FATE AND TRANSPORT OF ARSENIC IN DELAWARE SOILS: ASSESSING POTENTIAL IMPACTS ON WATER QUALITY

Final Report

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EXECUTIVE SUMMARY

The fate, cycling, and transport of arsenic (As) in Delaware's agricultural and urban/suburban 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 our ability to assess the risk of As to human and ecological health by increasing our understanding of the amounts, forms, solubility, and bioavailability of As in Delaware soils. Our research primarily focused on two settings: (i) agricultural cropland, especially situations where broiler litter, 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/suburban environments where past industrial activities resulted in soils with very high concentrations of As. The following are the major findings of this study, along with some suggestions for future research that could further increase our ability to prevent As from endangering human health and Delaware's ecosystems:

- Total arsenic concentrations in 22 benchmark soil series located on agricultural and forested lands (86 surface and subsoil samples) averaged 4.7 ± 3.5 mg kg^{-1} (ppm). The DNREC has proposed a total As value of 11 mg kg^{-1} as the "background" level that should be used to determine the need for and most appropriate approach to remediate sites where future land use is "…reasonably anticipated to be residential or unrestricted" (DNREC, 2005). In our study, 97% of agricultural and forested soils sampled were below the 11 mg kg^{-1} standard.

- Arsenic solubility in agricultural and forested soils, and thus the risk of As leaching to ground waters or being transported via runoff to surface waters, was determined to be very low, relative to environmental standards. For example, TCLP (toxicity characteristic leaching procedure) As concentrations in soils were always less than 1 mg kg^{-1} and averaged 0.1 ± 0.1 mg kg^{-1}. These TCLP-As values are also much lower than the USEPA standard of 100 mg As kg^{-1} to identify solid materials where As leaching could be potentially hazardous.

- Soils from farms where broiler litter (or other manures and fertilizers) had been applied in accordance with normal agronomic recommendations did not have unusually high soil total As concentrations and there was no evidence of significant As leaching into subsoils. However, due to difficulties getting access to broiler litter impacted soils, the number of farms sampled was quite limited. Additional sampling of soils where broiler litter applications have been made continuously at recommended, or higher, rates is suggested. Further, our calculations and field data suggest that regular application of broiler litter at agronomic rates could increase soil total As values above the current DNREC soil As standard (11 mg kg^{-1}) within one to two generations, which raises questions about the sustainability of As use in poultry production. A sustainable practice is generally assumed to be one that can be continued indefinitely with no adverse environmental effects. Although soil As levels in agricultural fields are now consistently below DNREC criteria, the potential for gradual buildup of soil As above environmental limits suggests it would be prudent to investigate alternatives to the use of organo-arsenicals in poultry production.

- Detailed laboratory studies of As sorption and desorption showed that Delaware's agricultural soils have good capacities to retain dissolved As that is released from litters, manures, fertilizers and other soil amendments. Subsoils had greater capacities to retain As than topsoils, primarily due to higher concentrations of aluminum and iron oxides, soil constituents known to sorb and tightly retain As. Arsenic sorption was greatest at the soil pH values recommended for crop production (pH 5.5 to 7.0). Kinetic studies showed that As sorption by soils occurred very rapidly (<< 60 minutes), followed by a slower, long-term phase that continued to remove As from solution for hours.

- Phosphate, present at high concentrations in many Delaware soils from long-term applications of manures and fertilizers, was preferentially sorbed by soils, relative to As, and thus has the potential to inhibit As sorption through competition for similar sorption sites on soil constituents. Desorption studies showed that solutions with high phosphate concentrations could displace previously sorbed As from soils, particularly subsoils.

- Greenhouse soil column leaching studies of the impact of broiler litter application rate on As leaching found litter application had little effect on dissolved As concentrations in leachate from topsoils. Less than 1% of added litter As was leached from soils and in virtually all leaching events litter did not significantly increase dissolved As concentrations in leachate relative to unamended soils. These results are consistent with findings from the laboratory sorption-desorption studies that showed Delaware soils have considerable capacity to retain As and thus protect shallow ground waters from As leaching.

- X-ray absorption near edge structure (XANES) and x-ray fluorescence (XRF) spectroscopy were used to provide direct *in-situ* speciation of As and its distribution and association with other elements, respectively, in broiler litters. These analyses showed that the organo-arsenical Roxarsone found in litters is rapidly converted to arsenate (As (V)) during litter storage. Consistent with past research (Sims and McCafferty, 2002) much (~50%) of the total As in litters was found to be water-soluble. Our results suggest that if litters are thoroughly incorporated with soils, soluble litter As will be sorbed quickly and will not be susceptible to significant losses by leaching or surface runoff. However, if bypass flow pathways (cracks, old root channels, macropores) predominate in soils with shallow water tables, soluble As in litters has the potential to leach through soil profiles to the water table. Similarly, if litters are applied to the soil surface, runoff may dissolve and transport As to nearby surface waters.

- Best management practices (BMPs) for broiler litters to prevent As losses to ground and surface waters should focus on production and storage areas and land application methods. Because much (>40-50%) of litter total As is easily soluble in water it is important to prevent direct interaction of litters with rainfall or snowmelt in settings where the potential for dissolved As transport to surface or ground waters is likely. In general, litters should be protected from rainfall and snow-melt during storage and all areas used to stockpile litters prior to land application should be cleaned up after storage to remove residual litter and soil from the upper few cm of the stockpile area. Chemical amendments, such as alum, can be used in poultry production houses to reduce As solubility in litters and thus the risk of dissolved As loss by runoff or leaching. Land application practices should be designed to prevent the buildup of As in soils; consideration should be given to establishing annual and cumulative As loading rates for crop land as has been done with biosolids. Broiler litters should be incorporated by tillage whenever possible to decrease the potential for dissolved As transport from surface-applied litters exposed to rainfall and snow-melt. Application of litter to poorly-drained soils, subject to anaerobic conditions, should be avoided because of the potential for reduction of As(V), the major form of As in litters, to As (III) a more toxic form of As.

- The urban soils from old industrial sites in Wilmington, DE had much higher total As concentrations and more complex As speciation than the agricultural or forested soils. The soils also contained very high concentrations of other metals and tended to be high in pH and calcium. Visual inspection showed most were not natural soils but were mixtures of soil, fill materials, and occasionally debris. Leachable (TCLP) and bioavailable (PBET, Mehlich 3) As were significantly correlated with total As. A rapid sequential chemical fractionation procedure found these soils varied widely in the distributions of total As into exchangeable, sorbed, and resistant As pools. Encouragingly, the fractionation method successfully identified As fractions that were well-correlated with bioavailable As. This suggests these methods could be used to identify soils of differing risk to human health and for further, more detailed investigation into As speciation by methods such as x-ray absorption fine structure (XAFS) analysis.

- Direct speciation of As in contaminated soils from old tannery sites, using μ-XRF and μ-extended x-ray absorption fine structure (EXAFS) spectroscopy, identified arsenate, arsenite, orpiment, and realgar as the As-bearing species present in these soils. It appears that some of the initial As substances used in the tanning process persist in soils at these sites.

- Future research should focus in two key areas: (i) evaluation of best management practices to reduce the risk of As loss from broiler litters in high risk situations, such as surface-applied litters, litter storage areas, and soils with significant bypass flow; and (ii) improving our understanding, using advanced speciation techniques and bio-indicators, 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).

There are many long-standing environmental concerns about surface and ground water quality in the Mid-Atlantic U.S. Historically, the primary pollutants of interest in Delaware have been nutrients, such as N and P, but there are also growing concerns about the effects of trace metals from industrial, municipal, and agricultural sources on ground water quality and human health. Arsenic (As) is a ubiquitous contaminant in soil/water environments due to natural geological processes and anthropogenic inputs. Over the past few decades, the health of humans, farm animals, wildlife, microorganisms, and some plants in the U.S. has been jeopardized by As contaminating soil and water because of its high carcinogenic, phytotoxic and biotoxic characteristics. Long-term human exposure to As in drinking water can result in bladder, lung, skin, kidney, immunological, neurological, and endocrine effects. The USEPA announced that it was lowering the maximum contaminant level (MCL) for As in drinking water from 50 $\mu g\ L^{-1}$ (ppb) to 10 $\mu g\ L^{-1}$, and all water systems were expected to comply by January of 2006 (USEPA, 2001a). Recent data show there is still an unacceptable level of risk at the EPA's newly adopted 10 $\mu g\ L^{-1}$ MCL. For example, it has been shown that the consumption of drinking water with a concentration of only 3 $\mu g\ L^{-1}$ of As creates risk of bladder and lung cancer in 4 to 10 people per 10,000 people (National Research Council, 2001). This exceeds EPA's maximum acceptable level of risk of 1 in 1,000,000 people by 1000-fold.

A portion of As contamination in soil and aqueous environments is due to natural sources, with weathering of As-containing rocks being the main source, releasing 45,000 metric tons per year (Tamaki and Frankenberger, 1992). Arsenic is a major constituent in more than 245 minerals including sulfides, oxides, arsenites, and arsenates (Gao et al., 1994; Yan-Chu, 1994). Mineral distribution depends on the parent rock composition and the extent of weathering that has occurred. The concentration of As in sedimentary and igneous rocks ranges from 0.1 to 2,000 mg kg^{-1} (ppm). Sedimentary rocks have a mean As concentration of 13 mg kg^{-1} in shales and 25 mg kg^{-1} in coal, while igneous rocks have a lower mean concentration of 1.5 mg kg^{-1}. Metamorphic rocks contain less As, ranging from 0.4 to 18 mg kg^{-1} As. While As is mainly released into soil and aqueous environments through the weathering of rocks, it is also deposited into the atmosphere by volcanic and geyser activities (Smith et al., 1998). Volcanic activity and other natural sources of As contamination account for over half of As's atmospheric flow.

Arsenic concentrations in water range from 0.1 to 1 mg L^{-1} with a mean of 3 $\mu g\ L^{-1}$ in sea water, 1.7 $\mu g\ L^{-1}$ in river water, 1 $\mu g\ L^{-1}$ in precipitation, and 280 $\mu g\ L^{-1}$ in saline lakes (Gao et al., 1994). Long-term anthropogenic inputs (e.g., inorganic and organic arsenical pesticides, defoliants, wood preservatives, manures, biosolids) to soils have increased total As levels up to as high as 165 mg kg^{-1} (the average As concentration in uncontaminated soils is 5 mg kg^{-1}).

Arsenic and Poultry Production: Potential for Soil and Water Contamination: National surveys and research provide evidence that poultry production practices introduce As into the environment (Christen, 2001b). More than 11.4 million Mg of poultry litter (PL) were produced in the USA in 1996 and about 90% of this was land applied (Cabrera and Sims, 2000). Poultry litter can contain relatively high concentrations of certain trace elements such as Cu, Zn, and As, the sources of which are growth promoters and biocides added to poultry feed. Total As concentrations in PL vary. For example, Sims and Wolf (1994) found levels ranging from 0 to 77 mg kg^{-1}. Others have shown PL has As concentrations in this same range, for example, 30- 37 mg kg^{-1} (van der Watt et al., 1994), 43 mg kg^{-1} (Moore et al., 1998), 35 mg kg^{-1} (Jackson et al., 1999), 45 mg kg^{-1} (Sims and Luka-McCafferty, 2002), and 1-39 mg kg^{-1} (Jackson et. al., 2003). In comparison, the As concentrations set by USEPA as Aceiling concentration limits" and Apollutant concentration limits" for the land application of biosolids (sewage sludge) are 75 and 41 mg kg^{-1} (Christen, 2001a,b).

The Delmarva Peninsula is one of the most concentrated poultry production areas in the US. In 2000, 620 million broilers were produced, which resulted in manure and poultry litter (PL, a mixture of bedding such as wood shavings or sawdust and manure) containing approximately 26,000 kg of As (Poultry and Value Summary, 2000; Garbarino et al., 2003). Poultry litter is generally applied at the rate of 9-20 Mg ha^{-1} on agricultural lands, and its total annual As inputs on the Delmarva Peninsula are estimated between 20 and 50 metric tons of total As (Christen, 2001a). The main sources of As in PL are 4-amino-phenylarsonic acid (p-ASA) or 3-nitro-4-hydroxyphenly-arsonic acid (*Roxarsone*, abbreviated ROX), used as feed additives to prevent coccidiosis, increase weight gain and improve feed efficiency. ROX was used in about 70% of broiler industry operations from 1999-2000 (Chapman and Johnson, 2002). The organo-As compounds added to the feed are primarily excreted in the organo-As forms. For example, Morrison (1969) found that ROX constituted 36-88% of the total As in 10 PL samples. Jackson et al. (2003) found that the major As species in 40 PL extracts were either ROX or As(V). For 20 of the 40 PL samples, As(V) was the major As species in the water extract, showing that mineralization of the initial organo-As had occurred. The quantity of ROX excreted by a single broiler when fed the typical 45.4 g As ton^{-1} formulation is about 150 mg over the normal growth period of 42 days (equal to 43 mg of As; Garbarino et al., 2003). Feed spillage and digested materials can increase mean total As concentration in PL to 14-76 mg kg^{-1} (Moore et al., 1998). Thus, assuming PL is applied at ~7 Mg ha^{-1} (~ 3 tons ac^{-1}) about 100-530 g of As ha^{-1} could be added with each application. Addition of As to agricultural lands via PL is not specifically regulated at either the federal or state levels nor is nonpoint source pollution of soils by As considered under current nutrient management laws in Delaware. It is unclear whether total maximum daily load agreements (TMDLs) established between Delaware and USEPA to protect surface water quality will affect the application of As in PL to cropland.

Fate and Transport of Arsenic in Poultry Litter Amended Soils: The effects of continuous PL amendments on As contamination in Mid-Atlantic soil and water environments are not known. Limited data have shown ground water from agricultural fields of the Pocomoke River Basin in Maryland and Delaware had total dissolved As concentrations as high as 23 μg L^{-1} (Hancock et al., 2003). Moore et al. (1998) reported that initial dissolved As concentrations of > 200 μg L^{-1} were found in runoff water from a field that had been amended with 9 Mg PL ha^{-1} and after 7 days, the runoff dissolved As concentrations were still > 50 μg L^{-1}.

There is also evidence that the organic As in PL transforms to organic and inorganic As, primarily As (V) (Garbarino et al., 2003; Rosal et al., 2005; Cortinas et al., 2006). When PL samples were mixed with water (50 wt %) and the mixture was allowed to compost at 40C, the speciation of As converted from organo-As to As(V) in about 30 days. These studies suggest that after litter storage and land application and then the subsequent exposure to sunlight, elevated temperatures, and precipitation, As could undergo transformations to inorganic As species such as As(V) via photodegradation and microbial degradation processes. The As (V) is much more soluble and toxic than ROX and thus concerns exist that it could be sufficiently mobile in soils to potentially contaminate shallow ground waters, most of which are inter-connected with fresh and estuarine surface waters (Bednar et al, 2004; Brown et al, 2005). Brown et al. (2005) found As (V) was readily mobile in soil systems, and found ROX to be more mobile in the subsurface soil horizons. Arai et al. (2003) employed novel micro-focused x-ray absorption fine structure (XAFS) and x-ray fluorescence (XRF) spectroscopies to directly speciate As in PL samples and long-term PL amended soils. The predominant inorganic species in the PL was As(V). The As(V), which is more toxic than the organo-As species could sorb on soil components such as metal oxides or leach into waters. Jackson and Miller (1999) found that 72% of the total As in PL samples was water soluble, Jackson and Bertsch (2002) reported 71% of the As in PL samples was water soluble and, in a recent study by Garbarino et al (2003), 70-90% of As in dried PL samples from Kansas was water soluble. Rutherford et al. (2003) conducted sequential water extractions on soil samples taken from the Delmarva and Oklahoma areas that had been amended for long time periods with PL, and compared these to the same soils from forested areas that had no history of PL applications. Water-extractable As was 6.4 times higher for the PL-amended Delmarva soil than the unamended soil. They found that water-extractable As decreased with depth in the soils. Acid-extractable As and Fe increased with depth in the amended soils with concentrations of As being twice as high in the amended soil at all depths compared to the unamended field. The correlation between soil As and Fe suggests Fe-oxides in the soils could be retaining the As, however, this was not established by Rutherford et al. (2003).

Given ongoing environmental concerns and results of recent research, it is apparent that the fate of As in soils, especially in soils that are sandy, prone to leaching, that overlie shallow ground waters commonly used as sources of drinking water, and that are regularly amended with PL, needed to be studied further. There are very limited data available on the speciation and distribution of As in long-term PL-amended soils, the fate and transport of As added to these soils in PL, how competing ions such as phosphate, which is also found in large quantities in PL and in Delaware soils, affect As retention and release to leaching waters, and the potential to develop and use management practices that will mitigate As transport. For example PL is often amended with metal salts (e.g., aluminum sulfate or "alum") to reduce ammonia emissions and stabilize P such that it may be less mobile in soil and water environments. Alum amendments do lower water soluble P levels in litters, soils, and runoff (Sims and Luka-McCafferty, 2002). Moore et al. (1998) also reported trace metals were less mobile via runoff after PL was amended with alum. Sims and Luka-McCafferty (2002) conducted a large scale study on 200 farms on Delmarva to determine effects of alum on PL properties, elemental composition, and the solubility of inorganic elements such as P and As. With respect to As, total levels in untreated PL samples averaged 45 mg kg^{-1} and soluble As averaged 19 mg kg^{-1} while concentrations in alum-treated samples were lower, averaging 44 and 7 mg kg^{-1}, for total and soluble As.

As Contamination from Tannery Operations: Historical leather tanning practices employed an array of toxic metal compounds, resulting in high concentrations of arsenic in the area surrounding former tannery sites. The present development of these contaminated sites for housing and recreational purposes calls for a thorough assessment of the metal(oid) speciation in the underlying soil due to the potential mobilization of high levels of toxic metals into nearby ground and surface waters. Leather tanning practices in the late 1800's and early 1900's used several As compounds at various stages of the tanning process. Realgar (AsS) was slacked with lime ($CaCO_3$) to dehair finer leathers to achieve a lighter grain than could be produced via the use of sodium sulfide. Arsenic-based coloring agents such as Scheele's green ($CuHAsO_3$), Paris green ($Cu(AsO_2)_2Cu(C_2H_3O_2)_2$), and sodium arsenate leather preservatives (Columbia Encyclopedia, 2005) were also frequently used. In addition, $PbHAsO_4$ was a common insecticide at many industrial facilities (IPCS International program on chemical safety). Although these practices have been abandoned for decades and the tanneries closed, the surrounding soils remain contaminated with a mixture of As(II), As(III), and As(V).

Leather tanning was widespread along the Atlantic seaboard of the United States until the early 20th century. In Wilmington, Delaware, 128 tannery footprints were identified and subsequently clustered into 53 sites (http://www.tetratech-de.com/tanneries/contents.asp), and managed by the Delaware Department of Natural Resources and Environmental Control (DNREC). A preliminary investigation of one such site determined that the As was localized to a small (100 m^2) surface area and a depth of approximately 10 feet (3 meters). Thorough characterization of such sites for total and soluble As, and for the main species of As present in these soils or soil-like materials is essential to accurately access proper remedial actions.

Surprisingly, while tanneries are often sited as sources of As contamination, there is a noticeable lack of tannery site investigations in the literature; only two papers specifically deal with tannery contaminated As-sites (Davis et al., 1994; Sadler et al., 1994). In addition, neither of these studies uses XAFS to elucidate the As speciation, but rather relied solely on less definitive chemical extraction methods.

Quantifying Retention, Release, and Speciation of Metalloids and Metals in Soils: Pollution assessment and remediation efforts represent a significant financial burden for agriculture, industry, and government. Frequently, remedial actions are undertaken based on the total metal/metalloid burden because precise speciation information on the contaminants is not known. Although total content of metals can give insight into the degree of pollution, such analyses provide no information on bioavailability or the potential mobility of metals through soils to ground waters (de Groot, 1995). More effective, widely-used and accepted approaches to characterize the potential for As to move through soils to ground waters include: (i) chemical extraction; (ii) sorption-desorption studies; and (iii) chemical and spectroscopic studies.

Chemical extraction approaches use solutions of dilute acids, bases, chelates, or even water, to rapidly and inexpensively characterize the solubility and bioavailability of metals in soils. A variety of chemical extractants used alone, or in sequence, have been evaluated with As. Examples include deionized water, phosphate solutions, agronomic soil tests, and solutions specifically designed to extract As from Al and Fe oxides in soils (Rodriguez et al., 2003). These tests have been shown to be reasonably well correlated with the potential for As to leach through soils, to be bioavailable to plants, animals, and aquatic organisms, and to become soluble under anaerobic conditions that can occur in aquifers and in sediments from fresh and estuarine water bodies. Sequential extraction techniques use a series of progressively stronger and selective chemical extractants to partition As into soluble, Al-bound, Fe-bound, organic, and very recalcitrant residual phases in soils and sediments. These methods are very useful to conduct large-scale screening studies of a variety of soils, or sediments, to determine the distribution of As in the soil environment and to guide sampling efforts for more detailed characterization of the sorption-desorption and speciation of As in soils.

Sorption-desorption studies are widely used to obtain quantitative parameters needed for environmental fate and transport models that characterize the potential for a metal to leach to ground waters or be transported via overland flow processes to surface waters. *Sorption* refers to the binding of a metal to soil constituents (e.g., clays, Al or Fe oxides, carbonates) and *desorption* refers to the subsequent release of that metal from these constituents into the soil solution. Understanding sorption-desorption processes in soils and how they are affected by soil physical and chemical properties is critical to quantifying the concentration of As that will be in the soil solution and thus will directly interact with leaching or runoff waters. These studies are more time-consuming than chemical extraction methods but they provide numerical parameters, such as partition coefficients, sorption maxima, and binding strengths that are useful in modeling the potential for As to move through different soil profiles into shallow ground waters. Sorption-desorption studies are more process-oriented than chemical extractions and more valuable to our efforts to understand and quantify the relationship between As in solid phases (soils, sediments, aquifer materials) and aqueous phases such as leachate, ground water, or surface water.

Speciation is critical to predict the fate, transport, toxicity, and bioavailability of metals and metalloids. Many factors affect speciation including oxidation-reduction, pH, time, type and quantity of inorganic and organic sorbent phases, other ions, and organisms. These factors will determine whether a given contaminant will adsorb, precipitate, chelate, leach through the soil profile, or be absorbed by plants. Traditionally, speciation of metals/metalloids such as As in soils has been assessed by indirect approaches such as sequential extraction and/or modeling based on equilibrium data from laboratory studies (Manning and Goldberg, 1997; Manning and Suarez, 2000). These approaches are limited in their ability to assess the precise speciation of metals/metalloids in soils, primarily because of the heterogeneous nature within and among soils. Sequential extraction techniques, while useful for characterization purposes, may introduce artifacts by transforming chemical forms and may overlook minor but important phases. Extraction of sorbed As with subsequent chromatographic identification is another technique that has been employed to identify previously bound arsenic phases, yet fail to describe the actual sorption complex (Garcia-Manyes et al., 2002; Pongratz, 1998). To alleviate such shortcomings, more sophisticated techniques that provide direct identification of species (i.e., X-ray diffraction (XRD), thermal gravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS)) have been adopted to characterize metals in contaminated soils (Ding et al., 2000; Farquahr et al., 1996; Nesbitt et al., 1998). Despite their accurate descriptions of metal speciation relative to extraction approaches, these techniques may introduce artifacts from sample alterations, and detection limits are often far above background concentrations of the target metal.

XAFS spectroscopy is a technique that can provide detailed chemical and structural information about a specific absorbing element, be it a major component of a solid phase (crystalline and amorphous), a trace component of the bulk phase, or a surface-associated component (Bertsch and Hunter, 1998; Bertsch and Sayers, 1998). Several research studies have demonstrated the utility of XAFS to elucidate sorption mechanisms of metal ions on single-component metal oxides and clay mineral systems (Bargar et al., 1995; Charlet and Manceau, 1992, 1993; Fendorf et al., 1997; Scheidegger et al., 1998; Schlegel et al., 1999; Strawn and Sparks, 1999; Towle et al., 1997). Subsequently, XAFS studies have been performed using mixtures of oxides and clay minerals to better simulate metal sorption behavior in natural systems (Elzinga and Sparks, 1999; Scheckel and Sparks, 2000; Scheckel et al., 2000). These studies have enabled researchers to extend this technique one step further, allowing one to use

XAFS to successfully characterize metal-contaminated environmental samples (Hesterberg et al., 1997; Manceau et al., 1996; Morin et al., 1999; Morris et al., 1996; O'Day et al., 1998; Ostergren et al., 1999). While these studies have been critical in improving the understanding of metal sorption mechanisms in geomedia, one must realize that standard (bulk) XAFS probes an area of several millimeters in a sample, providing only an average speciation of the metal/metalloid of interest in a sample. This may pose a problem when one is analyzing XAFS data collected on heterogeneous samples since the spectrum may represent several species and without the proper database of reference samples the data are difficult to decipher (Hunter and Bertsch, 1998). Moreover, in samples where the metal/ metalloid may be present in numerous phases, the detection limit for minor species is indefinite and all species may not be represented upon spectral analyses since high Z elements in coordination to the central absorbing atom are preferentially represented over low Z elements (Manceau et al., 2000). Other techniques capable of probing an element in an environmental sample at a scale more indicative of the most reactive sites in soils (micron level) may give insight into spatial distribution of a contaminant. Using electron microscopy and electron microprobe analysis one can attain both quantitative (elemental composition) and qualitative (contaminant distribution) with good spatial resolution (< 1 μm) (Webb et al., 2000). However, the information gleaned from these techniques only provides elemental concentrations, making it difficult to distinguish between sulfide and sulfate, for example. One of the most promising techniques to examine heterogeneous soil and environmental samples is spatially resolved, micro-focused XAFS (μ-XAFS), whereby discrete regions within a complex mixture can be investigated on a micron scale (Manceau et al., 2000; Roberts, 2002). Advantages of using synchrotron-based radiation relative to standard electron probe microprobe techniques is the increased sensitivity to metal/metalloid concentrations and its ability to distinguish between phases. Examples of third generation synchrotron light sources are the Advanced Photon Source (APS) at Argonne National Laboratory and the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory where μ-XAFS analyses of soils can be conducted. Such bright light sources enable one to employ a beam size of several hundreds square micrometers (e.g., clay fraction scale) and increased detection limits at several hundred ppm loading levels. Since the micrometer scale of a mineral particle contains diverse reactive sites (e.g., oxide and organic matter coatings), μ-XAFS is extremely useful for gaining detailed data on contaminant speciation. In addition, μ-synchrotron X-ray fluorescence (μ-SXRF) spectroscopic analyses can also be conducted which provides significant information on elemental association with a targeted element.

At beamline 13-ID/GeoSoilEnviroCARS (GSECARS) at the APS and beamline 10.3.2 at the ALS state-of-art- μ-EXAFS (micro-extended X-ray absorption fine structure) spectroscopic analyses can be determined. Micro-XANES analyses can be performed at beamline X-26A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Thus, the ability to determine analyses of the entire micro-XAFS (micro-XANES and micro-EXAFS) spectra will provide not only the molecular symmetry and the oxidation state of As but also binding mechanisms at soil surfaces. Our group (Roberts, 2002; Nachtegaal et al., 2005) has used bulk XAFS, μ-SXRF, μ-XANES, and μ-EXAFS to determine the speciation of Zn in soils that had been heavily impacted by zinc smelting facilities. Analyses were also conducted on a variety of Zn-bearing mineral phases and synthesized Zn sorption samples to aid in identifying Zn species in the contaminated soils. Principal component and target transformation analyses were used to quantitate the major Zn species in the soils. Zinc mineral, adsorbed, and surface precipitate phases were found in the soils. Such techniques were employed in our studies to speciate As and accompanying metals in a tannery contaminated soil.

Understanding the fate and speciation of As in Delaware soils resulting from PL and other anthropogenic sources such as tannery wastes, and the factors affecting the fate and transport to ground waters of As added to soils is critical to assess the risk of As to ground water quality and to human and ecological health. Many Delaware soils are highly susceptible to As leaching to ground waters due to their sandy texture, low organic matter, clay, and metal oxide contents. Accordingly, the objectives of this study are:

OBJECTIVES:

1. To characterize the speciation and distribution of As in major Delaware soils, as impacted by long-term applications of all potential As sources, such as poultry litter (PL), biosolids, and other organic by-products or industrial wastes.
2. To determine factors controlling the retention, release, and potential mobility to ground waters of As in Delaware soils, as affected by soil properties and competing anions.
3. To quantify the potential for As leaching in Delaware soils, the As species in leaching waters, and the potential for best management practices to mitigate As leaching.
4. To speciate As in soils and determine the associations and distributions of As and other co-contaminating metals in tannery contaminated soils by a combination of chemical extraction, desorption, and molecular scale x-ray absorption and fluorescence spectroscopic approaches.
5. To lead, in cooperation with the University of Delaware *Institute of Soil and Environmental Quality* (ISEQ) and *Center for Critical Zone Research*, a multi-party discussion of the implications of the findings of this research to the quality of Delaware's environment.

OBJECTIVE 1: ARSENIC CONCENTRATIONS AND FORMS IN AGRICULTURAL AND URBAN CONTAMINATED SOILS IN DELAWARE

Soil samples were collected from agricultural, forested, and urban contaminated sites in Delaware to provide information on total soil arsenic (As), the solubility and bioavailability of soil As, the chemical forms of soil As, and the relationship between As forms and soil properties.

Agricultural and Forested Soils

Our initial objective was to obtain soil profile samples from benchmark soil series throughout Delaware to determine the effects of past land uses, soil type, and agricultural management practices (e.g., manure use, cropping systems) on soil As. We were particularly interested in comparisons between settings where broiler litter had been applied at different frequencies (e.g., not at all vs. every year vs. one-year in a three-year crop rotation) and forested areas adjacent to crop land receiving litter. These settings were important because one of the key goals in this project was to determine the effects of the application of litter on the amount and forms of As in Delaware's agricultural soils. Broiler litter is well-known to contain As, at concentrations from 30 to 60 mg As kg^{-1} litter, due to use of organic arsenicals, (i.e., Roxarsone), to control certain poultry diseases. We considered forests the best representation of background settings with minimal anthropogenic inputs of As. Unfortunately, we were unable to obtain as many cooperators for this part of the project as anticipated. To compensate for this we obtained soil samples from five University of Delaware (UD) farms in New Castle and Sussex counties. Details on the collection and analysis of all agricultural and forested soils are given below.

Cooperator Farm and Forest Soils: We collected soil samples from 13 soil profiles representing 10 of Delaware's benchmark soil series (Tables 1 and 2). Five of the 10 soil series were located on two farms in New Castle County with no history of animal manure application and provided a range in topography, drainage class, and soil properties typical to this geographic region: Elkton silt loam (fine-silty, mixed, active, mesic Typic Endoaquults), Reybold silt loam (fine-loamy, mixed, semiactive, mesic Typic Hapludults), Woodstown loam (fine-loamy, mixed, active, mesic Aquic Hapludults), Nassawango silt loam (fine-silty, mixed, semiactive, mesic Typic Hapludults), and Sassafras sandy loam (fine-loamy, siliceous, semiactive, mesic Typic Hapludults). The other five soil series were located on farms in Sussex County either on (i) crop land - Rumford sandy loam (coarse-loamy, siliceous, subactive, thermic Typic Hapludults), Sassafras sandy loam (fine-loamy, siliceous, semiactive, mesic Typic Hapludults), Corsica loamy sand (fine-loamy, mixed, active, mesic Typic Umbraquults), Downer sandy loam (coarse-loamy, siliceous, semiactive, mesic Typic Hapludults), Greenwich sandy loam (coarse-loamy, mixed, semiactive, mesic Typic Hapludults); or in (ii) forests immediately adjacent to the sampled crop land – Sassafras sandy loam (fine-loamy, siliceous, semiactive, mesic Typic Hapludults), Ingleside sandy loam (coarse-loamy, siliceous, semiactive, mesic Typic Hapludults), Greenwich loam (coarse-loamy, mixed, semiactive, mesic Typic Hapludults). Soil profiles sampled in Sussex County also represented the typical range in topography, drainage, and soil properties characteristic of this area. Manure application history ranged from infrequent (Rumford, Sassafras soils) to a regular part of the crop fertilization program (Corsica, Downer, Greenwich soils). Soil description and classification information at each site was provided by USDA-NRCS soil scientists who assisted in collection of the soil samples (Tables A-1 and A-2). A total of 42 distinct soil horizons were obtained for analysis.

Table 1. Selected properties of soil profiles for ten Delaware benchmark soil series on agricultural crop land at five poultry farms in Sussex County and two cash-grain farms in New Castle County.

Farm ID and								Total (EPA 3050B)	
Soil Series	Depth	pH	OM	Sand	Silt	Clay	ECEC	Al	Fe
	--cm--		---------------------%---------------------				-meq 100g^{-1}-	-----------mg kg^{-1}--------------	
	Sussex County Poultry Farms (Crop land)								
Farm #1 -Rumford	0-20	5.8	0.7	80	14	6	1.48	3028	2527
	20-40	5.7	0.1	81	9	10	1.13	2715	2175
	40-61	5.4	0.2	72	9	19	2.89	9782	6968
	61-81	5.3	0.2	74	10	16	2.99	9808	7360
Farm #2 - Sassafras	0-20	5.1	1.2	68	22	10	2.12	6942	6288
	20-40	5.9	0.8	52	23	25	4.89	12950	13809
	40-61	6.1	0.4	72	10	18	4.05	13815	13420
	61-81	6.5	0.2	80	4	16	2.30	5567	4944
Farm #3 - Corsica	0-30	4.7	7.4	79	14	7	5.88	14368	1883
	30-43	4.7	1.6	45	26	29	10.20	22245	12615
	43-81	4.4	0.7	30	35	35	12.36	23841	17785
Farm #4 - Downer	0-28	5.3	1.5	75	16	9	4.40	9658	4525
	28-45	5.8	0.7	69	18	13	3.21	11260	6096
	45-73	5.7	0.7	76	7	17	6.32	16063	10352
	73-101	5.7	0.2	67	16	17	1.38	6629	3349
Farm #5 - Greenwich	0-28	5.2	1.3	55	30	15	6.45	11174	7148
	28-53	5.6	0.5	55	28	17	12.31	14150	10337
	53-81	5.7	0.8	49	30	21	5.50	15282	14008
	81-109	5.9	0.2	73	13	14	4.83	13295	12024
	New Castle County Cash Grain Farms								
Farm #6 - Elkton	0-23	5.7	2.2	23	57	20	5.31	9014	6900
	23-43	4.9	0.9	15	57	28	3.28	9496	15688
Farm #6 - Reybold	0-23	6.5	2.1	31	48	21	6.60	13067	10580
	23-30	6.5	1.1	33	46	21	4.41	12851	10175
	30-56	6.5	1.0	23	50	27	5.07	18587	15934
Farm #6 - Woodstown	0-23	5.4	1.0	47	39	14	2.73	10054	5669
	23-46	5.6	0.4	39	42	19	2.79	14483	8214
Farm #7 - Nassawango	0-18	6.2	1.6	33	49	18	4.48	12151	11556
	18-76	6.7	0.9	19	48	33	4.48	20795	26182
Farm #7 - Sassafras	0-30	5.4	4.8	53	30	17	2.44	13524	14484
	30-56	5.1	0.6	53	28	19	1.94	12365	17923
	56-91	5.6	0.6	53	24	23	5.04	18248	32950

Table 2. Selected properties for soil profiles of benchmark Delaware soil series located in forests adjacent to crop land at three poultry farms in Sussex County.

								Total (EPA 3050B)	
Soil Series	Depth	pH	OM	Sand	Silt	Clay	ECEC	Al	Fe
	--cm--		------------------%-----------------				-meq 100g^{-1}-	-----------mg kg^{-1}--------------	
	Sussex County Poultry Farms (Forests)								
Farm #1 - Sassafras	0-10	5.0	4.6	65	27	8	4.49	4998	4268
	10-40	4.8	0.7	72	11	17	2.42	11817	10432
	40-61	4.7	0.3	70	14	16	3.05	11329	10131
	61-81	4.7	0.1	85	5	10	1.92	4674	4900
Farm #2 - Ingleside	0-15	4.2	5.3	70	24	6	3.75	3693	2952
	15-40	4.6	0.6	68	22	10	1.21	4969	3691
	40-61	4.5	0.3	62	24	14	1.10	5691	4441
	60-91	4.3	0.4	61	19	20	3.48	12873	13396
Farm #5 - Greenwich	0-8	5.3	4.6	49	36	15	13.31	12559	7010
	8-46	4.2	1.0	47	34	19	8.29	16562	8528
	46+	4.1	1.1	51	26	23	7.11	19104	15489

University of Delaware Farm Soils: We also obtained and analyzed 44 topsoil samples (0-20 cm) collected during development of nutrient management plans for crop land on five UD farms in New Castle and Sussex counties (Table 3).

These soils had a diverse range in cropping history and past manure/fertilizer use and represented 12 different soil series. Soil series sampled on the UD farms in New Castle County included: Kenansville (loamy, siliceous, subactive, thermic Arenic Hapludults), Matapeake (fine-silty, mixed, semiactive, mesic Typic Hapludults), Matawan (fine-loamy, siliceous, semiactive, mesic Aquic Hapludults), Othello (fine-silty, mixed, active, mesic Typic Endoaquults), Sassafras (fine-loamy, siliceous, semiactive, mesic Typic Hapludults), Woodstown (fine-loamy, mixed, active, mesic Aquic Hapludults). For farms associated with the UD Georgetown Research and Education Center in Sussex County, soil series sampled included: Elkton (fine-silty, mixed, active, mesic Typic Endoaquults), Evesboro (mesic, coated lamellic Quartzipsamments), Kalmia (fine-loamy over sandy or sandy-skeletal, siliceous, semiactive, thermic Typic Hapludults), Kenansville (loamy, siliceous, subactive, thermic Arenic Hapludults), Klej (mesic, coated Aquic Quartzipsamments), Matawan (fine-loamy, siliceous, semiactive, mesic Aquic Hapludults), Rumford (coarse-loamy, siliceous, subactive, thermic Typic Hapludults), Sassafras (fine-loamy, siliceous, semiactive, mesic Typic Hapludults), Woodstown (fine-loamy, mixed, active, mesic Aquic Hapludults).

Urban Contaminated Soils

Soil samples were also obtained, with the assistance of DNREC staff, from former industrial sites in Wilmington, Delaware where As contamination was suspected or previously confirmed. Three sets of soil samples were obtained from the following locations: (i) Walnut Street – in October of 2004, soil samples were collected at a former tannery site located under what is now a parking lot. Samples were obtained using split-auger cores and were taken at several depth intervals from surface to bedrock (water table depth at this time was ~ 2 m) at various site locations that had been pre-determined by DNREC; (ii) Christina Park – soil samples (0-20 and 20-40 cm) were taken in the park according to a map prepared by DNREC and also at a nearby athletic field; (iii) South Market Street – soil samples previously collected at this location were provided to us by DNREC staff. These soils were collected using geoprobes or test pits and consisted of surface and subsoil samples taken at several intervals to depths of ~2-3 m. Some characterization, analytical data, and site history information was also provided by DNREC for the South Market Street soil samples.

Soil Characterization and Analysis

After collection, all soil samples were air-dried, ground and sieved to pass a 2 mm screen, and analyzed, as appropriate to project objectives, for some or all of the following physical and chemical properties: (1) total elemental content (Al, As, B, Ca, Cu, Fe, K, Mg, Mn, P, S, Zn) by two acid digestion methods - USEPA 3051 (microwave-assisted) and USEPA 3050B (digestion block); (2) routine soil test analysis of the UD Soil Testing Program (pH, organic matter, soil test (Mehlich 3 (M3): 0.2 M CH_3COOH + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.13 M HNO_3 + 0.001 M EDTA) extractable elements (P, K, Ca, Mg, Al, B, Cu, Fe, Mn, S, Zn) and soil P saturation ratio (PSR = molar ratio of M3-P:M3[Al+Fe]); (3) textural class (percentage of sand, silt, and clay); (4) effective cation exchange capacity (ECEC) by summation of exchangeable (1M NH_4OA_c) Ca, K, and Mg and 1M KCl-exchangeable acidity; (5) TCLP-As (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); (6) plant-available (M3) soil As; (7) PBET-As (PBET = physiologically based extraction test for human ingestion of soils) using the modified PBET method developed by Fendorf et al. (2004) which extracts As from soils by equilibration with 1M glycine at pH 3.0 for 1 h at 35.6^{o}C.; and (8) Chemical fractionation of soil As - conducted for some soils using the method of Fendorf et al. (2004) that partitions soil As into three fractions: (i) water soluble and exchangeable As – extracted with 1M Mg SO_4 at pH 7.0 (1 h equilibration); (ii) As sorbed by amorphous metal (hydr)oxides, primarily Al and Fe – extracted with 0.2 M ammonium oxalate (pH 3.0) equilibrated in the dark for 4 h; and (iii) As associated with recalcitrant soil phases such as crystalline metal hydr(oxides), extracted by 12M HCl following a 12 h equilibration. Concentrations of As in all soil extracts were determined by inductively coupled optical emission spectroscopy (ICP-OES).

ARSENIC STATUS OF AGRICULTURAL AND FORESTED SOILS IN DELAWARE

General Characteristics of Agricultural and Forested Soils

Cooperator Farm and Forest Soils: The soil profiles on crop land and forests on cooperator's farms in New Castle and Sussex counties had physical and chemical properties (Tables 1, 2, A-1, and A-2) representative of the Coastal Plain and Piedmont soils that dominate Delaware's agricultural land base. All soils were acidic (pH < 7.0) throughout the soil profile but topsoils from crop land were in or near pH range recommended for crop production in Delaware (pH 5.6 - 6.0; Sims and Gartley, 1996). In contrast, soil pH values in forests which, unlike crop land, are not routinely limed to neutralize soil acidity, were quite acidic (pH 4.1 to 5.3; mean pH = 4.6). Soil organic matter contents were generally low (<3%) with only a few exceptions, such as the poorly drained Corsica soil on Farm #3 (OM=7.4%), and were slightly higher in New Castle County (1.4%) than Sussex County (1.0%). Forested topsoils had higher OM contents (4.8%) than corresponding agricultural topsoils on the same farms (1.1%) and subsoils had lower OM contents (mean = 0.6 ±0.4%) than topsoils (mean = 2.9 ±2.1%). The elemental composition of all soils on these farms was dominated by aluminum (Al; mean = 11797 ± 5153 mg kg^{-1}) and iron (Fe; mean = 9979 ± 6375 mg kg^{-1}); all other elements measured had concentrations < 2000 mg kg^{-1} (Tables A-3 and A-4). Total Al and Fe were also highly correlated with clay content (Al, r=0.77***; Fe, r=0.75***), reflecting both the composition of clay minerals (alumino-silicates) typical to Delaware soils and the association of amorphous Al and Fe (hydr)oxides with soil clays. The Coastal Plain soils of Sussex County were coarser textured, primarily sandy loams and loamy sands, than the finer-textured, primarily silt loam soils in the Upper Coastal Plain and Piedmont regions of New Castle County. The concentration of finer-sized particles (silt, clay) was consistently greater in subsoils than topsoils, reflecting the influence of long-term weathering processes that cause the illuviation of fine particles into lower soil horizons. Paralleling this trend, effective cation exchange capacity (ECEC) values tended to be lower in topsoils (1.48 to 6.60 meq 100 g^{-1}) than subsoils (1.10 to 12.4 meq 100 g^{-1}) and particularly increased in finer-textured subsoils where clay, silt, Al and Fe had accumulated.

The fertility status of all soil profiles was also assessed by measuring Mehlich 3 (plant available) nutrients (Tables A-5 and A-6). For these farms, most, but not all, topsoils from agricultural crop land were within, or slightly exceeded the agronomically optimum values used by the UD Soil Testing Program for major plant nutrients (optimum soil test ranges: P= 50-100; K= 91-182; Ca=500-1000; Mg=66-132 mg kg^{-1}) indicating that fertilizers and manures have been applied on these farms in a manner that is reasonably consistent with crop needs. The one exception noted was Farm #4 in Sussex County (Downer soil) where poultry manures have been applied regularly and soil test P (264 mg kg^{-1}) was in the excessive range (>100 mg P kg^{-1}). As would be expected, forest soils were generally lower in fertility than soils from adjacent crop land. Subsoils were also lower in fertility than topsoils, although some relatively leachable plant nutrients (e.g., K and S) were observed to accumulate in subsoil horizons.

The distribution of soil test P (phosphate, $H_2PO_4^{-1}$ or HPO_4^{-2}) and S (sulfate, SO_4^{-2}) in these soil profiles illustrates the typical patterns of anion retention by Delaware soils. The trend consistently observed for P, as shown in past research (Mozzafarri and Sims, 1994) is for accumulation in topsoils with increased leaching of P into subsoils gradually occurring as topsoils become more P-saturated (Sims et al., 2002). This is supported by the significant correlation (r=0.80**) determined between topsoil M3-PSR and the M3-P content in underlying subsoils. In contrast, for sulfate, known to be more leachable in Delaware soils than phosphate (Kline et al., 1986), accumulation often occurs in high clay/Al/Fe subsoils underlying sandy surface horizons. Thus, depending upon the relative mobility of the anion in question and the distribution of reactive soil constituents in the soil profile, anion accumulation can occur in both surface and subsoil horizons. This is an important consideration when assessing the risk of ground water contamination by an element such as As, which is primarily found in well-drained soils as arsenate (AsO_4^{-3}), a form that is usually intermediate in mobility in soils between phosphate and sulfate.

University of Delaware Farm Soils: The properties of topsoils obtained from five University of Delaware farms in New Castle and Sussex counties were similar in many respects to the topsoils collected from crop land on the cooperator's farms (Table 3). For example, soil pH and OM values averaged pH 6.2 ± 0.4 and 2.6 ±1.1% at the two UD farms in New Castle County and pH 6.0 ± 0.3 and 1.3 ±0.6% at the three UD farms in Sussex County. Also, although we did not measure total Al and Fe on topsoils from the UD farms, the mean values for M3-Al (863 mg kg^{-1}) and M3-Fe (225 mg kg^{-1}) were comparable to values for topsoils located on the cooperator's farms (M3-Al = 705 mg kg^{-1} and M3-Fe = 159 mg kg^{-1}). Note, however, that to meet the goals of this study we intentionally selected soil samples from fields on UD farms where cropping histories were more diverse than on cooperator's farms, including pastures and forage crops as well as grain crop rotations. We also chose soil samples where soil fertility ranges were more extreme, primarily due to wider variations in manure and fertilizer use, as evidenced by M3-P values which ranged from a low of 8 mg kg^{-1} in a corn field at the UD Middletown farm to a high of 1016 mg kg^{-1} in a dairy pasture on the UD Newark farm.

In summary, based on our soil analyses, the soil profile investigations conducted by USDA-NRCS (Tables A-1 and A-2), information obtained on site histories, and our professional experience, we believe that the 86 soil samples (42 soil horizons from 10 benchmark soil series and 44 topsoils from UD farms representing 12 benchmark soil series) used in this study provide a representative range of the physical and chemical properties, effects of past soil management practices, and current As status of Delaware's agricultural and forested soils.

Table 3. Soil series, land use information, selected chemical properties, and forms of soil arsenic (As) for agricultural topsoils (0-20 cm depth) at five farms on University of Delaware property in New Castle and Sussex Counties.

Site ID	Land Use	Soil Series	pH	OM	M3-P	M3-Fe	M3-Al	Total As	M3 As	TCLP As	PBET As
				---%---	mg kg^{-1}						
Newark Research and Education Center											
N1	Corn silage	MeB2, MeC2	5.3	2.1	50	110	973	4.9	0.54	0.07	0.52
N2	Alfalfa	MeB2, MeC2	6.5	2.4	54	111	1003	8.9	0.48	0.23	0.82
N3	Mixed grass	MeB2, MeC2	6.7	1.7	49	119	927	4.4	0.54	0.12	0.65
N4	Mixed grass	Ot, MtA	5.6	4.4	69	326	938	7.2	0.72	0.16	0.02
N5	Mixed grass	SaB2, MeB2	6.1	3.4	38	245	818	7.8	0.64	0.14	0.17
N6	Alfalfa	MeB2 (SaC3, KeA, WoA)	6.4	2.2	134	377	929	3.3	0.74	0.18	0.01
N7	Alfalfa	MeB2 (SaC3, KeA, WoA)	6.5	3.1	243	336	926	10.6	0.69	0.17	0.01
N8	Corn silage	MeB2, MeA, KeA	6.7	1.8	133	634	811	7.8	0.66	0.18	0.44
N9	Corn silage	MeB2, MeA, KeA	6.6	3.9	131	387	912	4.9	0.63	0.05	0.09
N10	Corn silage	MeB2 (SaC3, KeA)	6.3	2.1	68	428	927	6.6	0.50	0.09	0.70
N11	Grass hay	MeB2	6.0	2.6	177	279	981	19.6	1.36	0.26	0.93
N12	Dairy Pasture	KeA	6.6	6.0	1016	376	879	11.1	0.79	0.16	0.80
N13	Reed Canary	Ot	6.0	2.6	27	429	684	4.9	0.77	0.13	0.48
N14	Grain corn	MeA	6.2	2.4	54	290	894	17.9	0.97	0.18	0.25
N15	Grain corn	MeA	5.7	2.4	176	344	1004	10.6	1.05	0.19	0.44
Middletown Research and Education Center											
M1	Corn, wheat, soybeans; As of 2004 all orchardgrass	WsA	6.5	2.0	48	213	949	7.8	0.43	0.29	0.01
M2		WsA	6.2	3.5	22	428	1132	11.7	0.50	0.35	0.51
M3		MeA	6.5	1.9	46	152	671	7.8	0.62	0.24	0.01
M4		SaD3	6.4	1.6	15	287	746	6.1	0.56	0.13	0.64
M5		SaD3	6.6	2.0	18	294	803	3.8	0.75	0.28	0.55
M6		SaD3	5.1	1.6	32	170	752	8.3	0.53	0.40	0.87
M7		MeB2	5.8	1.5	11	454	779	6.1	0.59	0.14	0.23
M8		SmE	6.0	1.5	8	308	821	7.2	0.71	0.15	1.33

Table 3 (cont.). Soil series, land use information, selected chemical properties, and forms of soil arsenic (As) for agricultural topsoils (0-20 cm depth) at five farms on University of Delaware property in New Castle and Sussex Counties.

Site ID	Land Use	Soil Series	pH	OM	M3-P	M3-Fe	M3-Al	Total As	M3 As	TCLP As	PBET As
				---%---	mg kg^{-1}						
Georgetown Research and Education Center											
GT1	Corn, wheat, soybeans, vegetables	Mn	6.2	0.7	203	143	719	3.8	1.04	0.21	1.40
GT2		Mn	6.3	0.8	140	123	718	5.5	0.97	0.54	0.51
GT3		El	6.4	1.5	160	95	956	6.6	0.67	0.06	0.01
GT4		SaA	6.3	0.9	166	141	766	3.8	0.65	0.27	1.28
GT5		Kl	5.8	2.7	145	151	898	1.0	0.72	0.32	1.22
GT6		EvA	5.7	1.6	191	193	589	1.0	0.69	0.13	0.11
GT7		Kl	6.3	1.4	159	98	947	3.8	0.68	0.26	1.58
GT8		Ka	6.5	1.1	150	184	886	7.8	1.94	0.51	0.82
GT9		Ka	5.7	2.1	148	122	702	8.3	1.71	0.22	0.16
GT10		Kl	5.9	2.8	135	124	1081	7.8	1.03	0.59	0.98
GT11		SaA	6.1	1.2	82	103	717	8.9	1.14	0.31	0.18
GT12		Wo	5.9	1.0	108	127	1048	3.3	0.46	0.10	0.01
GT13		KbA	5.8	1.2	168	177	773	3.8	0.42	0.47	0.84
GT14		KbA	6.4	0.8	121	122	1236	2.7	0.31	0.37	0.94
GT15		EvA	6.2	1.3	122	101	615	2.1	0.37	0.40	0.45
D1		Wo	5.7	1.1	298	193	873	4.4	0.49	0.46	0.89
D2		Wo	5.9	1.4	112	154	867	2.1	0.37	0.14	1.23
D3		EvA	5.8	0.8	259	174	662	4.9	0.49	0.22	0.03
D4		EvA	5.6	1.0	78	119	673	2.7	0.47	0.38	0.73
W1		RuA	6.6	1.0	81	78	736	6.1	0.52	0.12	0.24
W2		EvA	5.8	1.2	121	72	1247	0.4	0.59	0.12	0.03

Arsenic Status of Agricultural and Forested Soils

Total As concentrations in 42 soil horizons on cooperator's farms in New Castle and Sussex counties ranged from below detection to 9.2 mg kg^{-1} (mean = 3.0 ± 1.9 mg kg^{-1}) by the EPA 3051 method and from 0.4 to 7.8 mg kg^{-1} (mean = 3.1 ± 1.7 mg kg^{-1}) by the EPA 3050B method (Table 4). Given the similarity between the two methods, for the remainder of this report we only present EPA 3051 values for total soil As because this is the standard method used for total elemental analyses of soils by the UD Soil Testing Program. In terms of trends related to geographic location, we noted slightly higher total As concentrations in agricultural soil profiles from New Castle county (mean = 4.1 ± 1.9 mg kg^{-1}) compared to those found in Sussex county (mean = 2.6 ± 1.8 mg kg^{-1}). However, total As concentrations were virtually identical for three farms in Sussex county (Farms #1, #2, #5) where soil profiles were sampled on crop land (mean = 2.8 ± 1.6 mg kg^{-1}) and in adjacent forests (mean = 2.6 ± 1.9 mg kg^{-1}). Unlike P and S, there were no clear trends or patterns for total As accumulation within these soil profiles, either in topsoils or in subsoil horizons high in clay, Al and Fe.

For the five UD farms in this study, the 44 topsoil horizons sampled had total As concentrations ranging from 0.4 to 19.6 mg kg^{-1} (mean = 6.4 ± 3.9 mg kg^{-1}). As noted with the cooperator's farms, total As values were somewhat higher for UD farms in New Castle County (mean = 8.2 ± 4.0 mg kg^{-1}) than UD farms in Sussex County (mean = 4.3 ± 2.5 mg kg^{-1}). When all data from cooperator's farms and UD farms were combined, the overall mean value for total soil As in 86 agricultural and forested soils from Delaware was 4.7 ± 3.5 mg kg^{-1}. In summary, our total soil As results show that 97% of the agricultural and forested soils in this study had total As concentrations below the "background" level (11 mg total As kg^{-1}) proposed by DNREC to determine the need for and most appropriate approach to remediate sites where future land use is "...reasonably anticipated to be residential or unrestricted" (DNREC, 2005) (Fig. 1a). Therefore, our findings suggest that past and current agricultural practices in Delaware have not resulted in elevation of soil total As concentrations to the point that widespread site remediation will be required at this time.

Table 4. Total, leachable (TCLP), and plant-available (Mehlich 3) arsenic (As) in soil profiles for ten Delaware benchmark soil series on agricultural cropland at five poultry farms in Sussex County and two cash-grain farms in New Castle County.

		Total As		TCLP	Mehlich 3
Soil Series	Depth	EPA 3050B	EPA 3051	As	As
	--cm--	--------------------------------------mg kg^{-1} ---------------------------------------			
		Sussex County Poultry Farms (Crop Land)			
Farm #1 -Rumford	0-20	1.2	2.8	0.02	0.2
	20-40	1.0	2.8	0.06	0.3
	40-61	2.9	3.4	0.19	0.2
	61-81	3.3	1.5	0.01	0.2
Farm #2 - Sassafras	0-20	2.8	5.4	0.05	0.2
	20-40	4.9	5.4	bd[†]	0.3
	40-61	4.7	0.8	0.03	0.1
	61-81	3.0	3.4	bd	0.2
Farm #3 - Corsica	0-30	0.4	2.1	bd	0.2
	30-43	0.9	0.5	0.02	0.2
	43-81	2.3	bd	0.02	0.3
Farm #4 - Downer	0-28	4.9	2.6	0.23	0.4
	28-45	3.5	1.1	0.06	0.3
	45-73	3.9	6.3	bd	0.2
	73-101	1.0	3.2	0.29	0.2
Farm #5 - Greenwich	0-28	3.6	2.6	0.12	0.3
	28-53	3.3	0.3	0.18	0.2
	53-81	4.0	3.2	0.05	0.2
	81-109	1.9	1.6	bd	0.1
		New Castle County Cash Grain Farms			
Farm #6 - Elkton	0-23	0.8	3.4	0.01	0.1
	23-43	1.2	2.5	0.09	0.0
Farm #6 - Reybold	0-23	5.0	3.3	0.22	0.1
	23-30	4.3	3.7	0.03	0.1
	30-56	5.8	4.8	0.03	0.0
Farm #6 - Woodstown	0-23	2.5	2.2	0.35	0.1
	23-46	1.2	2.1	0.01	0.1
Farm #7 - Nassawango	0-18	2.4	4.4	bd	0.1
	18-76	2.4	4.8	bd	0.0
Farm #7 - Sassafras	0-30	7.8	5.4	bd	0.2
	30-56	5.4	3.7	0.19	0.1
	56-91	5.8	9.2	0.14	0.1

[†] bd = below detection limit

Table 5. Total, leachable (TCLP), and plant-available (Mehlich 3) arsenic (As) in soil profiles of benchmark Delaware soil series located in forests adjacent to crop land at three poultry farms in Sussex County.

		Total As		TCLP	Mehlich 3
Soil Series	Depth	EPA 3050B	EPA 3051	As	As
	--cm--	mg kg^{-1}			
	Sussex County Poultry Farms (Forests)				
Farm #1 - Sassafras	0-10	2.9	1.5	0.06	0.1
	10-40	2.2	5.4	0.22	0.1
	40-61	2.0	1.5	bd[†]	0.1
	61-81	1.6	0.8	0.05	0.3
Farm #2 - Ingleside	0-15	5.2	0.2	0.09	0.3
	15-40	2.0	2.1	bd	0.0
	40-61	0.9	1.5	bd	0.2
	60-91	4.3	6.1	0.10	0.1
Farm #5 - Greenwich	0-8	5.1	4.2	0.08	0.3
	8-46	2.8	2.1	0.04	0.2
	46+	4.9	3.3	0.20	0.1

[†] bd = below detection limit

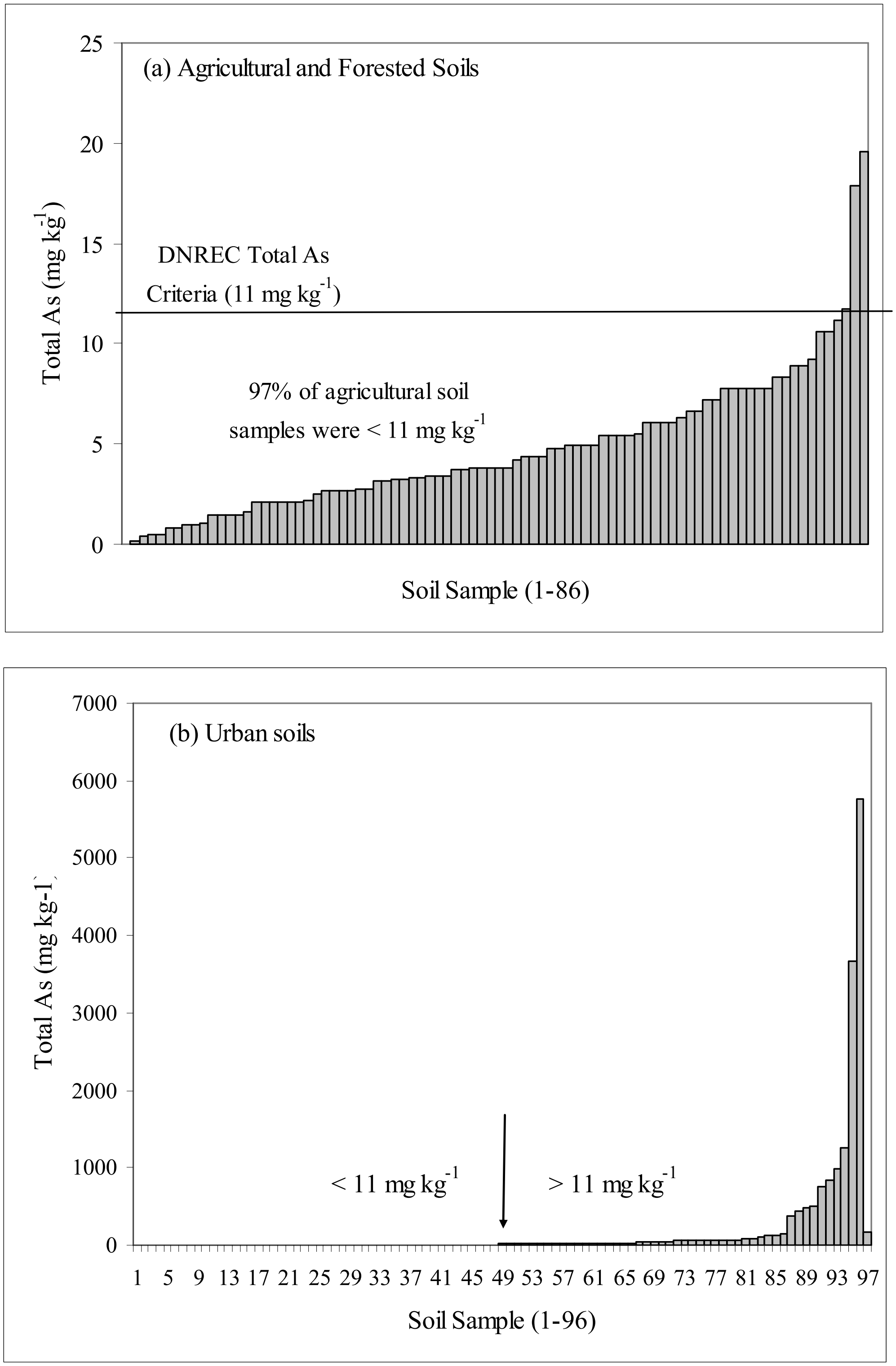

Figure 1. Comparison of total arsenic concentrations in (a) agricultural and forested soils obtained from cooperator's farms and University of Delaware farms and (b) urban soils collected at three locations in Wilmington, Delaware.

Scenarios for Effects of Long-term Broiler Litter Use on Soil Arsenic: Given the present concerns about the potential impact of broiler litter on soil As, it is useful to compare the soil total As values we measured with estimates of how litter applications would have been predicted to affect total As concentrations in Delaware soils since the use of organo-arsenicals by the poultry industry began in the 1960s. Assume, for example (Scenario #1), that broiler litter with a total As concentration of 40 mg As kg^{-1} had been applied at a rate of 9 Mg ha^{-1} every year for 40 years to a sandy loam soil in southern Delaware with an initial topsoil (0-20 cm depth) total As concentration of 2 mg kg^{-1} (mean As concentration in forested topsoils in this study). Assuming a bulk density of 1.4 g cm^{-3}, the total mass of soil in one hectare would be 2,800,000 kg ha^{-1}. In this example, the amount of total As initially present in the topsoil was 5,600 g As ha^{-1} and the total amount of As added in the litter during this 40-year period would have been 14,400 g ha^{-1}. If there was no loss of As from this soil by erosion, leaching, plant uptake, or volatilization, the soil total As concentration in 2005 would be predicted to be ~7 mg As kg $soil^{-1}$ (20 x 10^6 mg As in 2,800,000 kg soil). For this particular scenario, this represents an annual increase in soil total As of ~0.12 mg As kg^{-1} yr^{-1} due to broiler litter application. A more realistic scenario (Scenario #2) might assume broiler litter was not applied every year and that some added As was lost from topsoils by erosion, leaching to subsoils or in harvested crops. If we assume broiler litter was applied two years out of three, as might occur in a corn-soybean-corn rotation, and that 10% of added litter As was lost from topsoils, the predicted total topsoil As concentration in 2005 would be ~5 mg As kg^{-1}, or an annual increase of ~0.08 mg As kg^{-1} yr^{-1} due to broiler litter application. The soil total As value in Scenario #2 (~5 mg kg^{-1}) is similar to values we measured in topsoils on farms in Sussex County (3-5 mg kg^{-1}) and to total As values reported by the U.S. Geological Survey in 1984 for soils in Sussex County (4.9 mg kg^{-1}). All of these soil As concentrations, however, are higher than the median soil total As value of 1.2 mg kg^{-1} reported for 36 rural Coastal Plain soils in New Jersey (NJ statewide median soil total As = 5 mg kg^{-1}; Sanders, 2003). Clearly, additional scenarios could be conducted. However these calculations, and data from our study and past surveys of soil As in the region, suggest that long-term applications of broiler litter to crop land in southern Delaware should not have elevated soil total As to concentrations greater than the 11 mg kg^{-1} total As standard now proposed by DNREC. Finally, it is also useful to calculate the estimated number of years that broiler litter could be applied before exceeding an established upper limit, such as the 11 mg kg^{-1} DNREC soil As standard. Based on the assumptions used in Scenario #2 above for litter application rate and total As content, 10% losses of As added in litter, and an initial soil total As concentration of 5 mg kg^{-1}, it would require 75 years before topsoil total As values would be > 11 mg kg^{-1}. The fact that application of broiler litter at agronomic rates could increase soil total As values above the DNREC As standard within one or two generations does raise questions about the sustainability of As use in poultry production. A sustainable practice is generally assumed to be one that can be continued indefinitely with no adverse environmental effects. Based on the current criteria used by DNREC to identify soils where total As is of environmental and ecological concern (11 mg kg^{-1}), our calculations and field data suggest that it would be prudent to investigate alternatives to the use of Roxarsone or other organo-arsenicals in poultry production.

We conducted additional soil analyses (TCLP-As, M3-As, and PBET-As) to assess the potential risk of As in agricultural and forested soils to water quality and human health. Results from TCLP analyses conducted on soil profiles from cooperator's farms and topsoils on UD farms suggest that the risk of As leaching from these soils to ground waters is very low. As seen in Tables 4 and 5, the TCLP-As concentrations in soils on these farms and forests were always less than 1 mg kg^{-1} and averaged 0.1 ± 0.1 mg kg^{-1} on cooperator's farms and 0.2 ± 0.1 mg kg^{-1} on UD farms. The TCLP-As concentrations we measured in soils in this study are much lower than the regulatory value of 100 mg kg^{-1} established by the USEPA for TCLP-As in potentially hazardous solid materials[1]. Similarly, plant available soil As (M3-As) was extremely low, averaging 0.4 ± 0.4 mg kg^{-1} for the 86 topsoil and subsoil samples collected in this study. In comparison, for the same set of soils, mean values for M3-P and M3-S, the major soil anions that should compete with arsenate for plant uptake, were 82 ± 125 mg kg^{-1} and 30 ± 13 mg kg^{-1}, respectively. This suggests that As concentrations in the harvested portion of crops typically grown on these soils would be quite low and of little risk to the food chain. Finally, we also measured PBET-As for the 44 topsoils collected on five UD farms. The PBET method is an experimental procedure designed to assess the potential bioavailability of As (and other metals) in the human gastro-intestinal tract following soil ingestion. At present, there are no published criteria that quantitatively delineate the relative risk of PBET-As in soils. Despite this, we felt it would be useful to obtain some initial information on this test for agricultural and urban soils in Delaware. For the topsoils on the UD farms we found PBET-As concentrations ranging from 0.01 to 1.6 mg kg^{-1} (mean = 0.5 ± 0.4 mg kg^{-1}). Our results also showed that, over all soils, PBET extracted ~14% of total soil As. Higher but much more variable percentages of total As were extracted from the coarse-textured soils at the Georgetown farms (23 ± 28%) than from the finer textured soils at the UD Newark farms (6 ± 5%) (Table 3).

ARSENIC STATUS OF URBAN CONTAMINATED SOILS

Total As concentrations in the 96 soil samples collected from urban sites in Wilmington, Delaware were highly variable and ranged from below our analytical detection limit to as high as 5760 mg kg^{-1} (mean=177 ± 714 mg kg^{-1}; median=10 mg kg^{-1}; Tables 6 and 7). It is important to note that information provided by DNREC and observations we 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. The difference in elemental composition between the urban "soils" and agricultural topsoils is clearly shown in Tables A-3, A-4, and A-7. We also illustrate this in Figure 2 which compares the total soil content of Al, Ca, Cu, Fe, S, and Zn, elements often found in association with As in soil environments, for soils from the South Market Street location and agricultural soils from New Castle County. Note in particular the much higher concentrations of Ca and Mg in the urban soils compared to the agricultural soils. This suggests that some type of alkaline fill material, such as coal ash, may be a major component of the soil profile as this site.

For these urban sites, 50% of the soils exceeded the 11 mg kg^{-1} As background level proposed by DNREC in 2005 and thus would require some form of risk assessment to determine the need for site remediation (Fig. 1 (b)). 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." We found that 29% of the soils at these sites had total As concentrations > 40 mg kg^{-1} and that soils exceeding this action level were located close to the soil surface (< 1m) and at much deeper depths (> 2-3 m) in the soil profile (Tables 6 and 7).

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[1] The USEPA TCLP criteria for As is 5 mg L^{-1}. Based on the 1:20 soil:solution ratio used for a TCLP extraction, this criteria is equivalent to 100 mg TCLP-As kg^{-1} soil.

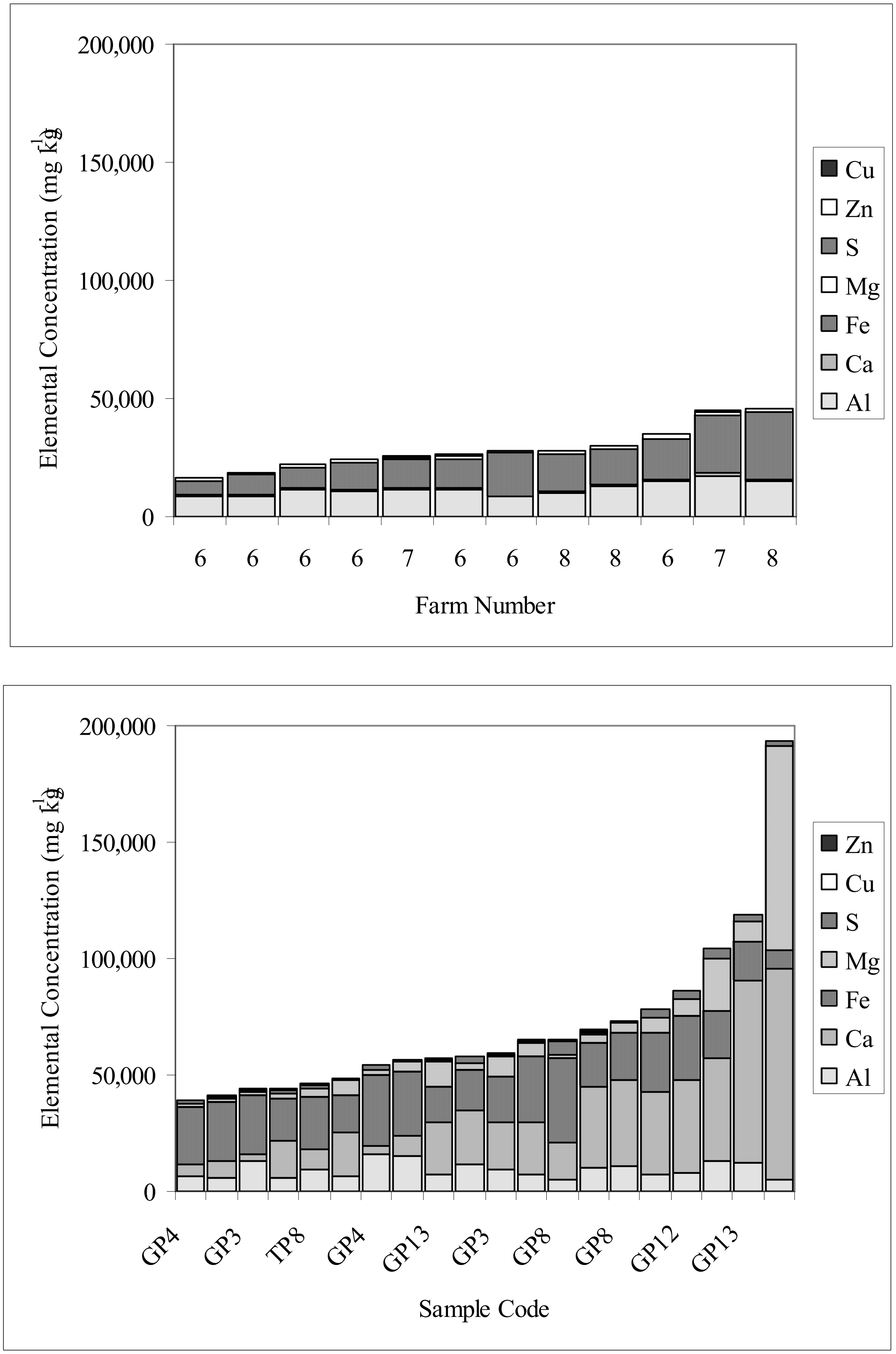


Figure 2. Comparison of total elemental composition of (a) agricultural soils in New Castle County, Delaware and (b) urban soils from Wilmington, Delaware.

Table 6. Total arsenic concentrations in topsoils and subsoils at two locations sampled with DNREC staff in Wilmington, Delaware.

Walnut Street			Christiana Park		
Sample ID	Depth	Total As	Sample ID	Depth	Total As
	----------m----------	----mg kg^{-1}----		---cm-----	----mg kg^{-1}----
#1	0.6 - 1.2	3.1	22	0-20	18
#3	1.8 - 2.4	0.8	22	20-40	12
	2.4 - 3.0	2.7	22	0-30	29
#4	0.3 - 0.9	387	23	0-20	14
	0.9 - 1.5	57	23	20-40	2.9
	1.8 - 2.4	0.1	27	0-20	12
	2.4 - 3.0	1.7	27	20-40	3.2
	4.3-4.9	1.0	32	0-20	11
	5.8-6.4	0.0	32	20-40	0.3
	7.3-7.9	0.1	2A	0-20	24
	8.8-9.4	0.0	2A	20-40	72
	10.3-10.9	0.0	2B	0-20	65
	13.4-14.0	0.0	2B	20-40	54
#5	0.3 - 0.9	3675	2C	0-20	14
	0.9 - 1.5	831	2C	20-40	985
	1.5-2.1	7.8	2D	0-20	59
	2.4 - 3.0	6.4	2D	20-40	7.0
	4.3-4.9	11	5A	0-20	10
	5.8-6.4	8.9	5A	20-40	55
	7.3-7.9	3.1	5B	0-20	90
	8.8-9.4	0.0	5B	20-40	5.3
	10.3-10.9	0.0	5C	0-20	23
#6	1.2-1.8	no data	5C	20-40	8.1
	1.8 - 2.4	6.0	5D	0-20	50
	2.4 - 3.0	6.2	5D	20-40	21
#7	0.3 - 0.9	130			
	1.2-1.8	102			
	1.8 - 2.4	13			
	2.4 - 3.0	0.0			
	4.3-4.9	4.2			
	5.8-6.4 top	0.0			
	5.8-6.4 bottom	0.0			
	7.3-7.9	0.0			
	8.8-9.4	0.0			
	10.3-10.9	0.8			
	11.9-12.5	1.6			
	13.4-14.0 top	1.1			
	13.4-14.0 bottom	0.0			
	14.9-15.5 top	2.3			
	14.9-15.5 bottom	5.0			
	16.4-17.0	0.8			
#8	0.9 - 1.5	70.0			
	1.8 - 2.4	2.5			
	2.4 - 3.0	3.6			
#9	0.3 - 0.9	4.0			
	1.8 - 2.4	3.3			
	2.4 - 3.0	0.6			
#10	0.3 - 0.9	32			
	1.2-1.8	484			
	1.8 - 2.4	10			
	2.4 - 3.0	8.4			
	3.0 - 6.4	1.1			

Table 7. 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							
ID	Type	Point	Depth	XRF-As	Total As	TCLP As	PBET As	M3-As	$MgSO_4$	Am-Ox	HCl	Residual†
			----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

†Residual = difference between EPA3051 total As and sum of $MgSO_4$, Am-Ox, and HCl As.

Table 8. Comparison of total and TCLP arsenic in selected topsoils and subsoils from two sites sampled with DNREC staff in Wilmington, Delaware.

Site	ID	Depth	Total As	TCLP-As
			-------------------mg kg^{-1}	----------------------------
		------m-------		
100 Walnut St.	5	0.9 - 1.5	503	12.7
	5	4.3-4.9	14	0.02
	7	0.3 - 0.9	130	0.69
	7	1.8 - 2.4	10	0.00
		-----cm-----		
Christiana Park	22	0-20	18	0.09
	22	20-40	12	0.06
	23	0-20	14	0.02
	27	0-20	12	0.03
	32	20-40	11	0.09
	2A	0-20	24	0.80
	2A	20-40	72	0.65
	2B	0-20	65	1.95
	2B	20-40	54	0.75
	2C	0-20	14	0.07
	2C	20-40	985	17.8
	2D	0-20	59	0.15
	5A	0-20	10	0.06
	5A	20-40	55	0.08
	5B	0-20	90	2.17
	5C	20-40	23	0.12
	5D	0-20	50	0.51
	5D	20-40	21	0.11

The leachability of As in all urban soils was assessed by TCLP extraction. Results showed that TCLP-As was significantly correlated with total As but that only one of the 96 samples (GP 14, deep sample, South Market Street site) exceeded the USEPA regulatory value (100 mg TCLP-As kg soil^{-1}) (Tables 7 and 8, Fig. 3). Based on the regression equation shown in Fig 3(b) (omitting one outlier shown in Fig. 3(a)), soil samples similar to those in this study with a total As value > ~5400 mg kg^{-1} would be expected to exceed the USEPA TCLP-As limit. We also found, using only the 20 soils from the South Market Street site, that bioavailable forms of soil As (PBET and Mehlich 3) were significantly correlated with total soil As (Fig. 4 a, 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 = 8-10 mg kg^{-1}). Data on soil test As values associated with As uptake are very limited and site specific; however, as an example, based on the regression equations in Fig 4(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}. Finally, we found that the percentage of total As extracted by PBET ranged from 10 to 76% and averaged 36 ± 19%, somewhat higher than the average percentages determined for agricultural and forested soils.

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. We conducted a relatively simple sequential chemical fractionation of the 20 soils from the South Market Street site using the method of Fendorf et al. (2004) to partition As into “easily exchangeable” ($MgSO_4$-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. Our general goal was to better characterize the variability in As speciation in urban contaminated soils. We also wanted to determine if there were any relationships between the chemical forms of As in these soils, soil chemical properties and leachable or bioavailable As. This information could then be used to guide the selection of soil samples for more complex speciation analyses using advanced spectroscopic methods such as XAFS or XANES. 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 (Tables A-7 and A-8, Fig. 5).

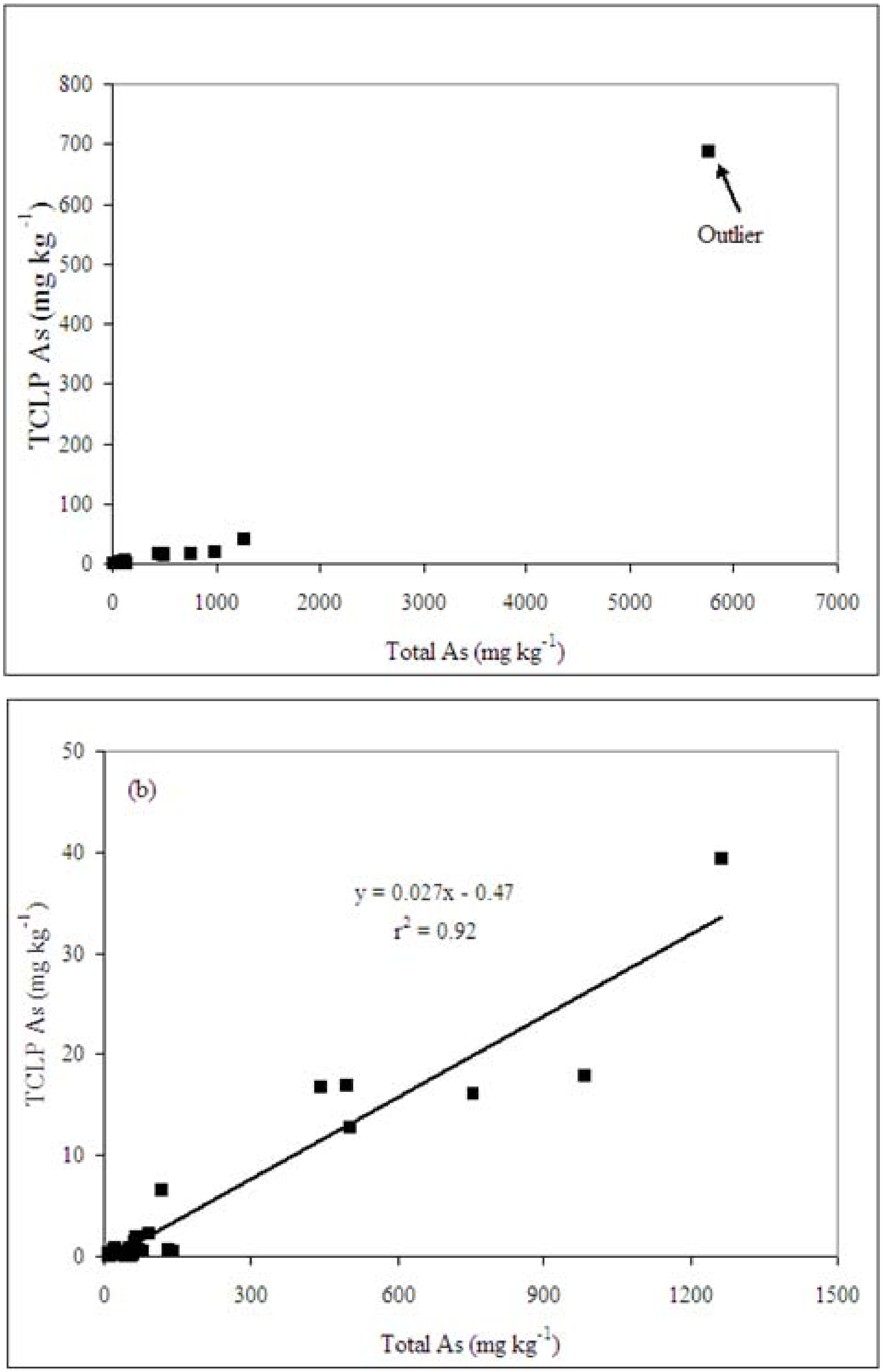


Figure 3. Relationship between total soil arsenic and TCLP-As for (a) all urban soils collected in Wilmington, Delaware and (b) all soils excluding the one outlier identified in (a).

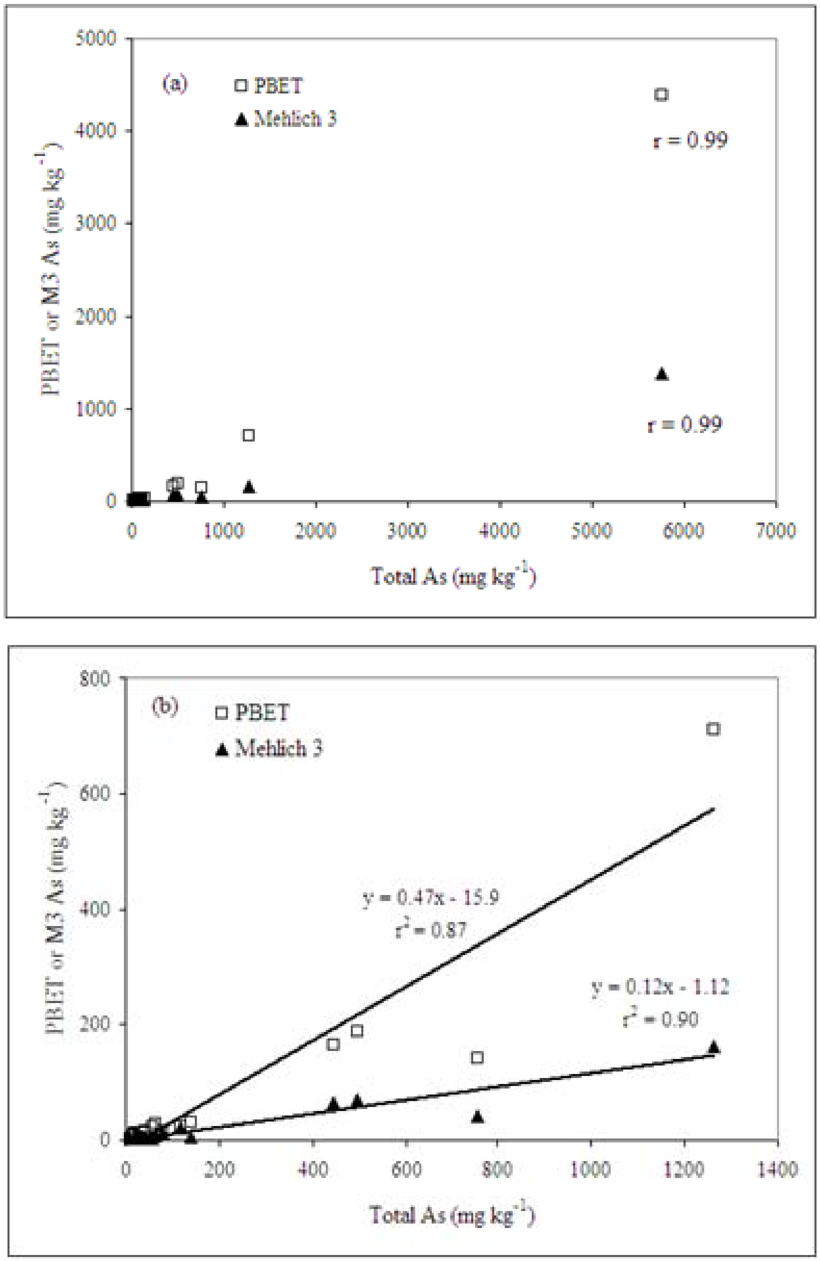


Figure 4. Relationship between total soil arsenic and either PBET-As or Mehlich 3-As for (a) urban soils collected in Wilmington, Delaware and (b) all urban in soils in (a), excluding one outlier with a total As concentration > 5000 mg kg^{-1}.

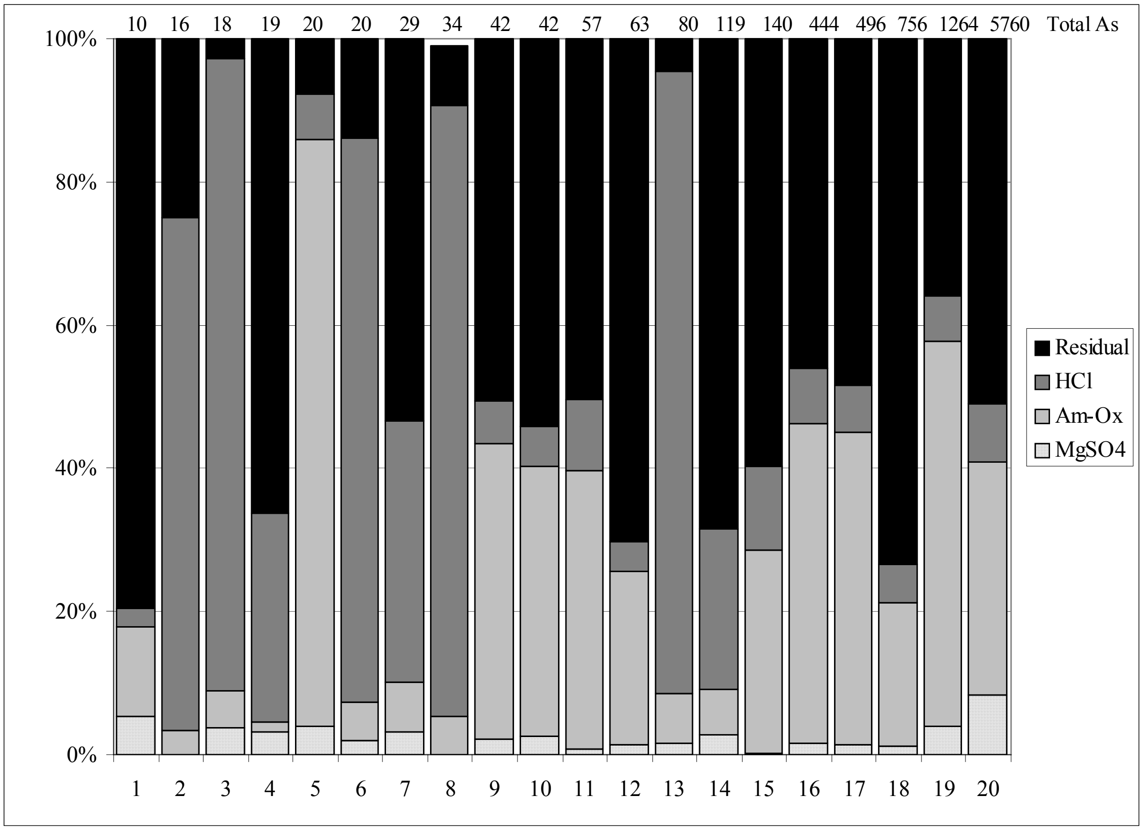


Figure 5. Sequential chemical fractionation of soil arsenic for 20 soils collected from an urban contaminated site in Wilmington, Delaware. Soils are in shown in order of increasing total As (value on top of each bar) from left to right.

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 ± 108 mg kg $^{-1}$ (2 ± 2%), 163 ± 432 mg kg^{-1} (25 ± 21%), 44 ± 103 mg kg^{-1} (29 ± 33%), and 236 ± 654 mg kg^{-1} (44 ± 25%). Despite this variability, closer examination of the fractionation results showed apparently at least two groups of soils at this site with clearly different trends in As speciation (Fig. 6(a)). In the first group, most As that could be extracted was removed by $MgSO_4$ and AmOx, while for the second group most of the extractable As was in the HCl fraction. The variability in chemical properties within each of the two groups of soils (Table 7) 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 #1 to have higher concentrations of organic matter, As, Ca, Mg, and S and slightly greater percentages of TCLP-As and PBET-As than soils in Group #2 (Table 9). As would be expected, the percentage of total As in the $MgSO_4$ fraction (water soluble and exchangeable As) and TCLP-As were well correlated (r=0.75). We also found significant linear relationships, 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 two subsets (Fig. 6b). However, chemical analyses provided no clear insight into the reasons for these two separate linear relationships.

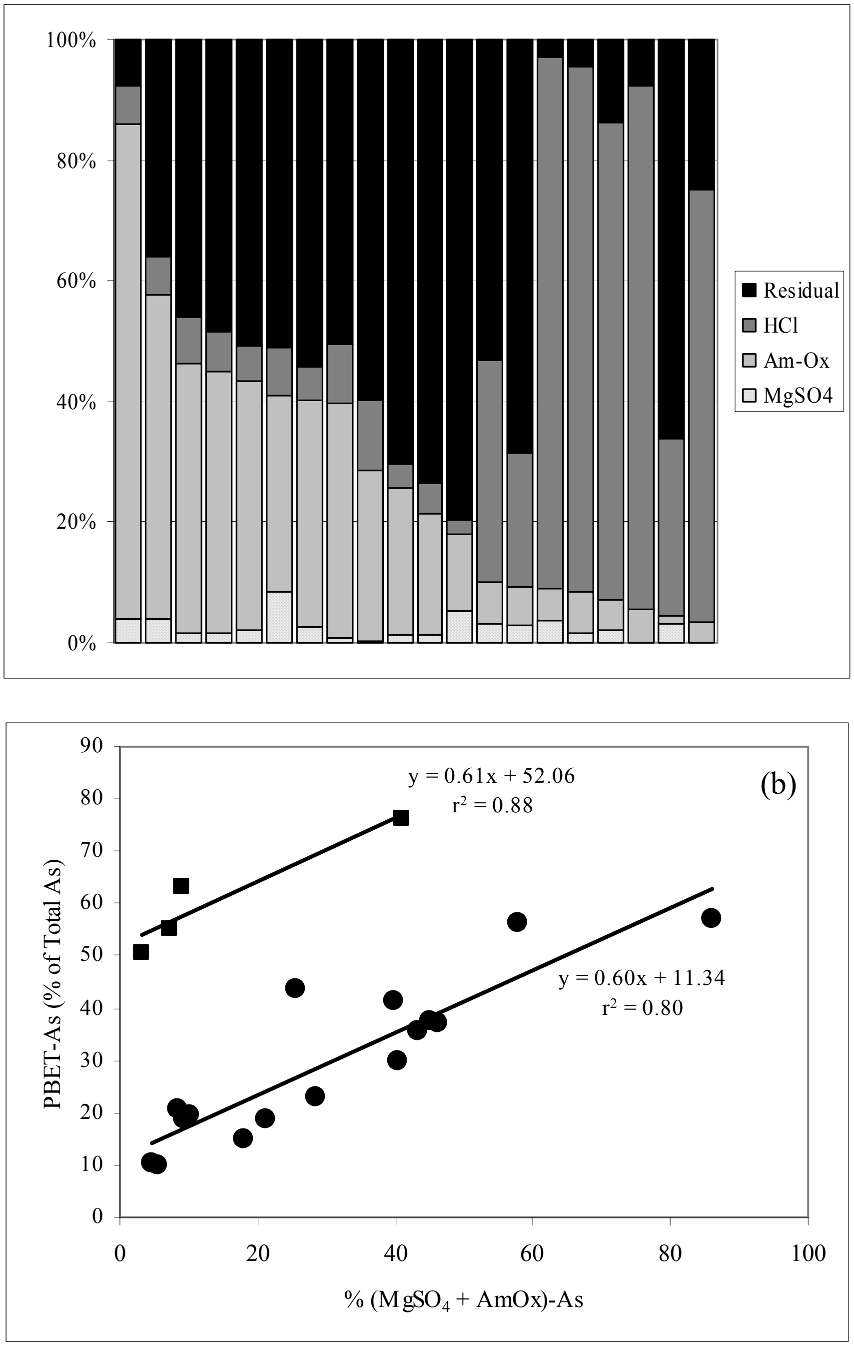


Figure 6. (a) Sequential fractionation of total As in 20 soils from an urban contaminated site in Wilmington, Delaware. Soils are presented, left to right, in descending order of [$MgSO_4$+ AmOx]-As and (b) Relationship between the percentage of total As extracted by [$MgSO_4$+ AmOx] and the percentage of PBET-As in these 20 soils.

Table 9. Comparison of the mean chemical properties of two groups of urban soils from the South Market Street site that exhibited different trends in the distribution of arsenic among three chemical fractions[†].

Soil Property	Group #1	Group #2
Percentage of Total As in fraction:		
$MgSO_4$	3	2
AmOx	38	5
HCl	7	63
Residual	52	30
pH	7.9	8.0
Organic matter (%)	4.0	2.9
Total (mg kg-1)		
As	966	86
Al	9,117	9,374
Fe	21,052	23,831
Ca	32,802	18,003
Mg	12,578	5,298
S	2,167	1,491
Cu	109	115
Zn	232	272
Percentage of Total As Extracted by		
TCLP-As	3	2
PBET-As	39	31
M3-As	10	8

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

In summary, sequential chemical fractionation analyses showed differences in relative extractability of As in these 20 urban contaminated soils. They also identified chemical fractions that are 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, cannot provide detailed chemical and structural information on the solid phases that control the fate and transport of As in soils. More advanced spectroscopic methods, such as EXAFS and XANES are required to provide definitive information on As speciation. Use of these more advanced methods to characterize As speciation in other urban soils is discussed later in this report.

OBJECTIVE 2: TO DETERMINE FACTORS CONTROLLING THE RETENTION, RELEASE, AND POTENTIAL MOBILITY TO GROUND WATERS OF AS IN DELAWARE SOILS, AS AFFECTED BY SOIL PROPERTIES AND COMPETING ANIONS

The studies reported on in Objective 2 were conducted with the aim of better understanding processes and mechanisms of As sorption/desorption in complex, heterogeneous, Delaware soils.

Arsenic Sorption by Soil Horizons: To determine the As retention capacity of Delaware soils

Sorption of arsenate (As(V)) by selected surface and subsoil horizons of soils sampled in Objective #1 was monitored as a function of time and at the measured pH range of these soils. The As(V) concentration (as $Na_2HAsO_4.7H_20$) reacted with the soils was based on typical application rates of As(V) in PL-amended soils and determined from isotherm studies where equilibrium As(V) in solution was assessed versus As(V) adsorption (Sims and Luka-McCafferty, 2002). Arsenate was studied since the recent research of Arai et al. (2003) and others (Gabarino et. al., 2003) has shown that the solid state speciation of As in aged PL is largely As(V). The reactors were mixed and maintained at constant pH. Eight of the agricultural soils were chosen to perform the isotherm and pH studies. The isotherm studies will provide insight into the amount of As the soils can sorb. The pH studies will help determine the effect of pH on the soils' ability to retain As. Preliminary kinetic studies determined that after 48 h there was a minimal increase in As sorption onto the soils, therefore all sorption studies were conducted for this period of time.

Subsequent to the initial experiments, the interaction of As(V)-PO_4 binary systems with selected soils was studied at soil pH values typical of soil profiles sampled in Objective #1 and at different As:PO_4 ratios (e.g., 1:1, 1:50, 50:1) using methods outlined above. The objective was to account for the effect of the presence of one oxyanion on sorption of another. An oxyanion is defined as a negatively charged polyatomic ion that contains oxygen. Many metals and nonmetals have the ability to form several different oxyanions depending on the oxidation state of the central atom. In Delaware's agricultural soils, PO_4 anions are very prevalent, due to long-term fertilization and manuring, and it is important to understand how As(V) and PO_4 compete for adsorption sites in soil profiles, thus impacting As(V) transport. Phosphate concentrations (as $Na_2HPO_4.H_20$) used in sorption studies were based on those found in the surface and subsurface horizons of Delaware soils.

Arsenic Desorption from Soil Horizons: The purpose of the desorption studies was to assess the extent and rate of release of native and freshly sorbed As from selected soil horizons using soils from Objective #1 (agricultural, forested, industrial contaminated). Desorption parameters in conjunction with previously determined chemical measures of labile As (e.g., soil test, easily desorbable, water soluble), will provide an index of As mobility in soils and thus its potential to leach to ground waters These data are also useful in assessing As bioavailability in soils and long-term residence time effects on As mobility. The soils were subjected to washing with 0.01*M* NaCl to mimic reactions with the soil solution, and with phosphate solutions (Na_2HPO_4) at concentrations realistic to those found in DE soils, to simulate competing PO_4 oxyanions in soils.

Arsenic Speciation of Poultry Litter: Arsenic speciation in source materials, such as manures, is vital in understanding how As will react once it enters soils. Poultry litter is a very heterogeneous material that contains a number of trace metals and basic nutrients that are beneficial for both the birds and as a fertilizer. It is often stored either in the house or in storage piles many times for years before application. Previous studies have found As(V) to be the predominant degradation product found in PL. However, there have not been any studies that examined this system over time. In our study, a series of PL samples were collected from a research poultry house at the University of Delaware Research and Education Center in Georgetown, DE. At the end of the experiment large amounts of PL were collected and placed into large bins, in order to simulate PL storage, and periodically sampled for analysis. Litter total As content was determined by the EPA 3050B method and water soluble As by standard methods. Litter As speciation was conducted by X-ray Absorption Near Edge Structure Spectroscopy (XANES) and elemental associations were determined by X-ray Fluorescence (XRF) mapping. All synchrotron work was done at beamline X26A at the National Synchrotron Light Source in Upton, NY.

Results of Arsenic Sorption and Desorption Studies

Arsenic Sorption by Soil Horizons: Due to the large volume of soil samples, eight soils were chosen to perform sorption experiments upon. The soils were chosen based on their texture, Fe and Al oxide content, P and As levels, and organic matter content. Table 10 provides a brief description of the soils used in the sorption studies.

The pH edge/envelope studies provide important information about the soils' ability to retain As under varying environmental conditions. Agricultural soils can experience a number of applications which can cause pH to change; such techniques include liming and applying fertilizer. Therefore, it is important to assess how these practices can affect As retention onto these soils. A number of pH studies were conducted to determine how a change in pH can alter As sorption. All pH studies were studied over a range of pH 3 to 10, a background electrolyte of 0.01M $NaNO_3$, a 5 g L^{-1} soil suspension, and an As concentration of 20 mg L^{-1} or 266 µM As(V) which is comparable to levels of total As found in PL samples. All sorption reactions were allowed to equilibrate for 48 h and pH was monitored using a pH stat. All reactions were completed in triplicate. These reaction conditions are similar to many other studies in the literature that have investigated As [and other metal(loid)] sorption on soil components and soils with the goal of better understanding sorption mechanisms.

The first pH studies were done in the traditional manner, where each soil was equilibrated separately at a different pH ranging from pH 3 to pH 10. After 48 h incubation, a sample was taken, analyzed for As and the total amount of As(V) sorbed calculated. In all cases subsurface soils sorbed more As than surface soils. Figure 7 demonstrates the importance of pH to As retention. As(V) is an oxyanion, which means that it has a negative net charge. Oxyanions traditionally sorb more at lower pHs than at higher pHs and tend to form what is known as an adsorption envelope, as seen in Figure 7. The soils retained more As(V) at the lowest pH values and then experienced another sorption maximum around pH 5.5 to 7. The target pH range for Delaware agricultural soils is from pH 5.5-6.5, similar to the pH values where greatest As sorption occurred. Based on these data, we chose a pH of 5.5 for the rest of the sorption studies.

A second pH sorption study was conducted in order to more directly assess As retention as the pH of the soil varies. Each of the soils were equilibrated to pH 5.5 and then the pH was increased or decreased and As sorption was measured (Fig. 8). These pH studies show that As sorption is most dominant in the pH range of 5.5 to 7; outside of this range, As retention decreases. Therefore, when land applying PL onto agricultural soils maintaining a pH over this range will maximize As retention by soils. In both studies, subsurface soils retained an average of 30-50% more As than surface soil horizons (Figs. 7 and 8). This is probably due to overall higher Fe and Al oxides and clay content in the subsoils (Table 10).

Soil Series	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	P 3050B (mg/kg)	As 3050B (mg/kg)	Fe 3050B (mg/kg)	Crystalline Fe (mg/kg)	Amorphous Fe (mg/kg)	Al 3050B (mg/kg)	Crystalline Al (mg/kg)	Amorphous AL (mg/kg)	pH	OM %	As (mg/kg) WS	P (mg/kg) WS
Elkton	0-23	23	57	20	442.5	0.8	6900	4926	2775	9014	321	2661	5.7	2.15	0.09	4.97
Elkton	23-43	15	57	28	83.2	1.2	15687	16601	4694	9495	544	2875	4.85	0.9	0.13	0.25
Sassafras	0-20	68	22	10	294.1	2.8	6288	5741	2797	6941	675	2950	5.1	1.2	0.15	2.01
Sassafras	20-40	52	23	25	130.9	4.9	13809	15878	2837	12950	1225	3708	5.9	0.8	0.05	0.39
Corsica	0-30	79	14	7	486.9	0.4	1882	325	709	14368	772	2987	4.65	7.4	0.13	4.65
Corsica	43-81	30	35	35	40.6	2.3	17785	4061	2284	23840	653	2047	4.35	0.65	0.02	0.04
Greenwich	0-28	55	30	15	384.5	3.6	7148	2185	2381	11173	1484	3958	5.2	1.25	0.09	2.11
Greenwich	53-81	49	30	21	164.9	4.0	14008	5711	1807	15281	1398	2088	5.7	0.8	0.02	0.29

Table 10. Physicochemical properties of soils investigated in the sorption experiments.

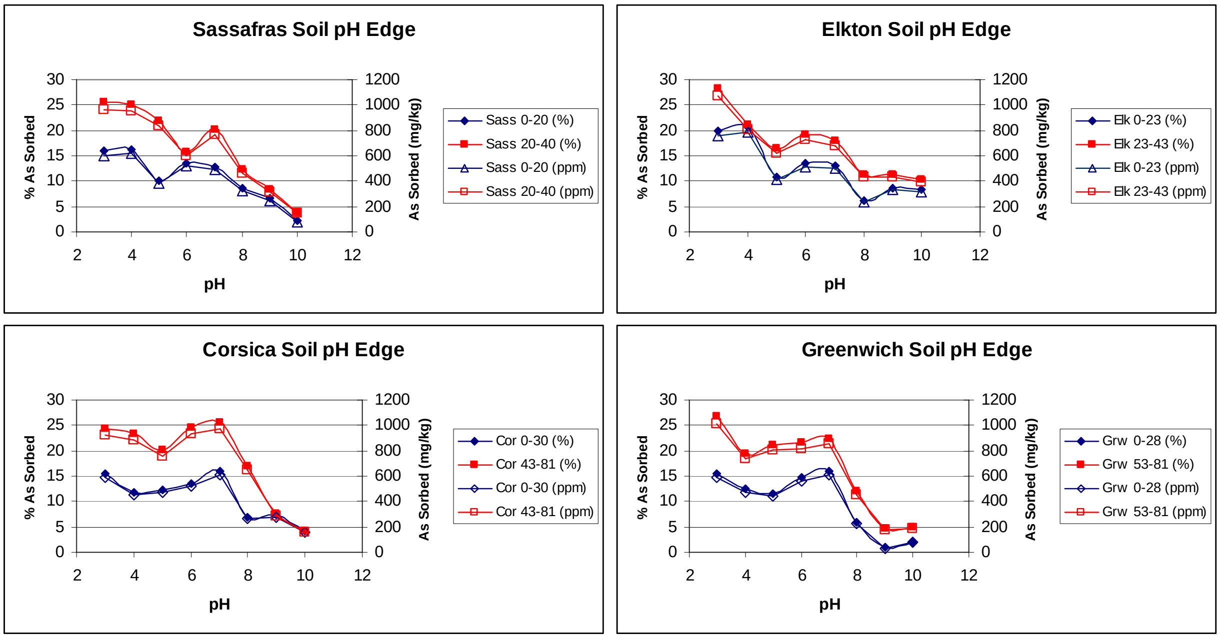


Figure 7. Arsenic sorption pH edge studies conducted on selected agricultural soils. Each soil - pH combination was allowed to equilibrate separately before sampling. Sorbed As is reported in ppm (mg kg^{-1}).

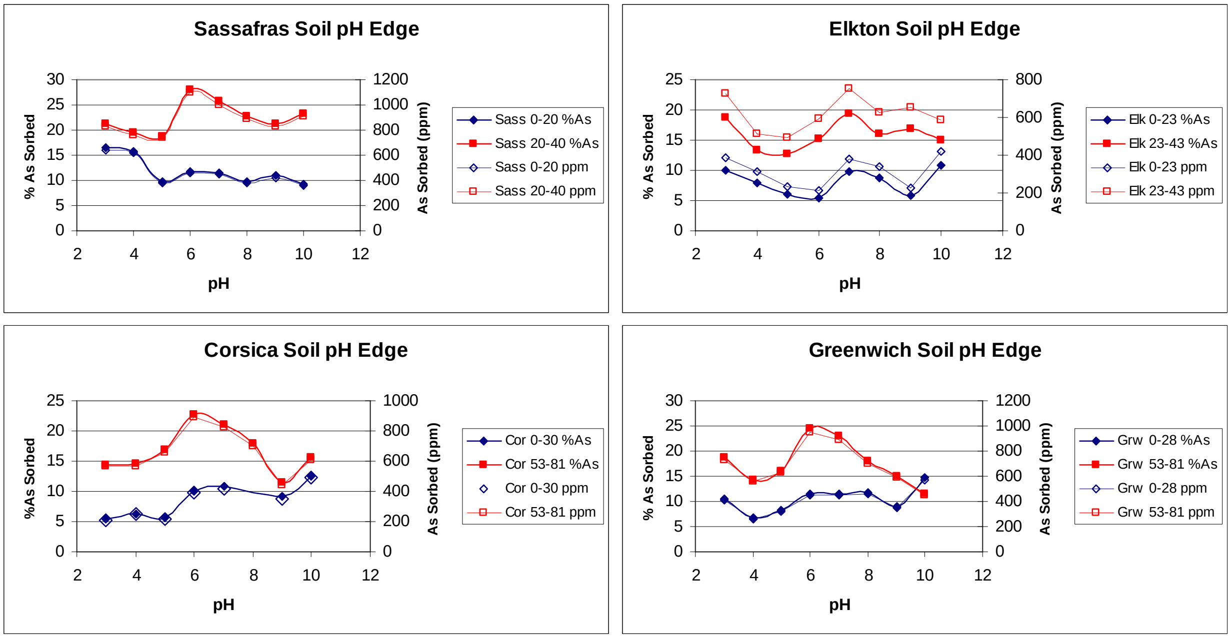


Figure 8. Monitoring As retention as pH increases or decreases from a pH of 5.5. Sorbed As is reported in ppm (mg kg^{-1}).

Sorption isotherms are used to describe the relationship between equilibrium concentrations of the sorptive and the quantity of sorbate on the soil surface (Sparks, 2003). Sorption isotherms were conducted to determine the maximum amount of As these soils could retain. The sorption isotherms were conducted similar to the pH edge studies with pH maintained at 5.5 and temperature and pressure were held constant. The concentrations used to determine the As sorption maximum were 5, 10, 25, 50, 75, 100, 250, 500, 750, 1000 µmol L^{-1} of As(V). Figure 9 depicts the relationship between the final (equilibrium) As concentration and As sorption by the soils. The final (equilibrium) concentration of As in solution is plotted against q, which is the amount of As per unit mass of soil. The following is the equation used to calculate q:

$$\frac{(C_oV_o) - (C_fV_f)}{m} = q$$

Where: C_o and C_f are the initial and final adsorptive (As) concentrations in mol L^{-1}, V_o and V_f are the initial and final sorptive volumes in liters and m is the mass of the sorbent (soil) in kg.

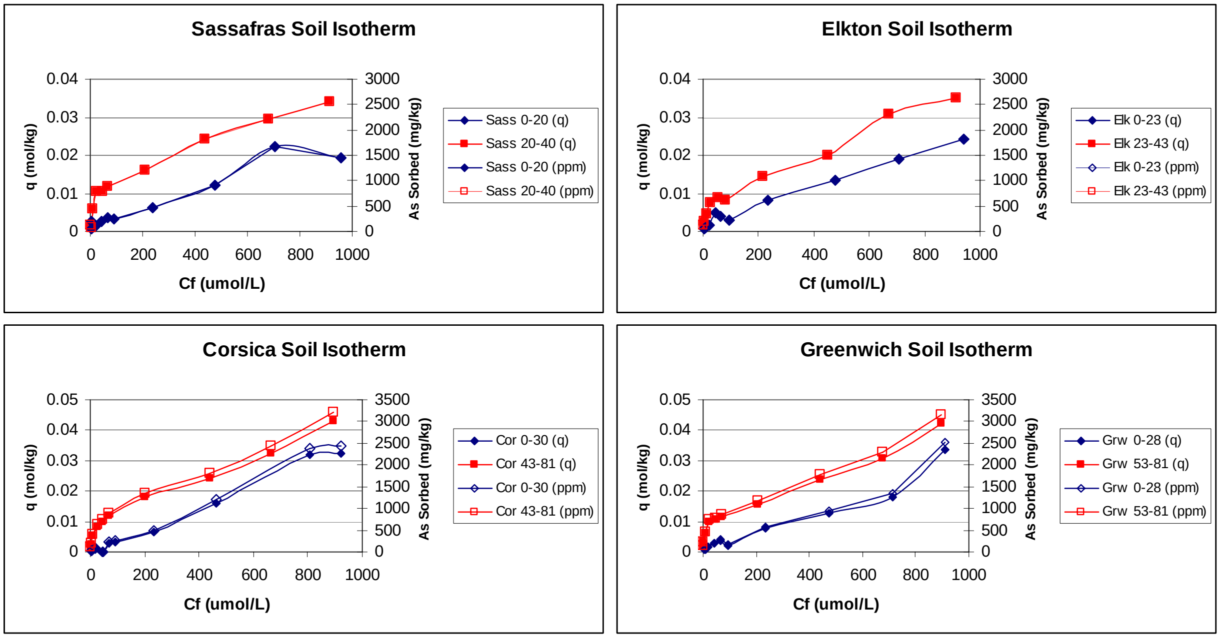


Figure 9. Sorption isotherms for the eight selected soils. Data are plotted C_f, final sorptive concentration vs. q, the amount of adsorption (sorbate per unit mass of sorbent).

The isotherms (Fig. 9) show sorption behavior similar to what was observed in the pH sorption envelopes (Figs. 7-8). The subsurface soil horizons sorbed more As than the surface horizons. The Langmuir equation is used to qualitatively determine the sorption maximum of a sorbate on a sorbent (Fig. 10). By applying the Langmuir equation the theoretical, maximum amount of As(V) that can be sorbed on the Delaware agricultural soils can be determined. The following linearized form of the Langmuir equation was used to determine As sorption maxima for the soils, where C is the final As concentration in solution, q is the amount of As sorbed, k is a constant related to binding strength and b is the sorption maximum.

$$C/q = 1/kb + C/b$$

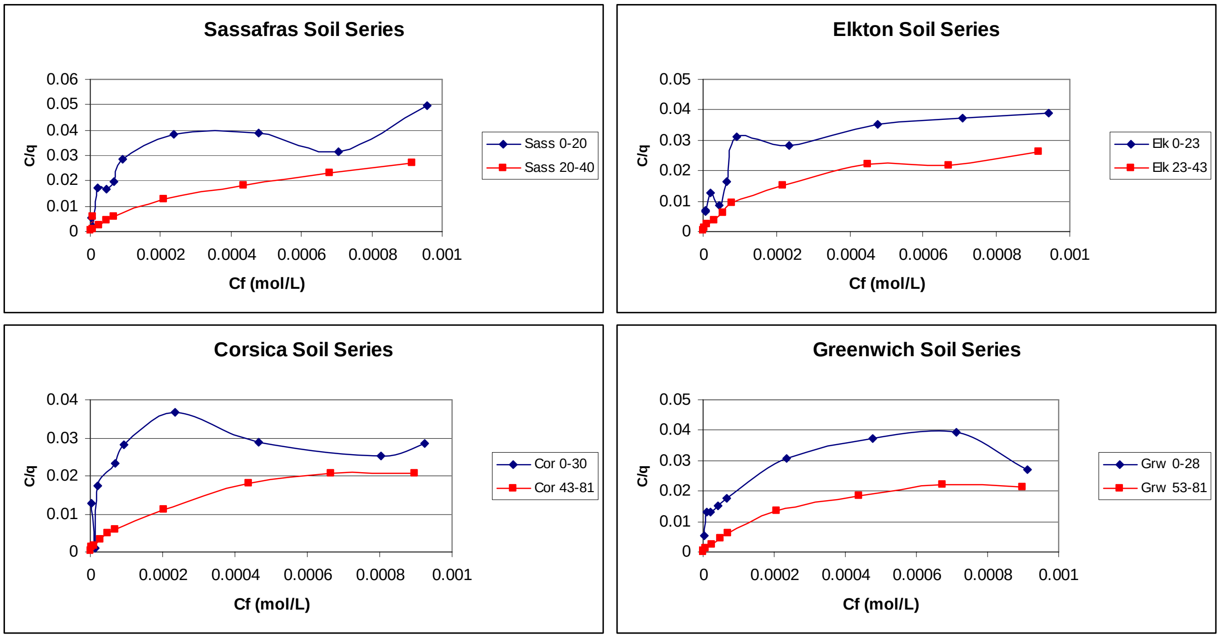


Figure 10. The Langmuir plots for the Delaware agricultural soils. C_f is the final As concentration in solution plotted against C/q (final As concentration/As sorbed). The slope of the lines will provide the sorption maximum.

Using the Langmuir equation and plotting C vs. C/q the sorption maxima were determined. The linear portion of the plot is most commonly used to describe the sorption capacity of soils and model systems. The initial linear portion of the graph is depicted in Figure 11 for each of the soils. The sorption maxima were calculated from the slopes of these lines.

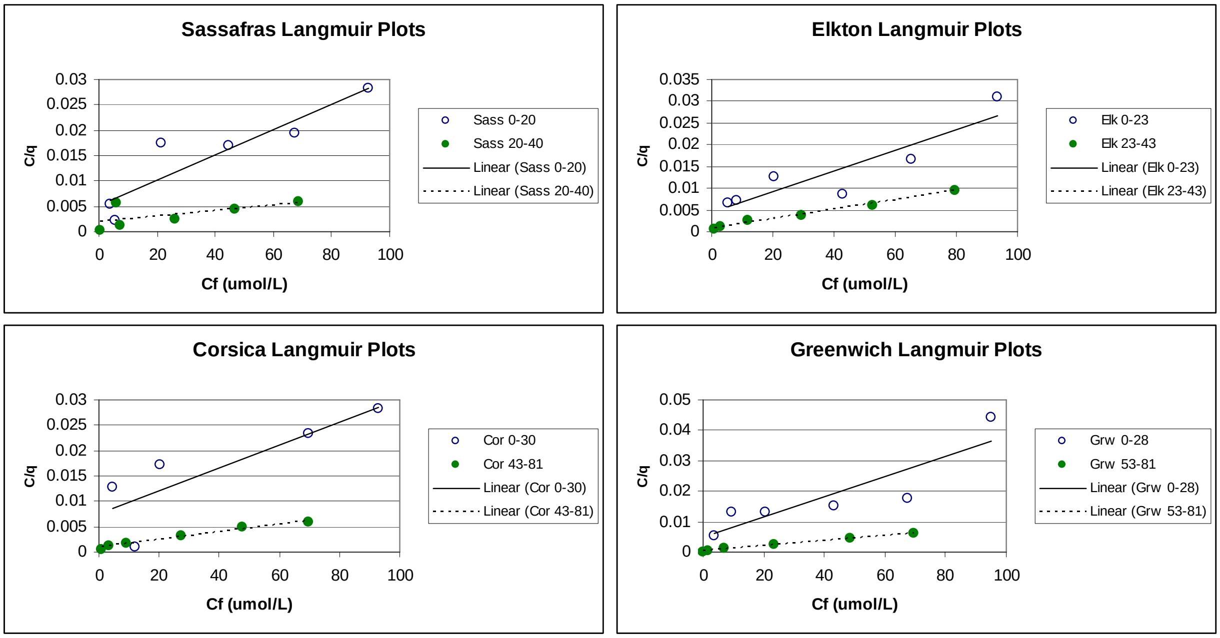


Figure 11. Initial linear portion of Langmuir plots (Fig. 10) that are used to calculate the sorption maxima.

The sorption maxima, for a particular soil depth, for each of these soils were similar (Table 11). According to the calculations, the subsurface soils had the ability to retain more As than surface soils. The Sassafras and Corsica soils displayed the greatest ability to sorb As, 18.3 μmol g^{-1} (1367 mg kg^{-1}) and 13.1 μmol g^{-1} (980 mg kg^{-1}) respectively. The pH edge sorption values were estimated at pH 5.5 and at the field soil pHs from the pH edge plots. When comparing Langmuir sorption maxima values (Table 11) with what is present in the soils, one can see that on average, the soil is now retaining a small percentage of the total As it can sorb.

Soil Series (cm depth)	Langmuir Calculated pH 5.5 (ppm)	pH edge Estimated at pH 5.5 (ppm)	pH edge Estimated pH of the soil (ppm)
Sassafras 0-20	302.4	449	473
Sassafras 20-40	1367.0	715	850
Elkton 0-23	312.7	464	425
Elkton 23-43	709.7	675	716
Corsica 0-30	334.1	493	455
Corsica 43-81	980.7	849	870
Greenwich 0-28	224.8	503	465
Greenwich 53-81	902.0	812	815

Table 11. Calculated Langmuir sorption maxima and sorption maxima derived from pH edges at pH 5.5 and the pH of the soils, where values are in ppm or mg kg^{-1}.

The Langmuir sorption maximum calculations provide important information about As sorption onto these soils. The agricultural soils commonly found in Sussex County, Delaware appear to be able to retain a significant amount of As. If the surface soils are not able to retain the As, it would appear that the subsurface soils should have the ability to sorb the remaining As that leaches through. The presence of phosphate however, may inhibit As retention on the soils.

Competitive Studies:

Oxyanions are dominant in poultry litter and the litter applied soils. When trying to determine arsenate sorption by soils, it is important to note the role that other oxyanions such as phosphate play in the retention of As. Phosphate and As(V) behave similar chemically, they are of similar size and charge, and previous studies have found that P will out compete As for sorption sites. There is at least 100 times more P than As found in Delaware agricultural soils, and at times up to 1000 times more P than As in PL. Therefore, it is worthwhile to study the impact that P has on As sorption.

A series of As and P competitive studies were conducted to determine which oxyanion was preferred in these soils and to suggest possible sorption mechanisms. The first of the experiments was a simple As and P competition study. We used 1:1, 1:50 and 50:1 ratios of As:P based on past published studies that have investigated the mechanisms of competitive oxyanion sorption on soils. The concentrations were 4 ppm As to 4 ppm P, 4 ppm As to 200ppm P, and 200 ppm As to 4 ppm P (note: ppm = mg L^{-1}). The oxyanions were introduced at the same time and measurements were made at 24 and 48 h.

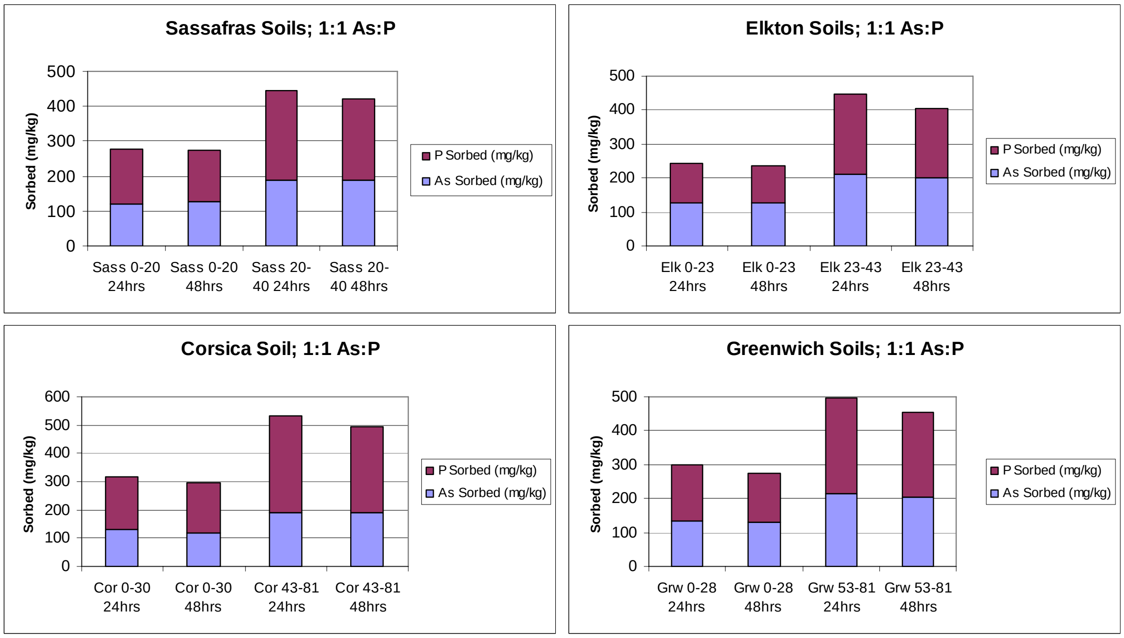


Figure 12. Amount of As and P mg kg^{-1} sorbed by soils after 24 and 48 h at a 1:1 As:P ratio.

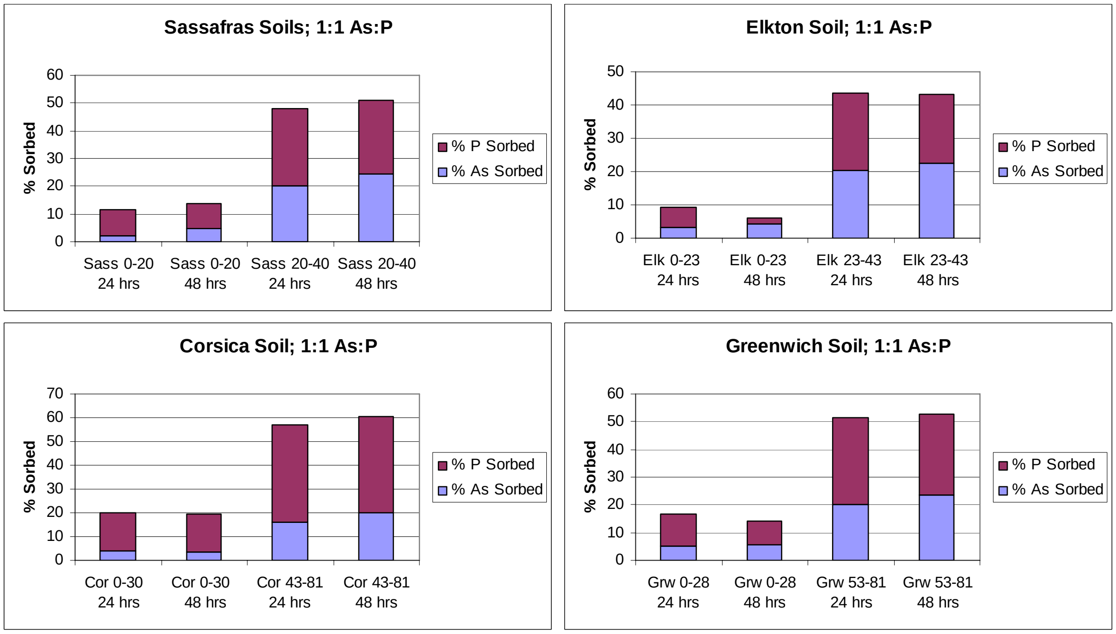


Figure 13. Amount of As and P (%) sorbed by soils after 24 and 48 h at a 1:1 As:P ratio.

The 1:1 competitive study demonstrated that the soils prefer P over As when introduced together at the same concentration, 4 mg L^{-1} (Figs. 12 and 13). In most cases the amount of P and As sorbed increased with time (Figs. 12 and 13). In all cases the subsurface soils sorbed more of the oxyanions than the surface soils. This would indicate that when P and As are introduced together, P may out compete As for sorption sites.

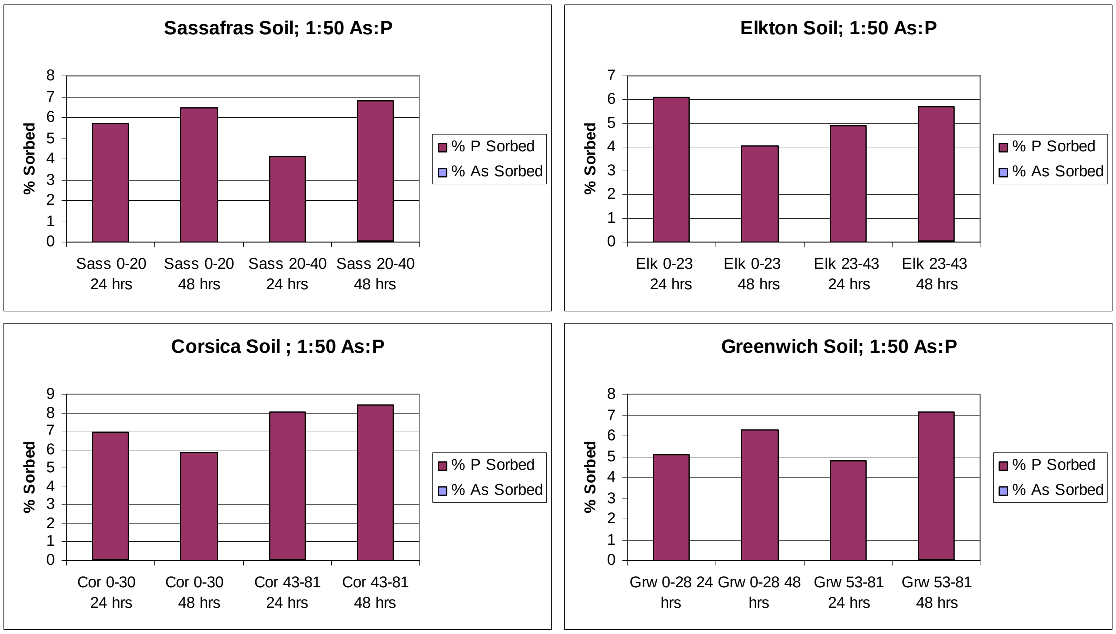


Figure 14. The amount of As and P (%) sorbed onto the soils after 24 and 48 hours at a 1:50 As:P ratio.

When As and P were introduced together at a 1:50 ratio, there was minimal As sorption (<1 μmol g^{-1}) [Fig. 14]. These results indicate that when P is in excess, it is preferred over As(V).

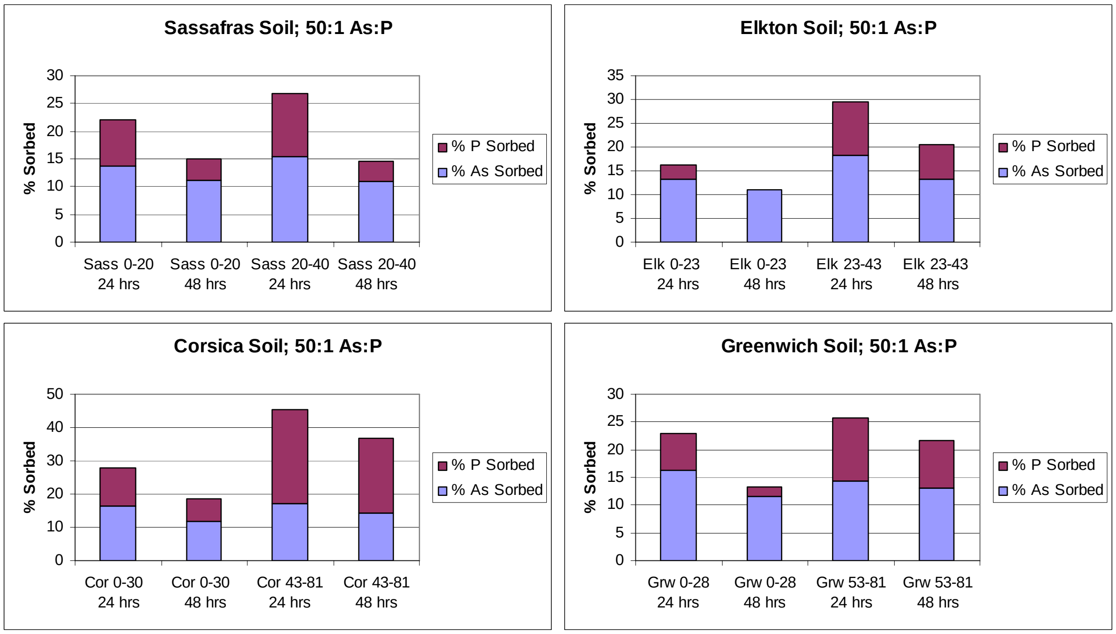


Figure 15. Amount of As and P (%) sorbed by soils after 24 and 48 h at a 50:1 As:P ratio.

When As and P were introduced at a 50:1 As:P ratio more As was sorbed than P (Fig. 15). However, in contrast with the 1:50 As:P study, a noticeable amount of P was bound to the soil. Even though As was in excess in solution, P was still taken up by the soil.

Three soils were chosen to perform a series of kinetic sorption studies. These studies helped determine how quickly As sorption processes occur in these soils. The Corsica surface and subsurface soils, and the Sassafras subsurface soil were chosen based on their ability to sorb As.

The first of the studies examined As sorption by soils to determine how quickly the As sorbs onto the soil surface without the presence of an inhibiting compound. Arsenic sorption exhibited typical kinetic behavior, a rapid increase in sorption followed by a slow uptake over time. Most of the As sorption occurs within the first 60 minutes (Fig. 16). The maximum amount of As sorbed was similar to what was seen in the pH edge and isotherm experiments.

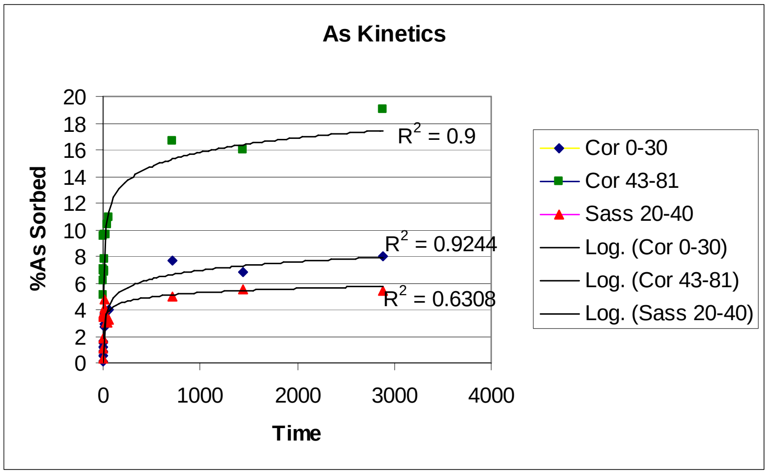


Figure 16. As sorption with time conducted on Corsica 0-30 cm, 43-81 cm, and Sassafras 20-40 cm depth soils.

The 1:1, 1:50 and 50:1 As:P ratio studies were conducted upon these soils over time to assess arsenic's ability to adhere to the soil in the presence of P (Figs. 17-19). All experiments were kept at a pH of 5.5, had a background electrolyte of 0.01*M* NaNO3, 5g L^{-1} soil suspension, and were monitored for 48 hours. The concentrations were 4 ppm As to 4 ppm P, 4 ppm As to 200 ppm P, and 200 ppm As to 4 ppm P.

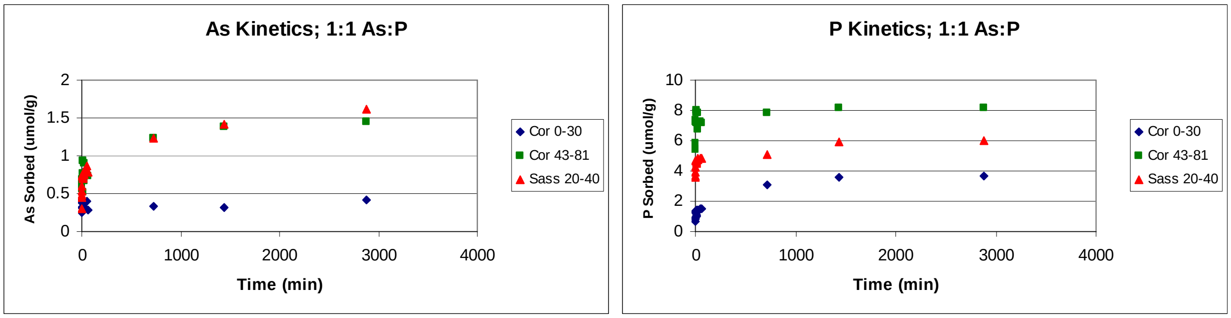


Figure 17. 1:1 As:P kinetic studies conducted on Corsica 0-30 cm, 43-81 cm, and Sassafras 20-40 cm depth soils.

The 1:1 As:P kinetic study demonstrates that when introduced at the same time at the same concentration, the soils prefer P over As. In all cases the soils immediately sorbed more P than As. The final percent sorbed for all experiments is noted in Table 12. The Corsica soils sorbed significantly more P than As, while the Sassafras soil sorbed an equal amount of both oxyanions. Once again the subsurface soils sorbed more of both As and P.

Soil	Treatment	% As Sorbed	% P Sorbed
Cor 0-30	1As:1P	5.70	16.91
Cor 43-81	1As:1P	21.45	41.68
Sass 20-40	1As:1P	23.16	28.65
Cor 0-30	1As:50P	2.32	7.37
Cor 43-81	1As:50P	5.17	5.28
Sass 20-40	1As:50P	4.00	6.12
Cor 0-30	50As:1P	17.23	11.63
Cor 43-81	50As:1P	6.26	21.12
Sass 20-40	50As:1P	15.55	11.97

Table 12. Percent As and P sorbed at the end of 48 h for each of the three soils and treatments in Figs. 17-19.

Table 12 illustrates the effect that As and P concentrations have on the soils' ability to retain these compounds. When one oxyanion is in excess, sorption of the other was inhibited. One trend that should be noted is that when P is in excess, As sorption is reduced. However, when As was in excess, there was still a significant amount of P sorption.

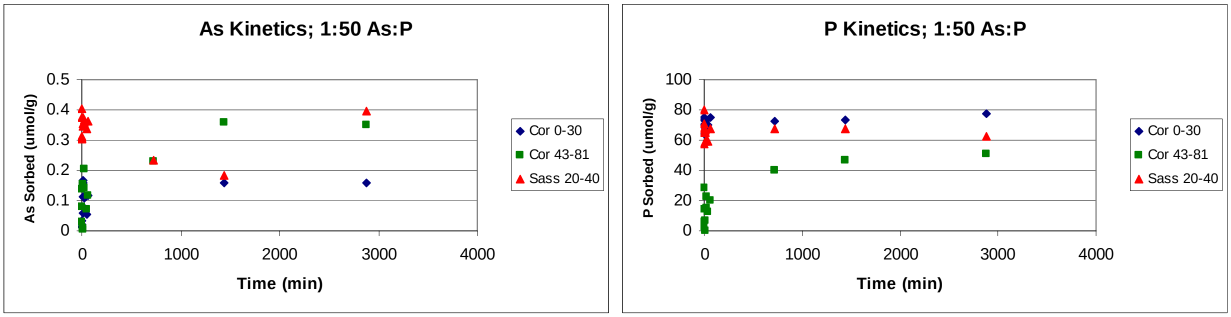


Figure 18. 1:50 As:P kinetic studies conducted on Corsica 0-30 cm, Corsica 43-81 cm, and Sassafras 20-40 cm depth soils.

Figure 18 depicts the uptake of As and P when in a 1:50 As:P ratio. Table 12 demonstrates that the amount of As sorbed was greatly reduced when the P concentration increased.

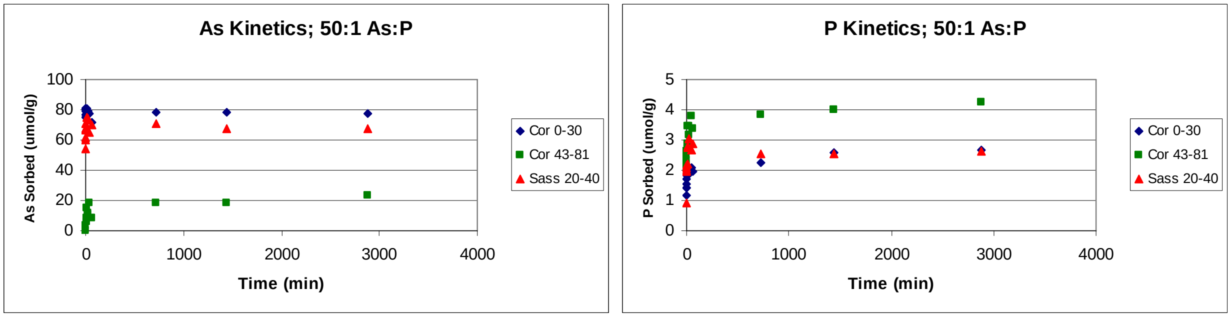


Figure 19. 50:1 As:P kinetic studies conducted on Corsica 0-30 cm, Corsica 43-81 cm, and Sassafras 20-40 cm depth soils.

Figure 19 illustrates the uptake of As and P when in a 50:1 As:P ratio. Most of the sorption was completed within the first 60 minutes. Table 12 demonstrates that the amount of P sorbed was reduced when the P concentration increased. This study implies that even when As was in excess, P can still be retained in significant amounts by the soil.

<u>Desorption Studies:</u> The purpose of the desorption studies was to assess the extent and rate of release of native and freshly sorbed As from selected soil horizons. Two separate experiments were completed. The first sorbed As(V) onto the selected soils, and then later introduced P into the system to determine how readily P can displace As. Then the inverse of this experiment was conducted to determine how readily As can displace P.

The first experiment assessed P's ability to remove As from the soil (Fig. 20). The first step was to sorb As(V) onto the soil and allow the solution to equilibrate for 24 h. The soil was then washed with 0.01*M* NaCl and the solution analyzed for arsenic to see how readily As was desorbed from the soil. Then a 4 ppm P solution was added to the soil and allowed to react for 24 h. The soil was then sampled and analyzed for As and P. This experiment monitors how tightly bound As was and determined if P could displace As from the soil surface.

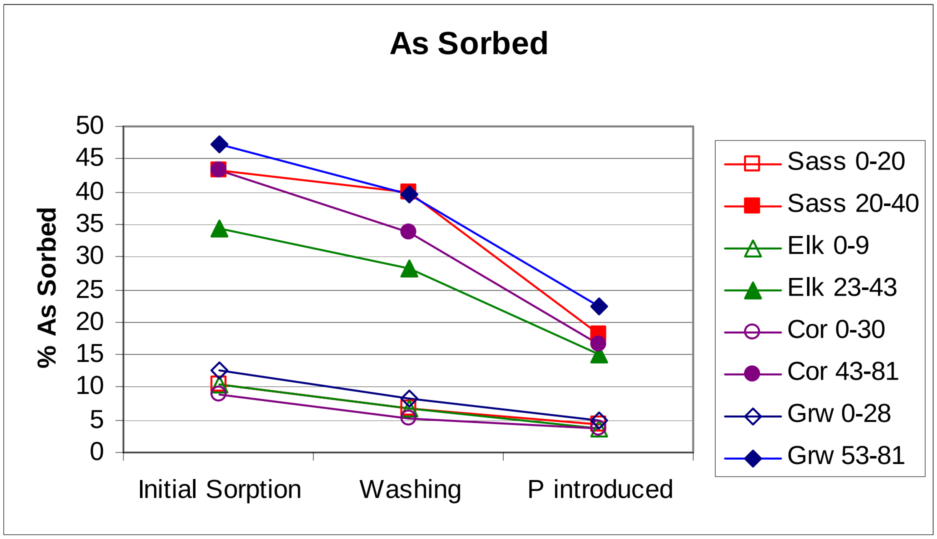


Figure 20. As removal from the soils after washing and P introduction.

Arsenic removal from the soil surface is shown in Figure 20. The greatest impact was seen in the subsurface soils, where at least 20% of the initially sorbed As was removed by the end of the experiment. Figure 20 depicts the % As sorbed in the beginning, after washing and after P was introduced for each of the eight soils. It appears that P had the ability to displace a significant amount of As from the soil surface. More As was displaced with P than with the NaCl electrolyte.

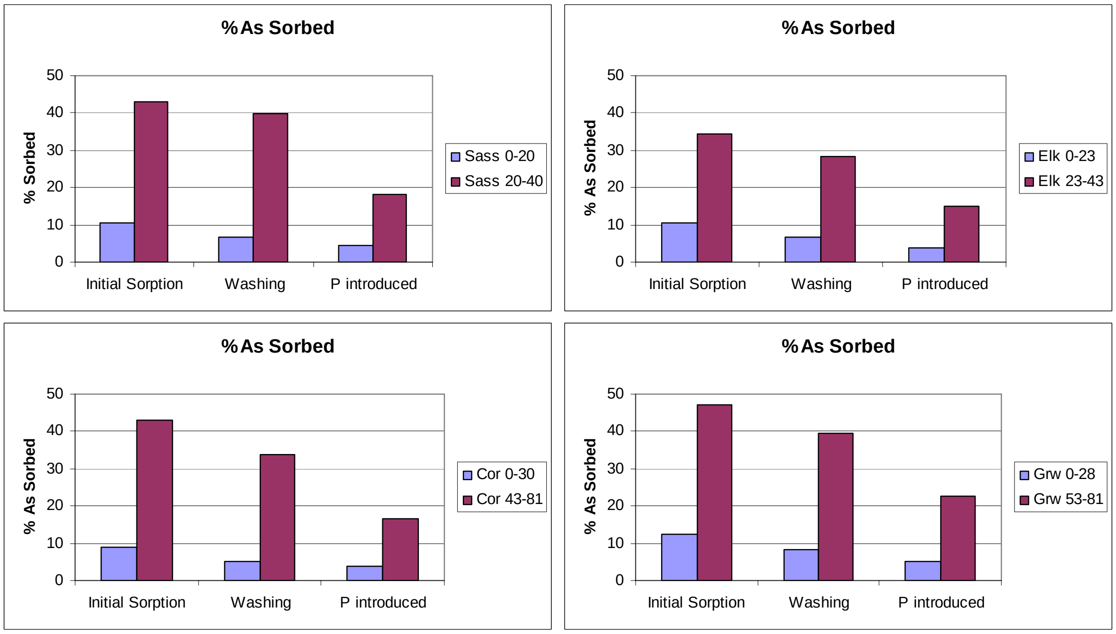


Figure 21. Percent As sorption before and after 0.01*M* NaCl addition and P sorption.

Figure 21 demonstrates what percentage of the initial As added remained sorbed to the soil surface after the washing and the introduction of P to the system. Figure 22 shows the soils' ability to sorb P when As is already present in the soil system.

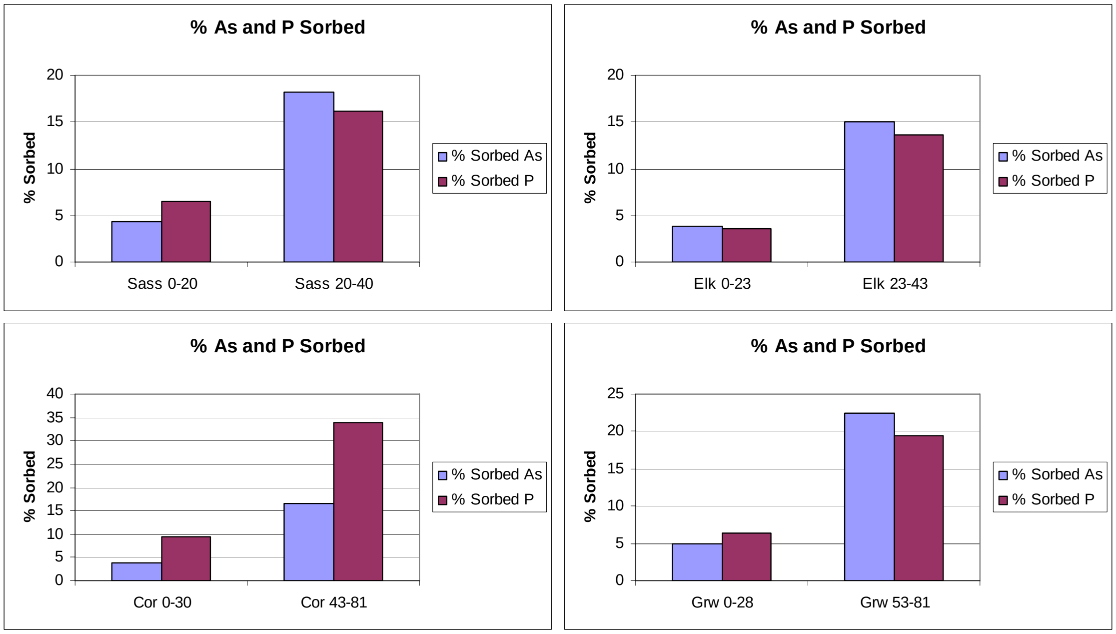


Figure 22. Percent As and P concentrations sorbed at the completion of the As then P sorption study after washing and P introduction.

In most cases more As remained sorbed than P, although the presence of P could displace a significant portion of As. This indicates that As is tightly bound to soils and may not easily be desorbed. The Corsica subsoil (43-81cm) sorbed significantly more As and P than other soils, indicating that texture and the presence of Fe and Al oxides play a role in As sorption.

The purpose of the second experiment was to assess As's ability to remove previously bound P from soils (Fig. 23). The first step was to sorb PO_4 onto the soil and take a sample after 24 hours. The soil was then washed with 0.01M NaCl to simulate soil solution, and then the solution was analyzed for P. As(V) was then added to the solution and allowed to react for 24 h.

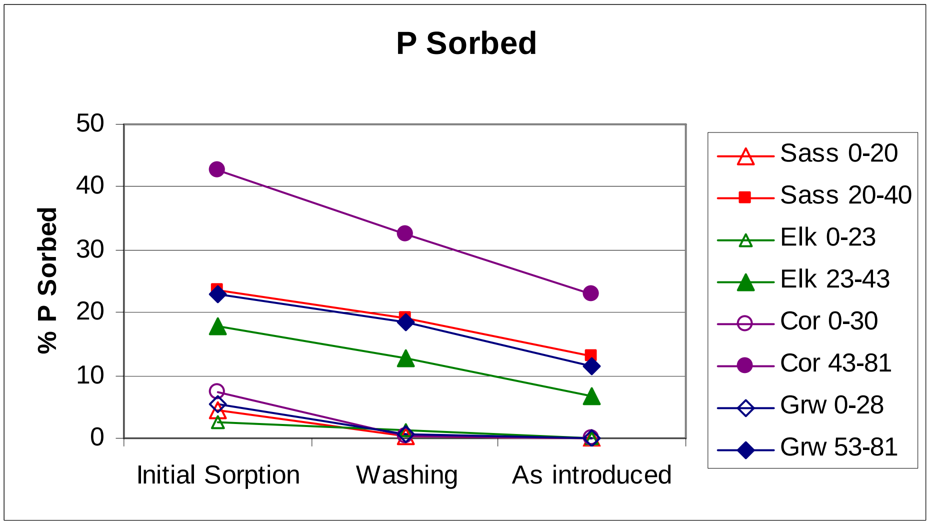


Figure 23. P removal from the soils after washing and As introduction.

Figure 23 shows a significant amount of P was displaced in all soils. All soils showed the impact of the washing, which indicates that P can be removed. Comparing this graph to the initial As sorbed experiment, it seems that As is more tightly bound than P in Delaware soils. This would indicate that once As is sorbed onto the soils it is less likely to be removed.

Figure 24 shows the percentage of P sorbed in the beginning, after washing and after As was introduced. It appears that As has the ability to desorb a significant amount of P from the soil surface.

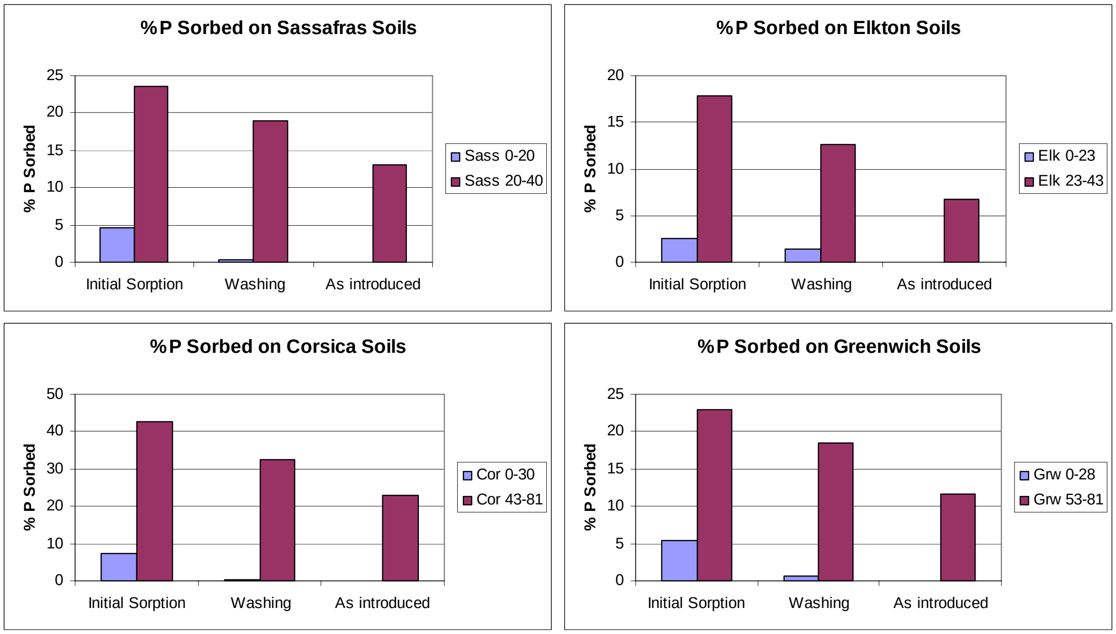


Figure 24. Percent P sorption before and after 0.01M NaCl addition and As sorption.

It is evident that the topsoils are not able to retain as much P as the subsurface soils (Figure 24). This could be due to the fact that there already is a significant amount of P bound to these soils. Once again the Corsica subsurface soil sorbed more P than any other soil. In all cases As had the ability to completely remove P from the surface soils (Fig. 25).

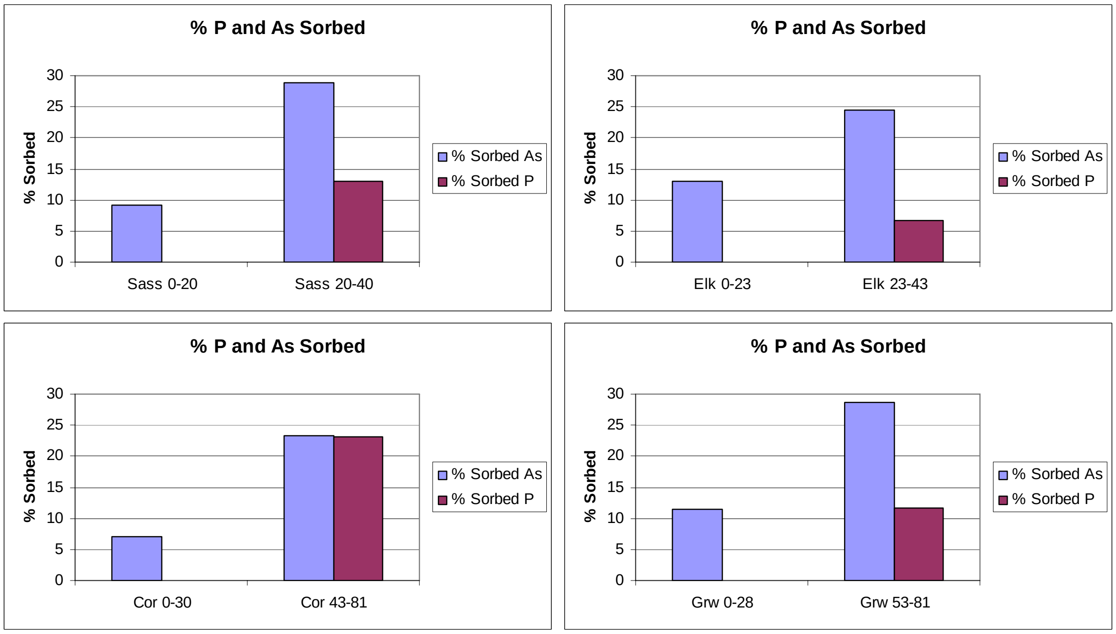


Figure 25. Percent As and P concentrations sorbed at the completion of the P then As sorption study, after washing and As introduction.

These studies indicate that As has the ability to displace sorbed P from the soil surface. As stated above, it would appear that As may adhere more tightly to the soil surface than P.

Arsenic Speciation of Poultry Litter

Since accumulation of As in litter amended soils was not seen, As speciation of the source material was investigated. The PL collected during the poultry house study in Georgetown, DE was analyzed for As content; some data are included in Figure 26. Arsenic content in the litter averages around 20 mg kg^{-1}. The As in the fresh litter, litter collected inside the house, is more than 50% water soluble. As storage time increases the amount of water soluble As decreases.

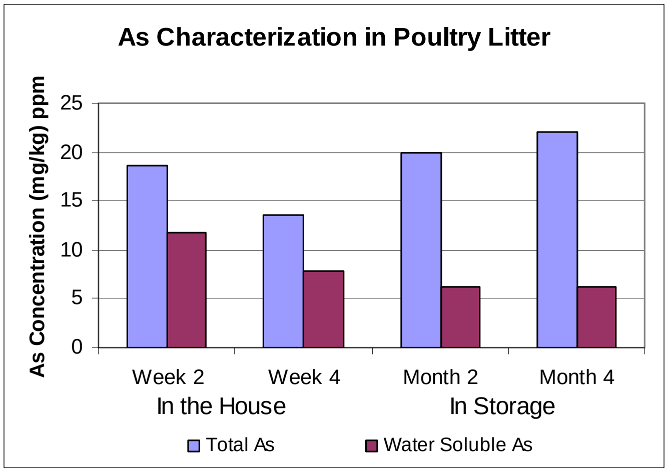


Figure 26. Arsenic content in poultry litter.

Arsenic speciation in systems is difficult when there are large amounts of P present. Colorimetric techniques cannot be determined due to interference with phosphate. Due to such difficulties, XANES was used to speciate the arsenic in the PL. The XANES analyses demonstrate that ROX appears to persist in the PL for an extended amount of time (Figure 27). However, as time increases, there is an increase in inorganic As species, in particular As(V). PL is often stored either in the house or in piles for an extended period of time before being land applied. The XANES data shown in Fig. 27 would imply that most of the ROX is degraded into other inorganic As(V) and organic As species.

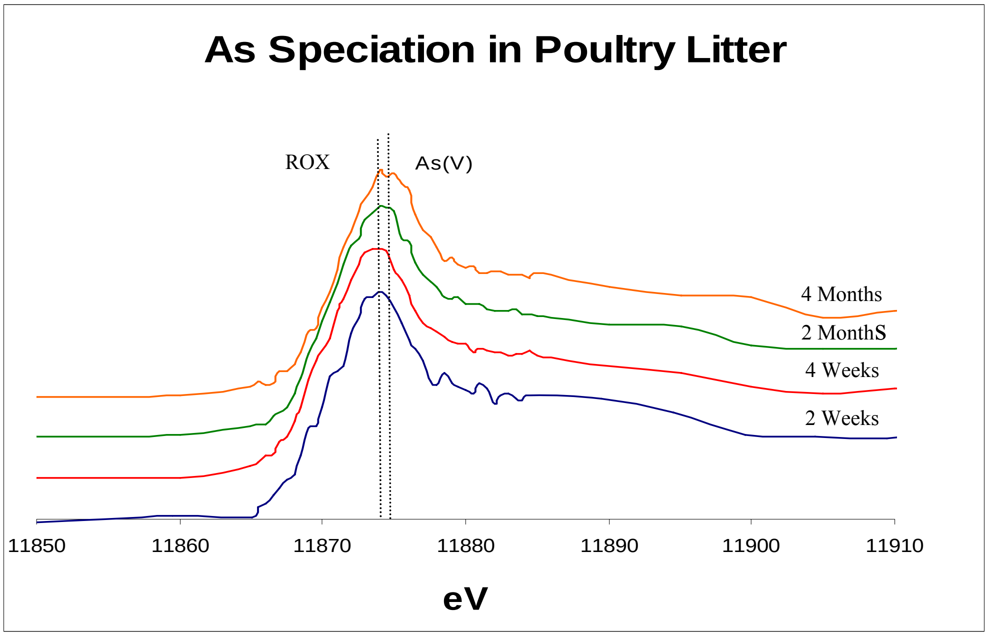


Figure 27. XANES analyses show that Roxarsone is the predominant As species in all the samples. Analyses show that as time increases, the amounts of inorganic As, particularly As(V) increases. As time increases the peak shifts to the right, which indicates a reduction of ROX and an increase in As(V).

XRF mapping is another technique used to gain information about the system. As distribution is concentrated mostly to hotspots, or areas where As is concentrated (Figure 28 and 29). There are a series of other trace metals that are found in PL that may be of concern and may play a role in As speciation. Copper, manganese and zinc are all found in high amounts in PL and are often seen in association with As. Figure 30 is a correlation plot of As vs. Cu. Each point on this plot is a pixel on the map. This plot demonstrates that Cu and As are commonly found in the same places. Similar plots are found for Mn.

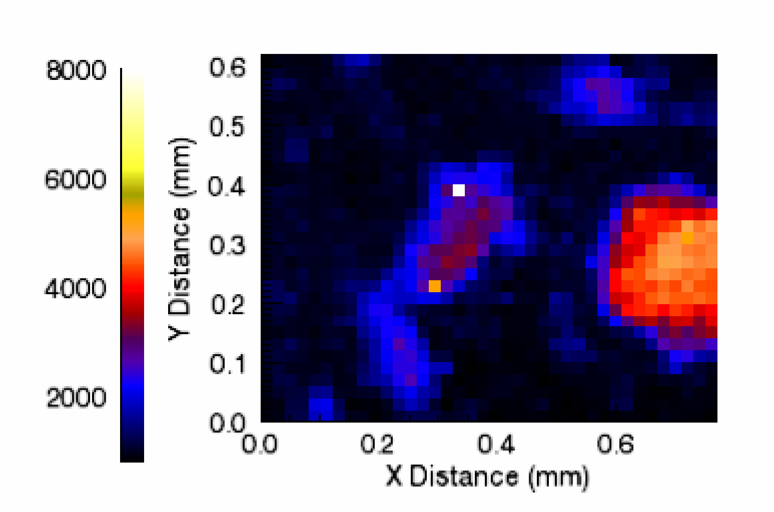


Figure 28. X-ray Fluorescence map of As in poultry litter. As is not evenly distributed, it tends to form concentrated “hot spots”, as denoted by the yellow and orange areas

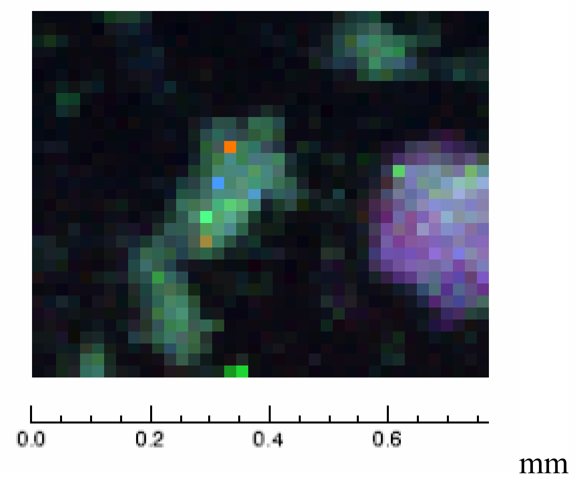


Figure 29.

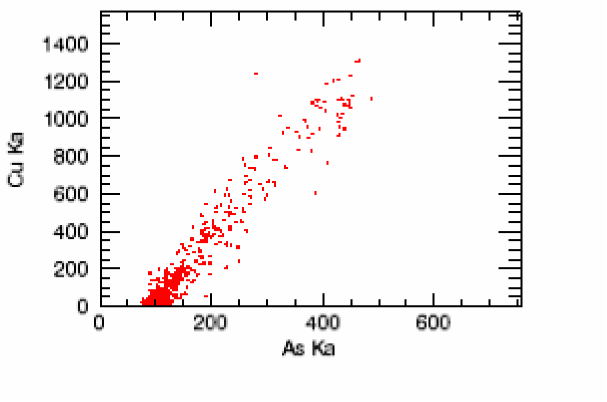


Figure 30.

Figure 29. XRF map showing As (red) distribution with regards to Cu (blue) and Mn (green). The purple color indicates areas where As and Cu are present at the same spot.

Figure 30. Correlation plot of As vs. Cu. This plot demonstrates that there appears to be a strong relationship between As and Cu.

This study provides important information about As speciation in poultry litter. When working with complex natural systems it is imperative to understand the source of the problem. Knowing what As species are being introduced to the system can provide a better understanding of As transport in soil systems.

OBJECTIVE 3: EFFECT OF BROILER LITTER ON ARSENIC LEACHING FROM DELAWARE SOILS

The effect of broiler litter 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 leaching from soils.

Column Study #1

Agricultural topsoils (0-20 cm) for this column study were obtained from two Sussex County poultry farms (Table 1; Farm #2 and Farm #3). The soil series at Farm #2 was a Sassafras sandy loam (fine-loamy, siliceous, semiactive, mesic Typic Hapludults) and at Farm #3 was a Corsica loamy sand (fine-loamy, mixed, active, mesic Typic Umbraquults).

Broiler litter had been applied to crop land at both sampling locations in the past. Note that soil test P values (M3-P) at the two sites (Sassafras = 47 mg kg^{-1} and Corsica = 86 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 broiler litter and fertilizer applications had been consistent with crop nutrient requirements. Bulk soil samples were collected 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. Three soil samples were collected during the mixing process for characterization of soil physical and chemical properties. Soils were analyzed for pH, OM, particle size (% sand, silt, clay), Mehlich 3 soil test extractable elements (P, K, Ca, Mg, Al, B, Cu, Fe, Mn, S, Zn), and for total As, TCLP-As, and M3-As. We also conducted As sorption isotherms for each soil, by a standard batch method used to measure P sorption parameters (Graetz and Nair, 2000). In brief, 2 g of each soil were equilibrated in triplicate for 24 h with 30 mL of each of six As solutions (0, 1, 2.5, 5, 10, 25, and 50 mg As L^{-1}, in 0.01 *M* $NaNO_3$). The solutions were centrifuged, filtered (0.45 μm Millipore membranes), and analyzed for As by ICP-OES. Results were used to calculate As sorption maxima for the soils using the Langmuir method as outlined by 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 was 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 the greenhouse. To minimize the potential of 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 (1 in) of rainfall. Broiler litter was surface applied to columns before event #8 at rates of 0, 4.5, 9.0, 13.5, 18.0, and 22.5 Mg ha^{-1} (equal to 0, 2, 4, 6, 8, and 10 tons ac^{-1}). The litter was obtained from a cooperator's farm and had been well-mixed, sieved to remove large particles and subsampled for total As analysis by the EPA 3051 microwave digestion method; litter total and water-soluble As were 43 mg kg^{-1} and 22 mg kg^{-1}. Based on this analysis, total As application rates to soil columns, on an areal basis, were 194, 388, 582, 776, and 970 g As ha^{-1}.

Three replications of each broiler litter rate were used, resulting in a total of 36 soil columns (2 soils x 6 litter rates x 3 reps) that were arranged in the greenhouse in a randomized complete block design. After broiler litter 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 μm Millipore membranes and refrigerated until analysis for As by ICP-OES. Note that, despite our efforts to prevent edge flow, this apparently occurred with 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 μg L^{-1}) than other columns in the study (mean=11 μg L^{-1}). Because we believe these high As concentrations were an artifact of a experimental leaching problem (edge flow) with these columns, we did not use these data and treated the results statistically as missing data. However, figures showing all data, including these outliers, are provided for review in the Appendix (Fig. A-2). 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. Residual broiler litter 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) and 15-20 cm (bottom) sections of all columns were extracted with the TCLP solution as described in Objective 1 and analyzed for TCLP-As by ICP-OES.

Column Study #2

We conducted a second column leaching study to: (i) modify the RO water addition method to further minimize edge flow; and (ii) evaluate As leaching from two additional soils, a sandy soil with no history of litter application (Evesboro loamy sand - mesic, coated, lamellic Quartzipsamments), obtained at the UD Research and Education Center; and a fine-textured soil (Matapeake silt loam – fine-silty, mixed, semiactive, mesic Typic Hapludults) from the UD Newark Farm with a much higher silt and clay content than the other soils from Sussex County (Corsica, Sassafras, Evesboro) used in Column Study #2. We used the same broiler litter as in Column Study #1 and two litter rates (0 and 9 Mg ha^{-1} – the litter rate commonly used to meet crop nitrogen requirements). Therefore, in this study there were 24 soil columns (4 soils x 2 litter rates x 3 replications) arranged in a randomized complete design in the greenhouse. Prior to leaching, soils were prepared, columns packed, and litters applied in an identical manner to Column Study #1. 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 we used small IV bags 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. We leached the columns eight times before application of the broiler litter and 22 times after litter application for a total of 30 leaching events (2.54 cm of water per event). After each event, all leachate was collected, volumes measured, samples filtered through 0.45 μm Millipore membranes and refrigerated until analysis of selected samples for As by ICP-OES. Using this method we noted evidence of edge flow for only one column (colored leachate for the Matapeake soil, PL rate = 9 Mg ha^{-1}). As in Column Study #1, we omitted data from this column from our statistical analyses of results. At the end of the final leaching event, as in Column Study #1, we removed any residual litter, then sectioned soil columns in 5-cm increments and measured TCLP-As on the 0-5 cm (top) depth.

Laboratory Incubation Study

A laboratory incubation study, using the same soils, broiler litter, and litter application rates as in Column Study #1, was also conducted to assess the potential effects of litter on As leachability under more static and better controlled conditions. The two soils (Corsica and Sassafras) were amended with dried, ground broiler litters, adjusted to field moisture capacity with deionized water, and incubated in the dark in sealed 250-mL polyethylene containers with small holes in the container tops for aeration. Subsamples were collected immediately after initiating the incubation (T0) and after 21 d (T21) and analyzed for TCLP-As as described above.

Broiler Litter Characterization

The broiler litters used in the column leaching and laboratory incubation studies, and litters obtained from previous research investigating the effects of alum [$Al_2(SO_4)_3$] on the solubility of P and trace elements (Sims and McCafferty, 2002), were analyzed for various forms of As. In addition to total As, we also determined leachable As (TCLP), bioavailable As (PBET), and As in three chemical fractions (easily exchangeable, sorbed to amorphous oxides of Al and Fe, and crystalline/recalcitrant As) by the sequential extraction method of Fendorf et al. (2004). Our goal was to assess the effectiveness of alum as a litter treatment "BMP" for the prevention of As leaching and to reduce the bioavailability of As in litters and litter-amended soils.

RESULTS AND DISCUSSION

EFFECT OF BROILER LITTER ON ARSENIC LEACHING FROM DELAWARE SOILS

Soil Properties in Column Studies

Properties of the agricultural topsoils used in Column Study #1 (Corsica, Sassafras) and Column Study #2 (Corsica, Sassafras, Evesboro, Matapeake) are provided in Table 13. In general, as with the agricultural soils collected on Cooperator and UD farms, these soils were moderately acidic (pH 5.1-6.4), with low-medium organic matter contents (1.6-2.4%) and varied in texture from sandy loam (Evesboro) to silt loam (Matapeake). Total As concentrations in the four soils ranged from 2.1 to 9.5 mg kg^{-1}.

Column Study #1

The leaching method used in Column Study #1 resulted in very uniform leachate volumes for all treatments and for the two soils (Fig. A-1). For example, for the Corsica soil, the mean values for leachate volumes collected for the six broiler litter rates (0, 4.5, 9, 13.5, 18, and 22.5 Mg ha^{-1}) during the 24 leaching events were 86, 92, 93, 98, 104, and 99 mL, respectively. Mean leachate volumes for the same litter rates in the Sassafras sandy loam were 87, 91, 88, 94, 90, and 99 mL. 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 $\mu g\ L^{-1}$ prior to the application of broiler litter containing 43 mg As kg^{-1}. The influence of broiler litter application rate on leachate As concentrations from these two soils in the next 16 leaching events is shown in Figure 31 for soil columns with no edge flow and Figure A-2 for all soil columns.

Table 13. Selected chemical and physical properties of four Delaware topsoils (0-20 cm depth) used in two greenhouse column studies investigating the effects of broiler litter applications on arsenic (As) leaching†.

Soil Property	Corsica	Sassafras	Evesboro	Matapeake
pH	5.7	5.1	5.4	6.4
OM (%)	4.4	1.6	2.0	2.4
Sand (%)	59	67	74	17
Silt (%)	27	16	14	61
Clay (%)	14	17	12	22
<u>As (mg kg^{-1})</u>				
Total As	2.1	5.4	1.5	9.5
TCLP As	0.04	0.08	0.01	0.11
M3 As	0.4	0.8	0.6	1.0
As sorption maxima	222	156	130	238
<u>Mehlich 3 (mg kg^{-1})</u>				
Al	1043	588	744	713
Fe	164	145	154	305
P	219	73	216	218
S	27	15	17	18

†The Corsica and Sassafras soils were used in both column studies; the Evesboro and Matapeake soils were only used in column study #2.

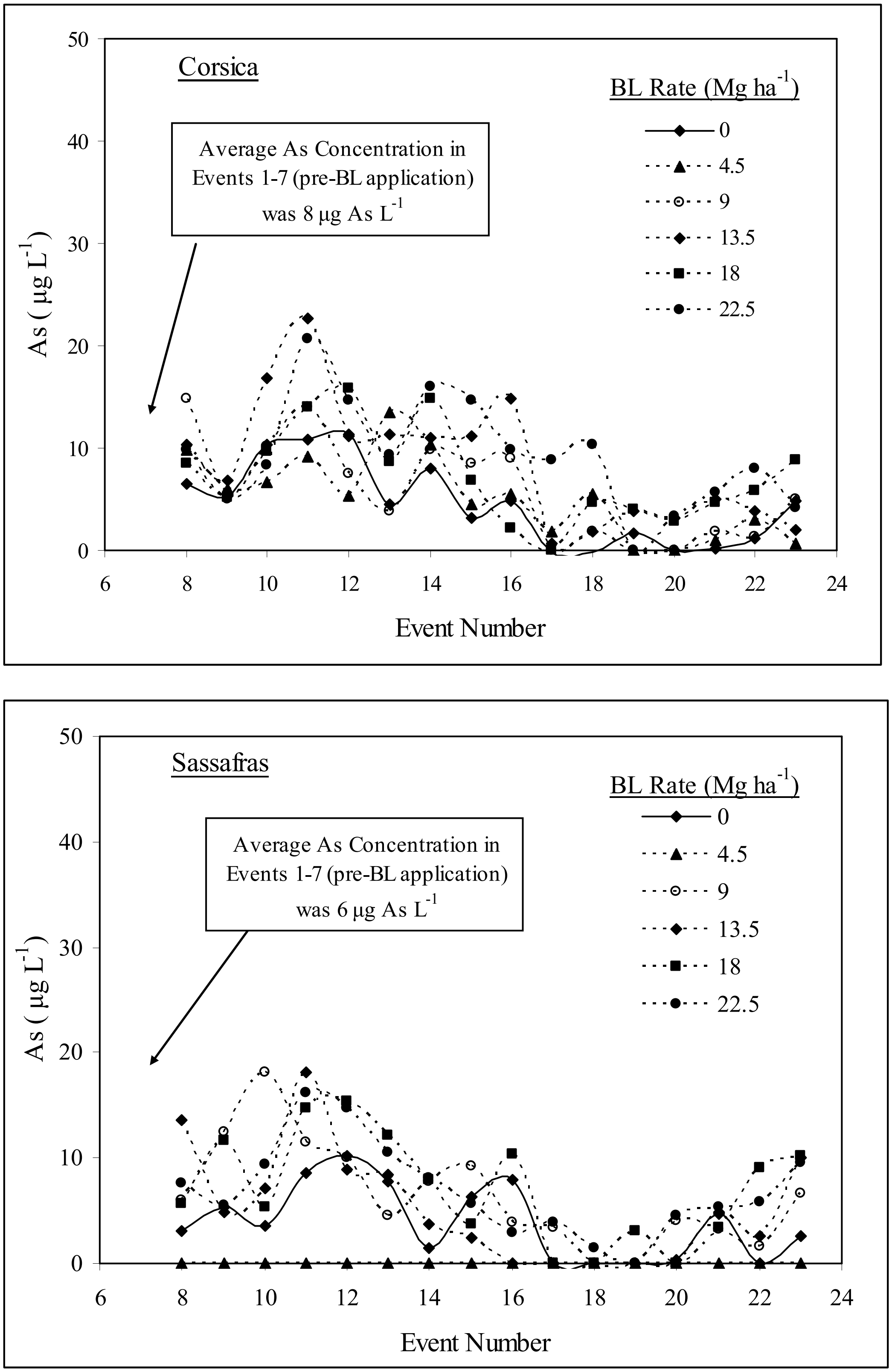


Figure 31. Effect of broiler litter (BL) application rate on total dissolved arsenic concentrations in leachate from the (a) Corsica and (b) Sassafras soils during Column Study #1.

The general trend observed (with no edge flow included for the Sassafras soil) was for broiler litter 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 broiler litter applications only resulted in significant increases in leachate As concentrations from the Corsica soil during leaching events 11 ($P < 0.05$), 17, and 18 ($P < 0.10$) (Fig. 31). 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 areal basis (no edge flow), during Column Study #1 ranged from 4 to 8 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 (Table 14).

Table 14. Effect of broiler litter application on the total mass per area of arsenic (As) leached and the percentage of As added in litter leached from two Delaware soils in Column Study #1.

Soil and Broiler Litter Rate	Total Mass As Leached	Percentage As Leached
-----Mg ha^{-1}-----	----------g ha^{-1}---------	------------%------------
Corsica		
0	4	-
4.5	5	0.6
9	5	0.5
13.5	9	0.9
18	6	0.4
22	8	0.5
Sassafras		
0	3	-
4.5	nd†	nd
9	5	0.7
13.5	5	0.3
18	6	0.4
22	6	0.3

†nd = no data

If the Sassafras soil columns where edge flow apparently occurred were included, the mass of As leached ranged from 3 to 27 g As ha^{-1} and the percentage of added broiler litter As leached varied from 3 to 9% (Table A-9).

We also measured TCLP-As in the 0-5 and 15-20 cm depths of all Corsica and Sassafras soil columns to provide an assessment of As leachability in litter-amended soils at the conclusion of the column leaching study. Litter applications increased TCLP-As slightly in the 0-5 cm depth, from 0.1 mg kg^{-1} in the control soils to 0.3 mg kg^{-1} in the Corsica soil and 0.2 mg kg^{-1} in the Sassafras soil, at the highest broiler litter rate (22.5 Mg ha^{-1}). These TCLP values were well below the USEPA standard (100 mg TCLP-As kg^{-1}) and similar to values observed in agricultural crop land and forested soils from Cooperator and UD farms (Tables 3 and 4).

A laboratory incubation study using the same two soils (Corsica and Sassafras), broiler litter, and litter application rates as Column Study #1 resulted in similar trends for TCLP-As (Table A-10). Immediately after litter application (T0), TCLP-As concentrations ranged from 0.4 (control) in the un-amended soils to 0.6 mg kg^{-1} (Corsica) and 0.8 mg kg^{-1} (Sassafras) soils at the highest litter rate (22.5 Mg ha^{-1}). Average values, over all litter rates and for both soils, for TCLP-As were 0.6 ± 0.1 mg kg^{-1} initially and 0.5 ± 0.1 mg kg^{-1}after 21 days incubation at field capacity and room temperature. The laboratory study provides additional evidence that broiler litter applications, even at extremely high rates relative to agronomic recommendations, will only slightly increase soluble/leachable As concentrations in Delaware soils.

Column Study #2

As observed in Column Study #1, leachate volumes were very consistent between soils and the two broiler litter rates in all events (Fig. A-3). For all 24 soil columns, mean leachate volumes in the 30 leaching events ranged from 113 to 129 mL (overall average leachate volume = 123 ± 28 mL). Arsenic concentrations in column leachate also exhibited similar trends as in Column Study #1 (Fig. 32; as mentioned above, data omit one outlier column for Matapeake soil – see Fig. A-4 for data for all columns). For the Corsica, Sassafras, and Evesboro soils, leachate As concentrations were always < 20 µg L^{-1} while slightly higher concentrations (20 – 30 µg L^{-1}) were observed with the Matapeake soil which had the highest soil total As concentration in Column Study #2 (9.5 mg As kg^{-1}; Table 16). 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 broiler litter. 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 broiler litter application. As noted above (see discussion on As sorption in Objective 2), it appears likely that any dissolved As released from the broiler litter 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 13, Fig. A-5), equivalent to 309 to 533 kg As ha^{-1}, orders of magnitude greater than the amount of total As added in of broiler litter (194 to 970 g As ha^{-1} for litter rates of 4.5 to 22.5 Mg ha^{-1}).

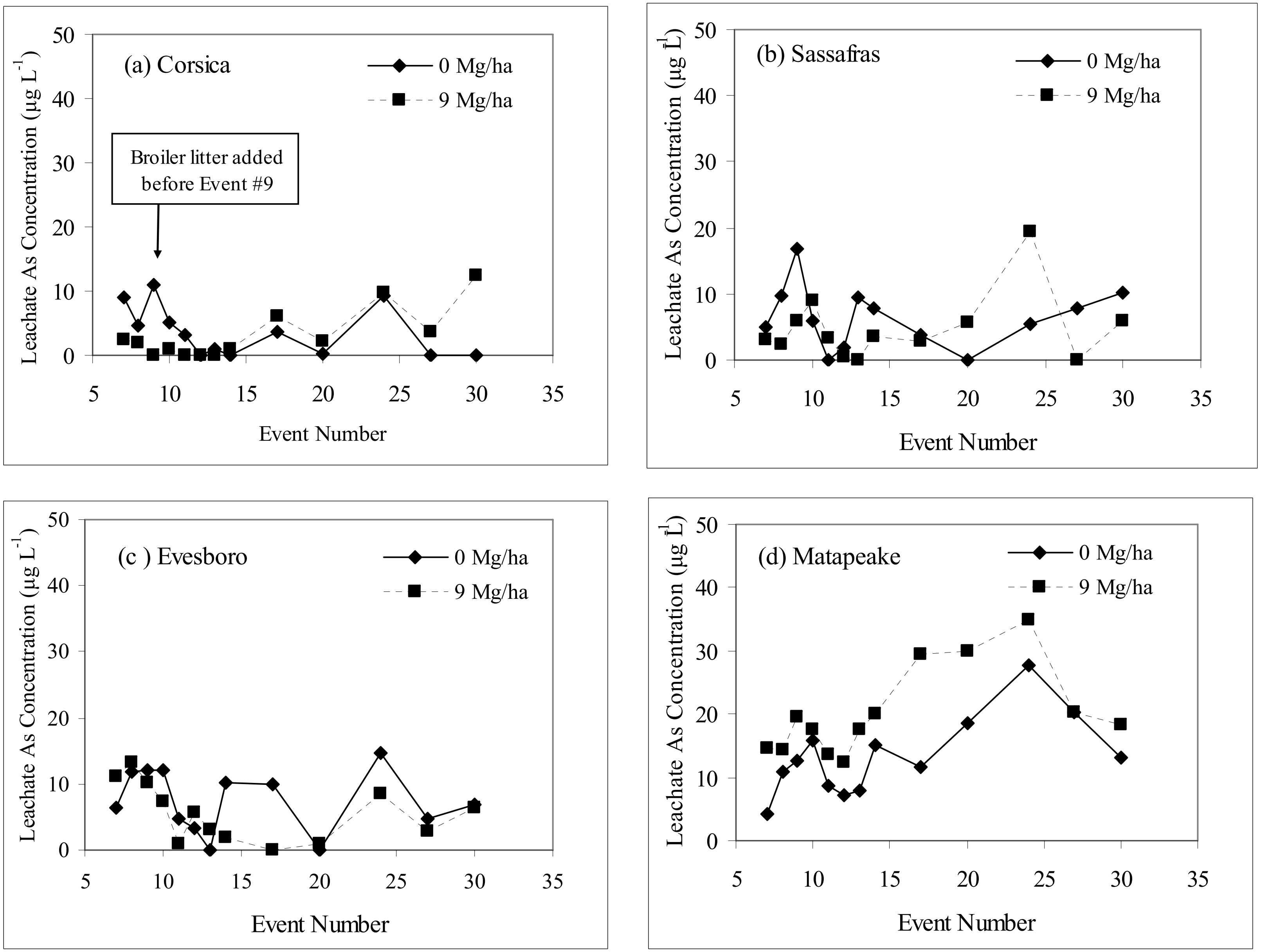


Figure 32. Effect of broiler litter (BL) application at 9 Mg/ha on total dissolved arsenic concentrations in leachate from the (a) Corsica, (b) Sassafras, (c) Evesboro and (d) Matapeake soils during Column Study #2.

BEST MANAGEMENT PRACTICES FOR BROILER LITTER ARSENIC

The development of best management practices (BMPs) for broiler litter As should have a clear goal, should be based on our knowledge of As transformations and mobility in litters and litter-amended soils, and must address production, storage, and land application of litters. For the purposes of the BMPs described below, it is assumed that the primary goal is to prevent As contamination of ground and surface waters. Other goals could include preventing human exposure to litter-borne As through inhalation or dermal contact, mitigating any potential food chain impacts of As on humans consuming crops grown on litter-amended soils and poultry products, and ingestion of soils with a history of litter application. While, based on recent studies (O'Connor et al., 2005), the need for BMPs that address these latter goals should be considered, they were not the focus of this project and thus are not directly addressed.

Our findings, and past research (Garbarino et al., 2003) indicate that the primary forms of As in broiler litters are (i) Roxarsone and (ii) arsenate [As (V), AsO_4^{-3}], an oxyanion known to react similarly in soils as phosphate ($H_2PO_4^-$, HPO_4^{-2}, PO_4^{-3}). Once excreted, Roxarsone may persist in litters for weeks, but appears to be gradually converted to As(V) by the actions of litter microorganisms. Since broiler litters typically remain in poultry houses for months, and even years, and can be stockpiled in storage areas for months before land application, it seems likely that the predominant form of As applied to cropland will be As(V). Much of the total As in litters is also easily soluble in water. Sims and Luka-McCafferty (2002) measured total and water-soluble As in litters collected from 200 poultry houses on the Delmarva Peninsula and reported that the mean values for total and water-soluble As were 45 ± 7 mg kg^{-1} and 19 ± 4 mg kg^{-1} or that ~ 42% of litter total As was solubilized by a single water extraction. The litters used in our As speciation and column leaching studies exhibited similar degrees of solubility in water (~50%). We also noted, for the column study litter, that 90% of litter total As could be extracted by the TCLP solution. The mean litter total As concentration reported by Sims and Luka-McCafferty (2002) was also slightly greater than the pollutant concentration limit (As = 41 mg kg^{-1}) used by USEPA to identify "exceptional quality" biosolids (sewage sludges) that can be land applied in a similar manner as fertilizers. Biosolids with total As concentrations > 41 mg kg^{-1} are subject to more stringent land application criteria such as annual (2 kg As ha^{-1}) and cumulative (41 kg As ha^{-1}) loading rates and record-keeping requirements. Similar standards have been established by the state of South Carolina for poultry producers. Given the rather high solubility of As in litters and the fact that the total As values are similar to those used to regulate land application of another organic soil amendment (biosolids), we suggest the following BMPs be used to prevent litter As from contaminating ground and surface waters:

Production and Storage BMPs for Broiler Litter As

- The use of chemical amendments to reduce As solubility in litters while in poultry houses should be considered. For example, alum [$Al_2(SO_4)_3$] applications, at proper rates, have been shown to reduce As solubility in poultry litters and decrease dissolved As concentrations in runoff (Sims and Luka-McCafferty, 2002; Moore et al., 1998). Past research suggests that alum hydrolyzes in moist, alkaline litters to form Al hydroxides that sorb dissolved As and phosphate, in much the same manner as occurs in soils. As part of the present study, we compared the solubility and speciation of As in litters from the study of Sims and Luka-McCafferty (2002) and found that, relative to untreated litters, alum treatment reduced litter As solubility and bioavailability and shifted the distribution of As from predominantly labile forms ($MgSO_4$-As) to more stable species (HCl-As, Residual As; Table 15).

Table 15. Comparison of As forms and solubility in unamended and alum-treated broiler litters collected in the study of Sims and Luka-McCafferty (2002).

	Arsenic Extraction Method							
Sample ID	Total	Water	TCLP	PBET	$MgSO_4$	AmOx	HCl	Residual
	----------------------	--------------------	--------------------	----------mg kg^{-1}	----------	--------------------	--------------------	--------------------
Control Litters								
516	50	16	29	24	21	0.5	7	22
528	36	12	23	19	15	0.4	6	15
534	41	15	30	23	17	0.3	5	18
570	45	19	36	26	24	0.4	4	16
581	43	24	34	27	24	0.2	4	15
582	42	24	28	22	21	0.4	4	17
599	42	17	29	22	24	0.5	5	12
Mean	43	18	30	23	21	0.4	5	16
Std. Dev.	4	5	4	3	4	0.1	1	3
% of Total As		42	70	55	49	1	12	38
Alum Litters								
132	44	9	16	19	8	1.4	4	30
133	43	8	17	18	9	1.4	5	28
148	49	15	26	27	14	1.7	6	27
149	48	14	24	24	14	1.0	5	28
172	43	14	17	19	8	1.6	5	28
178	36	5	12	15	7	0.7	4	24
182	38	5	16	18	8	2.1	5	23
183	45	9	16	18	13	1.3	6	25
199	42	3	15	20	10	1.7	13	18
Mean	43	9	18	20	10	1.4	6	26
Std. Dev.	4	4	4	4	3	0.4	3	4
% of Total As		21	41	46	23	3	14	60

- Broiler litters should be protected from direct contact with rainfall during storage to prevent dissolved As losses from litter stockpiled in fields. Litters stored in agricultural fields prior to land application should be covered with plastic or similar materials or stacked in a manner that prevents rainfall and snowmelt from entering stockpiles and leaching As from the litter.
- Litters should be stockpiled on impermeable surfaces designed to prevent dissolved As from leaching into soils or running off to surface waters after litters are removed and transported to agricultural fields for land application. Alternatively, any residual litter and the upper few cm of soil remaining after stockpiled litter is moved should be removed and re-distributed in fields at litter As application rates similar to those associated with normal crop production.
- Similarly, should poultry production or storage facilities be demolished and the land converted to other uses, residual litter and soil should be removed in a manner that is protective of the environment.

Land Application BMPs for Broiler Litter As

- Consideration should be given to the need to establish annual or cumulative As loading rates for broiler litters with higher As concentrations (e.g., > 41 mg As kg^{-1}), as has been done by USEPA for biosolids and South Carolina for poultry manures and litters (see above). Assuming the identical loading rate standards adopted by USEPA were also used for litters (Annual loading rate limit = 2 kg As ha^{-1}, Cumulative limit = 41 kg As ha^{-1}) and a litter As concentration of 45 mg kg^{-1}, the maximum amount of "as-is" broiler litter that could be applied to a crop field annually, assuming a litter moisture content of 25%, would be ~60 Mg ha^{-1} (~26 tons ac^{-1}), well above the amount of litter normally recommended for crop rotations in Delaware. The maximum cumulative litter application would be 1215 Mg ha^{-1} or ~540 tons ac^{-1}. If litter were to be applied once per year at a typical agronomic application rate (9 Mg ha^{-1} = 4 tons ac^{-1}), this would limit litter applications in a given field to a total of ~135 years.
- Litters applied for crop production purposes at normal agronomic rates should be incorporated whenever possible to prevent rainfall and snow melt interactions with surface-applied litter - which could lead to dissolved As losses in runoff. New application equipment that can incorporate litters in no-tillage systems (e.g., "zone tillage") should be investigated as an application BMP.
- Avoid litter applications shortly before predicted rainfall events to minimize the potential for As runoff or leaching into subsoils and shallow ground waters.
- Application practices should not result in direct deposition of litters in streams, ponds, or artificial drainage ditches where litter As could easily be solubilized.
- Soil erosion control practices should be implemented per USDA-NRCS recommendations to prevent the loss of As bound to clays, silts, and organic matter, the most easily erodible soil particles.
- Applying litters to agricultural soils that are low-lying, poorly drained, and susceptible to flooding should be avoided. In these settings soils, and litters, can become anaerobic, resulting in the conversion (microbial reduction) of As(V) to As(III), a more toxic and mobile form of As.

OBJECTIVE 4: TO SPECIATE AS AND DETERMINE THE ASSOCIATIONS AND DISTRIBUTIONS OF AS AND OTHER CO-CONTAMINATING METALS IN TANNERY CONTAMINATED SOILS USING A COMBINATION OF CHEMICAL EXTRACTION, DESORPTION, AND MOLECULAR SCALE X-RAY ABSORPTION AND FLUORESCENCE SPECTROSCOPIC APPROACHES

Methods:

Sample collection

Site access was granted to DNREC at a former tannery site, located under what is currently a parking lot near the Riverfront area of Wilmington. Samples were drawn from split-auger cores taken at various locations on site as pre-determined by DNREC, and were taken at every available depth interval from surface to bedrock. Soil samples were removed from the split auger and stored in air tight containers until analysis. Samples were collected in October of 2004, at which time the water table was at approximately 5-6' below the surface.

Chemical Analyses

The pH and pe of each sample were determined by mixing ~0.5 g soil with ~10 mL DDI water, settling for 20 minutes, and measuring using a combination electrode. Titrations for pH-dependent batch desorption were determined at various ionic strengths. Desorption isotherms were performed by suspending 1 g L^{-1} of soil into 0.1 M, 0.01 M, or 0.001 M $NaNO_3$ electrolyte solutions for 24 hours. The suspension was then placed on a pH stat and the pH incrementally decreased, letting the suspension equilibrate for 48 hours at each pH. Prior to re-adjusting the pH, 10-mL aliquots of the soil suspension were drawn and the equivalent volume of electrolyte solution replaced into the soil suspension. The samples were centrifuged and analyzed for total As by GF-AA.

Direct Speciation of Tannery Contaminated Soil

Some of the soil samples with As concentrations above 100 mg kg^{-1} (Hole 5, 3-5 feet, Hole 7, 1-3 feet, Hole 7, 4-6 feet) [See Table 6] were air dried and lightly ground before mounting on Kapton tape for micro-XAS and micro-XRF analysis. These were the only samples examined due to the extensive time necessary to run and analyze the experiments, the need to examine samples with higher As contents, and the fact that some of the samples could not be analyzed because they contained large amounts of rock materials,

All μ-XRF and μ-XAS analyses were conducted at the Advanced Light Source (Lawrence Berkeley National Lab in Berkeley, CA) on beamline 10.3.2. Samples were mounted on Kapton tape, affixed to the x,y,z sample stage, and positioned at 45° to the x-ray beam. For micro-XRF mapping, the beam energy was set such that fluorescence signals from all elements of interest (e.g., As, Fe, Ni, Zn, Co, Pb, etc.) were emitted and subsequently detected by a multi-element solid-state detector located 90° to the incident beam. Sample spots were quickly mapped at coarse resolution (2 μm x 2 μm) to identify smaller regions of interest (i.e. "hotspots") or distinct metal correlations that were then re-mapped using smaller step sizes and shorter dwell times for better resolution. From the fine maps, specific points of interest were identified from which to collect μ-EXAFS spectra from 100 eV below to 500 eV above the As K-edge of 11.874 keV. After background subtraction, normalization, and chi transformation, principle component analysis (PCA) and target transformation were used to determine the primary metal species present in the samples (Manceau et. al., 2002).

Results:

Soil characteristics

The measured pe and pH of all samples are given in Figure 33 as an overlay of the standard As pe-pH diagram. While all samples had a measured pH well within the $HAsO_4^{-2}$ or $H_2AsO_4^-$ region, the pH of the samples spanned 3 orders of magnitude from pH = 5.42 at 40 feet depth in hole #7, to pH = 9.07 at 50 feet depth. Surface samples (0-10 feet depth) ranged from 6.62-8.35. The pe values ranged from about 7 to 11.

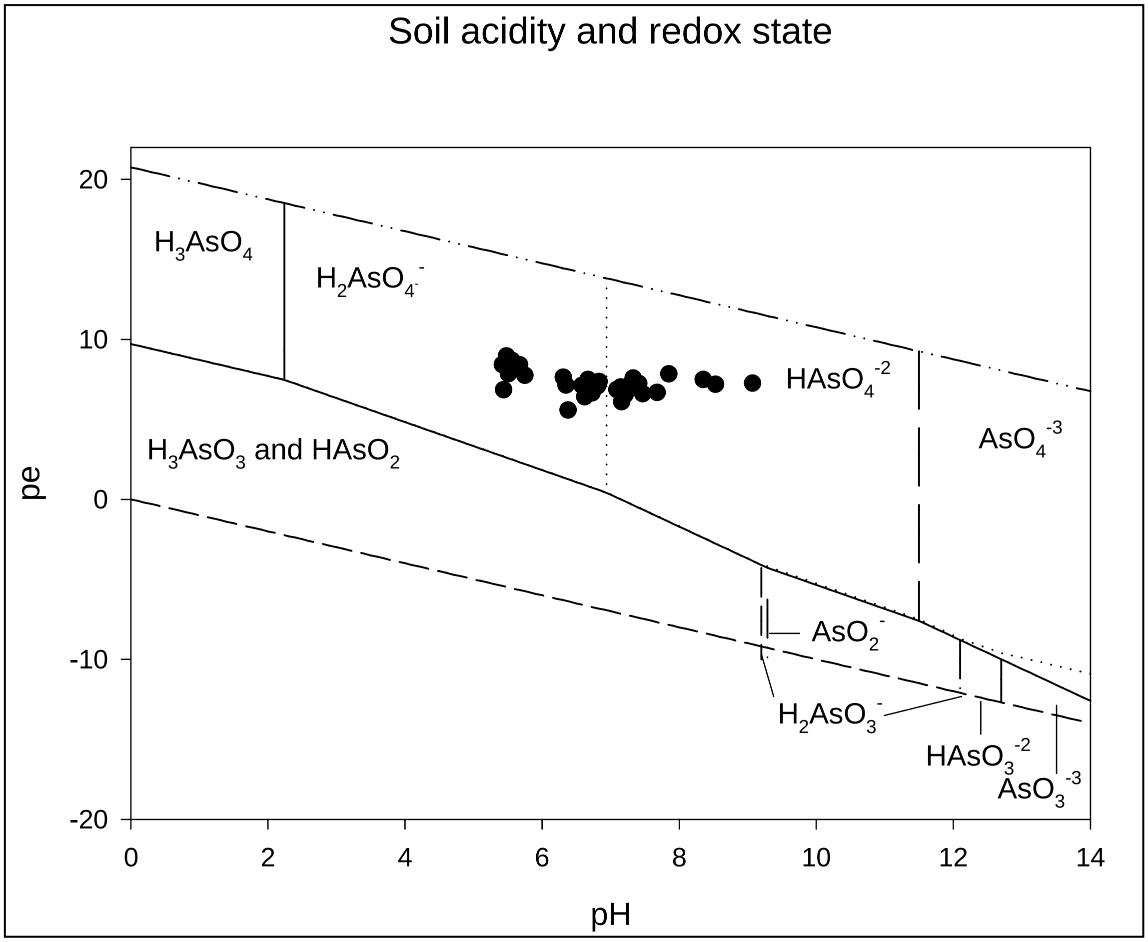


Figure 33. pe-pH of all soil-water suspensions plotted against the characteristic As-speciation diagram. Data points for the soil samples are represented by black filled circles.

Desorption characteristics

The mobility of As was determined by varying pH, ionic strength, and dissolved oxygen (DO) concentration systematically. These experiments were intended to mimic various macro-scale changes possible at the site and to evaluate the potential mobility of As. The results of these experiments are illustrated in Figure 34. The presence of dissolved oxygen increased the amount of As released from the soil. Increasing the electrolyte solution also had an effect on the amount of As released. The 0.01*M* $NaNO_3$ had the greatest impact on As desorption.

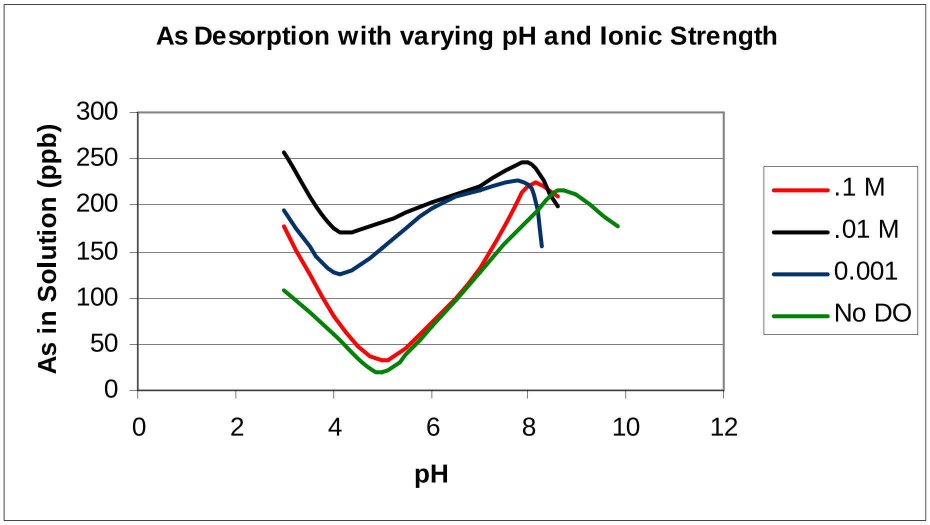


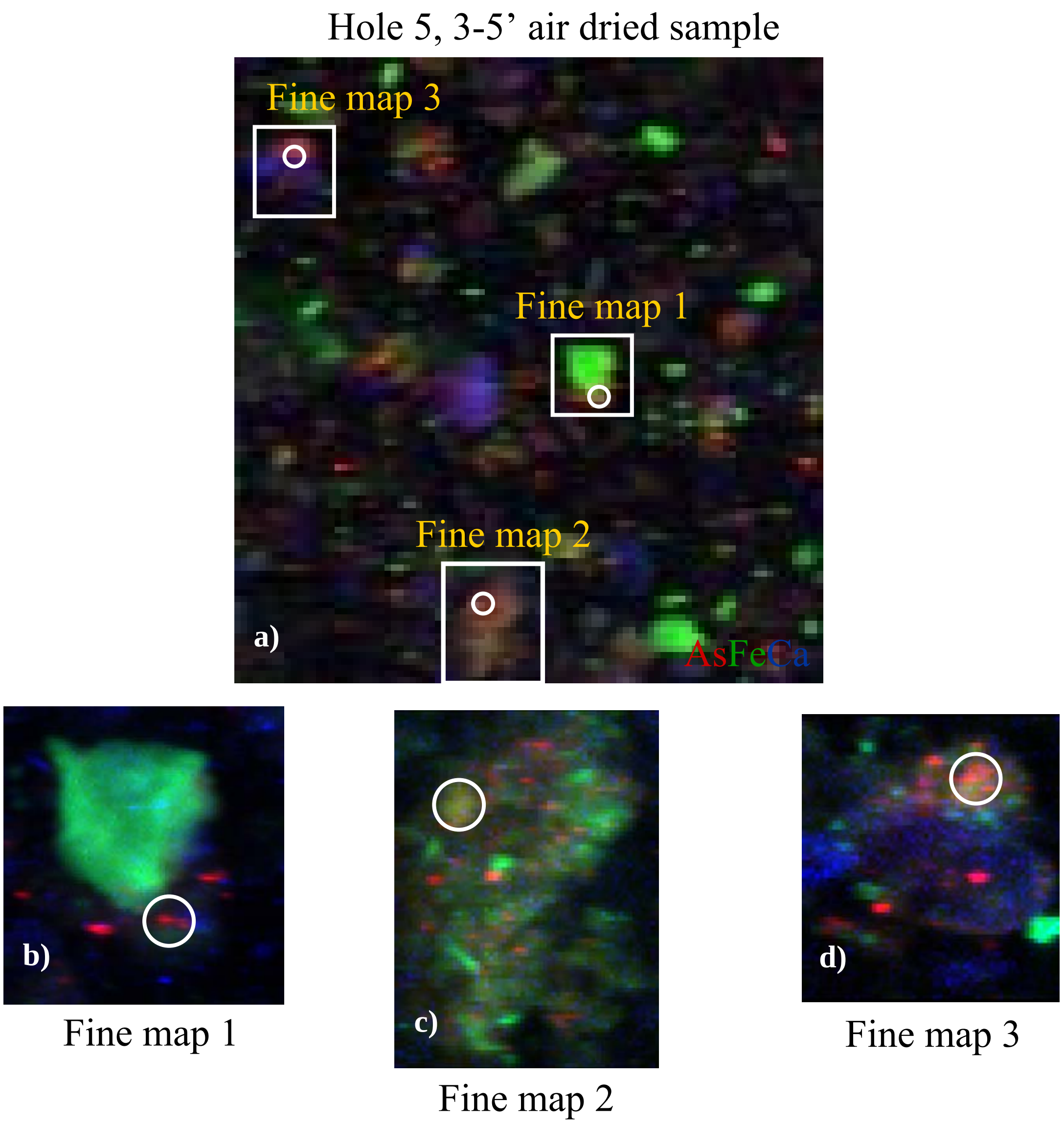
Figure 34. Solubilized concentration of As (ppb=μg L^{-1}) in solution) from a 1 g L^{-1} soil suspension at 0.1, 0.01, and 0.001 *M* $NaNO_3$ with varying pH. Temperature was kept constant at 25° C and DO was at equilibrium with the atmosphere.

Micro-XRF and Micro-XAS Data Analyses

Micro-XRF mapping images (Fig. 35) show two distinct As environments; diffuse sorbed As concentrations, as well as bright, highly concentrated “hot-spots”. While the diffuse, sorbed regions exhibit a correlation between As and other metals, such as Zn and Mn, the “hot-spots” have no such co-localization. Because no other metals are present in the “hot-spots”, the arsenic in these locations is most likely in a relatively pure mineral phase, such as realgar, pararealgar, or orpiment. In addition, the high energy line used for these experiments cannot detect light elements (above Al on the periodic table), making mapping of these elements nearly impossible.

From the μ-XRF maps, various spots were chosen from which to collect μ-EXAFS spectra. Background-corrected and normalized spectra from all spots are stacked in Fig. 36. It is immediately evident that several As oxidation states and mineral phases are present in the soil samples, as evidenced by the presence of a split white line. In some cases, mineral phases predominate (e.g., Hole 5, 3-5 inches, region 1, spot 3), while in others, a combination of mineral phases and As (III) and As(V) species occur (e.g., Hole 5, 3-5 inches, region 2, spot 2).

The full chi spectra were Fourier transformed to a radial distance function. The first shells were then selected up to a range of 2.6Å and back-transformed to create a filtered first shell chi function. Principle component analysis (PCA) was performed on the set of 15 total μ-EXAFS spectra to determine the minimum number of components necessary to fully describe the data set. The results from the PCA show that only three equations are needed to reconstruct every spectrum within the data set. These three equations translate to a combination of three possible species that are present within the sample. The PCA of the total spectra were also target transformed with standard spectra to determine the SPOIL values of each standard (see Table 15). The standards falling within the “excellent” and “good” ranges were then selected to use for a LLSF for phase/species determination. The species indicated by the SPOIL values represent the four possible oxidation states of As; As(II)-S, As(III)-S, As(III)-O, and As(V)-O confirming the data shown in Fig. 36, and the oxidation state analyses shown in Table 16, that indicates a combination of arsenate, arsenite, and As-bearing minerals such as orpiment and realgar. This further indicates the heterogeneous nature of the samples.



Fine map 1

Fine map 2

Fine map 3

Figure 35. a) Coarse XRF map of powder mounted, air dried sample from Hole 5, 3-5' in depth (2 x 2 mm). b) Fine map 1 of area of interest with small, high intensity As signal (red area). c) Fine map 2 of area of interest with diffuse, low intensity As signal (greenish yellow area). d) Fine map 3 of area of interest with mixture of As signal intensities (red and greenish yellow area). White circles indicate locations where μ-EXAFS spectra were collected.

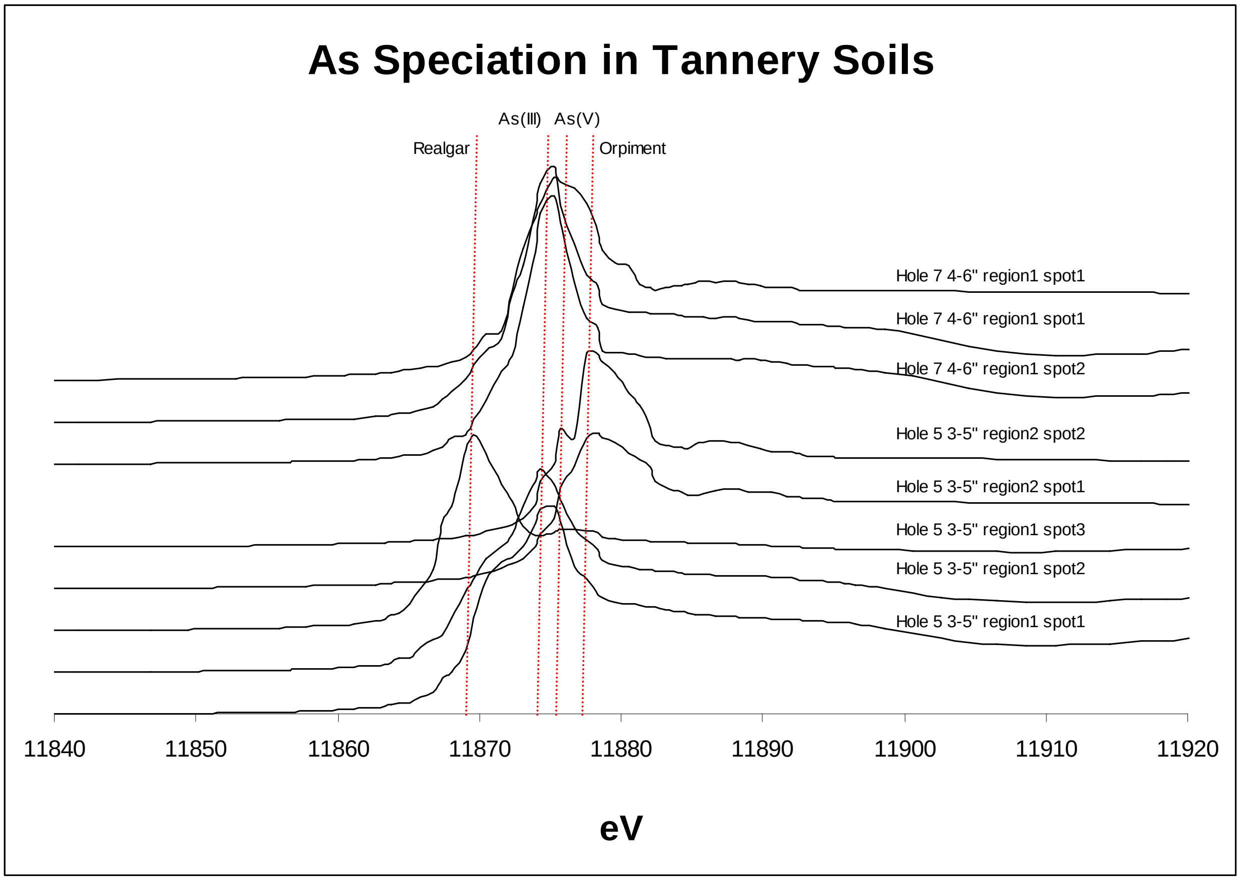
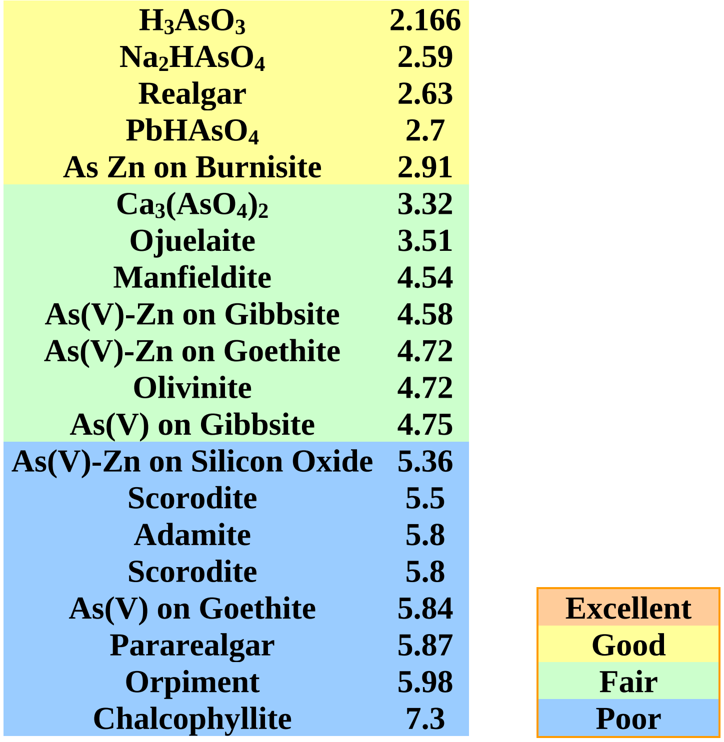


Figure 36. Background-corrected and normalized μ-EXAFS data collected from all locations in the three soil samples from Hole 5, 3-5’ depth, Hole 7, 1-3’ depth and 4-6’ depth. Energy levels where As mineral phases, realgar and orpiment, and As(III) and As(V) occur are shown as comparisons to the soil samples.



H_3AsO_3	2.166
Na_2HAsO_4	2.59
Realgar	2.63
$PbHAsO_4$	2.7
As Zn on Burnisite	2.91
$Ca_3(AsO_4)_2$	3.32
Ojuelaite	3.51
Manfieldite	4.54
As(V)-Zn on Gibbsite	4.58
As(V)-Zn on Goethite	4.72
Olivinite	4.72
As(V) on Gibbsite	4.75
As(V)-Zn on Silicon Oxide	5.36
Scorodite	5.5
Adamite	5.8
Scorodite	5.8
As(V) on Goethite	5.84
Pararealgar	5.87
Orpiment	5.98
Chalcophyllite	7.3

Excellent
Good
Fair
Poor

Table 16. SPOIL values computed from all the µ-EXAFS locations. Note: The species that fall within the "good" range represent the major possible oxidation states. It was from these results that As(III), As(V), and realgar were chosen for comparison.

Sample	AsO_4	AsO_3	Orpiment	Realgar
5, 3-5' 1.1	0.36721	**1.32479**	0	0.19922
5, 3-5' 1.2	0.41908	**0.93097**	0	0.18358
5, 3-5' 1.3	0	0.44788	0.5001	**0.513**
5, 3-5' 2.1	0.12456	0	**0.56205**	0.29977
5, 3-5' 2.2	0.15925	0	**0.557**	0.25926
7 1-3' 1.1	**1.06923**	0	0.14972	0
7, 1-3' 1.2	**1.09203**	0	0.23258	0
7, 4-6' 1.1	0.4451	0	0.80053	**1.83122**

Table 17. Oxidation state analysis of all µ-EXAFS locations using linear least squares fitting to standards of the four possible oxidation states. The values in bold indicate which form of As is predominant at each location. Location 5 contains arsenite, orpiment and realgar. Location 7 is dominated by arsenate and realgar. It appears that some of the initial arsenic substances used in the tanning process continue to persist in the fill material and soils.

OBJECTIVE 5: TO LEAD, IN COOPERATION WITH THE UNIVERSITY OF DELAWARE *INSTITUTE OF SOIL AND ENVIRONMENTAL QUALITY* AND THE UNIVERSITY OF DELAWARE *CENTER FOR CRITICAL ZONE RESEARCH*, A MULTI-PARTY DISCUSSION OF THE IMPLICATIONS OF THE FINDINGS OF THIS RESEARCH TO THE QUALITY OF DELAWARE'S ENVIRONMENT

A workshop will be conducted at the end of the project by the UD *Institute of Soil and Environmental Quality* and the UD *Center for Critical Zone Research.* Results of this project and other comparable studies will be reviewed and discussed relative to ongoing concerns about As in Delaware soils. The University will work with DNREC staff and other appropriate cooperators in the organization of this workshop.

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APPENDIX

TABLES AND FIGURES

Table A-1. Soil classification information for agricultural and forested soil profiles on five farms in Sussex County, Delaware.

Farm ID	Soil Series	Horizon	Depth	Color	Texture	Structure	Consistence	Boundary	Clay Particles	Pores	Roots	Coarse Fragments
			--in--									
Agricultural Cropland												
Farm #1	Rumford		0-8		Sandy loam							
			8-16		Loamy sand							
			16-24		Sandy loam							
			24-36		Sandy loam							
Farm #2	Sassafras		0-8		Sandy loam							
			8-16		Sandy clay loam							
			16-24		Sandy loam							
			24-36		Sandy loam							
Farm #3	Corsica	Ap	0-12		Loamy sand							
		Eg	12-17		Sandy clay loam							
		Btg	17-32		Clay loam							
Farm #4	Downer	Ap	0-11		Sandy loam							
		E	11-18		Sandy loam							
		Bt	18-29		Sandy loam							
		C/Bt	29-40		Sandy loam							
Farm #5	Greenwich		0-11		Sandy loam							
			11-21		Sandy loam							
			21-32		Loam							
			32-43		Sandy loam							
Forest												
Farm #1	Sassafras		0-4		Sandy loam							
			8-16		Sandy loam							
			16-24		Sandy loam							
			24-36		Loamy sand							
Farm #2	Ingleside		0-4		Sandy loam							
			8-16		Sandy loam							
			16-24		Sandy loam							
			24-36		Sandy loam							
Farm #5	Greenwich		0-3		Loam							
			3-18		Loam							
			18+		Sandy clay loam							

Table A-2. Soil classification information for agricultural soil profiles on two farms in New Castle County, Delaware.

Site and Soil Series	Horizon	Depth	Color	Texture	Structure	Consistence	Boundary	Clay Particles	Pores	Roots	Coarse Fragments
		--in--									
Farm #6 - Elkton	Ap	0-9	10YR 4/2	silt loam	weak medium subangular blocky	-	-	-	-	-	-
	Btg1	9-30	2.5Y 6/1	silt loam	weak coarse prismatic parting to moderate medium subangular blocky	-	-	-	-	-	-
	Btg2	30-48	2.5Y 6/2	silt loam	-	-	-	-	-	-	-
	Btg3	48-52	2.5Y 6/1	silt loam	-	-	-	-	-	-	-
	Cg1	52-58	5Y 6/1	silt loam	-	-	-	-	-	-	-
	2Cg	58-60+	5Y 6/1	sandy loam	-	-	-	-	-	-	-
Farm #6 - Reybold	Ap	0-9	10YR 4/3	silt loam	weak medium blocky parting to moderate fine granular	very friable	abrupt smooth	-	common fine tubular	few fine	-
	BE	9-12	10YR 4/4	silt loam	moderate medium subangular blocky	friable	clear smooth	-	common fine tubular	few fine	-
	Bt1	12-22	10YR 4/6	loam	moderate medium subangular blocky	friable	-	common continuous 7.5YR 4/6	common fine & medium tubular	not apparent	-
	Bt2	22-34	10YR 4/6	loam	moderate coarse subangular blocky	friable	-	common continuous 7.5YR 4/7	-	not apparent	-
	BC	34-50	10YR 5/6	silt loam	weak coarse subangular blocky	friable	-	-	-	not apparent	-
	2BC	50-60	7.5YR 5/6	loamy sand	single grain	loose	-	-	-	not apparent	-
	2C	60-70	10YR 4/6	loamy sand	single grain	loose	-	-	-	not apparent	-
	3C	70+	10YR 5/4	silt loam	massive	friable	-	-	-	not apparent	-

Table A-2 (cont.). Soil classification information for agricultural soil profiles on five farms in New Castle County, Delaware.

Farm ID and Soil Series	Horizon	Depth	Color	Texture	Structure	Consistence	Boundary	Clay Particles	Pores	Roots	Coarse Fragments
		--in--									
Farm # 6 - Woodstown	Ap	0-9	10Yr 4/2	loam	weak coarse subangular blocky	friable	abrupt smooth	-	common fine & medium tubular	few fine & medium	0%
	Bt1	9-18	10YR 5/4	loam	moderate medium subangular blocky	friable	clear smooth	few thin patchy	common fine & medium tubular	not apparent	0%
	Bt2	18-32	10YR 5/4	loam	strong medium subangular blocky	friable	-	common on ped faces	few fine	not apparent	0%
	BC	32-45	10YR 5/4	loam	weak medium subangular blocky	very friable	-	-	-	not apparent	5%
	2C1	45-66	7.5YR 5/6	loamy sand	single grain	loose	-	-	-	not apparent	2%
	2C2	66-72	7.5YR 5/6	loamy sand	single grain	loose	-	-	-	not apparent	2%
Farm #7 - Nassawango	Ap	0-7	10YR 4/3	silt loam	weak coarse subangular blocky	friable	wavy smooth	-	few fine & medium	common fine & very fine throughout	-
	Bt	7-30	10YR 4/6	silt loam	moderate medium subangular blocky	firm	-	-	-	common fine in cracks	-
	2BC	30-46	10YR 5/6	sandy loam	-	friable	-	-	-	-	-
	2C1	46-55	10YR 5/4	loamy sand	-	loose	-	-	-	-	-
	2C2	55-60	10YR 6/4	loamy coarse sand	-	loose	-	-	-	-	-
	2C3	60-72	10YR 5/4	sandy loam	-	very friable	-	-	-	-	10% quartzite & chert

Table A-2 (cont.). Soil classification information for agricultural soil profiles on five farms in New Castle County, Delaware.

Site and Soil Series	Horizon	Depth	Color	Texture	Structure	Consistence	Boundary	Clay Particles	Pores	Roots	Coarse Fragments
		--in--									
Farm #7 - Sassafras	Ap	0-12	10YR 4/3	sandy loam	weak coarse subangular blocky	friable	abrupt smooth	-	common fine & few medium	few fine & medium	-
	BE	12-20	10YR 5/4	sandy loam	weak coarse subangular blocky	friable	clear smooth	-	common earthworm tubes	few fine & medium	-
	Bt	20-36	10YR 5/6	sandy clay loam	moderate medium subangular blocky	friable	-	few medium continuous	-	few fine & medium	-
	BC	36-55	10YR 4/6	loam	-	friable	-	-	-	-	-
	C	55-72	10YR 5/4	loamy sand	-	very friable	-	-	-	-	-

Table A-3. Total elemental analysis for agricultural and forested soil profiles on five farms in Sussex County, Delaware.

Farm ID and Soil Series	Depth	P	K	Ca	Mg	Mn	Zn	Cu	Fe	B	S	Al	As
	--in--	------------mg kg^{-1}------------											
Agricultural Cropland													
Farm #1 - Rumford	0-8	302	208	350	334	39	18	9.0	2785	1.4	71	3432	2.8
	8-16	184	178	215	372	30	11	5.9	3967	1.8	25	4293	2.8
	16-24	147	827	394	622	48	16	5.5	8517	3.9	44	14851	3.4
	24-36	132	720	439	554	45	16	5.8	9539	3.8	68	12458	1.5
Farm #2 - Sassafras	0-8	269	355	304	538	121	28	7.2	6466	2.8	105	7714	5.4
	8-16	144	624	659	988	100	22	3.5	14704	5.6	68	14458	5.4
	16-24	116	407	562	640	64	15	1.5	11910	5.1	49	10279	0.8
	24-36	73	244	445	276	41	9	2.2	7396	2.9	39	8231	3.4
Farm #3 - Corsica	0-12	395	648	1020	360	22	16	7.0	1480	2.2	226	10163	2.1
	12-17	39	534	306	431	22	12	9.8	10546	5.7	98	13802	0.5
	17-32	33	584	265	495	17	17	15.2	16080	8.6	119	15182	-1.7
Farm #4 - Downer	0-11	442	229	500	370	64	24	14.0	3446	2.4	93	5399	2.6
	11-18	176	197	341	514	55	14	5.8	5107	1.8	23	6368	1.1
	18-29	139	397	512	543	68	16	8.8	9069	4.4	23	8712	6.3
	29-40	40	202	229	229	26	8	2.9	3236	1.5	13	5191	3.2
Farm #5 - Greenwich	0-11	322	303	680	789	136	21	9.6	5951	2.7	96	7348	2.6
	11-21	163	373	492	991	110	20	8.6	8574	4.5	45	9902	0.5
	21-32	143	523	566	1044	47	19	11.4	13319	6.8	38	11212	3.2
	32-43	84	350	342	563	33	11	6.7	7804	4.3	29	6980	1.6

Table A-3 (cont.). Total elemental analysis for agricultural and forested soil profiles on five farms in Sussex County, Delaware.

Farm ID	Depth	P	K	Ca	Mg	Mn	Zn	Cu	Fe	B	S	Al	As
	--in--	---mg kg^{-1}---											
Forest													
Farm #1 - Sassafras	0-4	209	479	483	598	59	18	2.1	4812	3.2	189	6209	1.5
	8-16	110	574	164	1012	49	22	3.1	9745	4.0	50	13016	5.4
	16-24	90	452	64	578	40	15	3.6	9307	3.5	88	11804	1.5
	24-36	66	259	41	322	26	10	2.4	6535	2.6	71	7492	0.8
Farm #2 - Ingleside	0-4	159	196	197	398	35	13	4.6	3914	2.4	218	4791	0.2
	8-16	73	168	101	541	32	10	0.0	3985	1.6	36	5674	2.1
	16-24	85	171	87	683	43	13	-1.6	6087	2.0	48	7294	1.5
	24-36	138	318	47	726	50	16	1.8	12259	3.6	115	10469	6.1
Farm #5 - Greenwich	0-3	205	324	435	858	144	20	7.0	6563	4.2	231	10039	4.2
	3-18	105	292	254	1149	127	21	7.2	8679	4.5	68	13420	2.1
	18+	105	424	148	1027	92	21	12.5	14176	7.2	115	12223	3.3

Table A-4. Total elemental analysis for agricultural soil profiles on five farms in New Castle County, Delaware.

Farm ID and Soil Series	Horizon	Depth	P	K	Ca	Mg	Mn	Zn	Cu	Fe	B	S	Al	As
		--cm--	mg kg^{-1}											
Farm #6 - Elkton	Ap	0-23	392	532	975	872	107	34	4.7	8226	32	214	8370	3.4
	Btg1	23-43	89	285	452	537	21	15	2.2	18293	66	123	8367	2.5
Farm #6 - Reybold	Ap	0-23	364	516	1084	1499	182	32	5.6	12062	47	198	11265	3.3
	BE	23-30	313	376	873	1357	191	30	5.0	11499	44	134	10623	3.7
	Bt	30-56	286	544	913	1801	161	33	6.9	17119	65	121	14865	4.8
Farm #6 - Woodstown	Ap	0-23	208	330	461	840	76	23	3.5	6387	25	112	8475	2.2
	Bt1	23-46	123	447	488	1238	57	21	4.9	9053	35	68	11484	2.1
Farm #7 - Nassawango	Ap	0-18	380	545	872	1300	306	35	5.8	11535	45	173	11533	4.4
	Bt	18-76	397	714	968	1981	143	37	8.9	24243	91	125	17428	4.8
Farm #8 - Sassafras	Ap	0-30	652	831	556	1214	814	43	6.0	15480	60	200	12854	5.4
	BE	30-56	432	652	315	1151	324	28	3.9	16241	61	127	10060	3.7
	Bt	56-91	464	1529	727	1566	111	36	7.7	28393	110	166	15143	9.2

Table A-5. Routine soil test analysis for agricultural and forested soil profiles on five farms in Sussex County, Delaware.

									Mehlich 3											
Site ID	Horizon	Depth	Sand	Silt	Clay	OM	pH	PSR	P	K	Ca	Mg	Mn	Zn	Cu	Fe	B	S	Al	As
		--cm--	-----------------%---------------						---mg kg^{-1}---											
Agricultural Cropland																				
Farm #1 - Rumford		0-20	80	14	6	0.7	5.8	0.240	119	63	267	40	10	4.5	4.8	97	0.22	8	385	0.15
		20-40	81	9	10	0.1	5.7	0.123	76	60	213	40	6	1.3	2.7	124	0.20	8	479	0.26
		40-61	72	9	19	0.2	5.4	0.023	18	145	403	101	7	0.5	1.1	71	0.28	26	661	0.15
		61-81	74	10	16	0.2	5.3	0.008	7	179	422	76	2	0.3	1.4	61	0.23	45	727	0.20
Farm #2 - Sassafras		0-20	68	22	10	1.2	5.1	0.072	47	99	253	38	43	4.0	2.9	119	0.34	11	502	0.19
		20-40	52	23	25	0.8	5.9	0.003	2	122	557	145	17	0.6	1.0	280	0.49	16	619	0.28
		40-61	72	10	18	0.4	6.1	0.003	2	94	484	126	7	0.2	1.2	52	0.30	20	535	0.12
		61-81	80	4	16	0.2	6.5	0.006	4	66	437	72	10	0.3	1.2	45	0.32	21	522	0.22
Farm #3 - Corsica	Ap	0-30	79	14	7	2.4	5.6	0.092	86	136	462	82	5	2.3	1.0	132	0.32	16	752	0.16
	Eg	30-43	45	26	29	2.8	4.8	0.065	83	156	472	103	4	2.2	1.2	250	0.55	40	995	0.28
	Btg	43-81	30	35	35	1.0	4.1	0.001	2	87	203	89	2	0.6	0.7	251	0.36	55	985	0.26
Farm #4 - Downer	Ap	0-28	75	16	9	1.3	5.2	0.332	264	82	348	42	19	9.1	6.0	95	0.20	13	649	0.42
	E	28-45	69	18	13	0.5	5.6	0.092	75	98	229	53	12	1.2	1.4	106	0.17	10	661	0.26
	Bt	45-73	76	7	17	0.8	5.7	0.016	13	120	417	105	8	0.4	0.9	62	0.15	12	669	0.19
	C/Bt	73-101	67	16	17	0.5	5.8	0.013	9	87	292	71	7	0.3	0.6	66	0.13	10	556	0.19
Farm #5 - Greenwich		0-28	55	30	15	1.5	5.3	0.089	87	106	371	43	29	2.4	2.0	98	0.29	16	805	0.26
		28-53	55	28	17	0.7	5.8	0.022	21	74	305	59	30	0.8	0.9	208	0.34	12	735	0.16
		53-81	49	30	21	0.7	5.7	0.003	3	74	440	93	3	0.2	0.7	184	0.29	26	670	0.18
		81-109	73	13	14	0.2	5.7	0.004	3	55	299	77	3	0.3	0.3	217	0.25	25	568	0.14

Table A-5 (cont). Routine soil test analysis for agricultural and forested soil profiles on five farms in Sussex County, Delaware.

									Mehlich 3											
Site ID	Horizon	Depth	Sand	Silt	Clay	OM	pH	PSR	P	K	Ca	Mg	Mn	Zn	Cu	Fe	B	S	Al	As
		--cm--	----------------%---------------						---mg kg^{-1}---											
Forest																				
Farm #1 - Sassafras		0-10	65	27	8	4.6	5.0	0.024	20	219	410	122	17	3.2	1.8	179	0.47	16	643	0.07
		10-40	72	11	17	0.7	4.8	0.004	4	82	122	30	2	0.9	2.5	146	0.25	19	809	0.09
		40-61	70	14	16	0.3	4.7	0.001	1	44	98	34	2	0.3	1.3	53	0.14	58	696	0.10
		61-81	85	5	10	0.1	4.7	0.002	1	31	97	37	2	0.4	1.6	34	0.20	53	540	0.30
Farm #2 - Ingleside		0-15	70	24	6	5.3	4.2	0.019	17	86	184	25	10	1.7	2.0	187	0.17	18	732	0.25
		15-40	68	22	10	0.6	4.6	0.004	3	11	60	9	3	0.3	1.3	52	0.22	16	541	0.00
		40-61	62	24	14	0.3	4.5	0.005	4	15	64	11	4	0.2	1.4	78	0.18	27	625	0.19
		60-91	61	19	20	0.4	4.3	0.239	116	61	262	40	10	4.3	4.5	93	0.13	7	377	0.14
Farm #5 - Greenwich		0-8	49	36	15	7.4	4.7	0.007	11	92	333	76	28	2.4	0.8	165	0.41	33	1374	0.32
		8-46	47	34	19	1.6	4.7	0.002	3	31	78	14	16	0.7	0.7	70	0.13	29	1130	0.24
		46+	51	26	23	0.7	4.4	0.001	1	36	60	15	4	0.3	0.6	182	0.30	73	893	0.07

Table A-6. Routine soil test analysis for agricultural soil profiles on five farms in New Castle County, Delaware.

									Mehlich 3											
Farm ID and Soil Series	Horizon	Depth	Sand	Silt	Clay	OM	pH	PSR	P	K	Ca	Mg	Mn	Zn	Cu	Fe	B	S	Al	As
		--cm--	-----------------%---------------						----------mg kg^{-1}----------											
Farm #6 - Elkton	Ap	0-23	23	57	20	2.2	5.7	0.065	52	67	714	172	23	3.4	1.49	379	2.23	26	519	0.08
	Btg1	23-43	15	57	28	0.9	4.9	0.002	2	19	357	144	2	0.4	0.41	400	1.97	31	602	0.00
Farm #6 - Reybold	Ap	0-23	31	48	21	2.1	6.5	0.031	25	74	794	220	56	1.6	0.98	136	1.48	21	623	0.09
	BE	23-30	33	46	21	1.1	6.5	0.020	16	28	607	139	56	1.1	0.75	151	1.30	15	610	0.06
	Bt	30-56	23	50	27	1.0	6.5	0.005	5	37	684	170	27	0.5	0.62	150	1.32	20	726	0.02
Farm #6 - Woodstown	Ap	0-23	47	39	14	1.0	5.4	0.024	18	46	292	75	19	1.2	0.76	117	0.82	18	598	0.06
	Bt1	23-46	39	42	19	0.4	5.6	0.003	3	33	370	105	14	0.4	0.40	333	1.77	22	618	0.09
Farm #7 - Nassawango	Ap	0-18	33	49	18	1.6	6.2	0.018	17	33	597	121	111	2.0	1.35	220	1.45	21	710	0.07
	Bt	18-76	19	48	33	0.9	6.7	0.002	2	38	763	238	17	0.2	0.58	149	1.25	17	775	0.07
Farm #8 - Sassafras	Ap	0-30	53	30	17	2.4	5.4	0.047	51	102	321	61	93	2.1	1.31	138	0.90	23	873	0.16
	BE	30-56	53	28	19	0.6	5.1	0.018	17	60	188	73	53	0.3	0.38	100	0.71	43	785	0.13
	Bt	56-91	53	24	23	0.6	5.6	0.005	4	57	596	164	12	0.2	0.32	124	0.99	50	705	0.07

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

Table A-8. 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	As	Al	Fe	Ca	Mg	P	S	Cu	Mn	Zn
		----m----		--%--										
GP	3	0-1.0	8.4	1.6	0.9	1077	343	10227	436	506	15	16	54	19
GP	3	1.6-1.8	6.1	2.9	1.7	612	357	1569	134	250	19	23	38	114
GP	4	0-1.0	7.5	2.3	0.3	699	235	1887	175	154	35	9	49	23
GP	4	1.8-2.7	7.7	1.7	0.7	550	362	2706	510	388	23	8	33	35
GP	7	1.8-2.1	7.8	2.2	0.6	413	269	7354	636	674	7	20	78	104
GP	8	0-1.3	9.6	2.8	0.3	1116	173	18857	562	392	8	38	30	38
GP	8	1.5-2.0	8.0	6.8	4.4	24	502	5459	590	767	20	26	19	101
GP	12	0-1.3	8.1	2.5	0.9	1042	293	8873	403	441	13	24	39	42
GP	12	1.4-2.1	8.0	3.1	64.7	646	366	9210	1456	1399	17	15	59	63
GP	12	1.4-2.1	8.0	3.2	69.8	642	358	10345	1524	1521	15	16	53	64
GP	13	0.2-0.9	7.8	2.7	12.7	648	206	4337	434	90	67	146	25	168
GP	13	1.3-1.9	8.1	2.9	41.9	383	374	18589	1282	1606	25	5	79	22
GP	14	0-1.3	8.3	1.2	20.1	305	202	4101	608	59	33	20	30	49
GP	14	2.4-2.9	9.3	8.1	1386.1	20	420	16495	4219	1155	24	16	57	35
TP	2	2.0-2.1	7.4	5.1	8.2	121	440	5834	228	310	40	42	41	92
TP	3	2.3-2.4	7.5	11.0	3.3	799	258	11509	732	281	7	34	41	159
TP	4	2.0-2.1	9.0	2.8	162.0	421	613	9755	2481	1895	6	8	35	20
TP	7	2.1-2.3	7.5	2.7	2.1	457	488	2948	246	464	10	16	66	34
TP	8	2.0-2.1	7.3	3.4	6.4	635	575	5086	548	741	9	13	86	37
TP	10	1.5-1.8	7.7	2.2	3.4	787	419	4147	463	413	16	29	38	34

Table A-9. Effect of broiler litter application on the total mass per area of arsenic (As) leached and the percentage of As added in litter leached from two Delaware soils in Column Study #1[†]. Data for all 36 soil columns, including those with apparent edge flow, are included.

	Arsenic - All data	
Soil and Broiler Litter Rate	Total Mass Leached	Percentage of Litter As Leached
-----Mg ha^{-1}-----	----------g ha^{-1}---------	------------%------------
Corsica		
0	4	n/a
4.5	5	0.6
9	5	0.5
13.5	9	0.9
18	6	0.4
22	8	0.5
Sassafras		
0	3	n/a
4.5	18	8.6
9	34	8.9
13.5	35	5.7
18	20	2.3
22	27	2.5

Table A-10. Effect of poultry litter on TCLP-As in two Delaware soils during a 21 day laboratory incubation study.

Soil Series	PL Rate	TCLP - As	
		Day 0	Day 21
	---Mg ha--	----------------mg kg^{-1}---------------------	
Corsica	0	0.42	0.45
	4.5	0.50	0.43
	9	0.56	0.50
	13.5	0.62	0.44
	18	0.63	0.53
	22.5	0.64	0.63
Sassafras	0	0.40	0.47
	4.5	0.51	0.54
	9	0.58	0.58
	13.5	0.53	0.53
	18	0.57	0.63
	22.5	0.76	0.60

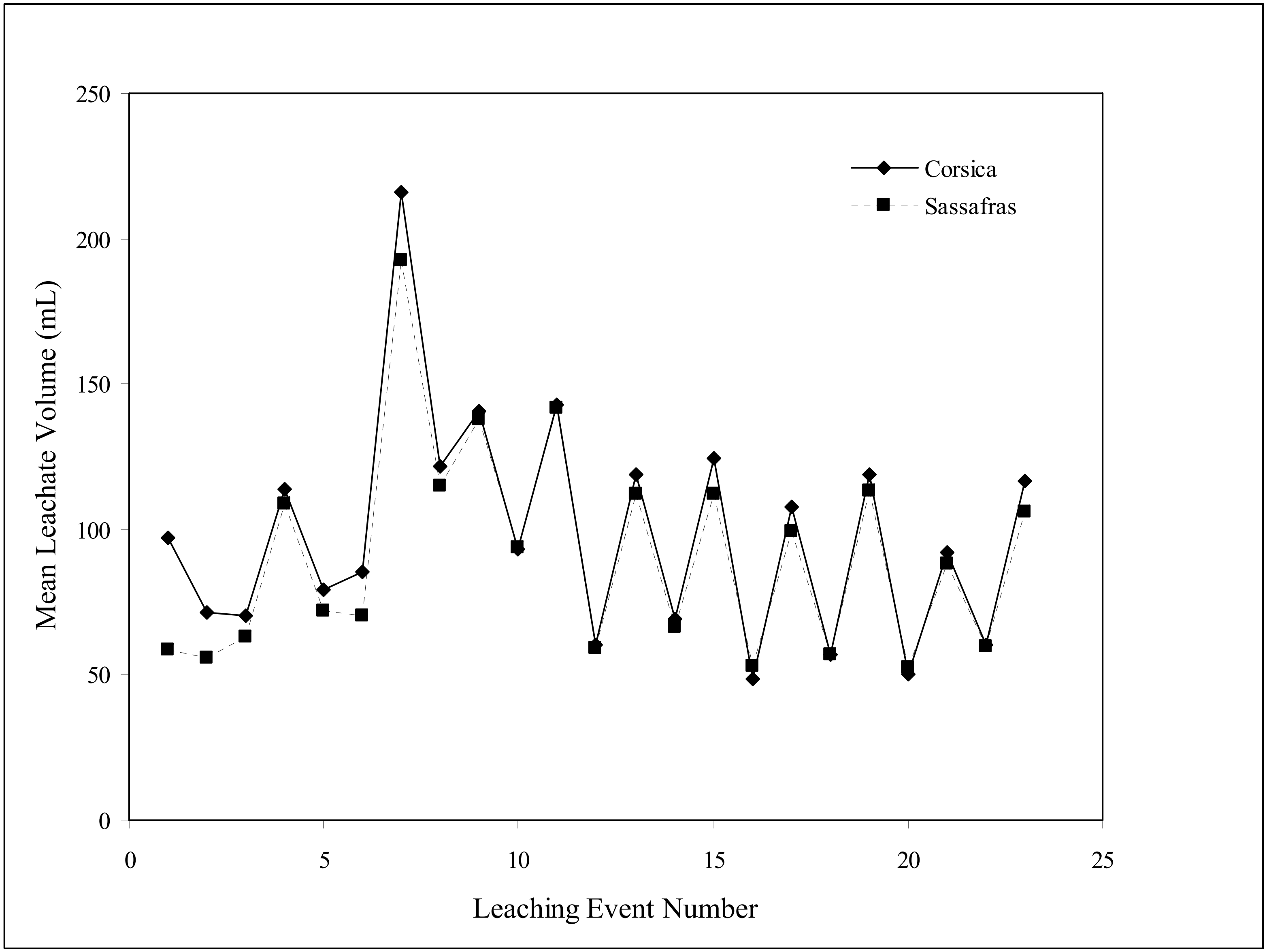
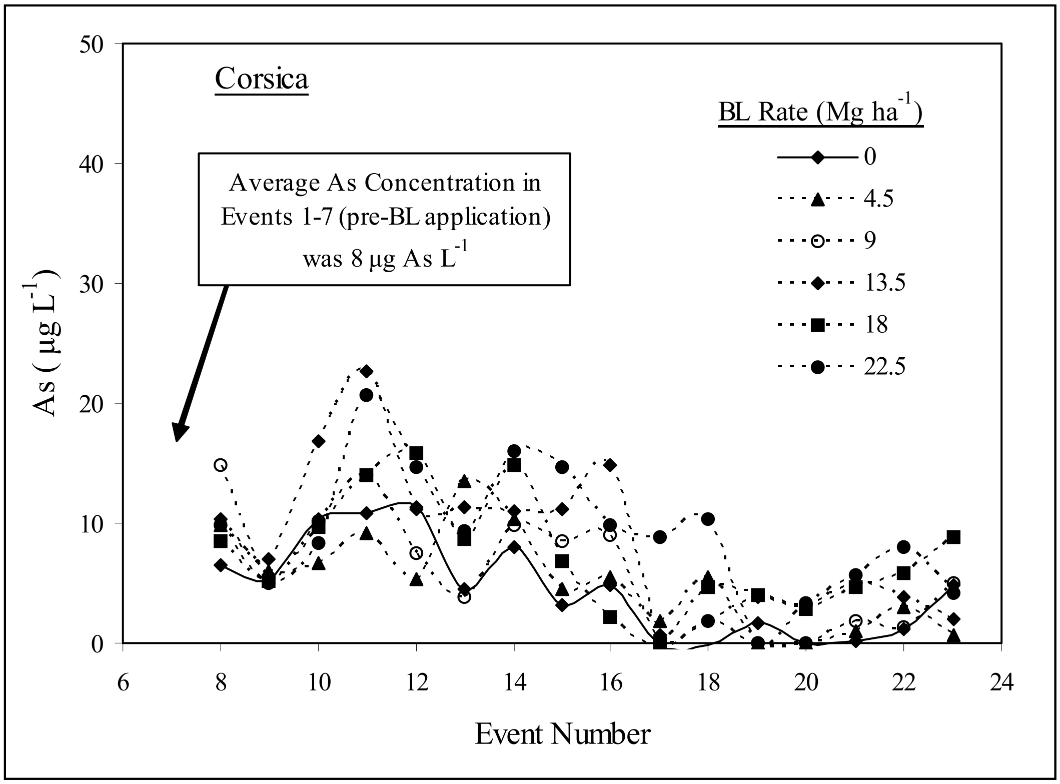


Figure A-1. Mean leachate volumes for the Corsica and Sassafras soils used in a greenhouse column study (Column Study #1) to evaluate the effects of broiler litter on As leaching. Values are averages of all litter rates for each leaching event.



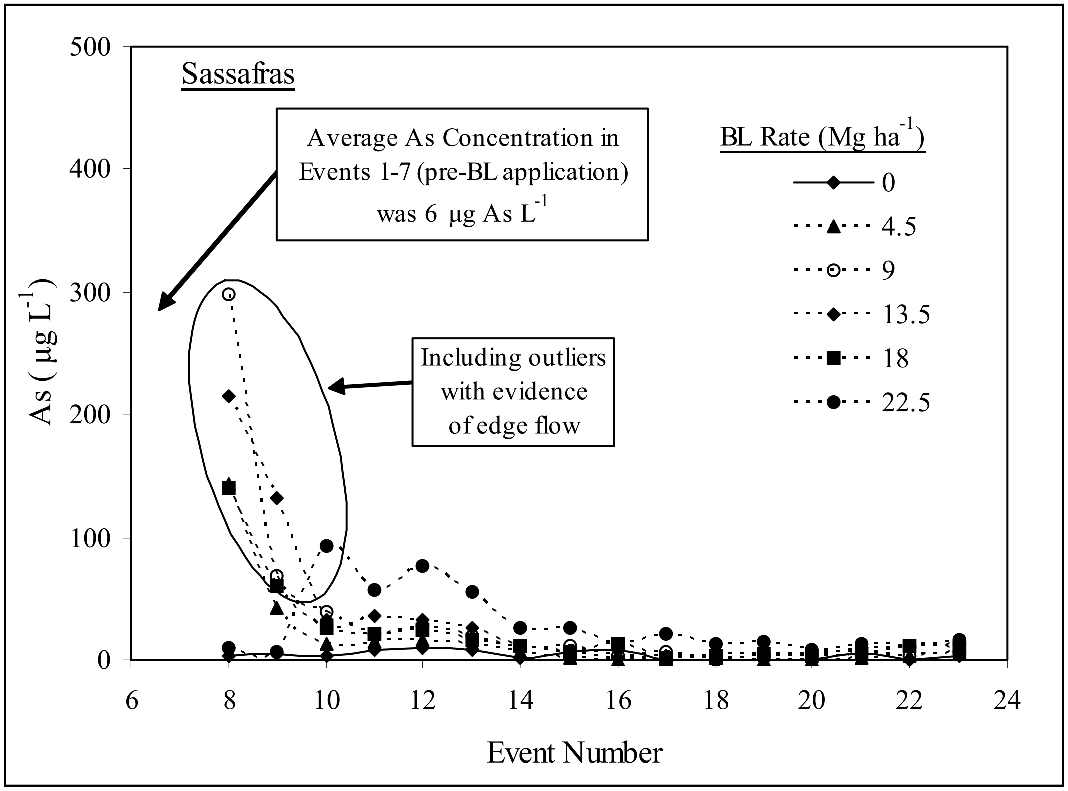


Figure A-2. Effect of broiler litter (BL) application rate on total dissolved arsenic concentrations in leachate from the (a) Corsica and (b) Sassfras soils during Column Study #1. Note: leachate concentrations include results from outlier columns where edge flow occurred.

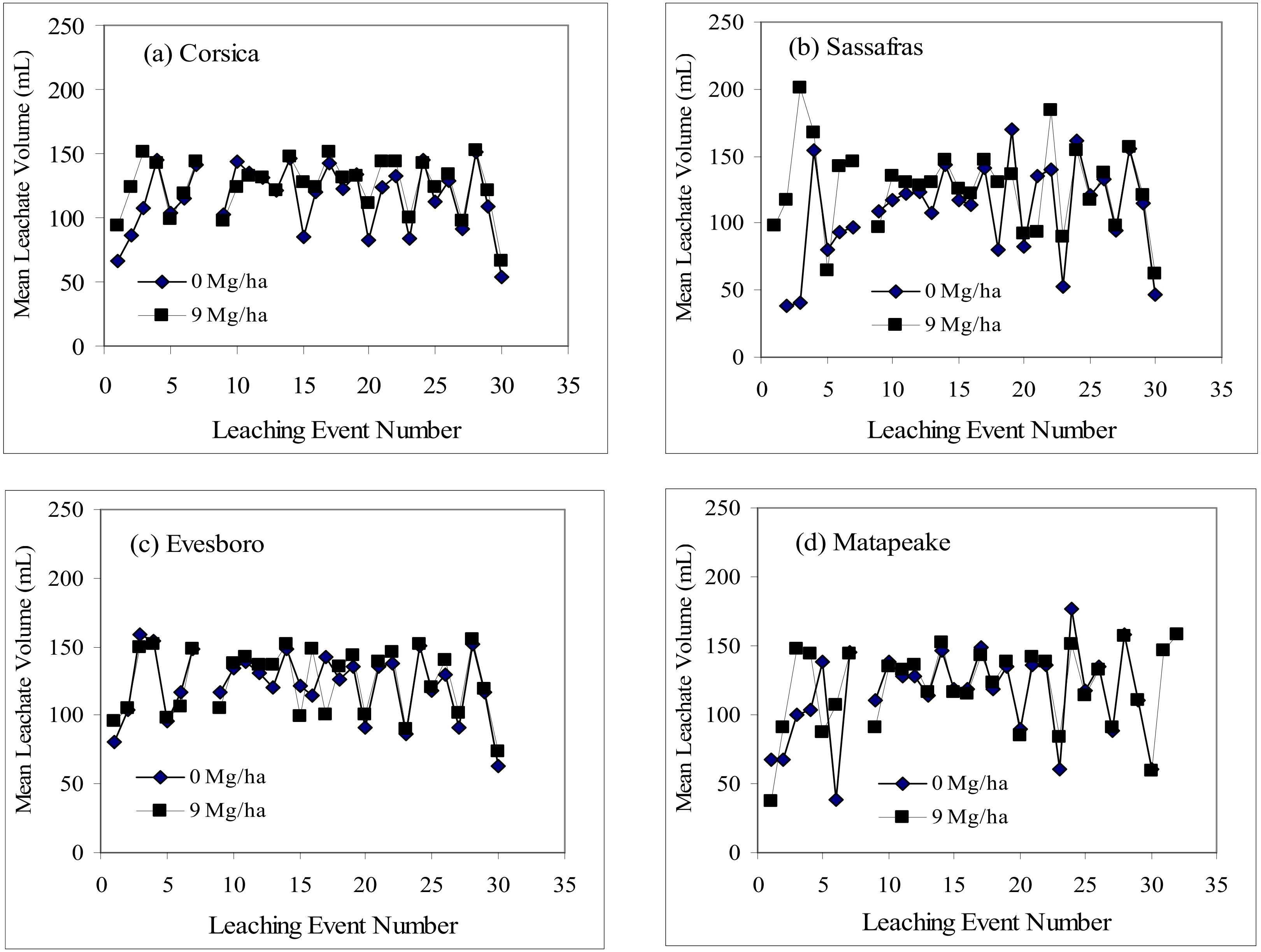


Figure A-3. Mean leachate volumes for the four soils used in Column Study #2 to evaluate the effects of broiler litter on As leaching. Values are averages of all litter rates for each leaching event.

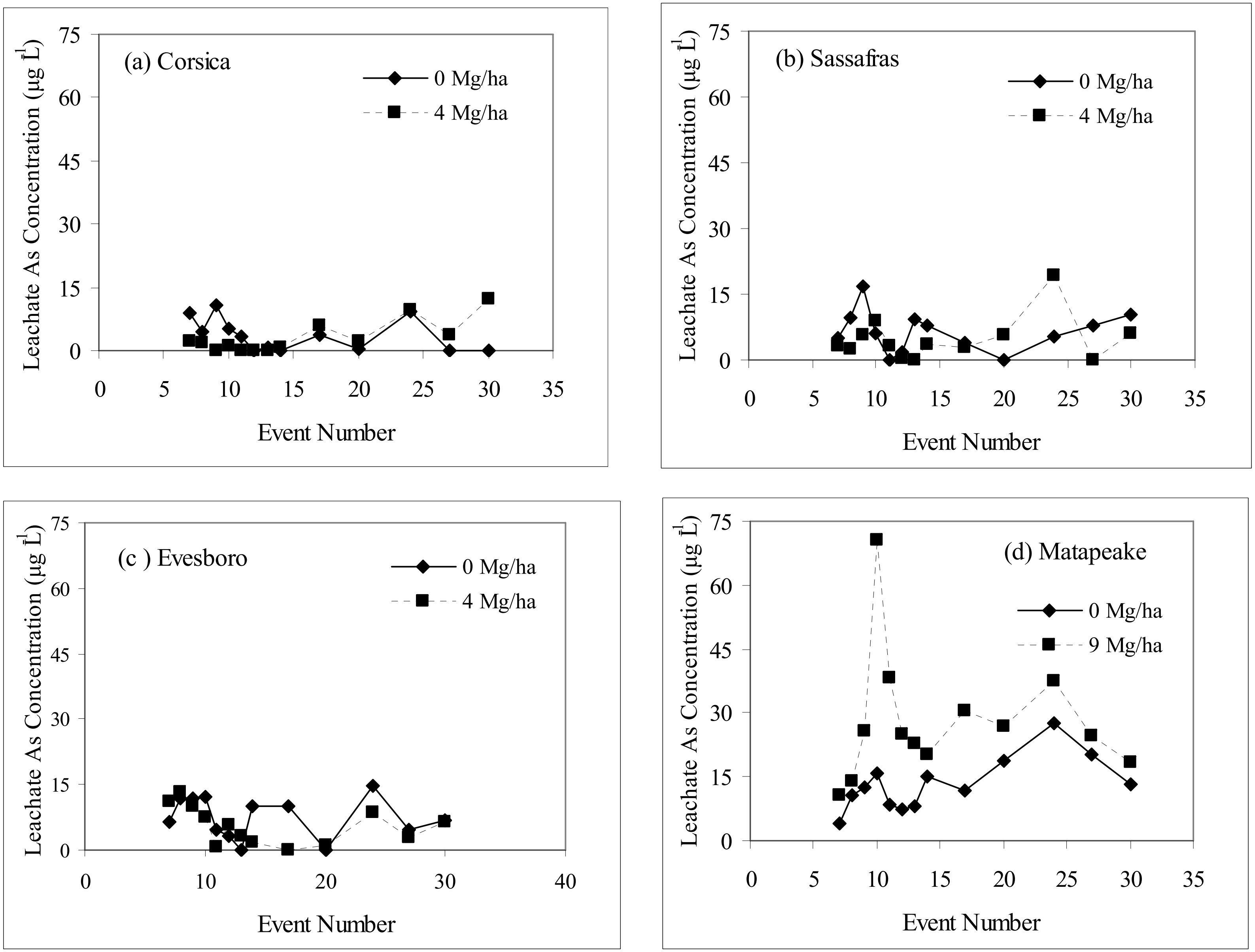


Figure A-4. Effect of broiler litter (BL) application rate on total dissolved arsenic concentrations in leachate from four soils during Column Study #2. Note: leachate concentrations include results from outlier columns (Matapeake only) where edge flow occurred.

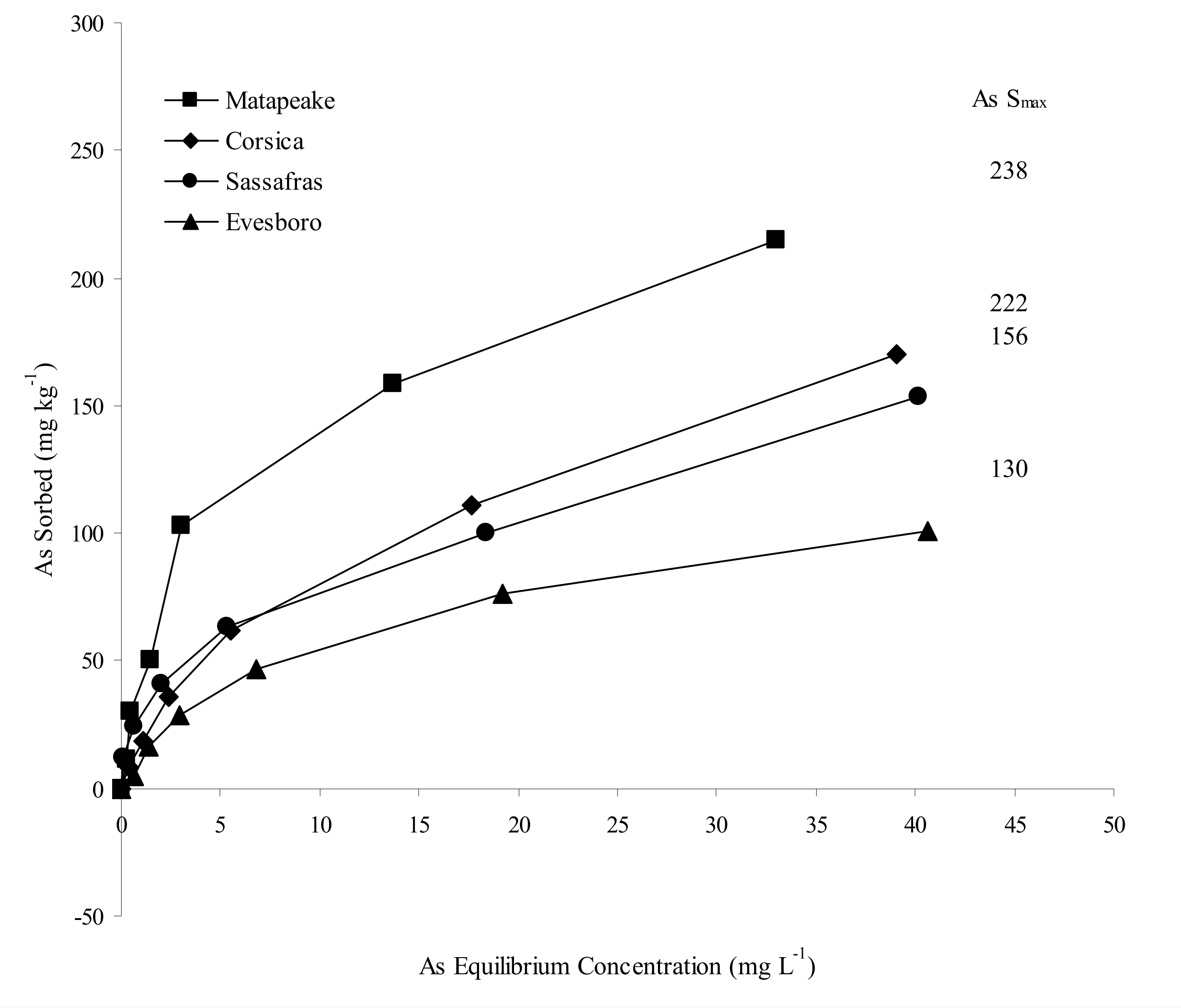


Figure A-5. Arsenic sorption isotherms for the four Delaware soils used in greenhouse column studies to evaluate the effects of broiler litter on As leaching.