

**FATE, TRANSPORT, AND BIOAVAILABILITY
OF ARSENIC IN MANURED AND CONTAMINATED
SOILS OF DELAWARE**

by

Sheila May Gardner

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Science in Plant and Soil Sciences

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TABLE OF CONTENTS

LIST OF TABLES	vi
LIST OF FIGURES	viii
Abstract	x
Chapter 1	
LITERATURE REVIEW	1
<u>Introduction</u>	1
<u>Sources of Arsenic Introduction into the Environment</u>	4
Geogenic Sources.....	4
Anthropogenic Sources.....	6
Poultry Litter	8
Tanneries.....	14
<u>Interactions of Arsenic in the Environment</u>	17
Soil	17
Water and Sediments	22
Plants	23
Humans	25
<u>Conclusions and Research Objectives</u>	28
REFERENCES	29
Chapter 2	
CHARACTERIZATION OF ARSENIC IN AGRICULTURAL SOILS AND LEACHING OF ARSENIC IN SOILS AMENDED WITH POULTRY LITTER	43
<u>Introduction</u>	43
<u>Methodology</u>	49
Soil Collection and Characterization	49
Poultry Litter Collection and Characterization	52
Arsenic Leaching Experiments	53
Statistical Analysis.....	58
<u>Results and Discussion</u>	59
Arsenic Status of Delaware Soils.....	59
Arsenic Leaching Experiments	67
Effects of Alum on Arsenic Chemical Phases, Solubility, and Bioavailability in Poultry Litter	76
<u>Conclusions</u>	79
REFERENCES	82

Chapter 3	
EVALUATING LECHABILITY AND BIOAVAILABILITY OF	
ARSENIC IN CONTAMINATED TANNERY SOILS	86
<u>Introduction</u>	86
<u>Methodology</u>	89
<u>Results and Discussion</u>	90
Soil Characterization.....	90
Leachability – Toxicity Characteristic Leaching Procedure.....	93
Bioavailability – Physiologically Based Extraction Test and	
Mehlich 3	95
Correlations of Soluble and Bioavailable Arsenic with	
Chemical Phases	98
<u>Conclusions</u>	104
REFERENCES	105
Chapter 4	
SUMMARY OF FINDINGS AND FUTURE RESEARCH	107
<u>Major Findings</u>	107
<u>Future Research</u>	112
REFERENCES	114
APPENDIX.....	115

LIST OF TABLES

Table 2.1. Soil taxonomic classification for farm and forested soils collected in New Castle County and Sussex County, Delaware	50
Table 2.2. Soil properties and Total, Mehlich 3, and TCLP As concentrations for agricultural soils collected from New Castle County and Sussex County, Delaware	61
Table 2.3. Soil properties and Total, Mehlich 3, and TCLP As concentrations for forested soils collected in association with poultry farms in Sussex County, Delaware	63
Table 2.4. Predominant soil series and overview of selected soil properties and forms of soil As for agricultural soils at farms on University of Delaware property and cooperator farms in New Castle County and Sussex County, Delaware.	64
Table 2.5. Chemical and physical properties of four Delaware topsoils (0-20 cm depth) used in two greenhouse column studies investigating the effects of PL applications on As leaching.....	66
Table 2.6. Results of TCLP-As extractions on post-column study soil samples collected from 0-5 cm depth sections from soil columns of Column Study 1	72
Table 2.7. Comparison of As forms and solubility in unamended and alum-treated PLs collected in the study of Sims and Luka-McCafferty (2002)	78
Table 3.1. Arsenic status for 20 soils collected by DNREC staff in Wilmington, Delaware in a site investigation (South Market Street) for potential As contamination. These soil samples were collected with a geoprobe (GP) or from a test pit (TP).....	92
Table 3.2. Comparison of the mean chemical properties of three groups of urban soils from the South Market Street site that exhibited different trends in the distribution of As among three chemical fractions	103
Table A-1. Soil Classification information for agricultural soil profiles on five farms in New Castle County, Delaware.....	116-119

Table A-2. Soil classification information for agricultural soil profiles on five farms in Sussex County, Delaware	120
Table A-3. Soil classification information for three forested soil profiles collected in association from farm sites in Sussex County, Delaware	121
Table A-4. Total Elemental concentrations for agricultural soils collected from New Castle County, Delaware	122
Table A-5. Total elemental concentrations for agricultural soils collected from Sussex County, Delaware	123
Table A-6. Total elemental concentrations for forested soils collected from Sussex County, Delaware	124
Table A-7. Mehlich 3 elemental concentrations for agricultural soils collected from New Castle County, Delaware	125
Table A-8. Mehlich 3 elemental concentrations for agricultural soils collected from Sussex County, Delaware	126
Table A-9. Mehlich 3 elemental concentrations for forested soils collected from Sussex County, Delaware	127
Table A-10. Selected soil properties for 20 soils collected by DNREC staff in Wilmington, Delaware for a site investigation (South Market Street) for potential As contamination. These soil samples were collected with a geoprobe (GP) or from a test pit (TP)	128
Table A-11. Routine soil test results for 20 soils collected in Wilmington, Delaware for a site investigation (South Market Street) for As contamination. These soil samples were collected with a geoprobe (GP) or from a test pit (TP).....	129

LIST OF FIGURES

Figure 1.1. Roxarsone structure	9
Figure 1.2. Skeletal structures and degradation reactions of roxarsone to 3-amino-4-hydroxyphenylarsonic acid (3-HPPA)	11
Figure 1.3. Skeletal structures and degradation reactions of roxarsone to arsenite and arsenate	11
Figure 1.4. Skeletal structures and degradation reactions of arsenite into the arsonoalkyl acids Monomethylarsonic acid (MMA(V)), Monomethylarsonous acid (MMA(III)), Dimethylarsinic acid (DMA(V)), and Dimethylarsinous acid (DMA(III)), and the alkylarsines Trimethylarsine oxide (TMAO(V)) and Trimethylarsine (TMA(III))	12
Figure 1.5. Skeletal structures of realgar and sodium arsenate.....	16
Figure 2.1. Comparison of total As concentrations in agricultural and forested soils obtained from cooperators' farms in New Castle County and Sussex County and University of Delaware farms. The topsoil horizons of the Sassafras and Corsica soils were used in column studies of As leaching from poultry litter	60
Figure 2.2. Mean volumes of leachate collected for Corsica and Sassafras soil columns used in Column Study 1	68
Figure 2.3. Effect of PL application rate on total dissolved As concentrations in leachate from the Corsica and Sassafras soils during Column Study 1.	69
Figure 2.4. Mean leachate volumes for the four soils used in Column Study 2 to evaluate the effects of PL on As leaching. Values are averages of all litter rates for each leaching event	74
Figure 2.5. Effect of PL application at 9 Mg ha ⁻¹ on total dissolved arsenic concentrations in leachate from the (a) Corsica, (b) Sassafras, (c) Evesboro, and (d) Matapeake soils during Column Study 2	75

Figure 3.1. Comparison of total elemental composition of (a) agricultural soils in Sussex County, Delaware and (b) urban soils from Wilmington, Delaware	91
Figure 3.2. Relationship between total soil As and TCLP-As for (a) all urban soils collected in Wilmington, Delaware and (b) all soils excluding the one outlier identified in (a)	94
Figure 3.3. Relationship between total soil As and either PBET-As or Mehlich 3-As for (a) urban soils collected in Wilmington, Delaware and (b) all urban soils in (a), excluding one outlier with a total As concentration > 5,000 mg kg ⁻¹	96
Figure 3.4. Sequential chemical fractionation of soil As for 20 soils collected from an urban contaminated site in Wilmington, Delaware.....	99
Figure 3.5. (a) Sequential fractionation of total As in 20 soils from an urban contaminated site in Wilmington, Delaware. Soils are presented, left to right, in designated groups and descending order of [MgSO ₄ + AmOx]-As and (b) Relationship between the percentage of total As extracted by [MgSO ₄ + AmOx] and the percentage of PBET-As in these 20 soils.....	100
Figure 3.6. Relationship between the percentage of total As extracted by MgSO ₄ and the percentage of TCLP-As in the 20 soils collected from an urban contaminated site in Wilmington, Delaware	102
Figure A-1. Effect of PL application rate on total dissolved As concentrations in leachate from the (a) Corsica and (b) Sassafras soils during Column Study 1. Note: Leachate concentrations include results from outlier columns where edge flow occurred	130
Figure A-2. Image from 1921 Sanborn fire insurance map showing the historical tannery operations located at the property from which the urban soils samples were collected	131

ABSTRACT

Over the past several years, trace element contamination, specifically arsenic (As), in soils and water has become an alarming environmental issue. All metal/metalloids are potentially hazardous at some concentration (Langdon et al., 2003), and As is known to be carcinogenic, phytotoxic, and biotoxic at extremely low concentrations. The most toxic forms of As are arsine gas, followed by inorganic trivalent compounds, organic trivalent compounds, inorganic pentavalent compounds, and finally elemental As (Cullen and Reimer, 1989). Inorganic As has been listed by the United States Environmental Protection Agency (USEPA) as a Class A human carcinogen and has been linked to bladder, kidney, liver, lung, and skin cancers, as well as impaired nerve function (Research Triangle Institute, 1998). In 2001 the USEPA reduced the allowable levels of As for oral intake in drinking water from $50 \mu\text{g L}^{-1}$ to $10 \mu\text{g L}^{-1}$, and states have been required to comply with this regulations since 2006. Delaware has complied with this standard since 2001. In 2004, the Delaware Department of Natural Resources and Environmental Control (DNREC) established an Interim Arsenic Soil Cleanup Standard for Residential Properties at 23 mg kg^{-1} for surface soils from zero to two feet below ground surface, and 101 mg kg^{-1} for subsurface soils from two to six feet below ground surface, which was a change from the previous standard of

11 mg kg⁻¹. DNREC established the 10⁻⁵ cancer risk (the potential risk for one additional cancer death caused by exposure to a carcinogen in a human population of 100,000 in a lifetime) for As at 4 mg kg⁻¹, the hazard index value (the numerical value obtained by dividing a person's expected daily intake of a non-carcinogen by a level which is not expected to produce toxic effects) at 23 mg kg⁻¹, and the background level at 11 mg kg⁻¹. Delaware Senate Bill 68, introduced in April 2005, established an As cleanup level of 6 mg kg⁻¹; however, the bill was not passed into law based on previous research showing that the average background As concentration in Delaware soils is 11 mg kg⁻¹ (DNREC, 2008).

The primary sources of As introduction into the environment in Delaware are pesticides, poultry litter, and historical tanneries. An organic As compound known as Roxarsone is incorporated into poultry feeds to control Coccidiosis, increase growth rate, improve feed utilization, enhance pigmentation, and may be effective in suppressing Salmonella (Alpharma, 1999). Most of the As is excreted by the chicken and is incorporated into poultry litter (PL – a mixture of bedding material and manure). The use of PL as an agricultural soil amendment has been an ongoing process for many years on the Delmarva Peninsula, and it is apparent that the fate of As in soils, especially those that are sandy and prone to leaching, needs to be studied.

Arsenic compounds were used in tannery operations from the late 1800s through the 1960s. Many historical tannery sites located in Wilmington, Delaware are proposed to undergo redevelopment into residential communities. This has the potential to expose future residents, construction employees, and other individuals residing and working in

the vicinity of the historical tannery to dangerous levels of As contaminated soil. Several historic tanneries are also located very close to the Christina River, where high water tables predominate, thus causing an increased potential for As to be transported to the Christina River via groundwater.

The main focus of this research project was to evaluate the potential for leachability and bioavailability of As from soils amended with PL and soils potentially contaminated by historical tanneries. Two greenhouse column experiments were used to investigate the leaching of As from PL-amended soils. A number of additional analyses were used in conjunction with the greenhouse experiments to characterize soil physical and chemical properties as well as As concentrations and availability in Delaware soils and PL. Methods used were: Microwave Digestion (USEPA Method 3051; USEPA, 1994), Mehlich 3 (Mehlich, 1984), Toxicity Characteristic Leaching Procedure (TCLP; USEPA Method 1311; USEPA, 1992), Physiologically Based Extraction Test (PBET; Fendorf et al., 2004), Sequential Fractionation (Fendorf et al., 2004), and Sorption Isotherms (Graetz and Nair, 2000).

This research study revealed that the agricultural and forested soils sampled in Delaware were relatively low in total As concentration; however, the agricultural soils with historical PL application were relatively lower in soil test phosphorus than what would be expected of soils with consistent PL amendments; therefore, soils of Sussex County, Delaware that have received more consistent PL amendments may exhibit higher total As concentration. The As in PL is highly water soluble and can be available to run off into surface waters during high rainfall events; however, alum [aluminum sulfate;

$\text{Al}_2(\text{SO}_4)_3$] was determined to be a valuable best management practice (BMP) in that it creates more recalcitrant As compounds that are less soluble. Only three leaching events during *Column Study 1* exhibited significant increases in leachate As due to PL applications; however, no significant increases in leachate As concentrations were exhibited during the leaching events of *Column Study 2*.

Of the urban soils analyzed, 95 percent exceeded the 11 mg kg^{-1} As background level established by DNREC; however, only one sample had a TCLP-As concentration that was greater than the USEPA TCLP-As limit of 5 mg L^{-1} (100 mg kg^{-1}). The PBET-As concentrations revealed that a high percentage of the As in these urban soils was bioavailable and could be toxic, whether it be through ingestion, inhalation, or dermal contact. The sequential fractionation was correlated strongly to the total As concentration and provided information as to which phases were associated with leachable (TCLP) and bioavailable As (Mehlich 3 and PBET); however, due to the complexity of these samples, more advanced methods (EXAFS and XANES) would be required to provide definitive information on As speciation.

CHAPTER 1

LITERATURE REVIEW

Introduction

Tens of thousands of As contaminated sites exist worldwide today, with some soil As concentrations reaching as high as 26.5 g kg^{-1} soil (Hingston et al., 2001). These soil As levels present a risk to human health from the incidental ingestion of soil.

Regulations governing As contamination in waters are well defined, but the regulatory cleanup goals for remediation of contaminated soils are still under development and vary greatly among countries, states, and land uses (Chen et al., 2002). In 2001, the United States Environmental Protection Agency (USEPA) reduced the allowable levels of As for oral intake in drinking water from $50 \text{ } \mu\text{g L}^{-1}$ to $10 \text{ } \mu\text{g L}^{-1}$, and states have been required to comply with this regulation since 2006, and Delaware has been in compliance since 2001.

Since major concerns with As have focused on water contamination, many are not aware of other possible problems, including dietary intake of As through the food chain via uptake from contaminated soils, that may adversely effect human health (Arnt et al., 1997). Also, a recent concern has been the possibility of ingestion of As by breathing dust that originated from As contaminated sites. Since wind erosion occurs worldwide,

soil transported aerially from these contaminated sites can be re-deposited in more populated areas, thus potentially causing adverse effects.

Arsenic is known to be carcinogenic, phytotoxic, and biotoxic at extremely low concentrations (Langdon et al., 2003), and the most toxic forms of As are arsine gas, followed by inorganic trivalent compounds, organic trivalent compounds, inorganic pentavalent compounds, and finally elemental As (Cullen and Reimer, 1989). Inorganic As has been listed by the USEPA as a Class A human carcinogen and has been linked to bladder, kidney, liver, lung, and skin cancers, as well as impaired nerve function (Research Triangle Institute, 1998).

In Delaware the most significant potential hazards to human health from As have been identified as the land application of poultry litter (PL – a mixture of bedding material and manure) to cropland and contaminated soils at historical tannery sites.

An organic As compound known as Roxarsone is incorporated into poultry feeds to control Coccidiosis, increase growth rate, improve feed utilization, enhance pigmentation, and may be effective in suppressing *Salmonella* (Alpharma, 1999). Most of the As is excreted by the chicken and is incorporated into PL. The use of PL as an agricultural soil amendment has been an ongoing process for many years on the Delmarva Peninsula, and it is apparent that the fate of As in soils, especially those which are sandy and prone to leaching, needs to be studied. To develop a more environmentally sound management program for PL application, the mobility and bioavailability of As in soils must first be understood.

Several sites located within Wilmington, Delaware are known to have been used historically for tanneries. The tanning industry was established in Wilmington, Delaware as early as 1845, with the sumac process being the primary tanning method at that time (Scharf, 1888). The sumac process consisted of a mixture of leaves and bark from various trees that were crushed and mixed into a paste and applied to the hides. In the late 1800's several of the tanneries began incorporating automated machinery to increase production as, until that point, the sumac process was done completely by hand. During this change to automated machinery, several chemicals were introduced to provide a decreased processing time and more consistent dyeing (Thorp, 1909). Some of these chemicals have subsequently become a concern, including As-containing realgar (AsS , As_2S_2 , As_4S_4), which was used to dehair hides, and sodium arsenate (Na_2HAsO_4), which was used during the dyeing process.

After hides were treated with realgar or sodium arsenate, they were allowed to dry draped over beams running the extent of the buildings known as "beam houses". Decades of tannery operations being conducted in this manner resulted in contamination of soil and groundwater in the Wilmington, Delaware area. During the 1950's, the tannery industry began to decline in numbers in Wilmington; however, several tanneries operated through the 1960's (DNREC, 2001). Today, the sites of several of these former tanneries are proposed to undergo redevelopment, which has caused concerns to arise over public and worker safety. Little research has been previously conducted on tannery soils; therefore, it is important to better understand the characteristics and behavior of As in soils from these locations.

Several variables must be considered before evaluating As mobility and bioavailability in soils, such as: pH, organic matter, texture, redoximorphic potential, As source, and microbial populations and activity. Prior to initiating research on As of greatest relevance to Delaware, it is important to understand what past studies have shown about soil As contamination, including natural and anthropogenic sources, interactions and transport in the environment, and potential measures to mitigate concerns for human and ecosystem health.

Sources of Arsenic Introduction into the Environment

Geogenic Sources

One of the main sources of As in soils is the parent material from which the soils are derived (Chen et al., 2002). Arsenic is the 52nd most abundant element in the earth's crust, and the continental crust has an expected average concentration of 1.5 to 2.0 mg kg⁻¹ As (Mahimairaja et al., 2005). Arsenic is also a major constituent in more than 245 minerals (O'Neill, 1995). Certain types of parent material, such as sandstones, igneous rocks, shales, volcanic rocks, and coals (Irgolic et al., 1986), contain high amounts of As, which can be released as inorganic forms of As during weathering and subsequently transported by leaching through soils and surface runoff into rivers and lakes (Yan-Chu, 1994). The average concentrations of As in igneous rocks range from 1.5 to 3.0 mg kg⁻¹, while sedimentary rocks range from 1.7 to 400 mg kg⁻¹ (Smith et al., 1998). Even higher

As concentrations have been found in sulfide minerals and iron ores, such as arsenical pyrite (FeAsS), realgar (AsS , As_2S_2 , As_4S_4) and orpiment (As_2S_3) (Matera et al., 2003).

Geogenic contamination of As in soils and water has been reported worldwide, and some of the As values that have been determined in soils are: $1.7\text{--}56.7 \text{ mg kg}^{-1}$ in Bangladesh (Alam and Sattar, 2000), 110 mg kg^{-1} in southwest England (Mitchell and Barr, 1995), $11.5\text{--}28.0 \text{ mg kg}^{-1}$ in India (Amit et al., 1999), and up to 5000 mg kg^{-1} in southern Thailand (Williams et al., 1996). Elevated concentrations of As originating from natural geologic formations also exist in groundwaters of Argentina [$3,000 \text{ g L}^{-1}$ (Sbarato and Sanchez, 2001)], China [$1,088 \text{ g L}^{-1}$ to $1,354 \text{ g L}^{-1}$ (Guo et al., 2001)], Germany [10 g L^{-1} to 150 g L^{-1} (Heinrichs and Udluft, 1999)], Japan [293 g L^{-1} (Kondo et al., 1999)], Mexico [267 g L^{-1} to $1,070 \text{ g L}^{-1}$ (Gomez-Arroyo et al., 1997)], Taiwan [671 g L^{-1} (Chen et al., 1995)], United States of America [$12,000 \text{ g L}^{-1}$ (Schreiber et al., 2000)], and Vietnam [1 g L^{-1} to $3,050 \text{ g L}^{-1}$ (Berg et al., 2001)].

A recent example of As contamination in groundwater due to geogenic sources is in Bangladesh. In 1971 international agencies installed tube wells to access groundwater for drinking water purposes, because of surface water contamination from waterborne pathogens such as cholera and dysentery. Since the change from surface water usage to groundwater, infant mortality rates decreased from 247 per 1,000 births in 1971 to 112 per 1,000 births in 1996; however, since 1971, human mortalities of 20,000 have occurred in Bangladesh annually due to As poisoning. An estimated 50 million people are also at risk for severe health consequences (Pearce, 2001; Chaudhuri, 2004); therefore, the situation has been deemed “the worst mass poisoning in history” (Mead,

2005). Arsenic concentrations in groundwater of Bangladesh approach 2 mg L^{-1} , and it has been predicted that 200,000 to 270,000 people will die of cancer from drinking As contaminated water in Bangladesh alone (Tondel et al., 1999). The groundwater is also utilized for irrigation water for crops, particularly paddy rice (*Oryza sativa* L.) (Ninno and Dorosh, 2001). This results in elevated As concentrations in the soil and the potential for human exposure through rice consumption.

Anthropogenic Sources

Although parent material has a great impact on the As content in soils, it is anthropogenic sources that are of the most concern for human health. Most contamination occurs in urbanized regions of the world and cannot be attributed solely to geological factors. Arsenic contamination in soils results from human activities, such as: milling, mining, combustion, wood preservation, pesticide application (Carbonell-Barrachina et al., 1998), application of some animal manures as fertilizer, and in glass and electronics manufacturing (Ascue and Nriagu, 1994). For example, a major contamination area from mining is Villa de la Paz-Matehuala, San Luis Potosi (Mexico). Arsenic concentrations in the soils of this area of Mexico are between $19\text{--}17,384 \text{ mg kg}^{-1}$ (Razo et al., 2004). Nriagu and Pacyna (1988) estimated that $35 \times 10^6 \text{ kg yr}^{-1}$ As had been released into the environment by the mining and metallurgy industry, which represented 22% of the total As released into the environment worldwide. If As containing residues from mining operations are not controlled, then they are susceptible to movement by wind and water, especially in this area of Mexico (Razo et al., 2004).

Soil and water may be contaminated by As from pigments, pesticides, chromated copper arsenate (CCA) -treated wood, growth promoters, and emissions from fossil fuel combustion, as well as many other sources (O'Neill, 1990). Historically, inorganic As compounds have been used as pesticides, such as: lead arsenate, which was used on orchards to control such pests as the gypsy moth (*Lymtria dispar*), codling moth (*Cydia pomonella*), and apple maggot (*Rhagoletis pomonella*) (Peryea, F. J., 1998); CCA which was the main component used to protect wood from bacterial, fungal, and insect attacks; and methylated arsenicals, which were used as a defoliant for cotton (Hingston et al., 2001). Decades of widespread usage of CCA in treating wood have caused increased concerns about possible environmental contamination from the leaching of wood preservatives into soils (Cao et al., 2003). The extensive usage of lead arsenate and methylated arsenicals on orchard and cotton farmland has also raised concerns about environmental contamination due to the arsenic compounds being lost to surface waters by runoff and groundwaters by leachings. Due to the potential for environmental contamination, many of these products were banned in the United States (lead arsenate, sodium arsenate, and methylated arsenicals banned in 1988; CCA banned in 1993).

Sodium arsenate (Na_2HAsO_4) has also been used in cattle and sheep dips, debarking trees, and the control of aquatic weeds (Ascue and Nriagu, 1994). This compound has been found in a large variety of samples including those from sea and fresh water, sediments, soils, marine organisms, and plants (Burguera and Burgera, 1997). Atmospheric deposition contributes significantly to the geochemical cycle of As (Ganje and Rains, 1982; Smith et al., 1998). Other sources of As are sewage sludge and

animal manures (Nicholson et al., 1999). Losses of As from soils amended with these organic by-products occur through leaching and soil erosion (Alloway, 1995; Smith, 1996). The USEPA has established an As ceiling concentration limit (the maximum concentration of each pollutant allowed in biosolids for land application) and an As cumulative pollutant loading rate (the maximum amount of a pollutant that can be applied to a site over its lifetime) concentration of 75 mg kg^{-1} and 41 kg ha^{-1} , respectively, for land application of sewage sludge (Christen, 2001); however, no such guidelines have been established for animal manures. Since animal manures are used extensively as fertilizer on the Delmarva Peninsula, As contamination of soils and ground water has become a growing concern.

Poultry Litter

The aryl-organoarsenical compounds p-arsanilic acid (4-aminophenylarsonic acid) and Roxarsone (ROX: 3-nitro-4-hydroxyphenyl arsonic acid; Figure 1.1) are approved by the United States Food and Drug Administration (USFDA) for use as animal feed additives (Jackson and Miller, 2000). Roxarsone, the most commonly used additive, has been approved for use at a rate of 25 mg kg^{-1} to 50 mg kg^{-1} for broiler feeds to control Coccidiosis, primarily caused by *Eimeria tenella*, to increase growth rate, improve feed utilization, enhance pigmentation, and also may be effective in suppressing *Salmonella* (Alpharma, 1999); however, ROX is not allowed in layer feeds. Roxarsone is also approved to be combined with several other feed additives, such as Amprolium, Ethopabate, Baciracin Methylene Disalicylate, Bacitracin Zinc, Bambermycins, and

Decoquate, to prevent exposure to Coccidiosis from more severe *Eimeria* species (*E. acervulina*, *E. maxima*, *E. brunetti*, *E. necatrix*, and *E. mitis*). A five-day withdrawal period is required before slaughter (Feed Additive Compendium, 2007). Since ROX is 28.5% As, the As added to poultry feed ranges from 7.1 mg kg⁻¹ to 14.25 mg kg⁻¹ As (Alpharma, 1999).

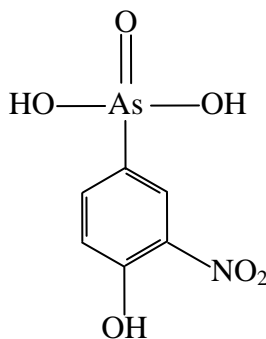


Figure 1.1. Roxarsone structure (3-nitro-4-hydroxyphenyl arsonic acid)

In 2000, roughly 70% of all chickens on starter rations and approximately 74% of those on grower rations in the United States (US) were fed ROX (Chapman and Johnson, 2002). According to Muir (2001), 8.26 billion chickens were produced in the US in 2000. At an average dosage of 45.4g of ROX per ton for the 42 days life cycle, chickens excrete about 150 mg of ROX in total. Given the percentages, roughly 5.8 billion chickens were fed ROX. The ultimate result is 9×10^5 kg of ROX, or, more specifically, 2.5×10^5 kg of As was present in the manure from these chickens (Rutherford et al., 2003). The use of ROX in poultry feeds has declined in recent years due to public concern; however, it is still the preferred coccidiostat used by the poultry industry.

The Delmarva Peninsula region produces over 600 million chickens and 1.5 million metric tons of manure annually, ranking second in the nation. Since it has

historically not been cost effective to transport the PL elsewhere, farmers have always used it for fertilizer, and by incorporating the PL into agricultural soils, approximately 20-50 metric tons of As have been introduced into the environment annually (Christen, 2001). No regulations exist for land application of metals in animal manures (USEPA, 1993).

Poultry litter contains As, copper (Cu), and zinc (Zn) (Kunkle et al., 1981), all of which are of concern because of their phytotoxicity (Schmidt, 1997). Total As concentrations in PL usually range from $<1 \text{ mg kg}^{-1}$ to 40 mg kg^{-1} (Nicholson et al., 1999; Jackson and Bertsch, 2001; Garbarino et al., 2003; Rutherford et al., 2003; Anderson and Chamblee, 2001; Jackson et al., 2003).

Roxarsone undergoes a series of aerobic and anaerobic reactions that transforms it into pentavalent and trivalent organic and inorganic compounds. Under anaerobic conditions, Stolz et al. (2007) found that the benzene ring of the ROX structure was oxidized first, which releases the inorganic trivalent H_2AsO_3^- . Stolz et al. (2007) did not find evidence of ROX degrading into organic As under aerobic conditions. Cortinas et al. (2006) also found that nitrogen-substituted phenylarsonic compounds degrade into As(III) under reducing conditions. Wershaw et al. (2000) stated that the three most likely degradation reactions of ROX are: i) the reduction of the nitro group (Figure 1.2); ii) rupture of the C-As bond (Figure 1.3); and iii) oxidative fission of the aromatic ring (Figure 1.4). Wershaw et al. (2000) also reported that the degradation product 3-amino-4-hydroxyphenylarsonic acid has been detected in the urine of hens fed ROX.

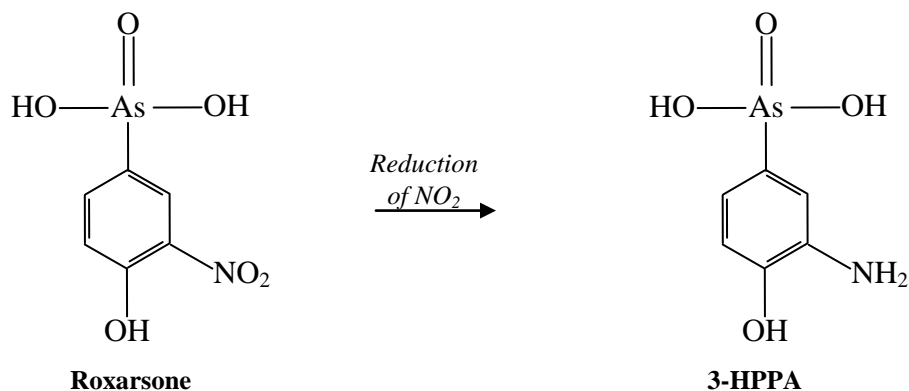


Figure 1.2. Skeletal structures and degradation reactions of roxarsone to 3-amino-4-hydroxyphenylarsonic acid (3-HPPA).

According to Wershaw et al. (2000) if ROX were to undergo microbial degradation, arsonoalkyl acids would be produced. Under anaerobic condition, arsonoalkyl acids could convert to alkylarsine, which is stable under anaerobic conditions; however, alkylarsine would be oxidized to the pentavalent AsO_4^{3-} .

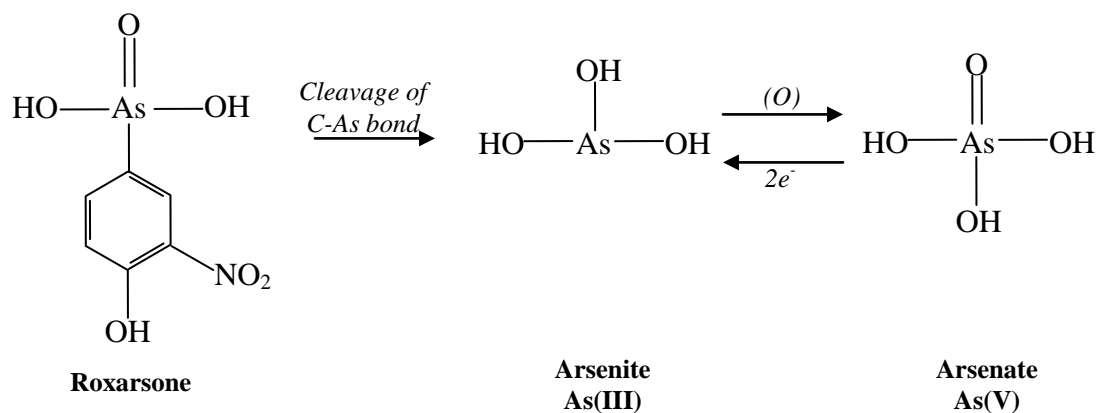


Figure 1.3. Skeletal structures and degradation reactions of roxarsone to arsenite and arsenate.

The research initiatives of Stolz et al. (2007), Cortinas et al. (2006), and Wershaw et al. (2000) indicated that 3-amino-4-hydroxyphenylarsonic acid, Monomethylarsonic acid (CH_3AsO_3 ; MMA(V)), Monomethylarsonous acid (CH_3AsO_2 ; MMA(III)), Dimethylarsinic acid ($\text{C}_2\text{H}_7\text{AsO}_3$; DMA(V)), Dimethylarsinous acid ($\text{C}_2\text{H}_7\text{AsO}_2$;

DMA(III)), Trimethylarsine oxide ((CH₃)₃AsO; TMAO(V)), Trimethylarsine ((CH₃)₃As; TMA(III)), AsO₄³⁻, H₂AsO₃⁻, as well as other As(III) compounds could be possible degradation products of ROX.

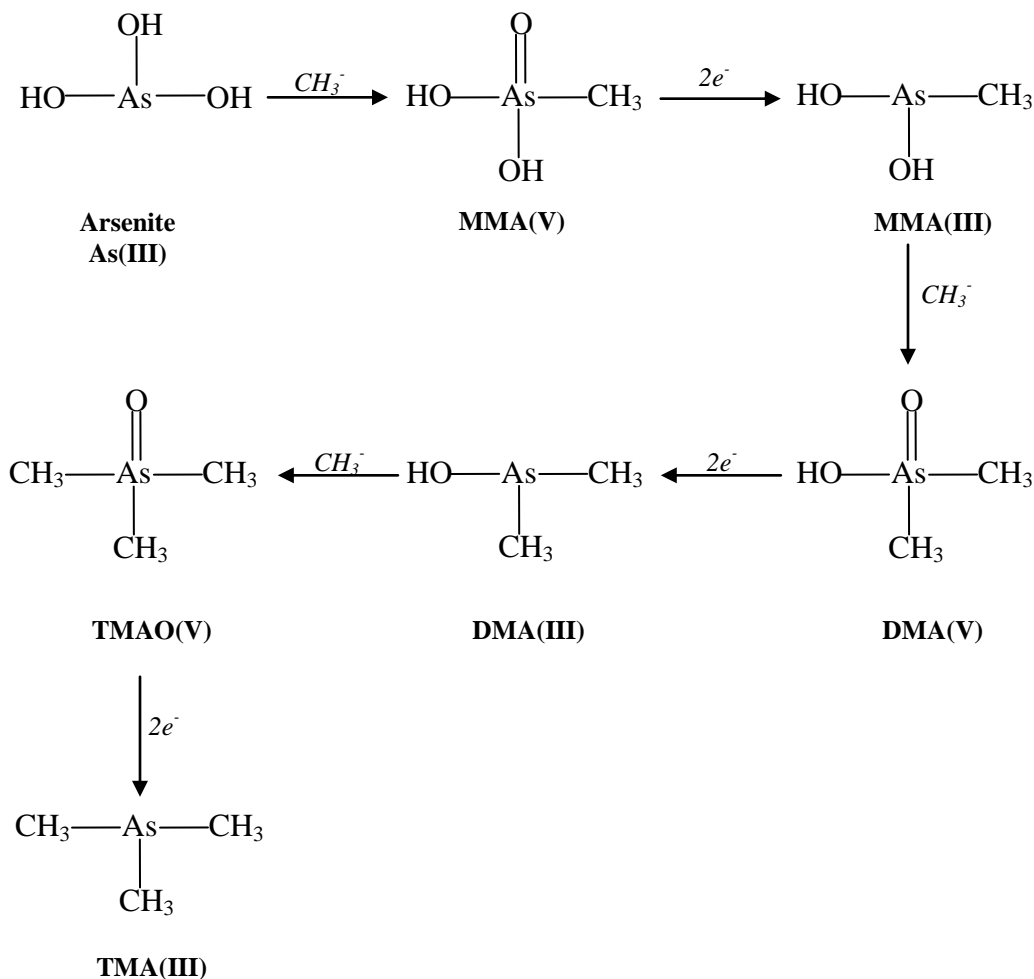


Figure 1.4. Skeletal structures and degradation reactions of arsenite into the arsonoalkyl acids Monomethylarsonic acid (MMA(V)), Monomethylarsonous acid (MMA(III)), Dimethylarsinic acid (DMA(V)), and Dimethylarsinous acid (DMA(III)), and the alkylarsines Trimethylarsine oxide (TMAO(V)) and Trimethylarsine (TMA(III)).

Garbarino et al. (2003) found that when PL samples were mixed with water and allowed to compost at 40°C, the As was converted from organo-As to As(V) in about 30

days. The major species of As in water extracts from PL were found to be ROX and As(V); however, minor quantities of As(III), dimethylarsinic acid (DMA), monomethylarsonic acid (MMA), 3-amino-4-hydroxyphenylarsonic acid were detected as well (Garbarino et al., 2003; Rutherford et al., 2003; Jackson et al., 2003; Cortinas et al., 2006; Stolz et al., 2007). Laboratory “composting” or “incubating” experiments simulate what would happen when the PL is added to the soil and biological aerobic processes take effect. However, in anaerobic conditions, bacteria of the genus *Clostridium* are selective in degrading ROX to inorganic As (Garbarino et al., 2003 and Cortinas et al., 2006), and since As(V) is a more soluble and more mobile form of As than ROX, it is more likely to sorb to soil components, leach into groundwaters, or runoff into surface waters.

Poultry litter has economic value as a phosphorus (P) fertilizer and as a beneficial soil amendment. The use of PL helps increase soil fertility and aeration and improves water-holding capacity (Gupta and Charles, 1999). It also enhances soil productivity and improves soil aggregate formation and stability. Water infiltration and the supply of plant nutrients, such as calcium (Ca), magnesium (Mg), and potassium (K), also increases (Kpombrekou-A, et al., 2002).

Over-application of PL can cause degradation of the soil, surface water, and groundwater quality if trace elements are present in sufficient concentrations (Kpombrekou-A et al., 2002). Since As is potentially a toxic element, ingestion or inhalation of As-bearing particles represents a potential health risk to humans (Sheppard, 1992), especially to farmers while working in poultry houses and applying PL to fields.

While laboratory methods have been developed to estimate the availability of As once ingested, no current research exists concerning As availability once inhaled.

Aluminum sulfate [alum; $\text{Al}_2(\text{SO}_4)_3$] is currently used to reduce ammonia-N concentrations in poultry houses. The alum is only applied at the beginning of each flock of birds produced; therefore, an initial pH of 4 to 5 occurs due to acidification caused by aluminum solubilization. However, the pH slowly rises to approximately pH 7 over the time the flock is in the house (Moore and Miller, 1994). It has been proposed that alum also reacts with soluble phosphate to form more stable aluminum phosphate precipitates (Moore and Miller, 1994). According to the research conducted by Peak et al. (2002), the phosphate compounds found in non-alum treated PL were aqueous phosphate, phytic acid, and dicalcium phosphate. However, in the alum treated PL (Al:P ratio >0.6) evidence of phosphate bound to aluminum oxides was found instead of the previously expected aluminum phosphate precipitate phases. As the pH gradually increases above pH 5, aluminum phosphate stability decreases greatly; therefore, it is possible that aluminum phosphate precipitation occurs that is followed by dissolution as time and pH increases. Since As and P react very similarly in the soil environment, it is proposed that As undergoes the same reactions in PL when treated with alum.

Tanneries

The Port of Wilmington has been known historically for tannery operations. Starting in 2001, DNREC began a tannery site initiative with the purpose to identify sites with a potential for soil and groundwater contamination from former tannery and hide

processing operations. Historical sources (such as Sanborn fire insurance maps) were utilized to identify former tannery sites, which were grouped into 52 “tannery complexes” by DNREC. The 52 “tannery complexes” consisted of over 400 individual parcels, which were mostly covered with buildings and/or parking lots (DNREC, 2002) and many tanneries were found to lie near the Christina River.

The tanning industry was established in Wilmington, Delaware as early as 1845, and the sumac process (a mixture of leaves and bark from trees crushed and mixed into a paste and applied to the hides) was used until the 1890’s. During the 1890’s, automated machinery was introduced into the tannery operations as well as As-containing chemicals. Tanneries were a major industry in Wilmington, Delaware until the 1950’s when operation numbers began to decline; however, several were identified on Sanborn maps through the 1960’s (DNREC, 2001).

The tannery process involved a strong As solution, which was used to de-hair hides and for dyeing purposes. Hides were soaked in vats of an As solution known as realgar (AsS , As_2S_2 , As_4S_4 ; Figure 1.5) and scraped by hand to remove the hair. Sodium arsenate (Na_2HAsO_4 ; Figure 1.5) was also used during the dyeing of hides to prevent discoloration of white portions (Thorp, 1909). Facilities in which these operations were carried out in were typically labeled as “beam houses,” in which hides were draped over beams to dry, and are identifiable on historic Sanborn maps. Chromium (Cr) salts were also used to finish the hides; therefore, both As and Cr are contaminants of concern in historical tannery sites (DNREC, 2002).

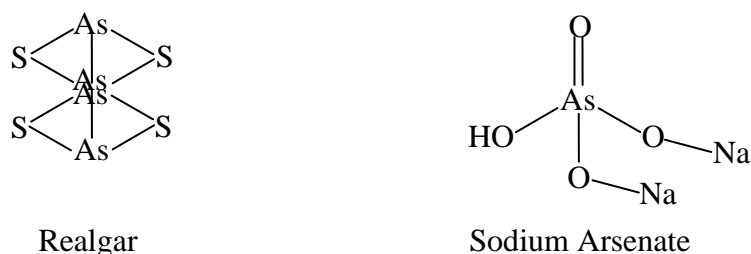


Figure 1.5. Skeletal structures of realgar and sodium arsenate.

Realgar occurs in nature in small quantities and is a brilliant red mineral, which can be used as a pigment when ground. It was used primarily for dehairing hides due to its inability to be mixed with other colors and a tendency to fade upon exposure to light as a dye. Sodium arsenate is a man-made compound that was used in dyeing alizarins and in calico printing to prevent discoloration of the white parts of a pattern so that other colors did not diffuse in the white portions (Thorp, 1909).

Even though tannery operations were distributed worldwide, few articles have been published concerning As contamination from tanneries. Sadler et al. (1994) reported that a formulation of 650 g L⁻¹ sodium arsenite was used as the active ingredient in a selected historical tannery in Queensland, Australia, although, other unregistered chemicals may have been used. It is known that sodium arsenite was used extensively at tannery sites and has been shown to be fairly mobile in sandy soils (Tammes and deLint, 1969). Sadler et al. (1994) collected soil samples from a site that was previously used as a waste disposal site for a tannery and used the Toxicity Characteristic Leaching Procedure (TCLP) to assess potential As mobility. A distilled water solution at a pH of 7.0 was used instead of the TCLP solution, which has a pH of 4.9, because the soil in the area from which the samples were collected would be leached with rainwater instead of

acidic leachate found in landfills and because As species are more mobile at pH 7.0 rather than pH 4.9. Sadler found that there was an inverse relationship between total As concentration and leachability, with the greatest mobility occurring in samples with the lowest total As concentrations.

Interactions of Arsenic in the Environment

Soil

The forms of As in the soil are influenced by the geologic source of the As, amount of phosphate (PO_4), aluminum (Al), iron (Fe), organic matter, pH, and the redox potential of the soil (Bhumbla and Keefer, 1994; Huang, 1994). Arsenic occurs as a number of different species in soils and aqueous environments, the most prevalent are the inorganic oxyanions arsenate (H_3AsO_4) and, under reducing conditions, arsenite (H_3AsO_3) (Bowell et al., 1994; Masscheleyn et al., 1991b; Onken and Hossner, 1996). Arsenic is found in nature with oxidation states of -3 , 0 , $+3$, and $+5$: arsines and methylarsines (3^-), elemental arsenic (0), arsenite (3^+), and arsenate (5^+) (Eisler, 1994; Fox and Doner, 2003).

Speciation of As in soils can be further influenced by microorganisms, which are involved in redox reactions, methylation, demethylation, and biosynthesis processes (Hiltbold et al, 1974; Tamaki and Frankenberger, 1992). In aquatic and terrestrial environments, manganese (Mn) oxides can also serve as catalysts and oxidize As(III) to As(V) (Oscarson et al., 1981a,b; Huang, 1991). The concentration and type of organic

forms of As present, primarily methylated species, are a direct result of microbial processes (Fox and Doner, 2003). Microbial activity can also affect mobilization of As under anaerobic conditions by both indirect or direct mechanisms. The indirect mechanism is the reductive dissolution of iron oxyhydroxide minerals, such as ferric arsenate (FeAsO_4), leading to the release of associated As into solution (Yamamura et al., 2003). The direct mechanism is the reduction of As(V) associated with a solid phase to the less adsorptive As(III). *Bacillus* sp. Strain SF-1, a dissimilatory arsenate-reducing bacteria (DAsRBs), achieves growth by the respiratory reduction of As(V) to As(III) (Ahmann et al., 1997; Zobrist et al., 2000). Arsenate reduction can also be achieved by various bacteria possessing cytoplasmic As(V) reductase (ArsC) (Cervantes et al., 1994; Xu et al., 1988).

Arsenate occurs mainly as the H_2AsO_4^- species between pH 2.5 and 6.5. Under oxidizing conditions, As exists as anionic As(V) and under reducing conditions As exists as As(III). Arsenate is predominate in aerobic soils with a pH>10, while As(III) is more dominant in anaerobic soils with a pH<6 (Sadiq, 1997). At pH values between six and 10, As(III) and As(V) exist simultaneously, and as soil pH is dependent upon numerous conditions and varies widely throughout the world, the natural soil pH can greatly effect the solubility and speciation of As.

The capacity of soils to retain As is dependent on different physio-chemical factors, such as hydration, pH, and crystallinity (Sadiq, 1997). Sorption-desorption, precipitation-dissolution, and oxidation-reduction reactions control the solubility of As. Sorption of As(V) has been found to decrease with increased pH (Goldberg and Glaubig,

1988; Darland and Inskeep, 1997; Jones et al., 1997; Raven et al., 1998). Arsenate is preferentially sorbed on hydrous oxides for pH values ranging from 4 to 7, while As(III) is preferentially sorbed at pH values ranging from 7 to 10 (Pierce and Moore, 1982). Studies have also shown that As(III), does not sorb as strongly as As(V) (Frost and Griffin, 1977; Pierce and Moore, 1982; Xu et al., 1991), and total soluble As concentrations often increase with decreased redox potential (Masscheleyn et al., 1991b; McGeehan and Naylor, 1994). Arsenate adsorption on humic substances is maximal at pH 5.5, and As(III) adsorption is maximal on humic substances at pH 8.5 (Thanabalasingam and Pickering, 1986). Arsenic may also be bound to solids through sorption by metal oxyhydroxide minerals or structural incorporation into minerals (Rochette et al., 1998). Significant amounts of As have also been found to adsorb to secondary aluminosilicates, imogolite, allophone, and ferrihydrite (Gustafsson et al., 1995). These minerals are more commonly found in Andisols and in Spodic horizons. The high positive surface charge density under low pH conditions makes these minerals effective sorbents for As(V) (Gustafsson and Jacks, 1995; Lindberg et al., 1997).

Since As(V) is less mobile in the environment than As(III), As(V) reduction to As(III), which may occur when soils become anaerobic, poses a threat to the environment as well (Rochette et al., 1998). Since As(V) solid phases are generally too insoluble to control equilibrium As(V) concentrations, precipitation-dissolution reactions involving As are often less important than sorption-desorption reactions (Robins, 1981; Sadiq et al., 1983; Dove and Rimstidt, 1985; Nishimura et al., 1987).

It was also found that the sorption capacity of As was linearly related to ammonium oxalate-extractable aluminum (Al), as well as to clay and ammonium oxalate-extractable Fe (Livesey and Huang, 1981). This suggests that As sorption occurs on Al and iron (Fe) oxides and sites of variable charge on clay minerals. It has been found that Fe oxides are the most important mineral component in determining a soil's overall capacity to adsorb As(III) and As(V) (Livesey and Huang, 1981; Manning and Goldberg, 1997). However, researchers have shown that at pH values above 6 or 7, As(III) adsorption by Fe oxides is greater than As(V) (Jain and Loeppert, 2000; Sun and Doner, 1998). Based on x-ray absorption fine structure spectroscopy surface complexation of As(V) at Fe oxide surfaces occurs primarily as a bidentate inner-sphere surface complex, although monodentate surface complexes are also possible (Waychunas et al., 1995).

Arsenic sorption on clay minerals is pH dependent (Frost and Griffin, 1977), and As(V) is more strongly sorbed than As(III) on these minerals (Lin and Puls, 2000). Since phosphorus (P) and As have similar chemical properties, Roy et al. (1986) found that adsorption of As(V) to a Cecil clay diminished substantially when phosphate (PO_4) was added, as well as that adsorption of PO_4 diminished in the presence of As(V). The addition of phosphorus (P) has been shown to substantially mobilize As(V) due to competition for binding sites at the oxide surface (Darland and Inskeep, 1997; Davenport and Peryea, 1991; Peryea, 1991).

Since As(V) adsorbs strongly onto organic and clay colloids, it is likely to persist in soils for a long time (Woolson, 1983). This is true for finer-textured soils with high Fe contents; however, soils of the Delmarva Peninsula are very sandy. Some of these soils

have argillic horizons which have enough clay content to adsorb As(V), yet some of them do not, which may lead to As leaching into the groundwater.

A leaching study conducted by Qafoku et al. (1999) showed that As leaching in a column containing mineral soil incorporated with As-rich poultry manure increased with the addition of monocalcium phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2$]. Arsenic concentration in the leachate was approximately 10 times higher when $\text{Ca}(\text{H}_2\text{PO}_4)_2$ was added compared to a calcium sulfate (CaSO_4) solution. With the addition of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ the concentrations of As found in the leachate were as high as $800 \mu\text{g L}^{-1}$.

Seiter (2009) conducted several experiments with Delaware soils varying in texture, pH, and organic matter content to: i) determine the amount of As sorbed over a pH range of 3 to 10, ii) determine the effect of P on As sorption, and iii) determine the extent and rate of As release from soils. The results indicated that: i) the subsurface soils sorbed more As than surface soils, ii) these soils retained more As(V) at the pH range of 3 to 4 and experienced another increase in As sorption around pH 5.5 to 7, which is similar to the natural pH of Delaware soils, iii) the soils exhibited a preference for P over As during the competition study, specifically during the 1:1 and 1:50 As to P ratios; however, a substantial amount of P was still sorbed during the 50:1 As to P ratio compared to the amount of As sorbed during the 1:50 As to P ratio, indicating a preferential reaction to P, iv) the soils experienced greatest desorption of As upon application of P; however, more As was retained than P was sorbed, indicating that As may not be as easily desorbed once sorbed, and v) As has the ability to desorb a

significant amount of P, which may indicate that As may be more tightly bound to the soil surface than P.

Water and Sediments

Surface and ground waters near former mining or smelting sites often contain elevated As levels. Arsenic also occurs naturally in the geothermal springs of Yellowstone National Park in Wyoming, in which As concentrations exceed 1.0 mg L^{-1} (Shakhashiri, 2000). Not all geothermal springs contain high concentrations of As, and the concentration of naturally occurring As in groundwater varies with climate and geology (Welch et al., 2000).

High As concentrations in soil water can also contribute to surface water and groundwater contamination. Since collecting and measuring soil pore-water samples is difficult, expensive, and prone to contamination or adsorption losses, water extractions of soils have been used to represent potential pore-water concentrations.

Arsenic has similar properties in water as it does in soils. Speciation of As in aquatic environments is critical in controlling the adsorption/desorption reactions with sediments. In water that is aerobic and acidic to near-neutral, As(V) is readily adsorbed very strongly by oxide minerals in sediments (Mahimairaja et al., 2005). Hasen et al. (2009) collected both sediment and groundwater samples from the Dularampur village under Bitikandi Union of Daudkandi upazila of Bangladesh, which lies east of the river Meghna in southeast Bangladesh and within the Heghna floodplain to research the direct redox relationship between the As-containing sediments and the As-contaminated

groundwater. Hasan et al. (2009) found that a moderate redox potential was indicated within the upper part of the aquifer (0 to 6.5 m below ground surface) by low dissolved concentrations of As ($<10 \mu\text{g L}^{-1}$) Fe, and HCO_3^- , but high dissolved concentrations of Mn, SO_4^{2-} , and NO_3^- . The deeper portions of the aquifer (6.5 m to 25 m below ground surface) were high in As ($10 \mu\text{g L}^{-1}$ to $100 \mu\text{g L}^{-1}$), Fe, and HCO_3^- concentrations, but low in Mn, SO_4^{2-} , and NO_3^- . Oxidative degradation by microorganisms of organic matter within the deeper sediments was most likely responsible for the redox reactions and subsequent dissolution of Fe(III)-oxyhydroxides, which is also reflected by the increased concentrations of Fe and As in the groundwater (Nickson et al., 2000; Bhattacharya et al., 2001; McArthur et al., 2004; Islam et al., 2005). The oxidation of organic matter is also indicated by the increase in concentrations of HCO_3^- and decrease in concentrations of NO_3^- and SO_4^{2-} (Appelo and Postma, 1999).

Even though most of the soils of the Delmarva Peninsula are well drained, a large portion of the land in southeastern Delaware is poorly drained and farmed only due to the presence of tax ditches. Southern Delaware is also prone to high water tables and a high density of poultry production operations, thus long-term manure applications. All of these factors together in the same area may result in As dissolution within the groundwater.

Plants

Arsenic has been found to be phytotoxic at an average toxicity threshold of 40 mg kg^{-1} for crop plants (Sheppard, 1992). Arsenic is not an essential element for plants, and

at high concentrations, it has been reported to interfere with metabolic processes and significantly inhibit plant growth (Marin, 1993; Miteva, 1998). Arsenic interferes with the pentose-phosphate pathway during photosynthesis, which often leads to death (Marques and Anderson, 1986; Tu and Ma, 2002). Uptake and accumulation of As by plants depends on the chemical form and concentration of the element in soil, soil properties, and presence of other ions (Baker et al., 1976; Khattak et al., 1991; Marin et al., 1992; Marin et al., 1993; Masscheleyn et al., 1991a). Arsenite has a greater ability to target and penetrate the plant cuticle than As(V), which can result in loss of turgor pressure within the plant cell (Adriano and Weber, 2001).

The distribution of As among plant parts is highly variable. Seeds and fruits generally have lower As concentrations than leaves, stems, or roots. Roots and tubers have higher As concentrations within the outer skin than the inner flesh (Peryea, 2001). Marin et al. (1992) reported that the different species of As had a specific relationship to translocation within rice (*Oryza sativa* L.). Marin et al. (1992) found that upon absorption, DMA was readily translocated to the plant shoot, while As(III), As(V), and MMA accumulated in the roots. Edible portions of fruit and vegetable foods seldom accumulate high concentrations of As, as most plants are harvested or are severely stunted before As concentrations pose a health risk (Ontario Ministry of the Environment, 2001).

When grown on both sandy loam/sand soils and finer textured clay loam/clay soils with equivalent soil As concentrations, plants grown on the sandier soils have higher total As concentrations than those grown on the finer textured soils. Arsenic becomes

less available for plant uptake at neutral soil pH and increased soil organic matter, and the addition of lime (CaCO_3) to soil generally tends to immobilize As (Moon et al., 2004). However, soils with high As concentrations amended with phosphate have been found to increase plant uptake of soil As (Peryea, 2001).

Studies have shown that 70 to 90% of the As present in PL is water-soluble (Garbarino et al., 2001; Jackson and Bertsch, 2001). Since PL is applied to cropland, questions and concerns have been raised about the ultimate fate of this As. Arsenic from PL can enter the pore water of the soil, thus becoming available for uptake by plants and other soil organisms.

Humans

Upon ingestion and absorption, the majority of inorganic As is rapidly cleared from the blood (half-life of one to two hours) (Cohen et al., 2006). Approximately 40 to 70% of As that is absorbed and metabolized is excreted within 48 hours. The signs of chronic long-term exposure to low concentrations of As are skin discolorations, chronic indigestion, and stomach cramps. Long term exposure can lead to skin, lung, kidney, and liver cancer as well as gangrene-like sores. Unfortunately, these cancers may not appear for 20 to 30 years depending on exposure (Flynn, 1998).

Arsenite has an affinity for sulfhydryl bonds and can alter protein structure, leading to disruptions of metabolic processes (Gochfeld, 1997). The binding of As(III) compounds with sulfhydryl groups has the potential to influence cellular glucose uptake, gluconeogenesis, fatty acid oxidation, and the production of glutathione. However if

discovered soon enough, the binding of As(III) with sulfhydryl bonds is often reversible before major damage occurs (Young, 2000).

Since there is a chemical similarity between phosphate compounds and As(V) compounds, As(V) may be substituted for PO₄ in vital compounds or reactions important to human health. Although As(V) does not interact directly with DNA, indirect effects of As(V) may create an alteration of gene expression via disruption of DNA methylation, inhibition of DNA repair, oxidation stress, or altered modulation of signal transduction pathways (Gamble et al., 2005; Cohen et al., 2006).

Rapid nationwide urbanization has tremendously increased the potential for human contact with contaminated soil. Soil ingestion from incidental hand-to-mouth activity by children is an alarming issue, and assessing human health risk associated with exposure to As contaminated soils has become very important (Sarkar and Datta, 2004). Most risk associated with As is from forms that are biologically available for absorption, or bioavailable, to humans. Studies involving the measurement of As in fecal excretion in humans indicated that almost 95% of oral intake of As(III) is absorbed (Bettley and O'Shea, 1975). Also, based on urinary analysis, it has been reported that monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are also easily and rapidly absorbed (75-85%) across the gastrointestinal tract (Buchet et al., 1981).

No laboratory method has currently been adopted by the USEPA as a standard method for evaluating bioavailability. In evaluating Superfund sites, baseline risk assessments have used the conservative estimate that all (100%) As present in soil is bioavailable by equating As bioavailability in water with that in soils (Rodriguez et al.,

1999). Since methods to evaluate risk assessment of As contaminated sites only consider total content, some studies have been conducted on immature pigs to simulate gastrointestinal function of children (Miller and Ullrey, 1987; Weis and LaVelle, 1991). Several of these *in-vivo* studies have shown that bioavailability of As in soils may be significantly less than that in water (Rodriguez et al., 1999). Yet, these studies are expensive and lengthy; therefore research efforts have been directed toward the development of chemical methods. Some *in-vitro* methods have been developed to compare to *in-vivo* results with varying degree of success (Davis et al., 1992; Rodriguez et al., 1999); however, these studies have only been conducted on severely contaminated waste disposal sites, and not marginally contaminated samples (Sarkar and Datta, 2004).

Fendorf et al. (2004) developed a simplified method to estimate As bioavailability in the instance of incidental ingestion. The first step in the bioavailability process has been deemed bioaccessibility, which has been defined as the fraction of a contaminant available for absorption into the gastrointestinal system of an organism (Ruby et al., 1996) and is dependent on the binding mechanism within soils (Ruby et al., 1992; Davis et al., 1993). Fendorf et al. (2004) also stated that as contaminated samples are aged, the potential for contaminant release should decrease due to amorphous compounds eventually developing into more stable crystalline structures. Fendorf et al. (2004) also developed a sequential fractionation method to be utilized in conjunction with the bioavailability extraction method to relate which As bound forms were considered bioavailable.

Conclusions and Research Objectives

As public concern over As impacts on human and ecosystem health increases worldwide, it is important to research and evaluate the potential for As contamination within Delaware due to PL and historical tanneries. Potential soil contamination and ground/surface water contamination should be evaluated as the land in Delaware is prone to high water tables, sandy soils, and receives plentiful rainfall throughout the year. Several methods were utilized in this research project to evaluate the potential for soil and ground/surface water contamination. The objectives of this research project were: i) to characterize total and extractable As content of soils as a result of historic tannery use and historical PL application, ii) to compare results from a greenhouse soil column study to laboratory leaching extraction methods, iii) to evaluate alum as a best management practice by characterizing total and extractable As content from alum-treated PL and untreated PL, and iv) to evaluate rapid chemical methods to assess As bioavailability.

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CHAPTER 2

CHARACTERIZATION OF ARSENIC IN AGRICULTURAL SOILS AND LEACHING OF ARSENIC IN SOILS AMENDED WITH POULTRY LITTER

Introduction

The aryl-organoarsenical compound roxarsone (ROX: 3-nitro-4-hydroxyphenyl arsonic acid) is approved by the United States Food and Drug Administration (USFDA) for use as an animal feed additive (Jackson and Miller, 2000). Roxarsone is typically used at a rate of 25 to 50 mg kg⁻¹ for broiler feeds to control Coccidiosis, primarily caused by *Eimeria tenella*, increase broiler growth rate, improve feed utilization, enhance pigmentation, and also may be effective in suppressing *Salmonella* (Alpharma, 1999). Roxarsone is also approved to be combined with several other feed additives, such as Amprolium, Ethopabate, Baciracin Methylene Disalicylate, Bacitracin Zinc, Bambermycins, and Decoquinate, to prevent exposure to Coccidiosis from more severe *Eimeria* species (*E. acervulina*, *E. maxima*, *E. brunetti*, *E. necatrix*, and *E. mitis*). A five-day ROX withdrawal period is required before slaughter (Feed Additive Compendium, 2007). Since ROX is 28.5% As, the total As concentration in poultry feed ranges from 7.1 to 14.2 mg kg⁻¹ As (Alpharma, 1999).

In 2000, roughly 70% of all chickens on starter rations and approximately 74% of those on grower rations in the United States (US) were fed ROX (Chapman and Johnson,

2002). According to Muir (2001), 8.26 billion chickens were produced in the US in 2000, thus ~5.8 billion chickens were fed ROX. At an average dosage of 45.4g of ROX per ton for the typical 42 day life cycle of a broiler, each chicken excretes about 150 mg of ROX, or its degradation products, in total. The ultimate result is that 9×10^5 kg of ROX, or, more specifically, 2.5×10^5 kg of As, was present in the manure from these chickens (Rutherford et al., 2003). Total As concentrations in PL usually range from <1 to 40 mg kg⁻¹ (Nicholson et al., 1999; Jackson and Bertsch, 2001; Garbarino et al., 2003; Rutherford et al., 2003; Anderson and Chamblee, 2001; Jackson et al., 2003). The use of ROX in poultry feeds has declined in recent years due to public concerns about the human and ecological impacts of As; however, it is still the preferred coccidiostat of the poultry industry.

The Delmarva Peninsula region produces over 600 million chickens and 1.5 million metric tons of manure annually, ranking second in the nation. Since, until recently, it has not been cost effective to transport the PL elsewhere, farmers have always used it for fertilizer, and by incorporating the PL into agricultural soils, approximately 20-50 metric tons of As have been introduced into the environment annually (Christen, 2001). The potentially toxic effects of As applied to cropland on aquatic ecosystems and human health is a longstanding and ongoing concern for the poultry industry and farmers who rely on PL as a nutrient source. With the advent of nutrient management legislation in Delaware, the relocation of PL to non-agricultural settings, such as the mushroom industry or for urban uses as a pelletized fertilizer, has become more common. This raises questions about the fate of As in urban and suburban settings as well as with

production agriculture. Even though the USEPA regulates land application of heavy metals in sewage sludge, no federal regulations exist for land application of metals in animal manures (USEPA, 1993).

Roxarsone undergoes a series of aerobic and anaerobic reactions in the environment that can transform it into pentavalent and trivalent organic and inorganic compounds. Under anaerobic conditions, Stolz et al. (2007) found that the benzene ring of the ROX structure was oxidized first, which releases the inorganic trivalent H_2AsO_3^- . However, they did not find evidence of ROX degrading into organic As under aerobic conditions. Cortinas et al. (2006) also found that nitrogen-substituted phenylarsonic compounds degrade into As(III) under reducing conditions. Wershaw et al. (2000) stated that the three most likely degradation reactions of ROX are: i) the reduction of the nitro group; ii) rupture of the C-As bond; and iii) oxidative fission of the aromatic ring and also reported that the degradation product 3-amino-4-hydroxyphenylarsonic acid was detected in the urine of hens fed ROX. According to Wershaw et al. (2006) if ROX were to undergo microbial degradation, arsonoalkyl acids would be produced. Under anaerobic conditions, arsonoalkyl acids could convert to alkylarsine, which is stable under anaerobic conditions; however, alkylarsine would be oxidized to the pentavalent AsO_4^{3-} . The research initiatives of Stolz et al. (2007) Cortinas et al. (2006), and Wershaw et al. (2000) indicates that 3-amino-4-hydroxyphenylarsonic acid, Monomethylarsonic acid (CH_5AsO_3 ; MMA(V)), Monomethylarsonous acid (CH_4AsO_2 ; MMA(III)), Dimethylarsinic acid ($\text{C}_2\text{H}_7\text{AsO}_2$; DMA(V)), Dimethylarsinous acid ($\text{C}_2\text{H}_7\text{AsO}$; DMA(III)), Trimethylarsine oxide ($(\text{CH}_3)_3\text{AsO}$; TMAO(V)), Trimethylarsine ($(\text{CH}_3)_3\text{As}$;

TMA(III)), AsO_4^{3-} , H_2AsO_3^- , as well as other As(III) compounds could be possible degradation products of ROX.

Garbarino et al. (2003) found that when PL samples were mixed with water and allowed to compost at 40°C, the As was converted from organo-As to As(V) in about 30 days. The major species of As in water extracts from PL were found to be ROX and As(V); however, minor quantities of As(III), dimethylarsinic acid (DMA), monomethylarsonic acid (MMA), 3-amino-4-hydroxyphenylarsonic acid were detected as well (Garbarino et al., 2003; Rutherford et al., 2003; Jackson et al., 2003; Cortinas et al., 2006; Stolz et al., 2007). Laboratory “composting” or “incubating” experiments usually simulate what would happen when the PL is added to the soil and aerobic microbiological processes take effect. However, in anaerobic conditions, bacteria of the genus *Clostridium* are selective in degrading ROX to inorganic As (Garbarino et al., 2003 and Cortinas et al., 2006), and since As(V) is a more soluble and more mobile form of As than ROX, it is more likely to leach into groundwaters, or be transported by runoff into surface waters.

Poultry litter has economic value as a phosphorus fertilizer, and also is a beneficial soil amendment. The use of PL helps increase soil fertility and aeration and improves water-holding capacity (Gupta and Charles, 1999). It also enhances soil productivity and improves soil aggregate formation and stability. Water infiltration and the supply of plant nutrients, such as calcium (Ca), magnesium (Mg), sulfur (S), potassium (K), and micronutrients also increases (Kpombrekou-A, et al., 2002). The long-term sustainability of PL use as a fertilizer, whether for agronomic crops or for

horticultural purposes, requires a clear understanding whether or not litter As is an environmental or human health problem. One area of particular concern is the loss of As from PL-amended soils to groundwaters by leaching or surface waters by runoff.

Aluminum sulfate [alum; $\text{Al}_2(\text{SO}_4)_3$] is currently used to reduce ammonia-N concentrations in poultry houses. The alum is only applied at the beginning of each flock of birds produced; therefore, an initial pH of 4 to 5 occurs due to acidification caused by aluminum solubilization. However, the pH slowly rises to approximately pH 7 over the time the flock is in the house (Moore and Miller, 1994). It has been proposed that alum also reacts with soluble phosphate to form more stable aluminum phosphate precipitates (Moore and Miller, 1994). According to the research conducted by Peak et al. (2002), the phosphate compounds found in non-alum treated PL were aqueous phosphate, phytic acid, and dicalcium phosphate. However, in the alum treated PL (Al:P ratio >0.6) evidence of phosphate bound to aluminum oxides was found instead of the previously expected aluminum phosphate precipitate phases. As the pH gradually increases above pH 5, aluminum phosphate stability decreases greatly; therefore, it is possible that aluminum phosphate precipitation occurs that is followed by dissolution as time and pH increases. Since As and P react very similarly in the soil environment, it is proposed that As undergoes the same reactions in PL when treated with alum.

While considerable research has been conducted to understand the processes of As transformation in PL; less is known about the fate and transport of As in soil after PL is land applied to soils where leaching is an established concern. Given the highly leachable nature of many Delaware soils and the shallow ground waters that predominate

in this region, there is a need to characterize the forms, solubility, and leaching behavior of As added to soils in poultry litter. There is also a need to identify and better understand best management practices (BMPs) that can reduce the potential for As leaching when PL is used as a soil amendment. One such BMP is the use aluminum sulfate [$\text{Al}_2(\text{SO}_4)_3$] as a PL amendment, commonly applied to reduce ammonia-N concentrations in poultry houses but also shown by Sims and Luka-McCafferty (2002) to decrease As solubility in PL. Consequently, the objectives of this research were: i) to obtain background information on the amounts of total, soluble, and bioavailable As in a wide range of Delaware soils, including but not limited to those with a history of PL application; ii) based on these background data, to quantify the leaching of As from poultry litter-amended soils with properties and total As concentrations representative of Delaware conditions; and (iii) to assess the effect of alum on the solubility and speciation of As in a wide range of poultry litters obtained from working poultry farms on the Delmarva Peninsula.

Methodology

Soil Collection and Characterization

To ensure that the soils selected for use in column studies of As leaching from poultry litter were representative of Delaware conditions, a wide range of agricultural and wooded soils were collected and analyzed for As forms and solubility and key physical and chemical properties. Several farm and wooded sites were selected throughout Delaware to characterize As concentrations in soils with various agricultural uses as well as soils with no history of agricultural use. Five farm sites were selected from New Castle County that had no known history of PL application (Farm 1 through Farm 5), five farm sites were selected from Sussex County that had a history of repeated PL applications (Farm 6 through Farm 10), and three wooded sites were selected from Sussex County that had no known history of agricultural use (labeled by corresponding farm from which soils were collected). Soils were classified taxonomically based on in-field conditions and one soil sample was collected from each horizon to a depth of approximately 100 cm (Table 2.1). A total of 42 soil horizons were collected, representing 10 benchmark soil series that are widely distributed in Delaware. In addition to the farm and wooded soils, 44 topsoil (0-20 cm) samples were obtained which had been collected during development of nutrient management plans for University of Delaware (UD) farms in New Castle and Sussex County, Delaware.

Table 2.1. Soil taxonomic classification for farm and forested soils collected in New Castle County and Sussex County, Delaware.

Farm Site Designation	Soil Series	Taxonomic Classification
New Castle County Cash Grain Farms		
Farm #1	Reybold	Fine-loamy, mixed, semiactive, mesic Typic Hapludults
Farm #2	Woodstown	Fine-loamy, mixed, active, mesic Aquic Hapludults
Farm #3	Sassafras	Fine-loamy, siliceous, semiactive, mesic Typic Hapludults
Farm #4	Elkton	Fine-silty, mixed, active, mesic Typic Endoaquults
Farm #5	Nassawango	Fine-silty, mixed, semiactive, mesic Typic Hapludults
Sussex County Poultry Farms (Crop Land)		
Farm #6	Sassafras	Fine-loamy, siliceous, semiactive, mesic Typic Hapludults
Farm #7	Rumford	Coarse-loamy, siliceous, subactive, thermic Typic Hapludults
Farm #8	Greenwich	Coarse-loamy, mixed, semiactive, mesic Typic Hapludults
Farm #9	Downer	Coarse-loamy, siliceous, semiactive, mesic Typic Hapludults
Farm #10	Corsica	Fine-loamy, mixed, active, mesic Typic Umbraquults
Sussex County Poultry Farms (Forested Land)		
Farm #7	Sassafras	Fine-loamy, siliceous, semiactive, mesic Typic Hapludults
Farm #6	Ingleside	Coarse-loamy, siliceous, semiactive, mesic Typic Hapludults
Farm #8	Greenwich	Coarse-loamy, mixed, semiactive, mesic Typic Hapludults

All 86 soil samples were air-dried, ground, and sieved to pass a 2-mm screen prior to experimental activities and laboratory analysis. The 86 soil samples were analyzed in triplicate for organic matter, pH, particle size distribution, total elemental (As, Al, B, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn) content (USEPA Method 3051; USEPA, 1994), Mehlich 3 (M3): $0.2\text{ M CH}_3\text{COOH} + 0.25\text{ M NH}_4\text{NO}_3 + 0.015\text{ M NH}_4\text{F} + 0.13\text{ M HNO}_3 + 0.001\text{ M EDTA}$) extractable elements (As, Al, B, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn; Mehlich 1984), and for easily leachable As by the Toxicity Characteristic Leaching Procedure (TCLP; USEPA Method 1311; USEPA, 1992). All elemental concentrations in soil digests or extracts were determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

The Mehlich 3 extraction was developed to evaluate the concentration that would potentially be plant available (Mehlich, 1984), and has been utilized as a form of bioavailability measurement. Samples were mixed with the Mehlich 3 extractant at a soil:solution ratio of 1:10 and placed on a reciprocating shaker at 180 oscillations per minute for five minutes. Samples were immediately filtered through a Whatman #41 filter paper, and extracts were analyzed for As by ICP-OES.

The TCLP method (toxicity characteristic leaching procedure using a leaching solution comprised of 0.1 M glacial acetic acid and 0.0643 M NaOH, with a final pH of 4.93 (USEPA, 1992)) was originally developed by the USEPA to evaluate the potential for contaminant leaching into groundwater from landfills. As the soils and groundwater of the Delmarva Peninsula are naturally slightly acidic, the TCLP method was selected to mimic in-field conditions for leachability. The samples were mixed with the TCLP

extractant at a dilution rate of 1:20 for 18 hrs in an end-over-end shaker, and then centrifuged at 2000 rpm for 13 minutes. Centrifugates were then vacuum filtered with through a 0.45 μm filter and analyzed for As by ICP-OES.

Poultry Litter Collection and Characterization

The PL used for the two column leaching studies was an untreated litter selected from a previously conducted research project in which the effects of alum on the solubility of P were investigated and came from a farm where ROX was used in poultry diets (Sims and Luka-McCafferty, 2002). Sixteen additional PLs from this study (7 control and 9 alum-amended) were also obtained to investigate the effects of alum on the solubility and speciation of litter As. All PL samples were analyzed in triplicate for total As (USEPA 3051), leachable As (TCLP), bioavailable As (M3 and PBET), and As in three chemical fractions identified by the sequential extraction method of Fendorf et al. (2004); the fractions included (i) easily exchangeable As (1M magnesium sulfate (MgSO_4)); (ii) As sorbed to amorphous oxides of Al and Fe (0.2M ammonium oxalate [Am Ox, $((\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O})$]); and (iii) crystalline/recalcitrant As (12M trace metal grade hydrochloric acid (HCl)). A soil:solution ratio of 1:20 was used for each extraction. Samples were extracted with 1M MgSO_4 for 1h, followed by 0.2M AmOx for 4 h in the dark, and then with 12M trace metal grade HCl for 12 h. Samples were rinsed with deionized water for 1h between each extraction. For each extraction samples were centrifuged at 2000 revolutions per minute (rpm) for 13 min and extracts were vacuum

filtered with a 0.2 μm filter. Rinse water was filtered using a 0.45 μm filter and discarded. Extracts were analyzed for As by ICP-OES.

The PBET method was adapted from Fendorf et al. (2004) and was developed to evaluate the potential for contaminants to be absorbed through the gastric system in the event that contaminated material is ingested. The PBET extractant consists of a mixture of 1 *M* glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) acidified to a pH of 3.0 with 6 *N* HCl. Samples were mixed with the extractant at a rate of 1:100 to simulate the ratio in the instance of incidental ingestion. Samples were then placed in a water bath for one hour at 35.6 °C to mimic conditions of the human stomach. Samples were then centrifuged at 2000 rpm for 13 minutes and gravity filtered using Whatman #542 filter paper. Extracts were analyzed for As by ICP-OES.

Arsenic Leaching Experiments

The effect of PL applications on As leaching from Delaware soils was investigated in two greenhouse column studies using a modification of the methodology developed by Maguire and Sims (2002) to study phosphorus (P) leaching from soils. Agricultural topsoils (0-20 cm) for study were obtained from two Sussex County farms that had with a history of PL use (Farms 6 and 10). The soil series at Farm 6 was a Sassafras sandy loam (fine-loamy, siliceous, semiactive, mesic Typic Hapludults) and at Farm 10 was a Corsica sandy loam (fine-loamy, mixed, active, mesic Typic Umbraquults). The Sassafras soil is a well-drained, sandy soil with low organic matter content, while the Corsica soil is a very poorly drained, sandy soil with high organic

matter content. Both fields had a history of PL application. Soil test P values (M3-P) at the two sites (Sassafras = 47 mg kg⁻¹ and Corsica = 164 mg kg⁻¹) were close to the optimum range for the agronomic crops grown on these farms (M3-P = 50–100 mg kg⁻¹), suggesting that PL and fertilizer applications had been consistent with crop nutrient requirements. Bulk soil samples were collected using an S-based sampling pattern across the agricultural field at each location and returned to the laboratory where they were air-dried, ground, sieved to pass a 2-mm screen and thoroughly mixed to ensure homogeneity. Subsamples were collected from both soils during the mixing process for characterization of soil physical and chemical properties. These soil samples were analyzed in triplicate for organic matter, pH, particle size distribution, total (USEPA 3051) elemental content, M3 extractable elements, and TCLP As. Arsenic sorption isotherms were also conducted by a standard batch method in which soils were equilibrated, at a 1:15 soil:solution ratio, with solutions containing concentrations of 0, 1.0, 2.5, 5.0, 10.0, 25.0, and 50.0 mg As L⁻¹, in 0.01M sodium nitrate (NaNO₃). Samples were then centrifuged at 2000 rpm for 13 minutes and vacuum filtered through a 0.45 µm filter. Extracts were analyzed for As by ICP-OES and Langmuir As sorption maxima for the soils were determined by the method of Gratz and Nair (2000).

Columns used in the greenhouse leaching study were cut from 15-cm (i.d.) PVC pipe to a length of 20 cm. For leachate collection, a hole was drilled into a 15-cm PVC endcap and a short tube filled with glass wool was glued into the hole. The endcaps were packed with sand that had been triple-rinsed with deionized water and securely attached to the bottom of each PVC column. The capped columns were then carefully packed with

the appropriate soils at bulk densities that corresponded to field conditions (Corsica = 1.25 g cm^{-3} ; Sassafras = 1.5 g cm^{-3}) and placed into racks in a greenhouse. To minimize potential edge flow (downward flow of water and dissolved solutes occurring between the packed soil and the side of the PVC column), paraffin wax was melted and poured slowly into a small gap created between the soil and the inside of each column. All columns were pre-wet by adding excess reverse osmosis (RO) water and left to drain to field capacity for two days prior to initiating leaching. Soil columns were then leached with RO water for two weeks (7 leaching events) to determine background As concentrations in leachate from unamended soils. The water was slowly applied by hand to minimize ponding and edge flow. Water added in each leaching event was equal to 2.54 cm of water to simulate the amount of rainfall in Sussex County, Delaware.

Poultry litter was uniformly applied to the column surface before leaching event #8 at rates of 0, 4.5, 9.0, 13.5, 18.0, and 22.5 Mg ha^{-1} . Based on the total As concentration in the PL (43.5 mg kg^{-1}) As application rates to soil columns, on an areal basis, were 194, 391, 587, 783, and 978 g As ha^{-1} .

Three replications of each PL rate were used, resulting in a total of 36 soil columns (2 soils x 6 litter rates x 3 replications) that were arranged in the greenhouse in a randomized complete block design. After PL application the columns were leached twice weekly (2.54 cm water per event) for eight weeks (16 post-litter application leaching events). Following each event, all leachate was collected, volumes were measured, leachate samples were filtered through $0.45 \text{ }\mu\text{m}$ Millipore membranes and refrigerated until analysis for As by ICP-OES. Despite efforts to prevent edge flow, this apparently

occurred in several Sassafras soil columns, as evidenced by a much darker color of the leachate samples obtained from these columns immediately after litter application than all other columns, which had clear leachates. Analyses of leachate from columns with colored leachates confirmed that they had markedly higher As concentrations in Event #8 (mean=336 $\mu\text{g L}^{-1}$) than other columns in the study (mean=11 $\mu\text{g L}^{-1}$). As these high As concentrations were an artifact of an experimental leaching problem (edge flow) with these columns, the data collected from these columns were omitted and the results were treated statistically as missing data. However, figures showing all data, including these outliers, are provided for review in the Appendix (Figure A-1). After completion of the first column leaching study, soil samples were collected from each column for analysis of potentially leachable As by the TCLP method. The soil was allowed to air-dry before post-column study sampling to assist in the removal of the soil from the columns. Residual PL on the soil surface was removed and soils were gradually extruded from the columns, sectioning them into 5 cm increments during this process. The 0-5 cm (top) sections of all columns and the 15-20 cm sections of the control and the 22.5 Mg ha^{-1} treatment rates were extracted with the TCLP solution and analyzed for As by ICP-OES.

A second column leaching study (*Column Study 2*) was conducted to: (i) modify the RO water addition method to further minimize edge flow; and (ii) evaluate As leaching from two additional soils that displayed different properties than the original soils used in *Column Study 1*. Along with the Sassafras and Corsica soils that were used in *Column Study 1*, a sandy soil with no history of PL application (Evesboro sandy loam - mesic, coated, lamellic Quartzipsamments), obtained at the UD Research and Education

Center in Sussex County; and a fine-textured soil (Matapeake silt loam – fine-silty, mixed, semiactive, mesic Typic Hapludults) from the UD Newark Farm (New Castle County) with a much higher silt and clay content than the other soils used in the column studies (Corsica and Sassafras) were used in *Column Study 2*. Bulk samples were collected from the topsoils (0-20 cm) from each location using an S-based sampling regime and returned to the laboratory where they were air-dried, ground, and sieved to pass a 2-mm screen and thoroughly mixed to ensure homogeneity. Soils were analyzed for organic matter, pH, particle size distribution, total (EPA 3051) elemental content, M3 extractable elements, TCLP As, and As sorption maxima as in *Column Study 1*. The same PL was used as in *Column Study 1*, but with only two PL rates (0 and 9 Mg ha⁻¹ – the rate commonly used to meet crop nitrogen requirements). Therefore, in *Column Study 2* there were 24 soil columns (4 soils x 2 litter rates x 3 replications) arranged in a completely randomized block design in the greenhouse. Prior to leaching, the soils and PL were prepared, and the columns packed in an identical manner to *Column Study 1*, with bulk densities for the Evesboro and Matapeake soils being 1.5 and 1.25 g cm⁻³, respectively. The modified water addition method in *Column Study 2* involved initially pre-wetting the soils by pumping water up through the bottom of each column with a peristaltic pump to better seal the soil-column interface. Also, during each leaching event small IV bags were hung directly over each column and close to the soil surface to slowly drip RO water onto the soil surface, resulting in a much more uniform water application. The columns were leached eight times before application of the PL and 22 times after PL application for a total of 30 leaching events (2.54 cm of water per event). After each event, all leachate

was collected, volumes measured, and samples were filtered through 0.45 μm Millipore membranes and refrigerated until analysis of selected samples for As by ICP-OES. Using this method evidence of edge flow was noticed for only one column during one leaching event (colored leachate for the Matapeake soil, PL rate = 9 Mg ha^{-1} ; leaching event 10). As in *Column Study 1*, data from this column for this event were omitted from statistical analyses of results. At the end of the final leaching event, as in *Column Study 1*, soil columns were allowed to dry to aid in soil removal, any residual PL was removed, then soil columns were sectioned into 5-cm increments and the 0-5 cm depth sections from each of the soil columns were analyzed for TCLP-As.

Statistical Analysis

Statistical analysis of the effect of broiler litter application rate on As concentrations in leachate at each leaching event in both column studies was conducted using the PROC GLM procedure of the Statistical Analysis System, Version 8.2 (SAS Institute, 2003). Separation of means was performed using least significant differences calculated with the GLM procedure with a probability value of 0.05 being used to determine if significant differences existed between litter rates.

Results and Discussion

Arsenic Status of Delaware Soils

The 86 soil samples collected from New Castle County and Sussex County, Delaware represented a wide range of soil types, textures, and total As concentrations and were characterized for key physical and chemical properties to determine which soils should be selected for the column studies. Total As concentrations in the soils ranged from 0 (below detection limit) to 19.6 mg kg⁻¹; however, only four of the 86 samples were above the 11 mg kg⁻¹ background concentration established by DNREC for As (Figure 2.1), and no samples were above the Interim Arsenic Soil Cleanup Standard for Residential Properties of 23 mg kg⁻¹. For the purpose of the soil column studies, limited soils were available to select from that were collected from Sussex County and that were historically amended with PL. The Sussex County farms soils were a Sassafras sandy loam, Rumford sandy loam, Greenwich loam, Downer loamy sand, and Corsica sandy loam (Table 2.1). The intent of characterizing these soils was to select two soil types for use in As leaching studies that were different in physico-chemical characteristics, yet typical of agricultural soils in Sussex County. The first soil series selected was the Sassafras sandy loam (Farm #6), due to its total As concentration, high sand percentage, and oxidized in-field conditions. The Sassafras soil series is a well drained soil with a seasonal high water table greater than 1.8 m below ground surface (NRCS, 2009b; Table 2.2). The second soil series selected was the Corsica sandy loam (Farm #10), due to its

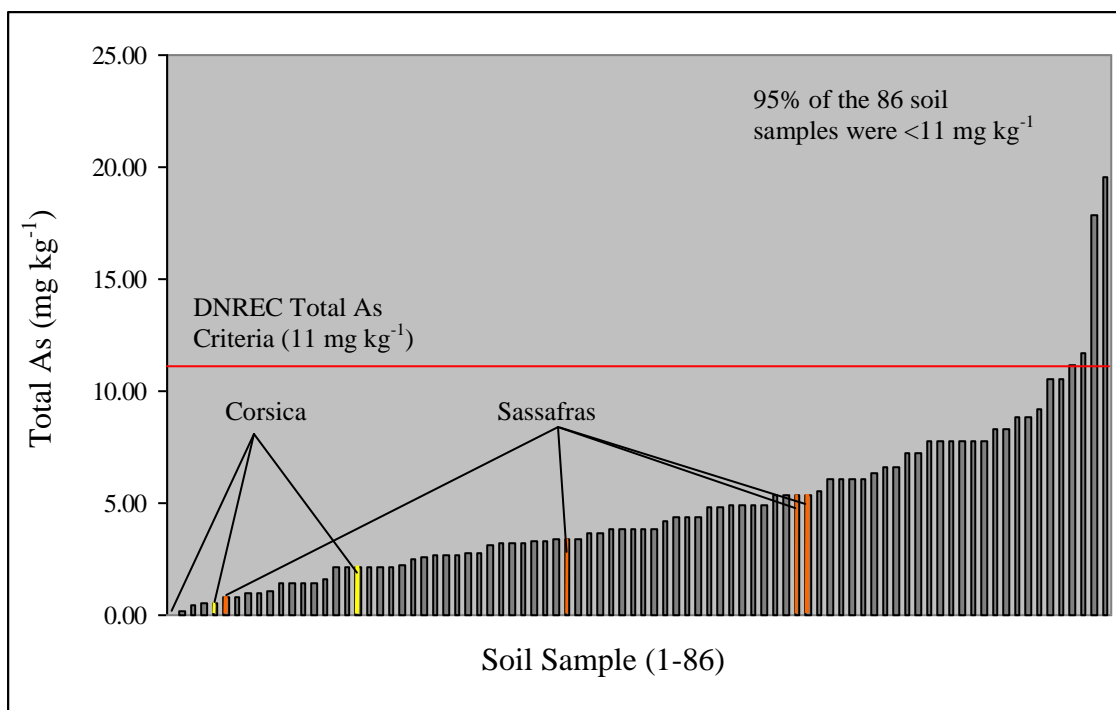


Figure 2.1. Comparison of total As concentrations in agricultural and forested soils obtained from cooperator's farms in New Castle County and Sussex County and University of Delaware farms. The topsoil horizons of the Sassafras and Corsica soils were used in column studies of As leaching from poultry litter.

Table 2.2. Soil properties and Total, Mehlich 3, and TCLP As concentrations for agricultural soils collected from New Castle County and Sussex County, Delaware.

Collected from New Castle County and Sussex County, Delaware.										
Farm Site Designation	Soil Series	Depth	pH	OM	Sand	Silt	Clay	Total	Arsenic M 3	TCLP
		cm		%					mg kg ⁻¹	
New Castle County Cash Grain Farms										
Farm #1	Reybold	0-23	6.5	2.1	31	48	21	3.3	0.09	0.22
		23-30	6.5	1.1	33	46	21	3.7	0.06	0.03
		30-56	6.5	1.0	23	50	27	4.8	bd	0.03
Farm #2	Woodstown	0-23	5.4	1.0	47	39	14	2.2	0.06	0.35
		23-46	5.6	0.4	39	42	19	2.1	0.05	0.01
Farm #3	Sassafras	0-30	5.4	4.8	53	30	17	5.4	0.16	0.43
		30-56	5.1	0.6	53	28	19	3.7	0.07	0.19
		56-91	5.6	0.6	53	24	23	9.2	0.04	0.62
Farm #4	Elkton	0-23	5.7	2.2	23	57	20	3.4	0.08	0.48
		23-43	4.9	0.9	15	57	28	2.5	bd	0.10
Farm #5	Nassawango	0-18	6.2	1.6	33	49	18	4.4	0.07	0.42
		18-76	6.7	0.9	19	48	33	4.8	0.04	0.29
Sussex County Poultry Farms (Crop Land)										
Farm #6	Sassafras	0-20	5.1	1.2	68	22	10	5.4	0.19	0.05
		20-41	5.9	0.8	52	23	25	5.4	0.28	0.43
		41-61	6.1	0.4	72	10	18	0.8	0.12	0.03
		61-81	6.5	0.2	80	4	16	3.4	0.22	0.44
Farm #7	Rumford	0-20	5.8	0.7	80	14	6	2.8	0.15	0.02
		20-41	5.7	0.1	81	9	10	2.8	0.26	0.06
		41-61	5.4	0.2	72	9	19	3.4	0.15	0.19
		61-81	5.3	0.2	74	10	16	1.5	0.20	0.01
Farm #8	Greenwich	0-28	5.2	1.3	55	30	15	2.6	0.26	0.59
		28-53	2.6	0.5	55	28	17	0.5	0.16	0.18
		53-81	5.7	0.8	49	30	21	3.2	0.18	0.53
		81-109	5.9	0.2	73	13	14	1.6	0.14	0.46
Farm #9	Downer	0-28	5.3	1.5	75	16	9	2.6	0.42	0.23
		28-46	5.8	0.7	69	18	13	1.1	0.26	0.06
		46-73	5.7	0.7	76	7	17	6.3	0.19	0.27
		73+	5.7	0.2	67	16	17	3.2	0.13	0.29
Farm #10	Corsica	0-30	4.7	7.4	79	14	7	2.1	0.27	0.44
		30-43	4.7	1.6	45	26	29	0.5	0.21	0.02
		43-81	4.4	0.7	30	35	35	bd	0.26	0.02

bd – Below Detection Limit

high organic matter content, high seasonal water table, and reduced in-field conditions.

The Corsica soil series is a very poorly drained soil with a seasonal high water table from 10 cm above ground surface to 15 cm below ground surface depending on seasonal fluctuation (NRCS, 2009a; Table 2.2). The Corsica soil also had a higher organic matter percentage than the other soils collected from Sussex County as well as New Castle County (Table 2.2, 2.3).

The total As concentration differed little between the soils collected from the cropland (Table 2.2) and the forested land (Table 2.3) of Sussex County; however, the soil samples collected from New Castle County averaged slightly higher in total As concentration (8.7, 7.3, and 4.1 mg kg⁻¹ As; Table 2.4) compared to the soil samples collected from Sussex County (4.3, 2.7, and 2.6 mg kg⁻¹ As; Table 2.4).

The TCLP As concentrations of the soils collected from Sussex County were similar to TCLP As concentrations of the soils collected from New Castle County; however, Mehlich 3 As concentrations were higher for the soils collected from New Castle County, which may be attributed to the higher clay content, and thus greater As sorption capacity, associated with the finer-textured soils found in New Castle County.

Comparison of the analytical results between the farm and wooded soils collected from Sussex County revealed that the total As content was only slightly higher in the farm soils than in the wooded soils, and little difference was found between the farm soils and forested soils for M3 and TCLP As. In contrast, Gupta and Charles (1999) collected samples from agricultural soils in eastern Maryland that had been amended with PL for approximately 15 to 20 years with applications occurring every other year and

Table 2.3. Soil properties and Total, Mehlich 3, and TCLP As concentrations for forested soils collected in association with poultry farms in Sussex County, Delaware.

Farm Site Designation	Soil Series	Depth cm	pH	OM	Sand %	Silt	Clay	Arsenic		
								Total	M 3	TCLP
								mg kg ⁻¹		
Farm #7	Sassafras	0-10	5.0	4.6	65	27	8	1.5	0.06	0.1
		10-40	4.8	0.7	72	11	17	5.4	0.22	0.1
		40-61	4.7	0.3	70	14	16	1.5	bd	0.1
		61-81	4.7	0.1	85	5	10	0.8	0.05	0.3
Farm #6	Ingleside	0-15	4.2	5.3	70	24	6	0.2	0.09	0.3
		15-40	4.6	0.6	68	22	10	2.1	bd	0.0
		40-61	4.5	0.3	62	24	14	1.5	bd	0.2
		60-91	4.3	0.4	61	19	20	6.1	0.10	0.1
Farm #8	Greenwich	0-8	5.3	4.6	49	36	15	4.2	0.08	0.3
		8-46	4.2	1.0	47	34	19	2.1	0.04	0.2
		46+	4.1	1.1	51	26	23	3.3	0.20	0.1

bd – Below Detection Limit

Table 2.4. Predominant soil series and overview of selected soil properties and forms of soil As for agricultural soils at farms on University of Delaware property and cooperator farms in New Castle County and Sussex County, Delaware.

Predominant Soil Series and Number of Fields Sampled	Statistic	pH	OM %	Arsenic		
				Total	M3 mg kg ⁻¹	TCLP
Newark Research and Education Center						
Matapeake, Sassafras, Kenansville (n=15)	Mean	6.2	2.9	8.7	0.7	0.2
	Std. Dev.	0.4	1.1	4.7	0.2	0.1
Middletown Research and Education Center						
Woodstown, Sassafras, Matapeake (n=8)	Mean	6.1	2.0	7.3	0.6	0.2
	Std. Dev.	0.5	0.7	2.3	0.1	0.1
Georgetown Research and Education Center						
Evesboro, Kalmia, Woodstown (n=21)	Mean	6.0	1.3	4.3	0.7	0.3
	Std. Dev.	0.3	0.6	2.5	0.4	0.2
New Castle County Cash Grain Farms						
Reybold, Woodstown, Sassafras, Elkton, Nassawango (n=12)	Mean	5.8	1.4	4.1	0.1	0.3
	Std. Dev.	0.6	1.2	1.9	0.1	0.2
Sussex County Poultry Farms (Crop Land)						
Sassafras, Rumford, Greenwich, Downer, Corsica (n=19)	Mean	5.3	1.0	2.7	0.2	0.2
	Std. Dev.	0.8	1.6	1.7	0.1	0.2
Sussex County Poultry Farms (Forested Land)						
Sassafras, Ingleside, Greenwich (n=11)	Mean	4.6	1.7	2.6	0.1	0.2
	Std. Dev.	0.4	2.0	1.9	0.1	0.1

found that total As concentrations in PL-amended fields were significantly higher (15.7 mg kg^{-1}) than total As concentrations in unamended fields (9.26 mg kg^{-1}). However, Arai et al. (2005) collected samples from agricultural fields in southern Delaware that had received PL amendments for over 30 years via surface application and did not find a significant difference between total As concentrations in PL-amended soils and unamended soils. Variations in total As concentrations in agricultural soils where PL has been applied are expected and are most likely due to differences in prior application rates and frequencies of application of PL. In the present study, as noted earlier, the soil test P values of the cropland soils from Sussex County were close to the agronomic optimum range ($50\text{-}100 \text{ mg kg}^{-1}$). This suggests that PL was applied less frequently and at lower rates on these farms than for many others in this area, thus much higher total soil As values in cropland compared to forest soils would not be expected. The situation may be different, however, on many other farms in Sussex County where the median soil test P value for agricultural soils was recently reported to be 169 mg kg^{-1} (Sims et al., 2008).

In summary, the agricultural topsoils selected for use in *Column Study 1* (Corsica, Sassafras) and *Column Study 2* (Corsica, Sassafras, Evesboro, Matapeake) were typical of the cropland in Delaware that receives PL applications. Soils were moderately acidic (pH 5.1-6.4), with low to moderate organic matter contents (1.6-4.4%) and varied in texture from sandy loam (Evesboro, Corsica, and Sassafras) to silt loam (Matapeake) (Table 2.5). Total As concentrations were relatively low, ranging from 0.7 to 9.5 mg kg^{-1} As. Arsenic in natural environments typically occur at an average concentration of 5 to 6 mg kg^{-1} (Peterson et al., 1981), and uncontaminated soils rarely exceed 10 mg kg^{-1} As (Adriano,

Table 2.5. Chemical and physical properties of four Delaware topsoils (0-20 cm depth) used in two greenhouse column studies investigating the effects of PL applications on As leaching.

Soil Property	Corsica	Evesboro	Matapeake	Sassafras
pH	5.7	5.4	6.4	5.1
OM (%)	4.4	2.0	2.4	1.6
Sand (%)	59	74	17	67
Silt (%)	27	14	61	16
Clay (%)	14	12	22	17
USDA Soil Texture	Sandy Loam	Sandy Loam	Silt Loam	Sandy Loam
<u>As (mg kg⁻¹)</u>				
Total As	0.7	1.5	9.5	3.7
TCLP As	0.04	0.40	0.58	0.08
M3 As	0.45	0.58	1.04	0.75
As sorption maxima	222	130	238	156
<u>Mehlich 3 (mg kg⁻¹)</u>				
P	186	216	218	98
Al	796	744	713	624
Fe	130	154	305	193

2001). The TCLP and M3 As concentrations were also very low for each of the soils used in the column studies compared to USEPA criteria for contaminated soils. Based on As sorption maxima, the finer-textured Matapeake soil, and the high OM Corsica soil with high M3-Al concentrations would be expected to retain more As leaching from PL than the sandy, low OM Evesboro and Sassafras soils.

Arsenic Leaching Experiments

The leaching method used in *Column Study 1* resulted in very uniform leachate volumes for all treatments and for the two soils (Figure 2.2). For example, for the Corsica soil, the mean values for leachate volumes collected for the six PL rates (0, 4.5, 9, 13.5, 18, and 22.5 Mg ha⁻¹) during the 24 leaching events were 87, 90, 93, 95, 106, and 100 mL, respectively. Mean leachate volumes for the same litter rates in the Sassafras sandy loam were 86, 89, 81, 94, 83, and 96 mL, respectively. Achieving reasonable uniformity in leachate volume between soils and across litter rates is necessary for comparisons of leachate As concentrations because extreme variations in leachate volume could dilute or concentrate As in the leachate.

Arsenic concentrations in the first seven leachates from the Corsica and Sassafras soil columns (total soil As = 2.1 and 5.4 mg kg⁻¹, respectively) averaged 8 and 6 µg L⁻¹, respectively, prior to the application of PL containing 43.5 mg As kg⁻¹. The influence of PL application rate on leachate As concentrations from these two soils in the next 16 leaching events is shown in Figure 2.3 for soil columns with no edge flow and Figure A-1 for all soil columns.

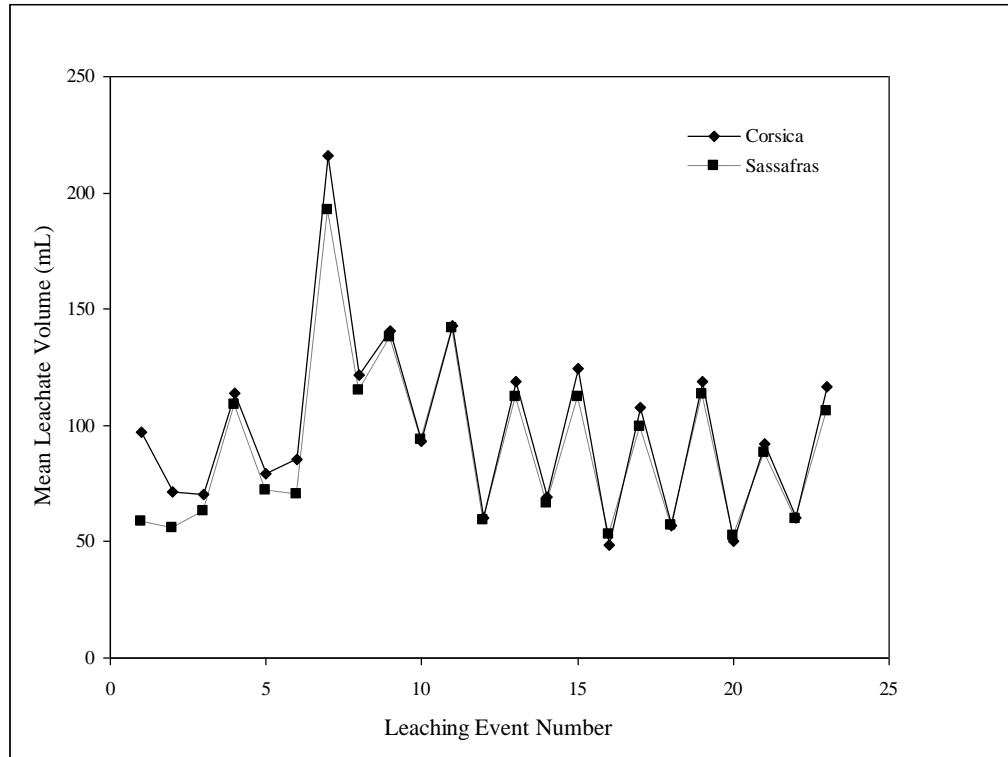


Figure 2.2. Mean volumes of leachate collected for Corsica and Sassafras soil columns used in *Column Study 1*.

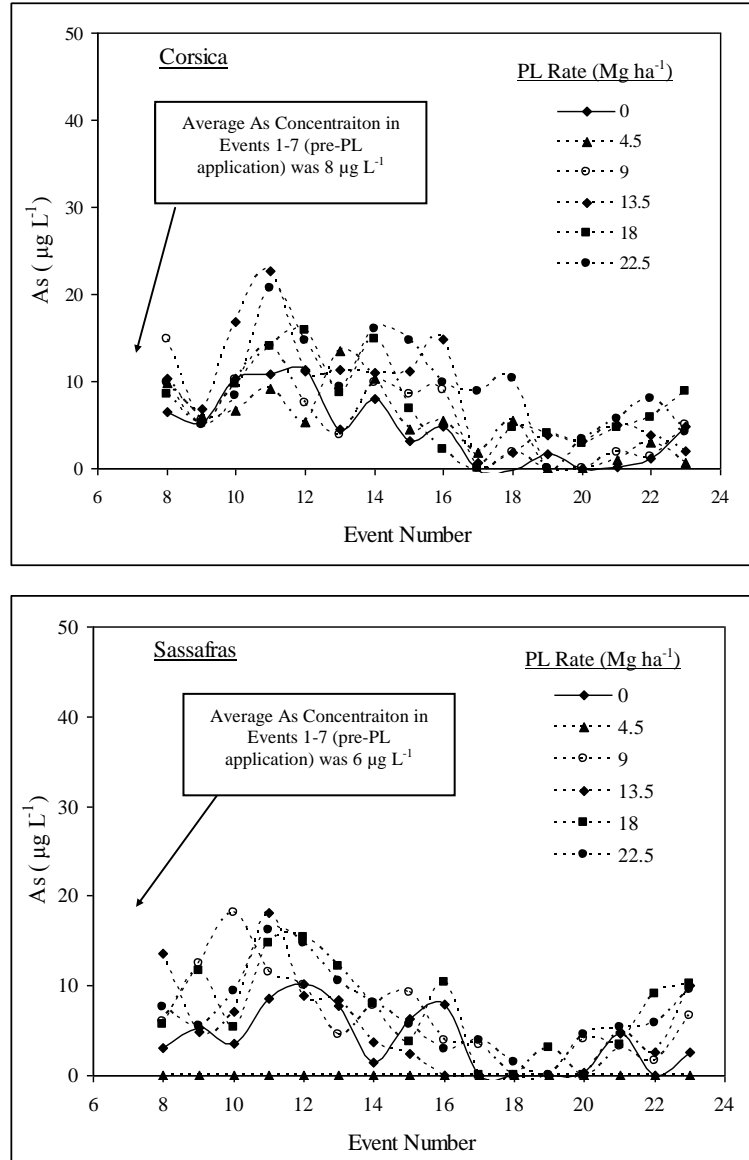


Figure 2.3. Effect of PL application rate on total dissolved As concentrations in leachate from the Corsica and Sassafras soils during *Column Study 1*.

The results of *Column Study 1* revealed that preferential flow existed in several of the columns. Even though leaching water was applied slowly in increments of 10 mL, it was apparent that some edge flow occurred in a few columns. Leachates dark in color were observed indicating the leaching events that resulted in preferential flow. For those treated columns in which preferential flow occurred, As concentration was much higher ($297.28 \mu\text{g L}^{-1}$) in comparison to those treated columns without preferential flow (non-detect). Soils used in both of the column studies had high affinities to adsorb As during the batch As isotherms. Therefore, As leachability is low from the soil itself; however, in the event of heavy precipitation events or PL application onto a soil with high macropore flow, the As concentration in leachate and runoff water would be much higher.

The general trend observed (with no edge flow included for the Sassafras soil) was for PL to cause little change or to slightly elevate As concentrations in leachate from the litter-amended soils relative to the control soils. However, statistical analyses of soil column leachate data showed that PL applications only resulted in significant increases in leachate As concentrations from the Corsica soil during leaching events 11 ($P < 0.05$), 17, and 18 ($P < 0.10$) (Figure 2.3). The only significant increase in leachate As concentration for the Sassafras soil occurred in event 8, immediately after litter application. The total mass of As leached, expressed on an aerial basis (no edge flow), during *Column Study 1* ranged from 4 to 9 g As ha⁻¹ for the Corsica soil and from 3 to 6 g As ha⁻¹ for the Sassafras soil; in all cases this amount of As leached was <1% of the total litter As added to these soils. If the Sassafras soil columns where edge flow apparently occurred were included, the mass of As leached ranged from 3 to 35 g As ha⁻¹ and the percentage of

added PL As leached varied from 2.3 to 8.9%. Pirani et al. (2006) conducted a leaching study utilizing two rates of PL, 5.6 and 11.2 Mg ha⁻¹, for two years. The soils in their study had total As concentrations of 2.7 to 5.1 mg kg⁻¹, similar to the Corsica and Sassafras soils used in *Column Study 1* (0.7 and 3.7 mg kg⁻¹). In their study, the total As concentration of the PL used in years 1 and 2 were 27 and 20.8 mg kg⁻¹, respectively. Pirani et al. (2006) also found no significant difference in As leaching between the control and litter treatments or between each year; however, during the first year a small spike in As concentration in the leachate of the high-litter treatment was observed that was associated with an increase in dissolved organic carbon (DOC) and a decrease in pH. They suggested that the increased DOC and the acidity of the leachate could have been responsible for the increased As solubility. As with the experiments conducted by Pirani et al. (2006), slight spikes in As concentration in the leachate water were experienced (no edge flow) during leaching events 11, 17, and 18. It is possible that these small spikes could be associated with an increase in DOC and decrease in pH making the As more readily available. However, as these parameters were not analyzed for throughout the experiments it is not possible to definitively attribute the As in the leachate to DOC and pH. This does suggest further research on the relationship between DOC and As in leaching situations is warranted.

Litter applications increased TCLP-As slightly in the 0-5 cm depth of soils collected from the columns at the end of the study, from 0.01 mg kg⁻¹ in the control soils to 0.32 mg kg⁻¹ in the Corsica soil and 0.12 mg kg⁻¹ to 0.21 mg kg⁻¹ in the Sassafras soil (Table 2.6). These TCLP values were well below the USEPA standard (100 mg TCLP-

Table 2.6. Results of TCLP-As extractions on post-column study soil samples collected from 0-5 cm depth sections from soil columns of *Column Study 1*.

Soil and Poultry Litter Rate	TCLP-As
Mg ha ⁻¹	mg kg ⁻¹
Corsica	
0.0	0.01
4.5	0.11
9.0	0.11
13.5	0.11
18.0	0.24
22.5	0.32
Sassafras	
0.0	0.12
4.5	0.15
9.0	0.09
13.5	0.13
18.0	0.21
22.5	0.16

As kg^{-1}) and similar to values observed in agricultural crop land and forested soils from Cooperator and UD farms (Table 2.2, 2.3, 2.4).

As observed in *Column Study 1*, leachate volumes were very consistent between soils and the two PL rates in all events in *Column Study 2* (Figure 2.4). Mean leachate volumes for each PL rate (0 and 9 Mg ha^{-1}) were 124 and 126 mL, respectively, for Evesboro, 117 and 126 mL, respectively, for Corsica, 116 and 119 mL, respectively, for Matapeake, and 109 and 127 mL, respectively, for Sassafras (overall average leachate volume = 123 ± 28 mL). Arsenic concentrations in column leachate also exhibited similar trends as in *Column Study 1* (Figure 2.5). Preferential flow was eliminated by using the IV bags with the exception of one replication of the Matapeake 9 Mg ha^{-1} leachate during leaching event 10. For the Corsica, Sassafras, and Evesboro soils, leachate As concentrations were always less than $20 \mu\text{g L}^{-1}$ while slightly higher concentrations ($20 - 30 \mu\text{g L}^{-1}$) were observed with the Matapeake soil which had the highest soil total As concentration in *Column Study 2* ($9.5 \text{ mg As kg}^{-1}$; Table 2.5). However, there were no statistically significant increases in leachate As concentrations in any event for any of the four soils in *Column Study 2* due to the application of 9 Mg ha^{-1} of PL. The total mass of As leached averaged 3, 4, 5, and 14 g As ha^{-1} for the Corsica, Sassafras, Evesboro, and Matapeake soils, respectively, and was not affected by PL application.

TCLP-As in the 0-5 cm sections of the soil columns was also measured at the completion of *Column Study 2*. TCLP-As values in the 0-5 cm section for the Evesboro soil remained the same (0.2 mg kg^{-1}) between the two treatment rates 0 Mg ha^{-1} and 9 Mg ha^{-1} .

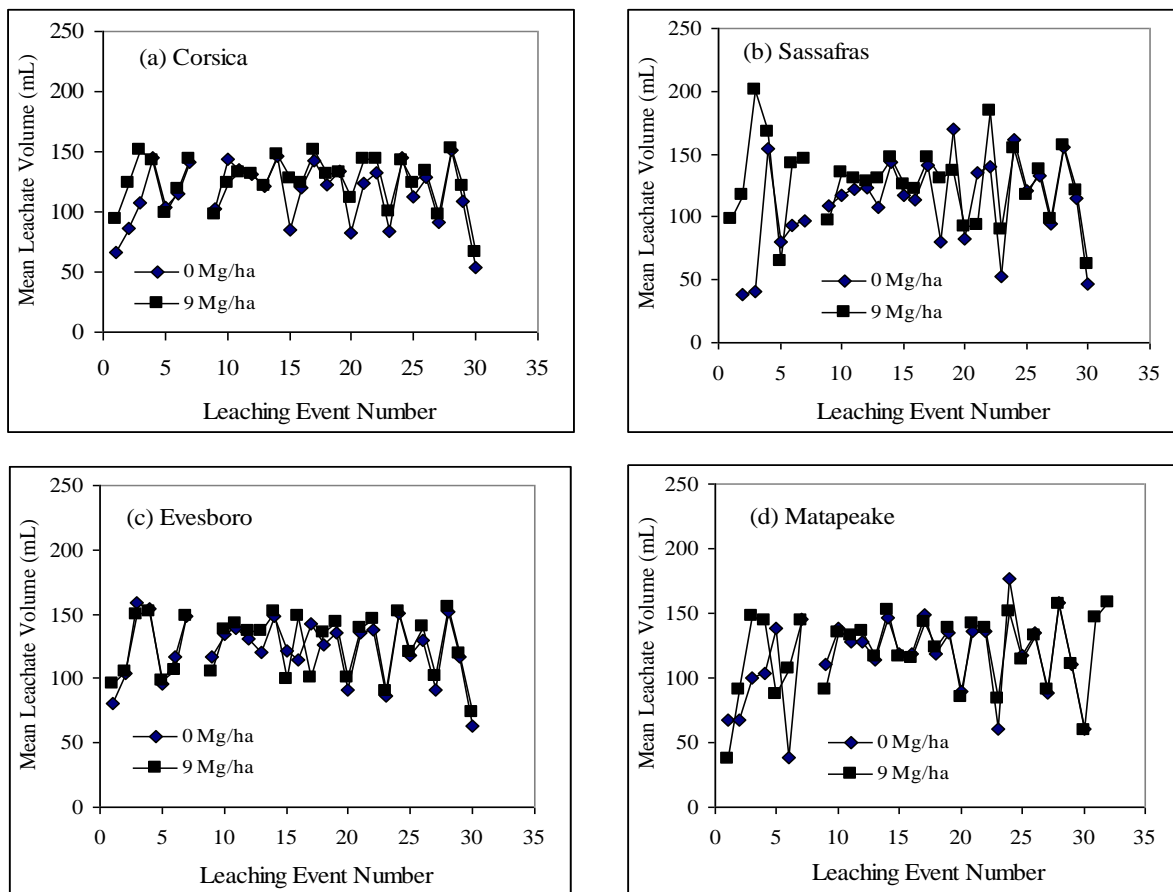


Figure 2.4. Mean leachate volumes for the four soils used in *Column Study 2* to evaluate the effects of PL on As leaching. Values are averages of all litter rates for each leaching event.

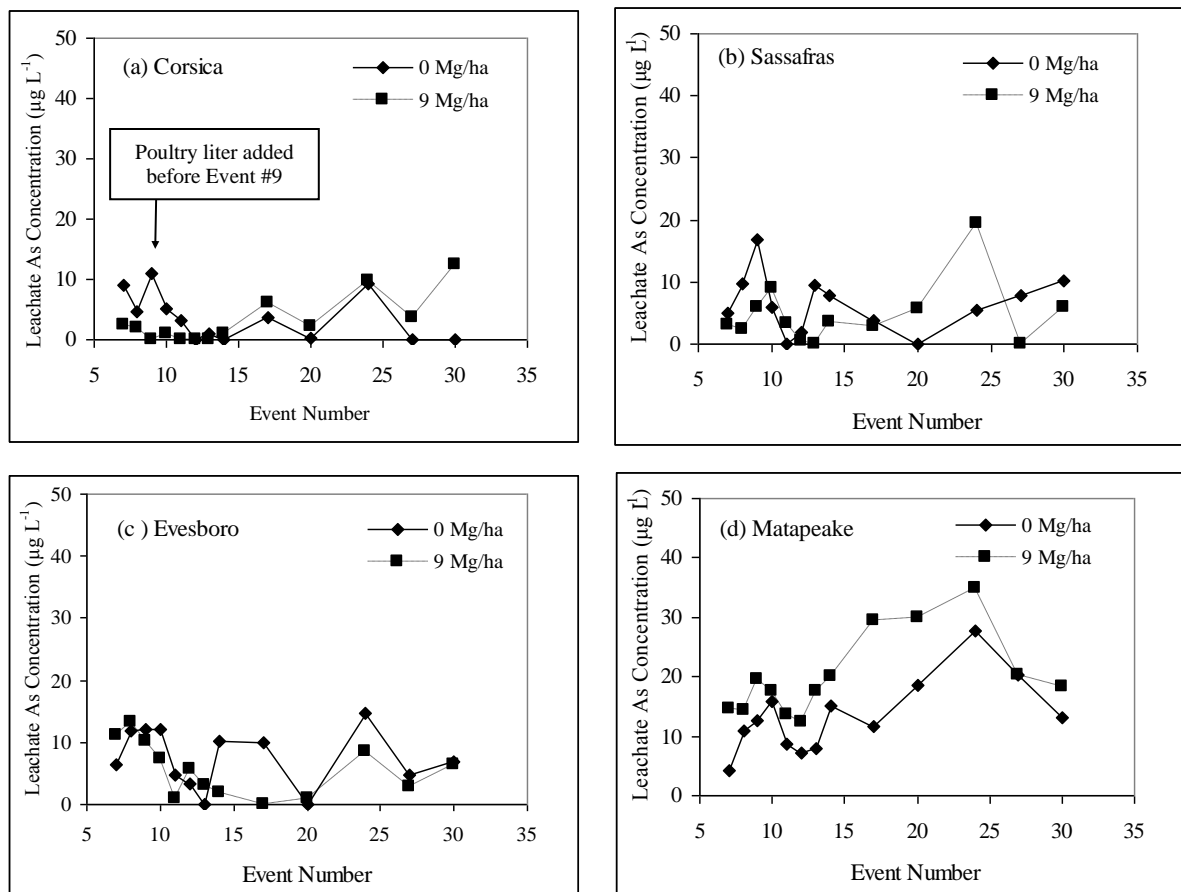


Figure 2.5. Effect of PL application at 9 Mg ha^{-1} on total dissolved As concentrations in leachate from the (a) Corsica, (b) Sassafras, (c) Evesboro, and (d) Matapeake soils during *Column Study 2*.

ha⁻¹ and decreased from 0.3 mg kg⁻¹ to 0.2 mg kg⁻¹, respectively, in the Corsica soil. The TCLP-As values in the 0-5 cm section for the Matapeake and Sassafras soils increased 0.1 mg kg⁻¹ between the treatment rates (0.4 mg kg⁻¹ to 0.5 mg kg⁻¹ for Matapeake; 0.3 mg kg⁻¹ to 0.4 mg kg⁻¹ for Sassafras). These TCLP values again were well below the USEPA standard (100 mg TCLP-As kg⁻¹) and similar to values observed during Column Study 1 and values obtained from Cooperator and UD farms (Table 2.2, 2.3, 2.4).

As noted in *Column Study 1*, it appears likely that any dissolved As released from the PL was rapidly sorbed by these soils, absent any type of bypass flow. Measured As sorption maxima for the four soils used in *Column Study 1* and 2 ranged from 130 to 238 mg kg⁻¹ (Table 2.5), equivalent to 309 to 533 kg As ha⁻¹, which is orders of magnitude greater than the amount of total As added from the PL during the column studies (194 to 978 g As ha⁻¹ for litter rates of 4.5 to 22.5 Mg ha⁻¹).

Effects of Alum on Arsenic Chemical Phases, Solubility, and Bioavailability in Poultry Litter

Water soluble, Mehlich 3, TCLP, PBET, and sequential fractionation extractions were conducted on the PL used in the two column leaching experiments as well as nine alum-treated litters and seven non-alum-treated (control) litters. Multiple PLs were selected to evaluate the extractable phases of As, determine if the alum influenced As extractability in PL, and determine if alum could be used as a best management practice to permanently decrease As solubility by converting it to forms that are stable in the soil environment As. Total As concentrations of the PLs ranged from 36 to 50 mg kg⁻¹ As for

the control litters and 36 to 49 mg kg⁻¹ As for the alum-treated litters; mean total As concentrations for the column study litter, control litters, and alum-treated litters were 43.5, 42.7, and 43.1 mg kg⁻¹ As, respectively (Table 2.7). Mean water soluble As for the column study litter, control litters, and alum-treated litters was 35.9 (82.5%), 18.1 (42.5%), and 9.1 mg kg⁻¹ (21.1%) As, respectively. Sims and Luka-McCafferty (2002) found that the average water soluble As was 19 mg kg⁻¹ for the untreated PL samples and 7 mg kg⁻¹ for the alum-treated PL samples, which is consistent with these results. Not only are the results consistent, but it can also be seen that long-term storage of the PL has not affected the water solubility of the As. Three previously conducted studies revealed slightly different percentages of the total As in PL was water soluble; 72% (Jackson and Miller, 1999), 71% (Jackson and Bertsh, 2001), and 70-90% (Garbarino et al., 2003). Even though these values vary slightly, there is still a common trend between them all that the As in PL is highly water soluble making it a concern to possibly leach into groundwater or to runoff into surface waters.

The sequential fractionation method of Fendorf et al.(2004), was used to characterize the forms of As in the control and the alum-treated litters. Results showed that the easily exchangeable portion significantly decreased and the residual portion significantly increased in the alum-treated litters compared to the control litters (Table 2.6). The amorphous oxide and crystalline/recalcitrant As phases were also slightly higher in the alum-treated litter. This suggests that treating PL with alum causes changes in the chemical species of As present, converting it to more recalcitrant forms that should

Table 2.7. Comparison of As forms and solubility in unamended and alum-treated PLs collected in the study of Sims and Luka-McCafferty (2002).

Sample ID	Total	Water	M3	TCLP	Arsenic				
					PBET	MgSO ₄	AmOx	HCl	Residual
					mg kg ⁻¹				
Column Study Litter	43.5	35.9	28.0	39.1	31.2	29.8	0.2	4.9	8.7
% of Total As		82.5	64.2	89.8	71.8	68.4	0.4	11.1	20.0
<u>Control Litters</u>									
516	50.0	16.0	26.8	29.3	23.8	20.8	0.5	6.6	22.1
528	36.0	12.0	17.9	23.1	18.7	15.2	0.4	5.4	14.9
534	41.0	15.0	25.0	29.6	22.9	17.3	0.3	5.3	18.1
570	45.0	19.0	29.5	35.7	26.2	24.2	0.4	4.3	16.1
581	43.0	24.0	24.7	33.5	26.9	24.0	0.2	3.5	15.3
582	42.0	24.0	22.2	28.1	22.2	20.5	0.4	3.9	17.2
599	42.0	17.0	24.1	29.4	22.5	23.8	0.3	4.9	13.0
Mean	42.7	18.1	24.3	29.8	23.3	20.8	0.4	4.8	16.7
Standard Deviation	4.2	4.5	3.6	4.0	2.7	3.5	0.1	1.0	2.9
% of Total As		42.5	56.9	69.8	54.6	48.8	0.8	11.3	39.1
<u>Alum-treated Litters</u>									
132	44.0	9.0	16.6	15.9	19.0	8.1	1.4	3.9	30.6
133	43.0	8.0	16.3	17.5	18.5	8.8	1.4	4.7	28.0
148	49.0	15.0	23.4	25.9	26.6	14.3	1.7	5.4	27.6
149	48.0	14.0	24.8	24.2	24.4	14.2	1.0	4.8	28.0
172	43.0	14.0	14.9	16.9	18.5	8.3	1.6	5.1	27.9
178	36.0	5.0	13.3	12.1	14.9	6.7	0.7	4.0	24.5
182	38.0	5.0	11.6	15.8	18.0	7.6	2.1	5.3	23.0
183	45.0	9.0	19.8	15.9	18.0	10.7	1.1	5.6	27.7
199	42.0	3.0	14.4	14.7	19.7	9.6	1.7	12.9	17.8
Mean	43.1	9.1	17.2	17.6	19.7	9.8	1.4	5.7	26.1
Standard Deviation	4.2	4.4	4.5	4.5	3.5	2.8	0.4	2.7	3.8
% of Total As		21.1	39.9	40.9	45.8	22.8	3.3	13.3	60.6

have a lower risk of loss to ground and surface waters; however, more advanced speciation methods (e.g., EXAFS) would be required to confirm the exact As species formed when alum is added to PL, as this has previously been conducted with P. Peak et al. (2002) found that phosphate was bound to aluminum oxides in alum-treated PL. It is expected that As would sorb to similar sites in PL when treated with alum, due to the similar reactivity of As and P.

Fendorf et al. (2004) developed the PBET method to give information on the reactive nature of contaminants and to allow a relationship between common procedures and bioaccessibility to be developed. When comparing the results between the Mehlich 3 and PBET extractions conducted on the PLs, a strong relationship can be seen. The r^2 -values for the relationships between M3-As and PBET-As were 0.69*** and 0.68*** for the control and alum-treated litters respectively. The same trend in r^2 -values was seen PBET-As is compared to MgSO_4 extractable As ($r^2 = 0.65$ and 0.86 , respectively). This indicates that the PBET method results correlate well with the plant available and easily exchangeable As in these unamended and alum treated litters.

Conclusions

Total As concentrations of the 86 agricultural and forested soils (surface and subsoil samples) averaged $4.7 \pm 3.5 \text{ mg kg}^{-1}$, and only five percent of the samples collected had total As concentrations greater than the 11 mg kg^{-1} background concentration established by DNREC for As. However, based on soil test P values for two of these soils (Sassafras and Corsica) that were selected for the column studies, these farms were likely to have

received only moderate application of PL. Thus, it is probable that many soils in Delaware have higher As concentrations due to PL application than those sampled.

During the column studies it became evident that the As in PL was highly water soluble resulting in a high potential for As to enter surface waters during high intensity rainfall events. The soils utilized in the column studies exhibited a high affinity for As sorption; however, previous research has shown that P is preferentially sorbed before As when P is present in much higher concentrations of As, which is the scenario during PL application in soils. This soil process may contribute to As release.

Macropore flow was also observed during the column studies, which revealed that As could leach directly into the groundwater via macropore flow (cracks, root channels, worm holes, etc.).

During the evaluation of alum, it became apparent that alum reacts with the As in the PL and forms more recalcitrant As compounds within the PL. Based on these results, alum could be utilized as a best management practice for PL to reduce the risk of As loss to ground and surface waters. While discontinuing the use of ROX would eliminate the incorporations of PL with high As concentrations onto agricultural land, it is highly unlikely that ROX would be banned. Therefore, it is imperative that best management practices (BMPs) be utilized when handling, storing, or applying PL.

While several conclusions can be made through this research study, additional questions have developed, such as: i) more advanced speciation methods (i.e., EXAFS) should be used to confirm exact As species that are formed when alum is added to PL and

ii) additional parameters (i.e., DOC and pH) should be measured throughout the column study to evaluate the effects of these parameters on As leaching.

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CHAPTER 3

EVALUATING LECHABILITY AND BIOAVAILABILITY OF ARSENIC IN CONTAMINATED TANNERY SOILS

Introduction

The City of Wilmington has been known historically for tannery operations. Starting in 2001, the Delaware Department of Natural Resources and Environmental Control (DNREC) began a tannery site initiative with the purpose to identify sites with a potential for soil and groundwater contamination from former tannery and hide processing operations. Historical sources (such as Sanborn fire insurance maps) were utilized to identify numerous former tannery sites, which were grouped into 52 “tannery complexes” by DNREC. The 52 “tannery complexes” consisted of over 400 individual parcels, which were mostly covered with buildings and/or parking lots (DNREC, 2002); however, many tanneries were found to lie near the Christina River.

The tanning industry was established in Wilmington, Delaware as early as 1845; and the sumac process (a mixture of leaves and bark from trees crushed and mixed into a paste and applied to the hides) was used until the 1890’s. However, during the 1890’s, automated machinery was introduced into the tannery operations as well as chemicals containing arsenic (As). Tanneries were a major industry in Wilmington, Delaware until

the 1950's when operation numbers began to decline; however, several were identified on Sanborn maps through the 1960's (DNREC, 2001).

The tannery process involved the use of strong chemical solutions containing As, which were used to de-hair hides and for dyeing purposes. Hides were soaked in vats of an As solution known as realgar (AsS , As_2S_2 , As_4S_4) and scraped by hand to remove the hair. Sodium arsenate (Na_2HAsO_4) was also used during the dyeing of hides to prevent discoloration of white portions (Thorp, 1909). Facilities in which these operations were carried out in were typically labeled as “beam houses,” in which hides were draped over beams to dry, and are identifiable on historic Sanborn maps. Chromium (Cr) salts were also used to finish the hides; therefore, both As and Cr are contaminants of concern in historical tannery sites (DNREC, 2002).

Realgar occurs in nature in small quantities and is a brilliant red mineral, which can be used as a pigment when ground. It was used primarily for dehairing hides due to its inability to be mixed with other colors and a tendency to fade upon exposure to light as a dye. Sodium arsenate is a man-made compound that was used in dyeing alizarins and in calico printing to prevent discoloration of the white parts of a pattern so that other colors did not diffuse in the white portions (Thorp, 1909).

Even though tannery operations were distributed worldwide, few articles have been published concerning As contamination from tanneries. Sadler et al. (1994) reported that a formulation of 650 g L^{-1} sodium arsenite was used as the active ingredient for an historical tannery in Queensland, Australia; however, other unregistered chemicals may have been used. It is known that sodium arsenite was used extensively at tannery

sites and has been shown to be fairly mobile in sandy soils (Tammes and deLint, 1969). Sadler et al. (1994) collected soil samples from a site that was previously used as a waste disposal site for a tannery and used the Toxicity Characteristic Leaching Procedure (TCLP) to assess potential As mobility; however, a distilled water solution at a pH of 7.0 was used instead of the TCLP solution, which has a pH of 4.9. The reasoning for this was that the soil in the area from which the samples were collected would be leached with rainwater instead of acidic leachate found in landfills and because As species are more mobile at pH 7.0 rather than pH 4.9. Sadler found that there was an inverse relationship between total As concentration and leachability, with the greatest mobility occurring in samples with the lowest total As concentrations.

The decades of tannery operation in Wilmington has led to serious concerns about soil and groundwater contamination in this highly populated urban area located on the banks of the Christina River. Today, the sites of several of these former tanneries are proposed to undergo redevelopment, which has caused concerns to arise over public and worker safety. Little research has been previously conducted on tannery soils; therefore, it is important to better understand the characteristics and behavior of As in soils from these locations. As such, the objectives of this research were to: i) characterize and evaluate the relationship between total, leachable, bioavailable, and chemical phase As concentrations in historic tannery soils, and ii) correlate the solubility and bioavailability to the chemical phases of As in historic tannery soils and how this information may be used for remediation projects.

Methodology

Soil samples from a tannery site which lies along South Market Street in Wilmington, Delaware were provided by DNREC. Samples were collected at varying depths from the surface to 2.9 m below ground surface using a geoprobe and advancing test pits. Samples were air dried, ground, and sieved to pass through a 2mm sieve. It is important to note that information provided by DNREC and observations made during sampling and of soils in the laboratory indicated that many of the urban “soil” samples collected were not true soils but were mixtures of the original soil and some type of fill material or in some cases were primarily fill material, including small pebbles, glass, concrete, and asphalt. A hydrocarbon odor was also noted in some of the samples during sample preparation. A 1921 Sanborn fire insurance map was also utilized to research the location of the historical tannery and depicts the orientation of the “beam house” (Figure A-2). Samples were analyzed for organic matter, pH, total elemental (As, Al, B, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn) content (USEPA Method 3051; USEPA, 1994), Mehlich 3 [(M3): $0.2\text{ M CH}_3\text{COOH} + 0.25\text{ M NH}_4\text{NO}_3 + 0.015\text{ M NH}_4\text{F} + 0.13\text{ M HNO}_3 + 0.001\text{ M EDTA}$] extractable elements (As, Al, B, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn; Mehlich, 1984), for easily leachable As by the Toxicity Characteristic Leaching Procedure (TCLP; USEPA Method 1311; USEPA, 1992), for bioavailable As by the Physiologically Based Extraction Test (PBET; Fendorf et al., 2004), and Sequential Fractionation (Fendorf et al., 2004) As. A discussion of each of these methods can be found in Chapter 2.

Results and Discussion

Soil Characterization

When comparing the elemental composition between the urban “soils” from old tannery sites and agricultural and forested topsoils in Delaware (Chapter 2), some clear differences are evident (Figure 3.1; Tables 3.1, A-4, A-5, A-6, and A-10). Total concentrations of Fe, K, Mn, and P were slightly higher in the urban soils than in the agricultural soils, and total concentrations of As, Ca, Cu, Mg, S, and Zn were much higher in the urban soils than in the agricultural soils. However, total concentrations of Al and B were lower in the urban soils than in the agricultural soils. The higher concentrations of Ca and Mg in the urban soils suggests that some type of alkaline fill material, such as coal ash, may be a major component of the soil profile at this site.

The pH of the urban soils (range 6.1 to 9.6, mean 7.96) was also higher than the pH of the agricultural soils (range 2.6 to 6.7, mean 5.6), which is consistent with the higher total Ca concentrations. The organic matter (OM) percentage in the urban soils (range 1.2 to 11.0, mean 3.56) was also higher than the OM percentage of the agricultural soils (range 0.1 to 7.4, mean 1.2); however, samples collected from lower depths (>1.0 m below ground surface) were higher in OM (range 2.7 to 11.0, mean 4.2) than samples collected from higher depths (<1.0 m below ground surface; range 1.2 to 2.8, mean 2.2), which is the inverse of what is found in agricultural settings. The higher OM also suggests that coal ash may have been used as a fill material within the deeper soils.

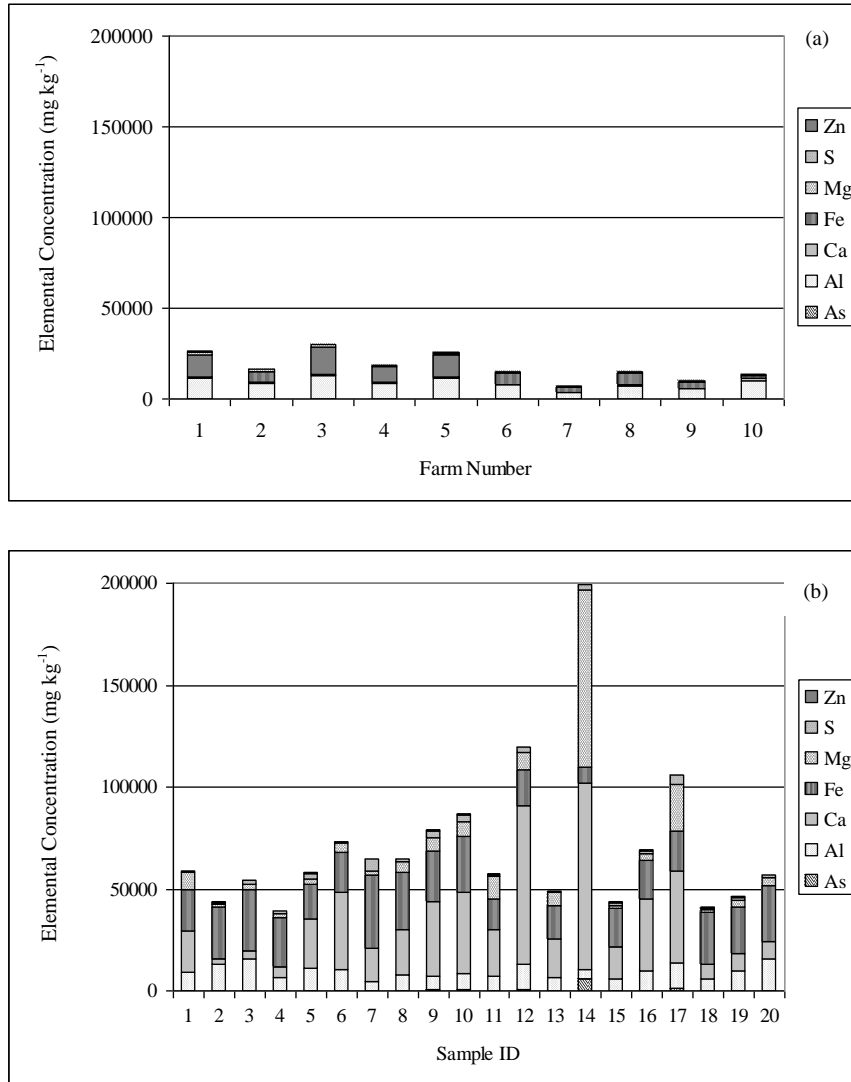


Figure 3.1. Comparison of total elemental composition of (a) agricultural soils in Sussex County, Delaware and (b) urban soils from Wilmington, Delaware.

Table 3.1. Arsenic status for 20 soils collected by DNREC staff in Wilmington, Delaware in a site investigation (South Market Street) for potential As contamination. These soil samples were collected with a geoprobe (GP) or from a test pit (TP).

Sample				DNREC	EPA 3051	TCLP	PBET	M3-	MgSO ₄	Am-Ox	HCl	Residual†
ID	Type	Point	Depth	XRF-As	Total As	As	As	As	As	As	As	As
m				mg kg ⁻¹								
1	GP	3	0-1.0	17.0	18	0.6	12	0.9	0.7	1.0	16.2	0.5
2	GP	3	1.6-1.8	83.6	34	0.4	3	1.7	0.0	1.8	29.2	2.5
3	GP	4	0-1.0	28.8	16	0.2	8	0.3	0.0	0.5	11.8	4.1
4	GP	4	1.8-2.7	13.9	10	0.3	2	0.7	0.5	1.3	0.2	8.0
5	GP	7	1.8-2.1	74.5	20	0.4	11	0.6	0.8	16	1.2	1.5
6	GP	8	0-1.3	27.9	19	0.4	2	0.3	0.6	0.3	5.6	12.7
7	GP	8	1.5-2.0	221	29	0.4	6	4.4	0.9	2.0	10.7	15.6
8	GP	12	0-1.3	60.1	20	0.2	11	0.9	0.4	1.0	15.5	2.7
9	GP	12	1.4-2.1	687	444	17	165	65	7.1	198	35	204
10	GP	12	1.4-2.1	554	496	17	187	70	7.3	216	32	241
11	GP	13	0.2-0.9	110.3	80	0.4	17	13	1.2	5.5	69.5	3.7
12	GP	13	1.3-1.9	956	756	16	141	42	9.3	152	39	556
13	GP	14	0-1.3	141	119	6.6	22	20	3.3	7.6	26.5	82
14	GP	14	2.4-2.9	6153	5760	688	4388	1386	484	1872	469	2935
15	TP	2	2.0-2.1	140	63	1.4	28	8.2	0.9	15	2.6	44
16	TP	3	2.3-2.4	322	57	0.0	23	3.3	0.5	22	5.6	29
17	TP	4	2.0-2.1	2433	1264	39	710	162	51	679	80	454
18	TP	7	2.1-2.3	51.3	42	0.3	13	2.1	1.1	16	2.3	23
19	TP	8	2.0-2.1	168	140	0.5	32	6.4	0.3	40	16	84
20	TP	10	1.5-1.8	35.8	42	0.0	15	3.4	0.9	17	2.4	21
Mean				614	471	39	290	90	29	163	44	236
Standard Deviation				1418	1286	153	978	308	108	432	103	654
% of Total As						8	61	19	6	35	9	50

Total As concentrations in the 20 soil samples collected from the historical tannery site in Wilmington, Delaware were highly variable and ranged from 10 mg kg⁻¹ to as high as 5760 mg kg⁻¹ (Table 3.1; mean=471 ± 1,286 mg kg⁻¹). For these urban sites, 95% of the soils exceeded the 11 mg kg⁻¹ As background level established by DNREC in 2005 and thus would require some form of risk assessment to determine the need for site remediation. A total As concentration of 40 mg kg⁻¹ was also identified by DNREC in 2005 as “...the concentration limit historically used for industrial sites as an action level and cleanup goal.” Out of the 20 historical tannery soils, 60% of the soils at this site had total As concentrations greater than 40 mg kg⁻¹; however, only 16% of the samples exceeding this action level were located within one meter of the soil surface.

Leachability – Toxicity Characteristic Leaching Procedure

The leachability of As in these urban soils was assessed by TCLP extraction, which has been developed by the USEPA to evaluate the potential for contaminant leaching into groundwater from landfills. The TCLP extraction concentrations varied from 0.0 to 688 mg kg⁻¹ As, with a mean of 39 mg kg⁻¹ (8%). Results showed that TCLP-As was significantly correlated ($r^2 = 0.92$) with total As but that only one of the 20 samples (GP 14, 2.4-2.9 meters below ground surface) exceeded the USEPA regulatory value (5 mg L⁻¹ or 100 mg kg⁻¹) (Table 3.1, Fig. 3.2). Dermatas et al. (2006) collected samples from a shooting range at 0 to 15 cm, 15 to 40 cm, and 40 to 55 cm below ground surface and found TCLP concentrations were 6.72, 8.26, and 0.02 mg L⁻¹ As, respectively, which correlated strongly ($r^2 = 0.93$) with the total As concentrations in the

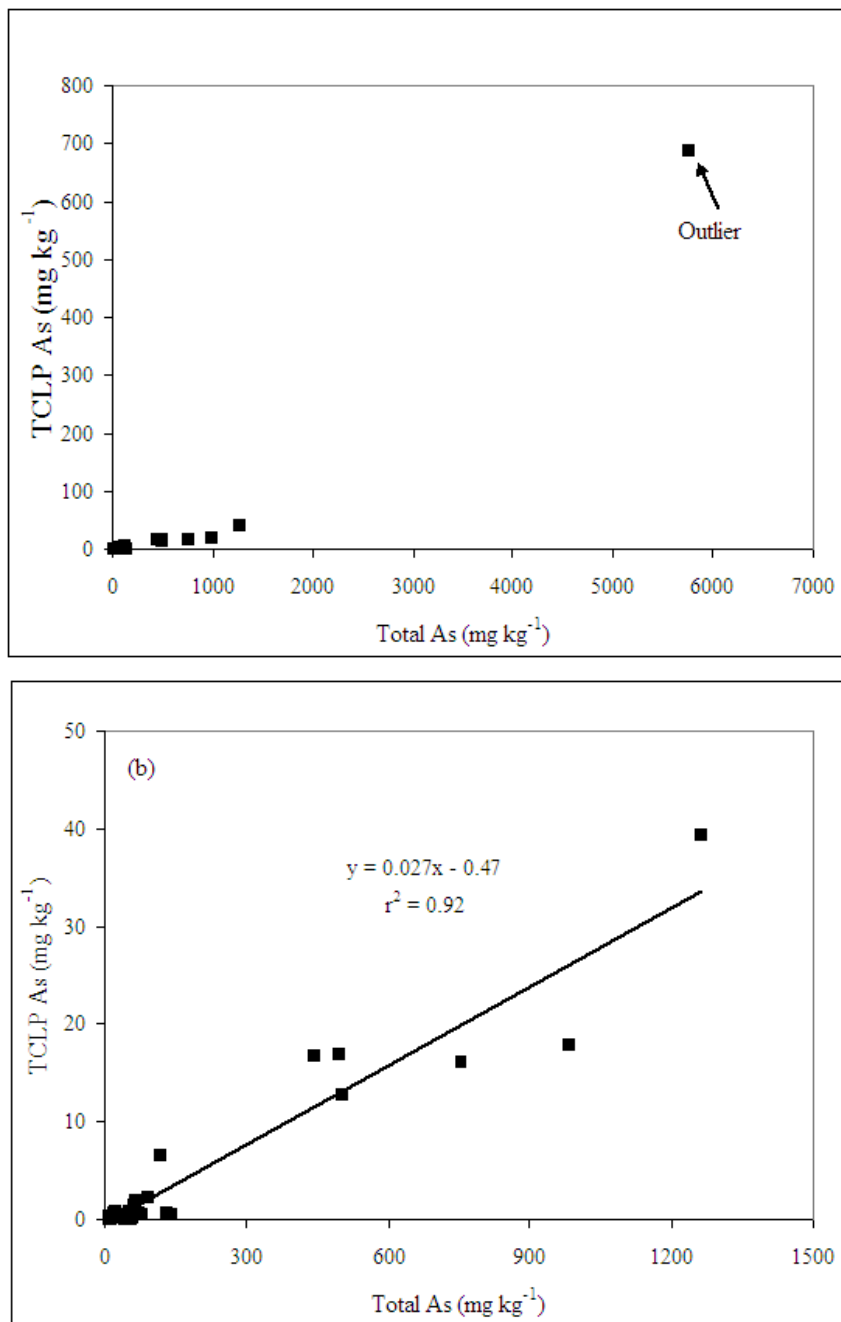


Figure 3.2. Relationship between total soil As and TCLP-As for (a) all urban soils collected in Wilmington, Delaware and (b) all soils excluding the one outlier identified in (a).

soils (1,057, 951, and 7.24 mg kg⁻¹, respectively). Devesa-Rey et al. (2008) reported that the TCLP extractions on sediment samples collected from the Anllóns River in Spain with a mean total As concentration of 75 mg kg⁻¹ (33 to 264 mg kg⁻¹) averaged 0.20 mg kg⁻¹ (0.07 to 0.39 mg kg⁻¹); however, no correlation data were provided by Devesa-Rey et al. (2008).

Based on the regression equation shown in Figure 3.2(b) (omitting one outlier shown in Fig. 3.2(a)), soil samples similar to those in this study with a total As value greater than approximately 5400 mg kg⁻¹ would be expected to exceed the USEPA TCLP-As limit (5 mg L⁻¹ or 100 mg kg⁻¹).

Bioavailability – Physiologically Based Extraction Test and Mehlich 3

Bioavailable forms of soil As (PBET and Mehlich 3) were significantly correlated with total soil As (Fig. 3.3 (a) and (b)). In some cases, M3-As concentrations were similar to values considered to be optimum for plant growth for the anionic plant nutrients phosphate and sulfate (optimum M3-P = 50 to 100 mg kg⁻¹ and M3-S = 8 to 10 mg kg⁻¹). Data on soil test As values associated with As uptake by plants are very limited and site specific; however, as an example, based on the regression equations in Fig 3.3(b), the total soil As values associated with M3-As ranges from 10 to 50 mg kg⁻¹ (similar to optimum soil concentrations for P and S) would be 93 and 426 mg total As kg⁻¹.¹ In a research project conducted by Peryea (2002) the total As concentrations and the M3-As concentrations also correlated well ($r^2 = 0.84$) on samples collected from an

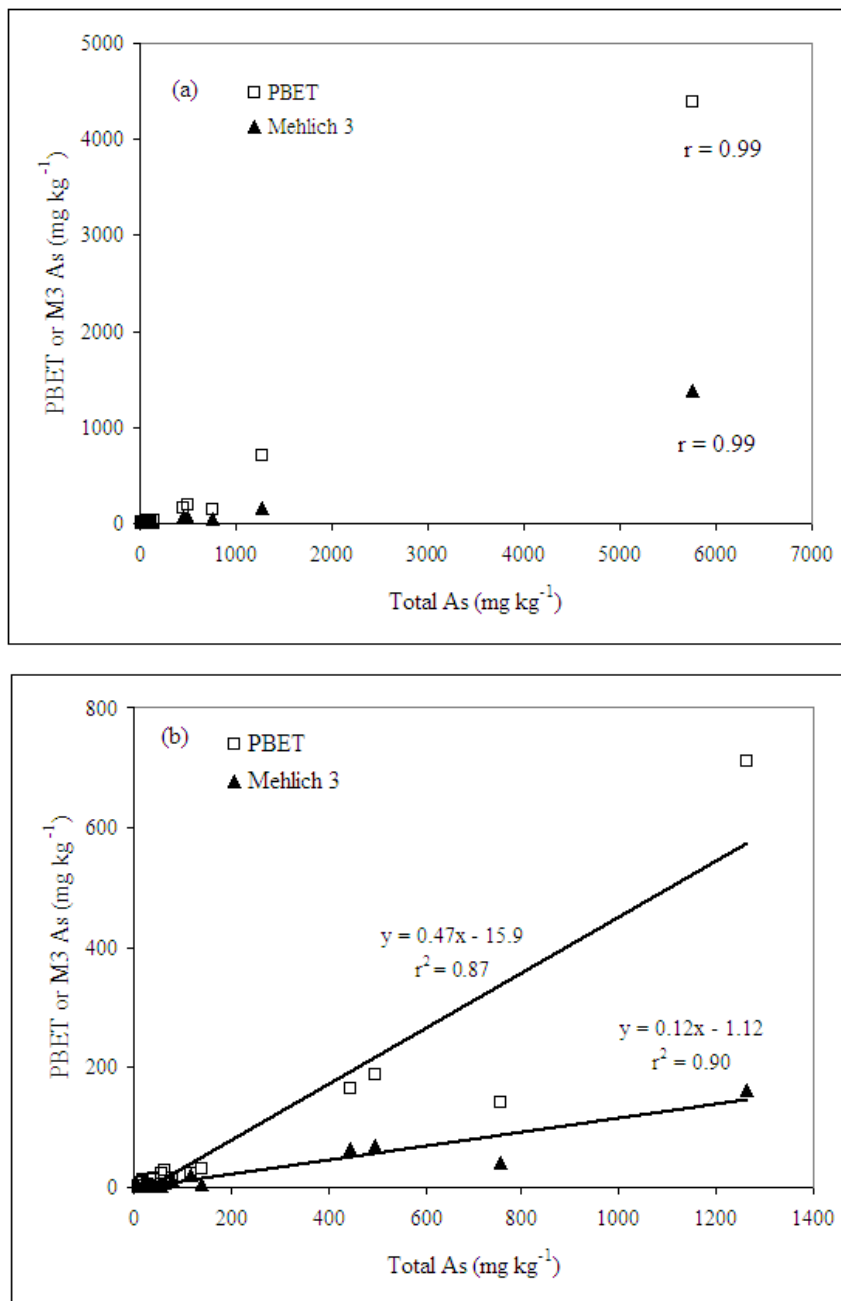


Figure 3.3. Relationship between total soil As and either PBET-As or Mehlich 3-As for (a) urban soils collected in Wilmington, Delaware and (b) all urban soils in (a), excluding one outlier with a total As concentration > 5,000 mg kg⁻¹.

apple orchard with historic use of lead arsenate.

The concentrations of the PBET As in these urban soils ranged from 2.0 to 4,388 mg kg⁻¹ with a mean of 290 mg kg⁻¹ (Table 3.1). The percentage of total As extracted by PBET ranged from 10% to 76% and averaged 61%, which is much greater than results reported by Devesa-Rey et al. (2008; 0.4 to 13.9 mg kg⁻¹; 1 to 11% of total As concentration) or Lombi et al. (2004; 235 mg kg⁻¹; 4.9% of total As concentration).

By utilizing the PBET data, it can be determined that up to 4.388 mg As could be absorbed by the human body for every one (1) g of soil incidentally ingested. According to the Ontario Ministry of the Environment (2001), sensitive individuals in exposed populations begin to display characteristics of As poisoning via oral intake at approximately 20 µg per kg of body weight per day (µg/kg/d). Therefore, human contact with soils with such high bioavailable-As concentrations, whether it be via dermal, inhalation, or ingestion, may be deadly.

Fendorf et al. (2004) utilized the PBET method to evaluate the bioaccessibility of As in contaminant-spiked soil samples that were incubated over a period of 400 days and reported that the greatest PBET-As concentrations were found during the first extraction with decreasing PBET-As concentrations thereafter. Fendorf et al. (2004) also stated that there is a limitation in bioaccessibility in that PBET concentrations are inversely proportional to ferric oxide content, which is consistent with the results for the GP-14 (2.4-2.9) sample. This sample had the highest concentration of total As (5,760 mg kg⁻¹), the highest PBET concentration (4,388 mg kg⁻¹; 76%), and the lowest total Fe concentration (7,816 mg kg⁻¹) of the urban soils utilized in this study. In the case where

total Fe concentration is lower, it can be expected that the extractability (leachable or bioavailable) would be greater as Fe oxides are primary sorption sites for As.

Correlations of Soluble and Bioavailable Arsenic with Chemical Phases

The range and variability of leachable and bioavailable As in these urban soils is undoubtedly due to the complexity in As speciation in the soils and fill materials at these sites. A relatively simple sequential chemical fractionation of the historic tannery soils was conducted using the method of Fendorf et al. (2004) to partition As into “easily exchangeable” ($\text{MgSO}_4\text{-As}$), “sorbed” (AmOx-As), and “recalcitrant” fractions. The difference between total As measured by the EPA3051 method and the sum of these three fractions represents residual soil As in extremely stable chemical forms. The general goal was to better characterize the variability in As phases in urban contaminated soils and to determine if there were any relationships between these chemical phases of As and soil chemical properties and leachable or bioavailable As. Consistent with the variability in total and soil test (M3) extractable elemental composition of these “soils”, the chemical fractionation results suggest complex As speciation and bioavailability at this site (Table 3.1, Figures 3.4, 3.5).

Mean As values (and percentage of total As in fraction) for the MgSO_4 , AmOx, HCl, and residual (difference between total As and sum of three fractions) pools were: $29 \pm 108 \text{ mg kg}^{-1}$ ($6 \pm 8\%$), $163 \pm 432 \text{ mg kg}^{-1}$ ($35 \pm 33\%$), $44 \pm 103 \text{ mg kg}^{-1}$ ($9 \pm 8\%$), and $236 \pm 654 \text{ mg kg}^{-1}$ ($50 \pm 51\%$). Despite this variability, closer examination of the

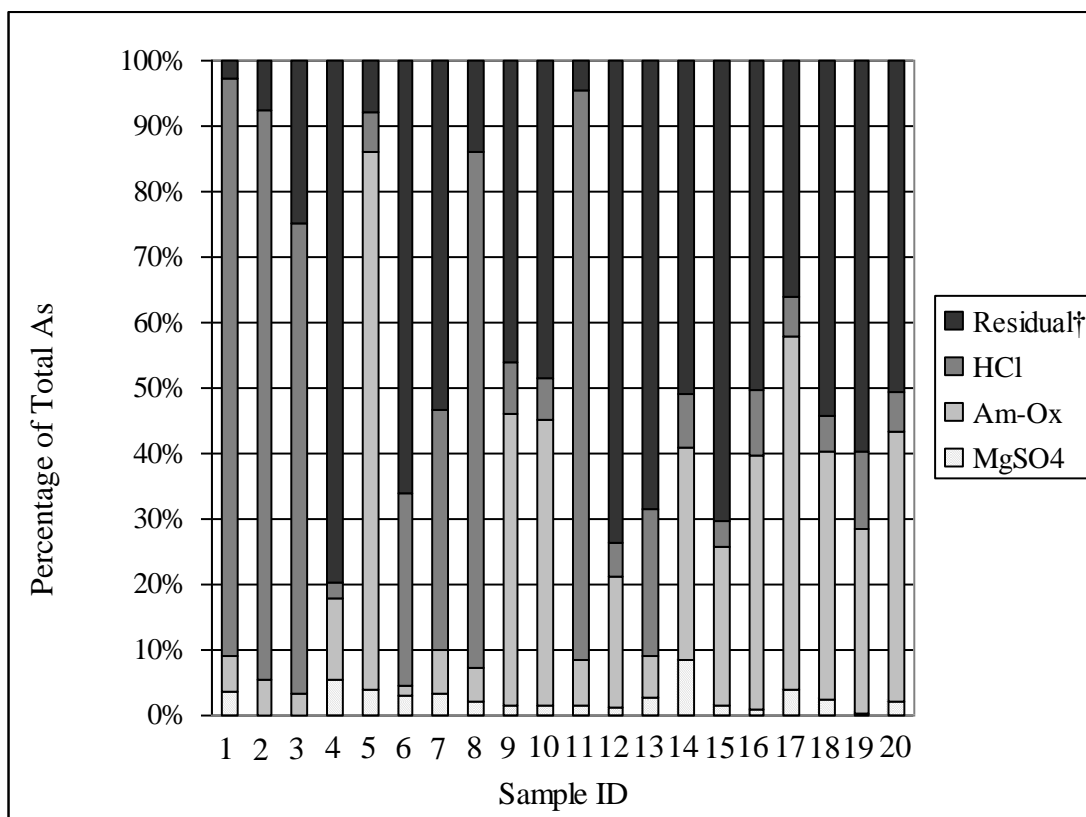


Figure 3.4. Sequential chemical fractionation of soil As for 20 soils collected from an urban contaminated site in Wilmington, Delaware. Soils are in shown in order of increasing total As (value on top of each bar) from left to right.

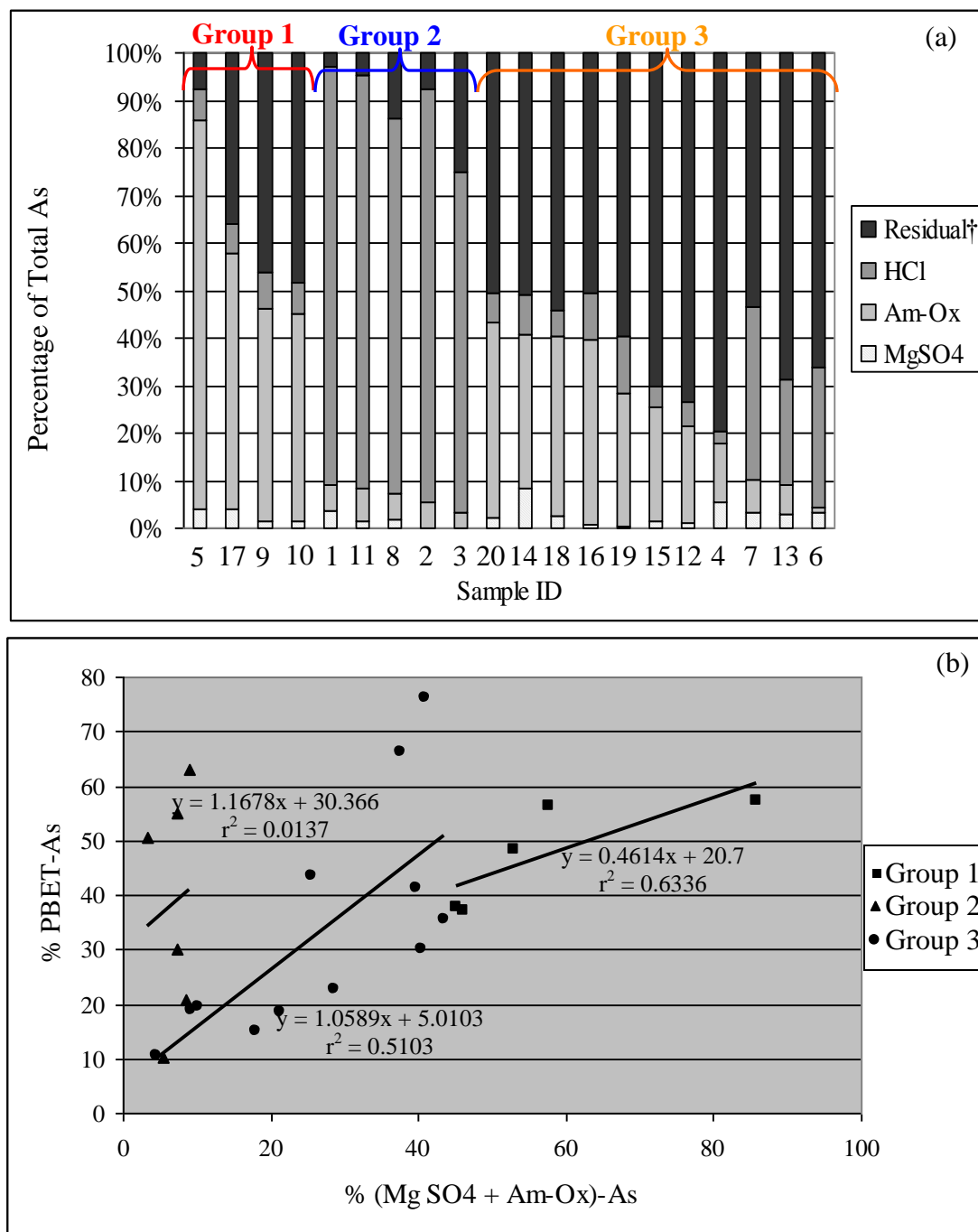


Figure 3.5. (a) Sequential fractionation of total As in 20 soils from an urban contaminated site in Wilmington, Delaware. Soils are presented, left to right, in designated groups and descending order of [MgSO₄+ AmOx]-As and (b) Relationship between the percentage of total As extracted by [MgSO₄+ AmOx] and the percentage of PBET-As in these 20 soils.

fractionation results showed three groups of soils at this site with clearly different trends in As phases (Fig. 3.5(a)). In the first group, most of the As that could be extracted was removed by MgSO_4 and AmOx ; for the second group most of the extractable As was in the HCl fraction; and for the third group, most of the As remained in the residual fraction. The variability in chemical properties within each of the three groups of soils (Table 3.1 and Table A-10) makes it difficult to draw any clear conclusions about the reasons for these differences in As fractionation although there was a slight trend for soils in Group #3 to have higher concentrations of organic matter, As, and Mg and slightly greater percentages of TCLP-As, PBET-As, and M3-As than soils in Groups #1 and #2 (Table 3.2). As would be expected, the percentage of total As in the MgSO_4 fraction (easily exchangeable) and TCLP-As were well correlated (Fig. 3.6; $r^2=0.56$). There was also a significant linear relationship, with similar slopes, between the percentage of total As in the two most labile fractions (% MgSO_4 -As + AmOx -As) and the percentage of PBET-As, when the data were split into three subsets (Fig. 3.5(b)). The relationship between % MgSO_4 -As + AmOx -As and % PBET-As for Group #2 ($r^2 = 0.01$) did not correlate as well as the data for Groups #1 and #3 ($r^2 = 0.63$ and $r^2 = 0.51$, respectively); however, this can be expected as approximately 85% of the total As is associated with the recalcitrant fraction (Table 3.2). Fendorf et al. (2004) reported that the exchangeable fraction (MgSO_4) was highly correlated with PBET concentrations ($r=0.98^{***}$ for A horizon soils and $r=0.98^{**}$ for B horizon soils). Unfortunately, chemical analyses provided no clear insight into the reasons for these separate linear relationships.

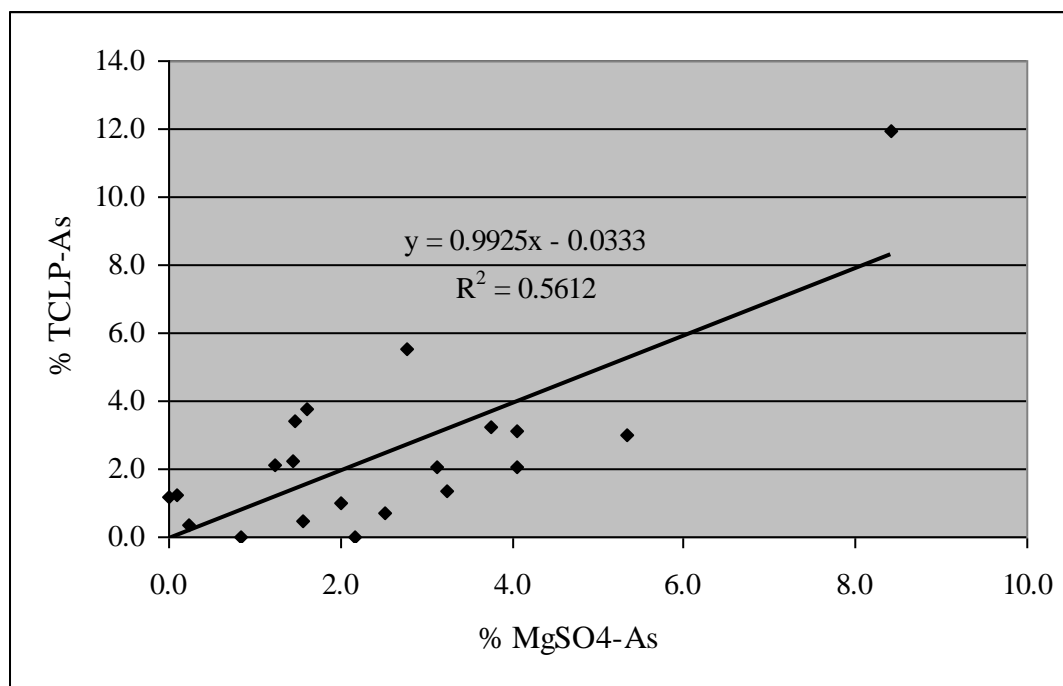


Figure 3.6. Relationship between the percentage of total As extracted by MgSO_4 and the percentage of TCLP-As in the 20 soils collected from an urban contaminated site in Wilmington, Delaware.

Table 3.2. Comparison of the mean chemical properties of three groups of urban soils from the South Market Street site that exhibited different trends in the distribution of As among three chemical fractions†

Soil Property	Group #1	Group #2	Group #3
<u>Percentage of Total As in fraction:</u>			
MgSO ₄	3.0	1.4	7.0
AmOx	50	6.0	30
HCl	7.0	85	8.0
Residual	40	8.0	54
pH	8.2	7.6	8.0
Organic Matter (%)	2.8	2.4	4.4
<u>Total (mg kg⁻¹)</u>			
As	556	34	640
Al	9,814	10,558	8,396
Fe	22,551	23,794	21,281
Ca	36,004	14,309	29,280
Mg	9,791	5,890	11,337
S	3,361	995	1,774
Cu	65	123	123
Zn	225	297	236
<u>Percentage of Total As Extracted by:</u>			
TCLP-As	3.0	1.1	10
PBET-As	48	30	66
M3-As	13	10	21

†Refer to Table 3.1 for detailed analyses of soils in Group 1 (Sample ID: 5, 9, 10, and 17), Group 2 (Sample ID: 1, 2, 3, 8, and 11), and Group 3 (Sample ID: 4, 6, 7, 12, 13, 14, 15, 16, 18, 19, and 20).

Conclusions

In summary, the urban soils provided by DNREC were not true soils and consisted of original soil, pebbles, glass, concrete, and asphalt. The total elemental concentrations varied greatly from the agricultural soils used in the column studies and exhibited characteristics of alkaline fill material. The total As concentrations of 95 percent of the urban soil samples was above the 11 mg kg^{-1} As background level established by DNREC, thus requiring a risk assessment for the site; however, only one soil sample had a TCLP concentration greater than the USEPA TCLP-As limit (5 mg L^{-1} or 100 mg kg^{-1}).

The TCLP concentrations were also determined to strongly correlate with total As concentrations; therefore the TCLP method would provide a good estimation of soil-As leachability.

Both bioavailability methods, Mehlich 3 and PBET, were strongly correlated with total As; however, the sequential chemical fractionation analyses showed differences in relative extractability of As in these 20 urban contaminated soils. Chemical fractions were also identified that were apparently related to the potential leachability (TCLP) and bioavailability (PBET) of As in these soils. However, chemical fractionation methods, while perhaps useful as a screening tool to rapidly and inexpensively identify soils with major differences in As species, they cannot provide detailed chemical and structural information of the As species that control the fate and transport of As in soils. More advanced spectroscopic methods, such as EXAFS and XANES would be required to provide definitive information on As speciation.

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CHAPTER 4

SUMMARY OF FINDINGS AND FUTURE RESEARCH

Major Findings

The fate, cycling, and transport of arsenic (As) in Delaware's agricultural and urban soils are areas of intense interest and environmental concern today. Past and ongoing anthropogenic activities have added As to Delaware soils creating questions about the potential for As to contaminate ground and surface waters. There are also concerns about As bioavailability and carcinogenicity when humans come into contact with or ingest soils that are contaminated with As. The overall goal of this study was to improve the ability to assess the risk of As to human and ecological health by understanding the amounts, solubility, and bioavailability of As in Delaware soils. This research project primarily focused on two settings: (i) agricultural cropland, specifically the situations where poultry litter (PL), well-known to be a long-term source of As to Delaware soils, had been used as a fertilizer for crop production; and (ii) contaminated soils in urban environments where past industrial activities resulted in soils with very high concentrations of As.

The 86 soil samples collected from agricultural and forested sites in New Castle County and Sussex County, Delaware represented a broad range of historic use, soil

types, textures, and total As concentrations, but all the soils exhibited characteristics of typical Delaware soils. The total As concentrations of the 86 soil samples averaged $4.42 \pm 3.72 \text{ mg kg}^{-1}$; however, only five percent of the samples were above the 11 mg kg^{-1} background concentration established by the DNREC for As.

The soils utilized for the column studies, Corsica, Evesboro, Matapeake, and Sassafras, were relatively low in As ranging from 0.7 to 9.5 mg kg^{-1} . The two soils collected from farms with historic PL application (Corsica and Sassafras) were low in total As concentration, 0.7 to 3.7 mg kg^{-1} , respectively; however, according to soil test phosphorus (STP) results, it is more likely that these two soils receive only moderate or inconsistent applications of PL. Therefore, it is probable that other soils in Delaware that have received consistent adequate PL applications to assist crop growth would have higher total As concentrations.

During the column studies, it became apparent that the As in PL was very water soluble. While the soils utilized in the column studies all exhibited a high affinity to sorb As, previous research has determined that P is preferentially sorbed before As when P is present at higher concentrations than As, which is the scenario during PL application to soil.

The results of *Column Study 1* revealed that preferential flow existed in several columns. While the data collected from the columns with preferential flow had to be omitted, valuable information was obtained through this observation. Since the As in PL is highly water soluble, the As could leach directly into groundwaters via macropore flow (root channels, worm holes, cracks, etc.), or runoff into surface waters during high

rainfall events. Statistical analysis of soil column leachate data showed that PL applications only resulted in significant increases in leachate As concentrations from the Corsica soil during leaching events 11, ($P < 0.05$), 17, and 18 ($P < 0.10$) and the Sassafras soil during leaching event 8. Prior research conducted by Pirani et al. (2002) discovered that spikes of As concentrations found in the leachate was also associated with an increase in dissolved organic carbon (DOC) and a decrease in pH. It is possible that the significant increases in As concentrations found during leaching events 11, 17, and 18 (Corsica) and 8 (Sassafras) may have been associated with the same phenomenon (increase in DOC, decrease in pH); however, these parameters were not measured during this research study. A future research objective derived from *Column Study 1* would be to conduct the same leaching study while measuring other parameters such as DOC and pH.

The procedure for *Column Study 2* was conducted to more adequately eliminate preferential flow paths. Preferential flow was eliminated with the exception of one column during one leaching event (Matapeake soil with treatment rate 9 Mg ha^{-1} replicate one during leaching event 10). As with the data from *Column Study 1*, the data collected from this column was omitted, as it was a product of preferential flow.

No significant increases in leachate As concentrations were observed during Column Study 2 as leachate As concentrations were consistently below $20 \mu\text{g L}^{-1}$ for the Corsica, Evesboro, and Sassafras soils and 20 to $30 \mu\text{g L}^{-1}$ for the Matapeake soil.

The TCLP-As concentrations obtained from the post column study 0 to 5 cm section of the soils of both *Column Study 1* and 2 were consistent between column studies

as well as with the data obtained from the 86 soil samples from New Castle County and Sussex County, Delaware.

Multiple PLs were selected to evaluate the extractable forms of As, determine if alum influenced As speciation in PL, and determine if alum could be used as a best management practice (BMP) to permanently decrease As solubility by converting it to forms that are stable in soil environments. The column study litter, seven non-alum-treated (control) litters, and nine alum-treated litters were utilized for this portion of the research study. The total As concentrations were consistent with previous research, 43.5, 42.7, and 43.1 mg kg⁻¹, respectively. The water soluble As concentration for the column study litter and the control litters was also consistent with previous research, 35.9 (82.5%) and 18.1 mg kg⁻¹ (42.5%), respectively, while the water soluble As concentration for the alum-treated litters was much less, 9.1 mg kg⁻¹ (21.1%).

The sequential fractionation method revealed that the easily exchangeable portion significantly decreased and the residual portion significantly increased in the alum-treated litters when compared to the control litters. This suggests that alum causes changes in the chemical speciation of the As in the PL, converting it to more recalcitrant and less soluble forms of As. Based on past research conducted by Peak et al. (2002) phosphate was bound to aluminum hydroxides in alum-treated PL. It is expected that As would sorb to similar sites in PL when treated with alum, due to the similar reactivity of As and P; however, more advance speciation methods would be required to confirm exact As species.

The PBET extractable As Concentrations correlated well with the Mehlich 3 and MgSO_4 As concentrations. This indicates that the PBET method extracts plant available and easily exchangeable forms of As.

The urban soils utilized in this research study were provided by the DNREC and consisted of original soil mixed with some type of fill material, including small pebbles, glass, concrete, and asphalt. The urban soils also had higher concentrations of Ca, Cu, Mg, S, and Zn and higher pHs when compared to the soils collected from agricultural settings, which indicates that some type of alkaline fill, such as coal ash was utilized at this site.

The total As concentrations of the 20 urban soils ranged from 10 to 5,760 mg kg^{-1} , of which 95% exceeded the 11 mg kg^{-1} As background level. The TCLP extraction ranged from 0.0 to 688 mg kg^{-1} and had a strong correlation with total As ($r^2 = 0.92$). However, only one sample exceeded the USEPA regulatory value (5 mg L^{-1} or 100 mg kg^{-1}). Based on the regression equation calculated, soil samples similar to those in this study with a total As concentration greater than 5,400 mg kg^{-1} As would be expected to exceed the USEPA TCLP-As limit.

The bioavailable extractions utilized, Mehlich 3 and PBET, were significantly correlated with total As ($r^2 = 0.90$ and $r^2 = 0.87$, respectively). The PBET As concentrations ranged from 2.0 to 4,388 mg kg^{-1} and averaged 290 mg kg^{-1} (61%), which was much higher than previously reported by Devesa-Rey et al. (2008) and Lombi et al. (2004). Fendorf et al. (2004) stated that the PBET concentrations were inversely related to ferric oxide content; however, this can be expected due to Fe being a primary sorption

site for As. The PBET data can be utilized to determine that up to 4.388 mg As could be absorbed by the human body for every one (1) g of soil incidentally ingested, which could be toxic based on the 20 µg per kg of body weight per day guideline established as a level in which characteristics of As poisoning begin to be displayed by the individual (Ontario Ministry of the Environment, 2001).

The results of the sequential fractionation revealed three distinctive groups; most of the As was extracted by MgSO_4 and AmOx for the first group, most of the As was extracted by HCl in the second group, and most of the As remained within the residual portion in the third group. The variability in chemical properties makes it difficult to draw any direct conclusions to the exact As speciation of these soils; therefore, more advanced speciation techniques would be required.

The TCLP results correlated well with the easily exchangeable (MgSO_4) fraction ($r^2 = 0.56$), and the relationship between % MgSO_4 + % AmOx and % PBET correlated well for groups 1 and 3 ($r^2 = 0.63$ and $r^2 = 0.51$, respectively), but not for group 2 ($r^2 = 0.01$). Unfortunately, chemical analysis provides no clear insight to these separate relationships.

Future Research

Future research should focus on: (i) conducting additional soil columns studies to evaluate which other parameters are effected by the addition of PL, (ii) conducting more advanced speciation techniques on the alum-treated litters and non-alum-treated litters to determine the different As species, determine which are more recalcitrant, and evaluate

how these compounds may react over time in the environment, (iii) evaluation of best management practices to reduce the risk of As loss from PL in high risk situations, such as surface-applied litters, litter storage areas, and soils with significant bypass flow, and (iv) improving understanding of the link between As speciation and bioavailability in urban contaminated soils where the risk of human exposure is high (e.g., residential development in former industrial areas) using advanced speciation techniques and bio-indicators.

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APPENDIX

Table A-1. Soil classification information for agricultural soil profiles on five farms in New Castle County, Delaware.

Farm Site Designation	Soil Series	Horizon	Depth cm	Color	Texture	Structure	Consistence	Boundary	Clay Particles	Pores	Roots	Coarse Fragments
Farm #1	Reybold	Ap	0-23	10 YR 4/3	Silt loam	Weak medium blocky parting to moderate fine granular	Very friable	Abrupt smooth	-	Common fine tubular	Few fine	-
		BE	23-30	10 YR 4/4	Silt loam	Moderate medium subangular blocky	Friable	Clear smooth	-	Common fine tubular	Few fine	-
		Bt1	30-56	10 YR 4/6	Loam	Moderate medium subangular blocky	Friable	-	Common continuous 7.5 YR 4/6	Common fine and medium tubular	NA	-
		Bt2	56-86	10 YR 4/6	Loam	Moderate coarse subangular blocky	Friable	-	Common continuous 7.5 YR 4/7	-	NA	-
		BC	86-127	10 YR 5/6	Silt loam	Weak coarse subangular blocky	Friable	-	-	-	NA	-
		2BC	127- 152	7.5 YR 5/6	Loamy sand	Single grain	Loose	-	-	-	NA	-
		2C	152- 178	10 YR 4/6	Loamy sand	Single grain	Loose	-	-	-	NA	-
		3C	178+	10 YR 5/4	Silt loam	massive	Friable	-	-	-	NA	-

Table A-1 (continued). Soil classification information for agricultural soil profiles on five farms in New Castle County, Delaware.

[illegible]

Table A-1 (continued). Soil classification information for agricultural soil profiles on five farms in New Castle County, Delaware.

Farm Site	Soil								Clay			Coarse
Designation	Series	Horizon	Depth	Color	Texture	Structure	Consistence	Boundary	Particles	Pores	Roots	Fragments
			cm									
Farm #3	Sassafras	Ap	0-30	10 YR 4/3	Sandy loam	Weak coarse subangular blocky	Friable	Abrupt smooth	-	Common fine and few medium	Few fine and medium	-
		BE	30-51	10 YR 5/4	Sandy loam	Weak coarse subangular blocky	Friable	Clear smooth	-	Common earthworm tubes	Few fine and medium	-
		Bt	51-91	10 YR 5/6	Sandy clay loam	Moderate medium subangular blocky	Friable	-	Few medium continuous	-	Few fine and medium	-
		BC	91-140	10 YR 4/6	Loam	-	Friable	-	-	-	-	-
			140-	10 YR	Loamy							
		C	183	5/4	sand	-	Very friable	-	-	-	-	-
Farm #4	Elkton	Ap	0-23	10 YR 4/2	Silt loam	Weak medium subangular	-	-	-	-	-	-
		Btg1	23-76	2.5 Y 6/1	Silt loam	blocky weak	-	-	-	-	-	-
		Btg2	76-122	2.5 Y 6/2	Silt loam	coarse prismatic	-	-	-	-	-	-
		Btg3	122- 132	2.5 Y 6/1	Silt loam	parting to moderate	-	-	-	-	-	-
		Cg	132- 147	5 Y 6/1	Silt loam	medium subangular	-	-	-	-	-	-
			147-		Sandy	blocky						
		2Cg	152+	5 Y 6/1	loam		-	-	-	-	-	-

Table A-1 (continued). Soil classification information for agricultural soil profiles on five farms in New Castle County, Delaware.

Farm Site Designation	Soil Series	Horizon	Depth cm	Color	Texture	Structure	Consistence	Boundary	Clay Particles	Pores	Roots	Coarse Fragments
Farm #5	Nassawango	Ap	0-18	10 YR 4/3	Silt loam	Weak coarse subangular blocky Moderate medium subangular blocky	Friable	Wavy smooth	-	Few fine and medium	Common fine and very fine throughout	-
		Bt	18-76	10 YR 4/6	Silt loam		Firm	-	-	-	Common fine in cracks	-
		2BC	76-117	10 YR 5/6	Sandy loam	-	Friable	-	-	-	-	-
		2C1	117- 140	10 YR 5/4	Loamy sand	-	Loose	-	-	-	-	-
					Loamy coarse sand							
		2C2	140- 152	10 YR 6/4		-	Loose	-	-	-	-	-
		2C3	152- 183	10 YR 5/4	Sandy loam	-	Very friable	-	-	-	-	10% quartzite and chert

Table A-2. Soil classification information for agricultural soil profiles on five farms in Sussex County, Delaware.

Farm Site	Soil								Clay			Coarse
Designation	Series	Horizon	Depth cm	Color	Texture	Structure	Consistence	Boundary	Particles	Pores	Roots	Fragments
Farm #6	Sassafras	-	0-20	-	Sandy loam	-	-	-	-	-	-	-
		-	20-41	-	Sandy clay loam	-	-	-	-	-	-	-
		-	41-61	-	Sandy loam	-	-	-	-	-	-	-
		-	61-91	-	Sandy loam	-	-	-	-	-	-	-
Farm #7	Rumford	-	0-20	-	Sandy loam	-	-	-	-	-	-	-
		-	20-41	-	Loamy sand	-	-	-	-	-	-	-
		-	41-61	-	Sandy loam	-	-	-	-	-	-	-
		-	61-91	-	Sandy loam	-	-	-	-	-	-	-
Farm #8	Greenwich	-	0-28	-	Sandy loam	-	-	-	-	-	-	-
		-	28-53	-	Sandy loam	-	-	-	-	-	-	-
		-	53-81	-	Loam	-	-	-	-	-	-	-
		-	81-109	-	Sandy loam	-	-	-	-	-	-	-
Farm #9	Downer	-	0-28	-	Sandy loam	-	-	-	-	-	-	-
		-	28-46	-	Sandy loam	-	-	-	-	-	-	-
		-	46-74	-	Sandy loam	-	-	-	-	-	-	-
		-	74-102	-	Sandy loam	-	-	-	-	-	-	-
Farm #10	Corsica	-	0-30	-	Loamy sand Sandy clay loam	-	-	-	-	-	-	-
		-	30-43	-	loam	-	-	-	-	-	-	-
		-	43-81	-	Clay loam	-	-	-	-	-	-	-

Table A-3. Soil classification information for three forested soil profiles collected in association from farm sites in Sussex County, Delaware.												
Farm Site	Soil								Clay			Coarse
Designation	Series	Horizon	Depth	Color	Texture	Structure	Consistence	Boundary	Particles	Pores	Roots	Fragments
			cm									
Farm #7	Sassafras	-	0-10	-	Sandy loam	-	-	-	-	-	-	-
		-	10-20	-	Sandy loam	-	-	-	-	-	-	-
		-	20-41	-	Sandy loam	-	-	-	-	-	-	-
		-	41-61	-	Sandy loam	-	-	-	-	-	-	-
		-	61-91	-	Loamy sand	-	-	-	-	-	-	-
Farm #6	Ingleside	-	0-10	-	Sandy loam	-	-	-	-	-	-	-
		-	10-20	-	Sandy loam	-	-	-	-	-	-	-
		-	20-41	-	Sandy loam	-	-	-	-	-	-	-
		-	41-61	-	Sandy loam	-	-	-	-	-	-	-
		-	61-91	-	Sandy loam	-	-	-	-	-	-	-
Farm #8	Greenwich	-	0-8	-	Loam	-	-	-	-	-	-	-
		-	8-46	-	Loam	-	-	-	-	-	-	-
		-	46+	-	Sandy clay loam	-	-	-	-	-	-	-

Table A-4. Total elemental concentrations for agricultural soils collected from New Castle County, Delaware.

Farm Site Designation	Soil Series	Depth cm	Total by Microwave Digestion										
			Al	B	Ca	Cu	Fe	K	Mg	Mn	P	S	Zn
			mg kg ⁻¹										
Farm #1	Reybold	0-23	11265.4	46.5	1084.3	5.6	12062.5	515.8	1498.7	182.1	364.3	198.2	31.7
		23-30	10622.7	44.0	873.3	5.0	11499.3	375.8	1357.1	191.2	312.9	134.5	30.0
		30-56	14865.4	64.6	913.4	6.9	17118.6	544.3	1800.6	160.7	285.7	120.5	33.1
Farm #2	Woodstown	0-23	8474.6	24.6	460.7	3.5	6387.4	330.4	839.8	76.4	208.3	112.0	22.8
		23-46	11483.9	34.6	487.9	4.9	9052.8	447.2	1237.9	57.2	123.3	67.9	21.1
Farm #3	Sassafras	0-30	12853.81	59.6	555.7	6.0	15479.5	830.7	1214.1	813.8	652.3	200.4	42.8
		30-56	10059.7	61.1	315.2	3.9	16241.3	651.7	1151.2	324.2	432.1	127.1	27.9
		56-91	15143.0	109.8	727.0	7.7	28392.6	1529.4	1565.6	111.0	463.9	165.7	36.1
Farm #4	Elkton	0-23	8370.3	31.7	974.6	4.7	8226.2	532.0	872.4	106.6	392.1	213.8	34.0
		23-43	8367.2	65.6	451.5	2.2	18293.1	285.3	537.1	21.4	88.9	122.7	15.0
Farm #5	Nassawango	0-18	11532.9	44.7	872.4	5.8	11534.5	544.7	1299.8	306.2	380.4	173.3	35.4
		18-76	17427.6	91.0	968.4	8.9	24243.1	713.7	1980.7	142.6	396.9	124.5	37.3

Table A-5. Total elemental concentrations for agricultural soils collected from Sussex County, Delaware.

Farm Site Designation	Soil Series	Depth cm	Total by Microwave Digestion										
			Al	B	Ca	Cu	Fe	K	Mg	Mn	P	S	Zn
			mg kg ⁻¹										
Farm #6	Sassafras	0-20	7714.3	2.8	304.1	7.2	6466.2	354.6	537.9	121.5	268.6	105.1	27.6
		20-41	14458.0	5.6	659.1	3.5	14704.0	623.5	987.9	100.5	144.2	67.5	22.4
		41-61	10279.0	5.1	561.8	1.5	11910.0	407.5	640.0	64.2	116.0	49.2	14.9
		61-81	8231.2	2.9	445.4	2.2	7395.8	243.9	275.8	40.5	73.4	38.8	8.7
Farm #7	Rumford	0-20	3431.5	1.4	349.8	9.0	2784.5	207.6	333.9	38.6	301.9	71.1	17.6
		20-41	4293.3	1.8	214.8	5.9	3967.3	178.3	372.2	30.3	183.6	24.8	10.5
		41-61	14851.0	3.9	393.8	5.5	8517.3	827.4	621.7	47.8	146.6	44.5	16.2
		61-81	12458.0	3.8	439.4	5.8	9539.3	720.1	553.7	45.1	131.8	68.3	16.3
Farm #8	Greenwich	0-28	7347.9	2.7	679.8	9.6	5950.9	302.7	789.5	136.3	321.6	96.2	21.4
		28-53	9902.0	4.5	492.3	8.6	8574.0	373.4	991.1	110.0	163.5	45.0	20.2
		53-81	11212.0	6.8	565.8	11.4	13319.0	523.4	1044.4	47.1	142.9	38.0	19.4
		81-109	6979.7	4.3	342.4	6.7	7803.6	349.6	563.5	33.4	84.1	28.6	10.8
Farm #9	Downer	0-28	5399.3	2.4	499.8	14.0	3445.6	228.8	369.9	63.9	442.3	92.6	23.7
		28-46	6367.9	1.8	341.2	5.8	5106.6	196.6	513.8	55.4	175.7	23.3	13.8
		46-73	8711.7	4.4	511.9	8.8	9069.1	397.4	542.6	68.4	139.0	22.5	16.3
		73+	5191.3	1.5	228.7	2.9	3236.2	201.8	228.8	26.2	39.6	12.6	7.7
Farm #10	Corsica	0-30	10163.0	2.2	1019.6	7.0	1480.2	647.6	360.4	22.3	394.8	226.3	16.5
		30-43	13802.0	5.7	305.8	9.8	10546.0	534.3	431.1	21.6	38.9	98.2	12.4
		43-81	15182.0	8.6	265.2	15.2	16080.0	583.8	495.4	17.1	32.8	119.2	16.5

Table A-6. Total elemental concentrations for forested soils collected from Sussex County, Delaware.

Farm Site Designation	Soil Series	Depth cm	Total by Microwave Digestion										
			Al	B	Ca	Cu	Fe	K	Mg	Mn	P	S	Zn
			mg kg ⁻¹										
Farm #7	Sassafras	0-20	6208.6	3.2	483.4	2.1	4811.9	479.2	597.9	59.4	209.2	188.8	17.9
		20-41	13016.0	4.0	164.1	3.1	9744.6	573.8	1011.6	49.3	109.9	50.1	21.7
		41-61	11804.0	3.5	64.3	3.6	9306.8	452.2	577.8	40.1	89.6	88.4	14.9
		61-81	7491.6	2.6	41.4	2.4	6534.7	259.0	321.6	26.0	65.6	71.2	9.9
Farm #6	Ingleside	0-20	4791.0	2.4	196.6	4.6	3913.9	196.4	397.7	35.1	159.3	217.9	13.2
		20-41	5673.7	1.6	100.7	0.0	3985.4	167.8	540.8	32.1	72.7	35.9	10.5
		41-61	7294.2	2.0	87.3	-1.6	6086.5	170.6	683.3	43.1	85.1	48.3	12.6
		61-81	10469.0	3.6	47.4	1.8	12259.0	318.3	726.3	50.2	137.7	114.8	16.2
Farm #8	Greenwich	0-7	10039.0	4.2	434.6	7.0	6563.1	323.6	858.0	143.8	205.1	230.9	20.1
		7-46	13420.0	4.5	254.2	7.2	8679.3	291.6	1149.3	127.4	105.4	68.1	21.1
		46+	12223.0	7.2	147.7	12.5	14176.0	424.3	1027.3	91.8	105.4	115.0	20.8

Table A-7. Mehlich 3 elemental concentrations for agricultural soils collected from New Castle County, Delaware.

Farm Site Designation	Soil Series	Depth cm	Mehlich 3										
			Al	B	Ca	Cu	Fe	K	Mg	Mn	P	S	Zn
			mg kg ⁻¹										
Farm #1	Reybold	0-23	623.3	1.5	794.3	1.0	135.9	74.3	219.6	56.0	24.7	20.5	1.6
		23-30	610.3	1.3	607.1	0.8	150.9	28.4	138.7	55.7	15.7	14.8	1.1
		30-56	726.4	1.3	684.3	0.6	150.0	36.8	170.2	27.2	5.0	20.4	0.5
Farm #2	Woodstown	0-23	598.2	0.8	291.5	0.8	116.9	46.1	74.9	19.5	18.1	18.0	1.2
		23-46	618.2	1.8	369.5	0.4	332.9	33.4	105.3	14.5	3.0	22.4	0.4
Farm #3	Sassafras	0-30	873.1	0.9	320.8	1.3	138.1	102.3	61.1	92.6	50.7	22.8	2.1
		30-56	785.2	0.7	188.3	0.4	99.5	60.3	72.8	52.7	17.1	42.8	0.3
		56-91	704.8	1.0	595.8	0.3	123.7	56.8	163.6	12.4	4.0	49.5	0.2
Farm #4	Elkton	0-23	518.5	2.2	714.4	1.5	379.4	67.0	172.4	23.3	52.2	25.5	3.4
		23-43	602.1	2.0	357.4	0.4	400.1	18.7	143.8	2.0	2.2	31.3	0.4
Farm #5	Nassawango	0-18	709.6	1.4	597.1	1.4	220.3	33.2	121.4	111.0	16.7	20.5	2.0
		18-76	775.4	1.2	762.8	0.6	149.1	38.4	238.4	17.3	2.1	17.4	0.2

Table A-8. Mehlich 3 elemental concentrations for agricultural soils collected from Sussex County, Delaware.

Farm Site Designation	Soil Series	Depth cm	Mehlich 3										
			Al	B	Ca	Cu	Fe	K	Mg	Mn	P	S	Zn
			mg kg ⁻¹										
Farm #6	Sassafras	0-20	502.4	0.3	253.1	2.9	119.0	98.9	38.2	43.1	46.5	10.6	4.0
		20-41	618.9	0.5	556.6	1.0	280.2	121.9	144.8	17.2	2.4	16.4	0.6
		41-61	534.7	0.3	483.9	1.2	51.6	94.3	125.9	6.8	2.1	20.3	0.2
		61-81	522.4	0.3	437.4	1.2	44.9	66.4	72.0	9.9	3.9	20.9	0.3
Farm #7	Rumford	0-20	385.2	0.2	267.3	4.8	97.4	62.9	40.5	10.4	118.8	7.6	4.5
		20-41	478.7	0.2	212.8	2.7	124.0	60.0	39.6	6.0	75.9	8.0	1.3
		41-61	660.6	0.3	402.6	1.1	71.3	145.5	100.8	7.3	18.0	25.7	0.5
		61-81	727.3	0.2	422.4	1.4	60.6	179.2	76.4	2.0	6.8	44.7	0.3
Farm #8	Greenwich	0-28	805.3	0.3	371.1	2.0	97.8	106.1	42.8	29.2	86.9	16.5	2.4
		28-53	734.7	0.3	304.5	0.9	208.3	73.6	59.2	29.5	20.8	12.3	0.8
		53-81	670.2	0.3	440.3	0.7	184.3	73.9	92.6	2.8	2.8	25.8	0.2
		81-109	567.7	0.3	299.3	0.3	217.2	54.9	77.1	2.6	3.2	25.3	0.3
Farm #9	Downer	0-28	648.5	0.2	348.3	6.0	95.4	82.3	41.9	18.7	264.2	13.2	9.1
		28-46	660.9	0.2	229.3	1.4	106.0	97.8	52.9	12.2	74.9	9.7	1.2
		46-73	668.8	0.1	417.0	0.9	62.2	120.0	104.6	7.7	12.5	12.1	0.4
		73+	436.7	0.1	151.0	0.4	70.7	42.8	34.6	5.3	5.1	8.4	0.2
Farm #10	Corsica	0-30	1069.3	0.6	750.4	1.8	192.0	227.8	127.9	5.9	164.3	25.4	4.1
		30-43	935.4	0.4	232.0	0.4	307.8	94.2	84.5	2.1	3.2	51.0	0.6
		43-81	1014.8	0.3	181.1	1.0	206.4	80.3	93.8	1.2	1.2	60.5	0.6

Table A-9. Mehlich 3 elemental concentrations for forested soils collected from Sussex County, Delaware.

Farm Site	Soil		Mehlich 3										
Designation	Series	Depth	Al	B	Ca	Cu	Fe	K	Mg	Mn	P	S	Zn
		cm	mg kg ⁻¹										
Farm #7	Sassafras	0-20	643.0	0.5	410.5	1.8	178.9	218.6	121.9	17.4	20.0	15.5	3.2
		20-41	809.1	0.3	121.5	2.5	145.9	81.8	29.9	2.5	3.8	19.0	0.9
		41-61	695.9	0.1	97.6	1.3	53.0	43.9	33.7	1.8	1.1	57.6	0.3
		61-81	540.2	0.2	96.8	1.6	33.6	31.3	37.0	2.3	1.3	53.0	0.4
Farm #6	Ingleside	0-20	731.9	0.2	184.5	2.0	187.1	86.5	25.4	9.9	17.5	17.7	1.7
		20-41	541.1	0.2	60.2	1.3	52.5	11.4	8.9	3.2	2.9	15.7	0.3
		41-61	624.5	0.2	63.8	1.4	78.1	15.4	11.2	4.3	3.6	27.5	0.2
		61-81	376.7	0.1	261.7	4.5	93.0	60.7	40.0	10.1	115.7	6.7	4.3
Farm #8	Greenwich	0-7	1373.7	0.4	333.1	0.9	165.3	91.8	76.5	28.0	10.9	32.7	2.5
		7-46	1129.6	0.2	77.7	0.8	69.7	31.3	13.8	15.8	3.2	28.7	0.7
		46+	892.7	0.3	60.3	0.7	181.9	36.2	15.3	4.0	1.3	73.2	0.3

Table A-10. Selected soil properties for 20 soils collected by DNREC staff in Wilmington, Delaware for a site investigation (South Market Street) for potential As contamination. These soil samples were collected with a geoprobe (GP) or from a test pit (TP).

Sample					Total										
Type	Point	Depth	pH	OM	Al	B	Ca	Cu	Fe	K	Mg	Mn	P	S	Zn
		m		%						mg kg ⁻¹					
GP	3	0-1.0	8.4	1.6	9176	2.4	20232	47	20032	1020	8636	340	358	840	121
GP	3	1.6-1.8	6.1	2.9	13180	1.6	2460	117	25384	790	1544	303	480	824	475
GP	4	0-1.0	7.5	2.3	15816	1.6	3956	56	30124	1666	2516	295	800	1660	173
GP	4	1.8-2.7	7.7	1.7	6600	0.4	4880	39	24752	556	1684	231	484	976	101
GP	7	1.8-2.1	7.8	2.2	11288	2.4	23808	66	17364	663	2612	372	456	2564	275
GP	8	0-1.3	9.6	2.8	10716	8.0	37340	100	19736	1129	4440	202	428	776	218
GP	8	1.5-2.0	8.0	6.8	4836	18.0	16192	124	36076	556	1876	183	556	5640	304
GP	12	0-1.3	8.1	2.5	7604	4.0	22188	83	28060	748	5736	261	400	1048	236
GP	12	1.4-2.1	8.0	3.1	7024	0.8	36000	73	25112	503	6492	440	512	3556	250
GP	12	1.4-2.1	8.0	3.2	8192	3.2	39568	77	27784	627	7096	497	556	3324	246
GP	13	0.2-0.9	7.8	2.7	7012	4.4	22708	314	15368	921	11020	290	1056	604	482
GP	13	1.3-1.9	8.1	2.9	12148	2.4	78240	19	17092	988	8496	526	592	3040	109
GP	14	0-1.3	8.3	1.2	6652	2.4	18944	79	15868	2007	6616	219	800	532	196
GP	14	2.4-2.9	9.3	8.1	4884	8.0	91120	63	7816	418	87400	205	852	2444	114
TP	2	2.0-2.1	7.4	5.1	5564	6.0	16236	527	18340	765	1852	210	624	1360	363
TP	3	2.3-2.4	7.5	11.0	9972	6.4	34932	185	19144	528	3292	247	400	1112	702
TP	4	2.0-2.1	9.0	2.8	12752	6.4	44640	45	19944	1281	22964	305	496	4000	127
TP	7	2.1-2.3	7.5	2.7	6000	2.8	6772	87	25464	634	1452	475	560	1080	127
TP	8	2.0-2.1	7.3	3.4	9536	0.8	8600	52	22656	1284	3368	526	460	1652	172
TP	10	1.5-1.8	7.7	2.2	15444	4.8	8828	80	27152	1738	4228	407	532	900	194

Table A-11. Routine soil test results for 20 soils collected in Wilmington, Delaware in a DNREC site investigation (South Market Street) for As contamination. These soil samples were collected with a geoprobe (GP) or from a test pit (TP).

Sample					Mehlich 3								
Type	Point	Depth	pH	OM	Al	Ca	Cu	Fe	Mg	Mn	P	S	Zn
		m		%	mg kg ⁻¹								
GP	3	0-1.0	8.4	1.6	1077	10227	16	343	436	54	506	15	19
GP	3	1.6-1.8	6.1	2.9	612	1569	23	357	134	38	250	19	114
GP	4	0-1.0	7.5	2.3	699	1887	9	235	175	49	154	35	23
GP	4	1.8-2.7	7.7	1.7	550	2706	8	362	510	33	388	23	35
GP	7	1.8-2.1	7.8	2.2	413	7354	20	269	636	78	674	7	104
GP	8	0-1.3	9.6	2.8	1116	18857	38	173	562	30	392	8	38
GP	8	1.5-2.0	8.0	6.8	24	5459	26	502	590	19	767	20	101
GP	12	0-1.3	8.1	2.5	1042	8873	24	293	403	39	441	13	42
GP	12	1.4-2.1	8.0	3.1	646	9210	15	366	1456	59	1399	17	63
GP	12	1.4-2.1	8.0	3.2	642	10345	16	358	1524	53	1521	15	64
GP	13	0.2-0.9	7.8	2.7	648	4337	146	206	434	25	90	67	168
GP	13	1.3-1.9	8.1	2.9	383	18589	5	374	1282	79	1606	25	22
GP	14	0-1.3	8.3	1.2	305	4101	20	202	608	30	59	33	49
GP	14	2.4-2.9	9.3	8.1	20	16495	16	420	4219	57	1155	24	35
TP	2	2.0-2.1	7.4	5.1	121	5834	42	440	228	41	310	40	92
TP	3	2.3-2.4	7.5	11.0	799	11509	34	258	732	41	281	7	159
TP	4	2.0-2.1	9.0	2.8	421	9755	8	613	2481	35	1895	6	20
TP	7	2.1-2.3	7.5	2.7	457	2948	16	488	246	66	464	10	34
TP	8	2.0-2.1	7.3	3.4	635	5086	13	575	548	86	741	9	37
TP	10	1.5-1.8	7.7	2.2	787	4147	29	419	463	38	413	16	34

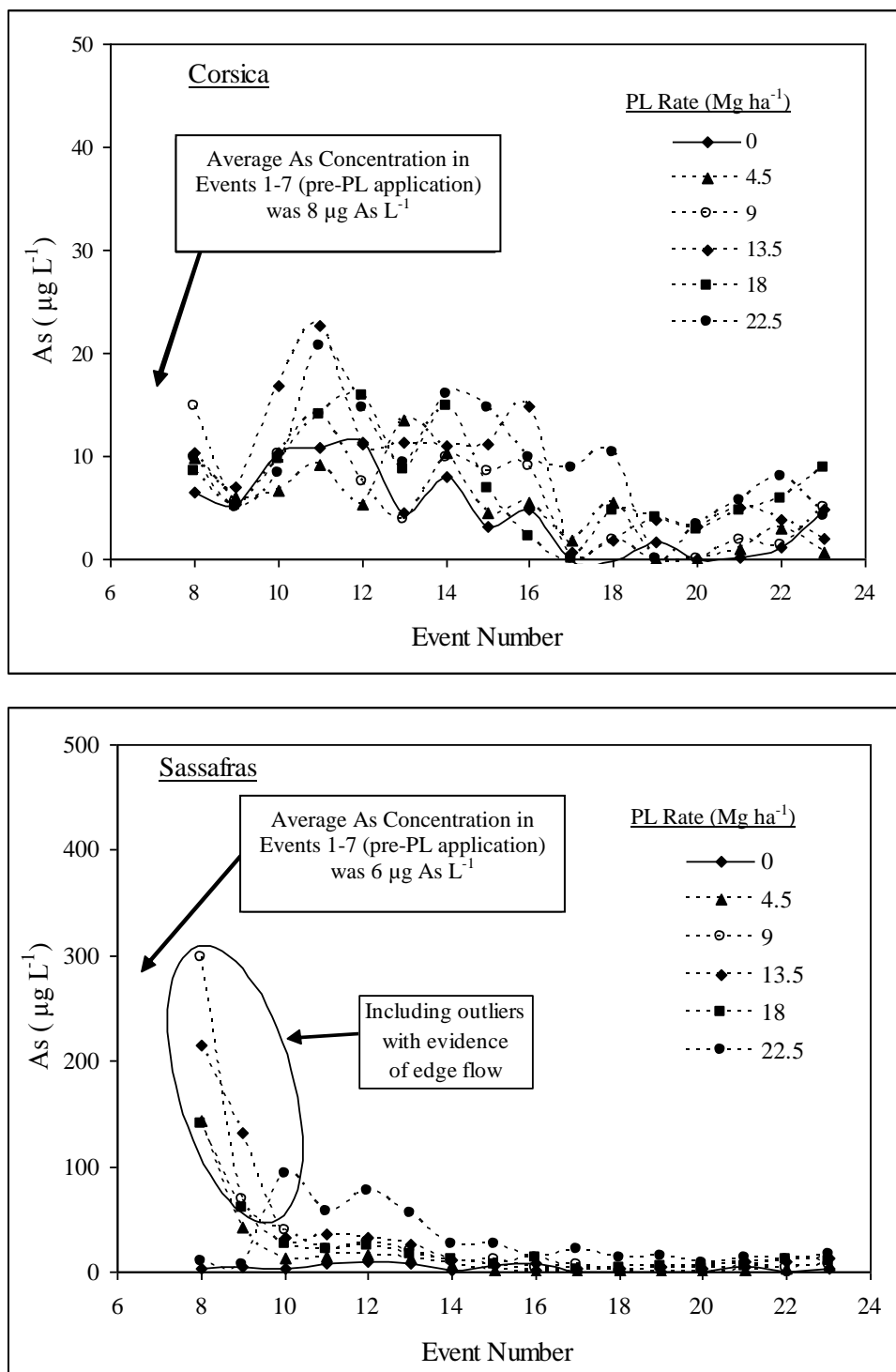


Figure A-1. Effect of PL application rate on total dissolved As concentrations in leachate from the (a) Corsica and (b) Sassafras soils during *Column Study 1*. Note: Leachate concentrations include results from outlier columns where edge flow occurred.

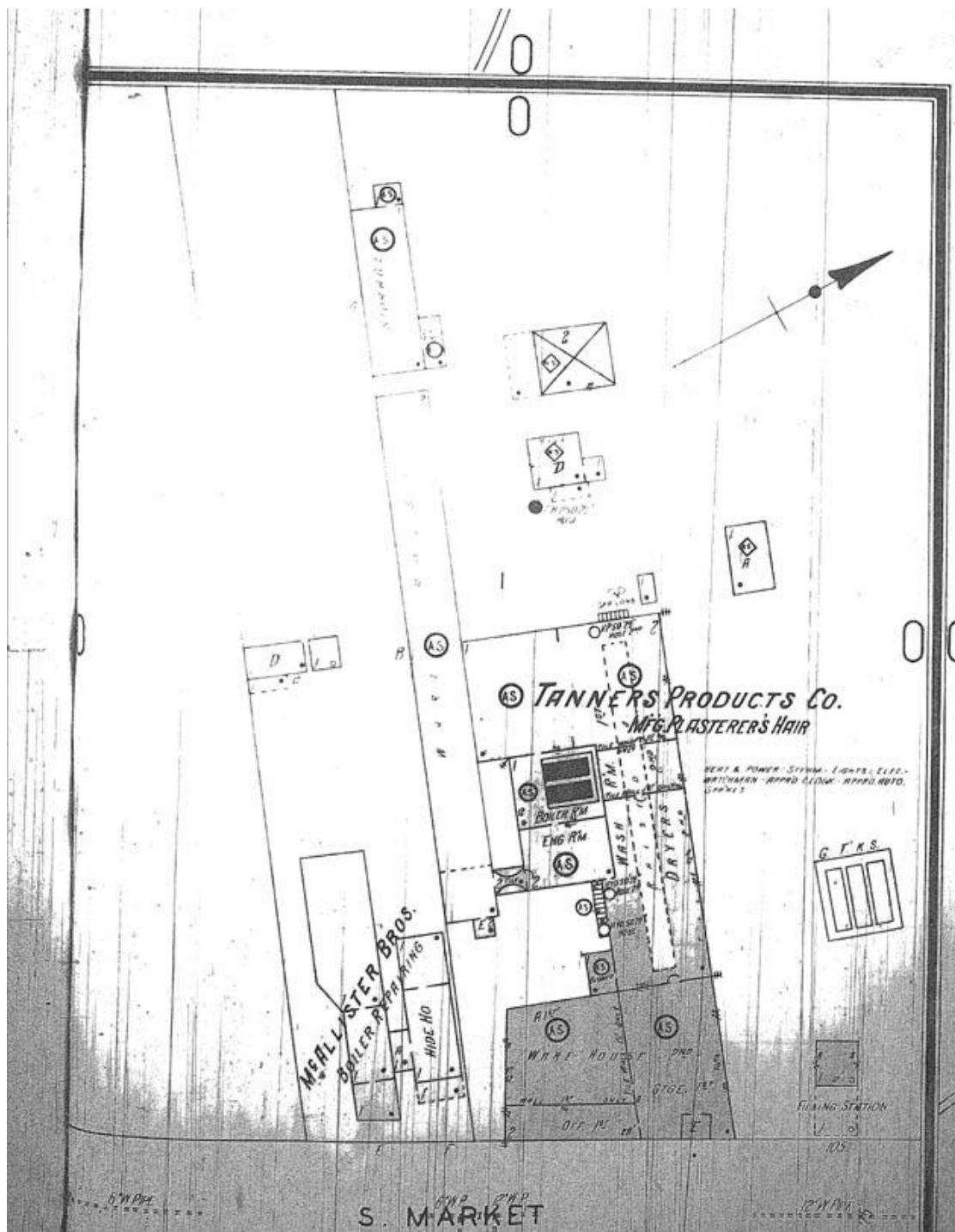


Figure A-2. Image from a 1921 Sanborn fire insurance map showing the historical tannery operations located at the property from which the urban soil samples were collected.