

**THE RELEASE AND MOBILITY OF TRACE ELEMENTS FROM
POULTRY LITTER: INSIGHTS FROM FIELD, LABORATORY AND
MODELING EXPERIMENTS**

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In

GEOSCIENCES

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ABSTRACT

Organoarsenic compounds and trace elements are added to poultry feed for disease control and improved productivity. These elements are excreted into poultry litter, which is land applied as fertilizer. This study utilized field and laboratory experiments to address the mobility of arsenic (As) and other litter-derived elements within the Broadkill River watershed, DE, a region of intense poultry production. For the first project, a litter application experiment was conducted at an instrumented field site in Sussex Co., DE. After establishing baseline geochemistry of soil water, ground water, and surface water at the site, poultry litter was then applied, followed by post litter application monitoring. Results showed low concentrations of As and other litter-derived elements in soil water; little impact was measured on ground or surface water. Mass balance calculations suggest that the majority of mass of leached elements was accounted for by uptake in underlying soils. The second project examined the impact of long-term litter application on chemical signatures of As, copper (Cu), zinc (Zn) and phosphorous (P) in stream sediments within the Broadkill River watershed. Sediment samples were collected from both upgradient and downgradient reaches within the watershed. Using GIS to overlay hydrology and land use, statistical relationships between As, Cu, Zn and P enrichment factors and land use were examined. Results did not show a relationship between these elements and agricultural land use, but did show a correlation between some of the elements and residential land use. The third project examined the influence of dissolved organic carbon (DOC) on the mobility of As, Cu, Zn and P using laboratory column experiments with soil from the field site. Two influent solutions were used: poultry litter leachate and a simulated solution of similar element concentrations, pH, and ionic strength but without DOC. Results showed that DOC enhanced the mobility of all four elements, but that even with DOC, 60-70% of the Zn, As and P mass was retained within the soil. Cu was fully mobilized by DOC. Patterns of breakthrough curves (BTCs) and mass calculations suggest that the behavior of these litter-derived elements in the column is controlled by both adsorption (including competitive) to soils and complexation with DOC.

DEDICATION

This dissertation is dedicated to God Almighty who has given me the grace, strength and wisdom to attain this milestone. His name will forever be praised in my life.

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ATTRIBUTION

Dr. Madeline Schreiber, Associate Professor of Geosciences in the Department of Geosciences at Virginia Tech, is co-author for Chapters 2, 3 and 4.

CHAPTER 1: INTRODUCTION

The use of organoarsenicals as poultry feed additives has increased dramatically as the industry has grown (Garbarino et al., 2003). Roxarsone (3-nitro-4-hydroxyphenylarsonic acid) is added to poultry feed at concentrations between 27 – 45 g per ton (Anderson and Chamblee, 2001). Trace metals, including Fe, Mn, Zn, Cu, and Se, are also routinely added as nutrient supplements (Han et al., 2000; Rutherford et al., 2003; Sims and Wolf, 1994). Roxarsone prevents intestinal parasites in poultry, promotes growth, allows for better feathering, increases egg production and also aids in pigmentation (Garbarino et al., 2003; O'Connor et al., 2005). Because poultry litter is rich in nutrients, more than 90% is land applied as fertilizer to farmland in the U.S (Jackson and Bertsch, 2001). However, as roxarsone uptake in tissue is low (Anderson and Chamblee, 2001), most of the As is excreted from the animals resulting in elevated concentration (15-77 mg/kg) of As and other trace elements in poultry litter (Anderson and Chamblee, 2001; Garbarino et al., 2003; Jackson and Miller, 1999; Sims and Wolf, 1994). Bednar et al (2003) estimated that with 8.3 billion poultry raised in the U.S annually, more than 350,000 kg of As as roxarsone or its biotransformation products are released to the environment from poultry litter use each year.

Studies have shown that 70-75 % of arsenic (As) from poultry litter is water soluble (Jackson and Miller, 1999; Rutherford et al., 2003), raising concern that poultry litter application may introduce excess As into the environment (Abernathy et al., 2003; Chen et al., 1996; Kessel et al., 2002). In 2001, the EPA lowered the Maximum Contaminant Level (MCL) for arsenic (As) in drinking water to 10 µg/L due to detrimental effects of As on humans (NRC, 2001). Because As is carcinogenic, locating sources and sinks of As is critical for protecting human and environmental health.

The research presented in this dissertation focuses on examining the pathways of organoarsenicals and other trace elements released from land-applied poultry litter on the Delmarva Peninsula, an area of intense poultry production within the U.S. To accomplish this objective, three separate research elements, organized as chapters, were conducted consisting of complementary field, laboratory and GIS/modeling experiments. The first chapter has been published in *Applied Geochemistry*, the second chapter is in the submission process to *Environmental Monitoring and Assessment*, and the third chapter will be submitted to the *Journal of Contaminant Hydrology*. The chapters are briefly described below.

CHAPTER 2: RELEASE OF ARSENIC AND OTHER TRACE ELEMENTS FROM POULTRY LITTER: INSIGHTS FROM A FIELD EXPERIMENT ON THE DELMARVA PENINSULA, DELAWARE

The objective of this chapter was to examine the release and mobility of As and other trace elements (Cu, Zn, and P) released from poultry litter application to a field site within the Delmarva Peninsula, DE. This study involved site instrumentation and background monitoring, followed by poultry litter application and a period of post application monitoring. Parallel laboratory experiments were conducted to quantify leaching rates of As and other trace elements from litter. A mass balance was also conducted to examine the fate of trace elements released from the litter.

CHAPTER 3: IMPACT OF POULTRY LITTER APPLICATION ON SEDIMENT CHEMISTRY OF THE BROADKILL RIVER ESTUARY SYSTEM, DELAWARE

The objective of this chapter was to investigate the impact of historical poultry litter application on the trace element chemistry of stream sediments in the Broadkill River watershed on the Delmarva Peninsula. This study involved collection of sediment samples from streams in the Broadkill watershed and construction of a GIS database combined with statistical analysis to examine relationships between trace element concentrations, land use, and geology.

CHAPTER 4: USING LABORATORY COLUMN EXPERIMENTS TO EXAMINE TRANSPORT OF ARSENIC AND TRACE ELEMENTS RELEASED FROM POULTRY LITTER

The objective of this chapter was to determine the extent to which litter-derived DOC influences the release and transport of As and other trace elements from litter into underlying sediment. Using sediment collected from the DE field site, column experiments were conducted using poultry litter leachate and simulated litter solution without DOC but similar concentrations of trace elements, pH and ionic strengths.

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CHAPTER 2

Release of Arsenic and Other Trace Elements from Poultry Litter: Insights from a Field Experiment on the Delmarva Peninsula, Delaware

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Abstract

We conducted a poultry litter application to examine field scale release and transport of trace elements from poultry litter into the subsurface. Field monitoring before and after litter application demonstrated increases in major ion, nutrient, and trace element concentrations in soil water after application, but concentrations of trace elements were all below regulatory standards. Using laboratory stepwise extractions of litter, projected leaching rates of trace elements are fastest for As, followed by Cu and Zn. Comparison of the projected (from laboratory extractions) to actual (measured in the field) trace element concentrations in litter show that laboratory-derived rates generally overpredict leaching, but the long-term projections of Cu and Zn concentrations remaining in litter are within 20% of the field measurement. Arsenic leaching from litter was underpredicted by the lab leaching model by over 100%, suggesting that other processes (perhaps biological) occurring in the field allowed for additional As to be leached/removed. Mass balance coupled with conservative tracer calculations reveal that the vadose sediment was the main sink for the trace elements, with lesser uptake of Cu and Zn (not As) by orchard grass (*Dactylis glomerata*). Overall, results of this study showed that the fate and transport of trace elements from poultry litter are controlled by their leaching rate from litter, adsorption, uptake in vegetation and dilution. An additional process affecting As is biotransformation.

Introduction

The use of organoarsenicals as poultry feed additives has increased dramatically as the industry has grown (Garbarino et al., 2003a). Until recent safety concerns prompted a voluntary withdrawal from the market in July 2011, roxarsone (3-nitro-4-hydroxyphenylarsonic acid) has been added to poultry feed at concentrations between 27 – 45 g per ton (Anderson and Chamblee, 2001a). Roxarsone acts as a coccidiostat by preventing intestinal parasites in poultry and also as a growth stimulant, a major economic advantage for U.S. poultry farmers (O'Connor et al., 2005). Because poultry litter is rich in nutrients, more than 90% is land applied as fertilizer to farmland in the U.S (Jackson and Bertsch, 2001). However, as roxarsone uptake in tissue is low (Anderson and Chamblee, 2001b), from a mass balance perspective, most of the As is excreted from the animals resulting in elevated concentration (15-77 mg/kg) of As in poultry litter (Anderson and Chamblee, 2001b; Garbarino et al., 2003b; Jackson and Miller, 1999). Bednar et al. (2003) estimated that with 8.3 billion poultry raised in the U.S annually, more than 350,000 kg of As as roxarsone or its biotransformation products are released to the environment from poultry litter use each year. In addition to As, other trace elements such as Fe, Mn, Zn, Cu, and Se are also routinely added as nutrient supplements (Han et al., 2000; Rutherford et al., 2003; Sims and Wolf, 1994) which result in elevated concentrations of these elements in in poultry litter.

In 2001, the EPA lowered the Maximum Contaminant Level (MCL) for As in drinking water to 10 µg/L due to its toxic and carcinogenic effects on humans (NRC, 2001). Concern about the possible role of poultry litter in releasing As to water supplies prompted several studies on the mobility of roxarsone and As derivatives in soils (Morrison, 1969). A report from USGS National Water-Quality Assessment (NAWQA) program documented As concentration up to 27 µg/L in groundwater near a litter applied field (Hancock et al., 2002). Brown et al. (2005) found low concentrations of As(V) in soil water underlying a litter applied site in the Shenandoah Valley of Virginia; soil water under an adjacent field where litter was not applied had no As. Recently, Church et al. (2010) reported on As release from a litter storage shed to drainage ditches at a site on the Delmarva Peninsula.

Biogeochemical processes play an important role in roxarsone release and subsequent transport. Several studies have demonstrated that roxarsone degrades during composting (Bednar et al., 2003; Garbarino et al., 2003b) and after land application of litter or from poultry

litter applied fields (Arai et al., 2003; Jackson et al., 2003; Rutherford et al., 2003). Degradation products include both organic and inorganic As species (As (III), As (V), roxarsone, 3-amino-4-hydroxyphenyl arsonic acid (3A4HBAA), 4-hydroxyphenyl arsonic acid (4HBAA), and dimethylarsinate (DMA) (Arai et al., 2003; Jackson and Bertsch, 2001; Rosal et al., 2005). Stolz et al. (2007) showed occurrence of rapid biotransformation of roxarsone from poultry litter by anaerobic Clostridia to 3A4HBAA and inorganic As species. In addition, photodegradation of roxarsone in poultry litter leachate was reported by Bednar et al. (2003).

Adsorption of roxarsone and As byproducts can also influence mobility. It is well known that As adsorbs strongly to metal oxides and clays, and that the adsorption is highly pH dependent (Stollenwerk, 2003 and references therein). Harvey (2006) conducted comparative pH stat studies of roxarsone and As(V) adsorption to goethite and found similar adsorption patterns, suggesting that the As(V) functional group on roxarsone was active in the adsorption process.

The fate and transport of organoarsenicals and other litter trace elements clearly depends on the extent to which these compounds interact with bacteria, minerals and organic matter in soils and sediments. Although studies have suggested that biogeochemical processes control arsenical behavior, there is very little understanding of how these processes together impact the mobility of trace elements at the field scale. The objective of this study was to examine the release and subsequent mobility of trace elements, including As, from poultry litter at the field scale. To achieve this, we implemented a litter application experiment at an instrumented field site and calculated a mass balance of trace elements released from the litter. We also conducted laboratory experiments to determine leaching rates of trace elements from the litter.

Study Area

The study area is in Sussex County, Delaware, within the Delmarva Peninsula of the Atlantic Coastal Plain Province. The peninsula contains five main aquifers, comprised of predominantly sand and gravels: the Potomac group (Patuxent and Patapsco), Magothy, Aquia, Piney Point, Miocene and the Columbia. These aquifers are separated by semi confining beds, composed of clay and silt (Drummond and Bolton, 2010). The stratigraphic units for these aquifers and confining beds dip gently from northwest to southeast with the exception of the Columbia aquifer, a surficial unconfined aquifer on the southeastern shore of the peninsula. The

Columbia is composed of Pliocene to Pleistocene sediments that are fluvial, littoral and shallow marine in origin (Drummond and Bolton, 2010). It consists of two main stratigraphic units, the Beaverdam sands and the Pensauken formation (Bachman and Wilson, 1984). Sediments are composed of predominantly coarse-grained feldspathic quartz sands and gravels, with interbedded light gray and brown silty clays. The aquifer is highly transmissive, and thus has been used extensively for irrigation purposes in the region (Drummond and Bolton, 2010).

The field site is a two acre plot (**Figure 2.1**) underlain by the Columbia aquifer, containing deposits of moderate to well-sorted sand with thin discontinuous silty clay lenses. Depth to the water table is approximately 3.1 m below ground surface (bgs). As the topography of the field area is flat, the horizontal hydraulic gradient is shallow (~ 0.002). The low-relief site drains to an unnamed stream contained within a wetland floodplain of a tributary to the Broadkill River. Prior to our experiments, this site had not received litter application for more than five years, making it an ideal site to establish baseline conditions before the application of poultry litter.

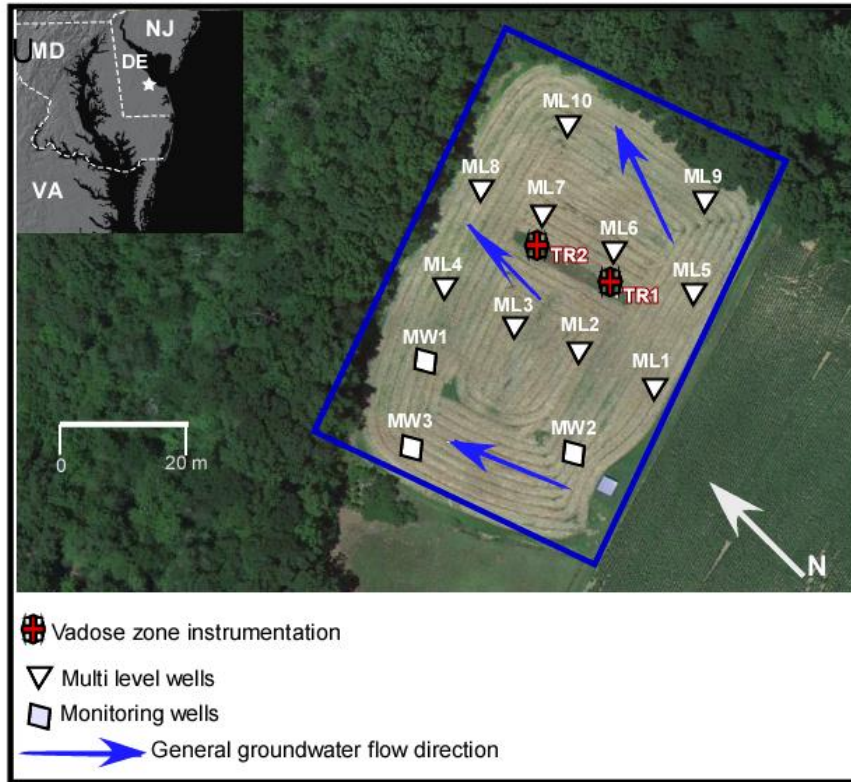


Figure 2.1 Location of field site in Sussex Co., DE (inset), and schematic base map of the field site showing locations of well nests (ML), monitoring wells (MW), and vadose zone instrumentation installed in trenches (TR). The vadose zone instrumentation consists of lysimeters, soil moisture sensors, and in situ redox probes (see Figure 2 for details). The general direction of groundwater flow is toward the forested wetland to the north. Aerial photo from Google Earth.

Methods and Materials

Site Instrumentation

The first phase of instrumentation, which occurred in Fall 2008, included installation of two transects of nested monitoring wells with each nest containing three wells, screened at depths of 2.4-3.4 m, 3.6-4.6 m, and 4.8-5.8 m bgs (**Figure 2.2**). During well installation, soil core samples were collected using direct push methods for particle size distribution and geochemistry. Immediately after installation, the wells were developed with a bailer to remove fine particles from the well screens. A shallow well was also installed in the hyporheic zone in the wetland adjacent to the field site.

The second phase of instrumentation was conducted in Spring 2009 and included installation of lysimeters, moisture sensors and redox loggers. A total of four zero-tension

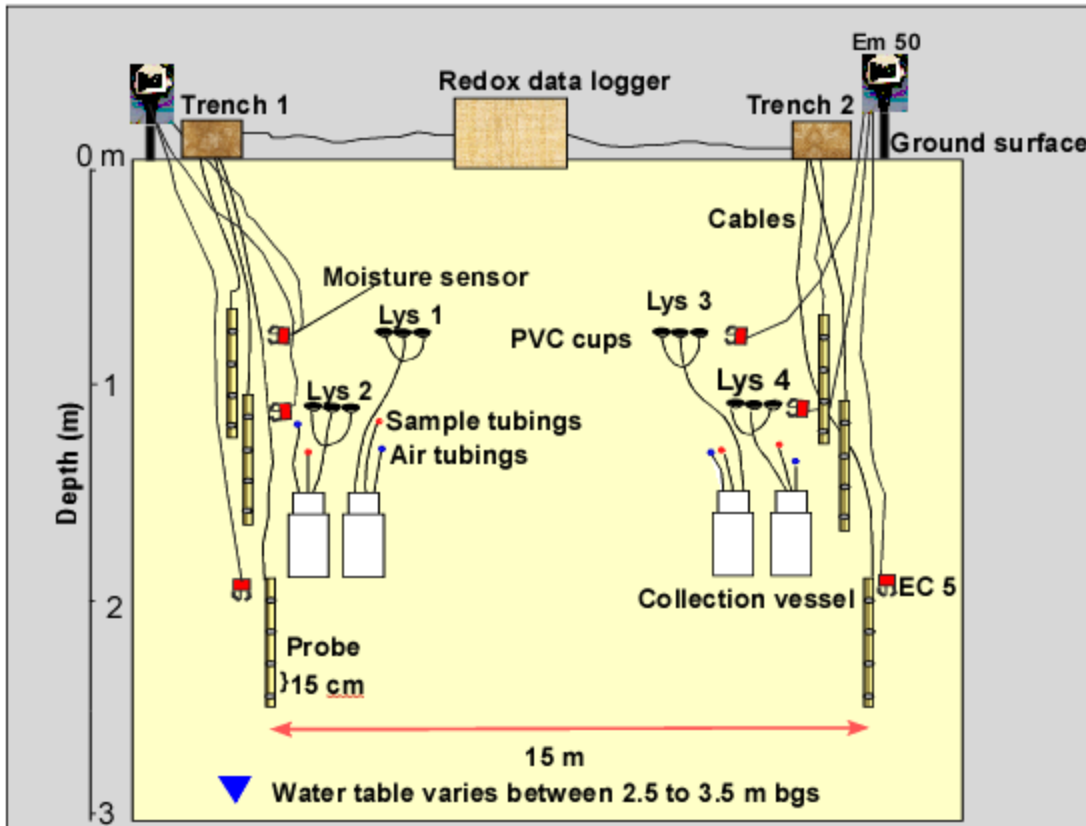


Figure 2.2. Schematic diagram of the vadose zone instrumentation. The instrumentation includes in situ redox probes, moisture sensors and lysimeters. Lysimeter air and sample tubes go to the surface. See Figure 1 for location of trenches.

lysimeters were constructed and installed; two installed at a depth of ~80 cm bgs and two installed at depth of 110 cm bgs. The lysimeter cups (PVC disks, diameter of each cup: ~15 cm) were filled with dried fine sand which was initially pre-treated with hydrochloric acid (HCl) and thoroughly rinsed with deionized water. Installation was done by digging two trenches with a small void in the walls of the trenches for lysimeter cups (lined with mesh and filled with sand), which were pressed tightly against the roof of the voids to ensure direct hydrological contact with the soil. Water intercepted by each of the three disks is routed through a tube to a 5 L collection vessel (**Figure 2.2**). Two pieces of tubing extended to the surface from water collection vessels at the bottom of the pit, one for collecting water through pumping and the other for air entry.

Soil moisture sensors (EC5, Decagon Devices, Inc.) were installed in the undisturbed part of the trench wall at depths of 75 cm, 110 cm, and 190 cm respectively (**Figure 2.2**). The sensor

prongs were connected by cable to a data logger (EM 50) at the surface. The data logger was programmed for an hourly continuous monitoring of relative changes in moisture condition of the soil. A tipping bucket precipitation gauge was also installed to collect precipitation data at the field site.

A redox monitoring system, the Hypnos 2.0 (after Vorenhout et al., 2004), was installed in the vadose zone to collect continuous measurements of soil redox potential. The Hypnos was calibrated by the manufacturer; we re-calibrated both the reference and measurement probes (six) by inserting them in Pt-Ag/AgCl solution for 24 hours. Results indicated that all six probes gave the expected value (220 ± 20 mv at 25° C). The systems redox probes were inserted into undisturbed section of the trenches at several depths (0.75 to 1.35 m, 1.35 to 1.95 m and 1.95 to 2.55 m) below the surface (**Figure 2.2**). Each probe is 0.60 m long and consists of four sensors which are evenly spaced at a distance of 0.15 m apart. The probes are connected to a data logger which collects hourly redox data. The data logger is also connected to Ag/AgCl reference electrode buried into the undisturbed soil. After the installation of the lysimeters, soil moisture sensors, and redox probes was complete, the trenches were backfilled with the original soil.

Water Sampling and Analysis

Prior to ground water sample collection, water levels were measured in all wells at each sampling event, which occurred on a monthly to quarterly basis from December 2008 to May 2010. The general direction of groundwater flow is towards the north and northwest (**Figure 2.1**).

Groundwater samples were collected under low flow after purging three well volumes with a peristaltic pump. Unstable parameters (water temperature, dissolved oxygen, specific conductance, and pH) were measured on site in flow cells after allowing them to stabilize prior to measurement. Soil water from lysimeters and water from the hyporheic zone well installed in the adjacent wetland was collected using a peristaltic pump. Lysimeters were fully purged after each sampling event. Surface water from the wetland was collected with pre-cleaned sampling containers. Duplicate samples were collected (1 duplicate per 20 samples) during each sampling event.

All water samples were filtered (0.45 μ m) in the field. Samples for cation and trace element analyses were acidified with trace metal grade nitric acid (HNO₃) in the field, while dissolved organic carbon (DOC) samples were preserved with concentrated hydrochloric acid (HCl). Alkalinity and anion samples were not preserved. Samples were chilled with ice until analysis. Sample bottles were cleaned thoroughly prior to sample collection using the following methods: trace metal grade HNO₃ washed for cations and trace elements; HCl washed for DOC, and soap with triple DI wash for all others.

Major anions (Cl, NO₃, and SO₄) were analyzed by Ion Chromatography (Dionex DX-120; detection limit 0.1 mg/L). Alkalinity was measured by titration with sulfuric acid (Hach method 8203; detection limit 1 mg/L). DOC was analyzed using a Shimadzu Carbon Analyzer (TOC-VCSN, Kyoto Japan, detection limit 0.1 mg/L). Arsenic was analyzed using Graphite Furnace Atomic Absorption Spectrophotometry with Zeeman background correction (GFAAS; Varian Spectra 220Z; detection limit 3 μ g/L). Analysis of other cations and trace elements (Al, Cu, Fe, Zn, Mn, Ca, Na, Mg, and P) was conducted using Inductive Couple Plasma-Atomic Absorption Spectrometry (ICP-AES) with detection limits varying between 3 and 175 μ g/L at the Virginia Tech Soil and Plant Analysis Laboratory (VTSPAL). Replicate analyses and laboratory blanks were run with each analytical method during every batch to ensure laboratory quality control.

Differences in the means of concentrations of major and minor ions between the samples collected to represent background and those collected after litter application were tested by locations using a paired t-test at a significance level of 0.05.

Soil Geochemistry and Particle Size Distribution

Soil cores collected during well installation were partitioned into sections based on observed changes in lithology. An additional set of cores was collected upon completion of the post-application monitoring. For each set of cores, samples from each section were sampled, dried, and sieved (< 2 mm fraction). The sieved fractions were analyzed for particle size analysis (PSA) and digested for chemical analysis, as described below.

Subsets of the sieved fractions were homogenized and analyzed for basic soil parameters (pH, organic matter (OM), cation exchange capacity (CEC)) at the VTSPAL. Samples were also digested using microwave digestion (CEM Mars Express) with EPA method 3052 (Agazzi and

Pirola, 2000) modified by substituting HCl for hydrofluoric acid (HF). The digestate was analyzed for As, Cu, Zn, Fe, Mn, Al, P, K, Na, and Mg by ICP-AES at the VTSPAL. A standard reference soil (SRM 2587) obtained from National Institute of Standards and Technology (NIST) was also extracted using the same method to determine the degree of trace element recovery of our method. Results of the microwave digestion of the reference soil showed recovery rates of 118, 84, 85, 88, 105, and 105% for Cu, Mn, Fe, P, Zn, and As, respectively, indicating that even without the use of HF, extractions of the trace elements were complete within experimental error. Duplicate samples of the soil were processed to ensure sampling quality control; replicate analyses and laboratory blanks were conducted to ensure laboratory quality control.

Particle size distribution of the sieved and homogenized soil samples was measured using the ASTM 152 H hydrometer method. Soil samples (40 g, sieved <2mm) were first decoagulated with 4% of sodium hexametaphosphate for 24 h. Modification to the method was based on recording temperature and hydrometer readings at various time intervals (from 1 min to 24 h), which eliminated the need for a temperature controlled water bath.

Poultry Litter Application

After eight months of background monitoring, the landowner cleared the field site and applied fresh poultry litter at the rate of 3-4 tons per acre on October 2, 2009. During application, litter samples were collected for laboratory analysis. Although no crop was planted after litter application, orchard grass, which had been planted at the field site previously, grew. Samples of the grass were collected before the first harvest in Spring 2010. After drying, the grass was ground using a mortar and pestle; a 0.5 g sample was extracted by microwave digestion (EPA method 3052).

Poultry Litter Extraction

Litter samples collected from the field (fresh, aged 53 d, aged 174 d) were brought to the laboratory, dried, disaggregated with a hand mill and sieved through a 2 mm sieve to remove detritus (wood shavings, feathers and twigs). The soluble fractions of trace elements were extracted from litter using 25 ml of 0.01M NaCl solution with 5 g dried, ground and sieved litter. The slurry was mixed on a wrist shaker for 5 d. Post extraction, the slurry was centrifuged (9000 rpm; 20 min), and the extracted supernatant filtered (0.45 μ m). Acid-soluble elements were

extracted by microwave digestion (EPA method 3052) using a 0.5 g homogenized litter sample. Trace elements in extracts were analyzed with ICP-AES, with the exception of chloride in soluble extracts, which was analyzed using a digital chloridometer (Labconco Corporation, Kansas, MO) and Ion Chromatography (Dionex DX-120; detection limit 0.1 mg/L) and As, which was analyzed using the GFAAS method described above.

In addition to the single extractions, we also conducted stepwise extractions, in which the fresh litter (5 g dried, ground and sieved) was extracted with 25 ml of 0.01 M NaCl for 5 d; the slurry was shaken, centrifuged, and supernatant extracted and filtered as described above. After the supernatant was decanted, an additional 25 ml of fresh 0.01 M NaCl solution was added, reacted for another 5 d and then for another 10 d. For each extraction, the supernatant was analyzed for trace elements using ICP-AES and GFAAS.

Speciation of As in soluble (0.01 M NaCl) extracts of a selected sample of litter leachate was conducted using IC-ICPMS (Ion Chromatography coupled with Inductively Coupled Plasma Mass Spectrometry) following the methods outlined in Garbarino et al. (2003b). Samples were preserved with 0.12 M EDTA (100 μ L for 10 ml sample) to maintain speciation (Garbarino et al., 2003b) prior to analysis. The As species, including As(III), As(V), and roxarsone, were separated on an AS7 column (Dionex IonPac 4x250 mm) using 2.5 mM HNO₃ in 0.5% methanol (0-1 min; 6-9 min) and 50 mM HNO₃ in 0.5% methanol (1-6 min) with a Dionex AGP-1 gradient pump. The speciated arsenic was then analyzed by ICPMS (X-series, Serial #X-0458). Quantification limits are approximately 5 μ g/L for As(III) and As(V) and 10 μ g/L for roxarsone.

Determination of Leaching Rates of Trace Elements from Poultry Litter

The rate of trace element leaching from poultry litter was determined using results of the acid digestion and stepwise extraction of fresh poultry litter. To calculate the leaching rate, we assumed that leaching is unopposed (once leached, solutes will not re-adsorb to the litter) and that leaching can be described by a first-order reaction, such that

$$\frac{dn_s}{dt} = -kn_s \quad (1)$$

where n_s is the number of moles of the trace element in the litter and k is the first order constant (1/t). We used the acid extractable data to represent the initial number of moles in litter (n_o), and

then at each time step, subtracted the number of moles extracted by the 0.01 M NaCl solution (n_{ext}) to determine the number of moles leached during each time step. At the start of the next extraction, the initial number of moles (n_1) was set to $n_0 - n_{ext1}$, and as follows, $n_2 = n_1 - n_{ext2}$ and $n_3 = n_2 - n_{ext3}$. As each of these stepwise extractions can be envisioned as different leaching experiments, the fraction of trace element remaining (α) was reset to 1 at the start of each extraction, such that $\alpha_0 = n/n_0$, $\alpha_1 = n_1/n_0$, $\alpha_2 = n_2/n_1$, and $\alpha_3 = n_3/n_2$. The value of k for each extraction step was then determined as

$$k_i = \frac{\ln(\alpha_i) - \ln(1)}{t} \quad (2)$$

where i represents the extraction step (1, 2 or 3), and t is the extraction time in days.

Mass Balance Calculations

To examine the fate of trace and other elements from the applied poultry litter, we calculated a mass balance of these elements within the vadose zone over the 174-d monitoring period. We assumed that the only input of elements during the monitoring period was the applied poultry litter, as no other soil amendments were applied during the monitoring period, and precipitation introduces negligible concentrations of trace elements. Output of trace elements can include leaching to soil water, surface runoff, and uptake by vegetation. For our calculations, we did not include surface runoff, as the surface topography is flat and there is no physical evidence (channel formation) at the site and we have never observed surface runoff, even during heavy rain events. The reservoir of trace elements was the 0.8 m column of sediment above the shallow lysimeter cups.

The mass input of elements released from the litter over the 174-d monitoring period was calculated as:

$$m_{i,in} = C_{i,totpl} f_{i,wspl} m_{pl} \quad (3)$$

where the $m_{i,in}$ is the mass (mg) of element i released from the litter, $C_{i,totpl}$ is the total concentration of element i in the litter (mg/kg), $f_{i,wspl}$ is the fraction of i of the total that leached from the litter, based on comparison of the 174-d aged litter collected from the field site to the fresh litter (note that this value is different from the water soluble fraction determined from the

lab experiments, as it is truly a measure of the mass of elements lost in the field during the experiment), and m_{pl} is the mass (kg) of poultry litter applied per 1 m² area. The mass of litter applied was based on a litter application rate over the trenches estimated at 4 tons per acre (0.89 kg per m²).

The mass of elements leached to soil water over the 174-d monitoring period was calculated as:

$$m_{i,leached} = \sum_{n=1}^3 (C_{i,sw} V_{i,sw})_n \quad (4)$$

where $m_{i, leach}$ is the mass (mg) of element i released into soil water from the three sampling events; $C_{i, sw}$ is the concentration of i measured in soil water, and $V_{i, sw}$ is the measured volume of soil water pumped from the lysimeter. The masses were summed for the three sampling events (11/24/09, 1/15/10, 3/25/10). Data from lysimeter 1 was used for calculating the mass output as it consistently contained water over the course of the experiment. To normalize to a 1 m² area for comparison to the input and storage, $m_{i,leached}$ was divided by the area of the three lysimeter cups (1.82 x 10⁻² m²).

The mass taken up into vegetation (orchard grass) was calculated as:

$$m_{i,uptake} = C_{i,veg} m_{veg} \quad (5)$$

where $m_{i, uptake}$ is the mass (mg) of element i taken up into vegetation, $C_{i, veg}$ is the total concentration of i in the orchard grass (mg/kg), and m_{veg} is the mass (kg) of vegetation yielded normalized to a 1 m² area, which in the case of orchard grass, was estimated as 2 tons per acre, or 0.449 kg/m² dry mass (Spitaleri et al., 2003).

The storage of elements was estimated by calculating the trace element uptake in the soil above the shallow lysimeters. To do this, we first compared the concentrations in the pre-application soil cores to those in the post-application cores collected at ML 6, adjacent to lysimeter 1. The stored mass of element i over the 174-d monitoring period was then calculated as:

$$m_{i,stored} = (C_{i,post} - C_{i,pre}) \rho_d V_{int} \quad (6)$$

where $m_{i, stored}$ is the mass (mg) stored in the soil column above lysimeter 1, $C_{i,pre}$ and $C_{i, post}$ are the concentrations of element i in a defined soil interval before and after litter application

(mg/kg), ρ_d is the estimated bulk density of the sediment (kg/m^3), and the V_{int} is the volume of the soil interval (m^3), normalized to 1 m^2 .

The accuracy of each mass balance component was examined using the error propagation method of Taylor (1982):

$$\frac{\delta C}{C} = \sqrt{\left(\frac{\delta x}{x}\right)^2 + \left(\frac{\delta y}{y}\right)^2 + \left(\frac{\delta z}{z}\right)^2} \quad (7)$$

where $\delta C/C$ is the fractional error in each mass balance component, and $\delta x/x$, $\delta y/y$, and $\delta z/z$ are the fractional errors for each source of error within each mass balance component. The fractional errors for the input include: the litter application rate (50%), the litter digestion, including weighing of sample and acid, and dilution errors (10%), and analysis of concentrations in the extract (10%). The errors for mass leached include: the estimate of functioning lysimeter area (33%, to account for a potential clog in one of the cups), analysis of concentrations in soil water (10%), and the measurement of soil water volume (10%). The estimated errors for uptake in vegetation include: the estimate of the orchard grass yield (50%), the grass digestion, including weighing of sample and acid, and dilution errors (10%), and analysis of concentrations in the extract (10%). The errors for storage include: sediment digestion (10%, including errors in weighing sediment and acid, and dilution errors), analysis of concentrations in the extract (10%) and the determination of sampling interval (25%, accounting for compaction of the sediment). Applying equation (7) to these estimates of experimental error, the uncertainties are approximately 52%, 36%, 52%, and 29%, for the mass input, leached, uptake, and storage components, respectively.

Calculation of Trace Element Retention Using Conservative Tracers

An alternative method to evaluate the retention of trace elements in the vadose zone is to compare the concentrations of trace elements in soil water to a conservative element that is also leached from litter. To do this, we first calculated the expected concentrations of trace elements in soil water, assuming conservative behavior, as:

$$C_{i,sw,exp} = \frac{C_{Cl,sw} C_{i,wspl}}{C_{Cl,wspl}} \quad (8)$$

where $C_{i,sw,exp}$ is the expected concentration of element i in soil water (mg/L), $C_{Cl,sw}$ is the concentration of chloride in soil water (mg/L, calculated as the difference between the maximum value measured after litter application and the measured background concentration), $C_{i,wspl}$ is the water soluble concentration of i in poultry litter (mg/kg) and $C_{Cl,wspl}$ is the water soluble concentration of chloride in poultry litter (mg/kg). This calculation assumed that chloride behaved conservatively in the vadose zone and that only the water soluble (not the acid extractable) concentrations from the litter were available for leaching.

We then calculated the fraction of element i retained in the sediment (F_r) as:

$$F_r = 1 - \frac{C_{i,sw,act}}{C_{i,sw,exp}} \quad (9)$$

The fraction of element retained from equation (8), which is based on measured concentrations of trace elements in soil water, can be compared to the fraction of mass retained (stored + vegetation) estimated by mass balance to provide an overall assessment of these different approaches.

Results

Litter Extractions

Trace Element Concentration and Speciation in Poultry Litter

Table 2.1 presents results of the water soluble and acid extractable elements in poultry litter for this and other studies. The total As concentration in the litter applied during this experiment ranges from 25 to 47 mg/kg, with an average concentration of 37 mg/kg (n=6). The soluble concentration of As in the litter ranged from 8 to 28 mg/kg, with an average of 21 mg/kg. Concentrations of other acid extractable and soluble ions in the poultry litter (P, S, Al, Fe, Zn, Mn, Cu) are all comparable to ranges of concentrations reported by other studies.

Speciation analysis of one of the fresh litter water extracts by IC-ICPMS indicates the presence of 2.5 mg/kg of As (III), 4.1 mg/kg of As (V) and 0.5 mg/kg of roxarsone. The sum of speciated concentrations (7.1 mg/kg) was slightly lower than the soluble As concentration of the extract (7.5 mg/kg) which may indicate the presence, albeit at low concentrations, of other As transformation products. Use of a reverse-phase separation method in other studies has documented the presence of 3-amino 4-hydroxybenzene arsonic acid (3A4HBAA), 4 hydroxybenzene arsonic acid (4HBAA), phenylarsonic acid (PAA), and dimethyl arsenate

(B'Hymer and Caruso, 2004; Rosal et al., 2005). As we did not use a reverse-phase method, we were not able to detect these species.

Table 2.1: Average acid and water soluble concentrations of trace elements in poultry litter.

Analyte	Extractable elements in poultry litter from this study (mg/kg) (n=6)			Extractable elements in poultry litter from other studies (mg/kg) (n varies, see footnotes)		
	Acid	Water	% Soluble	Acid	Water	% Soluble
As	37 ± 7	21 ± 8	57	28.7 ± 1 ^a 29 ± 3 ^a 29 ± 3 ^b 38 ± 37 ^c 17 ^d 20 ± 6 ^e 16 ± 10 ^f	22 ± 2 ^b 16 ^d	71-92
Cu	551 ± 53	89 ± 8	16	77 ± 1 ^a 359 ± 9 ^a 400 ± 12 ^b 396 ± 285 ^c 656 ^d 479 ± 230 ^f	200 ± 2.3 ^b 314 ^d	48-50
Mn	636 ± 57	32 ± 6	5	310 ± 10 ^a 410 ± 20 ^a 275 ^d 449 ± 119 ^f	7 ^d	3
Zn	701 ± 51	114 ± 34	16	320 ± 20 ^a 365 ± 4 ^a 430 ± 6 ^b 390 ± 175 ^c 247 ^d 373 ± 89 ^f	86 ± 1 ^b 18 ^d	7-20
P	24900 ± 1300	4100 ± 263	16	24000 ± 1300 ^b 17100 ± 3500 ^f	3900 ± 290 ^b	16-23

^aGarbarino et al (2003), n=3; note these are from 2 different samples of litter.

^bRutherford et al (2003), n=3

^cO'Connor et al (2005), n=8

^dJackson and Bertsch (2001), n=3

^eMorrison (1969), n=11

^fJackson et al (2003), n=40

Table 2.2 presents concentrations of water soluble and acid extractable solutes from fresh and aged poultry litter samples collected from the field site 53 d and 174 d after litter application. These results show that total (acid extractable) concentrations of all elements, with the exception

of Al, decreased in the litter over time. For example, total As decreased from 37 mg/kg to below detection limit (4 mg/kg) over the 174 d period, total Cu decreased from 551 to 438 mg/kg and total Zn decreased from 701 to 458 mg/kg. Water soluble concentrations differed, with some decreasing over time (As, Fe, Zn) and others increasing (Al, P, Cu).

Table 2.2: Acid extractable and water soluble concentrations of trace elements in fresh and aged litter from the field site. Results are averages of n=6 (fresh) or n=3 (aged) samples.

Analyte	Fresh litter (n=6) (mg/kg)		Aged 53 d (n=3) (mg/kg)		Aged 174 d (n=3) (mg/kg)	
	Acid	Water	Acid	Water	Acid	Water
As	37	21	32	15	< 0.6	< 0.6
Al	3170	15	3000	15	3800	29
Cu	551	89	507	95	438	105
Fe	1690	179	1590	204	1470	103
Mn	636	32	590	31	398	36
P	25000	4110	23500	6730	11100	5320
Zn	701	114	664	98	458	77

Leaching Rate of Trace Metals in Poultry Litter

Results of leaching rate calculations from the stepwise extraction (**Table 2.3**) showed that As leaches at the fastest rate from the litter followed by Cu and Zn. The calculated first-order rate constants (k_1 , k_2 , k_3) for the three extraction periods (0-5 d, 5-10 d and 10-20 d) decreased over time for all three trace elements. The time constant, $1/k$, describes how long it will take for the trace element concentration to decrease to 63% of its original value. Comparison of the average time constants yields a simple way of comparing the leachability of trace elements from litter. The average time constants ($1/k_{avg}$) for leaching of As, Cu and Zn were calculated as 18, 68 and 80 d, respectively (**Table 2.3**).

Table 2.3: First-order leaching rate constants of trace elements from poultry litter, based on step-wise laboratory extractions.

Analyte	k_1 (d^{-1}) (0-5 d)	k_2 (d^{-1}) (5-10 d)	k_3 (d^{-1}) (10-20 d)	k_{avg} (d^{-1}) (0-20 d)	Time constant ($1/k_{avg}$) (d)
As	1.4×10^{-1}	1.6×10^{-2}	3.7×10^{-3}	5.5×10^{-2}	18
Cu	3.7×10^{-2}	5.8×10^{-3}	6.8×10^{-4}	1.5×10^{-2}	68
Zn	3.5×10^{-2}	2.4×10^{-3}	4.1×10^{-4}	1.3×10^{-2}	80

In addition to providing information on the overall leaching behavior of trace elements, the first order rate constant from the last laboratory extraction period (10-20 d; k_3) can be used to predict trace element concentrations in poultry litter over time and compared with measured concentrations in poultry litter collected at the site 53 and 174 d after application (**Figure 2.3**). Results show that in early time (53 d), measured concentrations of As, Cu, and Zn in litter are greater than predicted using the lab leaching model. At later time (174 d), Cu concentrations in litter remain higher than predicted, but As and Zn concentrations are lower.

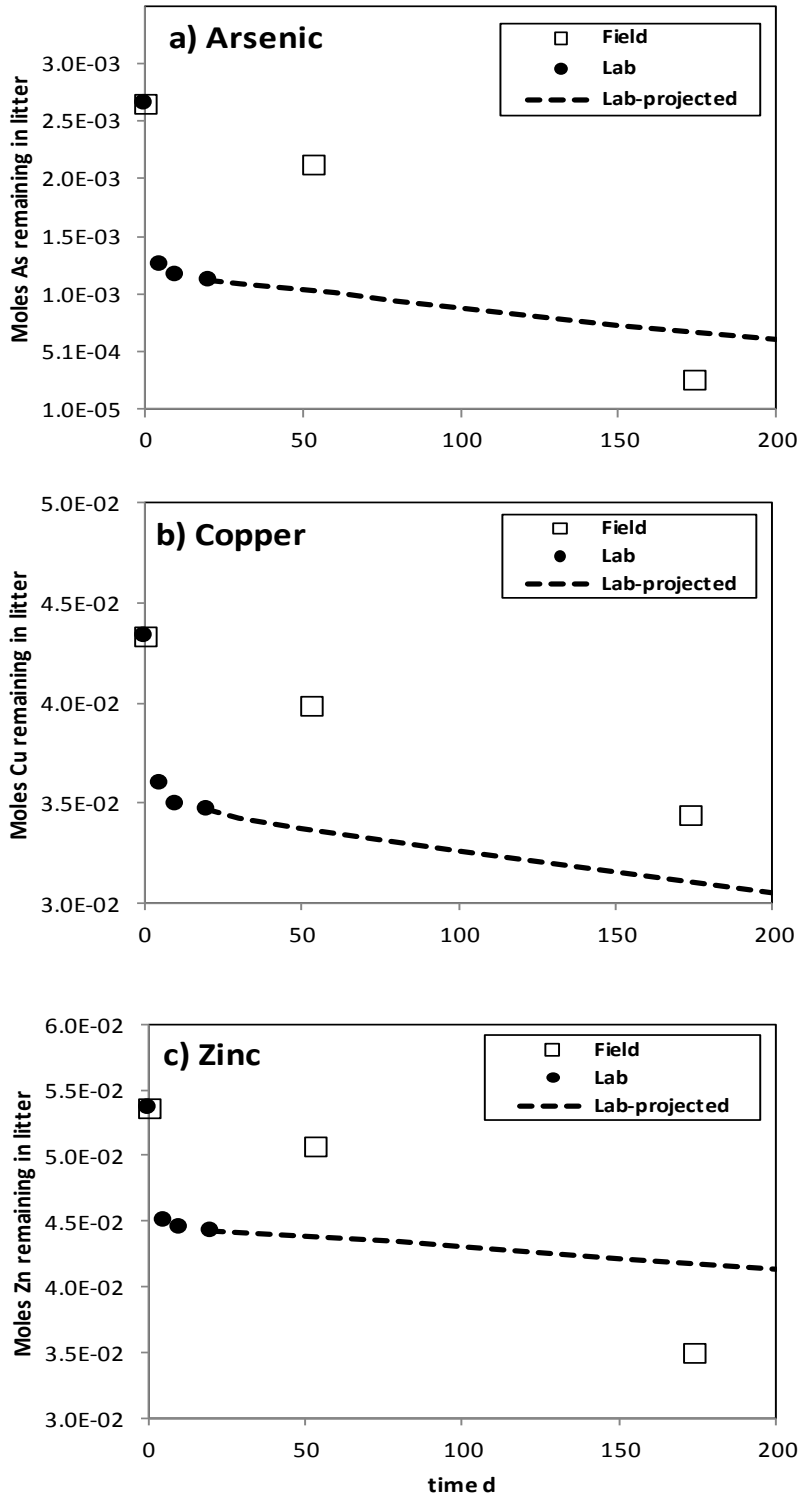


Figure 2.3. Measured and projected As, Cu, and Zn concentrations remaining in litter over time. Lab concentrations are from step-wise leaching experiments (0-20 d); lab-projected concentrations (20-200 d) are derived assuming first-order leaching, using the k_3 rate constant. Field values are measured from litter samples collected from the field at day 0 (day of application), day 53, and day 174.

Field Experiment

Hydrologic Conditions Before and After Litter Application

The water table at the site fluctuated over the monitoring period from 1.8 to 3.3 meters bgs, with highest elevations in the spring and lowest in the fall (data not shown). Horizontal hydraulic gradients were generally shallow (3.3×10^{-4} to 6.7×10^{-4}) over the monitoring period, reflecting the slow flow characteristics of this low-relief setting. Vertical hydraulic gradients, calculated using data from the well nests, were predominantly downward at the site; however, upward gradients were measured several times within well nests closest to the wetland (ML4, ML8), suggesting discharge of shallow groundwater to the forested wetland.

Soil moisture patterns (**Figure 2.4**) show progressive drying during the summer of 2009, which had little precipitation. From fall 2009 to spring 2010, increases in soil moisture in the shallow vadose zone (0.79 m, 1.09 m) occurred after precipitation events, with a ~14-30 days lag. The deepest soil moisture sensor (1.89 m) also responded to precipitation events, with a lag of 35-47 d. After one significant rain event (58 mm) on 10/27/09, the moisture content in the soil profile increased up to 85% in the 1.89 m interval, reflecting the rise of the water table and corresponding capillary fringe.

Hydrogeochemical Conditions Before and After Litter Application

The concentrations of cations, anions, nutrients, and trace elements, as well as basic field parameters, in soil water before and after litter application are presented in **Table 2.4**. Poultry litter application did not have a measurable impact on groundwater quality (data not shown).

Field Parameters

The pH of soil water was slightly acidic, characteristic of water within these coastal plain sediments which have low buffering capacity (Ritter and Chirnside, 1984). There was no observable change in pH after litter application. Dissolved oxygen (DO) was generally high, between 5 and 6 mg/L in soil water, reflecting dominantly aerobic conditions in soil water.

Table 2.4: Soil water geochemistry showing background and post litter application concentrations. Data from LYS1 and LYS3. bdl = below detection limit.

Analyte	Detection limit	Background concentration (n=5)		Post application concentration (n=6)	
		Range	Mean	Range	Mean
Ca (mg/l)	0.019	3.1-12.5	9.6	2.8-34.6	15.5
Mg (mg/l)	0.8	1.1-5.0	3.7	1.4-19.8	7.8
Na (mg/l)	0.26	3.7-14.7	5.9	3.2-13.1	9
K (mg/l)	0.175	2.0-4.1	2.9	2.2-16.4	7.3
As ($\mu\text{g/L}$)	2.5	bdl		2.7-4.3	3.5 ^c
Cu ($\mu\text{g/L}$)	3.0	bdl		3-18	10 ^c
Zn ($\mu\text{g/L}$)	4.0	7-28	16	4-59	31
Mn ($\mu\text{g/L}$)	3.0	3-21	14	5-21	12
Fe ($\mu\text{g/L}$)	8.0	bdl-4911		bdl-601	^c
P ($\mu\text{g/L}$)	27	bdl-167		bdl-325	^c
DOC (mg/l)	0.1	12.2-42.3	27.2	5.8-18.1	10.4 ^b
Cl (mg/l)	0.1	1.8-17.0	11.5	3.9-72.6	25
SO ₄ (mg/l)	0.1	4.2-7.7	6.7	18.7-65.3	38.5 ^a
NO ₃ -N(mg/l)	0.1	0.2-2.3	0.8	3.3-9.9	6.1 ^a
HCO ₃ (mg/l)	1	2-19	11	2-15	6
NH ₄ ($\mu\text{g/L}$)	13.5	14-700	423	39-1697	728
pH		5.6		4.1-5.2	4.7
SC ($\mu\text{S/cm}$)		110		78-564	232
DO (mg/l)		4.6		4.3-6.3	5.5
T °C		22.8		7.2-15.0	12.0

^a denotes post application concentration significantly higher (paired t test, $\alpha = 0.05$) than background concentration.

^b denotes post application concentration significantly lower (paired t test, $\alpha = 0.05$) than background concentration.

^c paired t test could not be conducted due to concentrations below detection limit.

No significant changes in DO were measured in soil water after litter application. However, continuous measurement of redox potential in the vadose zone (**Figure 2.5**) reveals several interesting patterns. Overall, the redox potential in the vadose zone is high (400-600 mV). However, approximately one month after litter application, a decrease (600 to 500 mV) in redox potential was measured at 1.25 m depth after a rain event, also observed in the 1.5 m interval (data not shown). In contrast, redox potential increased (500 to 600 mV) at the 2.2 m depth in response to the same rain event, likely due to the increase of the water table and corresponding capillary fringe.

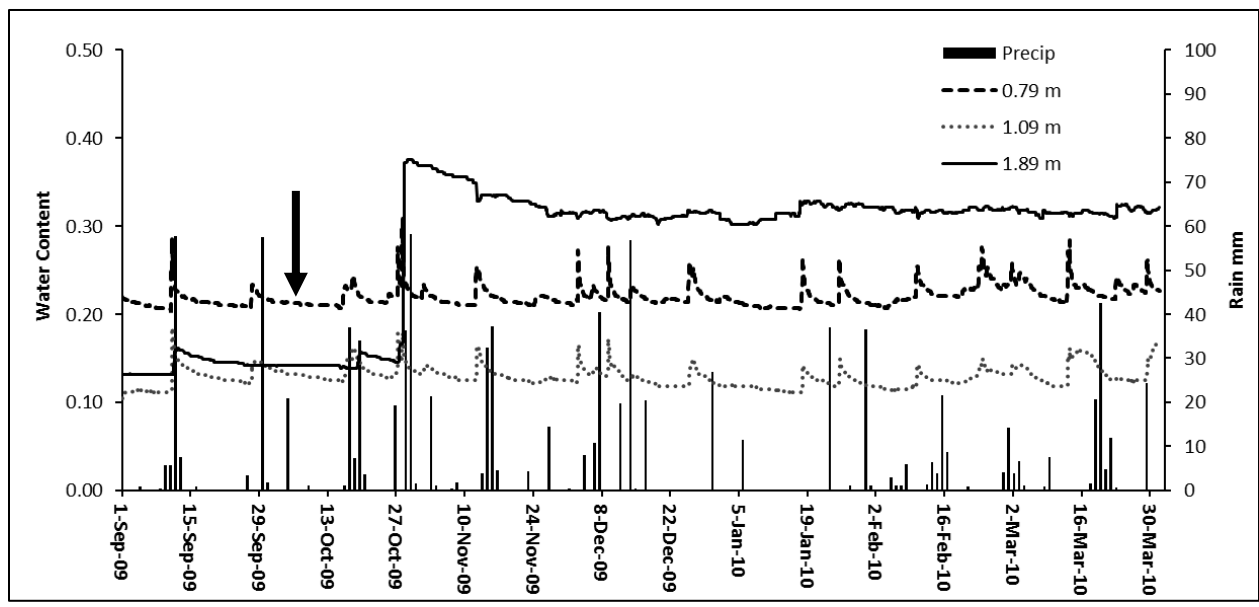


Figure 2.4. Daily rainfall and soil moisture content variation at depths 0.79, 1.09, and 1.89 m bgs from trench 1. The rain gauge did not measure snow precipitation. Arrow denotes date of litter application (10/2/09).

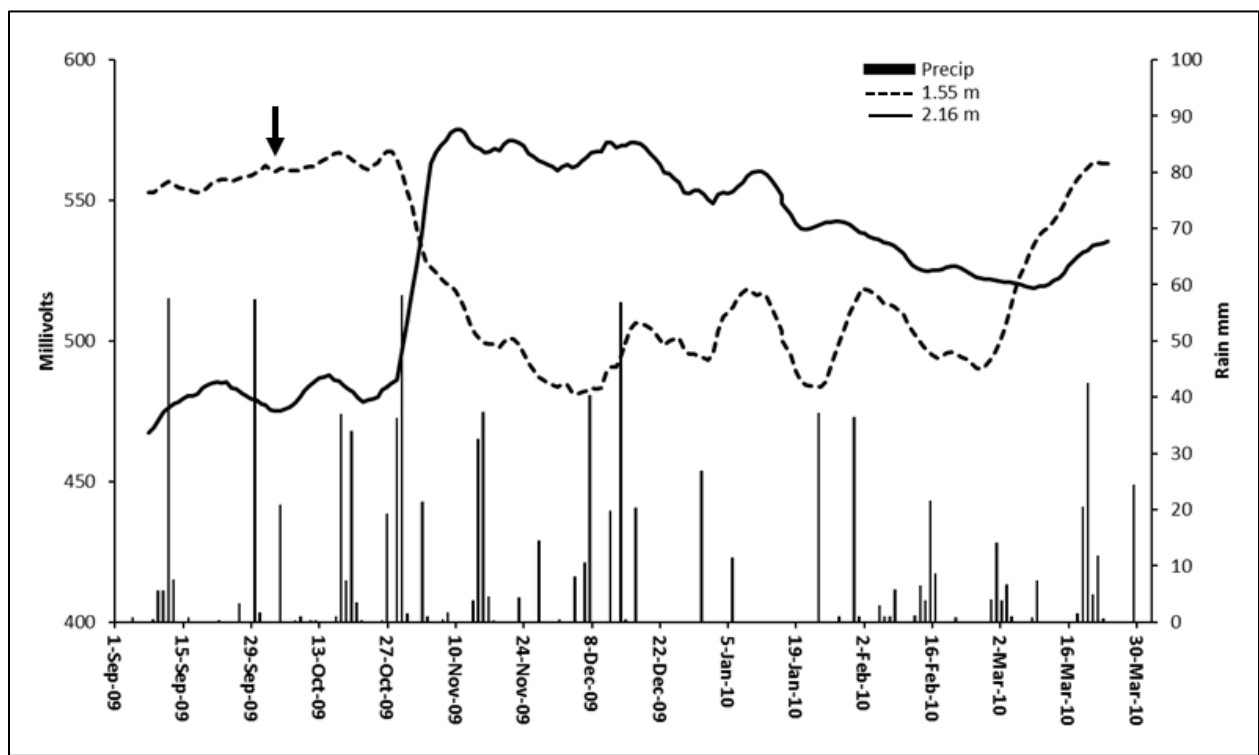


Figure 2.5. Continuous measurement of redox potential (millivolts) at 1.55 and 2.16 m bgs from trench 1, and daily rainfall data in mm. The redox data were corrected using the AgCl reference electrode buried within the shallow soil. The arrow denotes date of litter application (10/2/09). Data were processed using a 7-day moving average.

Major Ions

Examination of the major cation data reveals increases in concentration of most major ions after the application of poultry litter; elevated concentrations of major ions in the first sampling of the lysimeters (8/6/09) were likely due to disturbance of the soil during lysimeter installation (**Figure 2.6**). Concentrations of Cl, Ca, Mg and K spiked in the sample collected 53 d after litter application (11/24/09), returning to background measured levels during the next sampling event (105 d; 1/15/10) and remaining at background levels at 174 d (3/25/10). Sulfate concentrations were also elevated in both the 53 and 105 d sampling events, but returned close to background levels after 174 d. Paired t-tests show a statistically significant increase ($p < 0.05$) in the means of sulfate concentrations in soil water from the background to after litter application. None of the other major ions showed statistically significant differences in the means.

Nutrients (NO_3 -N, NH_4 , P, DOC)

Prior to litter application, concentrations of NH_4 in soil water were below the detection limit (13 $\mu\text{g/L}$) but increased above 1600 $\mu\text{g/L}$ at the next sampling event (105 d; 1/15/10) (**Figure 2.6**). The P background concentration was mostly below detection limit with the exception of one sampling event on the day of application (10/2/09) where the P concentration in soil water was 124 $\mu\text{g/L}$. Post application, P concentrations remained below detection limit until 174 d after litter application (3/25/10) where the concentration was 325 $\mu\text{g/L}$. NO_3 -N concentrations ranged from 0.2 to 0.9 mg/l in soil water before litter application; they increase to 9.9 mg/L at 53 d after application, subsequently decreasing to 6.6 mg/L (105 d) and 3.3 mg/L (174 d). In contrast to all of the other elements measured for this study, DOC concentrations decreased at 53 and 174 days. Paired t-tests show a statistically significant increase ($p < 0.05$) in the means of NO_3 -N concentrations from the background to after litter application, and a statistically significant decrease ($p < 0.05$) in the means of DOC concentrations in soil water from the background to after litter application. Due to below detection limit values for P at several monitoring events, paired t-test analyses could not be conducted.

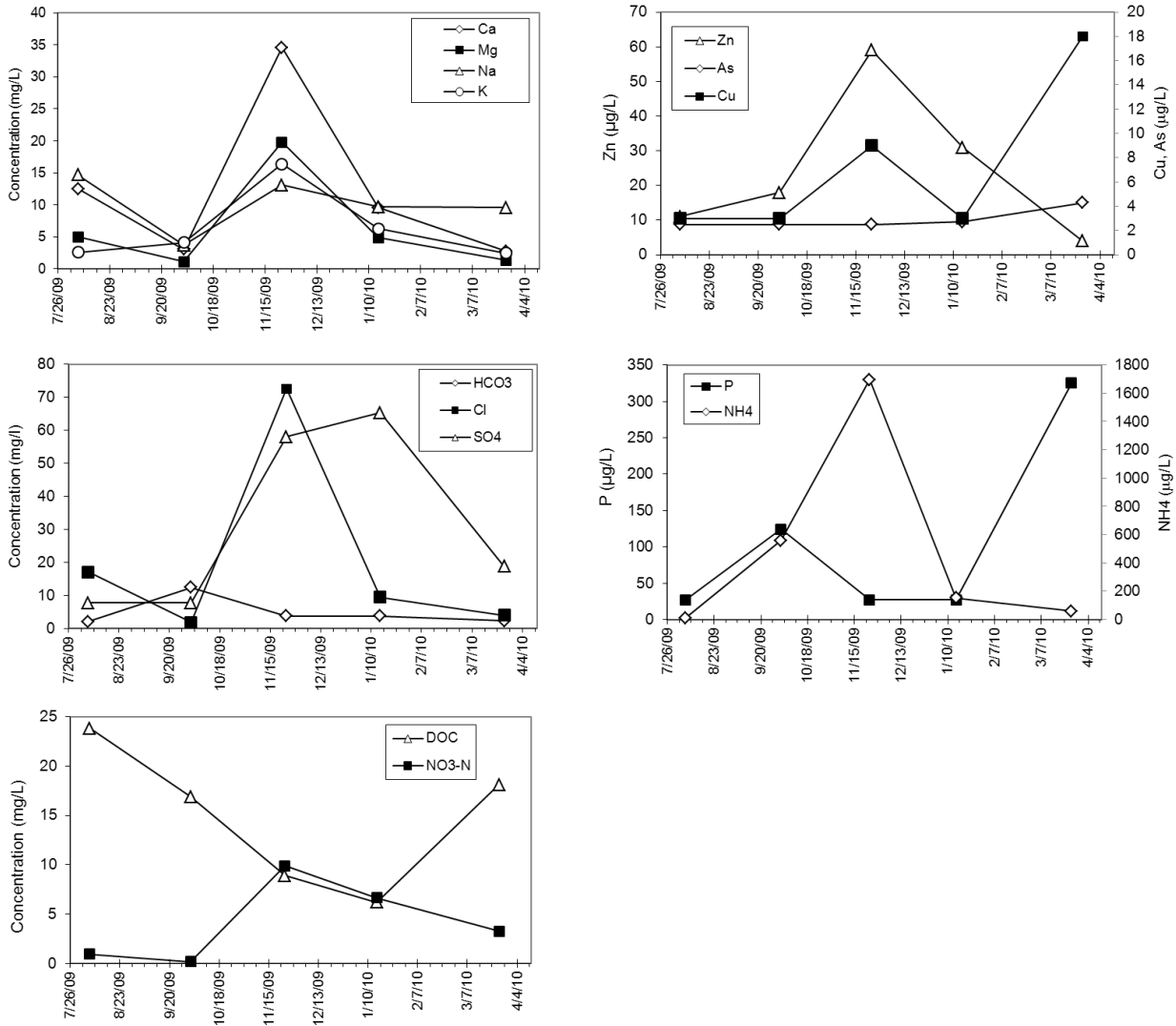


Figure 2.6. Time series plot showing patterns of water chemistry in lysimeter 1 before and after litter application. Litter was applied on 10/2/09, the day after the second sampling event. Concentrations below detection limit are plotted as the detection limit.

Trace Elements (As, Cu, Zn)

Prior to litter application, As and Cu concentrations in soil water were below detection limit ($\sim 3 \mu\text{g/L}$). Post application, Cu concentrations increased slightly to $9 \mu\text{g/L}$ at 53 d, declined to below detection limit at 105 d, and then increased again to $18 \mu\text{g/L}$ at 174 d (**Figure 2.6**). Arsenic showed a similar “slow bleed” pattern, with concentrations below detection in the 53 d sample, increasing just above detection limit at 105 d, and reaching a maximum of $4 \mu\text{g/L}$ at the

174 d sampling event. In contrast, Zn concentrations were detectable prior to application (11 and 18 µg/L in the two background events), spiked to 59 µg/L at 53 d, declined to 31 µg/L at 105 d. By 174 d, Zn concentrations in soil water were below detection. Due to below detection limit values for trace elements at several monitoring events, paired t-test analyses could not be conducted.

Soil Texture and Geochemistry

Textural determination through particle size analysis of the soil samples collected during well installation showed the presence of sand, loamy sand, loam, sandy clay loam and silty clay within the soil profile. Results of soil chemical analyses demonstrated depth dependent variation in geochemistry (**Figure 2.7**). It is also interesting to note that, after litter application, most of the trace elements accumulated in an interval located 0.65 to 0.8 m bgs; this increase is correlated with increase in Fe concentrations.

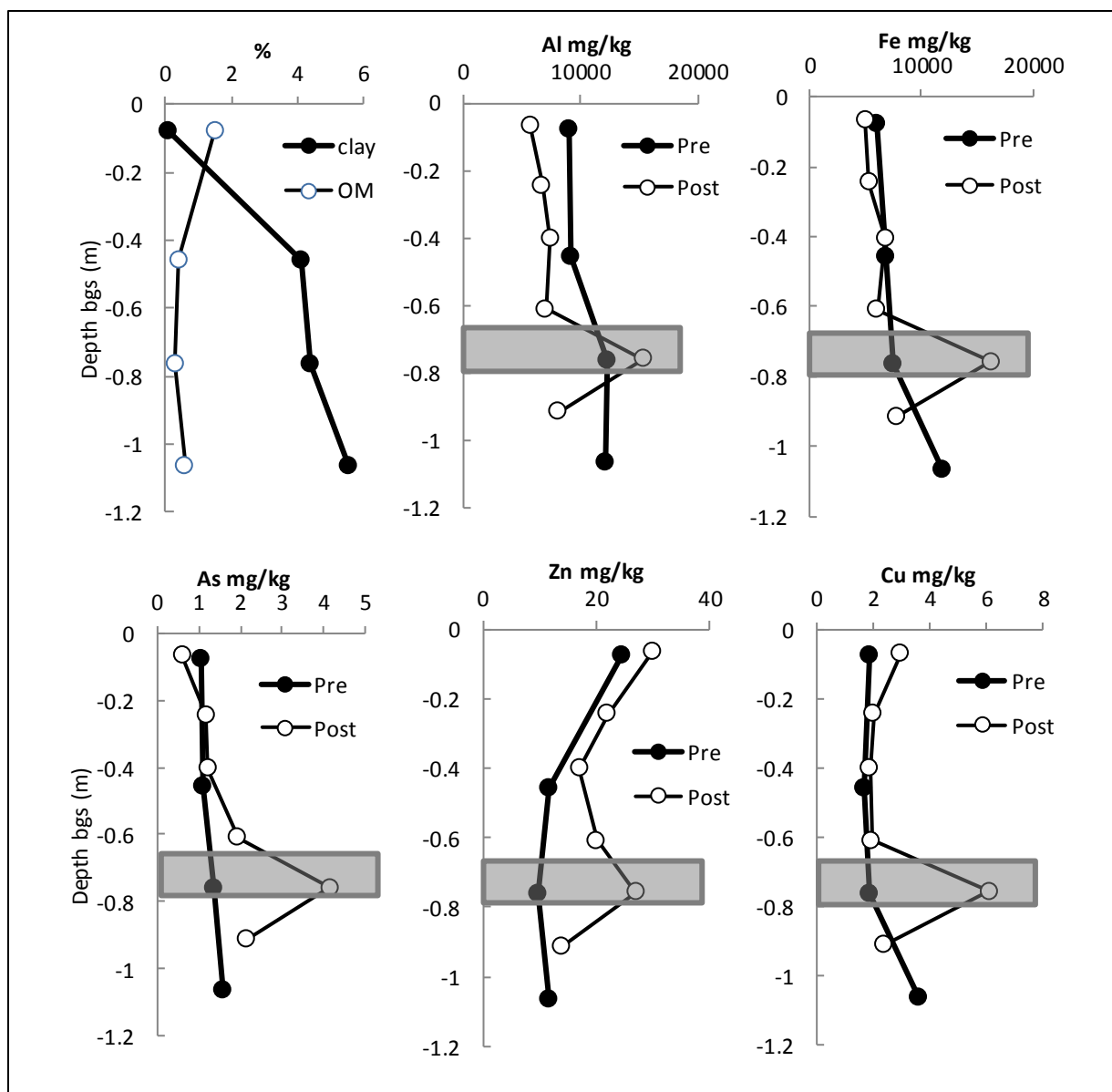


Figure 2.7. Subsurface soil chemistry from the ML6 borehole (see Fig 1 for location) showing baseline and post application concentrations of relevant elements. Organic matter and clay were measured before application only. Shaded region shows soil interval in which Al, Fe, As, Zn and Cu accumulated.

Trace Element Mass Balance

Results of the mass balance calculations, including the estimated error, are shown in **Table 2.5** and **Figure 2.8**. For As, Cu, and Zn, the mass taken up in storage (soil) is either equal to or greater than the mass released from litter. In comparison, less mass is estimated as lost through leaching to soil water (2-6%) or through uptake by vegetation (Cu 3%, Zn 13%, no

uptake for As). The calculation of trace element retention in the vadose zone, estimated using the soil water data and chloride as a conservative tracer (**Figure 2.9**), reveals a similar result as the mass balance calculation, namely that trace elements were retained in the vadose zone during the experiment. For As, Cu, and Zn the average % retention values were 96, 91, and 90%. The conservative tracer calculations also reveal retention of Fe and Mn (58 and 61%, respectively), which is supported by the post-application soil chemistry (**Figure 2.7**).

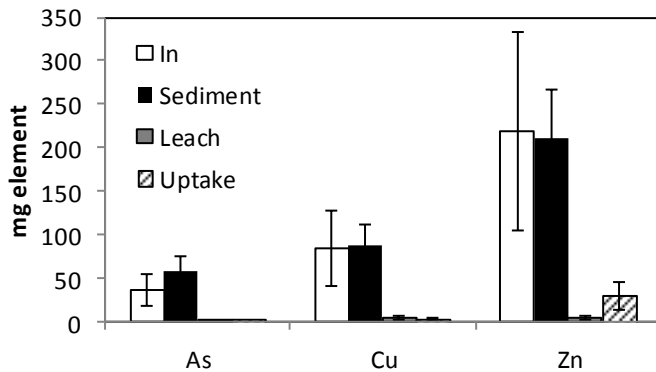


Figure 2.8. Mass balance of trace elements in vadose zone (0-0.8 m depth). Error bars represent estimated errors calculated using the propagation method of Taylor (1982).

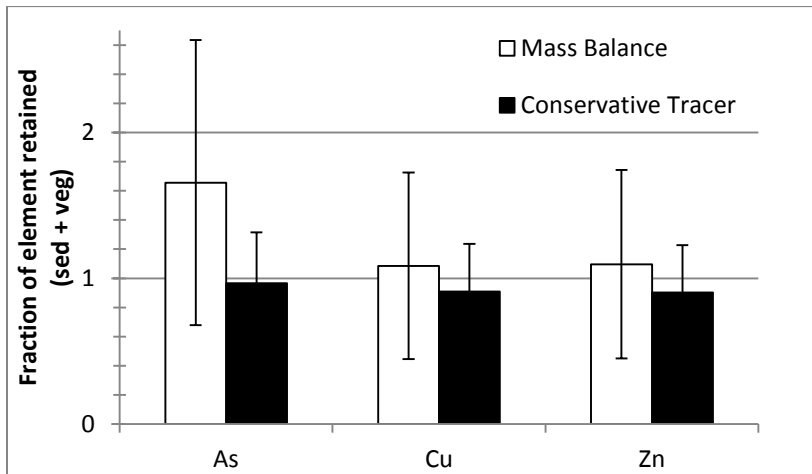


Figure 2.9. Comparison of mass balance and conservative tracer methods to estimate average fraction of trace element retained in vadose zone, through uptake to soil and vegetation. Error bars represent estimated errors calculated using the propagation method of Taylor (1982).

Table 2.5. Mass balance calculations

Mass Input: Release of elements from litter

Element	Conc litter (mg/kg)	Fraction released ^a	Mass released per m ² (mg)
As	40	1	36
Cu	551	0.17	84
Zn	701	0.35	219

^a determined by comparing fresh litter to 174 d litter collected from field

Mass Storage: Accumulation in soil^b

Element	Element Pre mg/kg	Element Post mg/kg	Interval of accumulation m	Area m ²	Bulk density soil kg/m ³	Mass stored per m ² (mg)
As	1.4	4.2	0.015	1	1400	59
Cu	1.9	6.12	0.015	1	1400	88
Zn	10	20	0.015	1	1400	210

^b using data from Hole (ML) 6; assumes element accumulates in limited interval (0.015 m; see Figure 8).

Mass Out: Leach to soil water

Element	Conc 1 (ug/L) ^c	Vol 1 ^c (L)	Conc 2 ^c (ug/L)	Vol 2 ^c (L)	Conc 3 ^c (ug/L)	Vol 3 ^c (L)	Mass Leach ^d per m ² (mg)
As	<2.5	0.8	2.7	1.25	4.3	2.7	1
Cu	9	0.8	<3	1.25	31	2.7	5
Zn	59	0.8	31	1.25	<4	2.7	5

^c 1 = 11/24/09, 2 = 1/15/10, 3 = 3/25/10; data from lysimeter 1

^d divided by lysimeter 1 area (3 disks, radius of each is 7.62 x 10⁻² m)

Mass Out: Uptake in orchardgrass

Element	Avg conc grass mg/kg	Crop yield kg/m ² ^f	Mass Uptake per m ² (mg)
As	1	0.449	<1
Cu	6	0.449	3
Zn	68	0.449	31

^f assume 2 tons dry crop yield/acre (Spitaleri et al., 2003)

Mass Balance (mg of element, ± error)

	Mass In (±52%)	Mass Stored (±29%)	Mass Out (±36%)
As	36 ± 19	59 ± 16	1 ± 0.4
Cu	84 ± 44	88 ± 24	8 ± 3
Zn	219 ± 114	210 ± 44	35 ± 13

Discussion

Trace Elements Released From Poultry Litter

The poultry litter used in our field experiment contained total concentrations of trace elements As, Fe, Cu, Zn, P, and Mn in a range similar to other studies. The water solubility of these elements from the litter varies, ranging from low (5%; Mn) to moderate (16%; Cu, Zn, P) to high (57%; As). Comparison of our water soluble data with those from other studies shows that our values for As (57%) and Cu (16%) are lower than in other studies (As 71-92%; Cu 50%), underscoring the variability of the chemical behavior of trace elements in litter.

Although the As species added to poultry feed was roxarsone, speciation of the fresh litter applied in our experiment revealed that only a small portion of the total As was roxarsone (6% of total), while As(III) and As(V) were the dominant As species (36% and 58%, respectively). Other studies have demonstrated a wide range in As species concentrations in litter (Arai et al., 2003; Garbarino et al., 2003b; Jackson and Bertsch, 2001; Rosal et al., 2005), reflecting the complex microbiological processing of As during composting of litter.

Leaching rates of trace elements from litter decrease over time and vary by element; arsenic is released from litter at the fastest rate, followed by Cu and Zn. Analysis of aged litter samples collected from the field site 53 d and 174 d after application confirmed that these trace metals are being leached from the litter. Based on the field samples, approximately 20% of total As was leached (37 to 32 mg/kg acid; 21 to 15 mg/kg soluble) within 53 d, while after 174 d, all of the initial As had been lost from the litter. Similar to As, concentrations of acid-extractable and soluble Zn in the litter decreased over time. However, Cu and P showed a different pattern, with acid extractable concentrations decreasing from litter application to 174 d, but the soluble concentration increased over that same period. This may suggest that some of the original soluble Cu and P in the litter were transformed to more soluble phases over time. The only element analyzed that did not decrease was Al; concentrations increased over the monitoring period, which likely reflects enrichment of Al in litter as other elements are leached.

Comparison of the projected (from laboratory extractions) to actual (measured in the field) concentrations of trace elements in litter show that lab projections generally overpredict leaching, but the long-term projections of Cu and Zn concentrations remaining in litter are within 20% of the field measurement. Arsenic leaching from litter was underpredicted by the lab leaching model by over 100%, suggesting that other processes (perhaps biological) occurring in

the field allowed for additional As to be leached/removed. Microbial processes can transform As to methylated volatile species (Andrewes et al., 2000; Cullen and Reimer, 1989), although this is thought to happen only under strongly reducing conditions. Because we did not measure volatile As species, we cannot currently address this question.

Impact of Litter Application on Water and Sediment Chemistry

After litter application, concentrations of most measured trace metals, nutrients and major ions in soil water increase compared to background concentrations. However, the timing of the measured peak concentrations varies. For the major cations and anions, nitrogen species, and Zn, measured maximum concentrations in soil water were measured at the first sampling event after application, reflecting rapid release of these elements from litter into the vadose zone. In contrast, Cu, As and P, show peak concentrations in soil water several months after litter application, indicating non-conservative behavior.

The decrease in DOC concentrations in soil water after litter application was unexpected, as litter contains high concentrations (69,000 mg/kg) of water soluble organic carbon, and the other water chemistry data support rapid flushing of water-soluble elements from the litter into soil water. In addition, a decrease in redox potential in the vadose zone was measured coincident with the first precipitation event after application, suggestive of an influx of leachate from the litter. Although DOC was likely released from the litter, it is possible that bacteria in the litter or vadose zone mineralized the DOC to CO₂, or that DOC adsorbed to sediment in the vadose zone, as has been shown in lab studies (Grafe et al., 2001). Currently, we do not have enough data from the field experiment to address the fate of DOC from the litter.

Comparison of soil chemistry before and after litter application indicates an increase of litter-derived trace elements in one interval in the vadose zone. Based on the positive correlation of trace elements in this zone with Fe, and to some extent, clay content, the most likely cause of trace element retention to soil was adsorption onto iron oxides and/or clay minerals.

Processes Controlling Transport of Trace Elements Released from Poultry Litter

The mass balance calculations of trace elements released from litter and monitored over 174 d suggest that most of the mass released from litter can be accounted for by accumulation in the vadose zone soil and through uptake into vegetation, with less than 6% lost through leaching

into soil water. Although these calculations are associated with large errors, they are supported by the calculations of trace element retention using the conservative tracer method. Despite the low mass loss to leaching observed during this experiment, it is important to recognize even a small loss of trace elements to water can result in violation of drinking water standards, as standards for elements like As are very low (10 $\mu\text{g/L}$). In the case of our field experiment, the occurrence of multiple significant precipitation events after litter application resulted in significant dilution of trace elements in soil water. Under different hydrologic (i.e., drier) conditions, trace element concentrations in soil and groundwater could be higher.

Overall, results of our field experiment indicate that retention (adsorption and vegetation uptake) and dilution played major roles in controlling trace element fate in the vadose zone. Due to the high concentrations of salts and DOC in the litter, we suspect that complexation of trace elements likely also impacted transport, but our dataset cannot be used to test this. Our litter speciation data showed that inorganic As species are the dominant form of As within litter, and as many previous studies have shown, mobility of As is strongly controlled by As speciation. Studies on biotransformation of roxarsone within the vadose zone sediments are in progress.

Acknowledgments

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CHAPTER 3

The Impact of Poultry Litter Application on Sediment Chemistry of the Broadkill River Estuary System, Delaware.

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Abstract

This project examined the impact of long-term poultry litter application on the chemical signatures of As, Cu, Zn, and P in stream sediments of the Broadkill River watershed within the Delmarva Peninsula, a region of intense poultry production. Thirty-seven sediment samples were collected from Broadkill River drainage systems and analyzed for litter-derived elements (As, Cu, Zn, P) and basic soil parameters such as particle size distribution, organic matter and soluble salts. Results showed that concentrations of elements in stream sediments are approximately log-normally distributed. Spatial variability in concentrations of elements was evident, with most elements increasing in concentration and enrichment from upgradient headwaters to downgradient reaches draining predominantly agricultural areas. Results of correlation analyses showed positive significant correlation among elements; elements were also positively correlated with percent clay and silt particles. Using GIS maps with overlays of hydrology and land use activities, statistical correlations between As, Cu, Zn and P enrichment factors and land use were examined. Results showed statistical significant relationships between As enrichment factors and residential areas within the watershed, but did not show a statistically significant relationship between element enrichment factors and agricultural land use. Factors that complicate this type of landscape-scale study include the presence of poultry processing plants, impoundments, changes in land use over time, and the influence of tides, all of which can have direct and indirect influences on element mobility.

Introduction

Over the past four decades, the organoarsenical roxarsone (3-nitro-4-hydroxyphenylarsonic acid) has been used as a poultry feed additive to increase growth, prevent intestinal parasites, and improve pigmentation (Garbarino et al., 2003; Rutherford et al., 2003). Because roxarsone uptake in tissue is negligible, the majority of the compound is excreted (Anderson and Chamblee, 2001; Moore et al., 1998; Morrison, 1969). Bednar et al (2003) estimated that with 8.3 billion poultry raised in the U.S annually, more than 350000 kg of As as roxarsone or its biotransformation products are released to the environment from poultry litter use each year. Trace metals such as Fe, Mn, Zn, Cu, and Se are also routinely added as nutrient supplements (Han et al., 2000; Rutherford et al., 2003; Sims and Wolf, 1994) resulting in elevated concentrations in poultry litter. Because poultry litter is rich in nutrients, more than 90% is land applied as fertilizer to farmland in the U.S (Jackson and Bertsch, 2001), raising concern that arsenic (As) and other trace elements may leach from the litter into hydrologic systems.

Previous studies on trace elements added to animal feed have shown that the elements can be mobilized into the environment. For example, Cu and Zn from litter can be mobilized to soil and drainage water (Aldrich et al., 2002; Han et al., 2000; Kingery et al., 1994; Moore et al., 1998; van der Watt et al., 1994). The fate of As from organoarsenical feed additives has not been studied as extensively. Several studies have documented As release from litter to soil water (Brown et al., 2005; Oyewumi and Schreiber, in press, 2012), drainage ditches (Church et al., 2010; Hancock et al., 2002) and into air near poultry farms (O'Connor et al., 2005). Studies have shown effects of long-term soil accumulation of As, and other trace elements derived from litter (Gupta and Charles, 1999; Han et al., 2000; Rutherford et al., 2003) although there are differences between results of these studies, mostly due to the complexities of biogeochemical reactions that influence trace element mobility.

In addition to litter application, there are other agriculture-related sources of trace elements to the environment. For example, Robinson and Ayotte (2004) showed that elevated As concentrations in stream sediment of regions in New England correlated with former agricultural areas that used arsenical pesticides. N'Guessan et al (2009) attributed anthropogenic contribution of cadmium in river sediments in France to fertilizer application. Also, Gimeno-García et al (1996) presented incidence of heavy metals from application of inorganic fertilizer

at a rice farm in Valencia Spain. Other anthropogenic sources of trace elements include mining activities (Garcia-Sanchez and Alvarez-Ayuso, 2003; Prusty et al., 1994), gasoline traffic emission (Nriagu, 1990; Won et al., 2007), biosolid or sewage sludge application (Sloan et al., 1998), urbanization (Sutherland, 2000; Wong et al., 2006), landfills (Looser et al., 1999), coal and oil combustion, manufacturing, and refuse incineration (Nriagu and Pacyna, 1988), among others.

Trace metal input into aquatic systems can also be through geogenic sources related to the processes of weathering, erosion and sedimentation (Nriagu, 1979; Viers et al., 2009; Vijver et al., 2008). Due to the range of sources of trace elements, it is challenging to decipher the impact of human activities on trace element release to the environment, especially at the landscape scale. Analysis of sediment chemistry in the context of land use and geology offers a useful method for identifying potential sources of trace elements to streams (Ciparis et al.; 2012; N'Guessan et al., 2009; Robinson Jr and Ayotte, 2006). Stream sediments are important environmental sinks and also play a critical role in controlling the mobility of trace elements within aquatic systems (Ikem et al., 2003; Rubio et al., 2000; Segura et al., 2006).

This research focused on examining the impact of historical and current use of poultry litter as fertilizer on the trace element chemistry of stream sediments within the Broadkill River watershed on the Delmarva Peninsula, Delaware, USA. The Broadkill River watershed is an agricultural region where poultry litter application as fertilizer is a common practice. Thirteen segments of the watershed have been listed as being impaired either from nitrogen, phosphorous, and/or enterococcus bacteria (EPA, 2006), indicating an agricultural influence on water quality (Denver et al., 2004). To address the research objective, we collected stream sediments from reference (upgradient, forested) and downgradient (agricultural, residential) sites in the watershed and analyzed them for trace elements and other physico-chemical parameters. Using these data, we calculated enrichment factors for trace elements of interest. Using geographic information systems (GIS), we delineated sub-watershed areas for each of the sampling points and determined the land use in each sub-watershed using land use/land cover (LULC) layers and hydrologic tools in GIS. Finally, we conducted statistical analyses to examine relationships between land use and stream sediment chemistry.

Study Area

The Broadkill River watershed (**Figure 3.1**) is located in Sussex Co., Delaware, which is the largest broiler-producing county in the U.S., producing over 200 million birds every year (USDA-NASS, 2012). The region lies within the Delmarva Peninsula on the Atlantic Coastal Plain (Field, 1980). Within the watershed, land use is dominantly agricultural (40%), with forest (21%), developed lands (13%) and wetlands (18%) as the other main land uses (EPA, 2006). The major crops grown are corn, soybeans, wheat and vegetables (Leytem et al., 2003; Ritter and Chirnside, 1984). The shallow subsurface geology in the watershed is comprised of the sands of the Columbia Formation (Pleistocene) (Ritter and Chirnside, 1984). Soils in the region consist mostly of sand, loamy sand, and silt loam (USDA-NRCS, 1974).

Originating near Milton, the Broadkill River is joined by Beaverdam Creek, Roundpole Branch, Pembedton Branch and Ingram Branch, among others (**Figure 3.1**), before discharging to Delaware Bay on the eastern (Atlantic) side of the peninsula (Dewitt and Daiber, 1973). Many of these tributaries are impounded resulting in formation of ponds (Reynolds, Wagamom, Waples, Laving, Diamond, and Red Mill). Also present in the watershed are poultry processing plants, as noted in **Figure 3.1**.

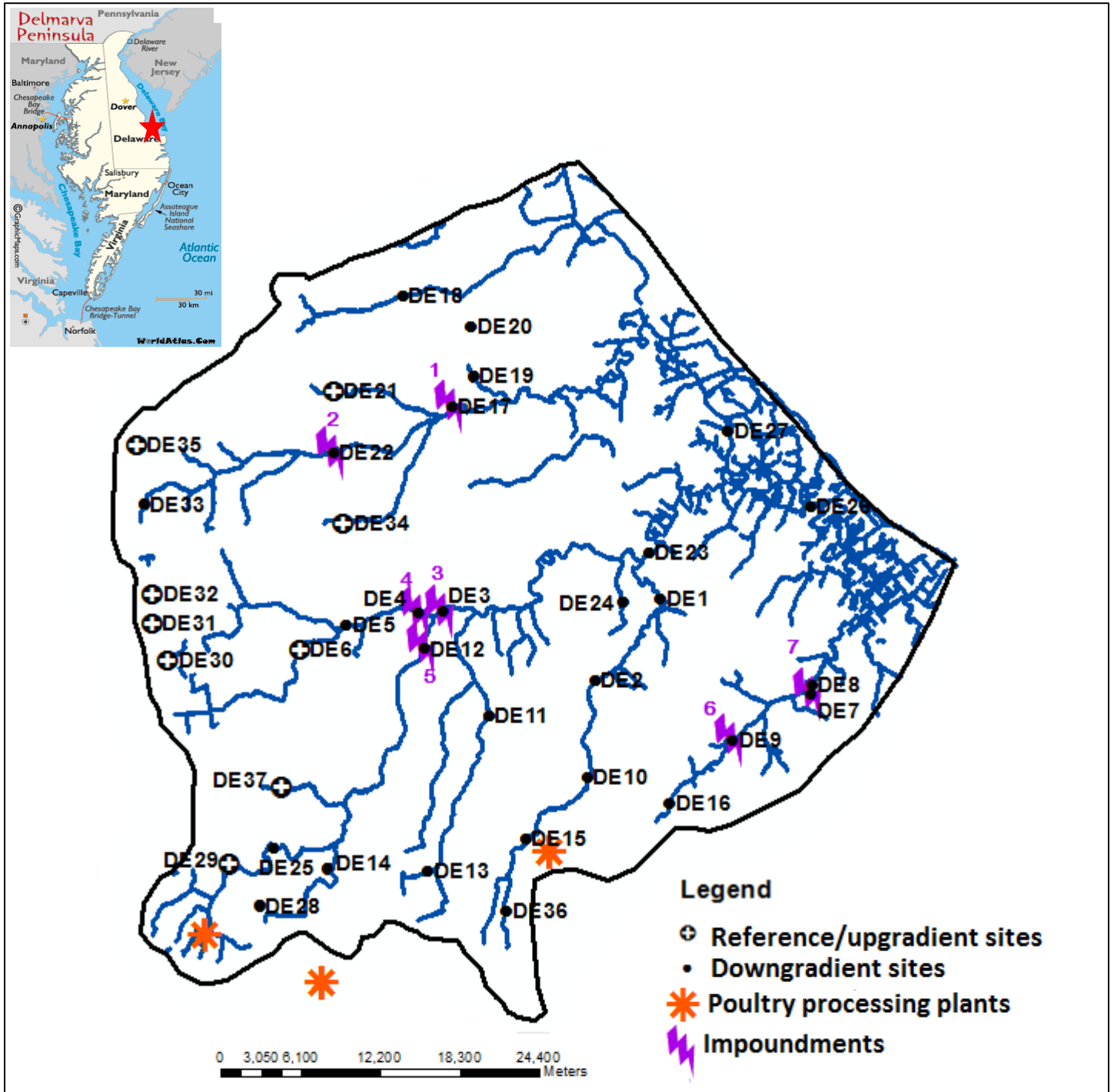


Figure 3.1: Study site shown with red star within the inset Delmarva Peninsula (WorldAtlas, 2012), and the outline of Broadkill River watershed, DE with streams, sampling locations and poultry processing plants, and impoundments : 1=Waples Pond, 2=Reynolds Pond, 3=Wagamon Pond, 4=Laving Pond, 5=Diamond Pond, 6/7: Red Mill Pond.

Methods

Selection of Sampling Sites

A total of thirty-seven monitoring sites within the Broadkill River watershed (**Figure 3.1**) were selected based on land use patterns and hydrology data within the watershed area (see section on geographic information system (GIS) below). Out of these thirty-seven sites, nine sites were identified as “reference” sites, which are defined as upgradient sites that are within the headwaters of the streams, draining predominantly forested areas. The remaining twenty-eight sites, defined as “downgradient” sites, were located within the remainder of the watershed and drain agricultural and residential/commercial, as well as forested areas. At each sampling site, the geographic coordinates were obtained with a portable hand held GPS unit (Trimble GPS Pathfinder Pro).

Sample Collection

Sediment samples were collected at each monitoring location. At most locations, samples were collected using stainless steel trowels that were cleaned with Alconox and water between sites. At these sites, sediments were collected from at least 10 locations from the top 0.1 m of the streambed. At a few sites where access to the streambed was limited, sediments were collected from an overhead bridge using an open jaw sampler. In these cases, sediment collection was limited to 1-2 locations within the river. After collection, sediments were homogenized in a stainless steel bowl, which was also cleaned between sites. During homogenization, rocks, twigs, leaves and other large debris were removed from the samples before packaging them into bags for transport to the laboratory.

Sample Preparation and Analyses

In the laboratory, sediment samples were air dried, thoroughly homogenized and sieved through a 2-mm sieve size for particle size analysis (PSA) using the ASTM 152H hydrometer method (ASTM, 2000). This procedure was slightly modified from the method described by Dane and Topp (2002) by taking temperature readings after each hydrometer readings to adjust for temperature variation.

Subsets of the dried and sieved sediment samples were digested with aqua regia in a microwave (CEM Mars Express) and analyzed for eight elements (Al, Cu, Fe, Mn, P, S, and Zn)

using Inductive Couple Plasma-Atomic Absorption Spectrometry (ICP-AES) with detection limits varying between 3 and 175 $\mu\text{g/L}$. Samples for As were analyzed using Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS; Varian Spectra 220Z) because of its lower detection limit (2.5 $\mu\text{g/L}$). A Certified Standard Reference Soil (#2587) obtained from the National Institute of Standards and Technology (NIST) was also extracted using the same method to determine the degree of element recovery. In addition to acid digestion, basic soluble soil properties, including cation exchange capacity (CEC), organic matter content (OM), pH, and soluble salts (SS) were analyzed in sediment samples at Virginia Tech Soil and Plant Analysis Laboratory (VTSPAL) using the methods described in Maguire and Heckendorn (2012).

Sources of GIS Data and Analyses

GIS Dataset: A digital elevation model (DEM), topography data, and land use/land cover (LULC) data at 30 m resolution for 2006 were obtained from the USGS seamless dataset (USGS, 2012). The locations of poultry processing plants were obtained from Google Earth. These datasets formed GIS layers for this study. Each layer was projected in ArcGIS software 10 (ESRI, Redlands, CA) to NAD 83 UTM zone 18.

GIS Analyses: First, the Broadkill River watershed was delineated into different subwatersheds (**Figure 3.2**), defined as upslope contributing areas to each of the sampling points. The delineation was conducted using the common approach (algorithm) for defining flow patterns from a DEM developed by Jenson and Domingue (1988). Initial joining of elevation quad sheets to a single layer was carried out using the mosaic function in ArcGIS 10 (ESRI, Redlands, CA). Precaution was taken to specify the processing extent to the flow direction layer in order to obtain subwatershed areas that are dependent on flow direction. This allows for a clear definition of upslope flow contributory areas for each sampling location. For statistical analyses, we determined both immediate upslope contributing areas of each sampling site (“individual” subwatershed) and cumulative upslope contributing areas for the downgradient sampling locations (“cumulative” subwatershed) by adding all land use areas draining the upper reaches of each sampling location.

The second GIS analysis involved reclassification of LULC data, which was conducted by combining different farming operations and croplands together as agricultural areas. Different

forest types, evergreen, rangeland, and shrub rangeland were lumped together as forested areas; family dwellings, multi-family dwellings, and mobile home parks/courts, were combined as residential areas; and all water bodies and wetlands were grouped together as wetlands/waterways. This resulted in four GIS LULC categories: residential, agricultural, forested, and wetlands/ waterways. Overlay of the reclassified LULC and subwatershed layer (**Figure 3.3**) allowed for the determination of the distribution of land use types within each subwatershed or upslope contributing area to each sampling location. Correlations were conducted using both individual and cumulative sub-watersheds.

Statistical Analyses

Statistical analyses were conducted using SAS / JMP 9.0 software packages (JMP®, Version 9) with significance level of α 0.05. Geochemical data in sediments were tested for normality using the Shapiro-Wilk W test ($p < 0.05$). In order to meet the assumption of normality and variance homogeneity of a parametric statistic, geochemical data were log transformed to obtain a more symmetrical distribution.

Prior to statistical analyses, we screened the sediment data for soluble salts (SS), under the assumption that the SS measure is a proxy for tidal influence. As one of the main objectives of this study was to examine connections between land use and stream sediment chemistry, the influence of tides would confound the signal. Two sites with high soluble salts content (> 2500 mg/kg; DE 26 and 27) were eliminated from statistical analyses. These sites are located within the Broadkill estuary, east of Route 9 (see **Figure 3.1**).

Two sample t-tests using unequal variances were used to examine differences in element concentrations between the reference upgradient and downgradient sites. Cluster analysis based on Ward's algorithm and Euclidean distance coefficient was used to obtain an overall estimate of resemblance between all pair of observations. Correlation analyses were used to determine the strength of association between geochemical parameters, organic matter (OM), and particle size distributions. Because the correlation and covariance matrices showed existence of strong inter relationship among measured variables, principal component analysis (PCA) was applied to study inter-related correlation patterns among observed variables. The proportion of variance explained by each component was used in the selection of significant components. The resulting orthogonal eigenvectors of principal components (PC) represent the weight of the correlated

data. Loading weights greater than 0.40 in each component were considered significant. Multiple linear regression analysis was used to examine relationships between the sediment physical and geochemical characteristics and land use types.

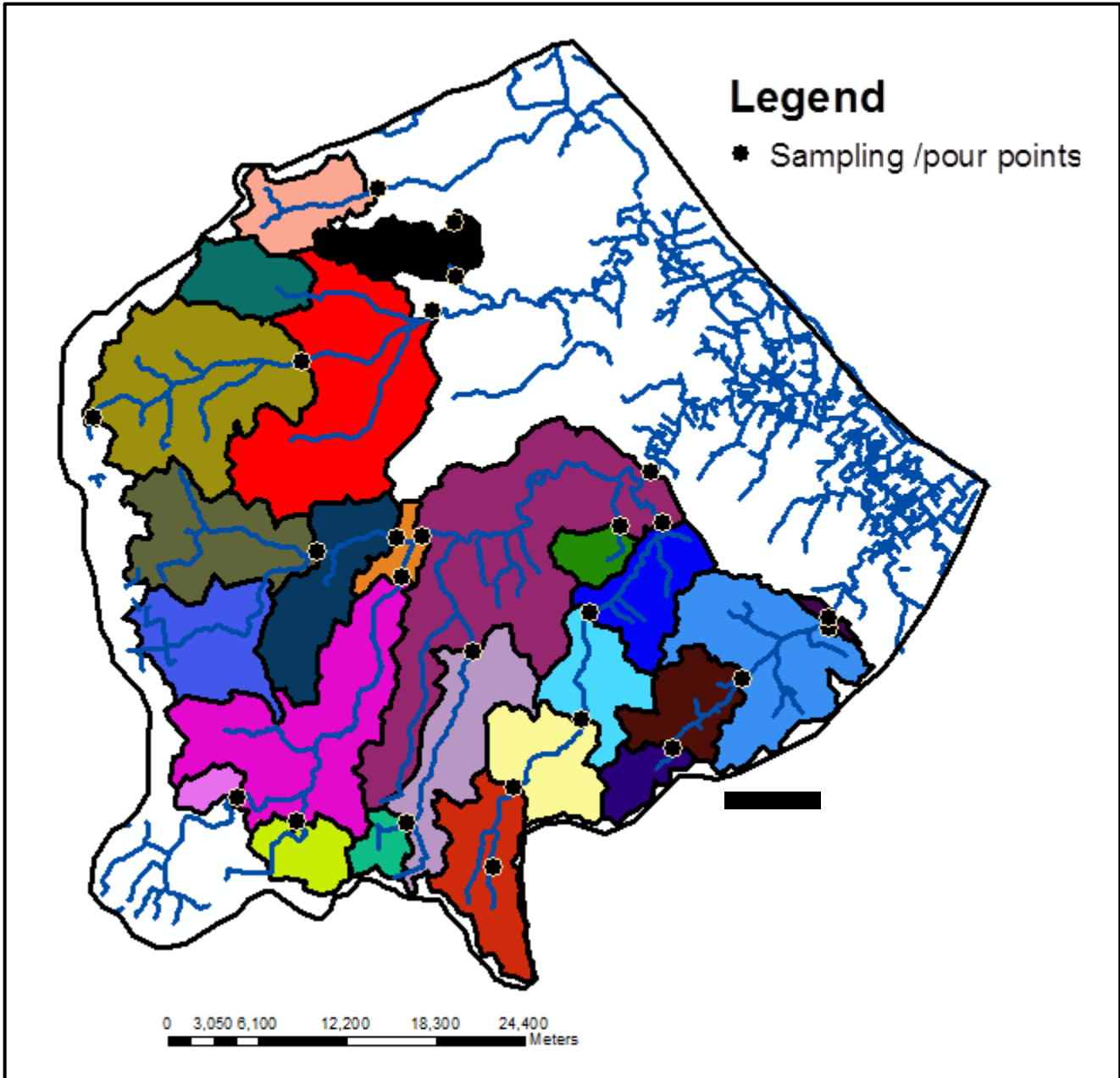


Figure 2.2: Delineated sub watersheds for sampling locations within the Broadkill River watershed. The sub watershed areas were determined in GIS using the sampling sites as pour points.

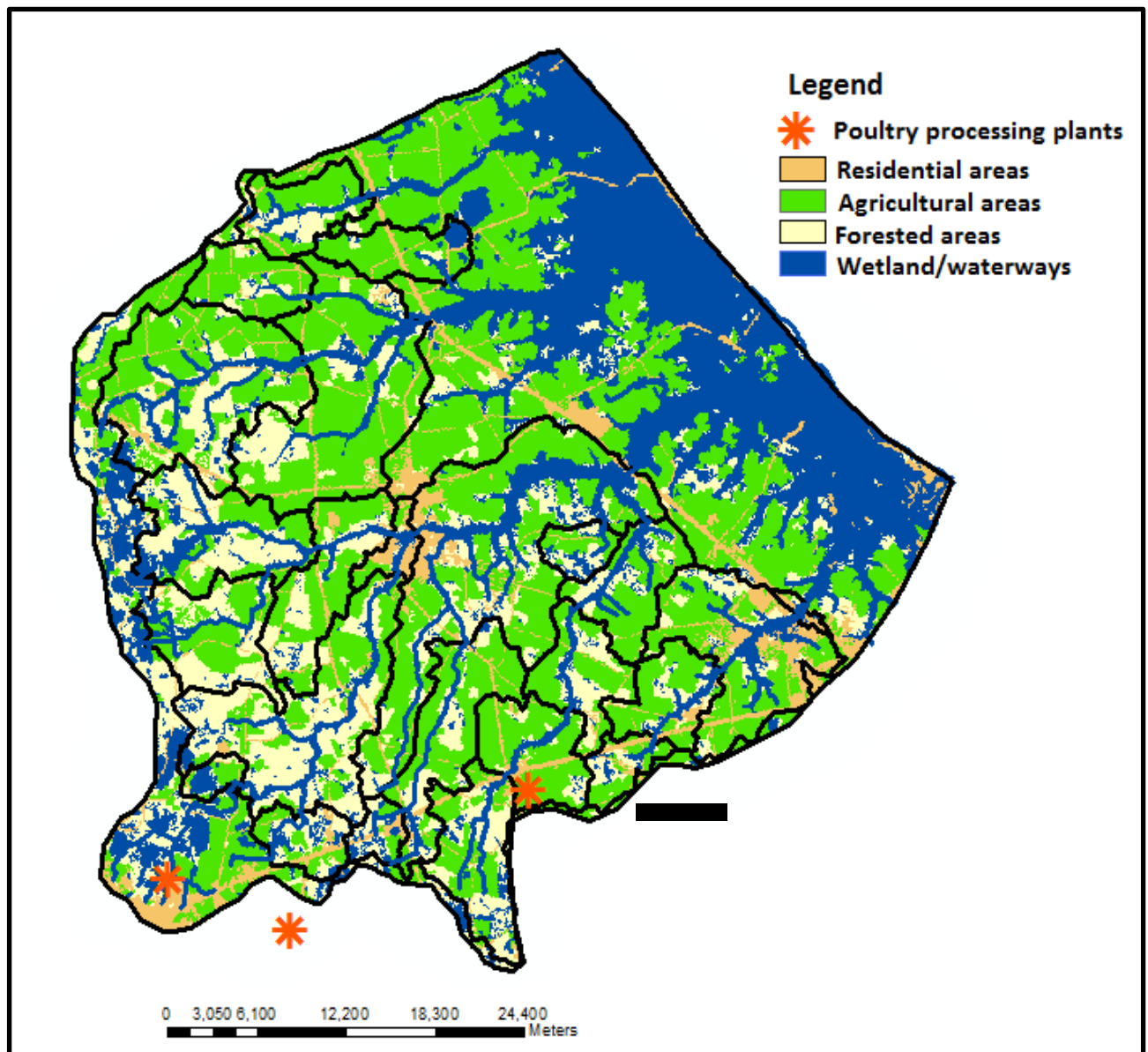


Figure 3.3: Land use distribution showing the four reclassified categories (Residential areas, forested areas, agricultural areas and wetlands/ waterways) overlain by sub watershed areas shown with black lines within the Broadkill River watershed.

Enrichment Factors (EF)

Enrichment factors (EF) are often used to allow comparison of element concentration in sediments or soil with its background or reference concentration within the same catchment (Förstner et al., 1990; Loska et al., 1997). Previous studies have utilized EFs to estimate the contribution of human activities to enhancing elements above background or reference concentrations. This approach has been used to examine the impacts of coal mining on metals in soils (Bhuiyan et al., 2010), the impacts of agricultural and industrial activities on trace elements concentration of stream sediments (Bourennane et al., 2010; N'Guessan et al., 2009), and the effect of urban runoff on sediment trace elements concentration (Mohiuddin et al., 2010; Rubio et al., 2000; Sutherland, 2000).

To determine background/reference concentrations, we utilized the data collected from our nine reference sites (see **Figure 3.1**). To examine if these data were reflective of background conditions, we searched the NURE HSSR (National Uranium Resources Evaluation Hydrogeochemical and Stream Sediment Reconnaissance) database to find samples of sediment geochemistry within the region. The NURE program sampled sediment from a total of 98, 76 and 60 sites within Sussex, Kent and New Castle Counties, Delaware between May and June 1978. However, out of 234 sites sampled, only 7 sites had As concentrations above detection limit (0.01 mg/kg; as reported by NURE); 142 sites had sediment Cu above the detection limit (detection limit for Cu not reported by NURE). It should be noted that the NURE data do not necessarily reflect reference concentrations, as samples were collected irrespective of land use. However, as our reference sites fall within the range of NURE data for both As and Cu, they were thus considered reasonable as references for this study.

Another issue in calculation of enrichment factors is the necessity of normalization to grain size and mineralogy, as these are correlated with trace elements and can thus bias the data. This normalization is typically conducted using concentrations of specific elements that are associated with finer grain sizes (Loring, 1990). Elements that have been used for grain size/mineralogic normalization are: Al (Pokrovsky et al., 2006; Sutherland, 2000 among others), Mn (Yongming et al., 2006), Ca (Loska, 2004), Fe (Bhuiyan et al., 2010; Emmerson et al., 1997; Schiff and Weisberg, 1999), Sc (Lee, 1994; N'Guessan et al., 2009) and Li (Loring, 1990).

For this study, we selected Al as our reference element to compensate for the effect of grain size and mineralogy component variations for several reasons: 1) Al is a major constituent

of fine grained estuary and coastal sediments (Hanson et al., 1993), 2) Al is not likely to have significant anthropogenic sources (Schropp et al., 1990); 3) Al is assumed to be relatively essentially immobile during weathering (Anand and Gilkes, 1984; Anderson and Hawkes, 1958; Chesworth et al., 1981); 4) Al has uniform distribution across our study sites and significant relationship with most of measured elements (After N'Guessan et al., 2009); 5) Al has been used successfully in other studies to reduce data variability for the purpose of sample inter-comparison (Hanson et al., 1993; Thorne and Nickless, 1981; Windom et al., 1989); and 6) Al has been used for normalizing metal concentration in estuary and coastal environments (Bruland et al., 1974; Din, 1992; Liaghati et al., 2003; Pokrovsky et al., 2006; Schropp et al., 1990; Sutherland, 2000; Trefry et al., 1985; Windom et al., 1989).

Enrichment factors were calculated after Sutherland (2000) using the following equation:

$$EF = \frac{Cn_{sample}/CAL_{sample}}{Cn_{background}/CAL_{background}}$$

where Cn_{sample} is the element concentration in the sediment sample, CAL_{sample} is the Al concentration in the sample, $Cn_{background}$ is the geometric average concentration of element in the reference sediment, and $CAL_{background}$ is the geometric average concentration of Al in the reference sediment.

In this study, we used population percentile values from frequency distribution plots of enrichment factors to operationally define three enrichment categories. EF values that fall between zero and 50th population percentiles ($EF \leq 50^{\text{th}}_{\text{percentile}}$) are classified as no to low enrichment, representing sites as sites within the range of natural variability. Sites with EF values within the inter quarter range ($50^{\text{th}}_{\text{percentile}} < EF < 75^{\text{th}}_{\text{percentile}}$) are classified as moderately enriched, while sites with EF values greater than the third quartile ($EF \geq 75^{\text{th}}_{\text{percentile}}$) are considered as significantly enriched.

Results

Particle Size Distribution and Physico-Chemical Characteristics of Sediments

Table 3.1 shows results of particle size distribution and basic physico-chemical parameters in the sediments. The sediment pH ranges from 5 to 8, with an average value of 6. Soluble salt (SS) concentrations range from 26 to 9170 mg/kg; samples with SS above 2500

mg/kg are italicized in bold (**Table 3.1**) and were not included in the statistical analyses. Organic matter (OM) fraction ranges from < 1 to 25%. The cation exchange capacity (CEC) values range from <1 to 15 meq/100g. Results of the particle size analysis (PSA) show that most sediments are classified as sand; other samples are classified as loamy sand, sandy loam and silty loam.

Sediment Chemistry

Results of acid extractable (aqua regia) concentrations of selected elements (As, Cu, Mn, P, S and Zn) in stream sediments are presented in **Table 3.2**. Concentration of elements in sediment from reference upgradient sites (italicized in bold) are at the tail end of the distribution of concentrations from downgradient sites (**Figure 3.4**). Results of t-test comparison of element concentrations in reference and downgradient geochemical data show that they are significantly different. Concentrations are approximately log normally distributed, confirmed by the Shapiro-Wilk W statistical test ($p < 0.05$); these are shown on probability plots presented in **Figure 3.5**.

The concentrations in sediment were compared with the lowest effect and severe effect levels proposed by the National Oceanic Atmospheric Administration (Buchman, 2008; Persaud et al., 1993). The lowest effect level (LEL) is the highest concentration that can be tolerated by most benthic organisms. The severe effect level (SEL) is the concentration above which pronounced disturbance of the sediment dwelling community can be expected. The comparison (**Table 3.3**) shows that the majority of the stream sediments are below the NOAA LEL values for As, Cu, Mn, and Zn with the exception of one sampling location with slightly higher concentration of As (DE 3, As: 6.4 mg/kg) than the LEL (6 mg/kg) and another location with higher Zn concentration (DE 13, Zn: 203 mg/kg) than the LEL (120 mg/kg).

Table 3.1: Result of particle size analysis and sediment physico-chemical parameters. CEC-cation exchange capacity, SS-soluble salts. Note that locations DE 26 and 27 (in bold) were removed from statistical analysis because of their high tidal influence denoted by high soluble salts (SS > 2500 mg/kg).

Site	Sand	Clay	Silt	OM	pH	CEC	SS
	%					meq+/100g	mg/kg
DE1	45	<2	54	5	5	10	2060
DE2	85	<1	14	3	7	10	128
DE3	94	<1	5	2	7	6	140
DE4	94	<1	5	1	7	2	77
DE5	37	1	62	9	6	9	400
DE6	91	<1	8	2	6	3	51
DE8	95	<1	4	<1	6	1	307
DE10	95	<1	4	<1	8	7	154
DE11	94	<1	5	<1	6	2	128
DE12	94	<1	5	1	7	9	410
DE13	87	<1	12	2	6	6	205
DE14	75	<1	24	8	6	7	102
DE15	91	<1	8	2	7	11	858
DE16	94	<1	5	2	6	4	128
DE17	90	<1	9	1	6	2	102
DE18	90	<1	9	1	7	4	128
DE19	34	4	62	7	5	5	77
DE20	52	<1	47	4	6	5	173
DE21	96	<1	3	<1	6	2	96
DE22	95	<1	4	<1	8	5	115
DE23	94	<1	5	2	6	4	832
DE24	73	3	24	25	5	15	1380
DE25	95	<1	4	<1	7	3	346
DE26	20	20	60	2	7	11	9170
DE27	93	1	6	<1	7	4	4390
DE28	40	4	56	9	6	11	141
DE29	95	<1	4	<1	7	3	384
DE30	97	2	1	<1	6	2	51
DE31	97	2	<1	<1	6	<1	26
DE32	93	<1	6	<1	6	2	64
DE33	85	1	14	9	5	7	115
DE34	92	<1	7	<1	6	1	51
DE35	95	<1	4	<1	6	<1	38
DE36	94	<1	5	<1	6	2	26
DE37	66	3	31	6	5	6	128

Table 3.2: Results of acid extractable (aqua regia) concentrations from sediment samples collected within the Broadkill River watershed. The values represent average concentrations of duplicate samples. The upgradient reference sites are italicized in bold. bdl= below detection limit. Note that locations DE 26 and 27 were removed from statistical analysis because of their high tidal influence reflected by high soluble salts (SS > 2500 mg/kg) shown in Table 1.

Analytes	Concentration in mg/kg							
	Al	Cu	Fe	Mn	P	S	Zn	As
Detection limit	0.96	0.72	1.92	0.72	6.48	10.8	0.96	0.6
DE 1	14100	11	15200	161	500	2800	91	4
DE 2	4440	10	5100	120	240	716	72	1
DE 3	2800	9	6140	350	212	362	42	7
DE 4	2500	2	1120	22	37	78	12	bdl
DE 5	17500	8	9700	160	381	994	77	3
DE 6	3300	1	1200	23	65	130	8	bdl
DE 8	1180	2	1320	14	48	140	16	bdl
DE 9	1400	bdl	1790	11	73	112	25	2
DE 10	3400	5	2800	38	121	102	30	bdl
DE 11	950	bdl	600	40	64	107	8	bdl
DE 12	1900	3	1700	34	98	514	14	bdl
DE 13	3500	11	5500	67	200	276	203	1
DE 14	5020	3	1400	14	130	658	32	bdl
DE 15	2600	11	4050	42	420	485	95	2
DE 16	1860	3	1430	18	88	268	24	bdl
DE 17	1890	2	1700	19	62	148	13	bdl
DE 18	3900	4	2830	28	100	150	52	bdl
DE 19	15000	11	9600	62	425	522	41	3
DE 20	11000	7	8600	180	414	234	37	3
DE 21	3060	bdl	1500	21	55	60	9	bdl
DE 22	4300	9	8090	115	100	1500	38	bdl
DE 23	7500	4	6560	68	240	1800	46	2
DE 24	17000	14	6500	118	900	3000	69	3
DE 25	3500	2	1110.	10	140	160	21	bdl
DE 26	19000	12	22200	156	680	1700	76	15
DE 27	3070	2	3070	17	74	782	14	2
DE 28	27400	13	7420	53	900	711	156	bdl
DE 29	4700	3	954	18	91	140	13	bdl
DE 30	7600	bdl	2010	8	25	70	20	bdl
DE 31	3400	1	1200	15	34	57	10	bdl
DE 32	5400	2	1160	12	56	70	10	bdl
DE 33	12600	7	4520	23	321	1100	24	bdl
DE 34	3140	1	940	8	73	87	7	bdl
DE 35	1500	bdl	460	6	11	15	3	bdl
DE 36	19000	4	5420	55	286	333	37	bdl
DE 37	3900	bdl	832	10	30	75	6	bdl

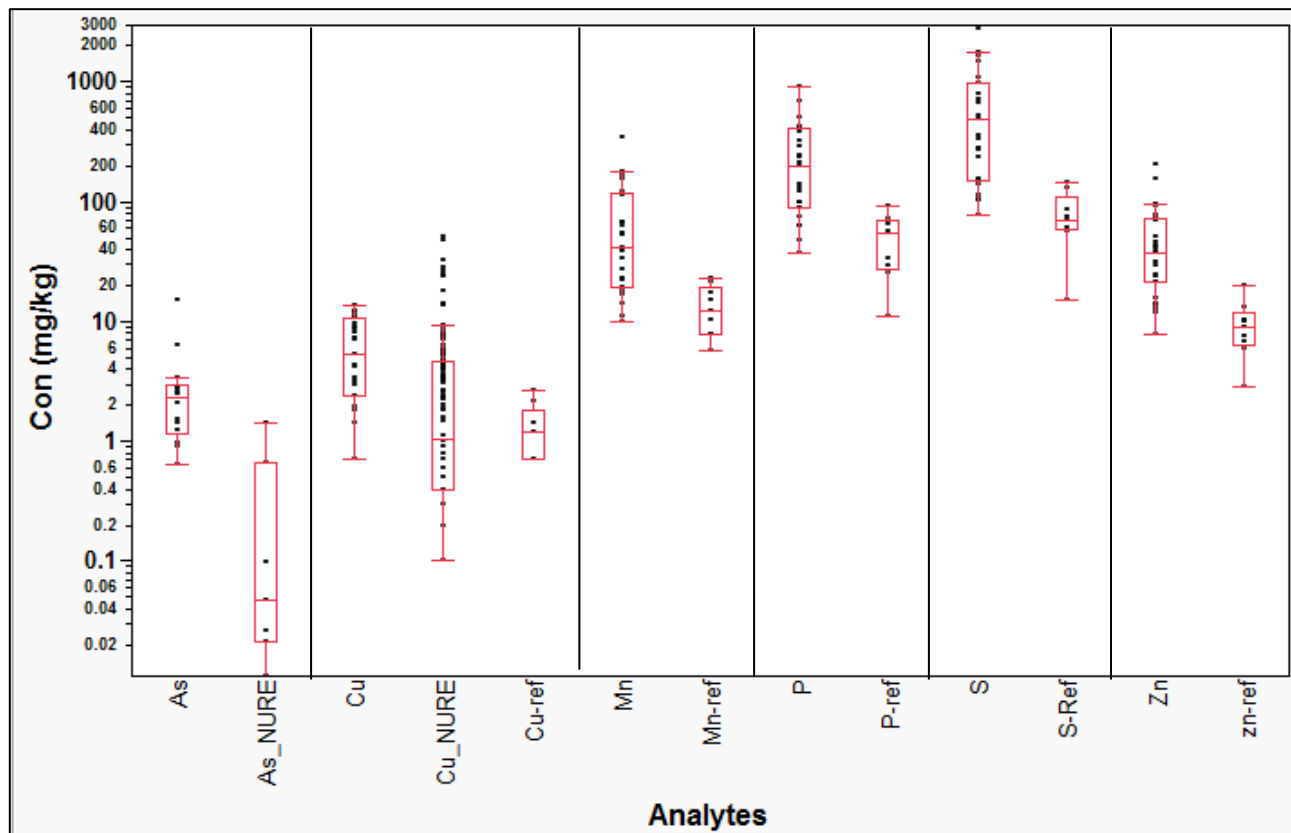


Figure 3.4: Boxplots of selected acid-extractable (aqua regia) elements in sediments from upgradient reference sites (n=9), downgradient sites (n=28), and NURE sites (n for As =7, n for Cu= 142). Eleven of the 28 sediments from the downgradient sites contained As concentrations below the detection limit of 0.6 mg/kg; these values were set at 0.6 mg/kg for graphing purposes. Values of As for the nine reference sites were all below 0.6 mg/kg and thus were excluded from the boxplot. There is a statistically significant difference (two sample t-test) between the reference upgradient sites and downgradient sites for all elements shown.

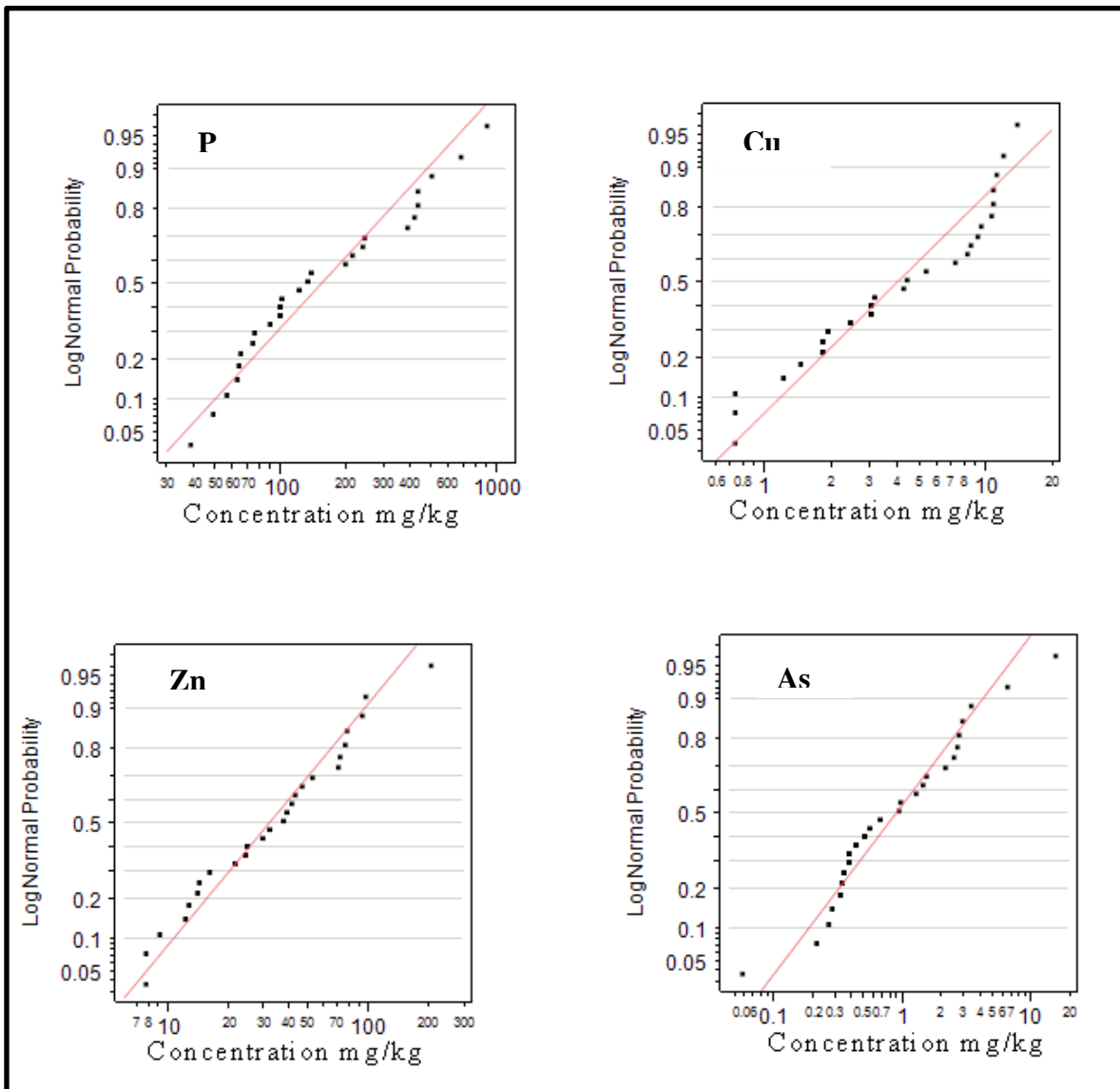


Figure 3.5: Log –probability plots of selected acid-extractable (aqua regia) element concentrations in sediment samples.

Table 3.3: Comparison of element concentrations in sediments from this study with screening limits from the National Oceanic Atmospheric Administration (NOAA) screening quick reference table (Buchman, 2008). GM = geometric mean concentration (mg/kg)
LEL= lowest effect level, SEL = severe effect level.

Concentrations in mg/kg							
Element	NOAA		Results from this study				
	LEL	SEL	GM	Min	Max	Exceed LEL n (%)	Exceed SEL n (%)
As	6	33	0.8	bdl	6.4	1(2.9)	0
Cu	16	110	4.6	0.7	14	0	0
Mn	460	1100	47	9.8	349	0	0
Zn	120	820	37	7.7	203	1(2.9)	0

Enrichment Factor (EF)

A summary of EF calculations for As, Cu, P, and Zn in the stream sediment samples and the classification of samples as low/no enrichment, moderate enrichment, and significant enrichment are presented in **Table 3.4**. Approximately half of our sampling sites have no or low enrichment of these four elements. Between 18 and 30% of the sites are moderately enriched, while 19 to 27% of the sites are significantly enriched. The spatial distribution of EFs generally show increased enrichment from the reference sites to downgradient sites for As, Cu, P, and Zn (**Figure 3.6**), with a few exceptions for sites located in impoundments or downgradient of poultry processing plants.

Table 3.4: Minimum, maximum and enrichment scales (No/low Enrichment: $EF \leq 50^{\text{th}}$ percentile, Moderate Enrichment: 50^{th} percentile $< EF < 75^{\text{th}}$ percentile, Significant Enrichment: $EF \geq 75^{\text{th}}$ percentile) for selected trace elements in sediment samples

Element	No/low Enrichment ¹ % (n)	Moderate Enrichment ² %(n)	Significant Enrichment ³ % (n)	Min EF	Max EF
Cu	52% (19)	24% (9)	24% (9)	0.2	13.2
P	54% (20)	18% (7)	27% (10)	0.2	13.3
Zn	52% (19)	24% (9)	24% (9)	0.7	24.1
As	50% (18)	30% (11)	19% (7)	0.1	104

Statistical Analyses

Because the elements data are approximately log normally distributed (**Figure 3.5**), we conducted a logarithmic transformation for these data prior to conducting statistical analyses in order to meet parametric statistic assumptions. Other data, including organic matter content, pH, CEC, and particle size, were not log transformed. As discussed in the methods, two sites with high soluble salts content (> 2500 mg/kg; DE 26 and 27) were eliminated from statistical analyses.

Correlation analysis shows that major and trace elements (Al, Cu, Fe, Mn, P, S, Zn, and As) are positively correlated with one another (Table 5). Likewise, a positive significant (>0.5) correlation exists between fine grain sizes (clay + silt) and Al, Cu, Fe and P, and a positive and less significant (0.4-0.5) correlation between clay+silt and Mn, S, Zn, and As. A similar positive and significant relationship exists between element concentrations and organic matter content as well with cation exchange capacity (**Table 3.5**). There were no significant correlations between these elements and pH. The inter-relationship between elements and OM, and fine grain sizes is further illustrated with cluster analysis (**Figure 3.7**). Two main clusters can be observed in the dendrogram: one between OM and fine grain sizes (clay +silt) and the other between all major and trace elements (Cu, As, Al, Fe, Mn, Zn, P and S). Clustering between elements can also be subdivided into four smaller clustering (between Cu and Zn, Al and Fe, Mn and Zn, and P and S) indicating their level of similarity.

Correlation analyses of sediment enrichment factors (EF) with LULC data for 2006, based on both individual and cumulative subwatersheds, are presented in **Table 3.6**. The individual subwatershed correlation analysis showed a positive significant relationship (~ 0.5) between residential areas and EF value of Mn (0.48), and As (0.60), however only Zn (0.46) has a significant relationship with residential areas in cumulative subwatershed correlation analysis. There is no other statistically significant relationship between EF values of elements and agricultural areas, forested areas, and wetland/waterways. Within this watershed, the percentage overall change in LULC data between 1992, 2001 and 2006 are presented in **Table 3.7**. Changes in land use between 1992 and 2006 were quantified in GIS. Over this 14 year period, residential areas and wetlands/waterways increased by 5.8% and 3.9%, respectively, while agricultural and forested areas decreased by 1.9% and 7.8%, respectively. Previous studies on land use within Sussex County, DE noted continuous change in land use areas due to urbanization, most significantly over the past 40 years (Duke et al., 2002; Mackenzie, 1989).

Table 3.8 presents results of principal component analysis (PCA) based on a variance-covariance matrix of the sediment geochemical data (centered and scaled). Two components were selected because they account for 99.76% variance in the dataset. The first component (PCI) is dominant, accounting for 97.5% of the total variance in the data. PCI is characterized by high positive loading (> 0.40 threshold) for Al, Cu, Fe, Mn, P, S, Zn, As, and Clay + Silt. The second component (PCII) accounts for only 2.26 % of the total variance; it is characterized by high positive loading (> 0.40 threshold) for S and OM. A scatter plot of PCI and PCII (**Figure 3.8**) based on element concentrations showed distinct differences in PC scores between the reference upgradient and downgradient sampling locations.

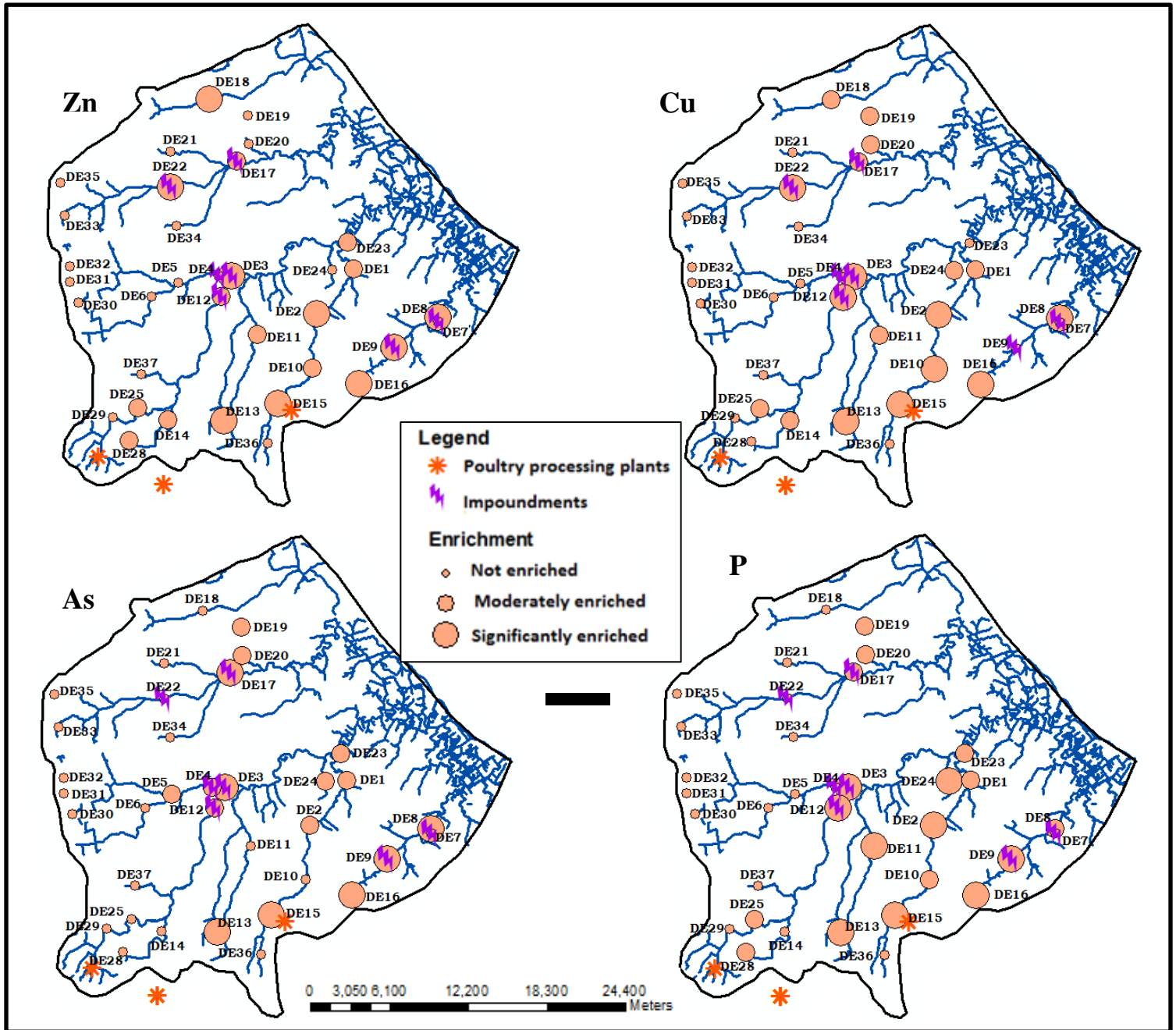


Figure 3.6: Spatial distribution of enrichment factor (EF) for acid-extractable (aqua regia) Zn, Cu, Zn, and P within the stream sediments of the Broadkill River watershed. Locations of impoundments and poultry processing plants are also shown. DE26 and DE27 are not included as the soluble salts concentrations were > 2500 mg/kg, indicating tidal influence.

Table 3.5: Correlation analysis of log transformed acid extractable (aqua regia) elements and selected physico-chemical parameters in sediments.

	<i>Al</i>	<i>Cu</i>	<i>Fe</i>	<i>Mn</i>	<i>P</i>	<i>S</i>	<i>Zn</i>	<i>As</i>	<i>OM</i>	<i>pH</i>	<i>CEC</i>	<i>OM</i>	<i>C+ S</i>
Al	1												
Cu	0.59	1											
Fe	0.71	0.86	1										
Mn	0.46	0.78	0.83	1									
P	0.70	0.87	0.83	0.74	1								
S	0.58	0.80	0.80	0.71	0.83	1							
Zn	0.55	0.86	0.85	0.69	0.83	0.74	1						
As	0.23	0.61	0.72	0.74	0.64	0.64	0.69	1					
OM	0.60	0.49	0.43	0.36	0.60	0.59	0.40	0.32	1				
pH	-0.27	0.05	-0.08	0.04	-0.12	-0.16	0.08	-0.02	-0.52	1			
CEC	0.48	0.76	0.63	0.60	0.76	0.76	0.70	0.57	0.73	-0.12	1		
OM	0.59	0.48	0.43	0.35	0.60	0.59	0.40	0.34	1.00	-0.52	0.73	1	
C+ S	0.69	0.50	0.59	0.46	0.60	0.47	0.46	0.41	0.56	-0.45	0.55	0.56	1

OM= Organic matter %

C+ S= Clay + Silt %

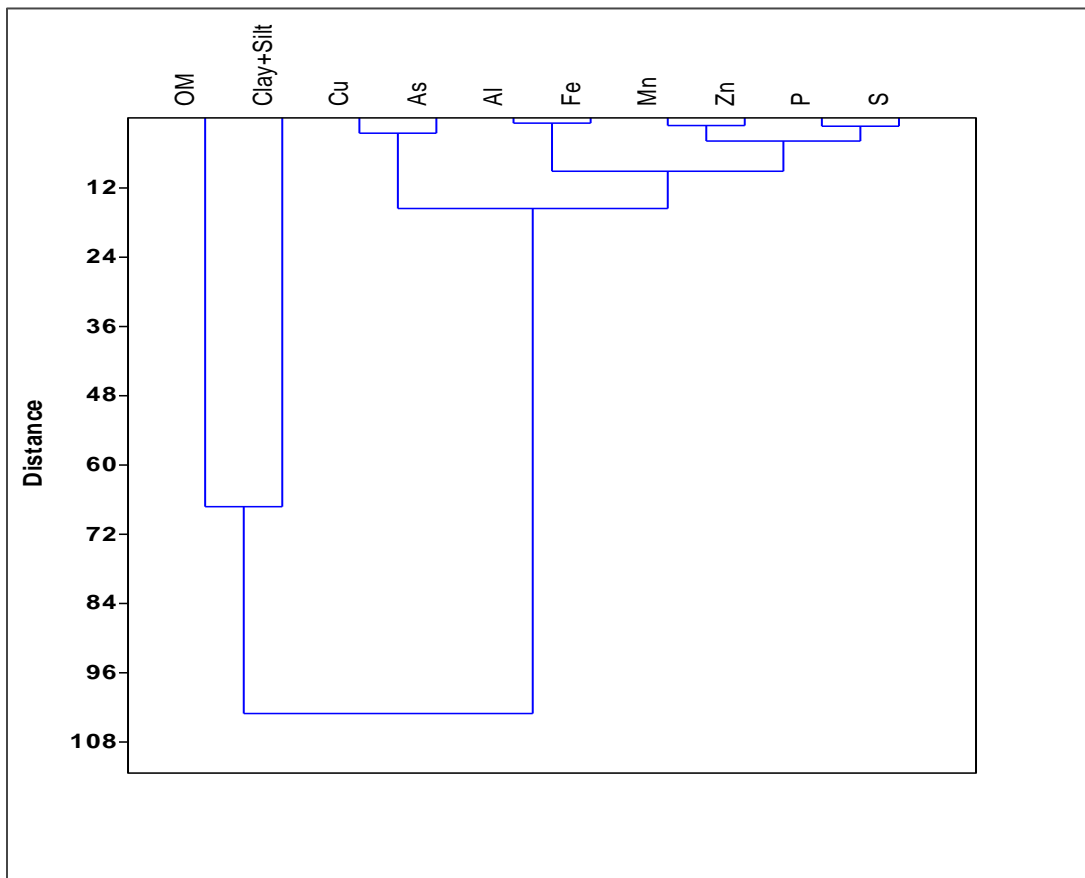


Figure 3.7: Cluster analysis on sediment geochemical data based on paired group algorithm and similarity measure using Gower similarity coefficients.

Table 3.6: Correlation analysis between sediment EF and land use types for 2006 within delineated individual (Ind) and cumulative (Cum) subwatershed areas. Significant (≥ 0.5) correlation values are italicized in bold.

	Type	<i>Cu</i>	<i>Fe</i>	<i>Mn</i>	<i>P</i>	<i>S</i>	<i>Zn</i>	<i>As</i>
Residential areas	Ind	0.33	0.43	<i>0.48</i>	0.15	0.04	0.20	<i>0.60</i>
	Cum	0.30	0.28	0.02	0.18	0.12	<i>0.46</i>	0.18
Agricultural areas	Ind	-0.25	-0.08	-0.05	-0.11	-0.09	-0.24	-0.16
	Cum	-0.20	0.03	0.02	-0.09	-0.05	-0.22	-0.02
Forested areas	Ind	0.10	-0.19	-0.24	0.10	0.29	0.18	-0.34
	Cum	0.24	0.07	0.20	0.15	0.29	0.17	0.09
Wetland/waterways	Ind	-0.07	-0.10	-0.13	-0.07	-0.14	-0.04	-0.05
	Cum	-0.07	-0.14	-0.15	-0.07	-0.18	-0.04	-0.09

Table 3.7: Percentage (%) overall change in land use area within the Broadkill River watershed determined from LULC data for 1992, 2001 and 2006 using GIS.

Year	1992	2001	2006
Residential areas	2.84	8.24	8.69
Agricultural areas	45.88	44.67	43.94
Forested areas	28.21	19.97	20.41
Wetland/waterways	23.06	27.12	26.97

Table 3.8: Principal Component Analysis (PCA) of selected element concentrations in sediment. Elements that are considered influential to the component are denoted by asterisk (*).

Initial Eigenvalues			
Components	Eigenvalues	Variance (%)	Cumulative (%)
1	734.64	97.5	97.5
2	17.04	2.26	99.76
Component loadings			
	Elements	PC I	PC II
	Al	0.68*	0.26
	Cu	0.58*	0.27
	Fe	0.58*	0.15
	Mn	0.41*	0.15
	P	0.63*	0.35
	S	0.46*	0.49*
	Zn	0.48*	0.20
	As	0.45*	0.14
	pH	-0.37	-0.37
	OM	0.58*	0.81*
	Clay+Silt	1.00*	-0.02

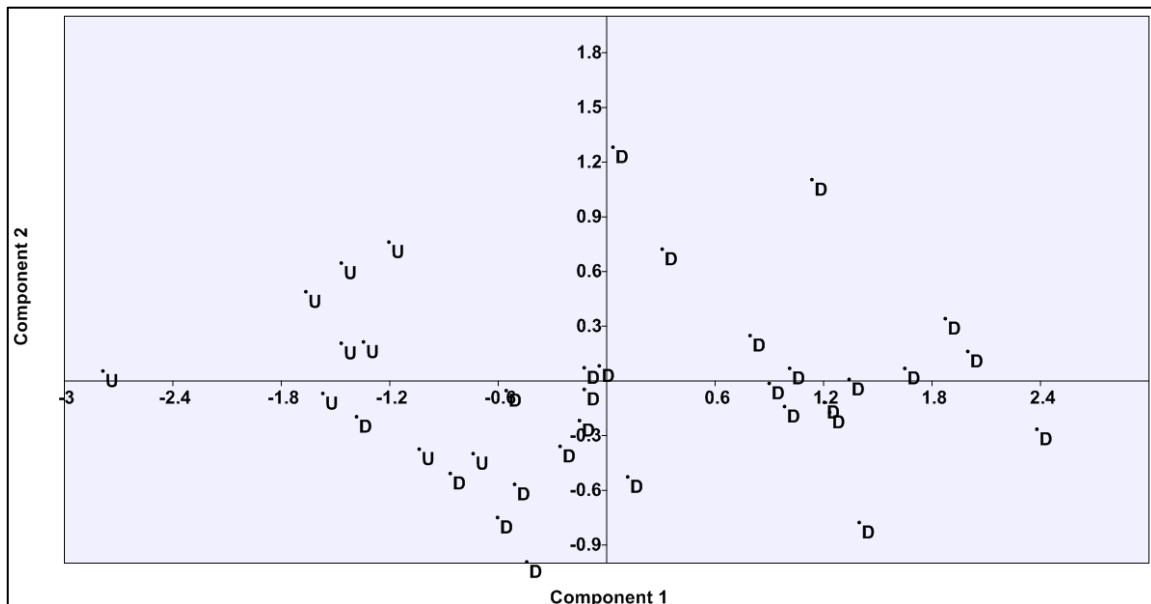


Figure 3.8: A scatter plot of PC scores I and II based on sediment concentrations. U represents upgradient, or reference, sites, while D represents downgradient sites.

Discussion

Trace Element Concentrations and Enrichment in Sediments

Overall, element concentrations in stream sediments from this watershed are lower than the lower effect level (LEL) with the exception of one site for As (6.4 mg/kg; LEL is 6 mg/kg) and another site for Zn (203 mg/kg; LEL is 120 mg/kg). None of the sediments had concentrations of elements that exceeded the severe effects level (SEL).

Despite the variability in element concentrations in sediments there is a statistically significant difference in As, Cu, Mn, P, S, and Zn concentrations between reference and downgradient samples. This difference is also apparent in the PCA analysis, where reference sites and downgradient sites fell within different quadrants of the PC plot.

The enrichment factor analysis also showed that majority of the sampling sites that are in the headwaters of streams within the Broadkill River watershed area have no to low enrichment with respect to As, Cu, P, and Zn, with the exception of three locations for Zn and P (DE 13, DE 16 and DE 28), and two locations for Cu and As (DE 13 and DE 16) respectively. Several of enriched locations are within impoundments (DE3, DE 8, DE 9, DE 12, DE 17, and DE 22, and others are located downgradient of a poultry processing plant (DE 13, DE 14, DE15, and DE 28). The presence of elevated concentrations of elements in impoundments/reservoirs is well-documented (e.g. Ashby et al., 1999), and is associated with stratification of the impoundment resulting in depletion of dissolved oxygen and reduction of elements, resulting in mobilization. The effluent discharge from poultry processing plants contains nutrients (N and P), carbon and some elements, including Cu and Zn; information about As is not available (DNREC, 2006; EPA, 2012). The relationship between poultry processing plants and element concentrations in stream sediments downstream of the plants is unclear based on our dataset; several sites located downgradient from plants show enrichments with respect to As, Cu, P and/or Zn while other sites do not show the effect.

Correlation analysis between fine grain sizes (clay + silt) and element concentrations in sediment showed significant positive correlation, suggesting partitioning of these elements in fine grain sizes. Although we did not conduct spectroscopic analysis of the sediments to determine direct associations between the studied elements and specific minerals, the association between trace elements and fine grain sizes has been observed in many studies (Hanson et al., 1993; Moore et al., 1989). Other studies (Adediran and Kramer, 1987; Bradl, 2004; Dong et al.,

2000; McKenzie, 1980; Violante et al., 2003) support the importance of element adsorption to clay minerals and metal oxides. The correlation between OM and Al, Cu, P and S also suggests adsorption of these elements to the OM fraction, which has also been observed in previous studies (Adediran and Kramer, 1987; Bradl, 2004).

The significant correlation between the studied elements, in addition to the cluster analysis and PCA results, points to an association between them. This association could result from: 1) affinity between these elements by virtue of similar source, 2) similar adsorptive characteristics between elements and minerals within the sediment, or 3) similar biogeochemical processes that are active in influencing their mobility.

Relationships Between Sediment Trace Elements Concentrations and Land use

Correlation analysis between sediment EF values and 2006 LULC data did not show any clear statistical significant relationship between agricultural areas and EFs. However, enrichment factors of several elements (As, Fe, Mn, and Zn) have significant, although weak, correlations with residential land use. It is important to note that the land use has changed significantly within the watershed over the past 30 years, as a result of progressive urbanization. Since 1992, the land area used for agriculture and forest has decreased, concomitant with an increase in land used for residential and commercial purposes. Thus, one possible reason for the correlation between these elements with residential land use is due to urbanization (land clearing and land development), resulting in erosion of previous agricultural soils to streams.

Conclusions

Results from this study suggest that litter-derived elements (As, Cu, Zn, P) in sediments from the Broadkill River watershed originate from both natural and anthropogenic sources. The natural sources are reflected by the no/low enrichment classification of approximately half of our sampling locations. In addition, the similarity of As and Cu concentrations for our reference upgradient sites with NURE data that were collected nearly four decades ago suggest natural, and not recent anthropogenic, inputs for these sites. However, statistically significant differences in element concentrations between our reference sites and downgradient sites point to anthropogenic sources of elements for many of these sites, resulting in approximately 25% of samples categorized as moderately enriched, and 25% categorized as significantly enriched with

respect to As, Cu, Zn and P. This is also supported by a positive and significant correlation of the enrichment factors of As, Zn and Mn with residential areas. Our results did not identify a connection between agricultural land use and element concentrations in stream sediments within the watershed. It should be noted that this type of landscape-scale study is complicated by changes in land use over time (conversion of farmland and forest to residential areas), the presence of point sources of elements (e.g. poultry processing plants), the presence of impoundments, which influence element cycling, and the influence of tidal dynamics.

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CHAPTER 4

Using Column Experiments to Examine Transport of Arsenic and Other Elements Released from Poultry Litter: Implications for Trace Element Mobility in Agricultural Watersheds

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Abstract

This study examined the effect of dissolved organic matter in poultry litter leachate on the fate and transport of litter-derived elements, As, Cu, P and Zn, using laboratory column experiments with soil collected from a field site on the Delmarva Peninsula, a region of intense poultry production. Treatments included leachate and simulated litter solution, which was prepared using similar concentrations of trace elements and major ions, as well as similar pH, ionic strength, but without DOC. Results of the experiments showed that DOC enhanced the mobility of all of the trace elements, but that even in presence of DOC, 60-70% of Zn, As and P were retained within the sediment. Cu was fully mobilized in solution and was not retained in the soil. Patterns of breakthrough curves (BTCs) and mass calculations suggest that the behavior of these trace elements in the column is controlled by both adsorption (including competitive) to soil and complexation with DOC. Although DOC mobilized trace elements in the column experiments, results from other field studies shows elevated Cu and Zn in topsoils to which litter has been applied over the long-term, indicating that complexation to solid organic matter will aid in retention of these elements at the surface. The implication of these findings is that the presence of DOC in poultry litter, in addition to the organic matter content and mineralogy of soils and underlying sediment, all strongly influence the mobility of trace elements derived from litter.

Introduction

Poultry litter application to enhance soil fertility is a common practice within the Delmarva Peninsula USA, an area of intense poultry production. Poultry litter contains trace elements, including organic arsenic (roxarsone; 3-nitro-4-hydroxyphenylarsonic acid) (Garbarino et al., 2003; Rutherford et al., 2003), and other elements such as Fe, Mn, Zn, Cu, and Se, which are routinely added to poultry feed as supplements (Han et al., 2000; Rutherford et al., 2003; Sims and Wolf, 1994). As trace elements are nutrients, they can improve soil fertility at low concentrations. However in excess, accumulation of trace elements in soil have the potential to restrict soil function, cause toxicity to plants, and contaminate the food chain (He et al., 2005). In addition, nutrients released from litter can contribute to eutrophication of streams and rivers,

resulting in formation of “dead zones” within critical estuaries such as the Chesapeake Bay and the Gulf of Mexico (Meyer-Reil and Köster, 2000).

Many laboratory studies have addressed specific processes that influence the mobility of litter-derived trace elements. For example, laboratory experiments on roxarsone have shown that it rapidly degrades to other forms of arsenic during composting (Garbarino et al., 2003) and land application of litter (Christen, 2001; Jackson et al., 2003). Studies have also shown that some bacteria are capable of breaking the arsenic-carbon bond (Pongratz, 1998) and releasing inorganic arsenic (Stolz et al., 2007). The released arsenic from poultry litter is more soluble (57-92 %) in comparison to Zn (7-20 %) and Cu (48-50 %) (Jackson and Bertsch, 2001; Jackson et al., 2003; Oyewumi and Schreiber, 2012; Rutherford et al., 2003), suggesting that As is more mobile than these other trace elements. In addition to bacterial processing, the mobility of trace elements from poultry litter depends on the extent to which these elements interact with minerals and organic matter (Boyle and Fuller, 1987; Lamy et al., 1993), properties of the metals itself, the quantity and type of soil binding sites, pH and competing ions in soil solution (Tyler and McBride, 1982). Adsorption of arsenic oxyanions to minerals, including metal oxides and clays, is well-documented (Stollenwerk, 2003). Adsorption of the cations Cu, Zn and Mn to minerals is also well-documented (Bradl, 2004; García-Sánchez et al., 1999). Complexation of trace elements with litter-derived DOC can also influence the release and mobility of these elements. For example, Li and Shuman (1997) showed that application of poultry litter to soil increased the migration of metals as organic complexes. The complexing ability of DOC is influenced by the dominant functional groups (carboxylic, alcoholic, carbonylic, phenolic and methoxylic) (Camobreco et al., 1996; Livens, 1991), and the pH of the systems because these functional groups exhibit acid-base behavior (Christensen and Christensen, 2000; Kerndorff and Schnitzer, 1980). Although trace element complexation has been studied in a range of environments, there have been few studies addressing the influence of this process in mobilizing As, in addition to other litter-derived trace elements, from litter and litter-applied soils.

In this study, we conducted laboratory column experiments to examine the interaction of leachate from poultry litter with soil from a field site in the Delmarva Peninsula, a region of intense poultry production. Result of a litter application experiment conducted at the field site (Oyewumi and Schreiber, 2012) showed that litter application resulted in slight increases in As, Cu, and Zn in soil water, with little to no impact on shallow groundwater. Mass balance

calculations suggested that uptake of trace elements (As, Cu, Zn and P) in the underlying soil could account for almost all of the mass input from the litter; less than 6 % of trace element mass was released to soil water. Due to the complexities of the field, we could not test the impact of DOC on trace element mobility. The purpose of conducting column experiments was to determine the extent to which litter-derived DOC influences the release and transport of elements (As, Cu, P, and Zn) from litter into underlying soil.

Materials and methods

Collection of Soil Samples for Column Experiments

Soil cores for the experiments were collected in Oct. 2011 from a field site in Sussex County, DE. Details of the field site are described in Oyewumi and Schreiber (2012). The field site had received litter applications in fall 2009 and spring 2010. Six cores (approximately 0.04 m in diameter) were collected to a depth of 1.5 m using direct push methods (Geoprobe). After collection, cores were capped, wrapped in aluminum foil, and transported to the lab in coolers.

Column Construction

In the laboratory, the soil cores were split, and the topsoil (A horizon; 0.3 m) was removed. The topsoil was removed from the sediment to allow for simulation of transport of the litter-derived trace elements in the vadose and saturated zone of the field site. The remaining soil (0.33 to 1.5 m depth) from the core samples was mixed to ensure homogeneity, during which roots, twigs and gravel were removed, and aggregate components were broken loose before packing them into columns.

The columns were constructed with polyvinyl chloride (PVC) tubes, capped at the top and bottom. The column length was 0.2 m and diameter was 0.034 m. A stainless steel wire mesh was placed inside the bottom cap to retain fine particles with the column during the experiment. In addition, a glass fiber filter was put on top of the packed soil to prevent loss of fines (After Strauss et al., 2011). Before soil was added to the column, a thin layer of acid washed and deionized water rinsed pure sand was put at the bottom of the column in order to allow uniform flow of the influent solutions. Columns were then incrementally packed with each increment compacted by weakly pressing with a clean pestle to provide a uniform compaction.

The soil were packed to simulate average field bulk densities (1300 to 1600 kg/m³) of undisturbed soil within Sussex County, Delaware (Sims et al., 2002; USDA-SCS, 1974). After packing, stainless steel mesh was placed on the top of the soil, followed by a glass fiber filter, before capping the top to prevent loss of fine particles. Teflon tubing was used to carry influent and effluent solutions.

Influent Solution Composition

Two types of influent solution were created for the column experiments. The first was a poultry litter leachate. Poultry litter was collected from a poultry farm near the field site, brought to the laboratory, dried, disaggregated with a hand mill and sieved through a 2 mm sieve to remove detritus (wood shavings, feathers and twigs). The water-soluble elements were extracted using 25 ml of deionized water on 5 grams of litter in a 50 mL centrifuge tube and placed on a wrist shaker for 5 days, after which the mixture was centrifuged (9000 rpm; 20 min), and the extracted supernatant filtered (0.45 micron). The litter leachate solution was then diluted by a factor of 20 for the experiments to simulate dilution of litter leachate with precipitation. The second solution was prepared using salts to simulate same concentrations as the leachate (Al, Fe, Ca, K, Na, Mg, P, S, Mn, Zn, As, and Cu). The pH and ionic strength were adjusted to match the litter leachate as close as possible. The pH was adjusted using sodium hydroxide and hydrochloric acid while the ionic strength was adjusted using CaCl₂.

Transport Experiments

The soil columns were initially saturated from the bottom with deionized water to facilitate air displacement, after which a degassed conservative tracer (0.01M Cl solution as CaCl₂, pH value of 7.65) was introduced using a peristaltic pump (VWR Mini-Pump Variable Flow) until approximately eight pore volumes were flushed through the column. The chloride solution was used to flush soil porewater and to characterize the hydrodynamic properties of the soil. Deionized water was then pumped through the column to flush the chloride solution. These three steps (DI, chloride, DI) were followed to pretreat all columns used in the experiments. Pore volume was calculated as the volume of water required to saturate the column; this was confirmed by the difference in weight of the saturated soil column and its dry weight (After Matocha and Hossner, 1999). **Figure 4.1** showed the image of the column set up for this study.

After pretreatment, separate columns were subjected to one of four treatments: 1) poultry litter leachate with 100 mg/L bromide (Br) as a conservative tracer (T1); 2) poultry litter leachate with no Br (T2); 3) simulated element solution with no dissolved organic carbon (DOC), and Br as a conservative tracer (T3), and 4) simulated solution without Br (T4). For each experiment, approximately 15 pore volumes of treatment solution were pumped bottom-up into the column. After the treatment, the columns were flushed with approximately five pore volumes of 0.01M CaCl₂ solution.

Effluent samples were continuously collected in 15 ml centrifuge tubes with a fraction collector (Isco Cynnet). The flow rate for each experiment was determined by weighing the eluted solution in the sample fractions. Three sub-samples were combined together that represented 30-45 minute intervals, depending on the flow rate. Samples for elements (As, Cu, Zn and P) were acidified with trace metal grade nitric acid (HNO₃). DOC samples were preserved with concentrated hydrochloric acid (HCl). After the completion of the experiments, columns were allowed to drain by gravity for five days after which they were opened and partitioned into three sections (bottom, middle and top), with each section thoroughly homogenized. The homogenized soil was acid digested and analyzed for elements to complete the mass balance.

Mass Balance of Trace Elements in Columns

We assumed the mass input of elements into the columns was only through introduction of the influent. The background soil concentration was determined after initial pretreatment with CaCl₂. The mass input of trace elements to the columns during the experiments was calculated as:

$$M_{i-in} - M_{i-out} = M_{i,stored}(\text{Change in storage}) \quad (1)$$

$$M_{i-in} = C_{inf-i}V_{in} \quad (2)$$

$$M_{i-out} = \sum(C_{eff-i}V_{out})i_{Total} \quad (3)$$

where M_{i-in} is the mass (mg) of element i in influent solution, C_{inf-i} is the concentration of a element i in influent solution, V_{in} is the total volume of influent solution, M_{i-out} is the mass of element i in effluent solution, which is calculated for each element i and summed to determine the total mass (mg), C_{eff-i} is the concentration of element i in effluent solution, V_{out} is the volume

of effluent solution, $M_{i,stored}$ (*change in storage*) is the mass (mg) of element i taken up or released by the soil, calculated as:

$$M_{i,stored} = (C_{i,post} - C_{i,pre})\rho_d V \quad (4)$$

where $C_{i,pre}$ and $C_{i,post}$ are the concentrations (mg/kg) of element i in the soil before and after the experiments, ρ_d is the bulk density of the column soil (kg/m^3), and V is the volume of the column. The change in storage can also be calculated by subtracting the mass in the effluent from the mass in the influent.

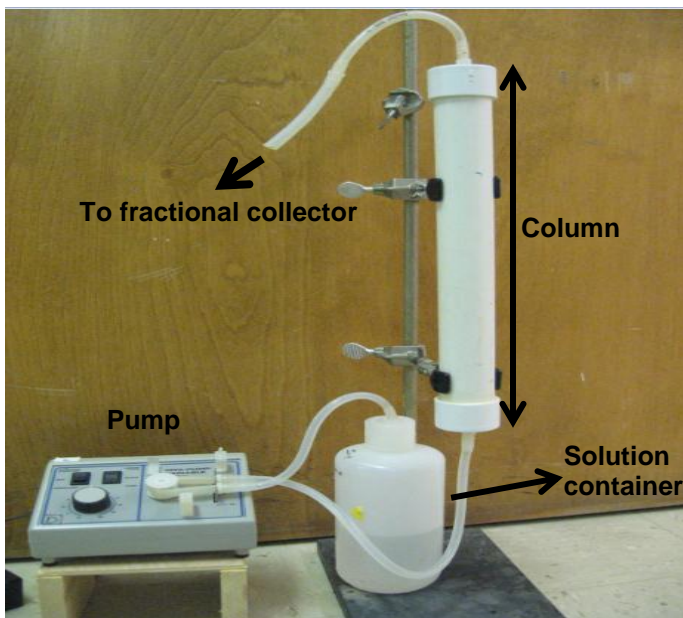


Figure 4.1: Column set up showing the introduction of the influent solution

Analytical Methods

Solids: The total porosity of the packed column was determined from the difference of the column weight before and after saturation using the oven-dried weight of soil. The bulk density was determined as the ratio of the weight of dry soil to the total volume of column. The moisture content of soil was measured using a thermogravimetry method (After Topp and Ferré, 2002). The homogenized soil sample was analyzed for particle size distribution using the ASTM 152 H hydrometer method (ASTM, 2000) described in Dane and Topp (2002). Basic soluble soil properties, including cation exchange capacity (CEC), organic matter content (OM), and pH

(Table 1) were analyzed at the Virginia Tech Soil and Plant Analysis Laboratory (VTSPAL) using methods described by Maguire and Heckendorn (2012). Subsets of the sediment samples were also digested with aqua regia in a microwave (CEM Mars Express) and analyzed for eight elements (Al, Na, Ca, Cu, Fe, K, Mn, P, and Zn) using Inductive Couple Plasma-Atomic Absorption Spectrometry (ICP-AES) with detection limits varying between 3 and 175 µg/L.

Solution: The influent solutions used in the experiments were analyzed for elements (As, Cu, P, and Zn), anions (Br, Cl, SO₄) and DOC. Samples for Cu, Zn and P were analyzed using ICP-AES at the VTSPAL. DOC samples were analyzed using a Shimadzu Carbon Analyzer (TOC-VCSN, Kyoto Japan). Samples for As were analyzed using Graphite Furnace Atomic Absorption Spectrophotometry with Zeeman background correction (GFAAS; Varian Spectra 220). Anion samples were analyzed using ion chromatography (Dionex DX-120). During pretreatment, conductivity in the effluent solutions was continuously monitored with a conductivity meter (Oakton conductivity meter Serial No 77994), and later converted to chloride concentrations with a set of calibration standards.

Parameter Estimation

Breakthrough curves (BTCs) were generated from effluent data by plotting the relative concentration (C/C_0) versus relative pore volume (V/V_0), where C is the measured effluent concentration, C_0 is the initial influent concentration, V is the sample volume collected, and V_0 is one pore volume. The pore velocity was calculated after Camobreco et al (1996) using the flow rate of influent solutions through the columns, column length and the pore volume as:

$$V = \frac{QL}{V_0} \tag{5}$$

Where V is the pore velocity, V_0 is the pore volume, Q is the flow rate of the influent solutions and L is the length of the column. The BTC of Cl was fitted to a 1D analytical solution of advection-dispersion equation (Ogata and Banks, 1961) to characterize the dispersion coefficient.

Results

Characteristics of the Column Soil and Solution

Table 4.1 presents results of the physical and acid extractable (aqua regia) ions in the homogenized soil samples used for column experiments. The soil is composed of predominantly sand (79-80%) with minor silt and clay (<20%). The soil is slightly acidic (pH 5), with an average organic matter fraction and cation exchange capacity of 0.3 % and 2.3 meq+/100g respectively. The average acid-extractable element concentrations shown in Table 1 were determined after initial pretreatment of the soil.

Table 4.2 presents the chemistry of the poultry litter leachate and the simulated litter solution. The pH of both solutions are similar (6.36, 6.57), however the EC value of simulated solution (1833 μ S/cm) is higher than that of poultry litter leachate (1262 μ S/cm). The ionic concentrations of elements are similar with the exception of Ca which we intentionally reduced in the simulated litter solution due to formation of apatite with phosphate, and nitrate. **Table 4.3** presents different types of treatment for each separate column.

Table 4.1: Basic physico-chemical characteristics of the homogenized soil sample used in the column experiments. Value is average of duplicate samples. OM = organic matter, CEC = cation exchange capacity

						Acid extractable (Aqua regia)							
Sand	Clay	Silt	OM	CEC	pH	Al	As	Cu	P	Zn	Fe	Mn	S
%				meq+/100g		mg/kg							
80	10	10	0.3	2.3	5	12,620	10	19	181	24	10,664	63	65

BTCs: Chloride

Figure 4.2 shows chloride BTCs obtained during the pretreatment stage for all four treatments. The breakthrough curves (BTCs) display a sharp front, characterized by early appearance of tracer in the effluent solution in less than 1 pore volume (and less than one hour into the experiment), which approached effluent relative concentration (C/C_0) of 1 in less than three pore volumes. Fitting the chloride BTC to the analytical solution of the advection-dispersion equation, the hydrodynamic dispersion coefficient values were estimated to be 0.75 (T1), 1.41 (T2), 1.49 (T3) and 1.49 cm^2/min (T4) (**Table 4.4**).

Table 4.2: Concentrations of major and minor ions in poultry litter leachate and simulated solution (mg/l unless noted) used for transport experiments. The simulated solution was based on the initial concentrations of elements in poultry litter. EC= Electrical conductivity, I= ionic strength.

Analytes (mg/l)	Solution 1: Litter leachate	Solution 2: Simulated solution
Al	0.02	0.05
Fe	0.34	0.34
Ca	0.16	19
K	206	408
Na	63	75
Mg	30	35
P	49	51
S	66	66
Mn	0.4	0.4
Zn	0.4	0.4
As	0.11	0.12
Cu	0.3	0.3
P	49	51
Cl	79	123
NO₃-N	<0.1	23
SO₄	162	173
DOC	400	<0.01
EC (uS/cm)	1262	1833
pH	6.57	6.36
I (M)	0.01	0.02

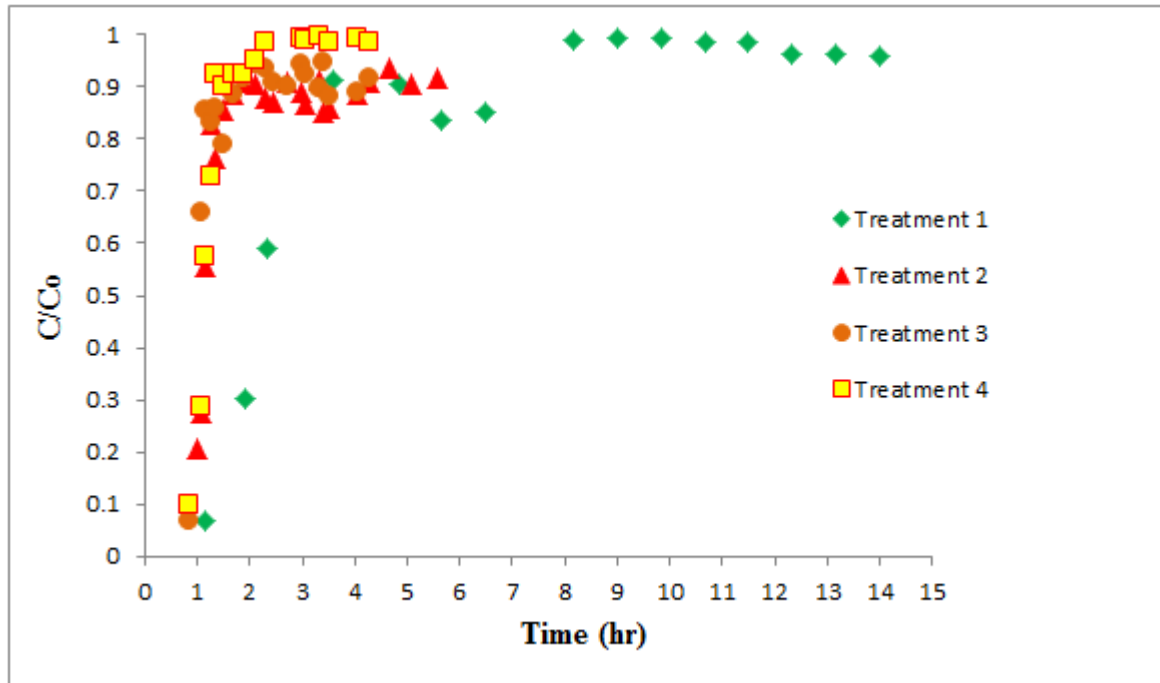


Figure 4.2: Breakthrough curves (BTCs) for chloride during initial flushing phase for treatments 1, 2, 3 and 4.

BTCs: Litter Leachate Experiment

Figure 4.3 shows the breakthrough curves in litter leachate treatments with (T1) and without Br (T2). Similar to Cl, the BTC for Br has a sharp front; the relative peak concentrations (C/Co) approached 1 within four pore volumes (PV). The DOC BTCs display a hyperbolic shape; the maximum C/Co was delayed in comparison with Br, reaching 1 at between 8 and 13 pore volumes. The DOC BTCs do not show differences related to the presence of Br.

The shape of the Cu BTC for T1 matches the Br peak; however, the maximum C/Co reached 2.5, indicating an additional source of Cu. Without Br, the Cu BTC displays a more gradual increase, and has a maximum C/Co of 1. The BTCs for Zn have a triangular shape, with a sharp increase in concentration, followed by a long tail. Similar to Cu, the Zn BTCs for T1 show higher eluted than influent concentrations, with C/Co values reaching up to 1.9 within five pore volumes. Without Br, the Zn BTCs also have a triangular shape, but have maximum C/Co values ~ 0.75 .

The BTCs for P and As are similar to each other, displaying a “shark-fin” shape, with a gradual increase in concentration, followed by a sharp decline during flushing. In comparison with Br, solute elution was delayed for both P and As. Unlike Cu and Zn, the maximum C/Co values for P and As are less than 1 (P: 0.5-0.6; As: 0.3-0.4). The similarity in BTCs between the T1 and T2 experiments shows a negligible effect of Br on the transport of these elements in leachate solution.

Table 4.3: Summary of column treatments.

Treatment	Solution type	Volume of influent (ml)	Flow rate (ml/min)	Bromide added
T1	Poultry litter leachate	799	0.76	Yes
T2	Poultry litter leachate	815	1.4	No
T3	Simulated litter solution	825	1.5	No
T3b	Simulated litter solution	830	1.53	No
T4	Simulated litter solution	837	1.49	Yes

BTCs: Simulated Trace Element Solution Experiment

Figure 4.4 shows the BTCs for the simulated solution. Without Br, the Cu BTC shows minimal breakthrough, with a maximum C/Co of 0.03-0.04. With Br, the Cu BTC remained steady at C/Co of 0.03-0.04, until late in the experiment, during the flushing period, when the C/Co value increased to greater than 8, signifying an additional source of Cu. The Zn BTCs also differed in the presence and absence of Br. Without Br, the Zn peak eluted late in the experiment (15 pore volumes), with a maximum C/Co of 0.1. With Br, the peak concentrations also eluted at ~ 15 pore volumes, but the maximum C/Co was much higher, approaching 0.7. The BTCs of As and P are similar to each other; they show a delayed response similar breakthrough time, with slightly higher peaks from P than for As. In contrast to Cu and Zn, more As and P mass is eluted in the solution without Br than is eluted with Br. Maximum C/Co values for As and P were 0.05 and 0.1 with Br and 0.2 and 0.3 without Br, respectively.

Table 4.4: Selected column physical and transport parameters

Parameters	Treatments			
	T1	T2	T3	T4
Bulk density (kg/m ³)	1685	1688	1700	1675
Porosity	0.35	0.34	0.35	0.35
1 pore volume (cm ³)	63	62	63	64
Pore velocity (cm/min)	0.48	0.90	0.95	0.93
Dispersion coefficient (cm ² /min)	7.5E-01	1.41	1.49	1.46

Comparison of BTCs: Litter Leachate Versus Simulated Solution

Figure 4.5 compares element BTCs in the litter leachate with Br (T1) with those in the simulated litter solution with Br (T4), to show the combined effect of DOC and Br on element transport. The BTCs show that Br enhanced release of Cu from the column soil, as effluent concentrations are greater than influent concentrations ($C/C_0 > 1$) in both the leachate and simulated experiments. This was also observed for Zn, but only in the leachate experiment. In the presence of Br, the transport of As and P was delayed in comparison with Cu and Zn, and the maximum C/C_0 values were considerably lower (< 0.6).

Figure 4.6 compares element BTCs in the leachate without Br (T2) with those in the simulated litter solution without Br (T3), to show the effect of DOC on the transport of elements. Comparison of the Cu and Zn BTCs shows much greater mass eluted in the leachate experiments; mass elution from the simulated solutions was negligible. Comparison of the As and P BTCs also shows greater mass eluted in the leachate experiments than in the simulated solutions, but the mass eluted in the simulated litter solutions (C/C_0 up to 0.2) was greater than for Cu and Zn ($C/C_0 < 0.1$). For As and P, both sets of BTCs (leachate and simulated) were delayed with respect to Cu and Zn.

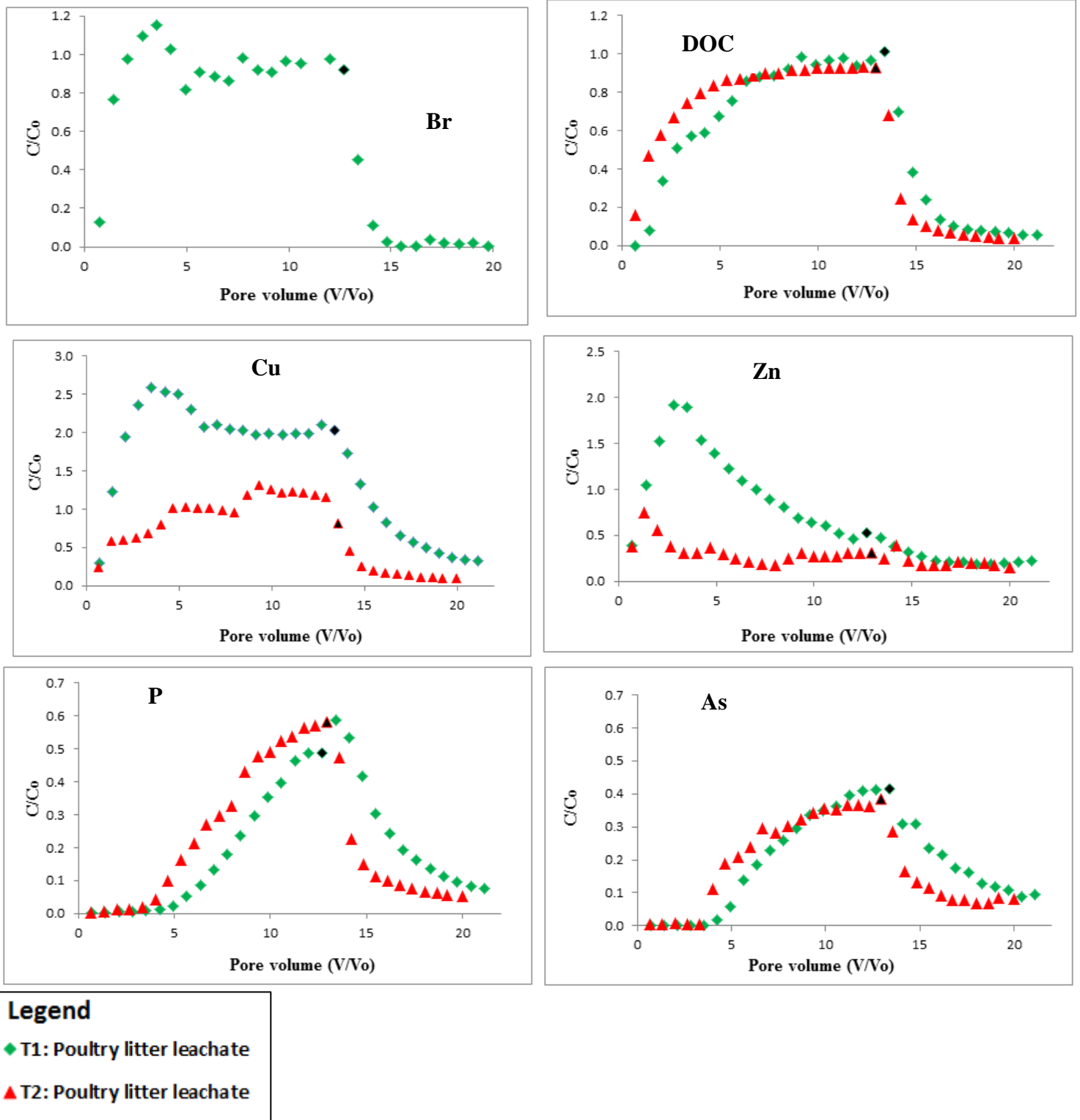


Figure 4.3: BTCs of Br, DOC, Cu, Zn, P and As in the poultry litter leachate treatments. T1 (green diamonds) has 100 mg/L of Br while T2 (red triangles) has no Br. Symbols filled with black represent the start of flushing with 0.01M CaCl₂ solution.

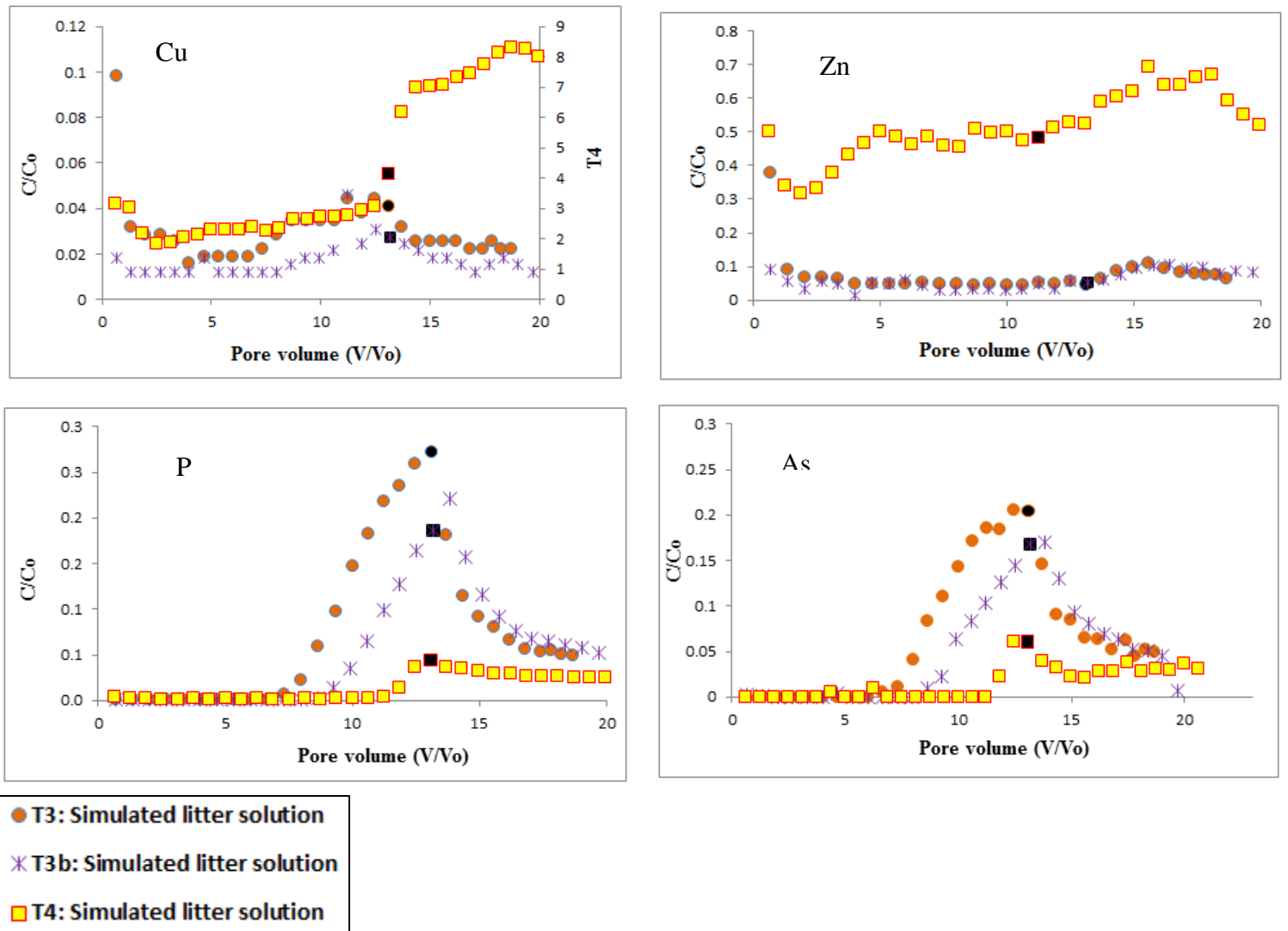


Figure 4.4: BTCs of Cu, Zn, P and As in the simulated solution treatments. T3 (brown circles; purple crosses) has no Br; T4 (yellow squares) has 100 mg/L Br. Symbols filled with black represent the start of flushing with 0.01M CaCl₂ solution. Note secondary y-axis for Cu, showing results of the T4 experiment.

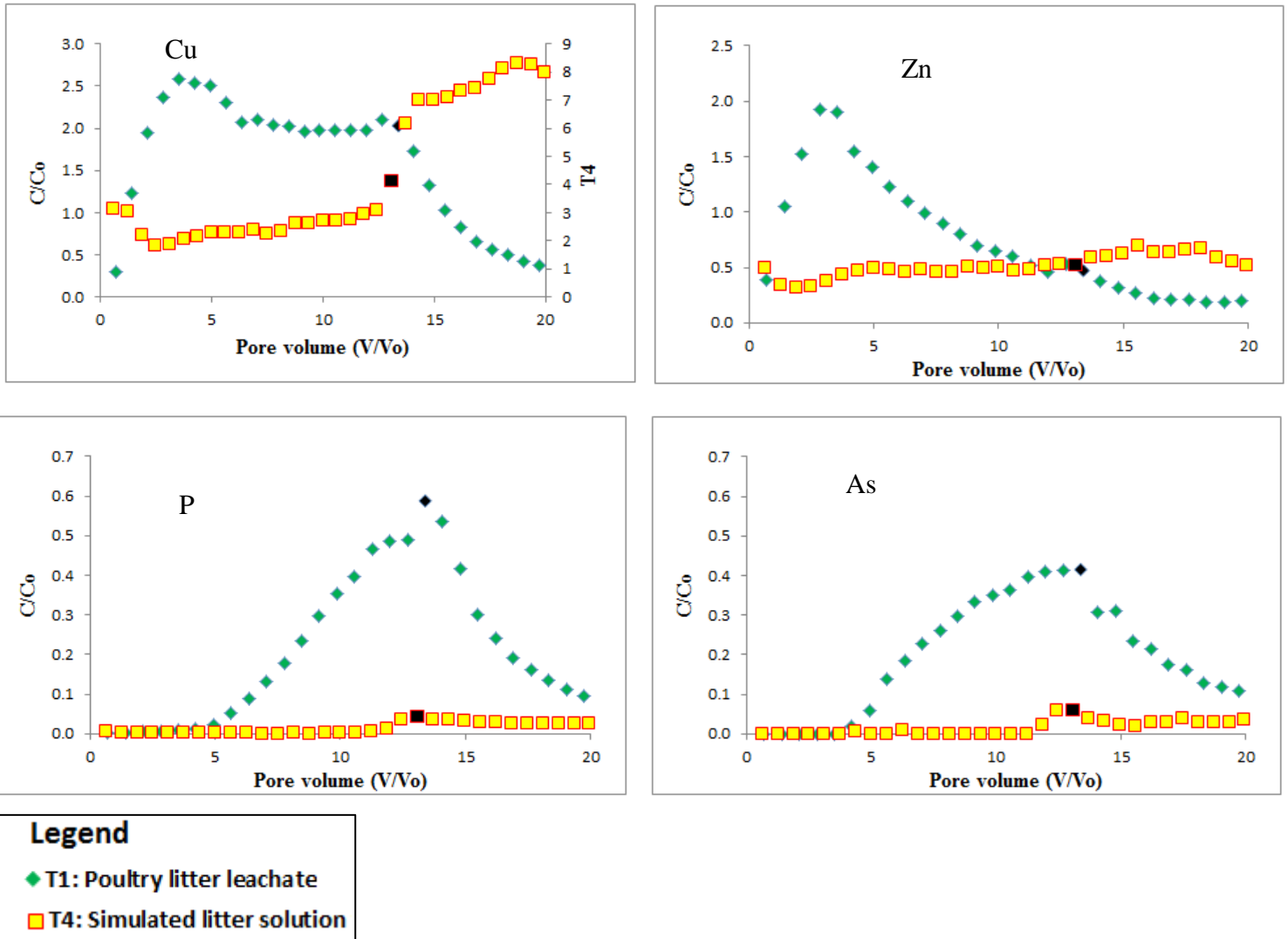


Figure 4.5: Comparison of the BTCs for Cu, Zn, P, and As from poultry leachate with Br (T1; green triangles) and simulated solution with Br (T4; yellow squares) showing the combined influence of DOC and Br. Symbols filled with black represent the start of flushing with 0.01M CaCl₂ solution. Note the secondary y-axis for the T4 Cu BTC.

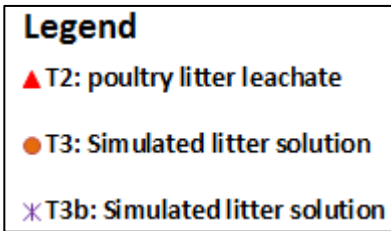
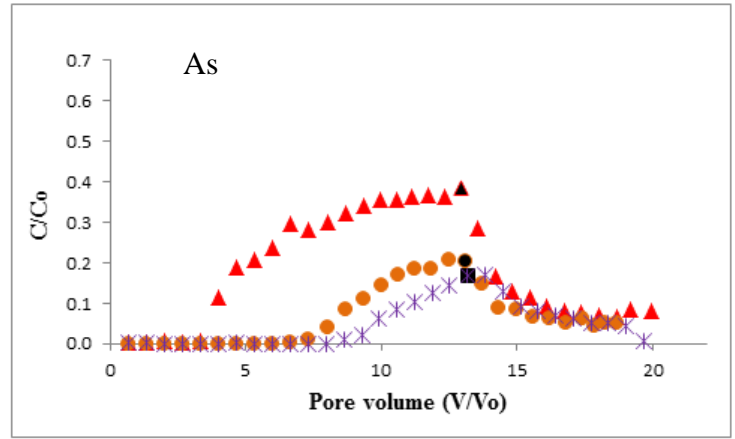
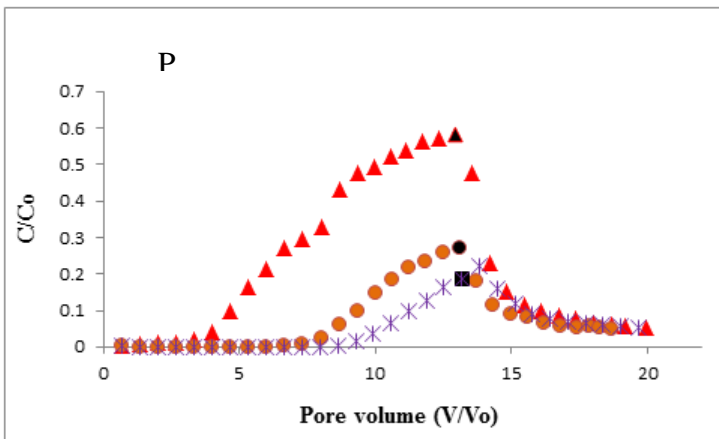
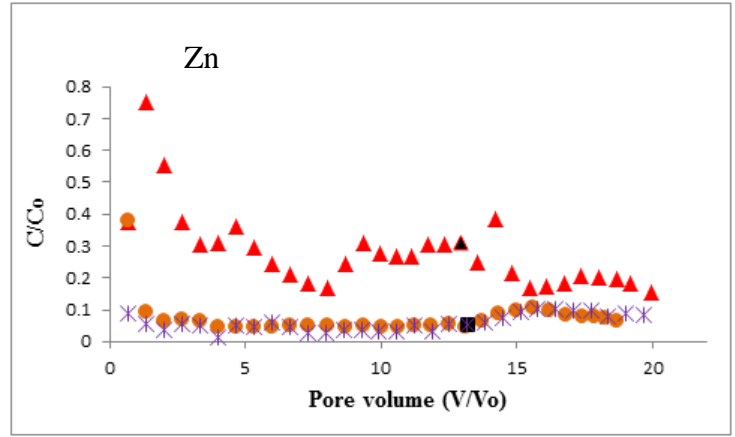
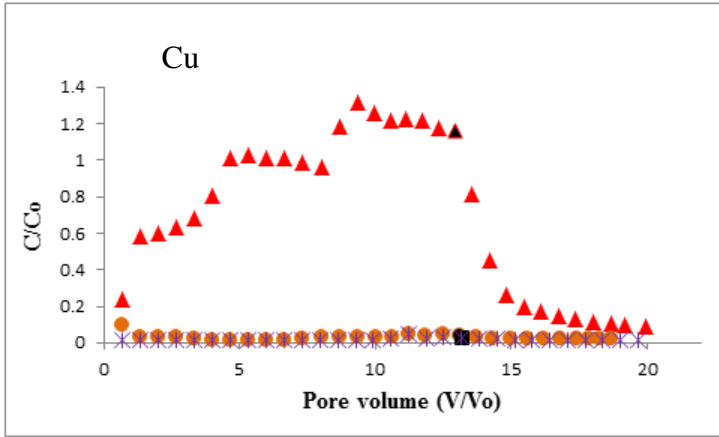


Figure 4.6: BTCs of Cu, Zn, P, and As from poultry leachate (T2; red triangles) and simulated litter solution (T3; brown circles, purple crosses) showing the effect of DOC in the absence of Br. Symbols filled with black represent the start of flushing with 0.01M CaCl₂ solution. Flow rates for each treatment are shown in the parentheses.

Mass Balance of Trace Elements in Columns

Results of mass balance calculations based on elution data are shown in **Table 4.5**. The influent masses had only slight differences between the experiments: As (0.087 to 0.104 mg), Cu (0.230 to 0.242 mg), P (38.8 to 41.6 mg), and Zn (0.32 to 0.36 mg). Using the solution data, the effluent mass was subtracted from the influent mass to determine the mass loss or gain during each experiment. We assumed that the only loss of mass was due to retention on soil, and that the only gain was due to release from soil. Calculations reveal that almost all of the Cu mass (95-97%) was retained in the simulated litter solution without Br; however, in leachate (T1 – with Br, T2 – no Br) and in simulated litter solution with Br (T4), Cu was released from soil. Zinc was retained in all experiments (28-90%), with exception of T1. For the leachate experiments, both with and without Br, As and P retention in the soil ranged from 62 to 68%. In the simulated litter solutions, As and P mass retention was 90-100%, also showing little effect of Br.

The change in storage of elements based on solid phase analysis of soil is shown in **Table 4.6**. Positive values indicate retention of mass; negative values indicate release. Comparison of the change in soil to the change in solution shows significant differences between these two methods of estimating change in mass storage. As the solution data are more accurate due to the fractional collection of samples, we will use the solution-based calculations of change in storage for interpretation.

Table 4.5: Mass balance calculations based on column elution data

<i>Mass in the influent solution (mg)</i>				
Treatments	As	Cu	P	Zn
T1	0.09	0.24	38.81	0.32
T2	0.09	0.24	39.59	0.33
T3	0.10	0.23	40.99	0.35
T3	0.10	0.23	41.23	0.35
T4	0.10	0.23	41.58	0.36
<i>Mass in the effluent solutions (mg)</i>				
Treatments	As	Cu	P	Zn
T1	0.030	0.66	14.90	0.43
T2	0.028	0.25	14.02	0.13
T3	0.001	0.01	4.38	0.04
T3	0.001	0.01	3.52	0.03
T4	0.000	1.22	0.93	0.26
<i>Mass difference between influent and effluent solutions(Inf-Eff, mg)</i>				
Treatments	As	Cu	P	Zn
T1	0.06	-0.42	23.91	-0.11
T2	0.06	-0.01	25.57	0.19
T3	0.10	0.22	36.60	0.31
T3	0.10	0.22	37.71	0.32
T4	0.10	-0.99	40.65	0.10
negative= released from sediments				
positive = retained to sediments				
<i>Percent mass lost or gained in solution</i>				
Treatments	As	Cu	P	Zn
T1	66.08	-176.72	61.61	-33.67
T2	68.46	-4.20	64.58	59.71
T3	99.04	95.00	89.31	89.55
T3b	99.26	96.86	91.46	90.50
T4	99.99	-428.48	97.76	28.32
negative= released from sediments				
positive = retained to sediments				

Table 4.6: Change in mass storage of elements in soil, shown as percent mass lost or gained within soil. Arsenic could not be calculated due to several soil samples with concentrations below detection limit.

% mass change of element			
Treatments	Cu	P	Zn
T1	-28.33	40.06	1.43
T2	135.46	61.65	30.52
T3	0.50	93.16	12.28
T4	54.11	73.37	313.18
if negative = decrease from background mass(mg)			
if positive = increase from background mass (mg)			

By comparing the effluent masses yielded from the different experiments, we can calculate the mass of element mobilized by Br and DOC (**Table 4.7**). To calculate the mass mobilized by Br in leachate, the mass in effluent for T2 (leachate without Br) can be subtracted from the mass effluent in T1 (leachate with Br). To calculate the mass mobilized by DOC, the mass in effluent in T3 (simulated litter solution without Br) can be subtracted from the mass effluent in T2 (leachate without Br). Results of these calculations suggest that 100% of the Cu in the leachate solution is mobilized by DOC. In the presence of Br, additional Cu is mobilized from soil. The release of Cu from soil is supported by a decrease in Cu measured in the soil from T1 experiment. In the leachate experiment, 28% of Zn is mobilized by DOC. In the experiments with Br, 86% of Zn was mobilized by Br. Addition of these percentages exceeds 100%, suggesting that some of the Zn mobilized by Br may have originated from the soil. However, no significant losses of Zn were measured in the soil. For both As and P, about one third of the mass in leachate was mobilized by DOC; but in contrast to Cu and Zn, these elements were not affected by Br. Both As and P showed measurable mass increases in soil during the T1 experiment, indicating that they were both retained in soil.

Table 4.7: Percent of element mass mobilized by Br and DOC in litter leachate. Values > 100% reflect release of element from soil.

	As	Cu	P	Zn
Mass mobilized by Br	1.57	173.64	2.17	86.52
Mass mobilized by DOC	27.99	104.3	24.91	28.1

Discussion

Effect of DOC on Trace Element Behavior

The presence of DOC in leachate influenced the mobility of all of the elements under study. The most significant impact was on Cu, which was 100% mobilized in solution in the presence of DOC. In the absence of DOC, approximately 96% of the mass was retained. For Zn, 28% of mass was mobilized by DOC. In the absence of DOC, 90% of Zn was retained. Cu and Zn both exhibit strong adsorption to metal oxides, a pH-dependent process that has been well-studied (Barrow et al., 1981; Kabata-Pendias and Pendias, 2000; Sparks et al., 1995; Tessier et al., 1985). However, in the presence of DOC, both of these elements form complexes with fulvic and humic acids (Bolter et al., 1975; Hsu and Lo, 2000; Li and Shuman, 1997; McBride, 1994). Han et al (2001) showed that Cu and Zn complexes in poultry litter amended soils are initially mobile, but that over time, they become more stable. This is supported by field studies showing elevated Cu and Zn concentrations in agricultural topsoil after years of poultry litter application, with much lower concentrations in mineral soils, suggesting retention of these elements through complexation with soil organic matter and limited mobility within the deeper profile (Brock et al., 2006; Codling et al., 2008; Kingery et al., 1994; Mitchell and Tu, 2006). The difference in mobility of Cu and Zn organic complexes can be explained by their complexation constants; Cu forms stronger complexes with humic and fulvic acids than does Zn (He et al., 2005).

In the absence of DOC, As and P were retained in the sediment column (99% and 91%, respectively). These results are supported by the literature, as adsorption of As and P to metal oxides is well-documented (El-Hoz and Apperley, 1996; Li et al., 2009; Liu et al., 2002; Stollenwerk, 2003). In a litter application experiment conducted at the field site where the soils were collected, As and P released from the litter were shown to be almost fully retained by the soil, and were concentrated in B horizon with elevated Fe and Al concentrations (Oyewumi and

Schreiber, 2012). In the presence of DOC, As and P were both mobilized (28% and 25%, respectively). The mechanisms for As mobilization could include complexation, as several recent studies have shown that As can form complexes with humic acids (Buschmann et al., 2006; Selim Reza et al., 2012) and can also form ternary complexes with Fe (Mikutta and Kretzschmar, 2011; Sharma et al., 2010). Another mechanism for As and P mobilization is competitive adsorption with DOC. A study by Grafe et al (2001) showed that DOC can compete with As for sorption sites on goethite. The delayed breakthrough of As and P in the leachate experiments supports this mechanism; comparison of the BTCs for the leachate vs. simulated litter solution shows an earlier breakthrough for the leachate solution than for the simulated litter solution. There is also the possibility of competitive adsorption between As and P, which is documented in the literature (Hongshao and Stanforth, 2001; Jackson and Miller, 2000; Roy et al., 1986; Violante and Pigna, 2002), but our dataset cannot be used to test this mechanism.

Effect of Br on Trace Element

Bromide was included in the experimental design to act as a conservative tracer, and was thus added to the influent of T1 and T4 experiments. Bromide had a marked effect on Cu and Zn mobility due to the strong complexes that Br forms with these two elements (He et al., 2005). In addition to complexing with these elements in solution, Br also appears to have complexed with Cu in the soil, resulting in “stripping” of Cu from the soil; this removal is supported by soil digestion results. Bromide did not have a strong influence on As and P in the leachate experiment. However, in the simulated litter solution, the presence of Br increases retardation of the As and P BTCs, and also decreases mass elution. The causes of this are currently not understood.

Trace Element Retention in Soil: Lab vs. Field

Results from T2, the experiment with leachate but no Br, which most closely reflects the field environment, show that about 60-68% of As and Zn released from litter is retained in this soil. In contrast, none of the Cu released from litter is retained. Comparison of these results to those from the field experiment (Chapter 2) is shown in **Table 4.8**. Trace element retention was greater in the field experiments than in the lab. Due to the complexities of the field, the cause of this difference is difficult to pinpoint. However, it is important to note the DOC concentrations in

the litter leachate differed considerably between the two experiments (6-18 mg/l in field, as measured in soil water vs. 440 mg/l in the lab, as measured in the influent solutions). Lower DOC concentrations, such as was measured in the field, would result in fewer complexes, allowing for more adsorption of elements on soil. Additional geochemical modeling will be conducted to test this idea.

Table 4.8: Comparison of mass retention of litter-derived elements in soils: Column experiments vs. field experiment (Chapter 2). NA = not analyzed.

	% Mass retained (field)	% Mass retained (lab T2)
As	98	66
Zn	98	60
Cu	94	0
P	NA	65

Implications for Mobility of Litter-derived Trace Elements

Results from this study show that Cu in litter leachate is mobile in soil with low organic content, due to complexation with DOC. However, if the Cu-complexes interact with organic soils, they will likely be retained, as has been shown in field studies. Thus, the mobility of Cu released from litter will be strongly influenced not only by the concentration (and form) of DOC in litter leachate, but also by the organic content of soil. If litter is applied to a field site with a thick layer of rich organic topsoil, Cu will likely be retained within the topsoil and not mobilized into soil and groundwater. However, in thin, organic-poor soils, there may be greater likelihood of mobilization.

As expected, due to their oxyanion form, As and P exhibit different behavior. In the column experiments, ~66% of the mass of As and P was retained within the soil, likely due to adsorption to metal oxides and clays. The remaining mass was mobilized in solution by DOC, either as complexes or due to competitive desorption by DOC. These results suggest that the mobility of As and P is less dependent on organic content of the soil, and more dependent on the metal oxide and clay content.

The behavior of Zn in the columns was influenced by both organic complexation and adsorption to minerals. In this study, about 60% of the Zn in litter leachate was retained in soil, and approximately 28% was mobilized, likely via complexation by DOC. Extrapolating to field conditions, these results suggest that some Zn will bind to organic-rich topsoil, but can also adsorb to minerals deeper in the profile.

The complexation of Br with Cu and Zn, which resulted in mobilizing soil-bound Cu in our experiments, is worth some discussion. Although Br was used in the experiments as a conservative tracer and would not be expected to be present in agricultural watersheds, the introduction of another strong complexing agent, such as EDTA or citric acid, to a site that has received litter application, could have a similar effect on mobilizing elements, and should be avoided. Additional speciation modeling will be conducted to test these ideas.

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