed to determine the predominant chemical species.

Speciation of Water-soluble Arsenic

The much higher recovery (8-12 times vs. initial values) of roxarsone at the end of the summer stockpiling in both the core and skin samples was unexpected (Table 4). Higher roxarsone levels in the core (vs. skin samples) were probably because of aerobic conditions in the skin layer resulting in greater degradation. As expected, roxarsone was not detected at the end of winter stockpiling (Table 4).

Table 4. Arsenic speciation data^[a] in the turkey litter^[b] prior to and at the end of stockpiling.

As specie, mg/kg	Summer stockpiling					Winter stockpiling				
	Initial conc. ^[c]	Final concentrations ^[d]				Initial conc. ^[c]	Final concentrations ^[d]			
		NR		NR+SIM			NR		NR+SIM	
		Core	Skin	Core	Skin		Core	Skin	Core	Skin
Roxarsone	0.11 ± 0.08	1.0 ± 0.2	0.93 ± 0.06	1.3 ± 0.3	1.02 ± 0.07	0.44 ± 0.33	ND ^[e]	ND	ND	ND
As(V)	1.2 ± 0.1	2.8 ± 0.7	1.02 ± 0.01	2.70 ± 0.04	0.8 ± 0.2	4.1 ± 0.3	6 ± 1	5.29 ± 0.05	7.7 ± 0.3	4.6 ± 0.4
MMA(V) ^[f]	0.12 ± 0.05	0.30 ± 0.03	0.08 ± 0.1	0.27 ± 0.03	ND	0.42 ± 0.03	0.47 ± 0.06	0.3 ± 0	0.58 ± 0.05	0.28 ± 0.04
DMA(V) ^[g]	1.10 ± 0.20	1.05 ± 0.09	1.00 ± 0.04	0.97 ± 0.02	0.50 ± 0.30	1.02 ± 0.03	2.4 ± 0.5	1.97 ± 0.02	2.30 ± 0.10	2.20 ± 0.20
p-ASA ^[h]	0.25 ± 0.03	0.06 ± 0.09	ND	0.07 ± 0.1	ND	0.3 ± 0.2	0.26 ± 0.01	0.2 ± 0	0.6 ± 0.5	0.2 ± 0.1
Identified WSE- As species	2.78	5.21	3.03	5.31	2.32	6.28	9.13	7.76	11.18	7.28
Total WSE-As	4.4 ± 0.6	7 ± 1	3.6 ± 0.7	6.4 ± 0.3	1.5 ± 0.6	13.2 ± 0.2	14 ± 3	13 ± 2	16 ± 3	13 ± 1
Species recovery (%)	63	74	84	83	154 ^[i]	48	65	60	70	56

^[a] Arsenic species measured by ion chromatography-inductively coupled plasma mass spectrometry (IC-ICP-MS) at Savannah River Ecology Laboratory, Aiken, SC (Jackson and Bertsch, 2001).

^[b] Only <2 mm fraction

^[c] Mean and standard deviation of four samples

^[d] Mean and standard deviation of two analytical replicates

^[e] Not detected

^[f] Monomethylarsonic acid

^[g] Dimethylarsinic acid

^[h] para-arsanilic acid

^[i] The major source of error was correctly estimating the area under the IC peaks for individual WSE-As species when the peak baselines were not flat or when peaks overlapped (B. Jackson, Dartmouth College, pers. com. 2006).

Based on WSE-As data, As(V) accounted for 27 ± 3% of the total WSE-As in the initial summer and winter stockpile litters and was the major degradation product in all samples which was consistent with the findings of Jackson and Miller (1999). Monomethylarsonic acid (MMA(V)), which is the precursor of DMA(V) (Fig. 1) accounted for ≤ 4% of the total WSE-As for all litter samples (before and after stockpiling) (Table 4). Based on the relative masses of the skin and the core samples, MMA(V) concentrations increased during stockpiling. The second most abundant constituent was DMA(V) which ranged from 8 to 33% of the total WSE-As species. While DMA(V) concentrations declined slightly during summer stockpiling, it increased substantially during winter stockpiling. Another coccidiostat, p-ASA was detected in most of the litter samples ranging from 0.06 to 0.6 mg/kg litter (Table 4); it was unclear if p-ASA was formed as a result of roxarsone degradation. As expected, all WSE-As species were present in higher concentrations in the core (vs. skin) probably due to leaching (Table 4).

Compared to total WSE-As concentration, the sum of the five identified water soluble As species ranged from 48 to 154%. Both, Jackson et al. (2003) and Garbarino et al. (2003) reported incomplete recoveries ranging from 29-69% and 40-90% of total WSE-As, respectively. Jackson et al. (2003) hypothesized that the unknown As species were likely aromatic in character, as they had high affinity for a styrene-divinylbenzene exchange column. The numerical increases in As(V) and DMA(V) concentrations during stockpiling (as opposed to percentage increase) were greater in the winter stockpiles versus the summer stockpiles. Given that roxarsone concentrations in the initial winter litter samples were quite low, increase in concentrations of As(V) and DMA(V) probably resulted from the degradation of other As species that were not identified. Absence of As(III) species such as arsenite and MMA(III) which are precursors of MMA(V) and DMA(V) was surprising; however, use of aerobic extraction procedure could have resulted in oxidation of As(III) species into As(V) species.

In this study, roxarsone nearly degraded completely during winter stockpiling; however, for reasons that were unclear, roxarsone concentrations increased during summer stockpiling. Since poultry litter may be stockpiled for months, depending on field and weather conditions, there is potential for some WSE-As species to leach into soil beneath the stockpiled litter. Stockpiling, particularly, during winter and wet months could increase anaerobic zones within and beneath the litter stockpiles. As a result, As(V) species could be reduced to the more toxic and mobile As(III) species.

Solid-Phase Arsenic Speciation in Turkey Litter Samples

Arsenic K-XANES spectra of 19 turkey litter samples are shown in Figures 11 (NR, stockpiles 1 and 2) and 12 (NR+SIM, stockpiles 3 and 4). Overall, spectra of these samples indicated that As was predominantly in the +5 oxidation state. However, two spectra (stockpile 3, summer – core and skin) show a significant proportion of As as As(III) (Fig. 12); the intensity of the As(V) peak at 8 eV (relative energy), is diminished and a shoulder at 4 eV is apparent.

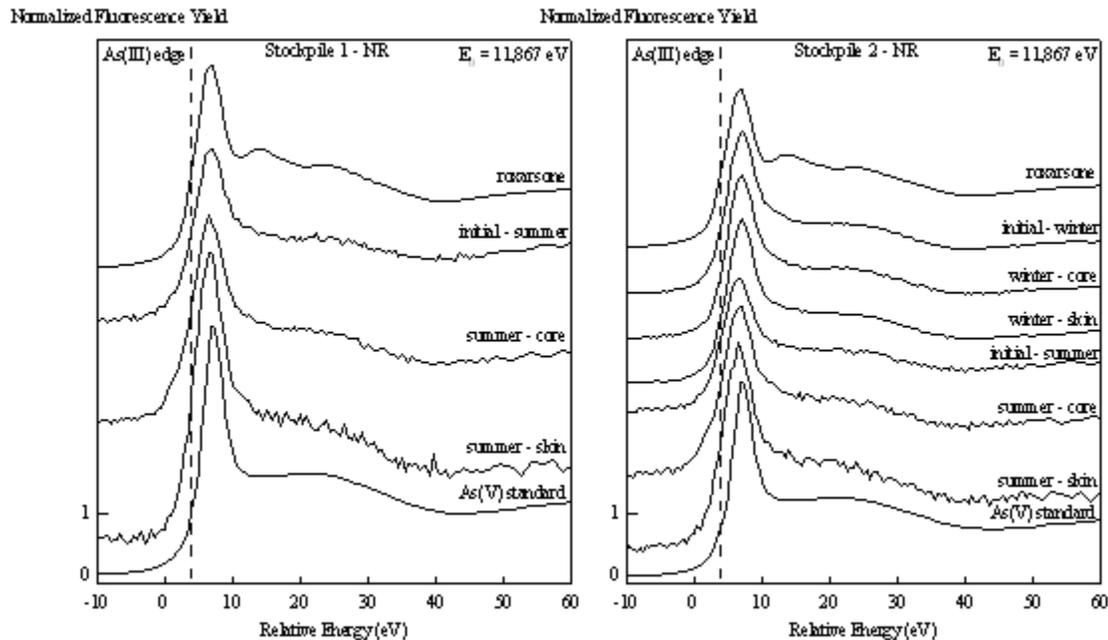


Figure 11. Stacked As K-XANES spectra for initial summer and winter TL samples, and TL core and skin samples taken after summer and winter stockpiling (only NR). Spectra of As(V) mineral standard and the As(III) edge position are included for oxidation state reference.

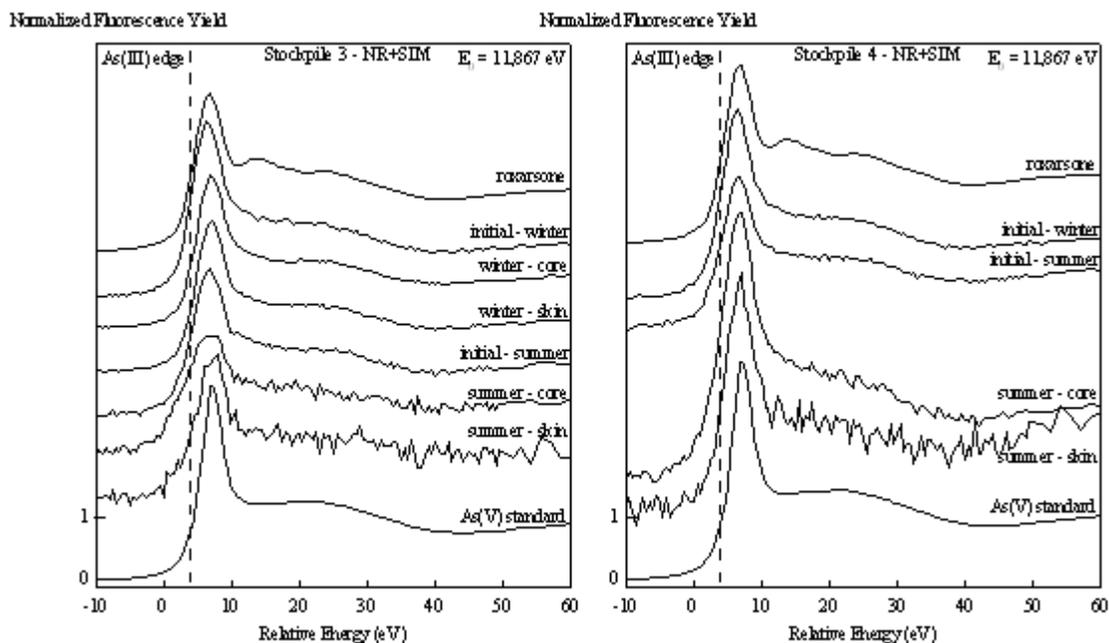


Figure 12. Stacked As K-XANES spectra for initial summer and winter TL samples, and TL core and skin samples taken after summer and winter of stockpiling (only NR+SIM). Spectra of As(V) mineral standard and the As(III) edge position are included for oxidation state reference.

Linear combination fitting (LCF) was performed using spectra of standards of As(V) and As(III) oxide, As(III)- and As(V)- adsorbed to boehmite (non-crystalline aluminum hydroxide), As(V) adsorbed to ferrihydrite (poorly-crystalline iron oxide), calcium arsenate (see Arai et al. 2003), p-arsanilic acid, roxarsone, and roxarsone-N (roxarsone with a reduced nitro group; 3-amino-4-hydroxyphenyl-arsonic acid) (Fig. 13). The fitting results are considered qualitative due to absence of spectra for DMA(V) (a major component of the turkey litter), and low As concentrations resulted in spectral noise and sloping baselines for some samples (e.g, stockpile 4 - summer core and skin, Fig. 12). Also, the spectrum for the As(III)-boehmite standard (Fig. 13) suggests that As(III) in this sample was partially oxidized to As(V), as evidenced by the development of a shoulder around 8 eV. Linear combination fitting was performed on all turkey litter samples (Figs. 11 and 12), except for the initial summer, and summer core and skin samples of stockpile 4 (noisy spectra).

The best linear combination fits, determined by χ^2 (goodness of fit), indicated that As(V) standards were most representative of components of the litter samples. Typically, the best fit components were As(V) (30-40% of total As) and roxarsone-N (50-70% of total As). The second best fits included As(V) and roxarsone. The summer core sample for stockpile 3 showed the most As(III) character, with ~41% As_2O_3 [As(III)], 19% As(III)-boehmite, ~23% calcium arsenate [As(V)], and ~17% As_2O_5 [As(V)] ($\chi^2 = 1.33$). The proportions of As(III)-boehmite in the fit is probably an overestimation due to partial oxidation of this standard (discussed above). Overall, best fits with predominantly As(V) character agree with the speciation data of the water-soluble extracts. Furthermore, best fits with roxarsone-N as one of the major components support the hypothesis that the non-recovered species from the aqueous-phase speciation analyses is a degradation product of roxarsone having aromatic ring character (discussed above) (Jackson et al. 2003).

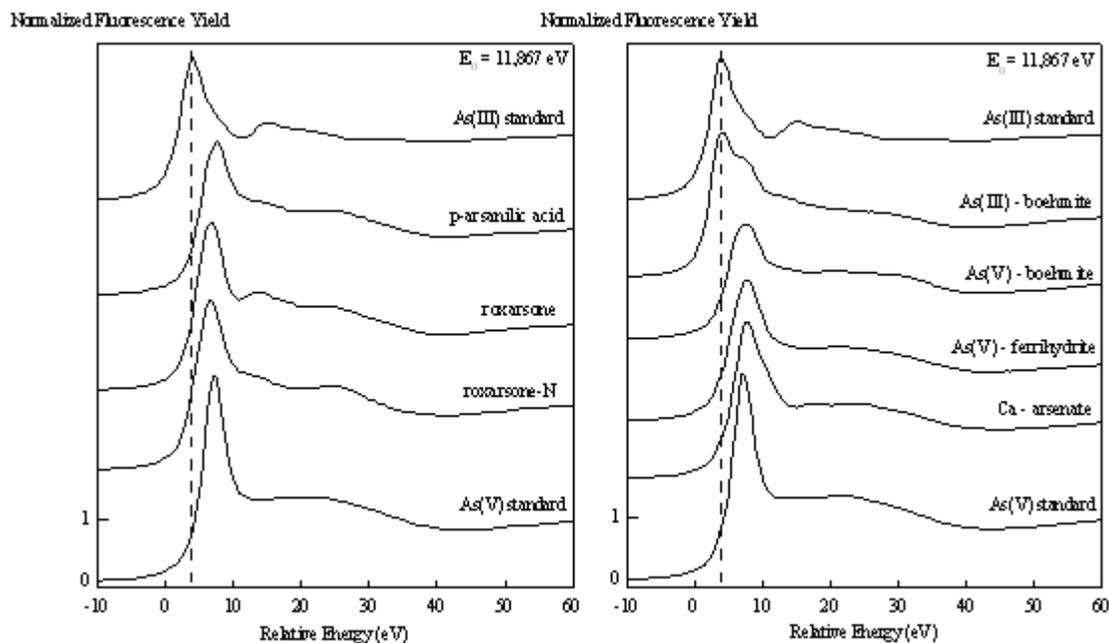


Figure 13. Stacked As K-XANES spectra for organo-As, inorganic As, and As adsorbed to mineral standards used to determine As oxidation states in TL and soil samples. Spectra of As(V) mineral standard and the As(III) edge position are included for oxidation state reference.

Summary: Transformations within Stockpiles

Except for total concentrations of C, N, and As, total concentrations of all other species increased during stockpiling, both during winter and summer; this may be attributed to large losses of C (only winter) and N through aerial emissions and leaching into the soil. At the end of stockpiling, concentrations (except total C, N, and As) were generally higher in the skin samples (vs. core). During summer stockpiling, as expected, due to leaching, concentrations of all water soluble constituents (except NO_3^- -N) decreased in the skin and increased in the core samples. However, during winter stockpiling, while the trend in the skin was similar to summer, concentrations of all water soluble constituents decreased in the core as well, indicating that the constituents may have leached into the soil below. Compared with initial concentrations, lower WSE-As concentrations in both skin and core samples in the winter stockpiles indicated leaching of WSE-As into the soil below.

Compared with initial concentrations, data from the speciation of water-soluble As indicated increased roxarsone concentrations in both the skin and core samples in the summer stockpiles; however, as expected, in the winter stockpiles, all the roxarsone had been degraded. In both the summer and winter stockpiles, the most abundant WSE-As specie was As(V). Generally, lower WSE-As species in the skin (vs. the core samples) was due to leaching from the skin into the core. Consistent with published studies, only 48 to 84% of the total WSE-As species were identified (except 154% in one case, Table 4). Solid phase As speciation using XANES corroborated the speciation of water-soluble As results indicating that As in the turkey litter was mainly in the As(V) form.

LEACHING FROM STOCKPILES

pH

Comparison of pH values in the soil beneath stockpiles versus outside the stockpile footprints provided information on the leaching of acidic or basic stockpile constituents into the soil. Change in pH in the

soil can affect transformation and hence, mobility and toxicity of constituents. Stockpiling of turkey litter resulted in elevated pH through out the sampling depth (Fig. 14).

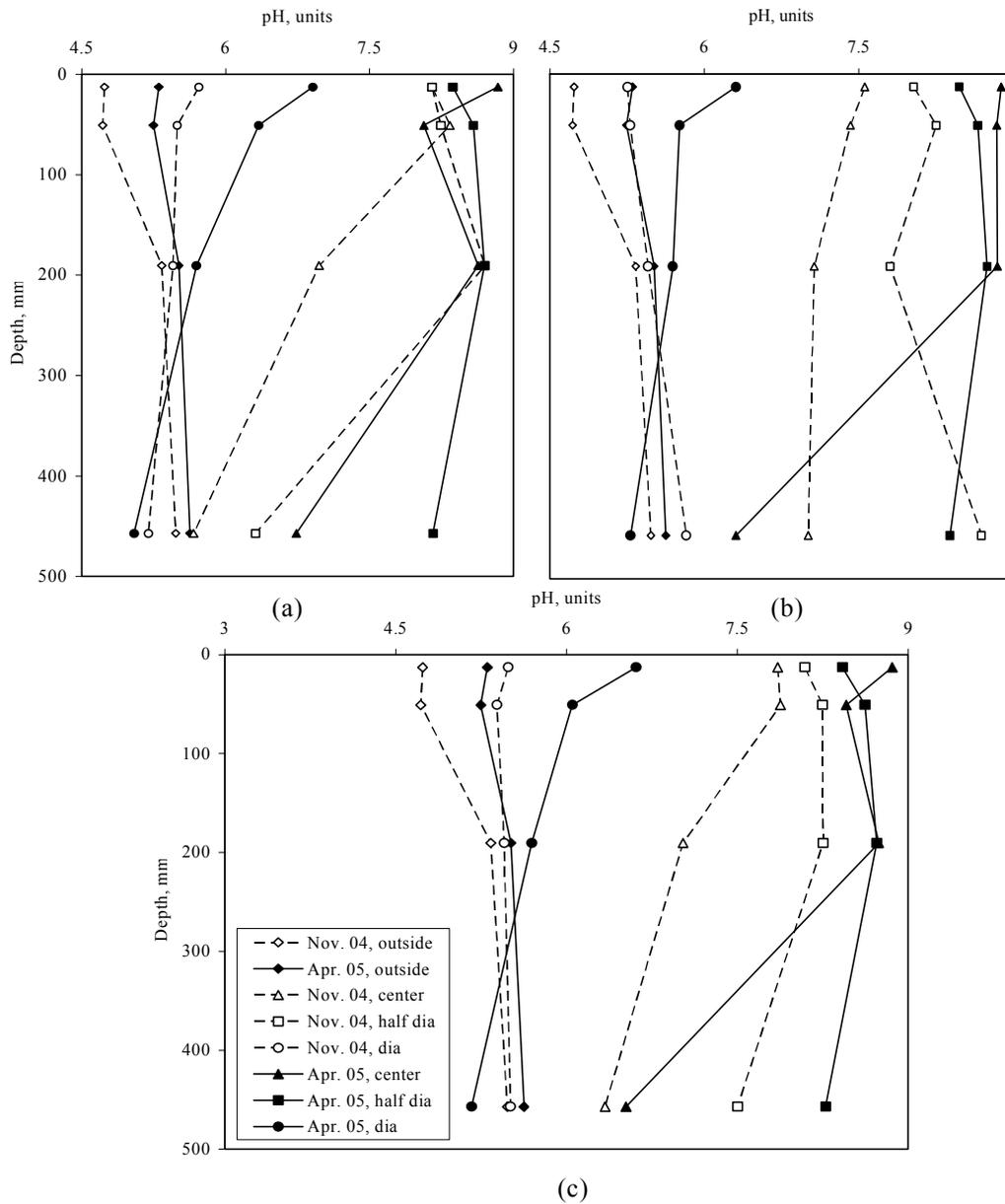


Figure 14. pH values in the soil beneath and outside the TL stockpile footprints based on average of (a) stockpiles 1 and 2 (NR), (b) stockpiles 3 and 4 (NR+SIM), and (c) all four stockpiles.

Compared with soil sampling locations beyond the stockpile footprints, the greatest increase in pH was observed at the half diameter followed by the center location; increase in pH at the diameter of the stockpile was only slight. It was observed that when rain fell on the stockpile, the top shed the rain and as it flowed downhill, it infiltrated into the stockpile sides; consequently, there was very little runoff from the stockpile edge. So, in the annulus (inner and outer diameters of ~1.5 and ~3 m, respectively) representing the half diameter portion of the stockpile there was likely greater mass of moisture as well as litter (as can be shown by geometry) compared with the center (1.5 m diameter cylinder) and the outer annulus (with inner and outer diameters of ~3 and 4.6 m, respectively). This likely resulted in greater changes in pH at the half diameter than at the center or diameter.

Application of simulated rainfall probably increased pH (vs. only natural rainfall) in the deepest layer (Figs. 14(a) & 14(b)), particularly during summer stockpiling. While greater depths of simulated rainfall (than applied in this study) could have resulted in larger differences between NR and NR+SIM even small depths of simulated rainfall applied after a long dry spell could have caused the stockpiles to absorb water like a sponge resulting in very little additional leaching.

Cumulative increase in pH was also observed as evidenced by greater pH at the end of winter vs. summer stockpiling in the 0-305 mm layer in all three locations (Fig. 14). In the deepest layer, pH was higher in summer than in winter at the center and at the diameter (Fig. 14).

Increased soil pH beneath stockpiled turkey litter in this study is consistent with the results of Gupta and Charles (1999) who reported that repeated poultry litter application resulted in higher pH down to 0.6 m depth compared with fields that received no poultry litter. In addition to lime in poultry diet, Hue (1992) proposed that ligand exchange reactions between anions of organic acids such as urate, phthalate, glycolate, pyruvate, and possibly, oxalate with terminal OH⁻ of Fe and Al oxides resulted in increased pH. Further, reduction of Mn and Fe oxides (mostly goethite) in localized, electron rich environments created by the rapid decomposition of manure also contributed to increased pH (Hue 1992). Additionally, leaching of ammonia, a weak base, from the stockpiles into the soil (discussed later) also likely contributed to increase in pH. Increase in soil pH from the 4.5-5.0 range to the 6-7.5 range results in maximization of relatively available P, mostly as orthophosphates which may not only increase WSE-P leaching but also enhance the mobility of WSE-As.

Electrical conductivity

Change in EC with depth and over time is due to change in concentrations of dissolved ions. Leaching of ions can affect fate and transport of turkey litter constituents. Turkey litter stockpiling resulted in elevated EC throughout the sampling depth (Fig. 15) with EC values beneath the stockpiles even at the deepest sampling depth being much higher than the corresponding locations outside. As expected EC values beneath the stockpiles decreased with increasing depth (Fig. 15).

For both summer and winter stockpiles, compared with outside the stockpile footprints, the greatest increase in EC was observed at half diameter followed by the center; increase in EC at the diameter of the stockpile was only slight. As explained earlier, higher EC values at the half diameter were likely due to greater moisture and salt availability compared with the center or the diameter. Larger difference in EC values between the half diameter and center (at the same depth) in November 2004 (vs. April 2005) was likely due to wetter conditions resulting in greater leaching. Wetter conditions also likely resulted in higher EC values (except at greatest depth) at the half diameter in November 2004 than April 2005 (all three locations) despite shorter interval for leaching. Lower EC values in the two shallow soil samples and higher values in the deeper samples beneath stockpiles 3 and 4 vs. stockpiles 1 and 2 (Figs. 15(a) and 15(b)) may be due to greater moisture availability for leaching that leached salts in the surface layer and deposited them deeper in the soil profile.

Gupta and Charles (1999) reported EC values of 111 to 119 $\mu\text{S}/\text{cm}$ in soils receiving no litter versus 270 to 182 $\mu\text{S}/\text{cm}$ in litter-treated soils, respectively, with increasing depth. In this study, adjusted for background EC and weighted based on depth, EC values in the sampling depth were 2202 and 2066 $\mu\text{S}/\text{cm}$, respectively, in November 2004 and April 2005. Reduced EC values in April 2005 despite greater loading and duration available for leaching could be attributed to immobilization into organic matter, complexation with uncharged aqueous solution, and perhaps, even some leaching into the soil below the 610-mm layer. Even in the deepest soil layer, in April 2005, the EC values under the stockpiles ranged from 120 to 2295 $\mu\text{S}/\text{cm}$ versus 28 $\mu\text{S}/\text{cm}$ beyond the stockpile. While increased EC in poultry

litter treated soils were attributed to leaching of metal cations by Gupta and Charles (1992), organic anions (Hue 1992) and NH_4^+ (discussed later) also likely contributed.

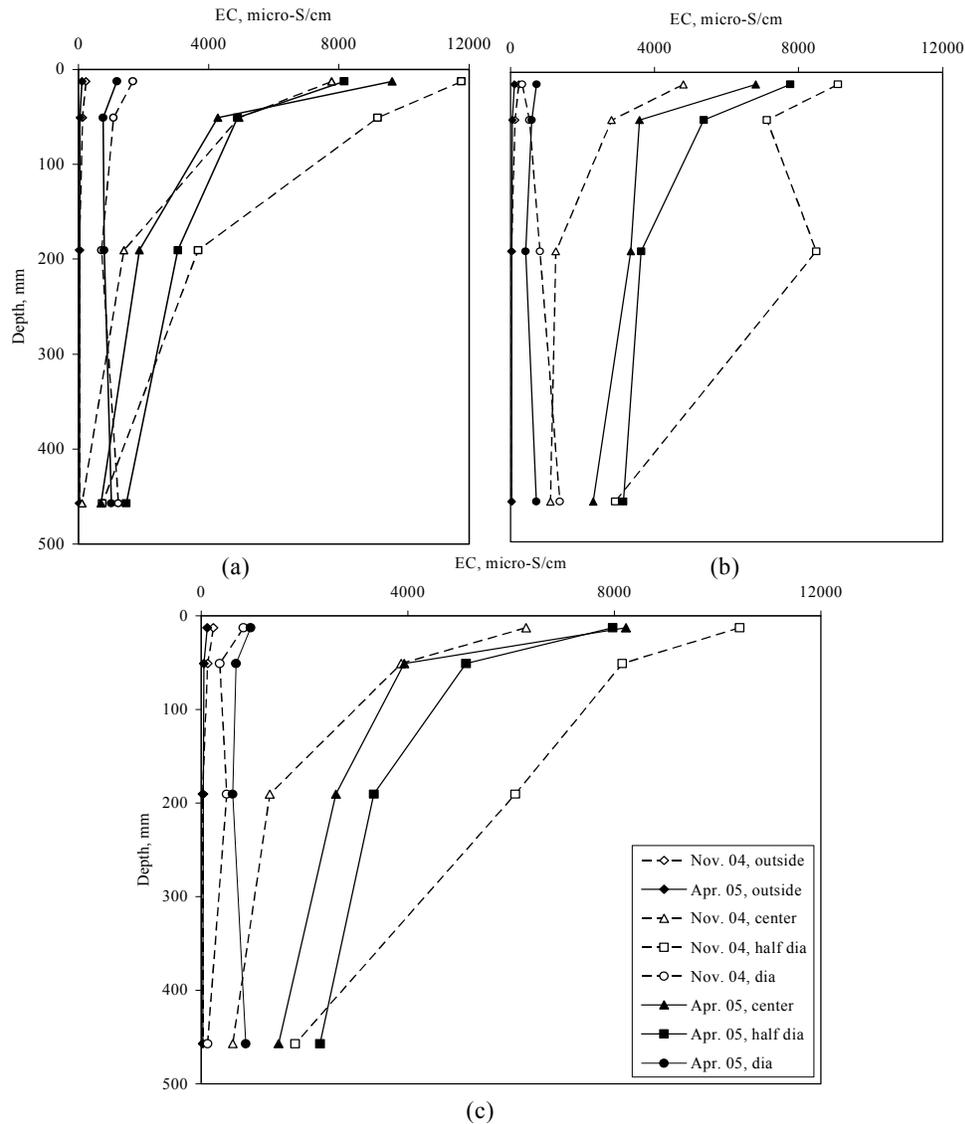


Figure 15. Electrical conductivity values in the soil beneath and outside the TL stockpile footprints based on average of (a) stockpiles 1 and 2 (NR), (b) stockpiles 3 and 4 (NR+SIM), and (c) all four stockpiles.

Carbon

Carbon, specifically, DOC can affect the fate and transport of turkey litter constituents by enhancing transformation rates and reducing sorption onto soil surface complexes. While total C concentrations decreased with increasing depth in the top two soil samples both beneath and beyond the stockpiles, total C concentrations in the bottom two layers were similar (Fig. 16). Lower total C in the surface layer beneath the stockpiles than beyond the stockpile footprints, particularly in November 2004 (Fig. 16), was unexpected. While the soil beyond the stockpile footprints had vegetation, there was no vegetation beneath the stockpiles. Mineralization of vegetation by the microbes in the N-rich litter may have resulted in formation of soluble C and N species that leached deeper into the soil over time.

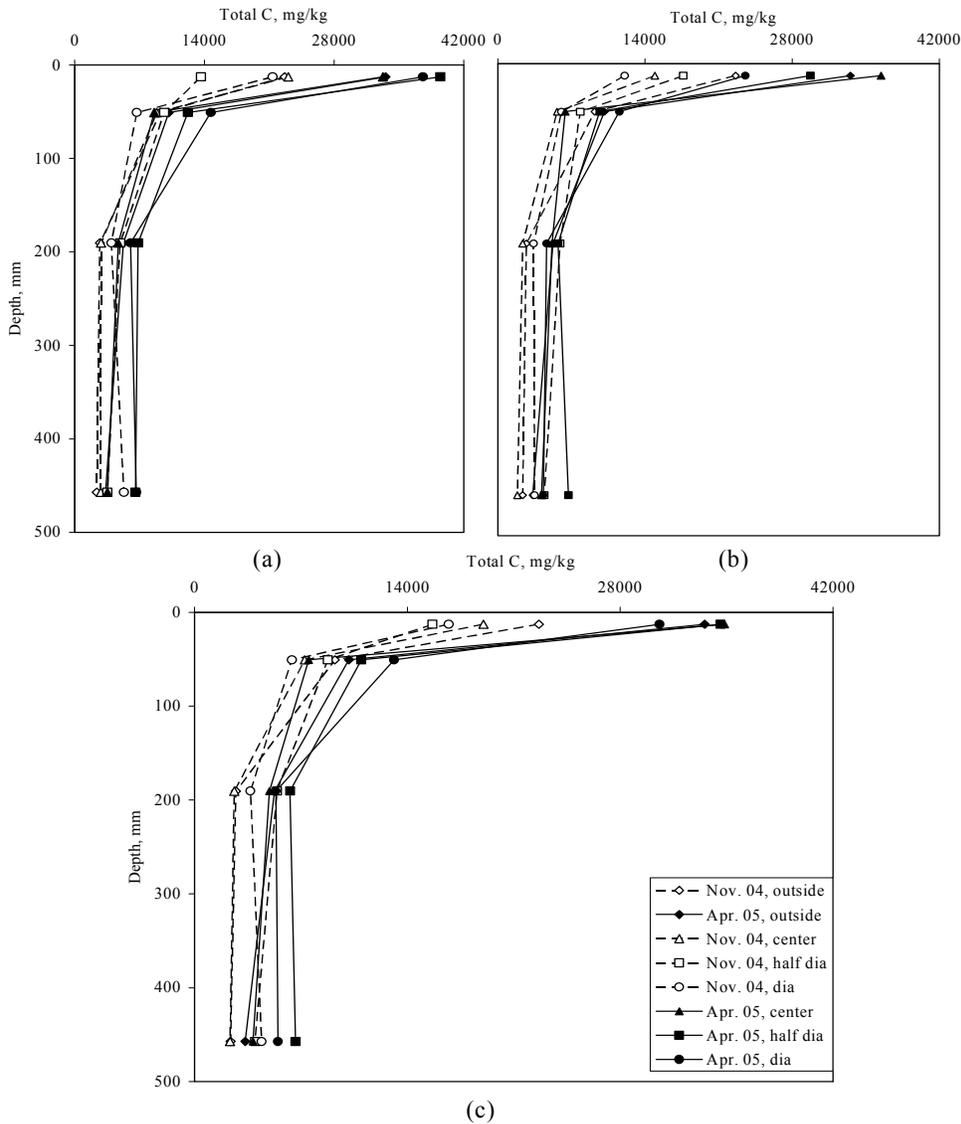


Figure 16. Total C concentrations in the soil beneath and outside the TL stockpile footprints based on average of (a) stockpiles 1 and 2 (NR), (b) stockpiles 3 and 4 (NR+SIM), and (c) all four stockpiles.

While total C concentrations beneath and beyond the stockpiles were similar at the same depth, DOC concentrations were substantially higher in much of the soil profile beneath the stockpiles (Fig. 17). At the surface, DOC levels beneath the stockpiles (half diameter, Nov. 04) was >75 times higher than outside while in the deepest sample it was >40 higher (Fig. 17(c)).

As with EC, greater DOC leaching was observed beneath the stockpiles, generally, at the half diameter followed by the center with little leaching at the diameter of the stockpile (Fig. 17). Simulated rainfall increased DOC leaching down to the deepest sampling layer in the half diameter and center (only winter stockpiles) (Fig. 17(b)). Since DOC concentrations in TL samples used for both the summer and winter stockpiles were comparable and total C higher in the winter stockpile (Table 3), higher DOC levels had been expected in April 2005 vs. November 2004 due to buildup in the soil over the winter. However, lower DOC concentrations at the half diameter beneath the winter stockpiles (NR+SIM) versus the summer stockpiles (NR+SIM) were likely due to reduced leaching from the stockpiles as well as redistribution of the DOC already present in the soil within the profile (Fig. 17). Consequently, there was

very little change in DOC concentration with depth in all except the surface sample, particularly in the stockpiles that also received simulated rainfall. Similarity in the EC (Fig. 15) and DOC (Fig. 17) profiles indicate that leaching of organic anions contributed substantially to the increase in EC.

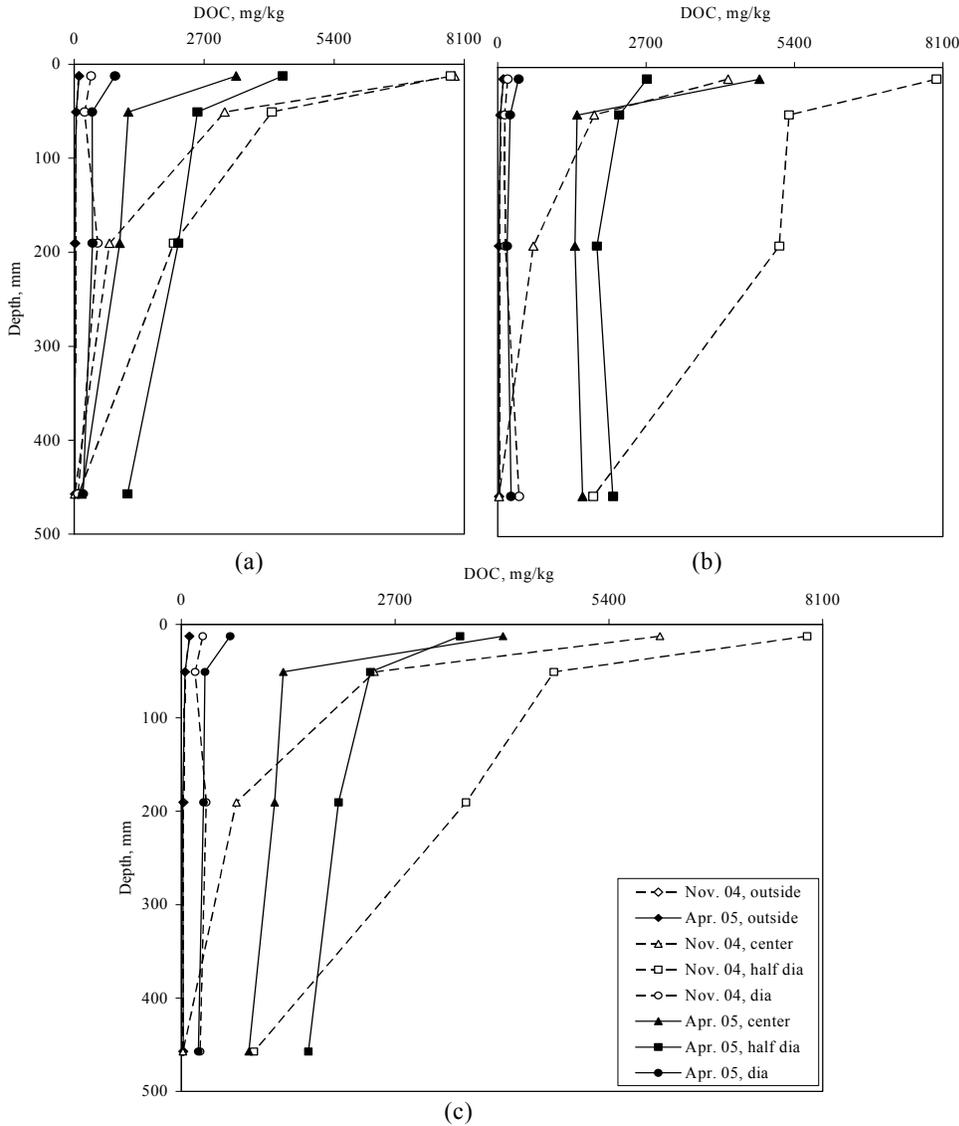


Figure 17. Dissolved organic C concentrations in the soil beneath and outside the TL stockpile footprints based on average of (a) stockpiles 1 and 2 (NR), (b) stockpiles 3 and 4 (NR+SIM), and (c) all four stockpiles.

Assuming a soil bulk density of 1600 kg/m^3 for the sampling depth, based on average DOC concentration (average of all locations for four stockpiles) and adjusted for background concentration, $\sim 24.9 \text{ kg}$ of DOC (2% of the total C in the summer stockpile) was leached from each stockpile into the top 610 mm of soil during summer stockpiling. At the end of the study, DOC in the sampling depth beneath each stockpile (adjusted for background concentration) was $\sim 17.4 \text{ kg}$ which was surprising since a greater mass of DOC was expected in the sampling depth. It was likely that DOC leached from the sampling depth (0-610 mm) into the soil layer below. Substantial DOC leaching as seen in this study has implications for As and metal mobility in the soil. Organic anions in DOC will compete with oxyanions of P and As, causing them to be desorbed thus enhancing their mobility (Redman et al. 2002). Availability of soluble organic C will also enhance mobility of metals/metalloids by forming aqueous complexes which in turn will

reduce solid-phase complexation that would have reduced metal and As mobility (Redman et al. 2002; Snoeyink and Jenkins 1980). Finally, by catalyzing redox reactions, DOC may enhance As mobility (Redman et al. 2002).

Phosphorus

Phosphorus, specifically, WSE-P can enhance the mobility of As species in the soil by competing with arsenates and arsenites for sites on soil surface complexes. Total P concentrations in the surface layer beneath the stockpiles were greater than outside the stockpile footprints. Also, total P decreased with increasing depth (Fig. 18).

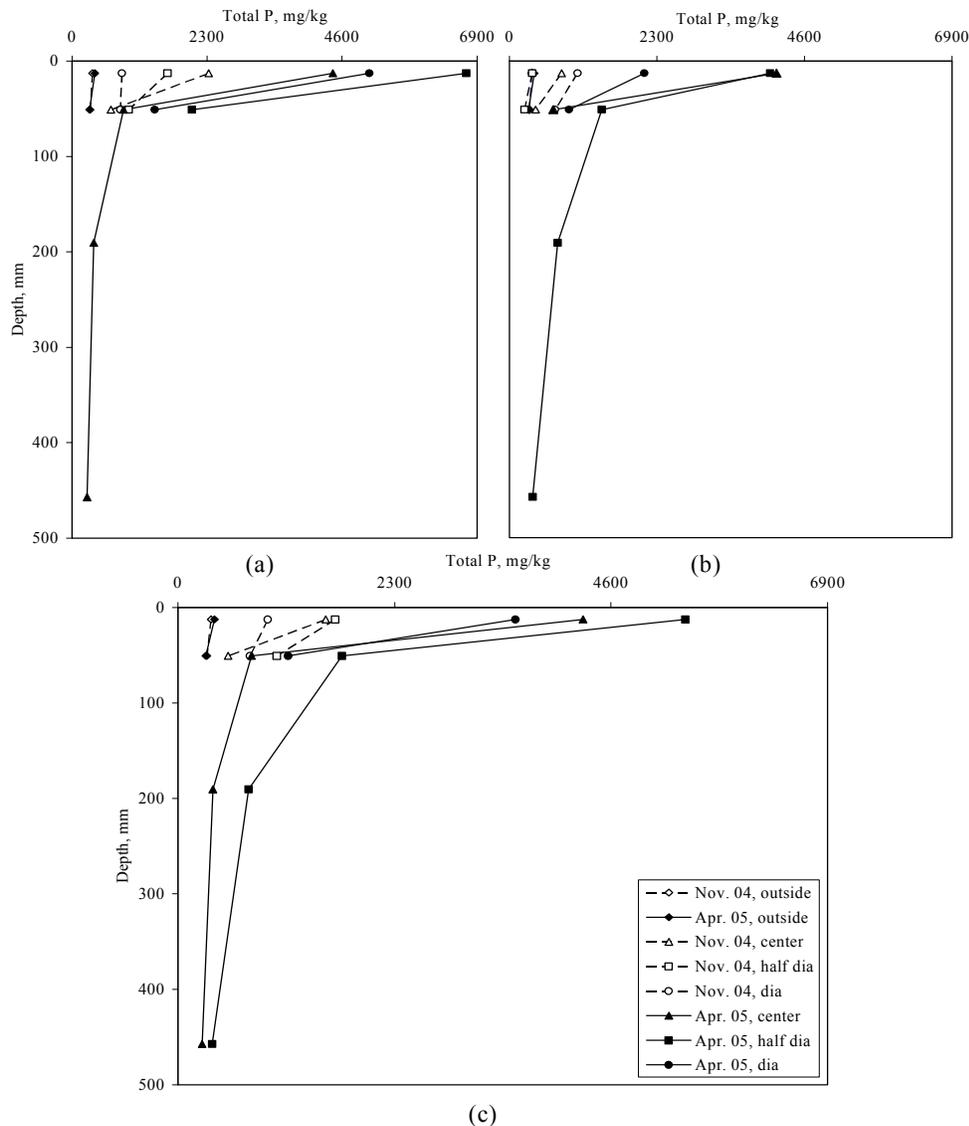


Figure 18. Total P concentrations in the soil beneath and outside the TL stockpile footprints based on average of (a) stockpiles 1 and 2 (NR), (b) stockpiles 3 and 4 (NR+SIM), and (c) all four stockpiles. For April 2005, data for the two deepest samples in the center and half diameter of the stockpile are based on samples from stockpiles 2 and 3, respectively.

Since total P concentrations for the two deepest samples were analyzed for one location (center or half diameter) each in one stockpile in April 2005 and no corresponding total P analyses were performed outside the stockpile, it is difficult to say conclusively if there was change in total P throughout the

profile. Total P in the 76-305 and 305-610 mm layers in the soil before stockpiling (Table 2) were 219 and 229 mg/kg, respectively. Since total P concentrations (averaged for stockpiles 2 and 3) in the 76-305 and 305-610 mm layers were 468 and 309 mg/kg, respectively, WSE-P leached down into the 76-305 mm layer, as discussed below.

Water soluble P concentrations in the soil samples beneath and outside the turkey litter stockpiles are presented in Figure 19. It seemed likely that there was substantial WSE-P leaching from the stockpiles down into the 76-305 mm soil layer (Fig. 19).

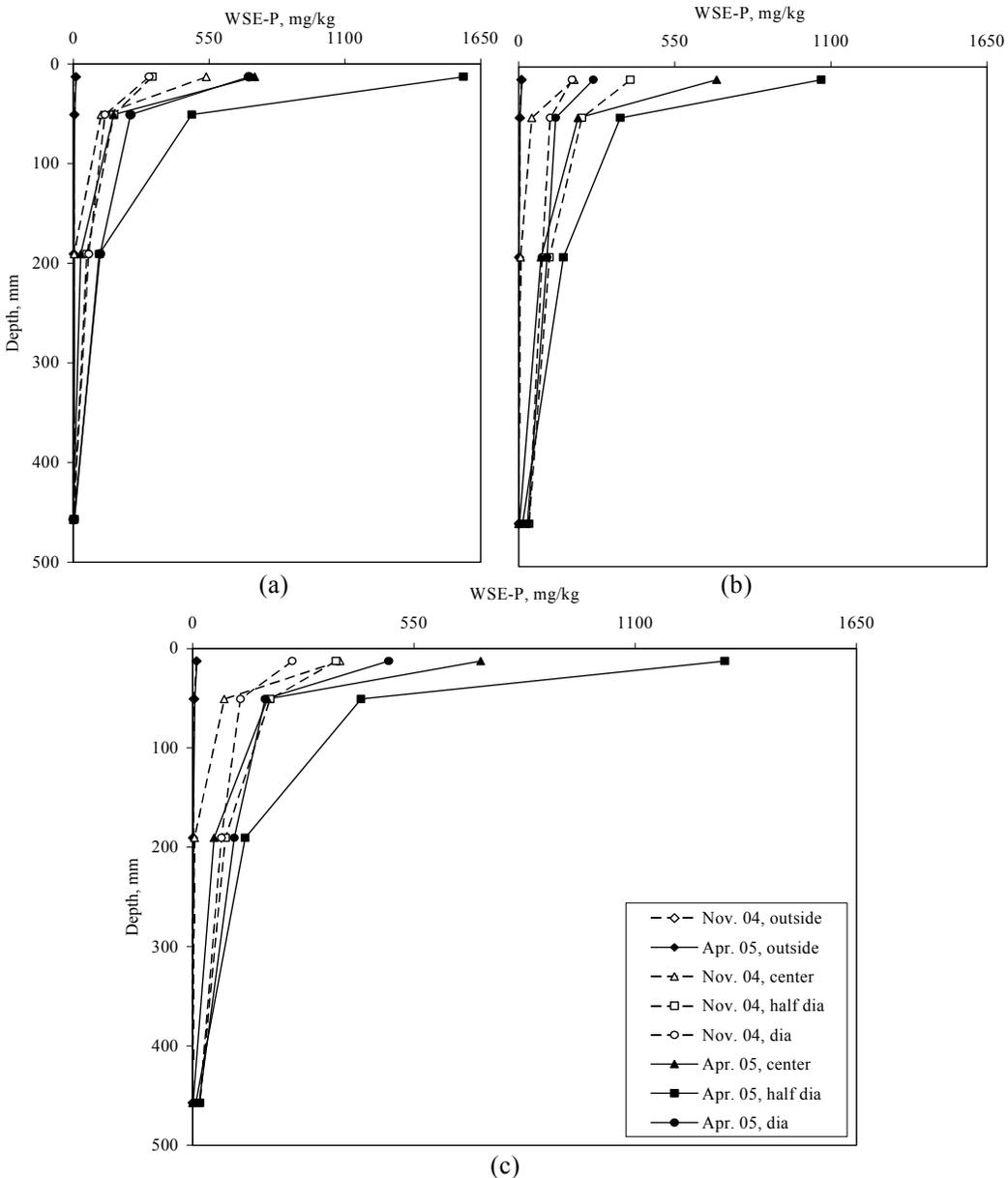


Figure 19. Water soluble P concentrations in the soil beneath and outside the TL stockpile footprints based on average of (a) stockpiles 1 and 2 (NR), (b) stockpiles 3 and 4 (NR+SIM), and (c) all four stockpiles.

When averaged for all four stockpiles, the highest WSE-P concentrations were observed at the half diameter (except the bottom layer), while the concentrations at the center and diameter were similar. In

the top two soil layers, WSE-P concentrations were higher in the NR stockpiles (Fig. 19(a)) versus NR+SIM stockpiles (Fig. 19(b)). However, in the two deeper layers, the trend was reversed. For example, in the lowest layer, average WSE-P concentration (averaged for all three locations) in the NR+SIM stockpiles were 2.4 times higher than in the NR stockpiles (Tables B3-B5; Appendix B). Hence, depending on other factors, even small depths of additional rainfall may increase leaching of WSE-P in the soil.

Compared with November 2004, average WSE-P concentrations (averaged for all three locations for all four stockpiles) in April 2005 in the top three layers were substantially higher, though the difference decreased with increasing depth (Fig. 18(c)). Greater WSE-P in the top three layers in April 2005 vs. November 2004 was likely due to much higher WSE-P in the winter stockpiles (Table 3), residual P from the previous stockpile, and leaching of WSE-P. There seemed to be substantial leaching of WSE-P from the stockpiles into the 76-305 mm layer because in April 2005, WSE-P concentration in that layer beneath the stockpile was 96.2 mg/kg compared with 1.4 mg/kg in the background. In the deepest layer, average WSE-P concentrations were 12.3 and 8.8 mg/kg, respectively, in November 2004 and April 2005 (Appendix B) whereas background WSE-P concentrations in November 2004 and April 2005 were 0.25 and <0.1 mg/kg (Appendix B), respectively.

Based on soil bulk density and average WSE-P concentration (adjusted for background concentration), ~0.76 kg of WSE-P (0.9% of the total P in the stockpile) was leached from each stockpile into the top 610 mm of soil during the summer stockpiling. At the end of the study, adjusted WSE-P mass in the sampling depth beneath each stockpile (adjusted for background concentration) was ~1.54 kg. Since the highest WSE-P concentration in the deepest layer was 16.6 mg/kg, it seemed unlikely that appreciable quantity of WSE-P had leached from the sampling depth. While no studies on P leaching losses from poultry litter stockpiles are available for comparison, Johnson et al. (2004) reported extractable P concentration of ~180 mg/kg in 0-300 mm soil layer. For 4 years, poultry litter (590 kg-P/yr-ha) had been applied to coastal Bermuda grass over-seeded with annual ryegrass on Darco loamy sand in Texas (Johnson et al. 2004). In this study, in the 0-305 mm layer, WSE-P concentration averaged 179 mg/kg. High WSE-P concentrations combined with wet (Fig. 7), and hence, anoxic conditions beneath much of the stockpile are likely to accelerate WSE-P leaching into the soil, especially if turkey litter is stockpiled at the same location. Increased WSE-P concentrations may in turn, increase mobility of As species.

Nitrogen

As would be expected, total N concentrations declined with depth though the lowest layer had slightly higher concentrations than the layer above it (Fig. 20) probably because the clay lens in the lowest layer reduced movement of soluble N species through it (discussed later). Reduced total N content of the surface layer beneath the stockpiles vs. outside the stockpiles (Fig. 20), particularly in November 2004 was likely due to mineralization of the surface vegetation and roots by the microbes in the N-rich litter resulting in the inorganic N species moving deeper into the soil.

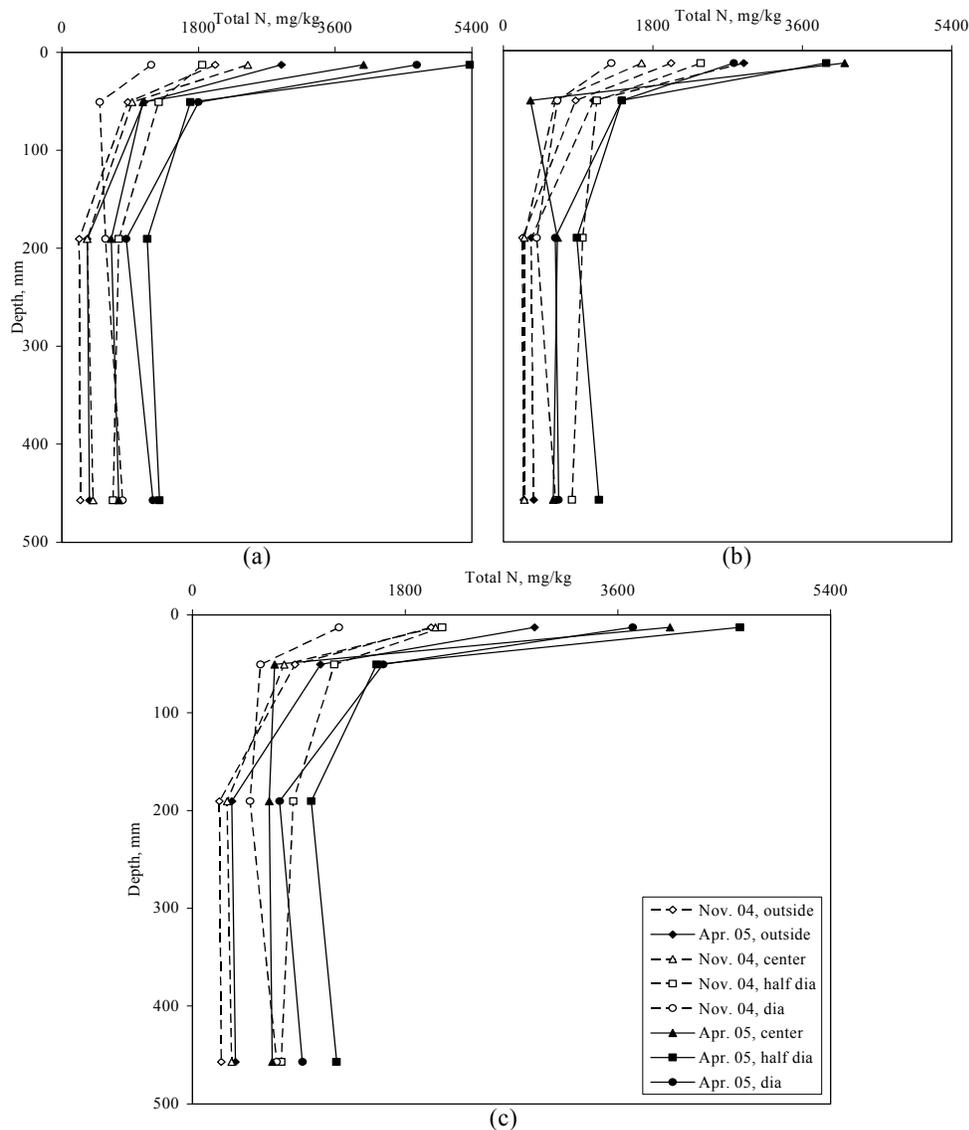


Figure 20. Total N concentrations in the soil beneath and outside the TL stockpile footprints based on average of (a) stockpiles 1 and 2 (NR), (b) stockpiles 3 and 4 (NR+SIM), and (c) all four stockpiles.

As would be expected, due to leaching from the stockpiles, NH_4^+ -N concentrations were much higher beneath the stockpiles than outside the stockpiles (Fig. 21). Evidence of NH_4^+ -N leaching was observed throughout the sampling depth (0-610 mm) (Fig. 21). Overall, the greatest NH_4^+ -N leaching beneath the stockpiles was observed at the half diameter followed by the center. As expected, there was very little NH_4^+ -N leaching at the diameter because aerobic conditions favored the formation of NO_3^- -N which then leached into the soil (discussed below). A wetter season and higher NH_4^+ -N and total N concentrations in the litter (Table 3) resulted in greater NH_4^+ -N concentrations in the soil profile at the half diameter during the summer stockpiling. It seemed that simulated rainfall did not affect NH_4^+ -N leaching into the top 76 mm. However, simulated rainfall affected the two deeper layers with the deepest layer showing a bigger change (Appendix B). Also noteworthy was the fact that in April 2005, particularly in the simulated rainfall stockpiles, compared with the 76-305 mm layer, the 305-610 mm layer had greater NH_4^+ -N concentration. The presence of clay lenses in the deepest layer probably resulted in accumulation of NH_4^+ -N. In fact, when collecting core samples, some soil samples from the deepest layer gave off a strong ammonia odor.

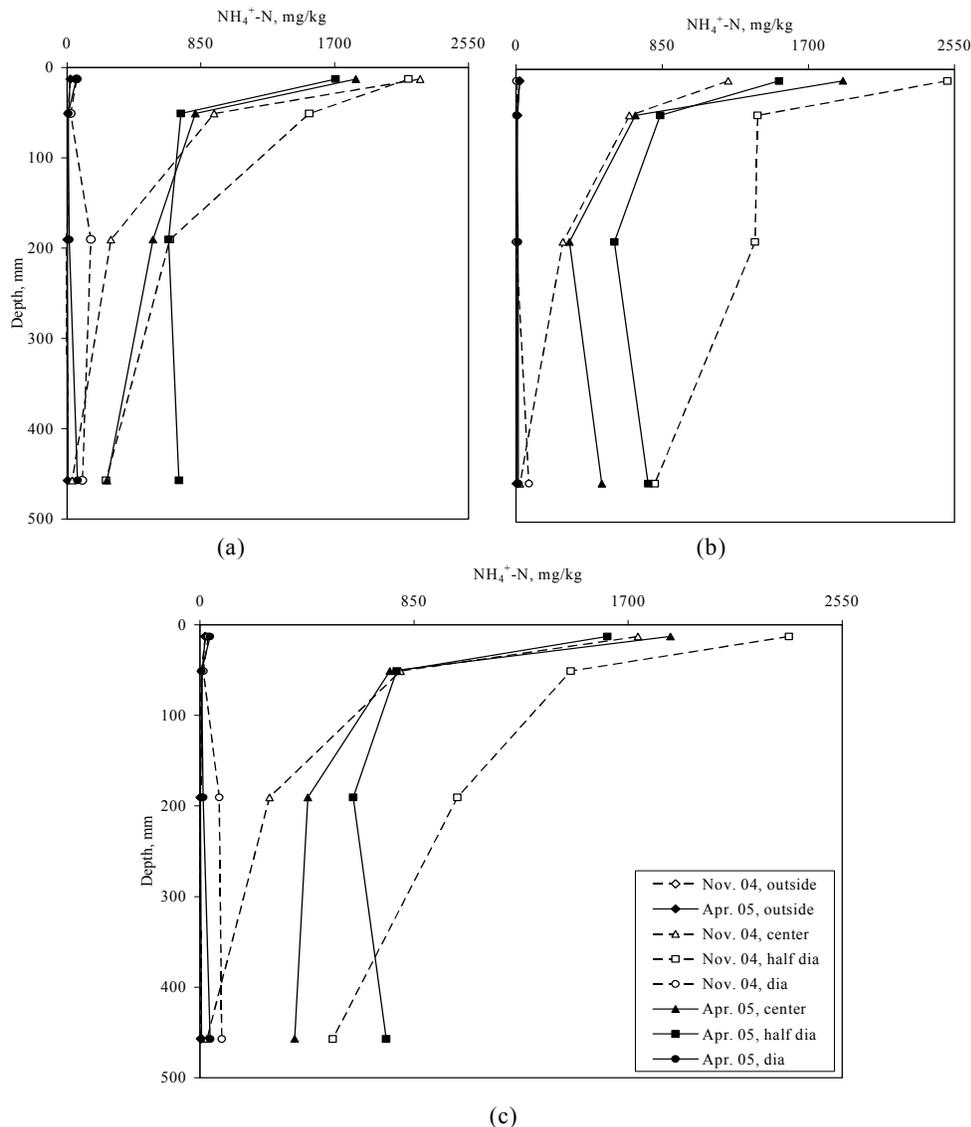


Figure 21. Ammonium-N concentrations in the soil beneath and outside the TL stockpile footprints based on average of (a) stockpiles 1 and 2 (NR), (b) stockpiles 3 and 4 (NR+SIM), and (c) all four stockpiles.

Based on soil bulk density and average $\text{NH}_4^+\text{-N}$ concentration (adjusted for background concentration), ~ 6.43 kg of $\text{NH}_4^+\text{-N}$ (3.7% of the total N in the stockpile) was leached from each stockpile into the top 610 mm of soil during the summer stockpiling. At the end of the study, $\text{NH}_4^+\text{-N}$ mass in the soil beneath each stockpile that was attributed to stockpiling was ~ 6.65 kg, indicating that a substantial portion of the $\text{NH}_4^+\text{-N}$ supplied by the winter stockpile or remaining in the soil profile may have been lost through N immobilization by soil microbes. Some of the $\text{NH}_4^+\text{-N}$ may have been fixed to clay or may have been reduced to N_2 . There is a possibility that when turkey litter is no longer stockpiled at the site, $\text{NH}_4^+\text{-N}$ in the surface layer will be oxidized to $\text{NO}_3^-\text{-N}$; however, in this study, based on results of $\text{NO}_3^-\text{-N}$ distribution in the profile (below), the likelihood of substantial nitrification seemed remote.

Compared with $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ represented a much smaller fraction of the total N in the soil profile beneath the stockpiles (Fig. 22). As expected, most of the $\text{NO}_3^-\text{-N}$ leaching occurred at the diameter (Fig. 22) where aerobic conditions allowed nitrification. It was surprising to note that $\text{NO}_3^-\text{-N}$ concentrations

in the soil profile beneath the NR+SIM stockpiles were lower than NR stockpiles (Fig. 22) since NO_3^- -N binds very weakly to soil and is mostly in soil solution. Despite a greater supply of N and longer duration available for leaching, NO_3^- -N concentrations in the soil profile were lower in April 2005 than in November 2004. This could be attributed to denitrification of NO_3^- to NO (when $\text{pH} < 5.5$), N_2O ($6 < \text{pH} \leq 6.5$), or N_2 (mainly at $\text{pH} > 6$) (Tisdale et al. 1993) since soil below the stockpile was likely moist (and hence anoxic) in some areas and there was adequate DOC for the denitrifying bacteria. The clay lens in the 305-610 mm layer likely reduced percolation through this layer resulting in an accumulation of NO_3^- -N in this layer compared with the much sandier 76-305 mm layer. However, some NO_3^- -N may have leached below the 610-mm depth.

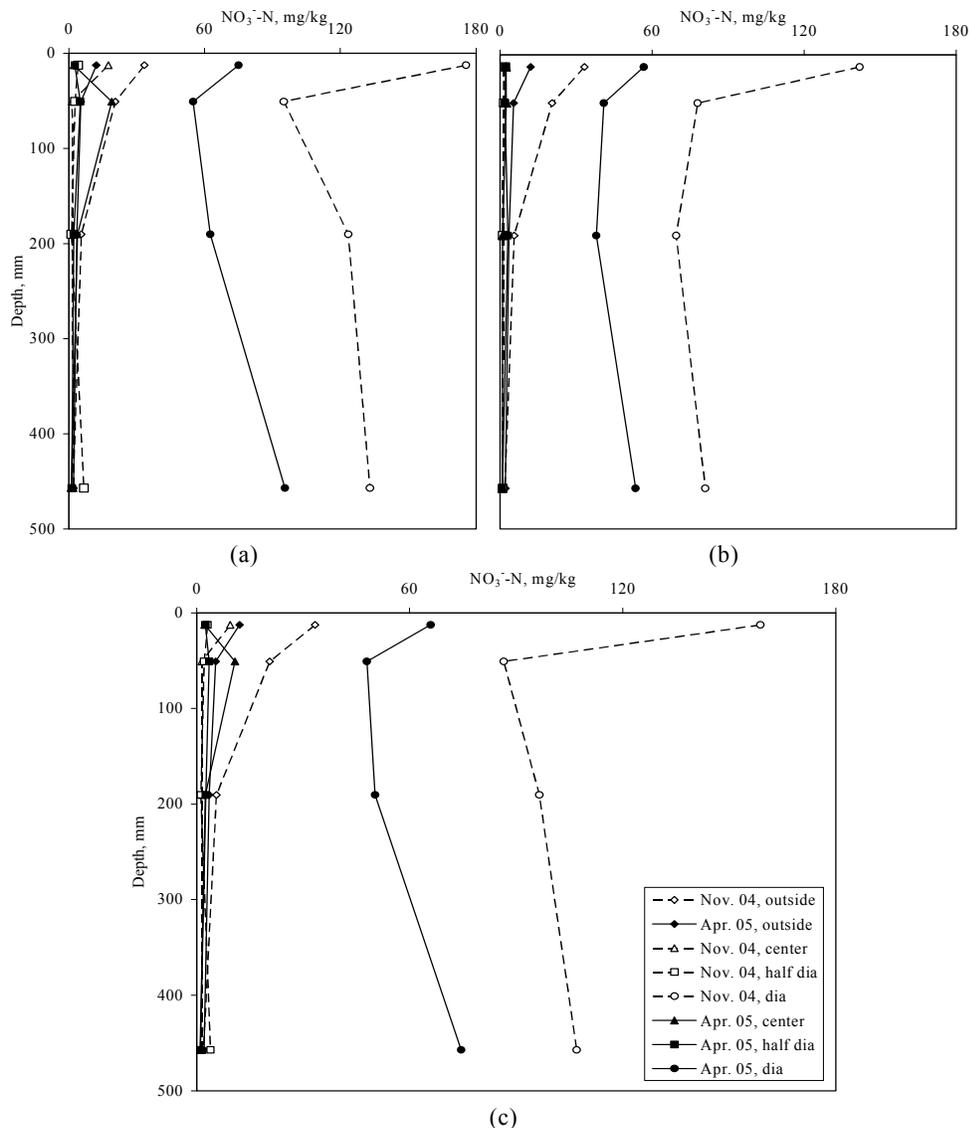


Figure 22. Nitrate-N concentrations in the soil beneath and beyond the TL stockpiles based on average of (a) stockpiles 1 and 2 (NR), (b) stockpiles 3 and 4 (NR+SIM), and (c) all four stockpiles.

Zhu and Schmidt (2000) reported 59 mg/kg in the 305-610 mm layer of sandy soil under a turkey manure stockpile that had been in place for 3 years. At the same depth, in this study, NO_3^- -N concentration at the diameter of the stockpile was 107.0 and 74.5 mg/kg, respectively after 162 and 337 d of the study. The total NO_3^- -N mass remaining in the sampling depth in November 2004 and April 2005 were ~ 0.5 and 0.3 kg, respectively. While repeated stockpiling at the same location may increase the risk of NO_3^- -N loading

to the shallow groundwater, denitrification may play a role in reducing NO_3^- -N loadings over time. However, while the DOC-rich leachate may reduce NO_3^- -N concentration in the water source, it may impair it in other ways and this requires further evaluation.

Arsenic

Turkey litter stockpiling resulted in build up of total As in the surface soil layer particularly in April 2005 (Fig. 23). Build up of total As in the surface layer was particularly high at the half diameter (Fig. 23).

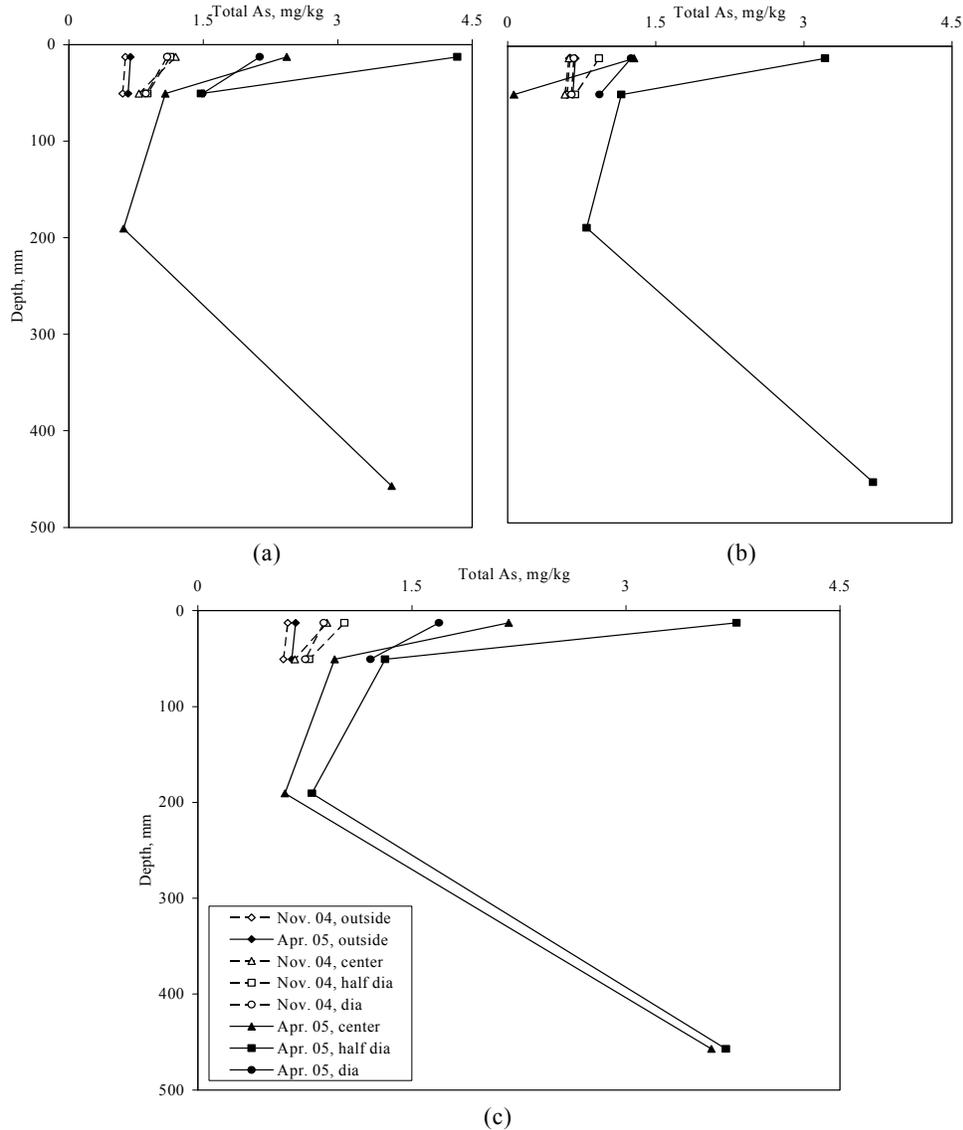


Figure 23. Total As concentrations in the soil beneath and outside the TL stockpile footprints based on average of (a) stockpiles 1 and 2 (NR), (b) stockpiles 3 and 4 (NR+SIM), and (c) all four stockpiles. For April 2005, data for the two deepest samples in the center and half diameter of the stockpile are based on samples from stockpiles 2 and 3, respectively.

Total As in the 76-305 and 305-610 mm layers (at the center in stockpile 2 and at the half diameter in stockpile 3) in April 2005 (Fig. 23) were comparable to the total As values determined prior to stockpiling in those two layers (Table 3) indicating that total As movement into the two deeper layers was not substantial.

Compared with total As, WSE-As provides a clearer picture of the impact of TL stockpiling on As contamination of the soil. Further, the type of As species moving into the soil is also an issue of concern. Water soluble As was not detected in any soil samples outside the turkey litter stockpile footprints in November 2004 while in April 2005, the maximum concentration detected was 0.01 mg/kg, much lower than in the soil samples beneath the stockpiles (Fig. 24). In April 2005, surface samples beneath the stockpiles had as much as 8-73% of the total As in the WSE-As form while in the deepest layer, it was 1-4% (Appendix B; Tables B2-B5). It seemed likely that there was substantial WSE-As leaching from the stockpiles down into the 76-305 mm soil layer (Fig. 24) as up to 49% of the total As in that layer was in the water soluble form.

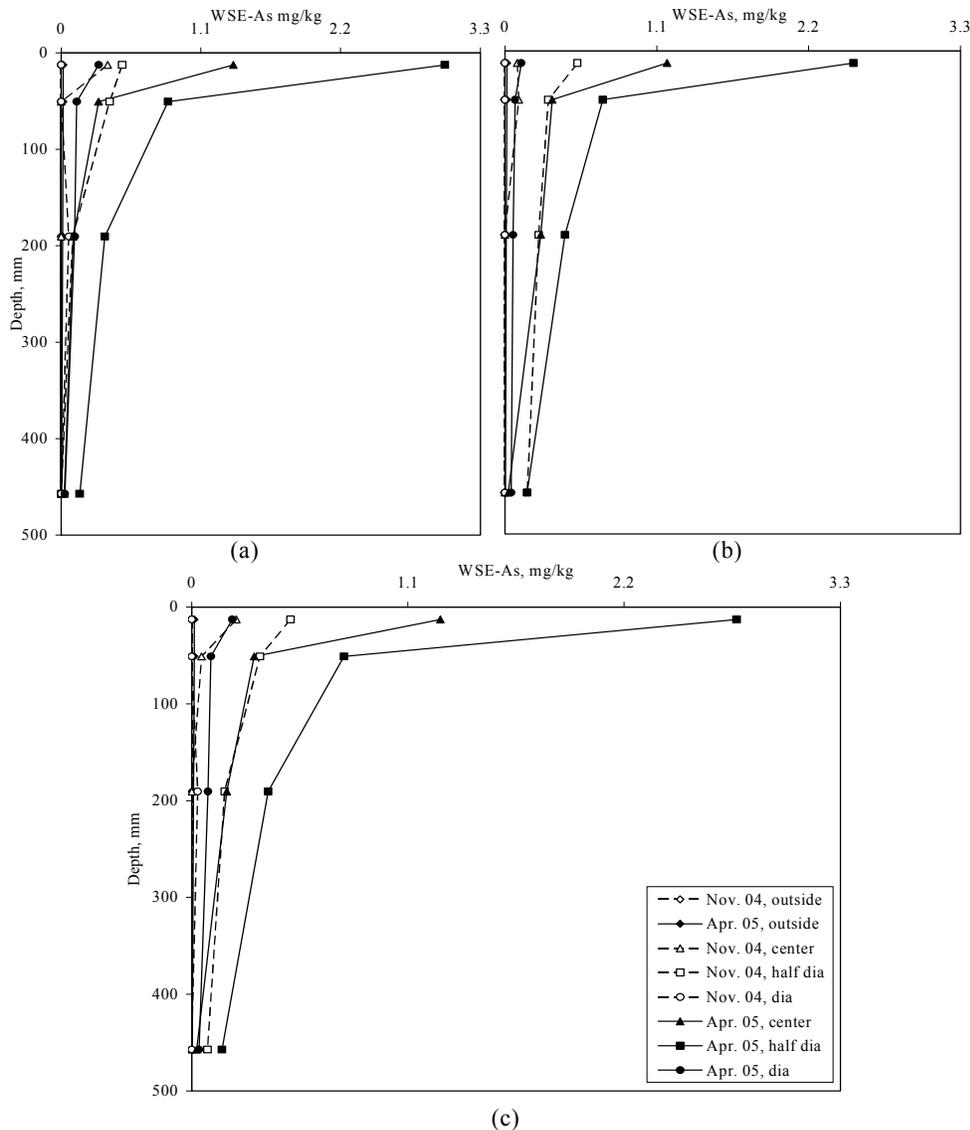


Figure 24. Water soluble As concentrations in the soil beneath and outside the TL stockpile footprints based on average of (a) stockpiles 1 and 2 (NR), (b) stockpiles 3 and 4 (NR+SIM), and (c) all four stockpiles.

The greatest WSE-As leaching was observed at the half diameter, followed by the center; there was very little leaching at the diameter (Fig. 24). There was no consistent difference in WSE-As concentrations by depth between the NR+SIM and NR stockpiles. In fact, in the April 2005 sampling, the surface samples

beneath the NR stockpiles received only natural rainfall had higher WSE-As; however, in the two bottom layers, the stockpiles that had also received simulated rainfall had slightly higher WSE-As. This indicated that even small depths of additional rainfall may affect WSE-As movement in the soil.

Compared with November 2004, average WSE-As concentrations (averaged for all three locations for all four stockpiles) in April 2005, the sampling depth was 3.5 times higher with the highest (6) and lowest (2) ratios observed in the surface and deepest layers, respectively. Total WSE-As masses in the sampling depth beneath each stockpile in November 2004 and April 2005 were ~1.0 g (4.2% of total As in the summer stockpile) and 3.3 g (3.9% of total As in summer and winter stockpiles), respectively. Hence, WSE-As concentrations proportional to total As loadings and duration of loading indicated that WSE-As increased with duration of stockpiling. It was unclear if solid phase complexation in the soil beneath the stockpiles should have reduced WSE-As concentrations. It seemed unlikely that there was leaching of WSE-As from the sampling depth into the soil below.

Arsenic K-XANES spectra of 37 soil samples are shown in Figures 25-33. Spectra were collected for selected soil samples taken beneath stockpiles 2, 3, and 4 at the center, half diameter, diameter, or between stockpiles. Each figure contains spectra of the As(V) standard and As(III) edge position for oxidation state reference. Overall, spectra indicated that As in these soil samples was predominantly in the +5 oxidation state. Due to low As concentrations (ranging from ~0.01 to 0.1 mmol-As/kg), LCF did not give satisfactory results (very high χ^2 values) or did not produce a fit. One sample containing the highest As concentration (Fig. 29 – winter, half-diameter 0-25 mm, stockpile 3) gave a satisfactory fit ($\chi^2 = 0.4$) of ~52% As_2O_5 [(As(V)], ~31% roxarsone-N [(As(V)], and ~17% As(III)-boehmite (possible overestimation of As(III)-boehmite character discussed above – see section Solid Phase Arsenic Speciation in Turkey Litter Samples).

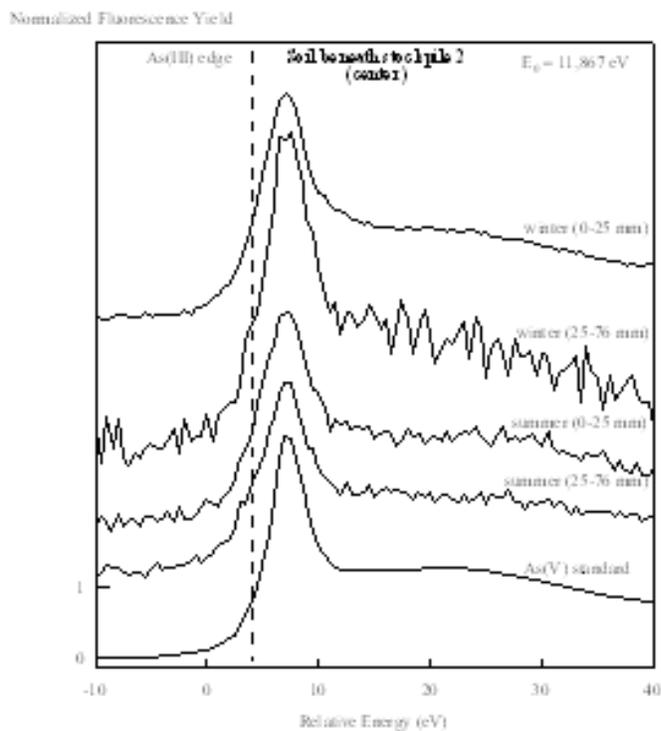


Figure 25. Stacked As K-XANES spectra of soil sampled beneath stockpile 2, center location, at two depths (0-25, 25-76 mm) for summer and winter stockpiles.

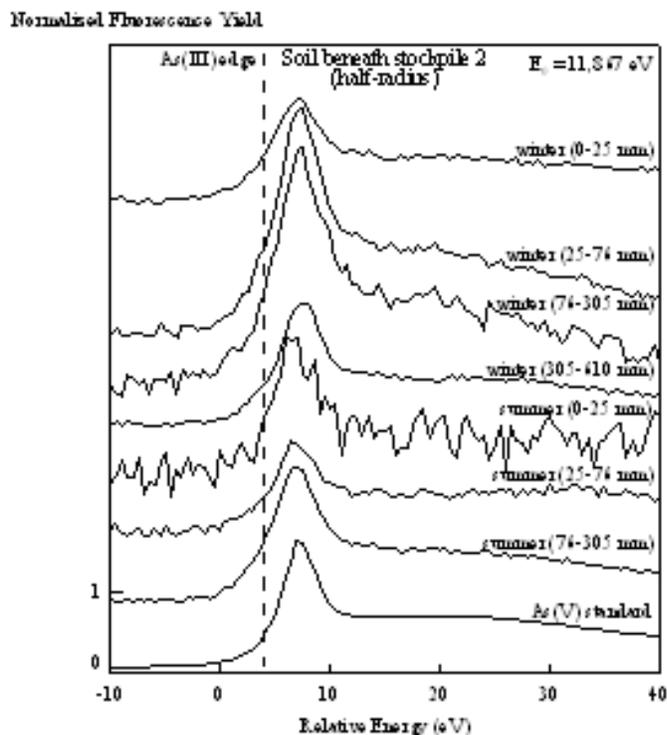


Figure 26. Stacked As K-XANES spectra of soil sampled beneath stockpile 2, half diameter, at all depths (0-25, 25-76, 76-305, 305-610 mm) for summer and winter stockpiles.

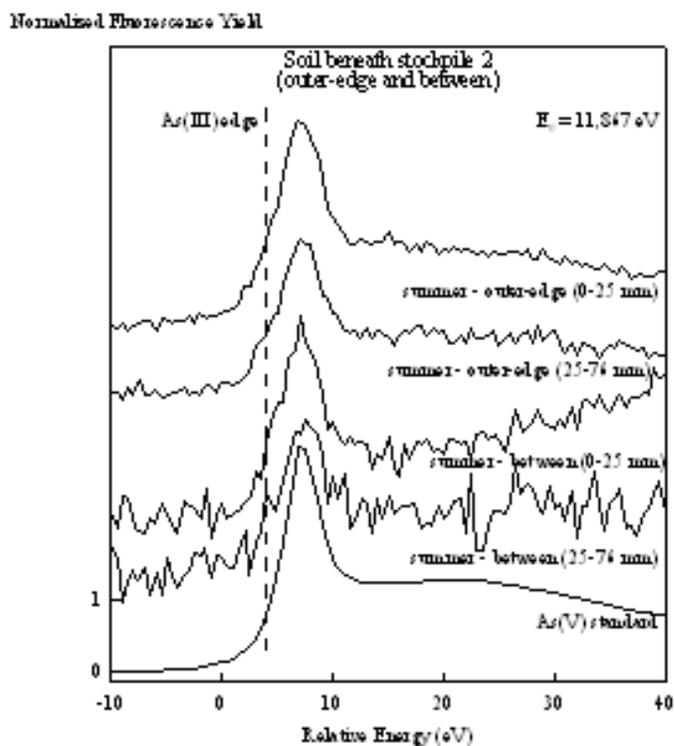


Figure 27. Stacked As K-XANES spectra of soil sampled beneath stockpile 2, diameter and between stockpile locations, at two depths (0-25, 25-76 mm) for the summer stockpiles.

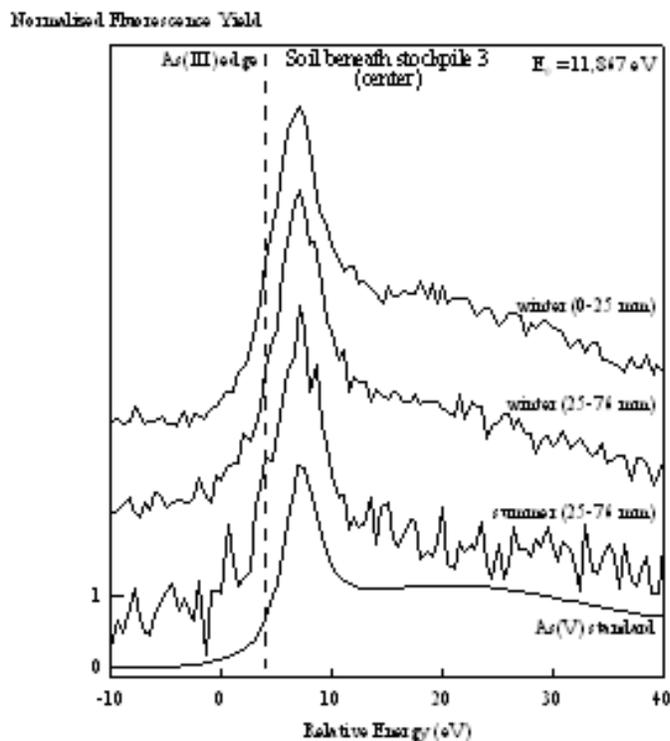


Figure 28. Stacked As K-XANES spectra of soil sampled beneath stockpile 3, center, at two depths (0-25, 25-76 mm) for summer and winter stockpiles.

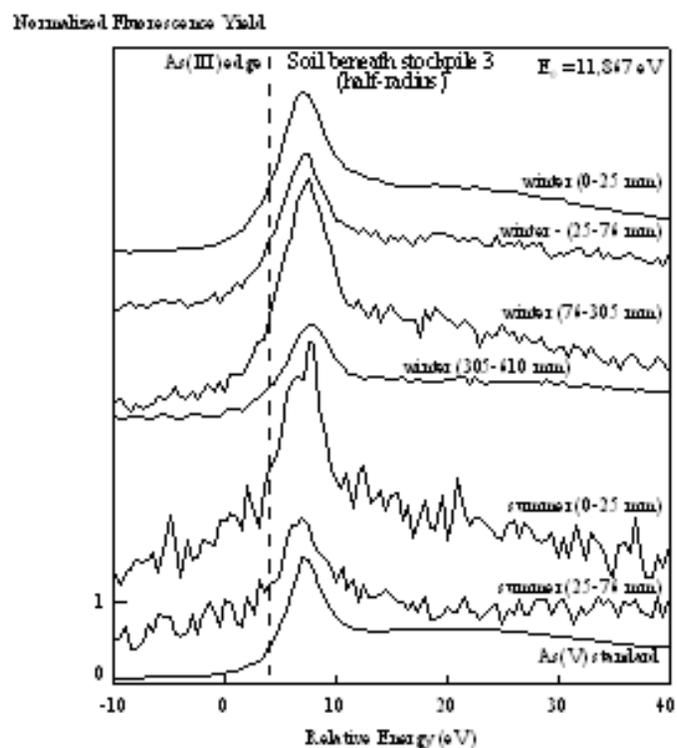


Figure 29. Stacked As K-XANES spectra of soil sampled beneath stockpile 3, half-diameter, at all depths for summer and winter stockpiles.

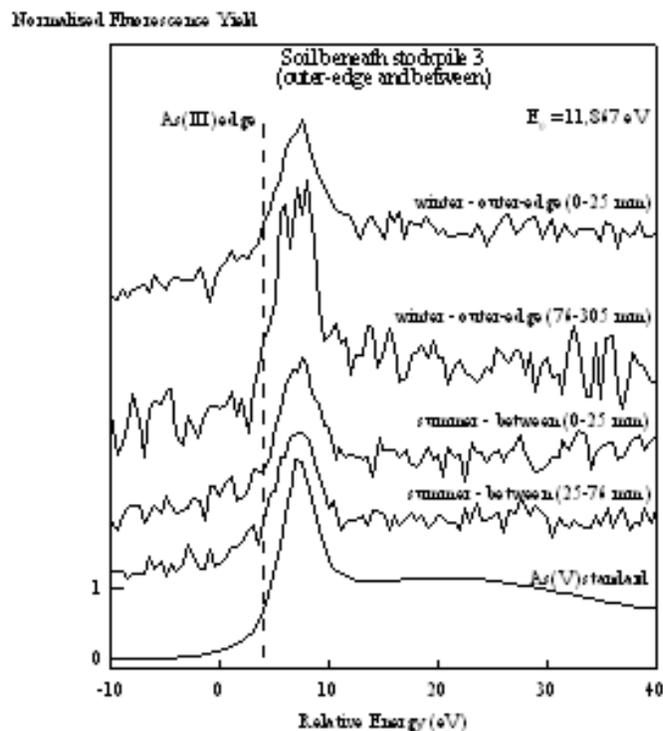


Figure 30. Stacked As K-XANES spectra of soil sampled beneath stockpile 3, at the diameter and between pile locations, at three depths (0-25, 25-76, 76-305 mm) for summer and winter stockpiles.

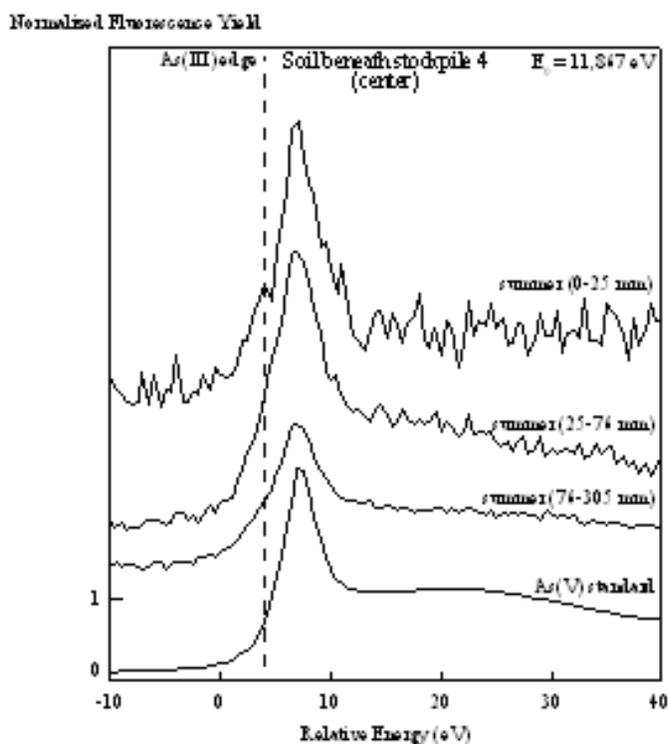


Figure 31. Stacked As K-XANES spectra of soil sampled beneath stockpile 4, center, at three depths (0-25, 25-76, 76-305 mm) for the summer stockpiles.

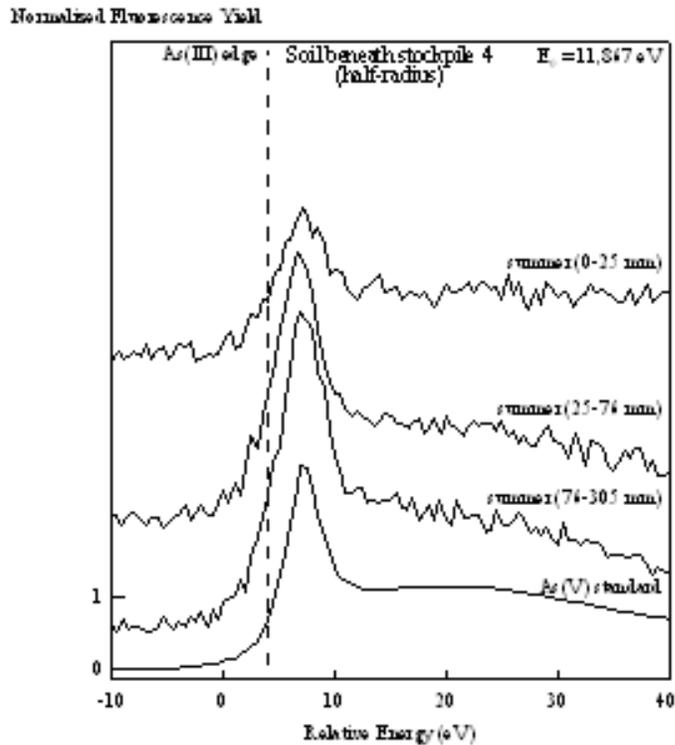


Figure 32. Stacked As K-XANES spectra of soil sampled beneath stockpile 4, half diameter, at three depths (0-25, 25-76, 76-305 mm) for the summer stockpiles.

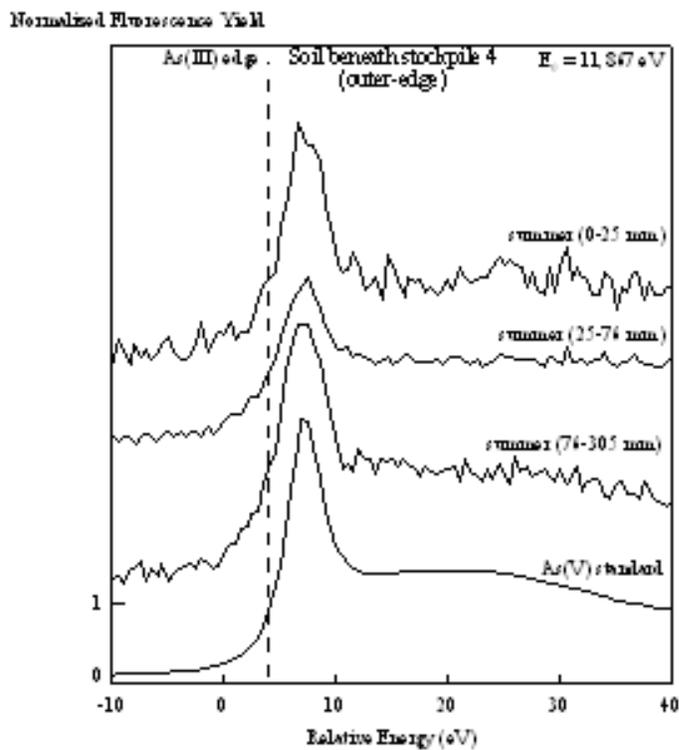


Figure 33. Stacked As K-XANES spectra of soil sampled beneath stockpile 4, outer-edge location, at three depths (0-25, 25-76, 76-305 mm) for the summer stockpiles.

Gupta and Charles (1999) reported that 15-20 years of litter application to cropland resulted in elevated As levels down to 600 mm. Gupta and Charles (1999) did not measure WSE-As; however, in this study, WSE-As leached into the soil from the stockpiles. Among the WSE-As species in the soil, As(V) was the most abundant specie; As (V) is generally considered to be less mobile than As (III) in soils. While WSE-As concentrations in the surface layer beneath the stockpiles ranged from 0.1 to 3.4 mg/kg (Table B3-B5-Appendix B), such low WSE-As concentrations were likely due to the low total As concentrations in the litter (~6 mg/kg-summer; ~16 mg/kg-winter) (Table 3). Arsenic mobility would be more of a concern under litter stockpiles containing greater As concentrations (e.g., up to 77 mg kg⁻¹) according to Sims and Wolf (1994). However, the soils beneath turkey litter stockpiles contained elevated P concentrations (Table B3-B5, Appendix B). Inorganic phosphate, which typically constitutes the dominant form of soil P (Stevenson 1994), competes with arsenate for sorption sites on soil particles (Violante and Pigna 2002). Such competitive sorption would potentially increase the mobility of As. Since DOC (Fig. 17) concentrations were about four orders of magnitude higher than WSE-As in the deepest layer and DOC can increase the mobility of As, the possibility of As species leaching deeper into the soil and contaminating the shallow groundwater over the longer term cannot be ruled out. The impacts of fluctuating water tables and high WSE-P and DOC levels on the possible reduction of As(V) species into the more toxic and mobile As(III) species requires further evaluation.

Copper, Manganese, and Zinc

Compared with soil samples outside the stockpile footprints as well as soil samples prior to stockpiling (Table 2), total Cu concentrations beneath the stockpiles were considerably elevated (Fig. 34). Averaged for all stockpiles and for the entire duration of the study, total Cu concentrations in the 0-25 and 25-76 mm depths were in the range of 103-172 and 15-45 mg/kg, respectively, versus 2.5 mg/kg (0-76 mm) (Table 2) prior to stockpiling and 12.5 mg/kg (0-100 mm) in poultry litter treated fields (Gupta and Charles 1999). While total Cu concentrations in the 76-305-mm and 305-610-mm samples were only determined beneath stockpiles 2 (center) and 3 (half diameter), average concentrations at those depths were higher by 385 and 170%, respectively, versus concentrations prior to stockpiling (Table 2). In the 300-600 mm depth in poultry litter treated fields, Gupta and Charles (1999) reported that total Cu concentrations averaged 5.1 mg/kg versus 8.2 mg/kg in the 305-610 mm depth in this study. Hence, it seemed likely that there was leaching of Cu down into deepest soil layer in this study, probably through complexation with organic ligands (DOC constituents) (Snoeyink and Jenkins 1980).

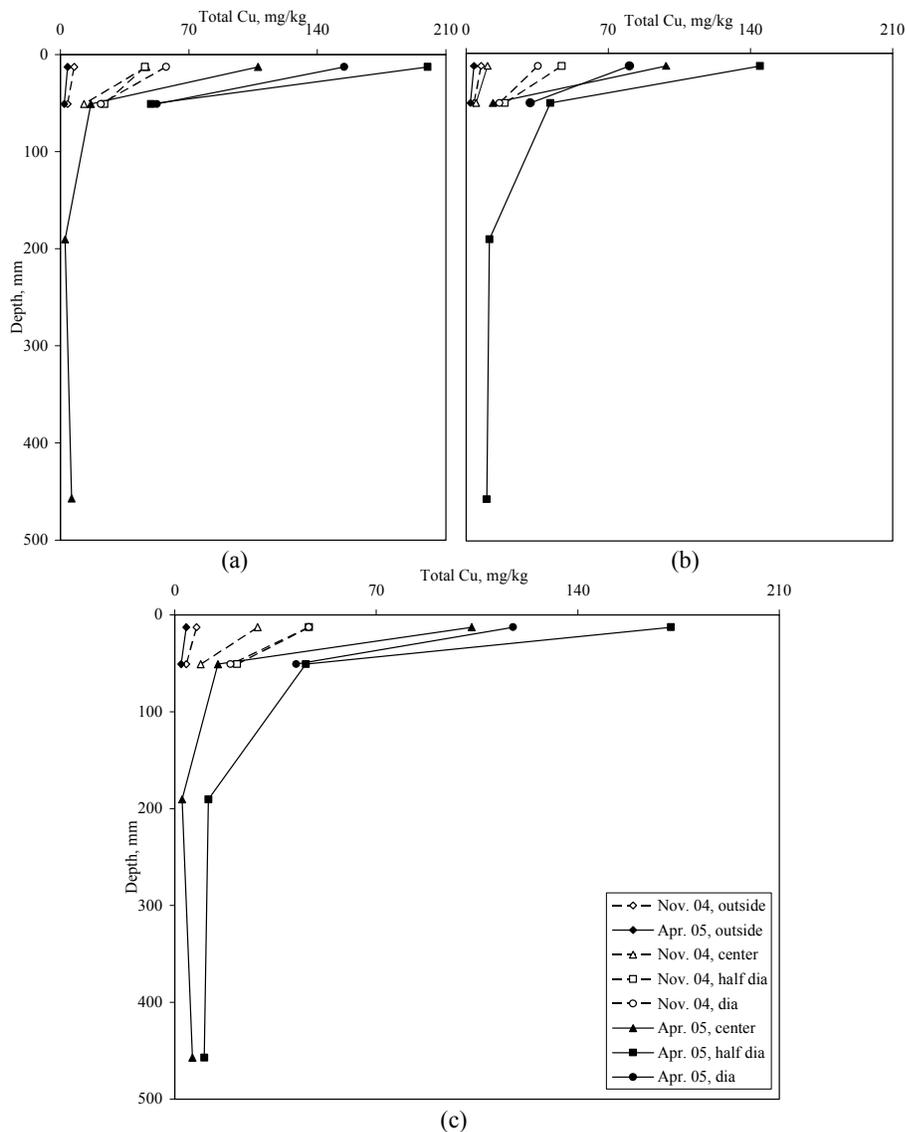


Figure 34. Total Cu concentrations in the soil beneath and outside the TL stockpile footprints based on average of (a) stockpiles 1 and 2 (NR), (b) stockpiles 3 and 4 (NR+SIM), and (c) all four stockpiles. For April 2005, data for the two deepest samples are based on stockpiles 2 (center) and 3 (half diameter).

Compared with soil samples outside the stockpiles as well as prior to stockpiling (0-76 mm layer) (Table 2), total Mn concentrations in the surface layer beneath the stockpiles were considerably elevated at the end of the study (Fig. 35). Averaged for all stockpiles and for the entire duration of the study, total Mn concentrations in the 0-25 and 25-76 mm depths were in the range of 138-165 and 24-46 mg/kg, respectively, versus 28.1 mg/kg (0-76 mm) (Table 2) prior to stockpiling and 33.1 mg/kg (0-100 mm) in poultry litter treated fields (Gupta and Charles 1999). Average total Mn concentrations (stockpiles 2 and 3) in the 76-305-mm and 305-610-mm samples were slightly lower than concentrations determined at the site prior to stockpiling (Table 2) indicating that the clay lens at the site probably had relatively high levels of background Mn.

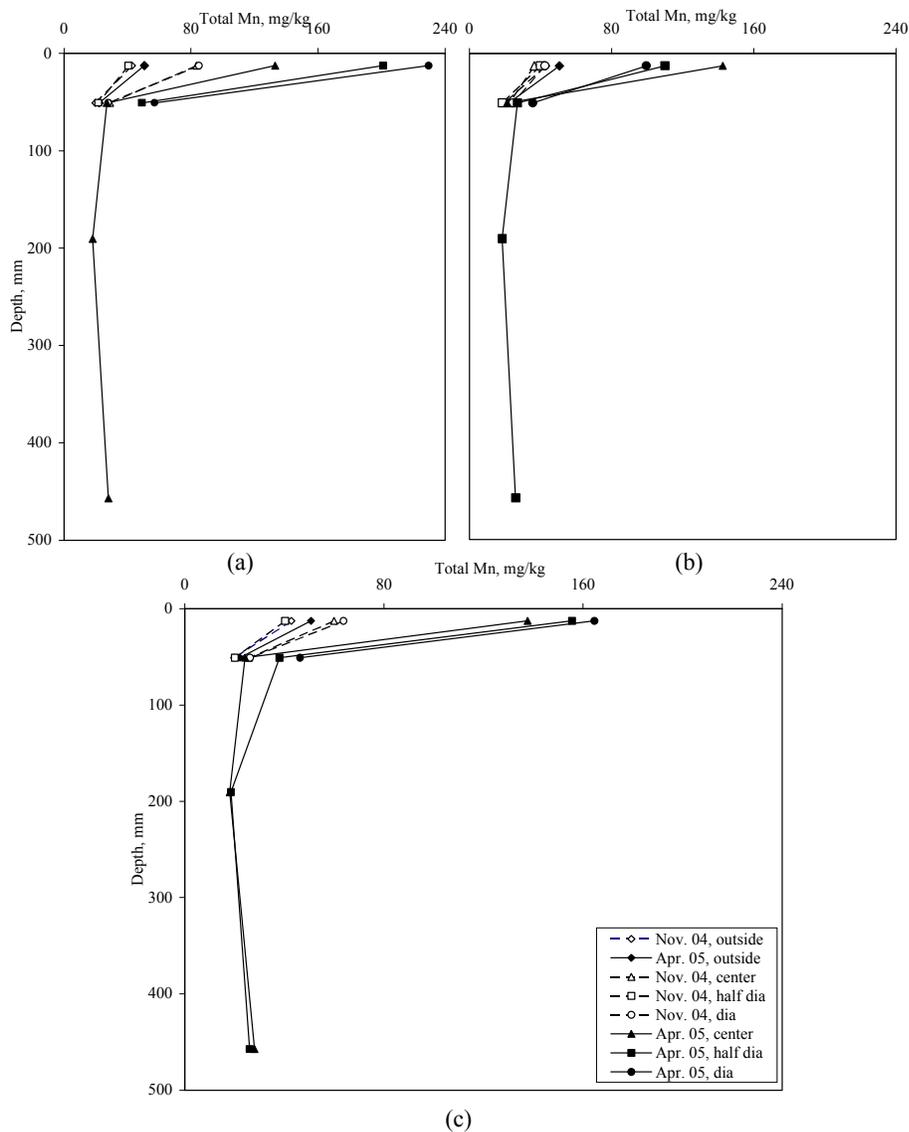


Figure 35. Total Mn concentrations in the soil beneath and outside the TL stockpile footprints based on average of (a) stockpiles 1 and 2 (NR), (b) stockpiles 3 and 4 (NR+SIM), and (c) all four stockpiles. For April 2005, data for the two deepest samples are based on stockpiles 2 (center) and 3 (half diameter).

Compared with soil samples outside the stockpiles as well as prior to stockpiling (0-76 mm layer) (Table 2), total Zn concentrations in the surface layer beneath the stockpiles were considerably elevated at the end of the study (Fig. 35). Averaged for all stockpiles and for the entire duration of the study, total Zn concentrations in the 0-25 and 25-76 mm depths were in the range of 161-192 and 21-58 mg/kg, respectively, versus 9.6 mg/kg (0-76 mm) (Table 2) prior to stockpiling and 31.4 mg/kg (0-100 mm) in poultry litter treated fields (Gupta and Charles 1999). Average total Zn concentrations (stockpiles 2 and 3) in the 76-305-mm samples were comparable to concentrations determined at the site prior to stockpiling (Table 2). However, total Zn concentrations under the stockpiles in the 305-610-mm samples were higher than concentrations prior to stockpiling. Hence, it was unclear if there was any Zn leaching from stockpiled turkey litter.

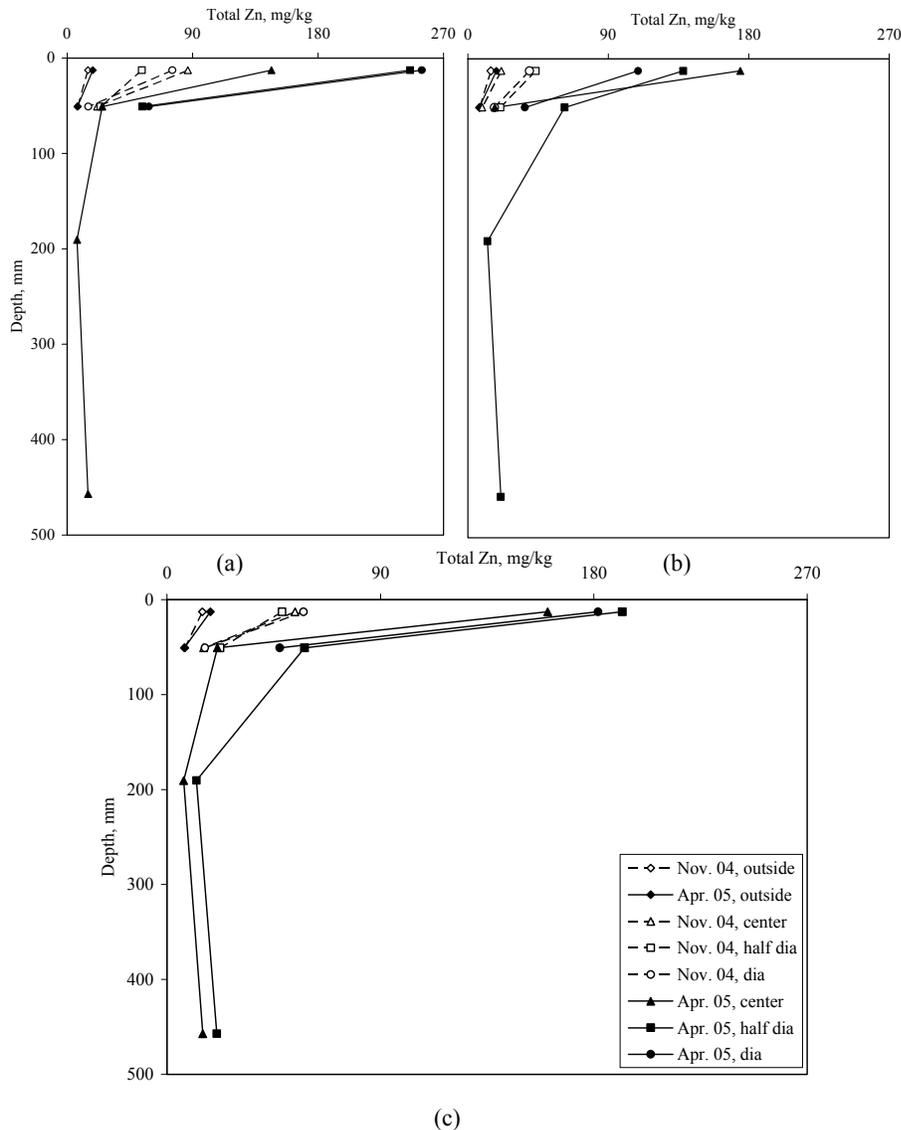


Figure 36. Total Zn concentrations in the soil beneath and outside the TL stockpile footprints based on average of (a) stockpiles 1 and 2 (NR), (b) stockpiles 3 and 4 (NR+SIM), and (c) all four stockpiles. For April 2005, data for the two deepest samples are based on stockpiles 2 (center) and 3 (half diameter).

All three metals (Cu, Mn, and Zn) shared some common trends. Total concentrations of all three metals were higher beneath the NR versus the NR+SIM stockpiles as was the case with total As (Fig. 23); the simulated rainfall depth was likely inadequate in increasing leaching from the NR+SIM stockpiles. Also, as with total As (Fig. 23), in the surface layer, the concentrations of all three metals were higher at the end of the study than at the end of summer stockpiling probably because all four species are conservative in nature. Based on the work of Gupta and Charles (1999) and the results of this study, TL stockpiling results in the accumulation of heavy metals on the soil surface; since heavy metals form complexes with organic ligands (Snoeyink and Jenkins 1980), over time, they may leach through the soil. However, there was evidence of total Cu leaching down throughout the sampling depth.

Summary: Leaching from Stockpiles

As expected, there were increased concentrations of pollutants species in the top 76 mm of the soil beneath the stockpiles as compared with the same soil depth outside the stockpile footprints. However, it

was surprising that concentrations of all species except DOC and $\text{NH}_4^+\text{-N}$ were lower beneath the NR+SIM stockpiles (top 76 mm) versus NR stockpiles. Concentrations of all species (except $\text{NO}_3^-\text{-N}$ and pH) were higher at the half diameter, followed generally by the center. Aerobic conditions favored the formation and leaching of $\text{NO}_3^-\text{-N}$ at the diameter while pH changes were highest at the center.

Leaching of constituents into the soil was affected both by the type of constituent and the time of stockpiling. Highly mobile constituents (such as EC, DOC, $\text{NH}_4^+\text{-N}$, and $\text{NO}_3^-\text{-N}$) and pH impacted the entire 610 mm depth of soil; slightly less mobile species such as WSE-As and WSE-P impacted mainly the top 305-mm depth though there was some evidence of leaching into the deeper layer. While soil samples were not analyzed for water soluble species of Cu, Mn, and Zn and total concentrations of the three metals were analyzed for only a few of the deeper samples, there seemed to be some leaching of Cu into the 76-305 mm depth. It had been expected that concentrations of constituents beneath the stockpiles would be higher at the end of winter stockpiling (also end of study) versus summer stockpiling. However, greater accumulation and leaching of constituents were mainly observed in species with lower reactivity and mobility such as WSE-As and WSE-P; however, compared with the summer litter, the winter litter had more than double the concentrations of both WSE-As and WSE-P (Table 2). Concentrations of highly reactive and mobile species (such as EC, DOC, $\text{NH}_4^+\text{-N}$, and $\text{NO}_3^-\text{-N}$) were in fact, generally, lower throughout the profile at the end of the study than after summer stockpiling probably due to transformation within the sampling depth as well as leaching below the sampling depth. Solid phase As speciation using XANES indicated that As in the soil was mainly in the As(V) form, consistent with the findings in the turkey litter after stockpiling.

CORRELATION OF MEHLICH 3 AND TOTAL CONCENTRATIONS IN THE SOIL

Based on zero intercepts, plots of Mehlich 3 concentrations of P, Cu, Mn, and Zn vs. total concentrations ($n=63$) in the 0-25 and 25-76 mm layers are given in Figures 37-40, respectively. The pH of the soil samples ranged from 4.7 to 8.9. Mehlich 3 concentration as percent of total concentration was specie dependent (Figures 37-40). Since data on total concentrations of P, Cu, Mn, and Zn in the deeper layers were limited, they were not included in the analysis. Similarly, correlations for turkey litter samples were not included since the Mehlich 3 extractant was intended for use with soil and not animal waste.

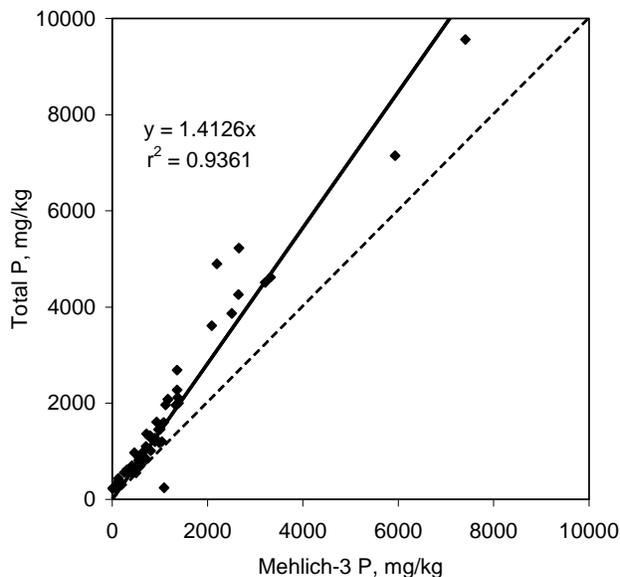


Figure 37. Correlation of Mehlich 3 P versus total P concentrations in the top 76 mm soil layer. The dashed line represents a 1:1 slope.

For Mehlich-3 P concentrations in the range of 4.6 to 7406 mg/kg, total P concentrations were ~141% of the Mehlich-3 P values (Figure 37). A very high r^2 value indicated that Mehlich 3 test was a very good indicator of total P concentration in Orangeburg loamy sand (top 76 mm) though it seemed to be even a better indicator when Mehlich 3 P concentrations are <1400 mg/kg due to less scatter in the data (vs. the full range). Penn and Sims (2002) reported that total P versus Mehlich-3 P r^2 values for Elsinboro (silty clay loam; pH = 6.6) and Woodstown (sandy loam; pH = 6.5) soils were 0.55 and 0.05, respectively. Hence, wide variability in r^2 values among the three soils (also Penn and Sims (2002)) were due to differences in soil properties and properties of the P sources.

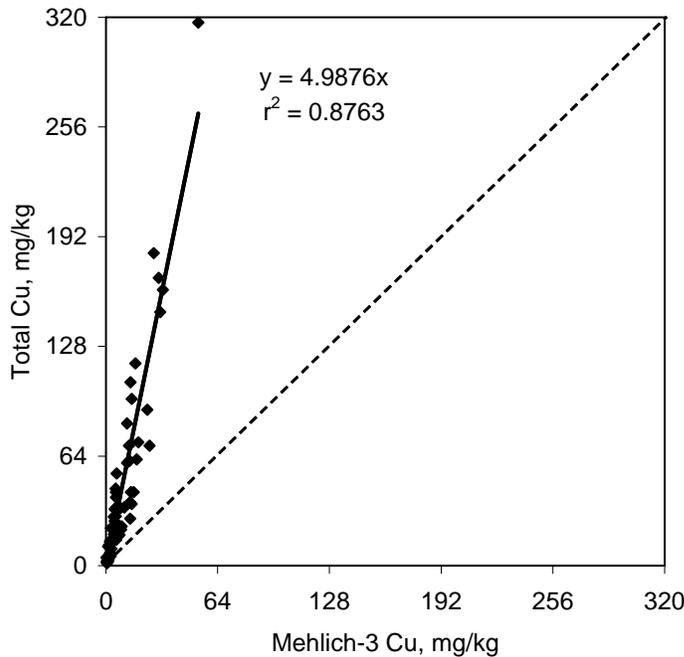


Figure 38. Correlation of Mehlich 3 Cu versus total Cu concentrations in the top 76 mm soil layer. The dashed line represents a 1:1 slope.

For Mehlich-3 Cu concentrations in the range of 0.3 to 53 mg/kg, total Cu concentrations were ~499% of the Mehlich-3 Cu values with a high r^2 value of 0.88 (Figure 38). Of the four species studied, Mehlich 3 Mn vs. total Mn yielded the lowest r^2 value of 0.80 (Figure 39) for Mehlich-3 Mn concentrations in the range of 4 to 267 mg/kg. However, the simpler Mehlich-3 method recovered the largest percentage (84%) of total Mn (vs. the P, Cu, and Zn). Close examination of Figure 39 indicated that Mehlich 3 Mn could be a much better predictor of total Mn when Mehlich-3 Mn concentrations <40 mg/kg. For Mehlich-3 Zn concentrations in the range of 0.3 to 209 mg/kg, total Zn concentrations were ~164% of the Mehlich-3 Zn values (Figure 40). An r^2 value of 0.97 (Figure 39) indicated that Mehlich-3 was an excellent predictor of total Zn in Orangeburg sandy loam (top 76 mm) though lower scatter of data when Mehlich-3 Zn <40 mg/kg indicated that it would perform even better in the lower ranges. No correlations of Mehlich-3 versus total concentrations of Cu, Mn, and Zn could be located in the literature for comparison with the results obtained in this study. Given that animal waste, particularly poultry litter has high concentrations of heavy metals, there is need for correlating Mehlich-3 concentrations with total concentrations of metals for benchmark soils.

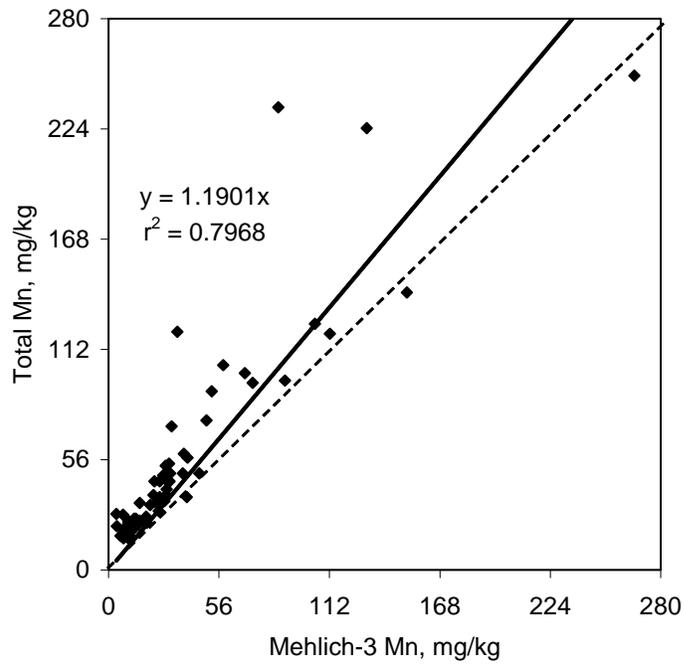


Figure 39. Correlation of Mehlich 3 Mn versus total Mn concentrations in the top 76 mm soil layer. The dashed line represents a 1:1 slope.

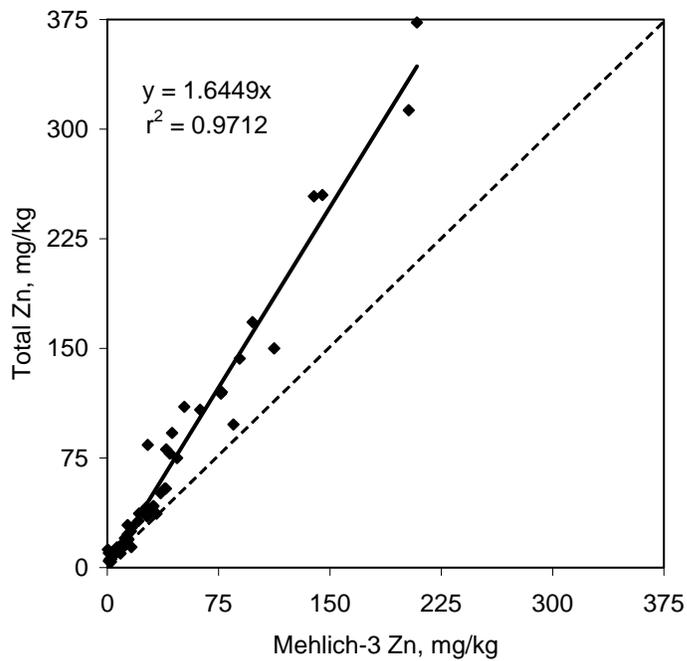


Figure 40. Correlation of Mehlich 3 Zn versus total Zn concentrations in the top 76 mm soil layer. The dashed line represents a 1:1 slope.

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APPENDICES

APPENDIX A. TURKEY LITTER DATA

Table A1. Chemical and physical properties^[a] of initial turkey litter samples (time 0 d) stockpiled in July 2004 (summer) and November 2004 (winter). Data reported at or below the limits of quantitation^[b] (LOQs) are in bold text.

Chemical and Physical Properties ^[a]	Initial litter ^[c] Stockpile 1		Initial litter ^[c] Stockpile 2		Initial litter ^[c] Stockpile 3		Initial litter ^[c] Stockpile 4		Initial litter Grand Mean ^[d]	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
pH	7.59 (0.02)	6.81 (0.01)	7.13 (0.04)	6.9 (0.01)	7.06 (0.02)	6.90 (0.01)	7.09 (0.03)	6.86 (0.01)	7.2 (0.2)	6.87 (0.03)
EC (mS/cm)	10.4 (0.1)	12.5 (0.4)	10.3 (0.2)	11.9 (0.2)	10.9 (0.2)	11.1 (0.2)	10.1 (0.1)	10.7 (0.2)	10.4 (0.2)	11.6 (0.4)
	(mg kg ⁻¹)									
Arsenic (As)	5.6 (0.1)	15 (1)	6.0 (0.1)	16.2 (0.4)	5.8 (0.1)	15 (1)	6.0 (0.1)	16.5 (0.3)	5.9 (0.1)	15.7 (0.4)
WSE-As	3.2 (0.2)	11.8 (0.2)	3.9 (0.1)	11.4 (0.1)	3.5 (0.1)	12.1 (0.2)	3.7 (0.2)	11.8 (0.1)	3.6 (0.2)	11.8 (0.2)
Copper (Cu)	542 (3)	710 (10)	580 (10)	663 (9)	550 (10)	673 (6)	561 (7)	684 (5)	560 (10)	680 (10)
Manganese (Mn)	685 (4)	910 (20)	762 (7)	822 (8)	720 (10)	840 (10)	718 (5)	870 (10)	720 (20)	860 (20)
Zinc (Zn)	690 (20)	1020 (20)	740 (30)	940 (20)	720 (20)	890 (60)	721 (6)	990 (10)	720 (10)	960 (30)
Iron (Fe)	1630 (30)	1410 (30)	1510 (20)	1390 (50)	1650 (90)	1380 (20)	1700 (100)	1520 (40)	1620 (40)	1430 (30)
Aluminum (Al)	1710 (20)	1270 (40)	1540 (30)	1180 (20)	1690 (40)	1160 (30)	1431 (8)	1240 (20)	1590 (70)	1210 (30)
	(g kg ⁻¹) ^[e]									
Carbon (C)	308 (2)	350 (2)	316 (1)	358 (2)	317.1 (0.7)	376 (1)	303 (2)	365 (3)	311 (3)	362 (6)
WSE-DOC	69 (1)	82 (1)	81 (1)	72.9 (0.2)	78 (1)	76 (3)	80 (1)	74.1 (0.3)	77 (3)	76 (2)
Nitrogen (N)	41.2 (0.1)	38.8 (0.3)	43.5 (0.1)	37 (1)	42.41 (0.07)	37.1 (0.4)	42.9 (0.2)	36.6 (0.8)	42.5 (0.5)	37.4 (0.5)
NH ₄ -N	14.5 (0.3)	10.31 (0.02)	15.3 (0.4)	9.25 (0.06)	15.2 (0.2)	10.13 (0.04)	14.8 (0.3)	9.9 (0.2)	15.0 (0.2)	9.9 (0.2)
NO ₃ -N (mg kg ⁻¹)	80 (20)	172 (8)	< 60 (0)	170 (2)	64 (9)	190 (10)	< 60 (0)	174 (4)	66 (5)	176 (4)
Phosphorus (P)	20.73 (0.07)	24.6 (0.4)	23.5 (0.3)	22.8 (0.9)	22.0 (0.2)	22.0 (0.4)	22.0 (0.2)	23.5 (0.5)	22.1 (0.6)	23.2 (0.6)
WSE-P	4.3 (0.1)	10.1 (0.2)	4.93 (0.09)	9.7 (0.2)	4.93 (0.03)	9.707 (0.004)	4.9 (0.2)	9.7 (0.3)	4.8 (0.1)	9.8 (0.1)
Moisture content ^[f] (fraction)	0.345 (0.001)	0.397 (0.001)	0.340 (0.005)	0.381 (0.002)	0.34 (0.0051)	0.379 (0.002)	0.329 (0.001)	0.38 (0.006)	0.338 (0.002)	0.384 (0.002)

^[a] pH and EC were measured at 1:2 turkey litter:water (Peters, et al., 2003). Solid Analytical Method (strong-acid extractable-preparation and analysis) using US-EPA SW-846 were 3050/6010 for ICP-OES analysis (As and P). US-EPA SW-846 3050/7210(Cu), 7460(Mn), 7950(Zn), 7380(Fe), 7020(Al) for AAS. Water-soluble extractable (WSE) As, P, and DOC measured by ICP-OES and total organic carbon analyzer on 1:10 litter:water extracts (Jackson, et al, 2003). Carbon and N were measured by combustion (Nelson and Sommers, 1996); ammonium-nitrogen (NH₄-N) and nitrate-nitrogen (NO₃-N) were measured colorimetrically in 0.5:30 litter:1 M KCl extracts (Peters, et al., 2003).

^[b] Limits of quantitation (LOQs) = to 10x the standard deviation of multiple measurements on a reagent blank or low concentration standard. LOQs determined in this study were: 0.59 mg As kg⁻¹; 0.27 mg Cu kg⁻¹; 0.48 mg Mn kg⁻¹; 0.38 mg Zn kg⁻¹; 3.3 mg Fe kg⁻¹; 24 mg Al kg⁻¹; 0.30 mg WSE-As kg⁻¹; 60 mg WSE-DOC kg⁻¹; 60 mg NH₄-N kg⁻¹; 60 mg NO₃-N kg⁻¹; 300 mg C kg⁻¹; 200 mg N kg⁻¹; 1.2 mg P kg⁻¹; 1.3 mg WSE-P kg⁻¹.

^[c] Data represent weighted means of analytical replicates of the <2 and >2 mm turkey litter fractions (% mass of each fraction). Standard errors of weighted means are shown in parentheses.

^[d] Data represent grand mean of concentrations measured in all four stockpiles (summer and winter). Standard errors of the stockpile means (summer and winter) are shown in parentheses.

^[e] Except where denoted.

^[f] Wet basis; data is for the <2 mm turkey litter fraction with standard errors shown in parentheses.

Table A2. Chemical and physical properties^[a] of summer turkey litter core and skin samples^[b] stockpiled (May - November 2004) for 162 d. Stockpiles 1 and 2 received natural rainfall (NR) and stockpiles 3 and 4 received natural rainfall plus simulated rainfall (NR+SIM). Data reported at or below the limits of quantitation^[c] (LOQ) are in bold text.

Chemical and Physical Properties ^[a]	Summer ^[d] Stockpile 1 NR		Summer ^[d] Stockpile 2 NR		Summer ^[d] Stockpile 3 NR+SIM		Summer ^[d] Stockpile 4 NR+SIM		Summer Grand Mean ^[e] NR		Summer Grand Mean ^[e] NR+SIM	
	Core	Skin	Core	Skin	Core	Skin	Core	Skin	Core	Skin	Core	Skin
pH	6.39 (0.01)	6.80 (0.03)	6.71 (0.01)	6.75 (0.02)	6.59 (0.01)	6.76 (0.02)	6.43 (0.01)	6.69 (0.01)	6.6 (0.1)	6.78 (0.03)	6.5 (0.1)	6.73 (0.04)
EC (mS/cm)	15.3 (0.2)	8.8 (0.2)	14.8 (0.9)	7.09 (0.09)	14.3 (0.6)	5.4 (0.2)	15.0 (0.1)	5.7 (0.2)	15.1 (0.3)	7.9 (0.9)	14.7 (0.4)	5.6 (0.1)
	(mg kg ⁻¹)											
Arsenic (As)	6.9 (0.4)	7 (1)	9.8 (0.7)	5.8 (0.3)	7.5 (0.4)	5.0 (0.1)	8.0 (1)	4.5 (0.2)	8 (1)	6.4 (0.6)	7.8 (0.2)	4.8 (0.3)
WSE-As	5.09 (0.04)	3.9 (0.1)	6.8 (0.1)	2.99 (0.03)	5.86 (0.03)	1.85 (0.04)	5.51 (0.04)	1.13 (0.03)	5.9 (0.7)	3.4 (0.5)	5.7 (0.1)	1.5 (0.4)
Copper (Cu)	645 (7)	830 (10)	780 (10)	878 (9)	712 (6)	770 (30)	740 (6)	730 (7)	710 (70)	850 (20)	730 (10)	750 (20)
Manganese (Mn)	763 (4)	1380 (10)	910 (20)	1450 (50)	830 (9)	1450 (10)	856 (7)	1456 (8)	840 (70)	1420 (40)	840 (10)	1453 (3)
Zinc (Zn)	1000 (100)	1320 (60)	1120 (30)	1410 (40)	1010 (50)	1330 (40)	1000 (20)	1350 (20)	1060 (60)	1370 (50)	1005 (3)	1340 (10)
Iron (Fe)	2150 (20)	2620 (90)	1710 (40)	2580 (30)	2000 (100)	2800 (20)	1650 (30)	2650 (20)	1900 (200)	2600 (20)	1800 (200)	2730 (70)
Aluminum (Al)	2100 (50)	2420 (90)	1520 (30)	2100 (100)	1730 (10)	2660 (50)	1710 (60)	2650 (80)	1800 (300)	2300 (200)	1720 (10)	2655 (6)
	(g kg ⁻¹) ^[f]											
Carbon (C)	318 (4)	309 (4)	343 (4)	282 (3)	348 (3)	307 (2)	343 (4)	310 (10)	330 (10)	300 (10)	346 (2)	309 (2)
WSE-DOC	89 (2)	39.3 (0.5)	103.9 (0.5)	28.8 (0.8)	100.6 (0.1)	17 (5)	65 (2)	9.6 (0.6)	96 (7)	34 (5)	80 (20)	13 (4)
Nitrogen	35.0 (0.6)	33.7 (0.3)	37.6 (0.3)	28.6 (0.3)	37.9 (0.7)	25 (1)	38.2 (0.6)	24.0 (0.8)	36 (1)	31 (3)	38.0 (0.1)	24.5 (0.3)
NH ₄ -N	12.5 (0.1)	3.84 (0.04)	18.4 (0.1)	2.92 (0.06)	16.9 (0.2)	1.57 (0.05)	13.6 (0.2)	2.00 (0.01)	15 (3)	3.4 (0.5)	15 (2)	1.8 (0.2)
NO ₃ -N (mg kg ⁻¹)	131 (4)	717 (7)	140 (2)	1000 (10)	136 (5)	1197 (7)	200 (6)	2100 (20)	136 (4)	860 (140)	170 (30)	1650 (450)
Phosphorus (P)	23.1 (0.7)	35.9 (0.9)	25.0 (0.5)	37.7 (0.5)	23.78 (0.04)	38.4 (0.3)	24.5 (0.3)	35.1 (0.4)	24 (1)	36.8 (0.9)	24.1 (0.4)	37 (2)
WSE-P	7.81 (0.09)	5.57 (0.08)	8.5 (0.3)	6.06 (0.09)	7.74 (0.01)	4.37 (0.02)	7.55 (0.09)	3.48 (0.01)	8.2 (0.3)	5.8 (0.2)	7.65 (0.09)	3.9 (0.4)
Moisture content ^[g] (fraction)	0.37 (0.006)	0.45 (0.008)	0.506 (0.003)	0.49 (0.019)	0.49 (0.01)	0.53 (0.011)	0.468 (0.004)	0.45 (0.008)	0.44 (0.055)	0.47 (0.018)	0.48 (0.009)	0.49 (0.038)

^[a] See Table A1 for methods description.

^[b] Skin is the surface thickness of ~150 mm.

^[c] See Table A1 for LOQ description.

^[d] See Table A1.

^[e] See Table A1.

^[f] Except where denoted.

^[g] See Table A1.

Table A3. Chemical and physical properties^[a] of turkey litter core and skin samples^[b] stockpiled during winter (November 2004 to April 2005) for 161 d. Stockpiles 1 and 2 received natural rainfall (NR) and stockpiles 3 and 4 received natural rainfall plus simulated rainfall (NR+SIM). Data reported at or below the limits of quantitation^[c] (LOQs) are in bold text.

Chemical and Physical Properties ^[a]	Winter ^[d] Stockpile 1 NR		Winter ^[d] Stockpile 2 NR		Winter ^[d] Stockpile 3 NR+SIM		Winter ^[d] Stockpile 4 NR+SIM		Winter Grand Mean ^[e] NR		Winter Grand Mean ^[e] NR+SIM	
	Core	Skin	Core	Skin	Core	Skin	Core	Skin	Core	Skin	Core	Skin
pH	7.67 (0.01)	6.84 (0.02)	7.71 (0.01)	6.89 (0.01)	8.19 (0.01)	7.56 (0.02)	7.87 (0.01)	7.62 (0.02)	7.69 (0.02)	6.87 (0.03)	8.0 (0.1)	7.59 (0.04)
EC (mS/cm)	9.26 (0.06)	6.52 (0.06)	10.34 (0.09)	6.1 (0.1)	11.18 (0.05)	5.4 (0.2)	8.4 (0.1)	5.4 (0.2)	9.8 (0.5)	6.3 (0.2)	9.8 (1)	5.4 (0)
	(mg kg ⁻¹)											
Arsenic (As)	15.0 (0.4)	17.1 (0.8)	13.6 (0.3)	14.9 (0.2)	16.05 (0.07)	17.0 (0.2)	16.3 (0.4)	15.94 (0.02)	14.3 (0.7)	16 (1)	16.2 (0.1)	16.5 (0.5)
WSE-As	10.59 (0.03)	7.0 (0.4)	8.94 (0.05)	6.04 (0.01)	11.57 (0.05)	6.58 (0.04)	10.2 (0.1)	7.84 (0.08)	9.8 (0.7)	6.5 (0.5)	10.9 (0.7)	7.2 (0.6)
Copper (Cu)	753 (8)	830 (7)	672 (8)	754 (4)	739 (6)	780 (10)	757 (2)	770 (4)	710 (40)	790 (40)	750 (10)	780 (10)
Manganese (Mn)	927 (6)	1080 (10)	867 (7)	1026 (5)	1040 (10)	1330 (20)	1110 (10)	1310 (10)	900 (30)	1050 (30)	1080 (30)	1320 (10)
Zinc (Zinc)	1078 (5)	1240 (30)	1050 (60)	1153 (7)	1220 (30)	1480 (30)	1251 (6)	1450 (40)	1060 (10)	1200 (50)	1240 (10)	1470 (10)
Iron (Fe)	1840 (40)	1750 (20)	1770 (10)	1730 (50)	1830 (20)	2160 (60)	1900 (60)	2140 (50)	1800 (40)	1740 (10)	1870 (30)	2150 (10)
Aluminum (Al)	1980 (40)	1930 (20)	2330 (30)	1840 (30)	1890 (30)	2360 (90)	2190 (40)	2490 (70)	2200 (200)	1890 (40)	2000 (200)	2430 (70)
	(g kg ⁻¹) ^[f]											
Carbon (C)	309 (2)	352 (5)	268 (7)	337 (4)	300 (2)	312 (7)	303 (9)	287 (2)	290 (20)	350 (10)	302 (1)	300 (10)
WSE-DOC	46 (3)	28.6 (0.4)	36.0 (0.4)	32.4 (0.8)	56.8 (0.2)	20.66 (0.02)	38.7 (0.5)	20.2 (0.3)	41 (5)	31 (2)	48 (9)	20.4 (0.2)
Nitrogen	33.0 (0.4)	33.8 (0.6)	30.4 (0.1)	32.8 (0.4)	31.71 (0.09)	33.4 (0.6)	32.55 (0.06)	31.2 (0.1)	32 (1)	33.3 (0.5)	32.1 (0.4)	32 (1)
NH ₄ -N	8.04 (0.02)	5.43 (0.09)	7.78 (0.09)	5.13 (0.08)	8.8 (0.3)	3.52 (0.06)	6.25 (0.06)	3.35 (0.03)	7.9 (0.1)	5.3 (0.1)	8 (1)	3.44 (0.07)
NO ₃ -N (mg kg ⁻¹)	133 (5)	289 (5)	29 (3)	370 (20)	290 (40)	360 (10)	28 (5)	110 (2)	80 (50)	330 (40)	200 (100)	200 (100)
Phosphorus (P)	26.8 (0.3)	29.9 (0.2)	24.8 (0.6)	28.8 (0.4)	29.2 (0.7)	34.4 (0.8)	30.5 (0.9)	34 (1)	26 (1)	29.4 (0.5)	29.9 (0.6)	34.2 (0.1)
WSE-P	5.26 (0.04)	4.3 (0.6)	4.66 (0.01)	4.04 (0.02)	5.32 (0.09)	2.75 (0.01)	4.0 (0.01)	2.79 (0.09)	5.0 (0.3)	4.2 (0.1)	4.7 (0.7)	2.77 (0.02)
Moisture content ^[g] (fraction)	0.363 (0.002)	0.48 (0.001)	0.304 (0.002)	0.511 (0.003)	0.33 (0.005)	0.499 (0.002)	0.36 (0.002)	0.52 (0.033)	0.33 (0.015)	0.50 (0.02)	0.34 (0.005)	0.51 (0.01)

^[a] See Table A1 for methods description.

^[b] Skin is the surface thickness of ~150 mm.

^[c] See Table A1 for LOQ description.

^[d] See Table A1.

^[e] See Table A1.

^[f] Except where denoted.

^[g] See Table A1.

APPENDIX B. SOIL DATA

Table B1. Chemical and physical properties^[a] of soil samples from four depths (0-25, 25-76, 76-305, 305-610 mm) prior to stockpiling litter in July 2004. Data reported at or below the limits of quantitation^[b] (LOQs) are in bold text.

Chemical and Physical Properties^[a]	Initial Soil^[c] (0-76 mm)	Initial Soil^[c] (0-76 mm)	Initial Soil^[c] (0-76 mm)	Initial Soil Grand Mean^[d] (0-76 mm)
pH	5.36 (0.06)	5.47 (0.05)	5.45 (0.04)	5.43 (0.01)
EC (uS/cm)	62 (2)	17.9 (0.5)	37.6 (0.7)	40 (20)
			(mg kg ⁻¹) ^[e]	
Arsenic (As)	1.09 (0.03)	0.81 (0.03)	0.9 (0.2)	0.9 (0.1)
WSE-As	0 (0)	0 (0)	0 (0)	0 (0)
Copper (Cu)	3.30 (0.06)	1.7 (0.3)	2.6 (0.9)	2.5 (0.8)
Mehlich 3-Cu	0.6	0.5	0.4	0.5(0.1) [20] ^[f]
Manganese (Mn)	33 (1)	24.6 (0.5)	26.8 (0.6)	28 (4)
Mehlich 3-Mn	9	7	7	8(1) [29] ^[f]
Zinc (Zn)	12.4 (0.9)	8 (1)	9 (1)	10 (2)
Mehlich 3-Zn	4	2	3	3(1) [30] ^[f]
Iron (Fe) (g kg ⁻¹)	3.79 (0.05)	2.58 (0.04)	2.9 (0.7)	3.1 (0.6)
Aluminum (Al) (g kg ⁻¹)	5.8 (0.3)	4.09 (0.04)	4.4 (0.2)	4.8 (0.9)
Carbon (C) (g kg ⁻¹)	16.6 (0.3)	14.2 (0.7)	9.9 (0.5)	14 (3)
WSE-DOC	44 (10)	36.8 (0.9)	33 (3)	38 (6)
Nitrogen (N)	1870 (60)	1570 (60)	1070 (60)	1500 (400)
NH ₄ -N	13.24 (0.04)	11.15 (0.06)	6.9 (0.4)	10 (3)
NO ₃ -N	19.3 (0.6)	10 (2)	15 (1)	15 (5)
Phosphorus (P)	363 (1)	299 (8)	290 (20)	320 (40)
Mehlich 3-P	93	106	101	100(7) [31] ^[f]
WSE-P	4.68 (0.03)	6.55 (0.09)	2.81 (0.07)	4.7 (1.9)
Moisture content (fraction)	0.06 (0.003)	0.06 (<0.001)	0.03 (<0.001)	0.05 (0.001)

Table B1. (continued).

Chemical and Physical Properties ^[a]	Initial Soil ^[c] (76-305 mm)	Initial Soil ^[c] (76-305 mm)	Initial Soil ^[c] (76-305 mm)	Initial Soil Grand Mean ^[d] (76-305 mm)
pH	5.66 (0.03)	5.73 (0.04)	5.83 (0.09)	5.74 (0.09)
EC (uS/cm)	34.5 (0.03)	22 (1)	16.7 (0.5)	24 (9)
	(mg kg ⁻¹) ^[e]			
Arsenic (As)	1.0 (0.1)	0.73 (0.07)	0.85 (0.04)	0.9 (0.1)
WSE-As	0 (0)	0 (0)	0 (0)	0.0
Copper (Cu)	2.7 (0.2)	1.3 (0.3)	1.5 (0.1)	1.8 (0.8)
Mehlich 3-Cu	0.7	0.4	0.5	0.5(0.2) [28] ^[f]
Manganese (Mn)	22 (1)	22 (1)	22.6 (0.2)	22.2 (0.4)
Mehlich 3-Mn	5	4	4	4.3(0.6) [19] ^[f]
Zinc (Zn)	6.3 (0.5)	18 (4)	5.9 (0.7)	10 (7)
Mehlich 3-Zn	1	0.5	1	0.8(0.3) [8] ^[f]
Iron (Fe) (g kg ⁻¹)	3.31 (0.08)	2.45 (0.04)	2.5 (0.1)	2.8 (0.5)
Aluminum (Al) (g kg ⁻¹)	5.2 (0.5)	3.97 (0.07)	4.5 (0.1)	4.6 (0.6)
Carbon (C) (g kg ⁻¹)	5.67 (0.06)	2.90 (0.1)	3.0 (0.1)	4 (2)
WSE-DOC	20 (2)	15.1 (0.8)	16 (1)	17 (3)
Nitrogen (N)	770 (60)	430 (60)	400 (0)	500 (200)
NH ₄ -N	0.56 (0.06)	0.2 (0.2)	0.46 (0.06)	0.4 (0.2)
NO ₃ -N	13.8 (0.3)	8.2 (0.5)	7.3 (0.1)	10 (4)
Phosphorus (P)	250 (10)	203 (8)	206 (4)	220 (30)
Mehlich 3-P	76	66	75	72(6) [33] ^[f]
WSE-P	2.23 (0.02)	1.1 (0.7)	0.94 (0.04)	1.4 (0.7)
Moisture content (fraction)	0.07 (<0.001)	0.06 (<0.001)	0.05 (<0.001)	0.05 (<0.001)

Table B1. (continued).

Chemical and Physical Properties ^[a]	Initial Soil ^[c] (305-610 mm)	Initial Soil ^[c] (305-610 mm)	Initial Soil ^[c] (305-610 mm)	Initial Soil Grand Mean ^[d] (305-610 mm)
pH	5.59 (0.02)	4.6 (0.1)	5.77 (0.02)	5.32 (0.6)
EC (uS/cm)	25.4 (0.5)	22.1 (0.5)	15.6 (0.4)	21 (5)
	(mg kg ⁻¹) ^[e]			
Arsenic (As)	3.5 (0.1)	4.1 (0.1)	2.2 (0.2)	3.3 (0.1)
WSE-As	0 (0)	0 (0)	0 (0)	0.0
Copper (Cu)	5.5 (0.3)	5.5 (0.2)	3.4 (0.3)	5 (1)
Mehlich 3-Cu	0.4	0.2	0.3	0.3(0.1) [6] ^[f]
Manganese (Mn)	33.3 (0.6)	24 (1)	28 (1)	28 (5)
Mehlich 3-Mn	3	2	7	4(3) [14] ^[f]
Zinc (Zn)	11.9 (0.5)	13.6 (0.1)	12 (1)	13 (1)
Mehlich 3-Zn	0.4	0.3	0.3	0.33(0.06) [3] ^[f]
Iron (Fe) (g kg ⁻¹)	13.58 (0.07)	16.5 (0.2)	9.0 (0.1)	13 (4)
Aluminum (Al) (g kg ⁻¹)	19 (2)	23.9 (0.6)	14.7 (0.7)	19 (5)
Carbon (C) (g kg ⁻¹)	4.3 (0.2)	2.9 (0.1)	2.0 (0.1)	3 (1)
WSE-DOC	9 (1)	10 (2)	10 (2)	10 (1)
Nitrogen (N)	900 (0)	900 (0)	500 (0)	800 (200)
NH ₄ -N	0.5 (0.4)	0.7 (0.6)	0.4 (0.1)	0.5 (0.2)
NO ₃ -N	4.5 (0.1)	2.1 (0.9)	1.8 (0.3)	3 (2)
Phosphorus (P)	253 (4)	255 (8)	187 (5)	230 (40)
Mehlich 3-P	6	1	7	5(3) [2] ^[f]
WSE-P	0.02 (0.04)	0.00 (0.01)	0.01 (0.01)	0.01 (0.01)
Moisture content (fraction)	0.12 (0)	0.13 (<0.001)	0.064 (0.003)	0.11 (0.004)

^[a] pH and EC were measured at 1:1 soil:water (Peters, et al., 2003). Solid Analytical Method (strong-acid extractable-preparation and analysis) using US-EPA SW-846 3050/6010 for ICP-OES analysis (As and P). US-EPA SW-846 3050/7210(Cu), 7460(Mn), 7950(Zn), 7380(Fe), 7020(Al) for AAS. Water-soluble extractable (WSE) As, P, and DOC were measured by ICP-OES and total organic carbon analyzer on 1:10 soil:water extracts (Jackson, et al, 2003). Carbon and N were measured by combustion (Nelson and Sommers, 1996) and ammonium-nitrogen (NH₄-N) and nitrate-nitrogen (NO₃-N) were measured colorimetrically on 1:10 soil:1 M KCl extracts (Peters, et al., 2003). Mehlich-3 extractations performed according to Mehlich (1984).

^[b] Limits of quantitation (LOQ) is equal to 10x the standard deviation of multiple measurements on a reagent blank or low concentration standard. LOQs determined in this study were: 0.30 mg As kg⁻¹; 0.30 mg WSE-As kg⁻¹; 0.59 mg P kg⁻¹; 1.3 mg WSE-P kg⁻¹; 300 mg C kg⁻¹; 10 mg DOC kg⁻¹; 200 mg N kg⁻¹; 1 mg NH₄-N or NO₃-N kg⁻¹; 0.27 mg Cu kg⁻¹; 0.48 mg Mn kg⁻¹; 0.38 mg Zn kg⁻¹; 3.3 mg Fe kg⁻¹; 24 mg Al kg⁻¹.

^[c] Data represent the mean and standard deviation (in parentheses) of 3 analytical replicates.

^[d] Data represent the grand mean of concentrations measured in all three initial soil samples. Standard deviations of those means are shown in parentheses.

^[e] Except where denoted.

^[f] Mehlich data is for single sample analysis. The mean of concentrations measured in all three soil samples is shown with standard deviations in parentheses. Percent of strong-acid extractable metal is in brackets.

Table B2. Chemical and physical properties^[a] of soils sampled between stockpiles at various depths (0-25, 25-76, 76-305, 305-610 mm) after 161 d(summer) and 162 d (winter) of stockpiling, respectively. Data reported at or below the limits of quantitation^[b] (LOQs) are in bold text.

Chemical and Physical Properties ^[a]	Soil Between ^[c] Stockpile 1 & 2 (0-25 mm)		Soil Between ^[c] Stockpile 2 & 3 (0-25 mm)		Soil Between ^[c] Stockpile 3 & 4 (0-25 mm)		Soil Between Stockpiles Grand Mean ^[d] (0-25 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
pH	4.87 (0.05)	5.43 (0.02)	4.81 (0.02)	5.43 (0.01)	4.53 (0.02)	5.05 (0.08)	4.7 (0.2)	5.3 (0.2)
EC (uS/cm)	210 (20)	121 (9)	190 (10)	95 (5)	310 (30)	120 (30)	240 (60)	110 (20)
	(mg kg ⁻¹) ^[e]							
Arsenic (As)	0.73 (0.06)	0.92 (0.04)	0.64 (0.01)	0.59 (0.01)	0.52 (0.02)	0.55 (0.04)	0.6 (0.1)	0.7 (0.2)
WSE-As	<0.3 (0)	0.01 (0)	<0.3 (0)	0.02 (0.01)	<0.3 (0)	0.01 (0.02)	<0.3 (0)	0.01 (0.01)
Copper (Cu)	15 (8)	4.4 (0.1)	3.5 (0.3)	3.0 (0.2)	4.1 (0.6)	4.3 (0.8)	8 (6)	3.9 (0.8)
Mehlich 3-Cu	3	1	1	1	1	1	2(1) [25] ^[g]	1(0) [26] ^[g]
Manganese (Mn)	45.4 (0.4)	53 (4)	45 (2)	45 (2)	38 (1)	54.0 (0.5)	43 (4)	51 (5)
Mehlich 3-Mn	26	27	24	22	26	29	25(1) [58] ^[g]	26(4) [51] ^[g]
Zinc	16.1 (0.2)	19 (2)	14.5 (0.4)	15 (1)	14 (4)	21 (3)	15 (1)	18 (3)
Mehlich 3-Zn	10	13	8	8	8	12	9(1) [60] ^[g]	11(2) [61] ^[g]
Carbon (g kg ⁻¹)	23 (1)	36 (4)	22 (4)	27 (3)	23 (1)	37 (5)	22.6 (0.6)	33 (6)
WSE-DOC	98 (4)	131.3 (0.3)	130 (10)	86.9 (0.1)	71 (5)	92 (2)	100 (30)	100 (20)
Nitrogen (N)	2100 (0)	3200 (300)	1900 (400)	2300 (300)	2000 (200)	3200 (400)	2000 (100)	2900 (500)
NH ₄ -N	31 (5)	33.0 (0.8)	21 (2)	23 (2)	12.1 (0.1)	5.3 (0.2)	20 (10)	20 (10)
NO ₃ -N	22.4 (0.8)	3.2 (0.2)	11.6 (0.2)	4.4 (0.4)	66 (2)	28.7 (0.7)	30 (30)	12 (14)
Phosphorus (P)	393 (3)	440 (10)	320 (20)	348 (2)	337 (6)	380 (6)	350 (40)	390 (50)
Mehlich 3-P	130	120	120	110	140	130	130(10) [37] ^[g]	120(10) [31] ^[g]
WSE-P	10.2 (0.5)	12 (1)	10.2 (0.2)	12.7 (0.6)	9.3 (0.2)	8.9 (0.2)	9.9 (0.5)	11 (2)
Moisture content (fraction)	0.895 (0.002)	0.919 (0.003)	0.921 (0.001)	0.934 (0.001)	0.89 (0.03)	0.939 (0.002)	0.90 (0.02)	0.93 (0.01)

Table B2. (continued).

Chemical and Physical Properties ^[a]	Soil Between ^[c] Stockpile 1 & 2 (25-76 mm)		Soil Between ^[c] Stockpile 2 & 3 (25-76 mm)		Soil Between ^[c] Stockpile 3 & 4 (25-76 mm)		Soil Between Stockpiles Grand Mean ^[d] (25-76 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
pH	4.71 (0.04)	5.44 (0.06)	4.77 (0.02)	5.34 (0.02)	4.68 (0.06)	4.96 (0.02)	4.72 (0.05)	5.2 (0.3)
EC (uS/cm)	140 (10)	56 (3)	120 (30)	48 (3)	120 (20)	50 (1)	130 (10)	51 (4)
	(mg kg ⁻¹) ^[e]							
Arsenic (As)	0.7 (0.1)	0.76 (0.09)	0.62 (0.05)	0.7 (0.1)	0.52 (0.04)	0.52 (0.01)	0.6 (0.1)	0.7 (0.1)
WSE-As	<0.3 (0)	0.0 (0)	<0.3 (0)	0.02 (0.01)	<0.3 (0)	0.02 (0.01)	<0.3 (0)	0.01 (0.01)
Copper (Cu)	5.7 (0.5)	3.05 (0.03)	3.3 (0.4)	2.0 (0.1)	2.8 (0.3)	1.5 (0.6)	4 (2)	2.2 (0.8)
Mehlich 3-Cu	3	0.8	1.1	0.8	1.2	0.5	2(1) [50] ^[g]	0.7(0.2) [32] ^[g]
Manganese (Mn)	20.0 (0.8)	24 (3)	21.2 (0.8)	25 (1)	18 (1)	17.3 (0.8)	20 (2)	22 (4)
Mehlich 3-Mn	7	9	8	10	7	6	7.3(0.5) [37] ^[g]	8(2) [36] ^[g]
Zinc	8.5 (0.2)	8.8 (0.9)	8.1 (0.7)	9.2 (0.1)	6 (1)	4 (1)	8 (1)	7 (3)
Mehlich 3-Zn	3	4	3	4	2	2	2.6(0.6) [33] [g]	3(2) [43] ^[g]
Carbon (g kg ⁻¹)	9.5 (0.5)	12.2 (0.4)	11 (1)	13.2 (0.8)	7 (1)	8.25 (0.07)	9 (2)	11 (3)
WSE-DOC	47 (1)	52 (2)	54 (8)	51 (3)	41 (2)	38 (1)	47 (7)	47 (8)
Nitrogen (N)	950 (70)	1250 (70)	950 (70)	1200 (0)	700 (200)	800 (0)	900 (200)	1100 (300)
NH ₄ -N	4 (2)	14 (1)	4 (3)	9.1 (0.4)	8 (4)	3 (2)	5 (2)	9 (6)
NO ₃ -N	23.75 (0.07)	4.9 (0.1)	23 (4)	3.9 (0.3)	14.95 (0.01)	7.3 (0.2)	21 (5)	5 (2)
Phosphorus (P)	310 (104)	335 (8)	340 (50)	279 (7)	280 (20)	276 (2)	310 (30)	300 (30)
Mehlich 3-P	110	120	110	120	130	140	120(10) [39] ^[g]	130(10) [43] ^[g]
WSE-P	4.0 (0.1)	5.48 (0.01)	2.94 (0.06)	5.88 (0.01)	4.0 (0.1)	4.55 (0.02)	3.6 (0.6)	5.3 (0.7)
Moisture content (fraction)	0.927 (0.001)	0.932 (0.001)	0.940 (0.001)	0.944 (0.001)	0.91 (0.03)	0.9639 (0.0003)	0.93 (0.02)	0.95 (0.02)

Table B2. (continued).

Chemical and Physical Properties ^[a]	Soil Between ^[c] Stockpile 1 & 2 (76-305 mm)		Soil Between ^[c] Stockpile 2 & 3 (76-305 mm)		Soil Between ^[c] Stockpile 3 & 4 (76-305 mm)		Soil Between Stockpiles Grand Mean ^[d] (76-305 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
pH	5.31 (0.03)	5.42 (0.01)	5.36 (0.03)	5.42 (0.05)	5.33 (0.02)	5.7 (0.04)	5.33 (0.03)	5.5 (0.2)
EC (uS/cm)	30 (2)	67 (8)	19.3 (0.7)	31 (3)	25.3 (0.7)	19 (3)	25 (5)	40 (30)
	(mg kg ⁻¹) ^[e]							
Arsenic (As)	NA ^[f]	NA	NA	NA	NA	NA	-----	-----
WSE-As	<0.3 (0)	0.02 (0.001)	<0.3 (0)	0.01 (0.01)	<0.3 (0)	0.0 (0)	<0.3 (0)	0.01 (0.01)
Copper (Cu)	NA	NA	NA	NA	NA	NA	-----	-----
Mehlich 3-Cu	0.6	0.4	0.3	0.4	0.4	0.4	0.4 (0.2)	0.4 (0)
Manganese (Mn)	NA	NA	NA	NA	NA	NA	-----	-----
Mehlich 3-Mn	3	3	4	5	3	4	3.3 (0.6)	4 (1)
Zinc	NA	NA	NA	NA	NA	NA	-----	-----
Mehlich 3-Zn	0.8	0.8	0.8	1	0.8	1	0.8 (0)	0.9 (0.1)
Carbon (g kg ⁻¹)	3.0 (0.6)	3.0 (0.3)	2.67 (0.06)	4.5 (0.4)	2.5 (0)	3.4 (0.8)	2.7 (0.3)	3.6 (0.8)
WSE-DOC	29 (4)	20 (3)	27 (4)	17.2 (0.8)	26 (1)	16 (1)	27 (2)	18 (2)
Nitrogen (N)	250 (60)	300 (0)	230 (60)	400 (0)	200 (0)	300 (100)	230 (305)	330 (60)
NH ₄ -N	1.6 (1.6)	1.0 (0.2)	0 (0)	2.6 (0.8)	2 (1)	2 (2)	1 (1)	1.9 (0.8)
NO ₃ -N	5.5 (0.5)	3.8 (0.2)	5.1 (0.3)	3.25 (0.02)	6.1 (0.1)	3.5 (1.4)	5.6 (0.5)	3.5 (0.3)
Phosphorus (P)	NA	NA	NA	NA	NA	NA	-----	-----
Mehlich 3-P	50	35	90	90	110	120	80 (30)	80 (40)
WSE-P	0.688 (0.004)	0.5 (0.3)	1.23 (0.04)	2.1 (0.1)	2.35 (0.02)	1.5 (0.2)	1.4 (0.8)	1.4 (0.8)
Moisture content (fraction)	0.95 (0.01)	0.956 (0.001)	0.956 (0.001)	0.958(0.0003)	0.9470(0.0004)	0.9559(0.0003)	0.951 (0.005)	0.957 (0.001)

Table B2. (continued).

Chemical and Physical Properties ^[a]	Soil Between ^[c] Stockpile 1 & 2 (305-610 mm)		Soil Between ^[c] Stockpile 2 & 3 (305-610 mm)		Soil Between ^[c] Stockpile 3 & 4 (305-610 mm)		Soil Between Stockpiles Grand Mean ^[d] (305-610 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
pH	5.62 (0.01)	5.47 (0.03)	5.49 (0.02)	5.56 (0.05)	5.33 (0.03)	5.85 (0.17)	5.5 (0.1)	5.6 (0.2)
EC (uS/cm)	26 (3)	31 (1)	30 (2)	23 (3)	26.7 (0.9)	31 (5)	28 (2)	28 (5)
	(mg kg ⁻¹) ^[e]							
Arsenic (As)	NA ^[f]	NA	NA	NA	NA	NA	-----	-----
WSE-As	<0.3 (0)	0.01 (0.0)	<0.3 (0)	0.0 (0)	<0.3 (0)	0.0 (0)	<0.3 (0)	0.003 (0.005)
Copper (Cu)	NA	NA	NA	NA	NA	NA	-----	-----
Mehlich-Cu	0.2	0.2	0.2	0.2	0.2	0.3	0.2 (0)	0.23 (0.06)
Manganese (Mn)	NA	NA	NA	NA	NA	NA	-----	-----
Mehlich-Mn	2	1	10	2	2	7	5 (5)	3 (3)
Zinc	NA	NA	NA	NA	NA	NA	-----	-----
Mehlich-Zn	0.6	0.2	0.8	0.3	0.8	0.3	0.7 (0.1)	0.27 (0.06)
Carbon (g kg ⁻¹)	1.85 (0.07)	3.33 (0.06)	3.1 (0.1)	3.3 (0.7)	2.2 (0.1)	3.6 (0.4)	2.4 (0.6)	3.4 (0.2)
WSE-DOC	17 (6)	21 (3)	40 (20)	22.1 (0.5)	8.7 (0.3)	25 (1)	20 (20)	23 (2)
Nitrogen (N)	200 (0)	475 (50)	300 (0)	350 (60)	230 (60)	270 (60)	240 (50)	360 (110)
NH ₄ -N	1.6 (0.7)	4 (1)	4 (6)	0.9 (0.1)	0.5 (0.8)	13.7 (0.3)	2 (2)	6 (7)
NO ₃ -N	1.7 (0.2)	2.6 (0.3)	1.8 (0.4)	1.6 (0.1)	2.3 (0.6)	2.0 (0.5)	1.9 (0.3)	2.1 (0.5)
Phosphorus (P)	NA	NA	NA	NA	NA	NA	-----	-----
Mehlich 3-P	0.7	0	6	4	8	20	5 (4)	8 (10)
WSE-P	<1.3 (0)	0.01 (0.06)	<1.3 (0)	0.0 (0)	<1.3 (0)	0.0 (0)	<1.3 (0)	0.003 (0.005)
Moisture content (fraction)	0.910(0.002)	0.855(0.003)	0.907(0.001)	0.910 (0.002)	0.911 (0.001)	0.899 (0.002)	0.909 (0.002)	0.89 (0.03)

^[a] See footnote in Table B1 for methods.

^[b] See footnote in Table B1 for limits of quantitation.

^[c] Data represent the mean and standard deviation (in parentheses) of 3 analytical replicates.

^[d] Data represent the grand mean of concentrations measured in all three soil samples (summer and winter). Standard deviations of those means are shown in parentheses.

^[e] Except where denoted.

^[f] Not analyzed.

^[g] Mehlich data is for single sample analysis. The mean of concentrations measured in all three soil samples (summer or winter) is shown with standard deviations in parentheses. Percent of strong-acid extractable metal is shown in parentheses for the 0-3 and 3-12 cm depths.

Table B3. Chemical and physical properties^[a] of soils sampled beneath center of litter stockpiles at various depths (0-25, 25-76, 76-305, 305-610 mm) after 161 d (summer) and 162 d (winter) of stockpiling, respectively. Data reported at or below the limits of quantitation[‡] (LOQs) are in bold text.

Chemical and Physical Properties ^[a]	Beneath Stockpile 1 ¹		Beneath Stockpile 2 ¹		Beneath Stockpile 3 ¹		Beneath Stockpile 4 ¹		Grand Mean ^[d]		Grand Mean ^[d]	
	Center NR (0-25 mm)		Center NR (0-25 mm)		Center NR+SIM (0-25 mm)		Center NR+SIM (0-25 mm)		NR (0-25 mm)		NR+SIM (0-25 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
pH	8.15 (0.01)	8.80 (0.02)	8.15 (0.05)	8.87 (0.01)	8.71 (0.04)	8.84 (0.01)	6.41(0.02)	8.93 (0.01)	8.2 (0)	8.84 (0.05)	8 (2)	8.9 (0.1)
EC(mS/cm)	6.1 (0.5)	9.3 (0.7)	9.5 (0.3)	10 (1)	7.3 (0.3)	8.9 (0.1)	2.3 (0.4)	4.7 (0.2)	8 (2)	9.7 (0.5)	5 (4)	7 (3)
------(mg kg ⁻¹) ^[e] -----												
Arsenic (As)	1.40 (0.07)	2.3 (0.1)	0.98 (0.08)	2.56 (0.04)	0.77 (0.05)	2.83 (0.03)	0.47 (0.04)	1.02 (0.02)	1.2 (0.3)	2.4 (0.2)	0.6 (0.2)	2 (1)
WSE-As	0.47 (0.02)	1.21 (0.02)	0.260 (0.001)	1.5 (0.1)	0.18 (0.01)	1.87 (0.03)	<0.3 (0)	0.48 (0.01)	0.4 (0.1)	1.4 (0.2)	0.24 (0.08)	1.2 (0.9)
Copper (Cu)	60 (3)	97.3 (0.7)	33.7 (0.2)	118 (5)	18.4 (0.7)	168 (1)	2.8 (0.5)	29 (1)	50 (20)	110 (10)	10 (10)	100 (100)
Mehlich 3-Cu	0	12	8	12	5	20	0.9	5	4(6) [8] ^[f]	12 (0) [11] ^[f]	3 (3) [30] ^[f]	10 (10) [10] ^[f]
Manganese(Mn)	90.7 (0.4)	125 (1)	76 (5)	141 (6)	57 (3)	251 (6)	16 (2)	34 (2)	80 (10)	130 (10)	40 (30)	140 (150)
Mehlich 3-Mn	50	90	50	110	40	180	8	20	50(0) [63] ^[f]	100(10) [77] ^[f]	20(20) [50] ^[f]	100(100) [71] ^[f]
Zinc (Zn)	92.1 (0.9)	143 (9)	80 (20)	150 (1)	37 (3)	310 (20)	5.7 (0.9)	36 (4)	86 (9)	147 (5)	20 (20)	200 (200)
Mehlich 3-Zn	40	70	40	80	20	130	2	25	40(0) [47] ^[f]	75(7) [51] ^[f]	10(10) [50] ^[f]	80(70) [40] ^[f]
Carbon (C) (g kg ⁻¹)	17.4 (0.7)	26 (2)	29 (2)	40.2 (0.4)	26 (2)	65 (4)	4.3 (0.2)	8 (1)	23 (8)	30 (10)	20 (20)	40 (40)
WSE-DOC (g kg ⁻¹)	7.67 (0.09)	2.9 (0.5)	8.1 (0.2)	3.8 (0.2)	5.9 (0.2)	7.8 (0.3)	2.49 (0.05)	1.7 (0.2)	7.9 (0.3)	3.4 (0.6)	4 (2)	5 (4)
Nitrogen (N) (g kg ⁻¹)	2 (0)	3.5 (0.4)	2.9 (0.1)	5 (0)	2.9 (0.3)	7.15 (0.07)	0.43 (0.05)	1.1 (0.1)	2.5 (0.6)	4.0 (0.7)	2 (2)	4 (4)
NH ₄ -N (g kg ⁻¹)	2.14 (0.05)	1.6 (0.2)	2.35 (0.03)	2.06 (0.02)	1.75 (0.04)	2.9 (0.3)	0.714(0.005)	0.95 (0.04)	2.2 (0.1)	1.8 (0.3)	1.2 (0.7)	2 (1)
NO ₃ -N	33.82 (0.01)	1.71 (0.03)	1.13 (0.04)	2.7 (0.8)	1.53 (0.07)	3.1 (0.4)	1.3 (0.5)	1.57 (0.05)	20 (20)	2.2 (0.7)	1.4 (0.2)	2 (1)
Phosphorus(P) (g kg ⁻¹)	2.69 (0.04)	4.3 (0.2)	2.0 (0.1)	4.6 (0.5)	1.33 (0.04)	7.1 (0.6)	0.30 (0.01)	1.18 (0.02)	2.3 (0.5)	4.4 (0.2)	0.8 (0.7)	4 (4)
Mehlich 3-P (g kg ⁻¹)	1.4	2.2	1.1	2.5	0.8	3.9	0.2	0.02	1.3(0.2) [57] ^[f]	2.4(0.2) [55] ^[f]	0.5(0.4) [63] ^[f]	2(3) [50] ^[f]
WSE-P (g kg ⁻¹)	0.60 (0.01)	0.78 (0.03)	0.48 (0.01)	0.691 (0.002)	0.38 (0.01)	1.02 (0.02)	0.007(0.001)	0.38 (0.01)	0.54 (0.09)	0.74 (0.06)	0.2 (0.3)	0.7 (0.5)
Moisture content (fraction)	0.86 (0.003)	0.821 (0.002)	0.846 (0.002)	0.744 (0.003)	0.860 (0.004)	0.660 (0.006)	0.956 (0.001)	0.899(0.004)	0.85 (0.01)	0.78 (0.05)	0.91 (0.07)	0.8 (0.2)

Table B3. (continued.)

Chemical and Physical Properties ^[a]	Beneath Stockpile 1 ¹ Center NR (25-76 mm)		Beneath Stockpile 2 ¹ Center NR (25-76 mm)		Beneath Stockpile 3 ¹ Center NR+SIM (25-76 mm)		Beneath Stockpile 4 ¹ Center NR+SIM (25-76 mm)		Grand Mean ^[d] NR (25-76 mm)		Grand Mean ^[d] NR+SIM (25-76 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
	pH	8.24 (0.03)	7.3 (0.01)	8.43 (0.01)	8.83 (0.04)	8.72 (0.04)	8.82 (0.02)	6.12 (0.02)	8.87 (0.02)	8.3 (0.1)	8 (1)	7 (2)
EC(mS/cm)	5.4 (0.2)	5.2 (0.2)	4.5 (0.2)	3.3 (0.6)	3.9 (0.1)	3.8 (0.2)	1.7 (0.2)	3.3 (0.6)	5.0 (0.6)	4 (1)	3 (2)	3.6 (0.4)
	(mg kg ⁻¹) ^[e]											
Arsenic (As)	0.89 (0.2)	1.38 (0.03)	0.67 (0.04)	0.77 (0.07)	0.59 (0.02)	0.80 (0.1)	0.57 (0.10)	0.89 (0.01)	0.8 (0.2)	1.1 (0.4)	0.58 (0.01)	0.85 (0.06)
WSE-As	<0.3 (0)	0.57 (0.003)	<0.3 (0)	0.01 (0.01)	0.20 (0.01)	0.29 (0.03)	<0.3 (0)	0.396(0.002)	<0.3 (0)	0.3 (0.4)	0.25 (0.07)	0.34 (0.07)
Copper (Cu)	16 (1)	28.5(0.1)	9.8 (0.3)	4.77(0.002)	7.4 (0.3)	11.1(0.8)	2.6 (0.4)	15.4 (0.4)	13 (4)	20 (20)	5 (3)	13 (3)
Mehlich 3-Cu	6	4	3	0.8	2	1	0.9	5	5(2) [38] ^[f]	2(2) [10] ^[f]	1.5(0.8) [30] ^[f]	3(3) [23] ^[f]
Manganese(Mn)	33 (3)	37 (1)	25 (2)	17 (3)	26 (2)	27 (2)	19 (1)	15.56 (0.02)	29 (6)	30 (10)	23 (5)	21 (8)
Mehlich 3-Mn	20	35	14	10	14	17	9	10	17(4) [59] ^[f]	20(20) [67] ^[f]	12(4) [52] ^[f]	14(5) [67] ^[f]
Zinc (Zn)	22.8(0.9)	36.9(0.8)	20.2(0.3)	13.3 (0.7)	13.9(0.7)	25 (2)	4.6 (0.3)	9.7 (0.1)	22 (2)	30 (20)	9 (7)	20 (10)
Mehlich 3-Zn	14	29	12	8	7	15	1	8	13(1) [59] ^[f]	20(10) [67] ^[f]	4(4) [44] ^[f]	12(5) [60] ^[f]
Carbon (C) (g kg ⁻¹)	6.1 (0.6)	9.8 (0.4)	11.7 (0.6)	7 (2)	8.1 (0.2)	8.4 (0.8)	3.2 (0.2)	4.5 (0.6)	9 (4)	8 (2)	6 (3)	6 (3)
WSE-DOC (g kg ⁻¹)	3.36 (0.06)	2.2 (0.03)	2.9 (0.3)	0.049 (0.002)	1.9 (0.1)	1.4 (0.1)	1.62 (0.05)	1.5 (0.1)	3.1 (0.3)	1 (2)	1.8 (0.2)	1.45 (0.07)
Nitrogen (N)	700 (100)	1300 (0)	1150 (70)	800 (200)	900 (0)	1000 (100)	350 (60)	550 (70)	900 (300)	1100 (400)	600 (400)	800 (300)
NH ₄ -N	940 (40)	1000 (80)	920 (60)	600 (100)	840 (70)	900(100)	480(10)	500 (80)	930 (10)	800 (300)	700 (300)	700 (300)
NO ₃ -N	1.1 (0.2)	37 (0)	1.9 (1.3)	0.99 (0.07)	0.99 (0.01)	2.6 (1.3)	1.7 (1)	2.4 (0.8)	1.5 (0.6)	20 (30)	1.3 (0.5)	2.5 (0.1)
Phosphorus(P)	700 (40)	1200 (20)	620 (30)	550 (10)	560 (70)	820 (10)	260 (20)	550 (40)	660 (60)	900 (500)	400 (200)	700 (200)
Mehlich 3-P	420	910	310	370	250	500	120	450	370(80) [56] ^[f]	600(400) [67] ^[f]	190(90) [48] ^[f]	480(40) [69] ^[f]
WSE-P	96 (1)	321 (8)	130 (10)	6.0 (0.3)	88 (3)	220 (30)	3.0 (0.1)	197 (5)	110 (20)	200 (200)	50 (60)	210 (20)
Moisture content (fraction)	0.917 (0.003)	0.8754 (0.0002)	0.9158 (0.0004)	0.911 (0.0003)	0.9243 (0.0005)	0.9058 (0.0003)	0.9467 (0.0005)	0.906 (0.002)	0.916 (0.001)	0.89 (0.03)	0.94 (0.02)	0.9059 (0.0002)

Table B3. (continued.)

Chemical and Physical Properties ^[a]	Beneath Stockpile 1 ^[c]		Beneath Stockpile 2 ^[c]		Beneath Stockpile 3 ^[c]		Beneath Stockpile 4 ^[c]		Grand Mean ^[d]		Grand Mean ^[d]	
	Center NR (76-305 mm)		Center NR (76-305 mm)		Center NR+SIM (76-305 mm)		Center NR+SIM (76-305 mm)		NR (76-305 mm)		NR+SIM (76-305 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
pH	5.79 (0.05)	8.46 (0.02)	8.16 (0.06)	8.88 (0.01)	8.47 (0.04)	8.88 (0.02)	5.67 (0.01)	8.82 (0.01)	7 (2)	8.7 (0.3)	7 (2)	8.85 (0.04)
EC(mS/cm)	2.5 (0.1)	2.0 (0.2)	0.28 (0.04)	1.8 (0.1)	0.7 (0.2)	2.74 (0.08)	1.80 (0.04)	3.9 (0.8)	1 (2)	1.9 (0.1)	1.3 (0.8)	3.3 (0.8)
	----- (mg kg ⁻¹) ^[e] -----											
Arsenic (As)	NA ^[g]	NA	NA	0.61 (0.02)	NA	NA	NA	NA	NA	NA	NA	NA
WSE-As	<0.3 (0)	0.07 (0.01)	<0.3 (0)	0.12 (0.01)	<0.3 (0)	0.3 (0.03)	<0.3 (0)	0.22 (0.03)	<0.3 (0)	0.10 (0.03)	<0.3 (0)	0.26 (0.06)
Copper (Cu)	NA	NA	NA	2.5 (0.2)	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-Cu	1	2	1	1 [40]	0.6	1	1	5	1 (0)	1.5 (0.7)	0.8 (0.3)	3 (3)
Manganese(Mn)	NA	NA	NA	18 (1)	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-Mn	14	9	9	8 [44] ^[f]	12	14	14	7	12 (4)	8.5 (0.7)	13 (1)	11 (5)
Zinc (Zn)	NA	NA	NA	7.0 (0.2)	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-Zn	1	2	3	3 [43] ^[f]	120	6	1	3	2 (1)	2.5 (0.7)	60 (80)	5 (2)
Carbon (C) (g kg ⁻¹)	3.2 (0.3)	5.3 (0.2)	2.45 (0.07)	4.2 (0.07)	2.6 (0.4)	6.4 (0.5)	2.2 (0.4)	4.0 (0.2)	2.8 (0.5)	4.8 (0.8)	2.4 (0.3)	5 (2)
WSE-DOC (g kg ⁻¹)	1.38 (0.03)	0.85 (0.09)	0.09 (0.01)	1.03 (0.09)	0.40 (0.05)	1.49 (0.09)	0.9 (0.05)	1.3 (0.05)	0.7 (0.9)	0.9 (0.1)	0.7 (0.4)	1.4 (0.1)
Nitrogen (N)	370 (60)	850 (70)	300 (0)	450 (70)	300 (0)	750 (70)	200 (0)	550 (70)	340 (50)	700 (300)	250 (70)	700 (100)
NH ₄ -N	424 (3)	550 (20)	132.6 (0.4)	540 (90)	260 (10)	291 (6)	285 (8)	330 (30)	300 (200)	550 (10)	270 (20)	310 (30)
NO ₃ -N	0.98 (0)	6 (3)	2.7 (0.1)	1.57 (0.05)	0.98 (0.01)	0.98 (0.09)	0.98 (0)	1.02 (0.07)	2 (1)	4 (3)	0.98 (0)	1.00 (0.03)
Phosphorus(P)	NA	NA	NA	400 (100)	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-P	30	30	70	160 [40] ^[f]	110	230	72	170	50 (30)	100 (90)	90 (30)	200 (40)
WSE-P	0.6 (0.1)	5.6 (0.4)	6 (3)	53 (3)	11.7 (0.8)	82 (1)	0.9 (0.1)	75 (10)	3 (4)	30 (30)	6 (8)	79 (5)
Moisture content (fraction)	0.9154 (0.0001)	0.887 (0.001)	0.92 (0.02)	0.920 (0.001)	0.931 (0.001)	0.920 (0.001)	0.9381 (0.0003)	0.925 (0.003)	0.918 (0.004)	0.90 (0.02)	0.935 (0.005)	0.923 (0.004)

Table B3. (continued.)

Chemical and Physical Properties ^[a]	Beneath Stockpile 1 ^[c]		Beneath Stockpile 2 ^[c]		Beneath Stockpile 3 ^[c]		Beneath Stockpile 4 ^[c]		Grand Mean ^[d]		Grand Mean ^[d]	
	Center NR		Center NR		Center NR+SIM		Center NR+SIM		NR		NR+SIM	
	(305-610 mm)		(305-610 mm)		(305-610 mm)		(305-610 mm)		(305-610 mm)		(305-610 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
pH	5.63 (0.02)	6.41 (0.02)	5.70 (0.03)	7.06 (0.05)	7.99 (0.01)	6.65 (0.02)	6.03 (0.05)	5.97 (0.02)	5.67 (0.05)	6.7 (0.5)	7 (1)	6.3 (0.5)
EC(mS/cm)	0.097 (0.004)	0.3 (0.007)	0.12 (0.01)	1.1 (0.2)	2.10 (0.07)	1.9 (0.2)	0.12 (0.01)	2.7 (0.4)	0.11 (0.02)	0.7 (0.6)	1 (1)	2.3 (0.6)
	------(mg kg ⁻¹) ^[e] -----											
Arsenic (As)	NA ^[g]	NA	NA	3.60 (0.03)	NA	NA	NA	NA	NA	NA	NA	NA
WSE-As	<0.3 (0)	0.02 (0.01)	<0.3 (0)	0.03 (0.01)	<0.3 (0)	0.03 (0.01)	<0.3 (0)	0.02 (0.01)	<0.3 (0)	0.03 (0.01)	<0.3 (0)	0.03 (0.01)
Copper (Cu)	NA	NA	NA	6.1 (0.7)	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-Cu	0.4	0.5	0.4	0.6 [10] ^[f]	0.2	2.3	0.3	0.9	0.4 (0)	0.55 (0.07)	0.25 (0.07)	2 (1)
Manganese(Mn)	NA	NA	NA	28 (4)	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-Mn	3	2	3	5 [18] ^[f]	4	12	6	14	3 (0)	4 (2)	5 (1)	13 (1)
Zinc (Zn)	NA	NA	NA	15 (1)	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-Zn	0.9	0.5	0.5	1 [7] ^[f]	9.6	3	0.2	2	0.7 (0.3)	0.8 (0.4)	5 (7)	2.5 (0.7)
Carbon (C) (g kg ⁻¹)	2.6 (0.1)	2.9 (0.4)	2.95 (0.07)	4.2 (0)	2.2 (0.1)	4.7 (0.2)	1.6 (0.2)	3.7 (0.2)	2.8 (0.2)	4 (1)	1.9 (0.4)	4.2 (0.7)
WSE-DOC	15.7 (0.2)	48 (3)	20.7 (0.2)	272 (12)	20.5 (0.3)	800 (100)	30 (10)	2300 (400)	18 (4)	160 (160)	25 (7)	1500 (1000)
Nitrogen (N)	425 (50)	750 (70)	400 (0)	750 (70)	300 (0)	700 (0)	200 (0)	500 (0)	410 (20)	750 (0)	250 (70)	600 (100)
NH ₄ -N	28 (1)	161 (5)	36.5 (0.5)	345 (9)	29 (2)	400 (30)	17 (0.03)	600 (40)	32 (6)	300 (100)	23 (8)	500 (100)
NO ₃ -N	2.6 (0.3)	0.99 (0.01)	1.3 (0.4)	1.00 (0.07)	1.1 (0.1)	0.95 (0.02)	0.98 (0)	0.90 (0.01)	2 (1)	1.00 (0.01)	1.0 (0.1)	0.93 (0.04)
Phosphorus(P)	NA	NA	NA	256 (6)	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-P	0	0	0	0.2 [0.1] ^[f]	5	50	2	20	0 (0)	0.1 (0.1)	4 (2)	40 (20)
WSE-P	<1.3 (0)	0.05 (0.07)	<1.3 (0)	0.4 (0.1)	<1.3 (0)	2.6 (0.7)	<1.3 (0)	2.2 (0.2)	<1.3 (0)	0.2 (0.2)	<1.3 (0)	2.4 (0.3)
Moisture content (fraction)	0.8402 (0.0003)	0.859 (0.001)	0.852 (0.001)	0.862 (0.001)	0.90 (0.06)	0.914 (0.001)	0.904 (0.001)	0.923 (0.001)	0.846 (0.008)	0.861 (0.002)	0.902 (0.003)	0.919 (0.006)

^[a] See footnote in Table B1 for methods.

^[b] See footnote in Table B1 for limits of quantitation.

^[c] Data represent the mean and standard deviation (in parentheses) of 3 analytical replicates.

^[d] Data represent the grand mean of concentrations measured for each treatment (NR and NR+SIM) for summer and winter. Standard deviations of those means are shown in parentheses.

^[e] Except where denoted.

^[f] Mehlich data is for single sample analysis. The mean of these analyses is shown with the standard deviation in parentheses. Percent of strong-acid extractable metal is shown in brackets for the 0-3 and 3-12 cm depths, and all depths for samples beneath stockpile 2 (winter).

^[g] Not analyzed.

Table B4. Chemical and physical properties^[a] of soils sampled beneath the half-radius of litter stockpiles at various depths (0-25, 25-76, 76-305, and 305-610 mm) after 161 d (summer) and 162 d (winter) of stockpiling, respectively. Data reported at or below the limits of quantitation^[b] (LOQs) are in bold text.

Chemical and Physical Properties ^[a]	Beneath Stockpile 1 ^[c]		Beneath Stockpile 2 ^[c]		Beneath Stockpile 3 ^[c]		Beneath Stockpile 4 ^[c]		Grand Mean ^[d]		Grand Mean ^[d]	
	Half-radius		Half-radius		Half-radius		Half-radius		NR		NR+SIM	
	NR (0-25 mm)		NR (0-25 mm)		NR+SIM (0-25 mm)		NR+SIM (0-25 mm)		(0-25 mm)		(0-25 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
pH	8.26 (0.02)	8.45 (0.06)	8.04 (0.02)	8.28 (0.02)	7.75 (0.01)	8.58 (0.02)	8.32 (0.02)	8.38 (0.01)	8.2 (0.2)	8.4 (0.1)	8.0 (0.4)	8.5 (0.1)
EC(mS/cm)	10 (2)	5.4 (0.8)	13.2 (0.3)	10.9 (0.6)	14.6 (0.2)	10 (1)	3.6 (0.6)	5.5 (0.4)	12 (2)	8 (4)	9 (8)	8 (3)
----- (mg kg ⁻¹) ^[c] -----												
Arsenic (As)	1.1 (0.1)	1.97 (0.02)	1.16 (0.02)	6.7 (0.4)	1.06 (0.04)	4.18 (0.05)	0.79 (0.04)	2.25 (0.02)	1.13 (0.04)	4.3 (3.3)	0.9 (0.2)	3 (1)
WSE-As	0.37 (0.02)	3.7 (0.2)	0.59 (0.01)	2.34 (0.07)	0.60 (0.01)	3.4 (0.2)	0.45 (0.02)	1.65 (0.03)	0.5 (0.2)	3 (1)	0.5 (0.1)	2.5 (1.2)
Copper (Cu)	22 (1)	83 (2)	70 (2)	317 (6)	61.2 (0.6)	182.40 (0.04)	33 (1)	107 (3)	50 (30)	200 (200)	50 (20)	150 (50)
Mehlich 3-Cu	3	10	10	40	10	20	4	10	7(5) [14] ^[f]	30(20) [15] ^[f]	7(4) [14] ^[f]	15(7) [10] ^[f]
Manganese(Mn)	22 (1)	96.2 (0.3)	59 (3)	306 (8)	45 (6)	120 (5)	35 (2)	100 (3)	40 (30)	200 (100)	40 (7)	110 (10)
Mehlich 3-Mn	9	80	30	200	30	90	30	60	20(10) [50] ^[f]	140(80) [70] ^[f]	30(0) [75] ^[f]	80(20) [73] ^[f]
Zinc (Zn)	29 (5)	119 (1)	78 (1)	370 (20)	51 (2)	168 (5)	36 (6)	108 (9)	50 (40)	200 (200)	40 (10)	140 (40)
Mehlich 3-Zn	10	70	40	150	30	70	20	50	30(20) [60] ^[f]	110(50) [55] ^[f]	25(7) [63] ^[f]	60(10) [43] ^[f]
Carbon (C) (g kg ⁻¹)	10 (1)	19.8 (0.7)	17.8 (0.2)	59 (4)	23 (1)	40 (2)	12 (1)	19 (2)	14 (6)	39 (3)	18 (8)	30 (20)
WSE-DOC (g kg ⁻¹)	5.5 (0.1)	7.4 (0.07)	10.1 (0.5)	1.30 (0.07)	11.3 (0.2)	1.7 (0.2)	4.7 (0.8)	3.7 (0.01)	8 (3)	4 (4)	8 (5)	3 (1)
Nitrogen (N) (g kg ⁻¹)	1.3 (0.07)	2.9 (0.1)	2.45 (0.07)	8 (1)	3.15 (0.07)	5.3 (0.5)	1.6 (0.1)	2.5 (0.3)	1.9 (0.8)	5 (4)	2 (1)	4 (2)
NH ₄ -N (g kg ⁻¹)	1.6 (0.08)	0.89 (0.03)	2.7 (0.1)	2.52 (0.03)	3.43 (0.04)	2.00 (0.02)	1.58 (0.07)	1.07 (0.01)	2.2 (0.8)	2 (1)	3 (1)	1.5 (0.6)
NO ₃ -N	1.1 (0.2)	2.1 (0.7)	7.08 (0.02)	3.1 (0.9)	2.9 (0.2)	2.9 (0.5)	1.2 (0.4)	1.7 (0.6)	4 (4)	2.6 (0.7)	2 (1)	2.3 (0.8)
Phosphorus(P) (g kg ⁻¹)	0.97 (0.04)	3.9 (0.1)	2.3 (0.1)	9.6 (0.3)	1.96 (0.07)	4.5 (0.6)	1.5 (0.03)	3.6 (0.04)	1.6 (0.9)	7 (4)	1.7 (0.4)	4.1 (0.6)
Mehlich 3-P	0.42	2.1	1.2	5.2	1.1	2.4	0.90	1.7	0.8(0.6) [50] ^[f]	4(2) [57] ^[f]	1.0(0.1) [60] ^[f]	2.1(0.5) [51] ^[f]
WSE-P (g kg ⁻¹)	0.15 (0.01)	1.43 (0.05)	0.48(0.01)	1.73 (0.06)	0.47 (0.01)	1.29 (0.04)	0.31 (0.01)	0.849(0.004)	0.3 (0.2)	1.6 (0.2)	0.4 (0.1)	1.1 (0.3)
Moisture content (fraction)	0.9013 (0.0004)	0.849 (0.001)	0.870 (0.003)	0.697 (0.006)	0.860 (0.002)	0.760 (0.002)	0.901 (0.001)	0.808 (0.004)	0.89 (0.02)	0.8 (0.1)	0.88 (0.03)	0.78 (0.03)

Table B4. (continued).

Chemical and Physical Properties ^[a]	Beneath Stockpile 1 ^[c] Half-radius NR (25-76 mm)		Beneath Stockpile 2 ^[c] Half-radius NR (25-76 mm)		Beneath Stockpile 3 ^[c] Half-radius NR+SIM (25-76 mm)		Beneath Stockpile 4 ^[c] Half-radius NR+SIM (25-76 mm)		Grand Mean ^[d] NR (25-76 mm)		Grand Mean ^[d] NR+SIM (25-76 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
	pH	8.26 (0.01)	8.49 (0.01)	8.22 (0.01)	8.67 (0.02)	8.11 (0.02)	8.74 (0.02)	8.40 (0.01)	8.58 (0.01)	8.2 (0.03)	8.6 (0.1)	8.3 (0.2)
EC(mS/cm)	7.9 (0.1)	4.5 (0.4)	10 (2)	5.3 (0.9)	10.1 (0.4)	5.2 (0.5)	4.2 (0.4)	5.5 (0.1)	9 (2)	4.9 (0.6)	7 (4)	5.4 (0.2)
	-----(mg kg^{-1}) ^[e] -----											
Arsenic (As)	0.92 (0.04)	1.56 (0.09)	0.83 (0.03)	1.39 (0.02)	0.74 (0.05)	1.1 (0.1)	0.63 (0.02)	1.2 (0.1)	0.88 (0.06)	1.5 (0.1)	0.69 (0.08)	1.2 (0.1)
WSE-As	0.30 (0.03)	0.74 (0.02)	0.46 (0.05)	0.94 (0.03)	0.34 (0.02)	0.82 (0.01)	0.29 (0.03)	0.60 (0.01)	0.4 (0.1)	0.8 (0.1)	0.32 (0.04)	0.7 (0.2)
Copper (Cu)	14.0 (0.5)	45 (2)	34 (1)	53.8 (0.6)	26 (1)	43 (1)	12.2 (0.6)	40 (3)	20 (10)	49 (6)	20 (10)	42 (2)
Mehlich 3-Cu	2	5	6	5	4	5	2	5	4(3) [20] ^[f]	5(0) [10] ^[f]	3(1) [15] ^[f]	5(0) [12] ^[f]
Manganese(Mn)	18.2 (0.9)	49 (4)	25 (2)	49 (1)	21 (1)	24 (1)	16 (1)	30 (2)	22 (5)	49 (0)	19 (4)	27 (4)
Mehlich 3-Mn	7	40	10	30	10	20	10	20	9(2) [41] ^[f]	35(7) [71] ^[f]	10(0) [53] ^[f]	20(0) [74] ^[f]
Zinc (Zn)	16 (2)	54 (1)	32 (4)	54 (2)	27.6 (0.2)	80 (30)	14 (3)	40 (4)	20 (10)	54 (0)	20 (10)	60 (30)
Mehlich 3-Zn	9	30	20	30	15	20	10	30	15(8) [75] ^[f]	30(0) [56] ^[f]	13(4) [65] ^[f]	25(7) [42] ^[f]
Carbon (C) (g kg^{-1})	6.5 (0.6)	10.6 (0.2)	12.9 (0.8)	13.9 (0.6)	10 (1)	8 (1)	6.0 (0.2)	11.0 (0.4)	10 (5)	12 (2)	8 (3)	10 (2)
WSE-DOC (g kg^{-1})	3 (1)	0.46 (0.01)	4.8 (0.7)	2.9 (0.08)	6.5 (0.6)	2.41 (0.04)	4.1 (0.3)	2.01 (0.07)	4 (1)	2 (2)	5 (2)	2.2 (0.3)
Nitrogen (N) (g kg^{-1})	0.9 (0.1)	1.6 (0.07)	1.7 (0.07)	1.83 (0.06)	1.4 (0.1)	1.2 (0.1)	0.85 (0.07)	1.7 (0.07)	1.3 (0.5)	1.7 (0.2)	1.1 (0.4)	1.4 (0.3)
NH ₄ -N (g kg^{-1})	1.26 (0.02)	0.706 (0.004)	1.815(0.002)	0.7 (0.2)	1.7 (0.1)	0.9 (0.2)	1.1 (0.1)	0.78 (0.06)	1.5 (0.4)	0.70(0.004)	1.4 (0.4)	0.84 (0.08)
NO ₃ -N	2.4 (1.4)	6.2 (5.5)	3.1 (0.2)	3.0 (1)	1.4 (0.2)	2.58 (0.06)	1.6 (0.3)	1.4 (0.3)	2.8 (0.5)	5 (2)	1.5 (0.1)	2.0 (0.8)
Phosphorus(P)(g kg^{-1})	0.58 (0.01)	2.00 (0.02)	1.36 (0.03)	2.1 (0.2)	1.30 (0.04)	1.28 (0.03)	0.96 (0.02)	1.60 (0.09)	1.0 (0.6)	2.05 (0.06)	1.1 (0.2)	1.4 (0.2)
Mehlich 3-P (g kg^{-1})	0.3	1.2	0.6	1	0.7	0.8	0.6	1	0.5(0.2)[50] ^[f]	1.1(0.1)[54] ^[f]	0.7(0.1)[54] ^[f]	0.9(0.1)[64] ^[f]
WSE-P (g kg^{-1})	0.078(0.004)	0.46 (0.01)	0.25 (0.02)	0.50 (0.01)	0.24 (0.01)	0.36 (0.01)	0.2 (0.1)	0.357(0.002)	0.2 (0.1)	0.48(0.03)	0.22 (0.03)	0.358(0.001)
Moisture content (fraction)	0.9095 (0.0002)	0.878 (0.002)	0.907 (0.001)	0.878 (0.002)	0.904 (0.001)	0.904 (0.001)	0.921 (0.002)	0.893 (0.001)	0.908 (0.002)	0.878 (0.000)	0.91 (0.01)	0.899 (0.008)

Table B4. (continued).

Chemical and Physical Properties ^[a]	Beneath Stockpile 1 ^[c]		Beneath Stockpile 2 ^[c]		Beneath Stockpile 3 ^[c]		Beneath Stockpile 4 ^[c]		Grand Mean ^[d]		Grand Mean ^[d]	
	Half-radius NR (76-305 mm)		Half-radius NR (76-305 mm)		Half-radius NR+SIM (76-305 mm)		Half-radius NR+SIM (76-305 mm)		NR (76-305 mm)		NR+SIM (76-305 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
pH	8.54 (0.03)	8.65 (0.03)	8.86(0.01)	8.74 (0.01)	8.37 (0.01)	8.7 (0.02)	7.24 (0.01)	8.8 (0.01)	8.7 (0.2)	8.7 (0.06)	7.8 (0.8)	8.8 (0.1)
EC(mS/cm)	3.4 (0.3)	2.7 (0.5)	3.9 (0.2)	3.4 (0.2)	7.9 (0.6)	4.5 (0.3)	9.0 (0.3)	2.8 (0.4)	3.7 (0.3)	3.1 (0.6)	8.5 (0.8)	4 (1)
	------(mg kg ⁻¹) ^[c] -----											
Arsenic (As)	NA ^[g]	NA	NA	NA	NA	0.80 (0.03)	NA	NA	NA	NA	NA	NA
WSE-As	<0.3 (0)	0.32 (0.01)	0.18 (0.01)	0.367(0.003)	0.33 (0.01)	0.41 (0.01)	0.16 (0.01)	0.46 (0.07)	0.24 (0.08)	0.34 (0.03)	0.2 (0.1)	0.44 (0.04)
Copper (Cu)	NA	NA	NA	NA	NA	11.6 (0.5)	NA	NA	NA	NA	NA	NA
Mehlich 3-Cu	2	2	2	2	1	1 [9] ^[f]	3	2	2 (0)	2 (0)	2 (1)	1.5 (0.7)
Manganese(Mn)	NA	NA	NA	NA	NA	18.5 (0.3)	NA	NA	NA	NA	NA	NA
Mehlich 3-Mn	5	8	9	9	9	10 [54] ^[f]	7	9	7 (3)	8.5 (0.7)	8 (1)	9.5 (0.7)
Zinc (Zn)	NA	NA	NA	NA	NA	12.5 (0.2)	NA	NA	NA	NA	NA	NA
Mehlich 3-Zn	3	5	6	9	6	8 [64] ^[f]	8	8	5 (2)	7 (3)	7 (1)	8 (0)
Carbon (C) (g kg ⁻¹)	4.8 (0.2)	8 (4)	5.1 (0.5)	6.0 (0.8)	5.8 (0.1)	7 (1)	6.1 (0.5)	4.6 (0.3)	4.9 (0.2)	7 (1)	6.0 (0.2)	6 (2)
WSE-DOC (g kg ⁻¹)	1.7700(.0002)	2.18 (0.04)	2.4 (0.5)	2.15 (0.07)	4.40 (0.09)	1.92 (0.2)	5.85 (0.07)	1.70 (0.2)	2.1 (0.4)	2.16 (0.02)	5 (1)	1.8 (0.2)
Nitrogen (N) (g kg ⁻¹)	0.75 (0.07)	1.3 (0.1)	0.75 (0.07)	0.95 (0.07)	0.9 (0)	1.1 (0.2)	1 (0)	0.7 (0)	0.8 (0)	1.1 (0.2)	0.95(0.07)	0.9 (0.3)
NH ₄ -N (g kg ⁻¹)	0.71 (0.04)	0.79 (0.01)	0.6 (0.2)	0.5 (0.2)	1.34 (0.07)	0.8 (0.1)	1.4 (0.01)	0.37 (0.08)	0.65 (0.09)	0.6 (0.2)	1.37 (0.04)	0.6 (0.3)
NO ₃ -N	0.98 (0)	3.4 (0.3)	1.4 (0.6)	1.06 (0.03)	1.3 (0.4)	3 (1)	0.98 (0)	3.0 (0.2)	1.2 (0.3)	2.2 (1.7)	1.1 (0.2)	3 (0)
Phosphorus(P)(g kg ⁻¹)	NA	NA	NA	NA	NA	0.75 (0.01)	NA	NA	NA	NA	NA	NA
Mehlich 3-P (g kg ⁻¹)	0.1	0.04	0.4	0.2	0.4	0.4 [53] ^[f]	0.5	0.5	0.3 (0.2)	0.1 (0.1)	0.5 (0.1)	0.5 (0.1)
WSE-P	10.18 (0.02)	38.6 (0.7)	98.8 (0.1)	171 (10)	100 (6)	167 (2)	117 (8)	147 (18)	54 (63)	105 (94)	109 (12)	157 (14)
Moisture content (fraction)	0.894 (0.001)	0.877 (0.001)	0.916 (0.002)	0.941 (0.002)	0.917 (0.001)	0.905 (0.001)	0.922 (0.001)	0.917 (0.001)	0.91 (0.02)	0.89 (0.02)	0.920 (0.003)	0.911 (0.009)

Table B4. (continued).

Chemical and Physical Properties ^[a]	Beneath Stockpile 1 ^[c]		Beneath Stockpile 2 ^[c]		Beneath Stockpile 3 ^[c]		Beneath Stockpile 4 ^[c]		Grand Mean ^[d]		Grand Mean ^[d]	
	Half-radius NR (305-610 mm)		Half-radius NR (305-610 mm)		Half-radius NR+SIM (305-610 mm)		Half-radius NR+SIM (305-610 mm)		NR (305-610 mm)		NR+SIM (305-610 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
pH	5.59 (0.08)	7.77 (0.06)	7.03 (0.01)	8.55 (0.01)	8.50 (0.03)	8.36 (0.04)	8.89 (0.05)	8.42 (0.01)	6 (1)	8.2(0.6)	8.7(0.3)	8.4 (0.04)
EC (mS/cm)	0.44 (0.01)	0.9 (0.1)	1.04 (0.07)	2.09 (0.06)	3.1 (0.3)	2.5 (0.04)	2.8 (0.3)	3.7 (0.5)	0.7 (0.4)	1.5 (0.9)	3.0 (0.2)	3.1 (0.8)
	----- (mg kg ⁻¹) ^[c] -----											
Arsenic (As)	NA ^[g]	NA	NA	NA	NA	3.7 (0.3)	NA	NA	NA	NA	NA	NA
WSE-As	<0.3 (0)	0.06 (0.002)	<0.3 (0)	0.23 (0.01)	0.14 (0.01)	0.155 (0.004)	0.183 (0.003)	0.17 (0.01)	<0.3 (0)	0.1 (0.1)	0.16 (0.03)	0.16 (0.01)
Copper (Cu)	NA	NA	NA	NA	NA	10.2 (0.2)	NA	NA	NA	NA	NA	NA
Mehlich 3-Cu	1	1	2	1	1	2 [20] ^[f]	1	1	1.5 (0.7)	1 (0)	1 (0)	1.5 (0.7)
Manganese(Mn)	NA	NA	NA	NA	NA	26 (3)	NA	NA	NA	NA	NA	NA
Mehlich 3-Mn	2	2	4	6	6	4 [15] ^[f]	5	7	3 (1)	4 (3)	5.5 (0.7)	6 (2)
Zinc (Zn)	NA	NA	NA	NA	NA	21 (8)	NA	NA	NA	NA	NA	NA
Mehlich 3-Zn	1	1	3	3	2	3 [14] ^[f]	3	2	2 (1)	2 (1)	2.5 (0.7)	2.5 (0.7)
Carbon (C) (g kg ⁻¹)	2.7 (0.1)	4.0 (0.7)	4.4 (0.4)	9.1 (0.8)	4.3 (0)	6.6 (0.1)	4.55 (0.07)	6.85 (0.2)	4 (1)	7 (4)	4.4 (0.2)	6.7 (0.2)
WSE-DOC (g kg ⁻¹)	0.036 (0.002)	0.235 (0.001)	0.157 (0.001)	1.98 (0.03)	1.72 (0.03)	1.83 (0.04)	1.75 (0.03)	2.4 (0.1)	0.10 (0.09)	1 (1)	1.73 (0.02)	2.10 (0.4)
Nitrogen (N)	500 (0)	900 (200)	850 (70)	1650 (70)	900 (0)	1150 (70)	750 (70)	1150 (70)	700 (200)	1300 (500)	800 (100)	1150 (0)
NH ₄ -N	120.9 (0.4)	420 (20)	375 (7)	1000 (100)	840 (40)	840 (40)	770 (10)	700 (30)	200 (200)	700 (400)	810 (50)	800 (100)
NO ₃ -N	9.9	1.03 (0.05)	3.4 (0.3)	1.6 (0.9)	0.98 (0)	0.7 (0.9)	1.2 (0.4)	1.07 (0.002)	7 (5)	1.3 (0.4)	1.1 (0.2)	0.9 (0.3)
Phosphorus (P)	NA	NA	NA	NA	NA	360 (20)	NA	NA	NA	NA	NA	NA
Mehlich 3-P	0	0	20	30	90	40 [11] ^[f]	110	60	10 (10)	20 (20)	100 (10)	50 (10)
WSE-P	<1.3 (0)	0.05 (0.07)	<1.3 (0)	7.8 (0.3)	25 (5)	11 (3)	48 (3)	14.4 (0.2)	<1.3 (0)	3.9 (5.5)	37 (16)	13 (2)
Moisture content (fraction)	0.852 (0.001)	0.850 (0.003)	0.845 (0.001)	0.850 (0.003)	0.896 (0.005)	0.880 (0.002)	0.906 (0.001)	0.900 (0.002)	0.849 (0.005)	0.852 (0.003)	0.901 (0.007)	0.89 (0.01)

^[a] See footnote in Table B1 for methods.

^[b] See footnote in Table B1 for limits of quantitation.

^[c] Data represent the mean and standard deviation (in parentheses) of 3 analytical replicates.

^[d] Data represent the grand mean of concentrations measured for each treatment (NR and NR+SIM) for summer and winter. Standard deviations of those means are shown in parentheses.

^[e] Except where denoted.

^[f] Mehlich data is for single sample analysis. The mean of these analyses is shown with the standard deviation in parentheses. Percent of strong-acid extractable metal is shown in brackets for the 0-25 and 25-76 mm depths, and all depths for samples beneath stockpile 3 (winter).

^[g] Not analyzed.

Table B5. Chemical and physical properties^[a] of soils sampled beneath the diameter (outer-edge) of litter stockpiles at various depths (0-25, 25-76, 76-305, and 305-610 mm) after 161 d (summer) and 162 d (winter) of stockpiling, respectively. Data reported at or below the limits of quantitation^[b] (LOQs) are in bold text.

Chemical and Physical Properties ^[a]	Beneath Stockpile 1 ^[c]		Beneath Stockpile 2 ^[c]		Beneath Stockpile 3 ^[c]		Beneath Stockpile 4 ^[c]		Grand Mean ^[d]		Grand Mean ^[d]	
	Diameter NR (0-25 mm)		Diameter NR (0-25 mm)		Diameter NR+SIM (0-25 mm)		Diameter NR+SIM (0-25 mm)		NR (0-25 mm)		NR+SIM (0-25 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
pH	5.82 (0.03)	6.84 (0.05)	5.62 (0.02)	6.98 (0.05)	5.28 (0.04)	6.62 (0.04)	5.23 (0.04)	6.00 (0.06)	5.7 (0.1)	6.9 (0.1)	5.3 (0.04)	6.3 (0.4)
EC(mS/cm)	1.67 (0.03)	1.3 (0.2)	1.67 (0.03)	1.11 (0.06)	1.02 (0.08)	0.75 (0.05)	0.64 (0.06)	0.70 (0.02)	1.672 (0.002)	1.2 (0.1)	0.8 (0.3)	0.73 (0.03)
----- (mg kg ⁻¹) ^[c] -----												
Arsenic (As)	1.24 (0.08)	2.4 (0.1)	0.95 (0.06)	1.86 (0.02)	0.67 (0.08)	1.2 (0.02)	0.67 (0.04)	1.3 (0.1)	1.1 (0.2)	2.1 (0.4)	0.67 (0)	1.3 (0.1)
WSE-As	<0.3 (0)	0.3 (0.02)	<0.3 (0)	0.29 (0.03)	<0.3 (0)	0.14 (0.01)	<0.3 (0)	0.097 (0.003)	<0.3 (0)	0.30 (0.01)	<0.3 (0)	0.12 (0.03)
Copper (Cu)	43 (4)	148 (3)	72 (2)	161 (1)	34 (1)	70 (5)	37 (2)	91 (6)	60 (20)	155 (9)	36 (2)	80 (20)
Mehlich 3-Cu	14	26	19	27	10	24	14	22	17(4) [28] ^[f]	26.5(0.7)[17] ^[f]	12(3) [33] ^[f]	23(1) [29] ^[f]
Manganese(Mn)	49 (3)	224.4 (0.7)	121 (9)	235 (5)	48 (3)	95 (4)	37 (2)	104 (9)	90 (50)	230 (8)	43 (8)	100 (6)
Mehlich 3-Mn	31	110	35	70	28	70	26	50	33(3) [37] ^[f]	90(30) [39] ^[f]	27(1) [63] ^[f]	60(10) [60] ^[f]
Zinc (Zn)	41 (6)	255 (3)	110 (9)	254 (5)	41 (3)	98 (6)	38 (4)	120 (7)	80 (50)	255 (1)	40 (2)	110 (20)
Mehlich 3-Zn	30	120	50	120	26	80	29	70	40(10) [50] ^[f]	120(0) [47] ^[f]	28(2) [70] ^[f]	75(7) [68] ^[f]
Carbon (C) (g kg ⁻¹)	18 (1)	39 (1)	25 (5)	36.2 (0.8)	13.1 (0.4)	24 (3)	11 (0.4)	23 (3)	22 (5)	38 (2)	12 (1)	23.5 (0.7)
WSE-DOC (g kg ⁻¹)	0.46 (0.01)	0.85 (0.05)	0.250 (0.004)	0.85 (0.06)	0.161 (0.002)	0.468 (0.001)	0.199 (0.003)	0.286 (0.001)	0.4 (0.1)	0.9 (0)	0.18 (0.03)	0.4 (0.1)
Nitrogen (N) (g kg ⁻¹)	2 (0)	4.9 (0.1)	2.8 (0.5)	4.45 (0.07)	1.35 (0.07)	2.8 (0.3)	1.25 (0.07)	2.8 (0.4)	2.4 (0.6)	4.7 (0.3)	1.3 (0.07)	2.78 (0.04)
NH ₄ -N	120 (10)	28 (3)	4 (1)	90 (5)	1.6 (0.3)	35.6 (0.4)	5 (1)	3 (2)	60 (80)	60 (40)	3 (2)	20 (20)
NO ₃ -N	137 (1)	90 (20)	214 (1)	65 (7)	136 (1)	31 (2)	148 (3)	82.5 (0.2)	180 (50)	80 (10)	142 (8)	60 (40)
Phosphorus(P) (g kg ⁻¹)	1.45 (0.06)	5.23 (0.04)	2.4 (0.2)	4.9 (0.1)	1.10 (0.08)	2.12 (0.06)	1.01 (0.07)	2.1 (0.1)	1.9 (0.7)	5.1 (0.2)	1.06 (0.06)	2.10 (0.03)
Mehlich 3-P (g kg ⁻¹)	2.0	2.2	1.1	1.8	0.7	1.3	0.8	1.1	1.6(0.6) [84] ^[f]	2.0(0.3)[39] ^[f]	0.8(0.1) [75] ^[f]	1.2(0.1)[57] ^[f]
WSE-P (g kg ⁻¹)	0.203 (0.01)	0.73 (0.02)	0.411 (0.001)	0.69 (0.04)	0.183 (0.004)	0.274 (0.004)	0.19 (0.01)	0.25 (0.01)	0.3 (0.1)	0.71 (0.03)	0.19 (0.01)	0.26(0.02)
Moisture content (fraction)	0.866 (0.001)	0.842 (0.003)	0.867 (0.003)	0.836 (0.003)	0.894 (0.001)	0.948 (0.005)	0.890 (0.003)	0.910 (0.002)	0.866 (0.001)	0.839 (0.004)	0.892 (0.003)	0.93 (0.03)

Table B5. (continued).

Chemical and Physical Properties ^[a]	Beneath Stockpile 1 ^[c]		Beneath Stockpile 2 ^[c]		Beneath Stockpile 3 ^[c]		Beneath Stockpile 4 ^[c]		Grand Mean ^[d]		Grand Mean ^[d]	
	Diameter NR (25-76 mm)		Diameter NR (25-76 mm)		Diameter NR+SIM (25-76 mm)		Diameter NR+SIM (25-76 mm)		NR (25-76 mm)		NR+SIM (25-76 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
pH	5.65 (0.01)	6.01 (0.04)	5.34 (0.02)	6.68 (0.03)	5.13 (0.02)	5.98 (0.07)	5.43 (0.05)	5.54 (0.04)	5.5 (0.2)	6.3(0.5)	5.3 (0.2)	5.8 (0.3)
EC(mS/cm)	1.21 (0.07)	0.84 (0.06)	0.95 (0.03)	0.70 (0.07)	0.68 (0.02)	0.48 (0.04)	0.38 (0.06)	0.71 (0.07)	1.1 (0.2)	0.8 (0.1)	0.5 (0.2)	0.6 (0.2)
	-----(mg kg^{-1}) ^[c] -----											
Arsenic (As)	1.0 (0.1)	1.86 (0.02)	0.72 (0.06)	1.12 (0.03)	0.66 (0.06)	0.89 (0.02)	0.63 (0.02)	0.97 (0.09)	0.9 (0.2)	1.5 (0.5)	0.65(0.02)	0.93 (0.06)
WSE-As	<0.3 (0)	0.11 (0.02)	<0.3 (0)	0.133(0.001)	<0.3 (0)	0.07 (0.01)	<0.3 (0)	0.078(0.001)	<0.3 (0)	0.12(0.02)	<0.3 (0)	0.07 (0.01)
Copper (Cu)	21.1 (0.5)	43 (1)	23 (1)	62 (1)	15.0 (0.3)	27.5 (0.2)	18 (2)	36 (1)	22 (1)	50 (10)	17 (2)	32 (6)
Mehlich 3-Cu	9	14	9	16	6	13	8	14	9(0) [41] ^[f]	15(1)[30] ^[f]	7(1) [41] ^[f]	13.5(0.7)[42] ^[f]
Manganese(Mn)	21.6 (0.8)	41.0 (0.6)	34 (1)	73 (7)	26 (1)	33.2 (0.6)	23 (1)	38 (1)	28 (9)	60 (20)	25 (2)	36 (3)
Mehlich 3-Mn	10	30	16	30	13	20	15	20	13(4) [46] ^[f]	30(0)[50] ^[f]	14(1) [56] ^[f]	20(0) [56] ^[f]
Zinc (Zn)	16 (4)	42.1 (0.8)	14.1 (0.8)	75 (10)	16.8 (0.6)	35 (5)	17.2 (0.2)	38 (2)	15 (1)	60 (20)	17.0 (0.3)	37 (2)
Mehlich 3-Zn	10	30	20	40	10	30	10	30	15(7)[100] ^[f]	35(7)[58] ^[f]	10(0) [59] ^[f]	30(0) [81] ^[f]
Carbon (C) (g kg^{-1})	6.9 (0.5)	16 (1)	6.6 (0.6)	13.0 (0.6)	7 (1)	10.9 (0.8)	5.2 (0.3)	12 (1)	6.8 (0.2)	15 (2)	6 (1)	11.5 (0.8)
WSE-DOC (g kg^{-1})	0.30 (0.01)	0.36 (0.03)	0.14 (0.01)	0.393(0.003)	0.112 (0.004)	0.23 (0.01)	0.140 (0.003)	0.21 (0.01)	0.2 (0.1)	0.38(0.02)	0.13 (0.02)	0.22 (0.01)
Nitrogen (N) (g kg^{-1})	0.80 (0)	2.05 (0.07)	0.75 (0.07)	1.56 (0.07)	0.70 (0.08)	1.35 (0.07)	0.60 (0)	1.5 (0.1)	0.78 (0.04)	1.8 (0.3)	0.65 (0.07)	1.4 (0.1)
NH ₄ -N	43 (1)	5.1 (0.3)	2 (2)	8.9 (0.1)	6 (2)	5.5 (0.9)	2 (2)	2.8 (0.7)	20 (30)	7 (3)	4 (3)	4 (2)
NO ₃ -N	79 (1)	53.8 (0.8)	111 (1)	56 (1)	76 (1)	24 (1)	80 (1)	57.9 (0.5)	100 (20)	55 (2)	78 (3)	40 (20)
Phosphorus(P)(g kg^{-1})	0.78 (0.03)	1.20 (0.06)	0.86 (0.02)	1.6 (0.2)	0.71 (0.02)	0.84 (0.04)	0.71 (0.02)	1.0 (0.1)	0.82 (0.06)	1.4 (0.3)	0.71 (0)	0.9 (0.1)
Mehlich 3-P (g kg^{-1})	0.6	0.8	0.6	0.8	0.5	0.68	0.60	0.64	0.6(0) [73] ^[f]	0.8(0)[57] ^[f]	0.6(0.1)[84] ^[f]	0.66(0.03)[73] ^[f]
WSE-P	118 (1)	193 (2)	137 (2)	270 (7)	101.3 (0.1)	119 (2)	121.0 (04)	210 (10)	130 (10)	230 (50)	110 (10)	160 (60)
Moisture content (fraction)	0.915 (0.001)	0.897 (0.001)	0.916 (0.001)	0.897 (0.004)	0.930 (0.002)	0.941 (0.001)	0.9231 (0.0003)	0.929 (0.001)	0.916 (0.001)	0.897 (0.000)	0.926 (0.005)	0.935 (0.008)

Table B5. (continued).

Chemical and Physical Properties ^[a]	Beneath Stockpile 1 ^[c]		Beneath Stockpile 2 ^[c]		Beneath Stockpile 3 ^[c]		Beneath Stockpile 4 ^[c]		Grand Mean ^[d]		Grand Mean ^[d]	
	Diameter NR (76-305 mm)		Diameter NR (76-305 mm)		Diameter NR+SIM (76-305 mm)		Diameter NR+SIM (76-305 mm)		NR (76-305 mm)		NR+SIM (76-305 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
pH	5.27 (0.03)	5.59 (0.03)	5.63 (0.03)	5.8 (0.02)	5.29 (0.08)	5.85 (0.03)	5.62 (0.04)	5.54 (0.04)	5.5 (0.3)	5.7 (0.1)	5.5 (0.2)	5.7 (0.2)
EC(μ S/cm)	121 (2)	641 (1)	1310 (50)	900 (100)	900 (100)	340 (30)	740 (10)	510 (40)	700 (800)	800 (200)	800 (100)	400 (100)
	-----(mg kg^{-1}) ^[e] -----											
Arsenic (As)	NA ^[g]	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
WSE-As	0.12 (0.01)	0.07 (0.01)	<0.3 (0)	0.14 (0.01)	<0.3 (0)	0.05 (0.01)	<0.3 (0)	0.07 (0.02)	0.2 (0.1)	0.11 (0.05)	<0.3 (0)	0.06 (0.01)
Copper (Cu)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-Cu	3	8	5	9	4	7	6	9	4 (1)	8.5 (0.7)	5 (1)	8 (1)
Manganese(Mn)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-Mn	8	8	8	8	9	9	10	14	8 (0)	8 (0)	9.5 (0.7)	12 (4)
Zinc (Zn)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-Zn	6	9	5	8	4	6	6	14	5.5 (0.7)	8.5 (0.7)	5 (1)	10 (6)
Carbon (C) (g kg^{-1})	4.5 (0.4)	7.2 (0.4)	3.45 (0.07)	4.9 (0.6)	3 (0)	5.0 (0.6)	4 (1)	4.4 (0.5)	4.0 (0.7)	6 (2)	3.4 (0.3)	4.7 (0.4)
WSE-DOC (g kg^{-1})	0.7 (0.1)	0.31 (0.01)	0.287 (0.003)	0.46 (0.01)	0.13 (0.01)	0.150 (0.002)	0.144 (0.001)	0.189 (0.004)	0.50 (0.3)	0.4 (0.1)	0.14 (0.01)	0.17 (0.03)
Nitrogen (N)	650 (70)	1050 (70)	500 (0)	650 (70)	400 (0)	650 (70)	400 (0)	600 (0)	600 (100)	900 (300)	400 (0)	630 (40)
NH ₄ -N	277 (2)	2.2 (0.2)	26 (1)	24.4 (0.4)	1 (1)	21 (3)	1 (1)	3 (1)	200 (200)	10 (20)	1 (0)	10 (10)
NO ₃ -N	156 (2)	72.1 (0.2)	91 (4)	52.9 (0.9)	79 (3)	27 (5)	60 (1)	49 (1)	120 (50)	60 (10)	70 (10)	40 (20)
Phosphorus(P)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-P	370	420	340	450	420	440	450	510	360 (20)	440 (20)	440 (20)	480 (50)
WSE-P	60.7 (0.4)	83 (1)	62.0 (0.9)	132 (2)	74.61 (0.03)	83 (2)	90.6 (0.2)	117 (1)	61 (1)	110 (30)	80 (10)	100 (20)
Moisture content (fraction)	0.914 (0.001)	0.873 (0.001)	0.93 (0.07)	0.916 (0.002)	0.931 (0.001)	0.923 (0.002)	0.9354 (0.0004)	0.927 (0.004)	0.92 (0.01)	0.89 (0.03)	0.933 (0.003)	0.925 (0.003)

Table B5. (continued).

Chemical and Physical Properties ^[a]	Beneath Stockpile 1 ^[c]		Beneath Stockpile 2 ^[c]		Beneath Stockpile 3 ^[c]		Beneath Stockpile 4 ^[c]		Grand Mean ^[d]		Grand Mean ^[d]	
	Diameter NR		Diameter NR		Diameter NR+SIM		Diameter NR+SIM		NR		NR+SIM	
	(305-610 mm)		(305-610 mm)		(305-610 mm)		(305-610 mm)		(305-610 mm)		(305-610 mm)	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
PH	5.41 (0.02)	5.08 (0.04)	4.98 (0.04)	5.01 (0.03)	5.51 (0.01)	5.06 (0.03)	6.14 (0.03)	5.51 (0.01)	5.2 (0.3)	5.05 (0.05)	5.8 (0.4)	5.3 (0.3)
EC ($\mu\text{S}/\text{cm}$)	1100 (100)	1060 (30)	1300 (100)	1000 (100)	1440 (50)	720 (50)	1300 (80)	710 (80)	1200 (100)	1030 (40)	1400 (100)	715 (7)
-----(mg kg^{-1}) ^[e] -----												
Arsenic (As)	NA ^[g]	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
WSE-As	<0.3 (0)	0.029 (0.001)	<0.3 (0)	0.03 (0.02)	<0.3 (0)	0.04 (0.01)	<0.3 (0)	0.05 (0.01)	<0.3 (0)	0.03 (0.001)	<0.3 (0)	0.05 (0.01)
Copper (Cu)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-Cu	3	7	2	5	6	6	5	7	2.5 (0.7)	6 (1)	5.5 (0.7)	6.5 (0.7)
Manganese(Mn)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-Mn	3	4	2	6	9	9	5	13	2.5 (0.7)	5 (1)	7 (3)	11 (3)
Zinc (Zn)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-Zn	2	4	1	3	3	5	2	4	1.5 (0.7)	3.5 (0.7)	2.5 (0.7)	4.5 (0.7)
Carbon (C) (g kg^{-1})	4.1 (0.2)	7.2 (0.5)	6.6 (0.6)	6.1 (0.1)	4 (0)	4.9 (0.2)	3 (0)	3.8 (0.7)	5 (2)	6.7 (0.7)	3.5 (0.7)	4.34 (0.8)
WSE-DOC (g kg^{-1})	0.08 (0.01)	0.1794(0.0004)	0.094(0.001)	0.187(0.002)	0.358(0.002)	0.206(0.003)	0.42 (0.03)	0.283 (0.001)	0.09 (0.01)	0.18 (0.01)	0.39 (0.04)	0.24 (0.05)
Nitrogen (N)	850 (70)	1300 (0)	750 (70)	1100 (0)	750 (70)	700 (0)	500 (0)	600 (100)	800 (70)	1200 (100)	600 (200)	650 (70)
NH ₄ -N	86 (1)	57 (2)	110 (1)	76 (2)	85.9 (0.8)	12 (2)	63.8 (0.5)	16 (5)	100 (20)	70 (10)	70 (20)	14 (3)
NO ₃ -N	152 (2)	96 (6)	114.1 (0.02)	98 (1)	100 (2)	55 (2)	62.0 (0.2)	52 (9)	130 (30)	97 (1)	80 (30)	54 (2)
Phosphorus(P)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Mehlich 3-P	60	90	20	140	170	260	210	310	40 (30)	120 (40)	190 (30)	290 (40)
WSE-P	<1.3 (0)	2.1 (0.1)	<1.3 (0)	2.37 (0.09)	34.5 (0.4)	18 (1)	37.7 (0.02)	44 (1)	<1.3 (0)	2.2 (0.2)	36 (2)	30 (20)
Moisture content (fraction)	0.8537 (0.0009)	0.8338 (0.0025)	0.8764 (0.0256)	0.8394 (0.0016)	0.8913 (0.0002)	0.9048 (0.0035)	0.9132 (0.0012)	0.8993 (0.0013)	0.87 (0.02)	0.837 (0.004)	0.90 (0.02)	0.902 (0.004)

^[a] See footnote in Table B1 for methods.

^[b] See footnote in Table B1 for limits of quantitation.

^[c] Data represent the mean and standard deviation (in parentheses) of 3 analytical replicates.

^[d] Data represent the grand mean of concentrations measured for each treatment (NR and NR+SIM) for summer and winter. Standard deviations of those means are shown in parentheses.

^[e] Except where denoted.

^[f] Mehlich data is for single sample analysis. The mean of these analyses is shown with the standard deviation in parentheses. Percent of strong-acid extractable metal is shown in brackets for the 0-25 and 25-76 mm depths.

^[g] Not analyzed.

APPENDIX C. QUALITY CONTROL DATA

Table C1. Mean concentrations, standard deviations, and percent recovery of metals (in parentheses) measured in the Standard Reference material[®] 2710 (Montana Soil) from the National Institute of Standards and Technology (NIST). The Standard Reference Material was digested with each batch of soil digests^[a].

Analyte	NIST ^[b] Reported “leachable” [“total”]	Measured Analyte Soil digest Batch 1	Measured Analyte Soil digest Batch 2	Measured Analyte Soil digest Batch 3	Measured Analyte Soil digest Batch 4	Measured Analyte Soil digest Batch 5	Measured Analyte Soil digest Batch 6	Measured Analyte Soil digest Batch 7	Measured Analyte Soil digest Batch 8	Measured Analyte Soil digest Batch 9
----- mg kg ⁻¹ ----- (% NIST “leachable” concentration) ^[c]										
Aluminum	18,000 [64,000 ± 800]	26,900 ± 400 (149 ± 2) ^[c]	26,700 ± 900 (148 ± 5)	29,100 ± 3500 (162 ± 19)	26,400 ± 1900 (147 ± 11)	23,500 ± 1100 (131 ± 6)	23,000 ± 1000 (128 ± 6)	23,500 ± 500 (131 ± 3)	23,300 ± 1300 (129 ± 7)	21,700 ± 600 (121 ± 3)
Arsenic	590 [626 ± 38]	609 ± 5 (103 ± 0.8)	616 ± 4 (104 ± 0.7)	611 ± 8 (104 ± 1)	620 ± 10 (105 ± 2)	541 ± 8 (92 ± 1)	550 ± 10 (93 ± 2)	560 ± 30 (95 ± 5)	543 ± 2 (92 ± 0.3)	538 ± 7 (91 ± 1)
Copper	2700 [2,950 ± 130]	2,820 ± 20 (104 ± 0.7)	2,818 ± 6 (104 ± 0.2)	2740 ± 10 (101 ± 0.4)	2,500 ± 100 (93 ± 4)	2,500 ± 100 (93 ± 4)	2610 ± 40 (97 ± 1)	2700 ± 100 (100 ± 4)	2580 ± 20 (96 ± 0.7)	2580 ± 30 (96 ± 1)
Iron	27,000 [33,800 ± 1000]	29,100 ± 1300 (108 ± 5)	31,000 ± 200 (115 ± 0.7)	30,300 ± 300 (112 ± 1)	36,000 ± 2000 (133 ± 7)	28,100 ± 700 (104 ± 3)	27,000 ± 1000 (100 ± 4)	28,600 ± 1300 (106 ± 5)	26,900 ± 400 (99 ± 1)	26,900 ± 300 (99 ± 1)
Manganese	7700 [10,100 ± 400]	8,380 ± 40 (109 ± 0.5)	9,480 ± 10 (123 ± 0.1)	8,498 ± 5 (110 ± 0.06)	6,930 ± 20 (90 ± 0.3)	7,200 ± 200 (94 ± 3)	7,300 ± 200 (95 ± 3)	7,400 ± 100 (96 ± 1)	7,160 ± 10 (93 ± 0.1)	7,210 ± 60 (94 ± 0.8)
Phosphorus	1060 [1,060 ± 150]	1,130 ± 20 (103 ± 2)	1,130 ± 20 (103 ± 2)	1,120 ± 10 (106 ± 1)	1,030 ± 20 (97 ± 2)	912 ± 9 (86 ± 0.8)	900 ± 20 (85 ± 2)	910 ± 40 (86 ± 4)	885 ± 8 (83 ± 0.8)	880 ± 10 (83 ± 1)
Zinc	5900 [6,952 ± 91]	6,100 ± 1500 (104 ± 25)	7,200 ± 200 (122 ± 3)	7,000 ± 100 (119 ± 2)	6,900 ± 400 (117 ± 7)	6,100 ± 200 (103 ± 3)	6,200 ± 200 (105 ± 3)	5,900 ± 300 (100 ± 5)	6,100 ± 100 (103 ± 2)	6,080 ± 70 (103 ± 1)
Replicates		2-3	2-3	3	3	3	3	2-3	2-3	3

^[a] Solid Analytical Method (preparation and analysis) using US-EPA SW-846 3050/6010 for ICP-OES analysis (As and P). US-EPA SW-846 3050/7020 (Al), 7210 (Cu) 7380 (Fe), 7460 (Mn), and 7950 (Zn) for AAS.

^[b] Mean concentrations and standard deviations of “leachable” and “total” analytes reported by the National Institute of Standards and Technology for the Standard Reference material[®] 2710 (Montana soil).

^[c] Data in parentheses is the % of NIST “leachable” analyte concentration.

Table C2. Percent recovery^[a] of selected metals/metalloids measured in spiked soil and turkey litter samples after acid digestion^[b].

Analyte	Initial Soil (0-76 mm)	Initial Soil (610-914 mm)	Initial Turkey Litter (<2 mm fraction)	Initial Turkey Litter (>2 mm fraction)
	Percent Recovery (%)			
Arsenic	97	88	94	94
Copper	93	91	106	99
Manganese	84	80	98	93
Phosphorus	100	104	108	150
Zinc	103	102	97	124

^[a] Percent recovery data are the average of two duplicate spikes.

^[b] Solid Analytical Method (preparation and analysis) using US-EPA SW-846 3050/6010 for ICP-OES analysis (As and P). US-EPA SW-846 3050/7210 (Cu), 7460 (Mn), and 7950 (Zn) for AAS.