Effect of Land-applied Arsenicals on the Soils of Alabama

by

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Abstract

Many agricultural practices apply arsenicals directly to land through agricultural practices. Over time, repeated land-application of arsenicals may result in accumulation of arsenic in the soil. This may be problematic especially when arsenicals are added with poultry manure, which contains phosphorus and organic matter that may increase arsenic solubility. In Alabama, little is known about the consequences of repeated application of arsenicals to the soil. The objectives of this study were to: 1) assess the extent of arsenic contamination with repeated poultry litter or arsenical herbicide application and 2) evaluate the impact of soil phosphorus content on arsenite, arsenate, roxarsone, and monosodium methane arsenate (MSMA) sorption and solubility.

For objective 1, sites with more than 10 years of repeated application of poultry litter and MSMA were sampled to determine the accumulation and distribution of arsenic within the profile. Soil samples at four different depths were characterized for soil pH, Mehlich-I extractable phosphorus, non-crystalline iron oxide fraction, total carbon content, and total soil arsenic content. With a few exceptions, there was a homogenous distribution of soil pH and non-crystalline iron oxide fraction with no definite pattern at sampled locations across depths. Phosphorus content ranged from 2.94 to 183.4 mg kg^{-1}. Total carbon content decreased from surface to subsoil. Soil arsenic content varied among sampled fields at location 1 and 2 and at certain depths at Sand Mountain Research and Extension Center (SMREC). At Tennessee Valley Research and Extension

Center, soil arsenic concentrations were consistent and near expected background levels. Although differences in soil arsenic concentrations were detected among fields at some locations, contamination of soils as a result of long-term poultry litter or MSMA application was inconclusive. Some control fields that did not have a history of poultry litter or arsenical herbicide application, had elevated levels of arsenic. This may be due to cotton production many years ago. Arsenicals were historically used as defoliants, herbicides, and pesticides and may still cause elevated background readings.

For objective 2, batch experiments were conducted on low and high phosphorus soils from an 80-year fertilization study at the SMREC in northern Alabama. Phosphorus loading had no influence on the sorption of arsenite, arsenate, roxarsone, or MSMA. Arsenite had greater sorption than arsenate. Roxarsone and MSMA did not sorb to soil colloids and resulted in slight desorption of native arsenic from soil. Thus, the potential for leaching and mobility of arsenic land-applied to Hartsells soils is much greater for arsenate, roxarone, and MSMA than arsenite.

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I. Literature Review

Natural occurrence of arsenic

Many forms of arsenic exist in nature. Naturally occurring arsenic of geological origin is found in rocks and soil, which eventually enters water and air by means of weathering, dissolution, and erosion. Arsenopyrite (FeAsS) is the most abundant arsenic-containing mineral present in the earth's crust and arsenobetaine is the major form found in marine animals (Francesconi and Kuehnelt, 2002).

Arsenic can also enter the environment through anthropogenic activities, such as through the use of herbicides, pesticides, defoliants, feed additives, and industrial wastes (Sarkar *et al.*, 2007). Many agricultural practices involve application of arsenicals directly to land through poultry manure and agrochemical applications. Over time, repeated land-application of arsenicals may result in accumulation of arsenic to toxic levels in the soil. Elevated concentrations of arsenic are known to cause harmful effects to human life due to prolonged exposure either from soil or drinking water. Health risks encountered from prolonged exposure to inorganic forms of arsenic, which are known to be more deleterious, can range from cancers (e.g., skin, lung, bladder, and liver) to other vascular diseases (Yosida *et al.*, 2007). Due to toxicity of arsenic, the U.S. Environmental Protection Agency (EPA) lowered the maximum contaminant level (MCL) of arsenic in drinking water to 10 µg L^{-1} (USEPA, 2001).

The availability and mobility of applied arsenicals in soil is influenced by different soil parameters such as pH, redox potential (Eh), organic matter, hydrous oxide minerals of iron, aluminum, manganese, clay minerals, and phosphorus content of soil (Goldberg, 1986; Hingston *et al*., 1972; Inskeep *et al*., 2002; Markis *et al*., 2008). This is especially critical when arsenicals are added with poultry manure, which already contains phosphorus and organic matter that can affect arsenic behavior in soil.

Effect of pH and redox potential on arsenic mobilization

The major oxidation states of arsenic encountered in soil and natural waters are the +5 and +3 states, which exist predominantly as the arsenate (AsO_4^{3-}) and arsenite (AsO_3^{3-}) oxyanions, respectively. The mobility of arsenic in soils is found to be a function of its oxidation state, which is influenced by the soil redox potential (Gulens *et al*., 1979). Among the two species, arsenite is considered more mobile and toxic than arsenate (McArthur *et al.*, 2001; Nimick, 1998). Studies indicate that As(V) has stable redox potentials greater than -100 mV at pH 8 and greater than 300 mV at pH 4. Below these redox potentials, As(III) is more stable (Cherry *et al.*, 1979).

Under neutral pH and aerobic conditions in soils, arsenic is immobilized by sorption or co-precipitation with metal oxides, involving both outer-sphere and inner-sphere complexation (Bissen and Frimmel, 2003; Sun and Doner, 1996). At low pH and reduced redox potential, arsenic mobility increases due to dissolution of metal oxides. Under such reduced conditions, sorption or co-precipitaion with sulfide minerals controls arsenic concentrations in solution (Harvey and Swartz, 2002; Masscheleyn *et al*., 1991).

The major processes controlling the activity of arsenate in soil are surface complexation and sorption reactions on clay minerals and hydrous oxide minerals of iron, aluminum, and manganese. This behavior is analogous to phosphate sorption and complexation reactions. In comparison, arsenite exhibits strong preference for hydrous oxides of iron (Goldberg, 1986; Hingston *et al.*, 1972). Both oxyanions exhibit the trend of either increasing sorption with decreasing pH or reaching a sorption maximum centered around the acid dissociation constant of the oxyanion (Inskeep *et al.*, 2002; Hingston *et al.*, 1972). The sorption capacity of arsenite on iron oxide is similar or much higher than arsenate with little pH dependence and with an adsorption envelope centered around pH 8. At lower pH, arsenate exhibits higher sorption on iron oxide. A reverse trend is observed in case of arsenite sorption on amorphous aluminum oxide (Manning and Goldberg, 1997).

Interaction of arsenic with organic matter

Dissolved organic matter (DOM) in soil solution influences arsenic mobility. Fulvic and humic acids form stable complexes with mineral surfaces thereby effectively blocking arsenic adsorption on iron oxides, alumina, quartz, or kaolinite (Abbt-Braun, 2002; Kaiser *et al.*, 1997; Graffe *et al.*, 2002). Organic anions also enhance arsenic leaching from soil material when arsenic is primarily associated with the metal oxide fraction (Lin *et al.*, 2002; Bauer and Blodau, 2006; Lombi *et al.*, 2000). The formation of aqueous arsenic-DOM complexes either by positively charged amino groups in DOM or by metal cation bridges may lead to greater mobility of arsenic (Saada *et al.*, 2003; Redman *et al.*, 2002). A small, but substantial, increase in arsenic mobility was observed due to high concentrations of dissolved organic carbon in wetland soils (Kalbitz and Wenrich, 1998).

Dissolved organic matter has the potential to chemically mobilize arsenic from iron oxides, soils, aquifers, and sediments. Considering only sorption competition reactions, pore water rich in DOM may release more than three times the amount of arsenic from soils than pore water deficient in DOM. With the small solute/solid ratios found in natural environments, this process has the potential to increase arsenic concentrations to levels exceeding drinking water standards (Bauer and Blodau, 2006).

Reductive dissolution of Fe(III)-oxide phases containing sorbed arsenic have shown solubilization of arsenic from aquifer sediments to groundwater (McArthur *et al.*, 2001). The highest concentration of arsenic in groundwater corresponds to the aquifer depth with the highest organic matter content and greatest microbial activity. At these depths, a high rate of reductive dissolution of Fe(III)-oxide phase is observed (Inskeep *et al.*, 2002). Detoxification of arsenite can occur by microbial oxidation of arsenite to arsenate during respiration (Cullen and Reimer, 1989).

Microbial degradation of organic matter in Bangladeshi sediments containing 10-30% arsenic contributed to reductive dissolution of metal oxides and release of arsenic bound to metal oxides and organic phases (Harvey and Swartz, 2002; Anwar *et al.*, 2003). Since DOM contains redox active functional groups, it can act as an electron shuttle between microorganisms, hydrogen sulfide, iron, and organic pollutants (Lovley *et al.*, 1996). Addition of arsenic to the solution containing DOM may result in both arsenate reduction and arsenite oxidation (Redman *et al.*, 2002).

Interaction of arsenic with minerals

Depending on the type of mineral and pH, adsorption behavior of both arsenic oxyanions varies. At high pH, arsenite is more strongly bound to soil components than arsenate (Manning and Goldberg, 1997, Raven *et al.*, 1998). There is a significant correlation between sorption of arsenate and oxalate extractable aluminum, iron, and clay

(Goldberg, 1986; Smith *et al*., 1998). Adsorption studies reveal that in natural systems arsenate is preferentially adsorbed to iron and aluminum oxide minerals compared to kaolinite, montmorillonite, calcite, and quartz (Fordham and Norrish, 1979; Livesey and Huang, 1981). Adsorption of arsenate on iron and aluminum hydroxides, e.g., goethite (FeOOH) and gibbsite [$Al(OH)_3$], increases with decreasing pH with maxima at pH 3, while arsenate adsorption on calcite and layer silicate minerals generally exhibits adsorption maxima in the pH range of 4 to 6 (Darland and Inskeep, 1997).

Arsenite exhibits greater sorption on goethite with little pH dependence, while arsenate has greater adsorption on gibbsite (Manning and Goldberg, 1997). Adsorption of arsenate on goethite, gibbsite, alumina, kaolinite, and montmorillonite increased at low pH and had adsorption maxima between pH 3 and 7. Arsenite exhibited somewhat similar behavior on these minerals and adsorption maximum was found at a pH range of 7 to 8. Adsorption of arsenate was greater than arsenite on alumina, amorphous iron hydroxide, kaolinite, and montmorillonite. However, arsenite adsorption often exceeded arsenate adsorption at pH above 7 on amorphous iron oxides (Gupta and Chen, 1978; Pierce and Moore, 1982; Jain and Loeppert, 2000; Goldberg and Johnston, 2001; Goldberg, 2002).

A shift in the point of zero charge (PZC) and a reversal of electrophoretic mobility with increasing ion concentration is used as evidence for strong specific ion adsorption and inner-sphere surface complex formation. Electrophoretic mobility (EM), which measures movement of charged particles across an applied electric field, denotes zero EM for the point of zero charge (PZC) of the particle (Goldberg, 2002; Hunter, 1981). No shifts in PZC during arsenite adsorption on amorphous aluminum oxide strongly indicate the formation of an outer or inner-sphere surface complex that did not affect the overall surface charge of the oxide (Goldberg and Johnston, 2001; Goldberg, 2002).

Variation in ionic strength can be used as an indicator to assess the type of complex formation during the adsorption process. Decreasing adsorption with increasing ionic strength is associated with formation of outer-sphere complexes, while formation of inner-sphere complexes has little dependence on ionic strength or may exhibit increasing adsorption with increasing ionic strength (McBride, 1997). Adsorption of arsenate on amorphous iron and aluminum oxides and arsenite on amorphous aluminum oxide had little dependence on ionic strength, suggesting formation of inner-sphere complexes, while arsenite adsorption on amorphous iron oxides exhibited decreasing adsorption with increasing ionic strength suggesting outer-sphere complexation (Manning and Goldberg, 1997; Goldberg and Johnston, 2001). As more pronounced effects of ionic strength on adsorption of arsenite are observed, it is concluded that arsenite is more weakly adsorbed than arsenate on oxide and mineral surfaces (Goldberg, 2002). At low arsenic concentrations, arsenate has a greater competitive effect on arsenite adsorption by amorphous iron oxide than that of arsenite on arsenate adsorption (Jain and Loeppert, 2000).

Interaction of arsenic with phosphorus

Similar chemical properties, such as tetrahedral geometry, atomic radii, bonding radii, ionization potential, electronegativities, and formation of oxyanions, are observed between phosphorus and arsenic (Markis *et al.*, 2008). Arsenate, phosphate, and molybdate are tetrahedral oxyanions that compete for adsorption sites on soil mineral surfaces (Cotton and Wilkinson, 1980; Murali and Alymore, 1983; Manning and Goldberg, 1996) and are estimated to occupy 0.61, 0.61, 0.31 nm^2, respectively on the goethite surface (Hingston, 1981; Manning and Goldberg, 1996).

Oxyanions of both arsenic and phosphorus exhibit similar chemical behavior in soils. Both of these oxyanions specifically adsorb on soil minerals especially on variable charge minerals (e.g., aluminum, iron, and manganese oxides; allophones; imogolite) by forming inner-sphere complexes. The surface coverage determines the formation of monodentate complexation, bidentate-binuclear complexation, and bidentate-mononuclear complexation in varying proportions (Violante and Pigma, 2002; Liu *et al.*, 2001).

Arsenic adsorption from solution to soil colloidal or mineral surfaces depends on the availability of sites for adsorption; however, presence of specifically adsorbed ligand ions such as phosphate have known to cause suppression of sorption processes unlike other ions such as chloride, nitrate, and sulfate (Smith *et al*., 2002). Arsenate desorption from iron oxides occurs with increasing pH and with competition from anions such as phosphate, and molybdate (Smith *et al*., 2002; Livesey and Huang, 1981). At high arsenate and low phosphate concentrations, competition for sites is reversed, suggesting that the mass action effect may dictate the extent of the adsorption of anions irrespective of the ligand ions (Barrow, 1974).

Phosphate competes with both arsenate and arsenite for adsorption in soils with limited sorption sites, but both phosphate and arsenic oxyanions are strongly retained in soils with unlimited sorption sites. However, increasing phosphate concentration in solution did not cause substantial decline in arsenate sorption, suggesting preferential sorption of arsenate and phosphate by oxide surfaces and some sites that may be common to both. Addition of phosphate to the soil decreased the sorption of arsenite, although this was less distinct in soils with relatively high sorption capacity (Smith *et al.*, 2002).

Studies on the competitive adsorption of arsenate and phosphate in soil revealed that though arsenate desorbed some previously adsorbed phosphate, a substantial portion of bound phosphate remained (Barrow, 1974; Hingiston *et al.*, 1971). This may be due to the fact that the goethite surface contains adsorption sites common to arsenate and phosphate, as well as sites that adsorb specifically one anion or another.

The adsorption envelopes and relative affinity of arsenate, phosphate, and molybdate for goethite and gibbsite surfaces are pH dependent and similar in magnitude, except for molybdate. Arsenate and phosphate have been found to compete for a similar set of surface sites, though some sites appear uniquely available for adsorption of either arsenate or phosphate (Manning and Goldberg, 1996).

Phosphate fertilization has a direct effect on arsenic mobility in soil. In soils with previous application of lead arsenate pesticides, application of phosphate fertilizers increased the mobility of arsenic in the soil (Peryea, 1991). The increased mobility is brought about by suppression of sorption and displacement of sorbed arsenic in soil (Sadiq, 1997; Peryea, 1991; Liu *et al.*, 2001). Application of high concentrations of phosphate (> 2 orders of magnitude of column capacity) yielded only 60% of arsenate recovery from the spiked column, suggesting that arsenate desorption kinetics play a pivotal role in arsenate transport through porous media (Darland and Inskeep, 1997).

Competitive effects of phosphate on arsenate adsorption were much greater than arsenate on phosphate sorption (Roy *et al.*, 1986). High applications of phosphate to arsenate polluted soils displaced large amounts (80% of the total) of arsenic in the soils

(Woolson *et al.*, 1973). The kinetics of sorption of arsenic and phosphorus on different soil minerals, organo-mineral complexes is influenced by the type and stability of surface complexes formed by their oxyanions and the effect of time on the electrical potential of the surfaces (Violante and Pigma, 2002).

Arsenicals from poultry

The poultry industry, specifically broiler (*Gallus gallus domesticus*) production, occupies a major portion of agriculture in the U.S. In the U.S., Alabama ranks third in broiler production after Georgia and Arkansas (McDonald *et al.*, 2009). The Alabama poultry industry is a multibillion-dollar corporate enterprise and a major business in the state, accounting for slightly more than 10% of the state's economy (Aksoy, 2008). This results in the production of 1.5 million metric tons of poultry manure or litter per annum (Aksoy, 2008; Mitchell, 2001). Poultry litter is comprised of manure and bedding material (Mitchell, 2001). Fresh litter is equivalent to a 3-3-2 (N-P_2O_5-K_2O) grade fertilizer and hence is used extensively in agriculture (Mitchell and Donald, 1995).

Disposal of poultry litter is becoming a major environmental concern since it is rich with nitrogen and phosphorus compared to other manures (Zhongqui *et al.*, 2009). Besides its nutrient content, poultry litter may also contain the organoarsenical roxarsone (3-nitro-4-hydroxyphenylarsonic acid). Roxarsone is a feed additive used to improve feed efficiency and control gut diseases in poultry. Most of the roxarsone is excreted unchanged in the manure, where it accumulates in the poultry bedding material. Poultry litter samples have been found to contain 30 to 60 mg roxarsone kg^{-1} litter (Morrison, 1969; Garbarino *et al.*, 2003). In Alabama, two-thirds of broiler production is concentrated primarily in the northern part of the state (Aksoy, 2008), where the majority of litter is land-applied. Thus, this region experiences a risk of arsenic and excess nutrient contamination from poultry litter disposal.

Application of poultry litter containing the organoarsenical roxarsone can contribute to arsenic in soil. Elevated concentrations of arsenic are reported in fields amended with poultry litter for more than 20 years in Oklahoma (Rutherford *et al.*, 2003) and Maryland (Gupta and Charles, 1999). In Delaware, arsenic accumulation was observed to be less than 15 mg kg^{-1} in the short-term poultry litter amended sites (Arai *et al.*, 2003). However, a study on the effects of soil depth on arsenic sorption with a variable history of broiler litter application indicated that arsenic sorption tended to decrease with increasing litter rate because of a lower arsenic concentration in the initial soil. This study also indicated an increased arsenic sorption with the depth because of the higher clay content of the subsoil compare to the surface (McDonald *et al.*, 2009). These arsenicals pose an environmental hazard and may eventually find their way to humans (Bellows, 20005; Christen, 2006, Jackson and Bertsch, 2001; Bednar *et al.*, 2002).

Anoxic conditions during the composting of poultry litter facilitates bacteria of the genus *Clostridium* in selectively degrading roxarsone into inorganic arsenic and other undefined organoarsenicals compounds (Stolz *et al.*, 2007). A study on the degradation of roxarsone revealed that under anoxic conditions and at room temperature the roxarsone undergoes a complete transformation into different arsenic containing components such as As(V), As(III), dimethylarsenic acid (DMA), and monomethlylarsonic acid (MMA) within about 48 hours (Garbarino *et al.*, 2003). This rate of transformation is directly proportional to temperature. The study also showed that when the litter extract was sterilized, roxarsone degradation was arrested for 10 days. This arrest suggests that bacterial processes were responsible for the roxarsone degradation.

Arsenate is the major arsenic species found in the litter-amended soil solution. The presence of an anoxic environment promotes the bacteriological reduction of arsenate into arsenite and the methylation of arsenate to dimethylarsenite (Garbarino *et al.*, 2003). Because arsenite and dimethylarsenite are generally more soluble than parent compound, there is a relatively greater possibility of arsenic being transported by leaching, surface runoff, erosion, or subsequent uptake by agricultural crops (Arai *et al.*, 2003).

Arsenicals from cotton and turf industries

About 75% of the total arsenic used in the U.S. for more than a century has been contributed from the application of organoarsenicals as herbicides (Onken and Hossner, 1996). Monosodium methanearsonate (MSMA) was registered for use by U.S. cotton producers in 1964 as a postemergent herbicide treatment for cotton. During its peak usage in Alabama cotton fields (1997), the herbicide MSMA was applied to 48% of cotton fields (~100,000 ha) and disodium methanearsonate (DSMA) was applied to 28% of cotton fields (~60,000 ha) (NASS, 2007). Application of MSMA is a common management practice for cotton, even in conservation tillage systems (Schwab *et al.*, 2002), but has declined in use due to glyphosate-ready cotton.

Application of DSMA and MSMA for control of weedy grasses, coupled with cotton's tolerance for these herbicides, made these herbicides an effective postemergent weed control throughout the cotton growing regions of U.S. When DSMA was applied in two directed applications for weed control during cotton production, no arsenic residues were detected in the cotton seeds. However, residual concentrations of arsenic were detected in the hay when sorghum, soybeans, and peanuts were grown subsequently in plots with DSMA application (Dickens and Hiltbold, 1967).

Increasing concentration of DSMA in the equilibration solution for the whole soils resulted in increased adsorption of DSMA on clay minerals. The rate of leaching of surface-applied DSMA varied for different soil types, but was found to be consistent with their adsorption capacities for DSMA. Differences in soil pH within the usual range had a little effect on leaching of DSMA. Under aerobic conditions, decomposition of methanearsonates was rapid and the amount of organic matter available had a direct effect on the decomposition rate (Dickens and Hiltbold, 1967).

During 1994-2001, MSMA was ranked among the top ten most commonly used herbicides used in turf production by the EPA. Since organoarsenicals are potentially toxic in the environment due to their high potential for leaching and runoff, the EPA has discouraged its use. A study in New Jersey, which hosts 2% of total golf courses in country, revealed that up to 3.2 million kg of arsenic per year were applied between 1920 and 1950 (Murphy and Aucott, 1998). Application of MSMA for weed control in golf courses remains a widely used practice (Bussey, 2004), and thus there is an increased interest to know the fate of applied arsenicals in the environment (Snyder and Cisar, 2002). Usage of MSMA in turf management creates a potential risk of arsenic toxicity to public and private wells in the near vicinity of golf courses (Snyder and Cisar, 2002).

According to the U.S. Geological Survey, waters near several golf courses in central Florida have elevated concentration of arsenic (Swancar, 1996). Arsenical herbicides are used extensively for turf management on golf courses throughout Florida and approximately 97% percent of the golf courses in Florida used MSMA (Ma *et al.*, 2002). Due to this extensive usage of arsenicals, elevated levels of arsenic have been found in the near vicinity (Feng *et al.*, 2005).

According to one study of four golf courses conducted in Hillsborough County, FL, total arsenic concentration in golf course lakes ranged from 0.1 to 124 µg L^{-1}. There was a temporal variation observed, which followed an annual pattern with the highest values observed during late spring and early summer. The detection of highest concentration coincided with the period when MSMA application occurred (Pichler, 2008).

Monosodium methanearsonate application to golf course greens leads to a variety of biochemical processes influencing the distribution of arsenic species. Appearance and disappearance of MMA before and after MSMA application suggests that MSMA is efficiently transformed by methylation and demethylation to other arsenic species, namely DMA and As(V) (Feng *et al*., 2005). After the formation of DMA, adsorption to the clay particles, leaching with the percolate water, demethylation to MMA, or further methylation to other volatile arsenic species (e.g., trimethylarsine) may occur. Presence of elevated concentrations of DMA in percolate indicates that leaching is a major pathway of arsenic biogeochemical cycling in soils (Feng *et al*., 2005).

Applied MSMA may eventually reach the surrounding water bodies through surface runoff or leaching. Lake sediments readily scavenge arsenic and therefore affect both the concentration of arsenic in the water column and its migration to groundwater (Belzile and Tessier, 1990). A change in the chemical properties of the sediment (i.e., redox, pH) may result in desorption of arsenic from the sediment and potential migration to groundwater (Pichler *et al*., 1999). Modifications in simple water chemistry (e.g., composition and concentration of major ions) also play an important role. Large concentrations of phosphate, bicarbonate, silicate and possibly organic matter can also increase release of arsenic due to the competition for the adsorption sites (Smedley and Kinniburgh, 2002).

References

Abbt-Braun, G., Huminstoffe-Vorkommen, Charakterisierung, and Reaktionen. 2002. Wasser-und Geotechnologie. 1:41– 50.

Aksoy, B., H.T. Cullinan, E.S. Norman, and M.R., Eden. 2008. Identification of optimal poultry litter biorefinery location in Alabama through minimization of feedstock transportation cost. Environ. Prog. 27:515-523.

Arai, Y., A. Lanzirotti, S. Sutton, J.A. Davis, D.L. Sparks. 2003. Arsenic speciation and reactivity in poultry litter. Environ. Sci. Technol. 37:4083-4090.

Barrow, N.J. 1974. On the displacement of adsorbed anions from soil: 2. Displacement of phosphate by arsenate. Soil Sci. 117:28-33.

Bauer, M., and C. Blodau. 2006. Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. Sci. of Total Environ. 354:179-190.

Bednar, A.J., J.R. Garbarino, J.F. Ranville, T.R. Wilderman. 2002. Presence of organoarsenicals used in cotton production in agricultural water and soils of southern United States. J. Agric. Food Chem. 50:7340-7344.

Bellows, B.C. 2005. Arsenic in poultry litter: organic regulations. ATTRA, National Sustainable Agriculture Information Service (verified 22 Jan, 2008).

Belzile, N., and A. Tessier. 1990. Interactions between arsenic and iron oxyhydroxides in lacustine sediments. Geochim. Cosmochim. Acta. 54:103-109.

Bissen, M., and F.H. Frimmel. 2003. Arsenic—a review: Part I. Occurrences, toxicity, speciation, mobility. Acta Hydrochim Hydrobiol 31:9-18.

Bussey, P. 2004. Goosegrass (*Elusine indica*) control with foramsulfuron in Bermuda grass (*Cynodon spp.*) Turf Weed Technol. 18:634-640.

Calace, N., A. Di Muro, E. Nardi, B.M. Petronio and M. Poetroletti. 2002. Adsorption isotherms for describing heavy-metal retention in paper mill sludges. Ind. Eng. Chem. Res. 41:5491-5497.

Cherry, A., A.U. Shaikh, D.E. Tullman, and R.V. Nicholson. 1979. Arsenic species as an indicator of redox conditions in groundwater. J. Hydrol. 43:373-392.

Chirsten, K. 2008. Chicken poop and arsenic. Environ. Sci. Technol. 40:2864-2865.

Cotton, F.A., and G. Wilkinson. 1980. Advanced inorganic chemistry. 4th ed. Wiley-Interscience, New York.

Darland, J.E., and W.P. Inskeep. 1997. Effects of pH and phosphate competition on the transport of arsenate. J. Environ. Qual. 26:1133–1139.

Dickens, R., and A.E. Hiltbold. 1967. Movement and persistence of methanearsonates in soil. Weeds 15(4):209-304.

Ehman, P.J. 1965. Effect of arsenical build-up in the soils on subsequent growth and residue content of crops. Proc. SWC 18:685-687.

Feng, M., J.E. Schrlau, R. Snyder, G.H. Snyder, M. Chen, J.L. Cisar, and Y. Cai. 2005. Arsenic transport and transformation associated with MSMA application on a golf course green. J. Agric. Food Chem. 53:3556-3562.

Fordham, A.W., and K. Norrish. 1979. Arsenate-73 uptake by components of several acidic soils and its implications for phosphate retention. Aust. J. Soil Res. 17:307–316.

Francesconi, K.A., and D. Kuehnelt. 2002. Arsenic compounds in environment. P. 51-94. In Frankenberger, W.T., Jr. (ed.) Environmental chemistry of arsenic. Marcel Dekker, NY.

Garbarino, J., A.J. Bednar, D.W. Rutherford, R.S. Beyer, and R.L. Wershaw. 2003. Environmental fate of roxarsone in poultry litter. I. degradation of roxarsone during composting. Environ. Sci. Technol. 37:1509-1514.

Goldberg, S. 1986. Chemical modeling of arsenate adsorption on aluminum and iron oxide minerals. Soil Sci. Soc. Am. J. 50:1154-1157.

Goldberg, S., and C.T. Johnston. 2001. Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling. J. Colloid Interface Sci. 234:204–216.http://soil.scijournals.org/cgi/external_ref?access_num=000166697700025&link_type=ISI

Goldberg, S. 2002. Competitive adsorption of arsenate and arsenite on oxides and clay minerals. Soil. Sci. Soc. Am. J. 66:413-421.

Grafe, M., M.J. Eick, P.R. Grossl, and A.M. Saunders. 2002. Adsorption of arsenate and arsenite on ferrihydrite in the presence and absence of dissolved organic carbon. J. Environ. Qual. 31:1115-1123.

Gulens, J., D. R. Champ, and R. E. Jackson. 1979. Influence of redox environments on the mobility of arsenic in ground water. Am. Chem. Soc. Symp. Ser. 93:81-95.

Gupta, G., and S. Charles. 1999. Trace elements in soil fertilized with poultry litter. Poult. Sci. 78:1695-1698.

Gupta, S.K., and K.Y. Chen. 1978. Arsenic removal by adsorption. J. Water Pollut. Control. Fed. 50:493-506.

Hingston, F.J. 1981. A review of anion adsorption. P. 51-90. *In* M.A. Anderson and A.J. Rubin (ed.) Adsorption of inorganics at solid-liquid interfaces. Ann Arbor Sci. Publ., Ann Arbor, MI.

Hingston, F.J., A.M., Posner, and J.P., Quirk. 1972. Anion adsorption by goethite and gibbsite. I. The role of proton in determining adsorption envelopes. J. Soil Sci. 23:117-192.

Hunter, R.J. 1981. Zeta potential in colloid science. Academic Press, London.

Harvey, C.F., C.H. Swartz, 2002. Arsenic mobility and groundwater extraction in Bangladesh. Science. 298:1602 – 1606.

Inskeep, W.P., and T.R. McDermott. 2002. Arsenic (V) /(III) cycling in soils and natural waters: chemical and microbiological processes. P. 183-215. *In* Frankenberger, W.T., Jr. (ed.) Environmental chemistry of arsenic. Marcel Dekker, NY.

Jackson, B.P., and P.M., Bertsch. 2001. Determination of arsenic speciation in poultry waste by IC-ICP-MS. Environ. Sci. Technol. 35(24):4868-4873.

Jackson, B.P., J.C. Seaman, and P.M. Bertsch. 2006. Fate of arsenic compounds in poultry litter upon land application. Chemosphere. 65: 2028-2034.

Jain, A., and R.H. Loeppert. 2000. Effect of competing anions on the adsorption of arsenate and arsenite by ferrihydrite. J. Environ. Qual. 29:1422–1430.

Kaiser, K., G. Guggenberger, and W. Zech. 1997. dissolved organic matter sorp0tion on subsoils and minerals studied by 13C-NMR and drift spectroscopy. Eur. J. Soil Sci. 48:301-310.

Kalbitz, K., and R. Wenrich. 1998. Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. Sci. Total Environ. 209:27-39.

Kuo, S. 1996. Phosphorous. *In* Methods of Soil Analysis Part 3: Chemical methods. Sparks, D.L. (ed.) Soil Sci. Soc. of America. Madison,WI.

Lin, H.T., M.C. Wand, and G.C. Li. 2002. Effects of water extracts of compost on the adsorption of arsenate by two calcareous soils. Water Air Soil Pollut. 138:359-374.

Liu, F., A. De Cristofaro, and A. Violante. 2001. Effect of pH phosphate and oxalate on the adsorption/desorption of arsenate on/from goethite. Soil Sci. 166:197–208.

Livesey, N.T., and P.M. Huang. 1981. Adsorption of arsenate by soils and its relation to selected chemical properties and anions. Soil Sci. 131:88–94.

Lombi, E., R.S. Sletten, and W.W. Wenzel. 2000. Sequentially extracted arsenic from different size fractions of contaminated soils. Water Air Soil Pollut. 124:319-32.

Lovley, D.R., E.L. Blunt-Harris, E.J.P. Philips, and J.C. Woodward. 1996. Humic substances as electron acceptors for microbial respiration. Nature 382:445-448.

Ma, L.Q., W. Harris, and J. Sartain. 2002. Environmental impacts of lead pellets at shooting ranges and arsenical herbicides on golf courses in Florida. Report # 00-03. Gainsville, FL: Florida center for Solid and Hazardous waste management, University of Florida.

Manning, B.A., and S. Goldberg. 1996. Modeling competitive sorption of arsenate with phosphate and molybdate on oxide minerals. Environ. Sci. Technol. 31:2005-2011.

Manning, B.A., and S. Goldberg. 1997. Adsorption and stability of As(III) at the clay-mineral water interface. Environ. Sci. Technol. 31:2005-2011.

Markis, K.C., J. Salazar, S. Quazi, S.S. Andra, D. Sarkar, S.B. Bach, and R. Dutta. 2008. Controlling the fate of roxarsone and inorganic arsenic in poultry litter. J. Environ. Qual. 37(3):963-971.

Masscheleyn, P.H., R.D. Delaune, and W.H.Patrick. 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environ Sci Technol. 25:1414–1419.

McArthur, J.M., P. Ravencroft, S. Safiullah, and M.F. Thirlwal. 2001. Arsenic in ground water: testing pollution mechanism for sedimentary aquifers in Bangladesh. Water Resour. Res. 37:109-117.

McBride, M.B. 1997. A critique of diffuse double layer models applied to colloid and surface chemistry. Clays Clay Miner. 45:598–608.

McDonald, M., K. R. Byre, D.M. Miller, and E.G. Edward. 2009. Broiler-litter application history and soil depths effects on arsenic sorption. Soil Sci. 174(12): 661-675.

Mitchell, C.C. and J.O. Donald. 1995. The value and use of poultry manures as fertilizer. An. Cir. Rosario: ANR-244 Ala. Coop. Ext. Serv., Auburn University, AL.

Morrison, J.L. 1969. Distribution of arsenic from poultry litter in broiler chickens, soil and crops. J. Ag. Food Chem. 17:1288-1290.

Murali, V., and L.A.G. Alymore. 1983. Competitive adsorption during solute transport in soils: 3. A review of experimental evidence of competitive adsorption and an evaluation of simple competitive models. Soil Sci. 136:279-290.

Murphy, E.A., and M. Aucott. 1998. An assessment of the amount of arsenical pesticides used historically in geographical area. Sci. Total Environ. 218:89-101.

National Agricultural Statistics Service, USDA. Alabama agriculture counts county data 2007. [Online]. Available at http://www.agcensus.usda.gov/Publications/2007/Full_Report/Volume_1,_Chapter_2_County_Level/Alabama/alv1.pdf (verified 2 March, 2009).

Nimmick, D.A., 1998. Arsenic hydrogeochemistry in an irrigated river valley- a reevaluation. Ground Water 36:743-753.

Onken B.M., and L.R. Hosner. 1996. Determination of arsenic species in soil solution under flooded conditions. Soil Sci. Soc. Am. J. 60:1385-1392.

Pierce, M.L., and C.B. Moore. 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. Water Res. 16:1247–1253.

Pichler, T., J. Veizer, and G.E.M. Hall. 1999. Natural input of arsenic into a coral-reef ecosystem by hydrothermal fluids and its removal by Fe(III) oxyhydroxides. Environ. Sci. Technol. 331:373-1378.

Peryea, F.J. 1991. Phosphate-induced release of arsenic from soils contaminated with lead arsenate. Soil Sci. Soc. Am. J. 55:1301–1306

Raven, K. P., A. Jain, and R. H. Loeppert. 1998. Arsenite and arsenate adsorption on ferri-hydrite: Kinetics, equllibrium, and adsorption envelopes. Environ. Sci. Technol. 32:344-349.

Redman, A.D., D.L. Macalady, and D. Ahmann. 2002. Natural organic matter affects arsenic speciation and sorption onto hematite. Environ. Sci. Technol. 36:2889-2896.

Roy, W.R., J.J. Hassett, and R.A. Griffin. 1986. Competitive coefficient for the adsorption of arsenate, molybdate, and phosphate mixtures by soils. Soil Sci. Soc. Am. J. 50:1176–1182.

Rutherford, D., A.J. Bednar, J.R. Garbarino, R. Needdham, K.W. Staver, and R.L. Wershaw. 2003. Environmental fate of roxarsone in poultry litter. Part II. Mobility of arsenic in soils amended with poultry litter. Environ. Sci. Technol. 37:1515-1520.

Saada, A., D. Breeze, C. Crouzet, S. Cornu, and P. Baranger. 2003. Adsorption arsenic(V) on kaolinite and on kaolinite-humic acid complexes, role of humic acid nitrogen groups. Chemosphere 51:757-763.

Sadiq, M. 1997. Arsenic chemistry in soils: An overview of thermodynamic predictions and field observations. Water Air Soil Pollut. 93:117–136.

Sarkar, D., K.C. Markis, V. Vandanapu, and R. Dutta. 2007. Arsenic immobilization in soils amended with drinking-water treatment residuals. Environ. Pollut. 146(2):414-419.

Schwab, E.B., D.W. Reeves, C.H. Burmester, and R.L. Rapper. 2002. Conservation tillage systems for cotton in Tennessee valley. Soil Sci. Soc. Am. J. 66:569-577.

Smedley, P.L., and D.G. Kinninburg. 2002. A review of the source, behavior and distribution of arsenic in natural waters. Appl. Geochem. 17:517-568.

Smith, E., R. Naidu, and A.M. Alston. 1998. Arsenic in the soil environment: A review. Adv. Agron. 64:149–195.

Smith, E., R. Naidu, and A.M. Alston. 2002. Chemistry of Inorganic Arsenic in Soils II. Effect of Phosphorus, Sodium, and Calcium on Arsenic Sorption. J. Environ. Qual. 31:557-563.

Sposito, G.. 1982. On the use of Langmuir equation in the interpretation of “adsorption” phenomena: The “two surface” Langmuir equation. Soil Sci. Soc. Am. J. 46:1147-1152.

Stolz, J.F., E. Perera, B. Kilonzo, B. Kail, B. Crable, F. Fisher, M. Ranganathan, L. Wormer, and P. Basu. 2007. Biotransformation of 3-nitro-4-hydroxybenzene arsenic acid (roxarsone) and release of inorganic arsenic by *Clostridium spp*. Environ. Sci. Technol. 41:818-823.

Swancar, A. 1996. Water quality, pesticide occurrence, and effects of irrigation with reclaimed water at golf courses in Florida. Tallahassee: USGS:86.

Snyder, G.H., and J.L. Cisar. 2002. An assessment of the risks associated with pesticides volatilized and dislodged from golf turf. Tallahassee: Florida department of environmental protection: 12.

Sun, X., and H.E. Doner. 1996. An investigation of arsenate and arsenite bonding structures on goethite by FTIR. Soil Sci. 161:865– 872

US Environmental Protection Agency (US-EPA). Pesticide industry sales and usage 1994-2001 market estimates [Online]. Available at http://www.epa.gov/oppbead1/pestsales/ (verified 5 May 2009).

United States Department of Agriculture-Natural Resources Conservation Service (USDA-NRCS), 2007. Soil Survey Laboratory Methods Manual [Online]. Available at ftp://ftp-fc.sc.egov.usda.gov/NSSC/Lab_Methods_Manual/SSIR42_2004_view.pdf (verified 20 January 2009).

US Environmental Protection Agency (US-EPA), 2007. Method 3051a- Microwave assisted acid digestion of sediments, sludges, soils and oils [Online]. Available at http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/3051a.pdf (verified 14 January 2009).

Violante, A., and M. Pigna. 2002. Competitive sorption of arsenate and phosphate on different clay minerals and soils. Soil. Sci. Am. J. 66:1788-1796.

Woolson, E.A., J.H. Axely, and P.C. Kearney. 1973. The chemistry and phytotoxicity of arsenic in soils: Effect of time and phosphorus. Soil Sci. Am. Proc. 37:254–259.

Yossida, T., H. Yamauchi, and S.G. Fan. 2007. Chronic health effects in people exposed to arsenic via the drinking water. Dose-water relationships in review. Toxicol. Appl. Pharmacol. 198:243-252.

Zhongqui, He, W. Honeycutt, I. A. Tazisong, Z. N. Senwo, and D. Zang. 2009. Nitrogen and phosphorus accumulation in pasture soil from repeated poultry litter application. Communications in Soil Sci. and Plant Anal. 40: 587-598.

II. Effect of long-term land application of arsenicals on Ultisols in northern Alabama

ABSTACT

In Alabama, many agricultural practices involve application of arsenicals directly to land by poultry manure and agrochemical applications. Long-term, repeated land-application of arsenicals may result in accumulation of arsenic to toxic levels in the soil. This is especially critical when arsenicals are added with poultry manure, which already contain phosphorus and organic matter that affect arsenic behavior in soil. The objective of the study was to assess the extent of arsenic contamination with repeated poultry litter or arsenical herbicide application. Pastures and cotton fields in northern Alabama with known poultry litter and MSMA applications for more than 10 years were selected. Soil samples at four different depths were characterized for soil pH, Mehlich-I extractable phosphorus, non-crystalline iron oxide fraction, total carbon content, and total arsenic. There were few differences in soil pH, non-crystalline iron oxide fraction, and total carbon among sampled locations across depth. No correlation was observed with these parameters and total soil arsenic. However, total carbon decreased from surface to subsoil. Phosphorus content was from low to medium with no effect on soil arsenic. Soil arsenic content varied by field at location 1 and 2, varied by field at certain depths at Sand Mountain Research and Extension Center and did not vary by field or depth at Tennessee Valley Research and Extension Center. Location 1 and 2 appeared to have fields with arsenic contamination, but the source of contamination was inconclusive. Control fields with no poultry litter or arsenical herbicide application were likely in cotton production many years ago. Arsenicals that were historically used in cotton

production as defoliants, herbicides, and pesticides may still be present in the soil and cause poor background readings for some control plots.

Introduction

Naturally occurring arsenic (As) of geological origin is found in rocks and soil, which eventually enters water and air by means of weathering, dissolution, and erosion. However, application of arsenicals directly to land during agricultural management practices, also contributed soil arsenic. Over time, repeated land-application of arsenicals may result in accumulation of arsenic to toxic levels in the soil. Health risks are associated with prolonged or acute exposure to arsenic (Yosida *et al.*, 2007) and hence contamination of soil and water poses a major threat to both human and animal life.

Agricultural practices that may have contributed arsenic to the soil are land applications of poultry litter or manure containing arsenic-based antimicrobials and application of arsenic-based chemicals including defoliants, herbicides, and pesticides to cotton, turf, and orchard trees (Rutherford *et al.*, 2003; Peryea, 1991). Fertilizers can also be a source of arsenic in soils (Smith *et al.*, 1998). Sodium arsenate and sodium arsenite were used extensively in the past to control boll weevil and defoliation of cotton, respectively (Sarkar *et. al.*, 2007). Monosdium methanearsonate (MSMA) and disodium methanarsonate (DSMA) were used for post-emergent control of annual grass weeds in cotton (Dickens and Hiltbold, 1967) and turf (Bussey, 2004). During its peak usage in Alabama cotton fields (1997), MSMA was applied to 48% of cotton fields (~100,000 ha) (NASS, 2007). Application of MSMA for weed control in golf courses remains a widely used practice (Bussey, 2004). Thus, repeated and long-term application of arsenicals has the potential to elevate the arsenic concentration in soil beyond background levels.

In the U.S., Alabama ranks third in broiler production after Georgia and Arkansas (McDonald *et al*., 2009). In Alabama, two-thirds of broiler production is concentrated primarily in the northern part of the state where 1.5 million metric tons of poultry manure and bedding waste or litter are land-applied per annum (Aksoy, 2008; Mitchell, 2001). The poultry litter is rich in nitrogen and phosphorus compared to other manures and is commonly applied as a fertilizer (Zhongqui *et al.*, 2009). Poultry litter may contain the organoarsenical roxarsone (3-nitro-4-hydroxyphenylarsonic acid), which is used as a feed additive in poultry operations to increase feed efficiency and control gut parasites (Rutherford *et al.*, 2003).

In poultry litter samples, 30 to 60 mg roxarsone kg^{-1} litter was detected (Morrison, 1969; Garbarino *et al.*, 2003). While this may seem minor, repeated application of arsenic-containing poultry litter has the potential to cause an increase of arsenic concentration in soil and or nearby water levels. Studies conducted in Oklahoma (Rutherford et al., 2003) and Maryland (Gupta and Charles, 1999) indicated that soils amended with poultry litter for more than 20 years caused increased concentration of arsenic in soil. Soils of northern Alabama are typically in the Ultisol soil order, which is characterized by low base saturation, eluviation of clay, and presence of kaolinite, gibbsite, and 2:1 clay minerals. These soil characteristics are known to affect sorption and mobility of arsenic. The different agro-climatic conditions and soil type found in northern Alabama may affect the mobility of land-applied arsenic differently than in Oklahoma and Maryland. Hence, it is necessary to study the behavior of added arsenicals, its sorption and mobilization under the influence of these soil characteristics. Poultry litter is land-applied at a rate of 4-5 tons per hectare as a fertilizer on cropland and pasture. Roxarsone, which may be present in the poultry litter, is highly soluble and readily degrades into inorganic arsenic species. Unfortunately, many of the degradation products are also soluble and more toxic than roxarsone, especially arsenite and dimethylarsenite. This may eventually lead to the mobilization of arsenic, which may pose a health hazard (Garbarino *et al.*, 2003). Presence of anoxic conditions during composting of poultry litter facilitates bacteria of the genus *Clostridium* in degrading roxarsone into inorganic arsenic and other undefined organoarsenicals compounds (Stolz *et al.*, 2007; Garbarino *et al.*, 2003). Thus, the potential of arsenic movement in the environment through leaching, surface runoff, or subsequent uptake by agricultural crops is relatively greater (Arai *et al.*, 2003).

Sorption and mobilization of arsenic in soil depends on soil pH, soil redox conditions, mineralogical composition, organic matter and phosphorus content of soil (Manning and Goldberg, 1996). Adsorption and mobilization of both arsenite and arsenate in soil is influenced by pH. At low pH, arsenate exhibits high sorption and low mobility, while arsenite exhibits this behavior at high pH (Manning and Goldberg, 1997; Inskeep *et al.*, 2002; Hingston *et al.*, 1972). Under neutral pH and aerobic conditions in soils, arsenic is immobilized by sorption and co-precipitation with metal oxides. Arsenic is released from metal oxides during dissolution, which typically occurs under low pH and reduced redox potentials (Bissen and Frimmel, 2003; Harvey and Swartz, 2002). In addition to metal oxides, sulfide minerals can also control arsenic concentrations in solution. Arsenic can sorb to or co-precipitate with sulfide minerals under low pH and reducing redox conditions (Harvey and Swartz, 2002; Masscheleyn *et al*., 1991).

Dissolved organic matter (DOM) has the potential to chemically mobilize arsenic from iron oxides, soils, aquifers and sediments by displacing sorbed arsenic (Bauer and Blodau, 2006). In contrast, arsenic sorption on iron oxides, alumina, quartz or kaolinite can be blocked by the formation of stable complexes by fulvic or humic acids with mineral surfaces (Abbt-Braun, 2002; Kaiser *et al.*, 1997; Graffe *et al.*, 2002). The formation of aqueous arsenic-DOM complexes either by positively charged amino groups or by metal-cation bridges with DOM may lead to greater mobility of arsenic (Saada *et al.*, 2003; Redman *et al.*, 2002).

Based on the type of mineral and pH, adsorption behavior of arsenic varies in soil. The major process controlling the activity of arsenic in soil is surface complexation or sorption reactions on hydrous oxide minerals of iron, aluminum, manganese, and clay minerals (Goldberg, 1986; Hingston *et al.*, 1972). Arsenic is preferentially adsorbed to iron and aluminum oxide minerals compared to kaolinite, montmorillonite, calcite, or quartz (Fordham and Norrish, 1979; Livesey and Huang, 1981). A study indicated that the adsorption of arsenate on goethite, gibbsite, alumina, kaolinite, montmorillonite increased at low pH and had adsorption maxima between pH 3 to 7, while arsenite exhibited increased sorption at high pH and had adsorption maxima at a pH range of 7 to 8 (Gupta and Chen, 1978; Pierce and Moore, 1982; Jain and Loeppert, 2000). At low arsenic concentration, arsenate has a greater competitive effect on arsenite adsorption by amorphous iron oxide than that of arsenite on arsenate adsorption (Jain and Loeppert, 2000).

Both phosphorus and arsenic exhibit similar chemical behavior in soils and are specifically adsorbed on soil minerals, especially on variable charge minerals. Thus, arsenic competes with phosphorus for adsorption sites in soils (Violante and Pigma, 2002; Liu *et al.*, 2001). Competitive effects of phosphorus on arsenic adsorption were much greater than arsenic on phosphorus sorption (Roy *et al.*, 1986). Application of phosphate fertilizers in soils with previous application of lead arsenate pesticides caused increased mobility of arsenic (Preya, 1991). The increased mobility is brought about by suppression of sorption and displacement of sorbed arsenic in soil (Sadiq, 1997; Peryea, 1991; Liu *et al*., 2001) and may result in leaching of arsenic from the root zone through the vadose zone to groundwater (McDonald *et al.*, 2009).

There are few studies available on arsenic in the soils of northern Alabama. The objective of the study was to assess the extent of arsenic contamination due to long-term repeated application of poultry litter and arsenical herbicides.

Materials and Methods

Pastures and cotton fields in Alabama with poultry litter (PL) and MSMA applications for more than 10 years were selected for study. Selected pastures received poultry litter from multiple chicken houses that were under different poultry management practices. All sites were located in the northern part of the state in the Sand Mountain and Tennessee Valley regions (Table 1). In addition to private land, sites at the Sand Mountain Research and Extension Center (SMREC) and Tennessee Valley Research and Extension Center (TVREC) were also selected. Areas with no known history of poultry litter or arsenical applications, but located near sampling sites with poultry litter and arsenical application, were evaluated to determine background levels of arsenic (control). All soils collected are in the Ultisol soil order. They are classified as a fine-loamy, siliceous, subactive, thermic, Typic Hapludults and a fine-loamy, kaolinitic, thermic Typic Paleudults, respectively.

A profile sample of 1-m depth was sampled using a 3-cm diameter hydraulic soil probe (Giddings Machine Co., Fort Collins, CO). The samples were collected at five different locations per field. In fields with variable topography, samples were taken from each landscape position (i.e., top of the hill, bottom of the hill and three samples from back slope/foot slope/shoulder positions). All sampling locations were recorded by global positioning system. Sampled cores were divided into the following depths: 0-20, 20-40, 40-60, >60 cm. Each depth was mixed thoroughly after removing extraneous materials for further sample preparation. The soil samples were air dried, sieved to pass a 2-mm sieve, and ground using mechanical grinder.

Total arsenic

To determine total soil arsenic, dried soil samples were microwave digested (US-EPA 3051a, 2007). Basically, a 0.5 g soil sample was microwave digested with 10 mL of concentrated nitric acid (Mars Xpress, CEM Corporation, NC). The digested samples were filtered and the volume made up to 100 mL. Potassium iodide was added to the digested samples on 1% w/v basis prior to analysis by hydride generation-atomic absorption spectrometry (HG-AAS) for determination of total arsenic (US-EPA 3051a, 2007). Potassium iodide converts As(V) to As(III), which improves the reaction kinetics of arsenic with sodium-borohydride during the hydride formation phase of the analysis.

For hydride generation, 0.6% sodium-borohydride in 0.5% sodium hydroxide was used. All samples were analyzed in duplicates. In the same matrix, working standards of 5, 10, 20, and 40 µg As L^{-1} concentrations were prepared using arsenic reference standard solution for AAS (Fisher Sci., NJ).

Soil characterization

Air-dried soil samples were characterized for soil pH, phosphorus, non-crystalline hydrous oxide (active) fraction of iron, and total carbon. Soil pH was determined potentiometrically in 1:2 (w/v) soil-water suspensions. Soil samples were extracted with Mehlich-I extractant solution in 1:4 (m/v) soil-extractant ratio (Kuo, 1996) and analyzed for phosphorus by inductively coupled plasma spectrometry (CIROS CCD model; Spectro Analytical Instruments, MA). Total soil carbon content was determined at 0-20 and 20-40 cm depths using the Carbon Analyzer^{TM} (Elementar-Variomacro, Germany). Non-crystalline hydrous (active) oxide fraction of iron in the soil was determined using dithionite-citrate extraction and atomic absorption spectrometry (USDA-NRCS, 2007).

Statistical Analysis

Statistical analysis was performed using the Proc Corr., MANOVA and Proc Mixed procedure at significance level $\alpha = 0.05$ (SAS 9.2; SAS Inc., Cary, NC) on soil pH, total arsenic, active iron oxide fraction and total carbon. The experimental design used was complete randomized design. Distribution of soil pH, total arsenic, active iron oxide fraction, and total carbon for different locations were formulated using the dynamic curve feature of Sigma Plot version 11 (Systat Corporation, San Jose, CA).

Results

Soils were analyzed for pH, Mehlich-I extractable phosphorus, total arsenic, active iron oxide fraction, and total carbon content to assess the impact of repeated application of arsenicals through routine management practices.

Soil pH

Soil pH varied from 4.25 to 6.28 (Table 2). At location 1, soil pH differed between control and field 3 at the surface; however, there were no other differences by depth with in a field or across fields at a depth. At location 2, differences were observed between the control and other fields for 20-40 cm depth and at 40-60 cm between the control and fields 1 and 2. And for >60 cm depth, only the control and field 2 differed. At the control site, the soil pH at the surface was greater than the subsoil. There was no difference between fields at any depth at SMREC, except at the control site where soil pH decreased from the surface to >60 cm depth. At TVREC, a difference was observed at 40-60 and >60 cm for the control and field 2. In field 1 and 2, soil pH increased with depth.

Mehlich-I extractable phosphorus

Mehlich-I extractable phosphorus varied from 2.94 to 183.4 mg kg^{-1} (Table 3). At location 1, phosphorus differed between control and field 1 and field 3 at 40-60 and 20-40 cm depth, respectively. Mehlich-I extractable phosphorus at the surface decreased with depth in all fields at this location. At location 2, no differences were observed amongst fields at any depth. Although Mehlich-I extractable phosphorus decreased with depth at all sites, only the control site was statistically significant. At SMREC, all fields had greater phosphorus at the surface than the control field, but at depths >20 cm only fields 1 and 2 were greater than the control field. Only fields 1 and 2 had decreasing phosphorus with depth. At TVREC, Mehlich-I extractable phosphorus differed among all fields at the surface and 20-40 cm depth (Table 3). At 40-60 cm depth, phosphorus varied between control and field 2 (Table 3). In field 1 and 2, phosphorus content decreased with depth.

Non-crystalline hydrous oxide fraction of iron

Non-crystalline hydrous oxide fraction varied between 1480 to 2525 mg kg^{-1} (Table 4). At location 1, no differences were found among fields, except at >60 cm depth where the iron oxide content was greater in field 1 compared to other fields at this site. At location 2, iron oxide content did not differ between any fields at a given depth or within a field by depth. At SMREC, iron oxide content was greater in field 3 compared to the control and other fields. No differences were found within any field with depth, except for the control field where iron oxide increased with depth. At TVREC, no differences among fields with depth were observed. Iron oxide content increased with depth in field 2.

Total carbon content

Total carbon content for the sampled locations was determined for the 0-20 and 20-40 cm depths and ranged from 0.29 to 1.78 (Table 5). At location 1, SMREC, and TVREC, total carbon did not differ from the control site at either depth. At location 2, total carbon was greater in field 1 compared to control and other fields at that location at 20-40 cm. At each site, total carbon was greater at the surface than at 20-40 cm.

Total arsenic content

The distribution of total arsenic at location 1 varied from 3.82 to 12.40 mg kg^{-1} (Fig. 1a). At all sampled depths, total arsenic concentration differed between control and fields 1 and 3. Within each field, arsenic was greatest at 40-60 cm for the control and field 1. In field 2, arsenic was greatest at 20-40 cm compared to other depths. Arsenic concentration in field 3 did not differ with depth.

Total arsenic concentration at location 2 ranged from 8.47 and 15.39 mg kg^{-1} (Fig. 1b). While the control and field 2 were consistently higher in total arsenic, they differed from fields 1 and 3 only at certain depth increments (Fig. 1b). Within each field, total arsenic did not differ with depth.

At SMREC, total arsenic content varied from 8.17 to 13.85 mg kg^{-1} (Fig. 1c). Surface concentrations of arsenic were greatest in field 3 and lowest in the control and field 1. At the 20-40 cm depth, field 3 was greater than field 1. No differences were observed between fields at 40-60 cm, but field 2 was lower than all other fields at >60 cm. Within the control field and field 2, arsenic at the surface was less than all other depths. Arsenic in fields 1 and 3 did not differ with depth. At TVREC, total arsenic content ranged from 3.20 to 5.73 mg kg^{-1} (Fig. 1d). Total arsenic did not differ among fields within a depth increment or within fields by depth.

Discussion

Soil pH

Soil pH at the sampled locations ranged from 4.25 to 6.28 (Table 3). Although some differences were observed by depth with in a field or across fields at a depth; overall, there was a relatively consistent distribution of soil pH at all sampled locations across depths. Decline of soil pH from surface to lower depth at control site of SMREC and at field 1 and 2 of TVREC is likely attributable to the liming practices followed during field maintenance. There was no correlation observed between soil pH and soil arsenic content. This may be due to the few differences in soil pH among all the sampled locations. Although mobility and sorption of arsenic oxyanions are a function of soil pH (Inskeep *et al.*, 2002; Hingston *et al.*, 1972), differences in arsenic among the locations or with depth cannot be attributed to pH variability.

Darland and Inskeep (1997) indicated that decreasing pH favors arsenate adsorption on the soil minerals, while arsenite adsorption increases at higher pH. A similar study by Manning and Goldberg (1997) found that adsorption of arsenate on goethite, gibbsite, alumina, kaolinite, montmorillonite increased at low pH and had adsorption maxima between pH 3 to 7, which subsequently declined at higher pH, while arsenite had adsorption maxima at pH between 7 to 8. They concluded that at high pH arsenite is more strongly bound to soil components than arsenate.

Mehlich-I extractable phosphorus

In general, low Mehlich-I extractable phosphorus (Table 4) was found at all the sampled locations except at SMREC (low to medium). Mehlich-I extractable phosphorus contents of the sampled locations are reported according to the Auburn University Soil Testing Laboratory ratings. The variability of phosphorus content at the sampled sites could be attributed to the different phosphorus management practices followed in the region. For example, each site had different rates of fertilization, variable rates of poultry litter addition, and cattle or crop management practices. Most sites exhibited decreasing phosphorus with depth indicating that the phosphorus was applied at the surface.

No correlation was found between Mehlich-I extractable phosphorus and soil arsenic content. The absence of the potential influence of phosphorus on the sorption and mobility of arsenic is likely attributable to the lower soil phosphorus content at the sampled locations, agronomic practices followed, and the background arsenic concentration. In general, arsenic and phosphorus compete for a similar set of surface sites; though some sites may be uniquely available for adsorption of either arsenic or phosphorus (Manning and Goldberg, 1996). Peryea (1991) reported that application of phosphate fertilizers in soils with previous application of lead arsenate pesticides caused increased mobility of arsenic. The increased mobility is brought about by suppression of sorption and displacement of sorbed arsenic in soil (Sadiq, 1997; Peryea, 1991; Liu *et al*., 2001) and may result in leaching of arsenic from the root zone through the vadose zone to groundwater (McDonald *et al*., 2009).

Non-crystalline hydrous oxide fraction of iron

Few differences were observed in the non-crystalline hydrous iron oxide content in all the sampled locations at all depths (Table 5). This may be due to the similarity in parent material, geological origin, and soil type. While the iron oxide fraction in soil greatly influences the behavior of arsenic (Fordham and Norrish, 1979; Livesey and Huang, 1981), variability in arsenic content among sites is unlikely due to the iron oxide fraction as little variability was observed. Goldberg (1986) and Hingston *et al.* (1972) indicated that the major process that controls the activity of arsenate in soil is its surface complexation or sorption reactions on hydrous oxide minerals of iron, aluminum, and manganese and clay minerals. In comparison, arsenite exhibits strong preference for hydrous oxides of iron only.

Total carbon content

At each location, the total carbon content decreased from the surface to the subsoil (Table 6). This is typical of most soils where organic matter is added to the soil via plant residue, manure, or poultry litter inputs. Mitchell and Donald (1995) and Jackson *et al.* (2006) reported that repeated application of poultry litter can increase the soil carbon content along with nitrogen and phosphorus.

Total carbon did not correlate with total soil arsenic concentrations. While it is not expected that carbon contents between sites would necessarily be correlated due to variable carbon management practices, no trends with depth in a single field indicates that arsenic is not bound entirely by organic matter. Soil arsenic concentrations were consistent with depth and in some cases increased with depth, while organic carbon decreased with depth. This may indicate a greater role in the oxide fraction and clay content on the arsenic mobility and sorption than soil carbon content (McDonald *et al.*, 2009). However, Jackson *et al.* (2006) reported that land application of poultry litter resulted in greater arsenic solubility due to competitive adsorption and complexation from increased dissolved organic carbon added in the litter. Bauer and Blodau (2006) reported that dissolved organic matter (DOM) has the potential to chemically mobilize arsenic from iron oxides, soils, aquifers and sediments by displacing sorbed arsenic.

Total arsenic content

Distinct differences in total soil arsenic content were found at location 1 among sites. The arsenic concentration in field 1 and 3 was approximately twice that of the control and field 2. Within a field, total arsenic increased slightly with depth for all fields, except field 3. Although differences were observed by depth with in a field or across fields at a depth, the relative homogenous distribution of arsenic concentration within a field suggests that arsenic was either geological in origin or applied anthropogenically and had some mobility in the soil profile. The two-fold increase between the control or field 2 and fields 1 and 3 suggests that arsenic accumulation may be attributable to management practices. At this location, soil pH, Mehlich-I extractable phosphorus, iron oxide fraction, and total soil carbon were relatively homogeneous. Thus, contributions due to native soil and or geology are unlikely. Repeated application of organic matter and phosphorus over time may contribute to arsenical leaching and eventual uniformity in the soil arsenic level within the profile.

At location 2, there were also distinct differences in total arsenic content among sites. However, at this location the arsenic concentration was higher in the control and field 2 than field 1 and 3. Although no poultry litter application was reported in the control field, the land had been in cotton production >30 years ago. Increased soil arsenic concentrations may be attributable to use of arsenical-based defoliants, herbicides, or pesticides during prior cotton production. Soil arsenic in fields 1 and 3 are at near the upper limit of 10 mg kg^{-1} expected in Alabama soils. Without reliable background soil arsenic levels, it is difficult to determine whether arsenic is native or anthropogenic. With similar parent material, homogeneous pH, and iron oxide fractions, it is unlikely that soil arsenic levels would differ significantly.

At SMREC, there was no definite pattern of soil arsenic distribution among fields. Soil arsenic in the control field and field 2 had increased slightly from surface to lower depths. The arsenic concentration was highest in field 3 at all depths. Soil arsenic in all fields is near or above expected background levels. It is not clear whether high arsenic concentrations in field 3 are attributable to recent application of poultry litter, prior cotton production, or from native soil arsenic.

At TVREC, soil arsenic content did not differ among fields or with depth within a field. Furthermore, concentrations were <5 mg As kg^{-1}, which is within the expected background level for this area. Soil arsenic distribution is most likely attributed to geological origin or similar history of arsenicals applied during cotton production not associated with MSMA. Other studies have shown leaching of arsenical herbicides (i.e., disodium methanearsonate [DSMA]). Dickens and Hiltbold (1967) found that leaching of surface applied DSMA was different for different soil types, but consistent with their adsorption capacities for DSMA. This study also indicated that residual concentrations of arsenic were detected in the hay when sorghum, soybeans and peanuts were grown subsequently in plots with DSMA application. Based on soil type and adsorptive capacity, surface application of DSMA exhibited varied leaching behavior.

Determination of whether repeated land-application of poultry litter or MSMA contributed to elevated soil arsenic levels was hindered by lack of reliable baseline arsenic levels at control sites. Soil arsenic may be attributable to geological origin, prior contribution of arsenical application during cotton production, and/or arsenicals from poultry litter. Continual leaching of arsenicals and saturation of binding sites may occur resulting in relatively homogeneous soil arsenic levels within a soil profile. Similar studies in Oklahoma (Rutherford *et al.*, 2003) and Maryland (Gupta and Charles, 1999) indicated that soils amended with poultry litter for more than 20 years caused an elevated concentration of arsenic in soil. Arai *et al.* (2003) found that the degraded products of poultry litter composting like arsenite and dimethylarsenite, are generally soluble, hence both roxarsone and some of its degradation products are relatively mobile and susceptible to leaching. Further investigations are needed to study biochemical changes that influence speciation of applied arsenicals as this has a potential influence on arsenic mobilization in soil.

Table 1: Description of sampling locations in northern Alabama.

Location Name	**County**	**Location details**
Location 1	Marshall/DeKalb	Control: 0 y of PL[†] application (pasture)
		Field 1: 15-20 y of PL application (pasture)
		Field 2: 15-20 y of PL application (pasture)
		Field 3: >50 y of PL application (pasture)
Location 2	Jackson/DeKalb	Control: 0 y of PL application (pasture)
		Field 1: >30 y of PL application (pasture)
		Field 2: >30 y of PL application (pasture)
		Field 3: >30 y of PL application (pasture)
SMREC	DeKalb	Control: 0 y of PL application (pasture)
		Field 1: >20 y of PL application (pasture)
		Field 2: >20 y of PL application (pasture)
		Field 3: >20 y of PL application (pasture)
TVREC	Limestone	Control: 0 y of MSMA[‡] application (pasture)
		Field 1: >10 y of MSMA application (cotton)
		Field 2: >10 y of MSMA application (cotton)

† PL, Poultry litter

‡ MSMA, Monosodium methanearsonate

Table 2. Mean soil pH at sampled fields in northern Alabama with known history of arsenical applications.

		pH			
		Field			
Location	**Depth (cm)**	**Control**	**Field 1**	**Field 2**	**Field 3**
Location 1[†]	0-20	5.31^{b}	5.60^{ab}	5.60^{ab}	6.03^{a}
	20-40	5.37	5.34	5.56	5.65
	40-60	5.45	5.17	5.12	5.61
	>60	5.37	5.15	5.05	5.63
Location 2	0-20	5.73^{A}	6.02^{AB}	6.03	6.10
	20-40	4.90^{Bb}	6.15^{ABa}	6.05^{a}	6.17^{a}
	40-60	5.09^{Bb}	6.19^{Aa}	6.01^{a}	5.89^{ab}
	>60	5.13^{Bb}	5.45^{Bab}	6.06^{a}	5.42^{ab}
SMREC	0-20	6.28^{A}	5.93	5.48	6.22
	20-40	6.11^{AB}	5.76	5.54	6.00
	40-60	5.58^{BC}	5.61	5.44	5.50
	>60	5.35^{C}	5.40	5.21	5.39
TVREC	0-20	5.74	5.63^{A}	5.55^{A}	
	20-40	5.54	5.18^{AB}	5.20^{A}	
	40-60	5.37^{b}	4.8^{Bab}	4.49^{Ba}	
	>60	5.29^{a}	4.67^{Bab}	4.25^{Bb}	

[†] Means in the same column at a single location followed by different capital letters differ at $\alpha \leq 0.05$. Means in the same row followed by different lowercase letters differ at $\alpha \leq 0.05$.

Table 3. Mean soil phosphorus (P) at sampled fields in northern Alabama with known history of arsenical applications.

		P (mg kg^{-1})			
		Field			
Location	**Depth (cm)**	**Control**	**Field 1**	**Field 2**	**Field 3**
Location 1†	0-20	42.21^{A}	55.4^{A}	42.78^{A}	28.05
	20-40	26.34^{Bab}	38.29^{ABa}	15.22^{Bbc}	7.50^{c}
	40-60	12.11^{BCb}	24^{BCa}	4.86^{Bb}	3.33^{b}
	>60	6.53^{C}	9.96^{C}	3.86^{B}	3.00
Location 2	0-20	45.36^{Aab}	31.29^{b}	102.21^{a}	38.64^{b}
	20-40	33.13^{AB}	24.66	86.55	19.1
	40-60	13.08^{BC}	14.47	48.53	6.29
	>60	5.85^{C}	13.7	28.43	2.94
SMREC	0-20	3.86^{c}	183.4^{Aa}	156.09^{Aa}	86.78^{b}
	20-40	2.52^{b}	148.72^{Aa}	126.8^{Aa}	44.93^{b}
	40-60	0.93^{c}	68.3^{Bab}	96.14^{Ba}	20.52^{bc}
	>60	0.55^{c}	42.1^{Bb}	88.87^{Ba}	4.24^{c}
TVREC	0-20	19.21^{c}	64.12^{Ab}	100.22^{Aa}	
	20-40	9.42^{c}	38.28^{Bb}	83.75^{Aa}	
	40-60	6.55^{b}	20.7^{BCab}	59.55^{ABa}	
	>60	3.76	19.23^{C}	28.91^{B}	

†Means in the same column at a single location followed by different capital letters differ at $\alpha \leq 0.05$. Means in the same row followed by different lowercase letters differ at $\alpha \leq 0.05$.

Table 4. Mean non-crystalline hydrous oxide fraction of iron at sampled fields in northern Alabama with known history of arsenical applications.

		Fe Oxide (mg kg^{-1})			
		Field			
Location	**Depth (cm)**	**Control**	**Field 1**	**Field 2**	**Field 3**
Location 1†	0-20	1941	1869^{B}	1706	1805
	20-40	1897	2005^{AB}	1931	1890
	40-60	1945	2014^{AB}	1945	1918
	>60	1878^{b}	2135^{Aa}	1907^{b}	1956^{ab}
Location 2	0-20	2204	2137	2194	2172
	20-40	2385	2277	2296	2327
	40-60	2368	2223	2282	2256
	>60	2284	2282	2204	2243
SMREC	0-20	1480^{Bb}	1659^{ab}	1717^{ab}	1854^{a}
	20-40	1703^{AB}	1805	1722	1875
	40-60	1755^{A}	1907	1690	1785
	>60	1820^{A}	1878	1785	1785
TVREC	0-20	2383	2362	2386^{B}	
	20-40	2456	2428	2464^{AB}	
	40-60	2482	2482	2509^{A}	
	>60	2494	2512	2525^{A}	

†Means in the same column at a single location followed by different capital letters differ at $\alpha \leq 0.05$. Means in the same row followed by different lowercase letters differ at $\alpha \leq 0.05$.

Table 5. Mean total carbon at sampled fields in northern Alabama with known history of arsenical applications.

		Total Carbon (%)			
		Field			
Location	**Depth (cm)**	**Control**	**Field 1**	**Field 2**	**Field 3**
Location 1[†]	0-20	1.23^{A}	1.11^{A}	1.78^{A}	1.72^{A}
	20-40	0.37^{B}	0.43^{B}	0.58^{B}	0.84^{B}
Location 2	0-20	0.93^{A}	1.46^{A}	1.48^{A}	1.20^{A}
	20-40	0.29^{Bb}	0.77^{Ba}	0.39^{Bab}	0.53^{Bab}
SMREC	0-20	1.28^{A}	1.39^{A}	1.20^{A}	1.37^{A}
	20-40	0.47^{B}	0.63^{B}	0.44^{B}	0.56^{B}
TVREC	0-20	1.26^{A}	0.68	0.93	
	20-40	0.74^{B}	0.41	0.40	

† Means in the same column at a single location followed by different capital letters differ at $\alpha \leq 0.05$. Means in the same row followed by different lowercase letters differ at $\alpha \leq 0.05$.

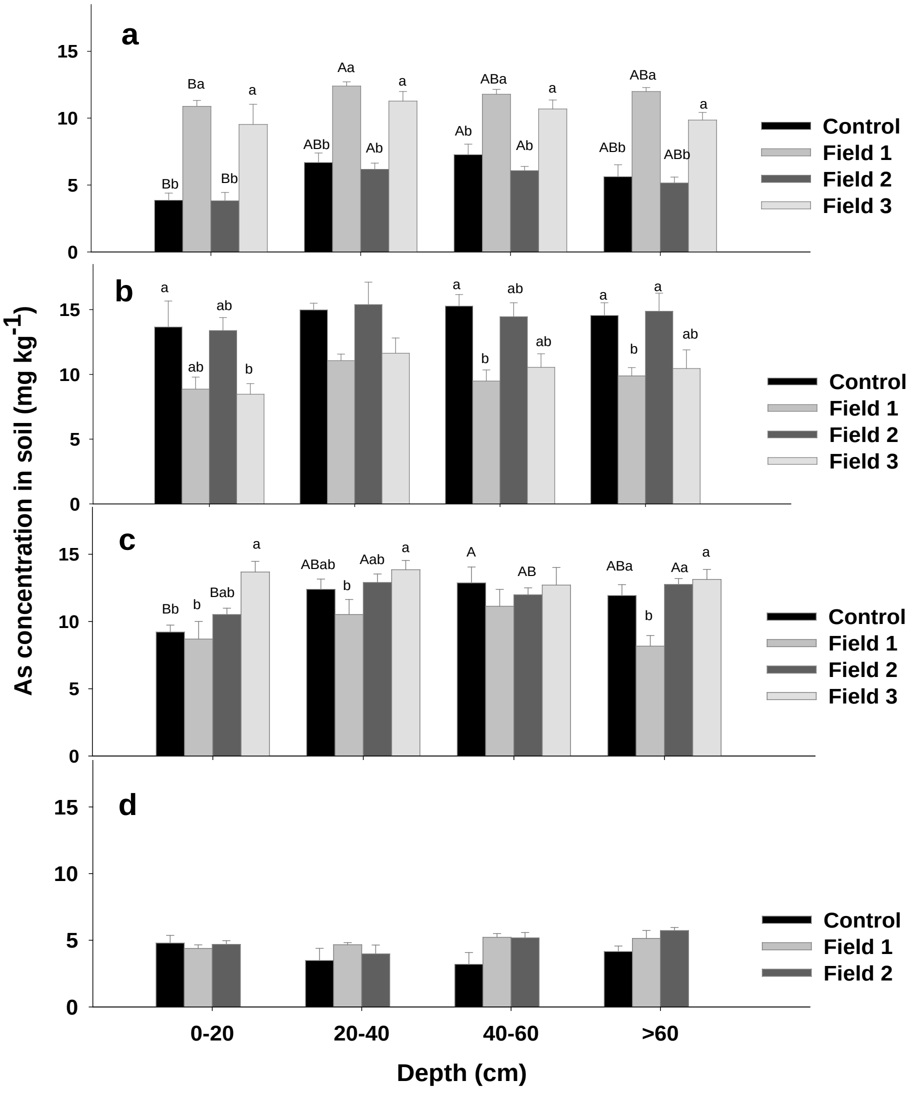

Figure 1. Total arsenic (As) concentrations at selected locations a) location 1, b) location 2, c) SMREC, and d) TVREC in northern Alabama. The control site at each location had no history of poultry litter addition or MSMA application. Fields 1-3 had poultry litter addition for >10 years; Fields 1-2 at TVREC had MSMA application for >10 years. Different uppercase letters indicate different arsenic concentrations within a field at $\alpha \leq 0.05$ and different lowercase letters indicate different arsenic concentrations within a depth across fields at $\alpha \leq 0.05$.

References

Abbt-Braun, G., Huminstoffe-Vorkommen, Charakterisierung, and Reaktionen. 2002. Wasser-und Geotechnologie. 1:41– 50.

Arai, Y., A. Lanzirotti, S. Sutton, J.A. Davis, D.L. Sparks. 2003. Arsenic speciation and reactivity in poultry litter. Environ. Sci. Technol. 37:4083-4090.

Bauer, M., and C. Blodau. 2006. Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. Sci. of Total Environ. 354:179-190.

Bissen, M., and F.H. Frimmel. 2003. Arsenic—a review: Part I. Occurrences, toxicity, speciation, mobility. Acta Hydrochim Hydrobiol 31:9-18.

Bussey, P. 2004. Goosegrass (*Elusine indica*) control with foramsulfuron in Bermuda grass (*Cynodon spp.*) Turf Weed Technol. 18:634-640.

Darland, J.E., and W.P. Inskeep. 1997. Effects of pH and phosphate competition on the transport of arsenate. J. Environ. Qual. 26:1133–1139.

Dickens, R., and A.E. Hiltbold. 1967. Movement and persistence of methanearsonates in soil. Weeds 15(4):209-304.

Fordham, A.W., and K. Norrish. 1979. Arsenate-73 uptake by components of several acidic soils and its implications for phosphate retention. Aust. J. Soil Res. 17:307–316.

Garbarino, J., A.J. Bednar, D.W. Rutherford, R.S. Beyer, and R.L. Wershaw. 2003. Environmental fate of roxarsone in poultry litter. I. degradation of roxarsone during composting. Environ. Sci. Technol. 37:1509-1514.

Goldberg, S. 1986. Chemical modeling of arsenate adsorption on aluminum and iron oxide minerals. Soil Sci. Soc. Am. J. 50:1154-1157.

Grafe, M., M.J. Eick, P.R. Grossl, and A.M. Saunders. 2002. Adsorption of arsenate and arsenite on ferrihydrite in the presence and absence of dissolved organic carbon. J. Environ. Qual. 31:1115-1123.

Gupta, G., and S. Charles. 1999. Trace elements in soil fertilized with poultry litter. Poult. Sci. 78:1695-1698.

Gupta, S.K., and K.Y. Chen. 1978. Arsenic removal by adsorption. J. Water Pollut. Control. Fed. 50:493-506.

Hingston, F.J., A.M., Posner, and J.P., Quirk. 1972. Anion adsorption by goethite and gibbsite. I. The role of proton in determining adsorption envelopes. J. Soil Sci. 23:117-192.

Harvey, C.F., C.H. Swartz, 2002. Arsenic mobility and groundwater extraction in Bangladesh. Science. 298:1602 – 1606.

Inskeep, W.P., and T.R. McDermott. 2002. Arsenic (V) /(III) cycling in soils and natural waters: chemical and microbiological processes. P. 183-215. *In* Frankenberger, W.T., Jr. (ed.) Environmental chemistry of arsenic. Marcel Dekker, NY.

Jackson, B.P., J.C. Seaman, and P.M. Bertsch. 2006. Fate of arsenic compounds in poultry litter upon land application. Chemosphere. 65: 2028-2034.

Jain, A., and R.H. Loeppert. 2000. Effect of competing anions on the adsorption of arsenate and arsenite by ferrihydrite. J. Environ. Qual. 29:1422–1430.

Kaiser, K., G. Guggenberger, and W. Zech. 1997. dissolved organic matter sorp0tion on subsoils and minerals studied by 13C-NMR and drift spectroscopy. Eur. J. Soil Sci. 48:301-310.

Kuo, S. 1996. Phosphorous. *In* Methods of Soil Analysis Part 3: Chemical methods. Sparks, D.L. (ed.) Soil Sci. Soc. of America. Madison,WI.

Liu, F., A. De Cristofaro, and A. Violante. 2001. Effect of pH phosphate and oxalate on the adsorption/desorption of arsenate on/from goethite. Soil Sci. 166:197–208.

Livesey, N.T., and P.M. Huang. 1981. Adsorption of arsenate by soils and its relation to selected chemical properties and anions. Soil Sci. 131:88–94.

Manning, B.A., and S. Goldberg. 1996. Modeling competitive sorption of arsenate with phosphate and molybdate on oxide minerals. Environ. Sci. Technol. 31:2005-2011.

Manning, B.A., and S. Goldberg. 1997. Adsorption and stability of As(III) at the clay-mineral water interface. Environ. Sci. Technol. 31:2005-2011.

Masscheleyn, P.H., R.D. Delaune, and W.H.Patrick. 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environ Sci Technol. 25:1414–1419.

McDonald, M., K. R. Byre, D.M. Miller, and E.G. Edward. 2009. Broiler-litter application history and soil depths effects on arsenic sorption. Soil Sci. 174(12): 661-675.

Mitchell, C.C. and J.O. Donald. 1995. The value and use of poultry manures as fertilizer. An. Cir. Rosario: ANR-244 Ala. Coop. Ext. Serv., Auburn University, AL.

Morrison, J.L. 1969. Distribution of arsenic from poultry litter in broiler chickens, soil and crops. J. Ag. Food Chem. 17:1288-1290.

National Agricultural Statistics Service, USDA. Alabama agriculture counts county data 2007. [Online]. Available at http://www.agcensus.usda.gov/Publications/2007/Full_Report/Volume_1,_Chapter_2_County_Level/Alabama/alv1.pdf (verified 2 March, 2009).

Pierce, M.L., and C.B. Moore. 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. Water Res. 16:1247–1253.

Peryea, F.J. 1991. Phosphate-induced release of arsenic from soils contaminated with lead arsenate. Soil Sci. Soc. Am. J. 55:1301–1306

Redman, A.D., D.L. Macalady, and D. Ahmann. 2002. Natural organic matter affects arsenic speciation and sorption onto hematite. Environ. Sci. Technol. 36:2889-2896.

Roy, W.R., J.J. Hassett, and R.A. Griffin. 1986. Competitive coefficient for the adsorption of arsenate, molybdate, and phosphate mixtures by soils. Soil Sci. Soc. Am. J. 50:1176–1182.

Rutherford, D., A.J. Bednar, J.R. Garbarino, R. Needdham, K.W. Staver, and R.L. Wershaw. 2003. Environmental fate of roxarsone in poultry litter. Part II. Mobility of arsenic in soils amended with poultry litter. Environ. Sci. Technol. 37:1515-1520.

Saada, A., D. Breeze, C. Crouzet, S. Cornu, and P. Baranger. 2003. Adsorption arsenic(V) on kaolinite and on kaolinite-humic acid complexes, role of humic acid nitrogen groups. Chemosphere 51:757-763.

Sadiq, M. 1997. Arsenic chemistry in soils: An overview of thermodynamic predictions and field observations. Water Air Soil Pollut. 93:117–136.

Sarkar, D., K.C. Markis, V. Vandanapu, and R. Dutta. 2007. Arsenic immobilization in soils amended with drinking-water treatment residuals. Environ. Pollut. 146(2):414-419.

Smith, E., R. Naidu, and A.M. Alston. 1998. Arsenic in the soil environment: A review. Adv. Agron. 64:149–195.

Stolz, J.F., E. Perera, B. Kilonzo, B. Kail, B. Crable, F. Fisher, M. Ranganathan, L. Wormer, and P. Basu. 2007. Biotransformation of 3-nitro-4-hydroxybenzene arsenic acid (roxarsone) and release of inorganic arsenic by *Clostridium spp*. Environ. Sci. Technol. 41:818-823.

United States Department of Agriculture-Natural Resources Conservation Service (USDA-NRCS), 2007. Soil Survey Laboratory Methods Manual [Online]. Available at ftp://ftp-fc.sc.egov.usda.gov/NSSC/Lab_Methods_Manual/SSIR42_2004_view.pdf (verified 20 January 2009).

US Environmental Protection Agency (US-EPA), 2007. Method 3051a- Microwave assisted acid digestion of sediments, sludges, soils and oils [Online]. Available at http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/3051a.pdf (verified 14 October 2009).

Violante, A., and M. Pigna. 2002. Competitive sorption of arsenate and phosphate on different clay minerals and soils. Soil. Sci. Am. J. 66:1788-1796.

Yossida, T., H. Yamauchi, and S.G. Fan. 2007. Chronic health effects in people exposed to arsenic via the drinking water. Dose-water relationships in review. Toxicol. Appl. Pharmacol. 198:243-252.

Zhongqui, He, W. Honeycutt, I. A. Tazisong, Z. N. Senwo, and D. Zang. 2009. Nitrogen and phosphorus accumulation in pasture soil from repeated poultry litter application. Communications in Soil Sci. and Plant Anal. 40: 587-598.

III. Effect of low and high soil phosphorus on the sorption and mobility of arsenite, arsenate, roxarsone and MSMA

ABSTRACT

Repeated land-application of relatively nutritionally-rich poultry litter may lead to high soil phosphorus levels in soil. Phosphorus competes with arsenic for adsorption sites. This may be problematic especially when arsenicals are added with poultry manure, which contains phosphorus and organic matter that may increase arsenic solubility. The objective of the study was to evaluate the impact of soil phosphorus on arsenite, arsenate, roxarsone, and monosodium methane arsenate (MSMA) sorption and solubility. Batch experiments were conducted on low and high phosphorus soils from a long-term fertilization study in the Sand Mountain region of northern Alabama, where land-application of arsenicals through agronomic practices occurs. Soil phosphorus had no effect on the sorption of arsenite, arsenate, roxarsone, and MSMA. Arsenite sorption was much greater than arsenate. Roxarsone and MSMA were not adsorbed to soil colloids and caused some desorption of native arsenic from the soil. Thus, there is a greater potential for leaching and mobility of arsenate, roxarsone, and MSMA in Hartsells soils than arsenite.

Introduction

Large applications of phosphorus to arsenate-polluted soils have been known to displace arsenic and increase its mobility in soils (Woolson *et al.*, 1973). The increased mobility of arsenic in the presence of phosphorus was brought about by suppression of sorption and displacement of sorbed arsenic in soil (Sadiq, 1997; Peryea, 1991; Liu *et al.*, 2001). In general, arsenic and phosphorus compete for a similar set of surface sites, though some sites may be uniquely available for adsorption of either arsenic or phosphorus (Manning and Goldberg, 1996). Phosphate competes with both arsenite [As(III)] and arsenate [As(V)] for adsorption in soils with limited sorption sites, but both phosphate and arsenic oxyanions are strongly retained in soils with unlimited sorption sites (Smith *et al.*, 2002). Increasing phosphate concentration in the soil solution causes substantial decline in arsenite sorption in soils with low sorption capacity unlike arsenate sorption in the same soils. This suggests preferential sorption of arsenate and phosphate by oxide surfaces and some sites that may be common to both (Smith *et al.*, 2002).

Phosphorus has a greater competitive effect on arsenic adsorption than arsenic on phosphorus sorption (Roy *et al.*, 1986). Studies on the competitive adsorption of arsenate and phosphate in soil revealed that though arsenate desorbed some previously adsorbed phosphate, a substantial portion of bound phosphate remained. Iron oxide surfaces in soil may contain adsorption sites common to arsenate and phosphate, as well as sites that adsorb specifically one anion or another (Barrow, 1974; Hingiston *et al.*, 1971). Increasing pH and competitive adsorption from phosphorus resulted in arsenate desorption from soil mineral complexes (Smith *et al.*, 2002; Livesey and Huang, 1981). At high arsenate and low phosphate concentrations, competition for sites is reversed, suggesting that the mass action effect may dictate the extent of the adsorption of anions irrespective of the ligand ions (Barrow, 1974). The sorption kinetics of arsenic and phosphorus on different soil minerals and other organo-mineral complexes is influenced by the type and stability of surface complexes formed by their oxyanions and the effect of time on the electrical potential of the surfaces (Violante and Pigma, 2002).

Arsenic and phosphorus share similar chemical properties like tetrahedral geometry, atomic and bonding radii, ionization potential, electronegativities and oxyanions (Markis *et al.*, 2008). Oxyanions of both arsenic and phosphorus are specifically adsorbed on soil minerals especially on variable charge minerals (aluminum, iron, and manganese oxides; allophones; imogolite) by forming inner-sphere complexes (Violante and Pigma, 2002; Liu *et al.*, 2001). The surface coverage determines formation of monodentate complexation, bidentate-binuclear complexation and bidentate-mononuclear complexation in varying proportions (Violante and Pigma, 2002; Liu *et al.*, 2001). Hence, soil phosphorus has a large influence on the sorption dynamics and mobilization of arsenic in soil. The objective of this study was to evaluate the impact of long-term high phosphorus management practices on the sorption and solubility of arsenite, arsenate, roxarsone and monosodium acid methane arsonate (MSMA) in soil.

Materials and Methods

Batch experiments were conducted to evaluate the effect of high soil phosphorus content on the sorption and solubility of arsenite, arsenate, roxarsone, and MSMA in soil. The soils selected for the study belonged to the Hartsells series (fine-loamy, siliceous, subactive, thermic, Typic Hapludults) from the Sand Mountain region of northern Alabama where land-application of arsenicals through agronomic practices has occurred. Soil samples used for the experiments were obtained from a long-term fertility experiment at the Sand Mountain Research and Extension Center that maintained consistent yearly fertilizer management for the last 80 years. The plots selected for the study were from no phosphorus fertilizer (low P) and high (~70 kg P_2O_5 ha^{-1}) phosphorus fertilizer addition (high P). Other nutrients, except nitrogen, were managed similarly. Nitrogen was applied at 100 kg N_2O ha^{-1} to the high P plots. There was no known history of arsenicals or poultry litter applied to the soil. From 1929 to 1992, row crops (e.g., corn and soybean) were rotated, but after 1992 the plots have been maintained in forage grass (e.g., *Festuca arundinacea*, *Cynodon dactylon*, and *Sericea lespedieza*). Soils were evaluated for pH, electrical conductivity, Mehlich-I extractable phosphorus, calcium, magnesium, potassium, active iron oxide fraction, and total arsenic (Table 1).

Soil pH and electrical conductivity (EC) were determined potentiometrically in 1:2 (w/v) soil:water suspensions. Soil samples were extracted with Mehlich-I extractant solution in 1:4 (w/v) soil:extractant ratio (Kuo, 1996) and analyzed for phosphorus, calcium, magnesium, potassium by inductively coupled plasma (ICP) spectrometry (CIROS CCD model; Spectro Analytical Instruments, MA). Non-crystalline hydrous (active) oxide fraction of iron in the soil was determined using dithionite-citrate extraction and atomic absorption spectrometry (USDA-NRCS, 2007).

Dried soil samples were microwave digested to determine the background total arsenic concentration in the soil. Basically, a 0.5 g soil sample was microwave digested with 10 mL of concentrated nitric acid according to the manufacturer’s settings for the EPA 5031a method (US-EPA 3051a, 2007; Mars Xpress, CEM Corporation, NC). The digested samples were filtered using an 8 µm filter and the volume made to 100 mL. Potassium iodide was added to the digested samples on 1% w/v basis prior to analysis by hydride generation-atomic absorption spectrometry (HG-AAS) for determination of total arsenic (US-EPA 3051a, 2007). Potassium iodide converts As(V) to As(III), which improves the reaction kinetics of arsenic with sodium-borohydride during the hydride formation phase of the analysis. For hydride generation, 0.6% sodium-borohydride in 0.5% sodium hydroxide was used. Standards were matrix-matched using digested blanks spiked with an arsenic reference standard solution for AAS (Fisher Sci., NJ).

Arsenite and arsenate solutions of 0.02, 0.2 1.5, 8, 15, 30, 60, and 120 mg As L^{-1} were prepared using sodium arsenite ($NaAsO_2$; Fisher Sci., NJ) and sodium arsenate ($Na_2HAsO_4.7H_2O$; MP Bio-Medicals LLC, France), respectively. Solutions for roxarsone and MSMA were prepared using 4-hydroxy-3 nitrobenzene arsenic acid (Acros Organics, NJ) and monosodium acid methane arsonate sesquihydrate (Chem Service, PA). Prepared solutions for roxarsone and MSMA were 0.43, 4.3, 8.52, 17.04, and 34.08 mg As L^{-1} and 0.7, 6.95, 13.89, 27.78, and 55.56 mg As L^{-1}, respectively. Concentrations were selected to span a wide range of arsenic concentrations including those found in poultry litter (e.g., 8-17 mg As kg^{-1}; Garbarino *et al.*, 2003). All solutions were prepared in 50 mM KCl.

Basically 50 mL of arsenic solutions, described above, were added to 100 mg high or low phosphorus soil in a 50-mL centrifuge tube and shaken for 24 hours. After shaking, the suspension was centrifuged at 1000 *g* for 20 minutes and filtered through 0.22 µm membrane syringe filter. Arsenic concentration in solution was determined by ICP. Adsorbed arsenic in the soil was calculated by difference of initial and measured solution (equilibrium) arsenic content.

Adsorption isotherms were obtained by plotting equilibrium arsenic concentration (C_{eq}; mg L^{-1}) against adsorbed concentrations (q; mg kg^{-1}). Langmuir and Freundlich models were applied to isotherm data to characterize the relationship between adsorbed and equilibrium concentrations (McDonald *et al.*, 2009; Sposito, 1989). Langmuir isotherm can be described as:

$$q = q_{max} K_L C / (1 + K_L C)$$

Where q is adsorbed concentration (mg kg^{-1}) in soil, q_{max} is the maximum sorption capacity (mg kg^{-1}), C is the equilibrium (final) concentration of the sorbate in solution (mg L^{-1}), and K_L is the Langmuir constant (McDonald *et al.*, 2009).

Freundlich isotherm can be described as:

$$q = K_f C^{1/n}$$

Where q is adsorbed concentration (mg kg^{-1}) in soil, C is the equilibrium (final) concentration of the sorbate in solution (mg L^{-1}), K_f is the Freundlich constant, and 1/n is a constant that describes heterogeneity of the sorption sites (McDonald *et al.*, 2009; Calace *et al.*, 2002).

Results

Arsenite [As(III)] sorption

Arsenite was readily adsorbed to both low and high phosphorus soils. Percent sorption began to stabilize at 98% adsorption when arsenite was added at 30 mg As L^{-1} (Fig. 2). There was a nearly linear increase of arsenite sorption with increasing equilibrium concentration (C_{eq}) (Fig. 3). Sorption ranged from 84 to 59,100 mg kg^{-1} in both soils.

Arsenite adsorption data were fit to Langmuir and Freundlich adsorption models. The Freundlich model was the best fit for both the soils with an R^2 of 0.914 and 0.9078 for low and high phosphorus soil, respectively (Fig. 4 and Table 7). The R^2 values for the Langmuir adsorption model were 0.0001 and 0.0124 for the high and low phosphorus soils, respectively. The slope of the fitted Freundlich model represents the parameter 1/n, which signifies the degree of sorption site heterogeneity (McDonald *et al.*, 2009; Sposito, 1989). The 1/n values for the low and high phosphorus soils were 1.4566 and 1.3295 (Table 6).

Arsenate [As(V)] sorption

Adsorption of arsenate to low and high phosphorus Sand Mountain soils was not more than 25% of added arsenate (Fig. 2). Maximal adsorption peaked at 20,000 mg As kg^{-1} when arsenic was added at 40 mg L^{-1} and decreased as equilibrium arsenic concentration increased (Fig. 5). No differences were observed between low and high phosphorus soils.

Arsenate adsorption data were fit to Langmuir and Freundlich adsorption models. The Freundlich adsorption model was found to have the best fit for the arsenate sorption data with an R^2 of 0.898 and 0.817 for low and high phosphorus soils, respectively (Fig. 6). The R^2 values for the Langmuir model were 0.0028 and 0.0451 for the high and low phosphorus soils, respectively. Using the Freundlich model, the heterogeneity factor for sorption sites, i.e., 1/n, was calculated as 1.1691 and 1.0215 for low and high phosphorus soils, respectively (Table 7).

Roxorsone and MSMA sorption

Negative adsorption of roxarsone and MSMA to Sand Mountain soils with low and high phosphorus status was observed at all arsenic loading rates (Fig. 7 and 8). Both roxarsone and MSMA exhibited increased desorption of arsenic with increased roxarsone or MSMA equilibrium concentrations (Fig. 9 and 10). Negative adsorption was nearly linear for both compounds.

Discussion

Effect of soil phosphorus

Sorption of arsenite, arsenate, roxarsone, and MSMA were not affected by the phosphorus status of the soil. Because phosphorus is known to compete with arsenic sorption (Roy *et al.*, 1986; Woolson *et al.*, 1973), it is surprising that sorption did not differ when phosphorus differed by a factor of more than 16 between the soils. Results from this study suggest that phosphorus does not compete with arsenic in these soils. This is supported by the low equilibrium phosphorus concentration (<0.2 mg L^{-1}) during the study. The results suggests that arsenic may be specifically adsorbed on soil minerals by forming inner-sphere complexes to sites that adsorb specifically one anion or another (Violante and Pigma, 2002; Liu *et al.*, 2001;Barrow, 1974; Hingiston *et al.*, 1971). Smith et al. (2002) reported that arsenic adsorption from solution to soil colloidal or mineral surfaces are determined by the availability of sites for adsorption. The kinetics of sorption of arsenate and phosphate on different soil minerals, and organo-mineral complexes is influenced by the type and stability of surface complexes and the effect of time on the electrical potential of the surfaces (Violante and Pigma, 2002).

Roxorsone and MSMA sorption

Roxarsone and MSMA were not adsorbed to soil colloids and actually stimulated some desorption of native arsenic from the soil. Retention of arsenic from organoarsenicals may require degradation into inorganic forms of arsenic before sorption to soil can occur (Garbarino *et al.*, 2003). Roxarsone and MSMA appear to have caused solubilization of sorbed arsenic from soil. Other studies have found contrasting results. Dickens and Hiltbold (1967) noted that increasing the concentration of disodium methanearsonate (DSMA) in the equilibration solution for the whole soils could result in increased adsorption of DSMA in soil. However, it was not clear whether the organoarsenical or degradation products of the organoarsenicals were retained. This process needs to be investigated as these arsenicals are often repeatedly applied to land through routine management practices involving application of poultry litter and arsenical herbicides. If degradation into inorganic forms does not occur, arsenic remains in solution and has the potential to leach through the soil profile.

Arsenite and arsenate adsorption isotherms

Arsenite sorption was much greater than arsenate sorption in both soils. When arsenic was added at concentrations >8 mg L^{-1}, arsenite adsorption was ~98%, while arsenate sorption was <25% for all arsenic concentrations supplied. Arsenite in solution was <2 mg L^{-1} even at the highest arsenic loading level. This suggests a very low potential for leaching, while arsenate equilibrium concentrations up to 100 mg L^{-1} suggests a high potential for leaching. Arsenate is the major species found in the litter amended soil extracts (Garbarino *et al.*, 2003) and repeated application of poultry litter to these soils through routine management practices is common. Thus, roxarsone and arsenate, a degradation product of roxarsone, are highly soluble and have the potential to leach in this soil.

Table 6. Soil properties for low and high phosphorus soils collected from a long-term fertilization study at the Sand Mountain Research and Extension Center.

Soil property	**Low P**	**High P**
pH	4.82	3.78
Electrical conductivity (dS m^{-1})	43.35	71.77
Mehlich-I extractable phosphorus (mg kg^{-1})	5.13	82.68
Mehlich-I extractable calcium (mg kg^{-1})	199.70	230.55
Mehlich-I extractable magnesium (mg kg^{-1})	35.35	29.43
Mehlich-I extractable potassium (mg kg^{-1})	92.05	41.22
Active iron oxide fraction (mg kg^{-1})	1803.25	1755.38
Total arsenic (mg kg^{-1})	9.71	8.55

Table 7. Summary of arsenite and arsenate adsorption coefficients of Sand Mountain high and low phosphorus (P) soils

Arsenic species	**Soil**	**Linear equation**	**$R^{2†}$**	**$1/n^{‡}$**
Arsenite	High P	Freundlich eq. y = 1.3295x + 4.4286	0.9078	1.3295
		Langmuir eq. y = -0.00005x – 0.0002	0.0001	-0.00005
	Low P	Freundlich eq. y = 1.4566x + 4.4163	0.9143	1.4566
		Langmuir eq. y = -0.0001x – 0.0001	0.0124	-0.0001
Arsenate	High P	Freundlich eq. y = 1.0215x + 1.6671	0.8071	1.0215
		Langmuir eq. y = 0.0001x - 0.0038	0.0028	0.0001
	Low P	Freundlich eq. y = 1.1691 + 1.4079	0.8979	1.1691
		Langmuir eq. y = 0.0004x – 0.0158	0.0451	0.0004

† Coefficient of variation

‡ slope describing the linear relationship between the natural logarithm of adsorbed arsenic concentration and the natural logarithm of equilibrium arsenic concentration and represents heterogeneity of sorption sites.

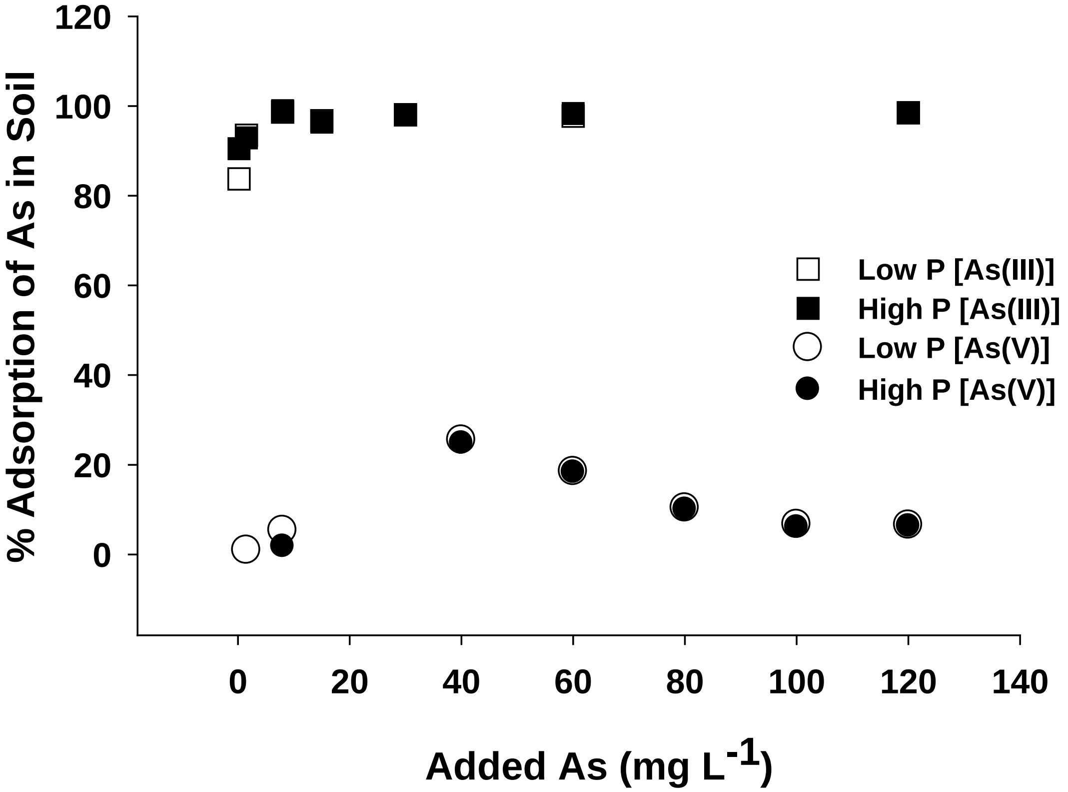

Figure 2. Percent adsorbed arsenic with respect to added arsenic as arsenite [As(III)] and arsenate [As(V)] in high and low phosphorus (P) soils.

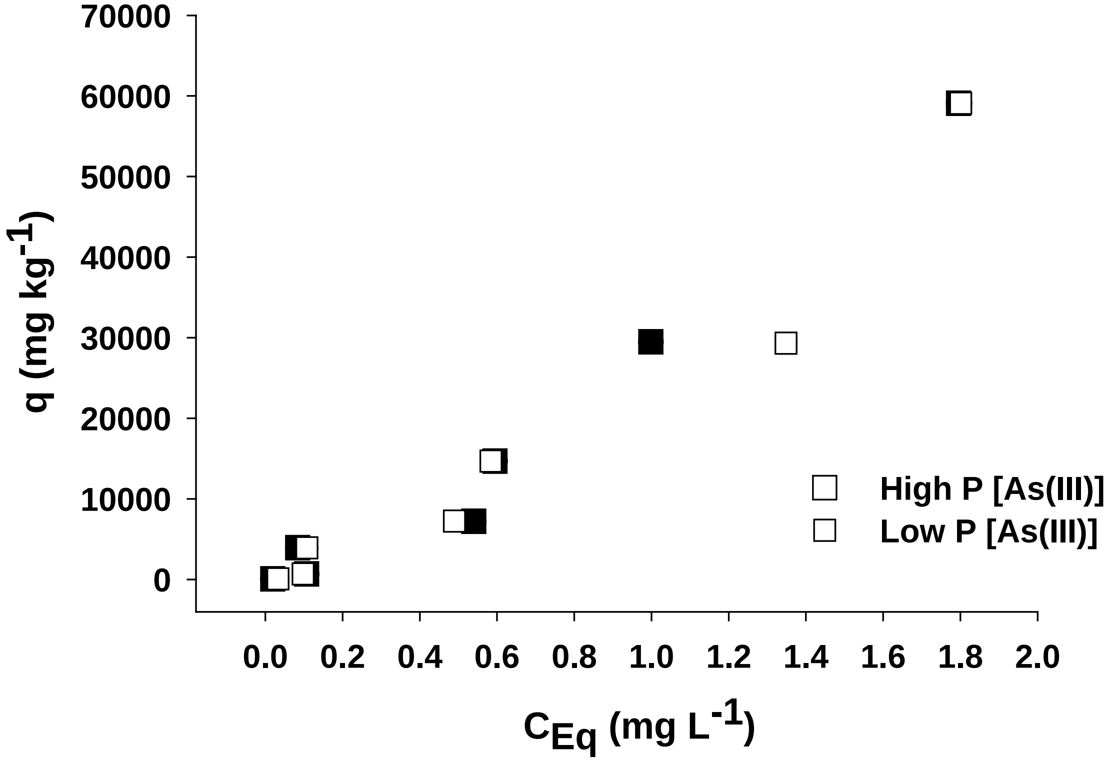

Figure 3. Relationship between sorbed arsenic concentration (q) and equilibrium arsenic concentration (C_{Eq}) from added arsenite in high and low phosphorus (P) soils.

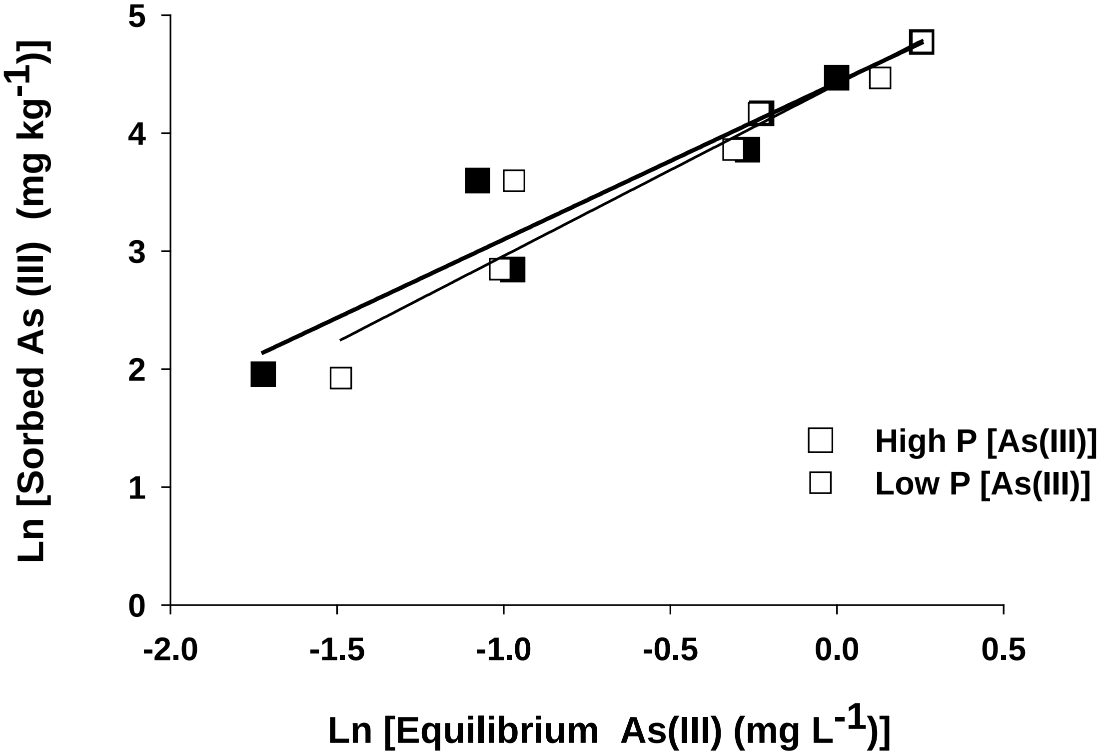

Figure 4. Arsenite sorption on high and low phosphorus (P) soils as described by the Freundlich model.

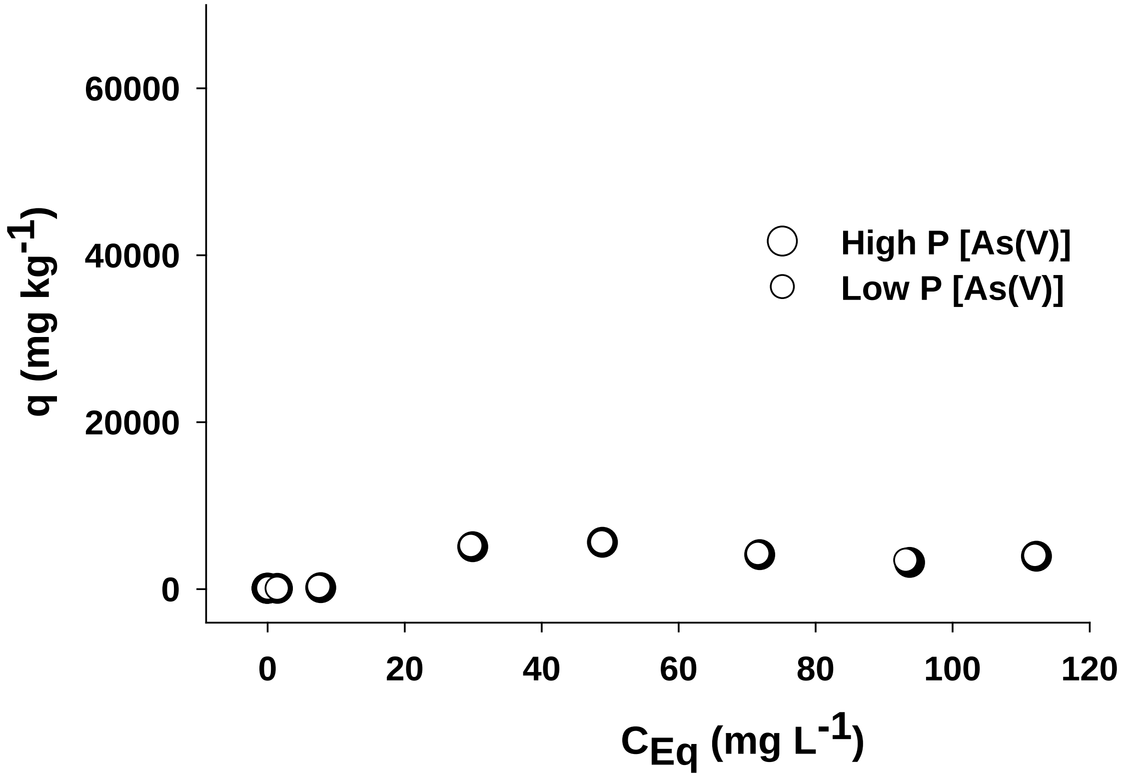

Figure 5. Relationship between sorbed arsenic concentration (q) and equilibrium arsenic concentration (C_{Eq}) from added arsenate in high and low phosphorus (P) soils.

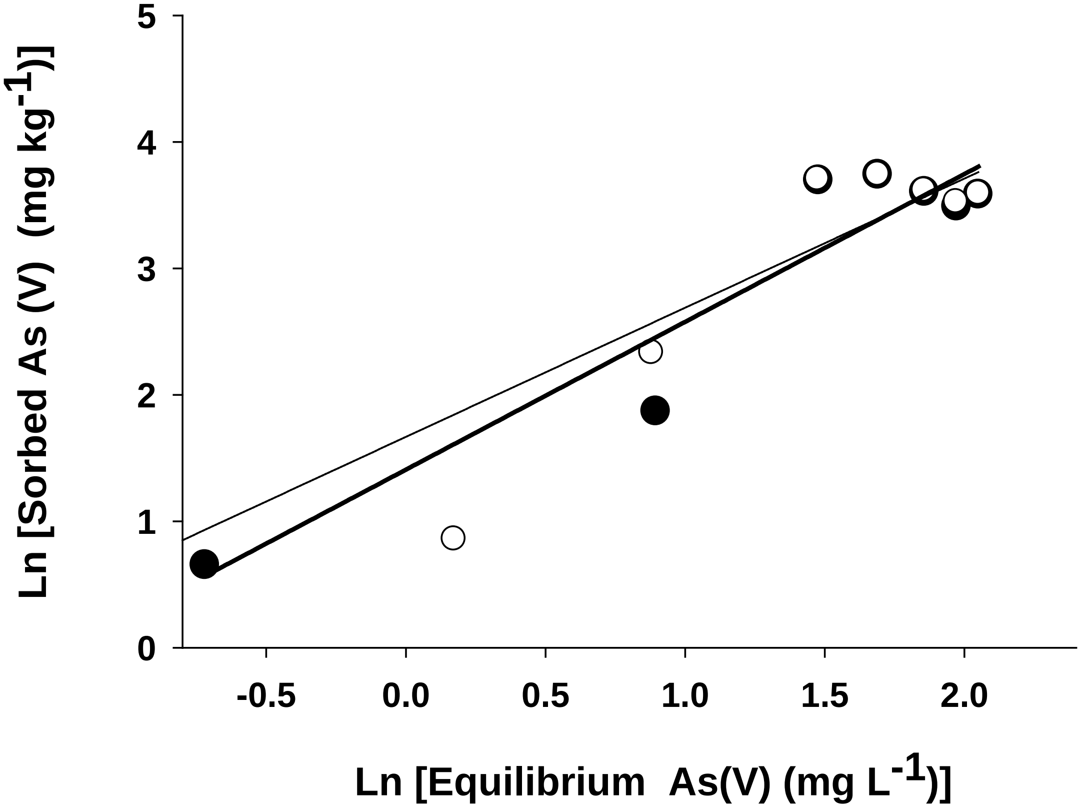

Figure 6. Arsenate [As(V)] sorption on high and low phosphorus (P) soils as described by the Freundlich model.

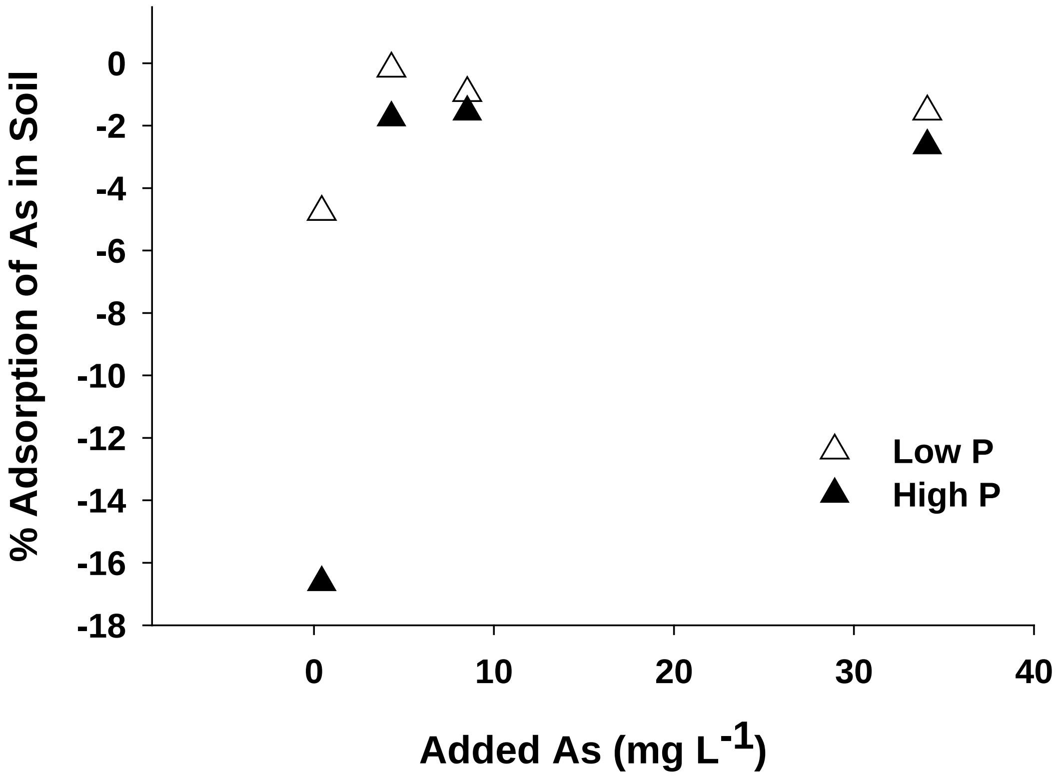

Figure 7. Relationship between percent adsorbed arsenic and added arsenic concentration from added roxarsone in high and low phosphorus (P) soils.

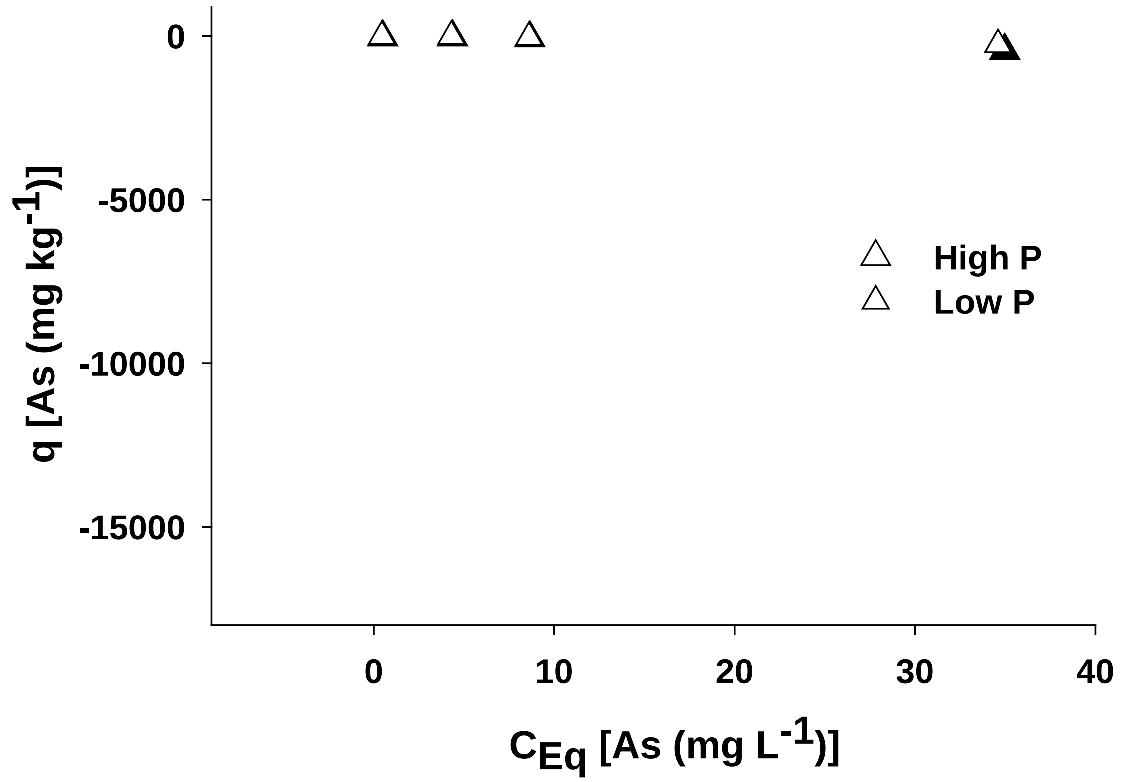

Figure 8. Relationship between sorbed arsenic concentration (q) and equilibrium arsenic concentration (C_{Eq}) from added roxarsone in high and low phosphorus (P) soils.

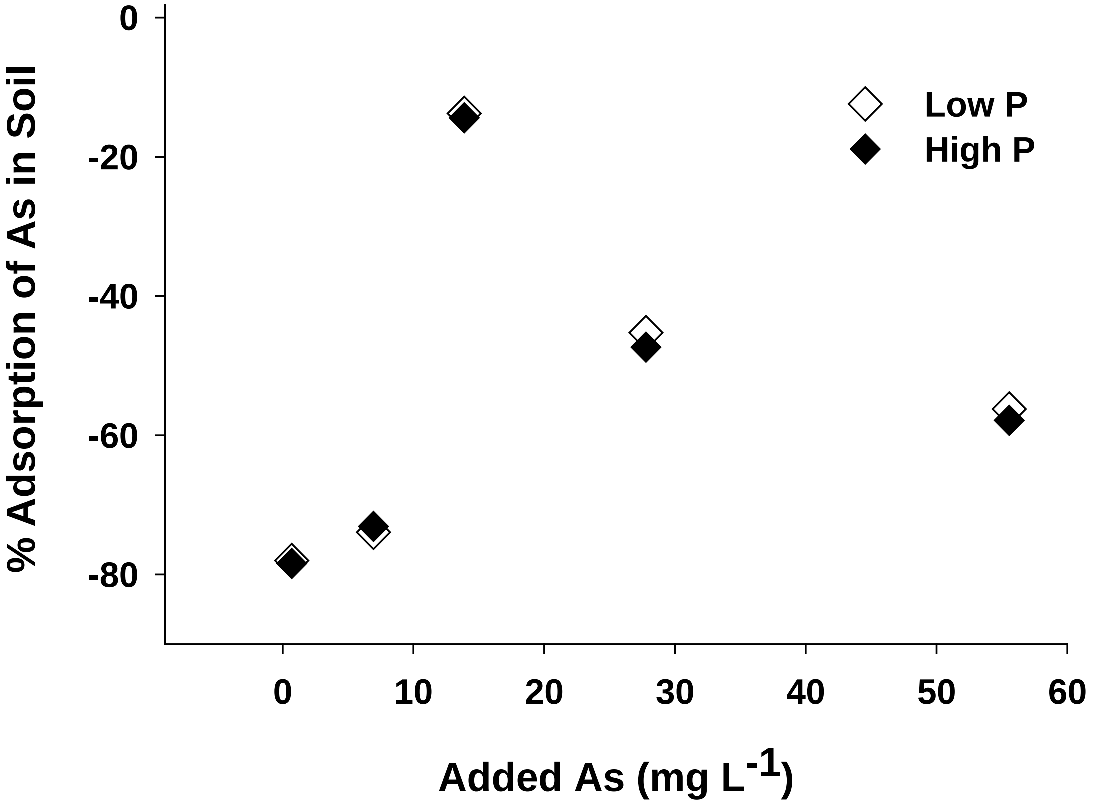

Figure 9. Relationship between percent adsorbed arsenic and added arsenic concentration from added MSMA in high and low phosphorus (P) soils.

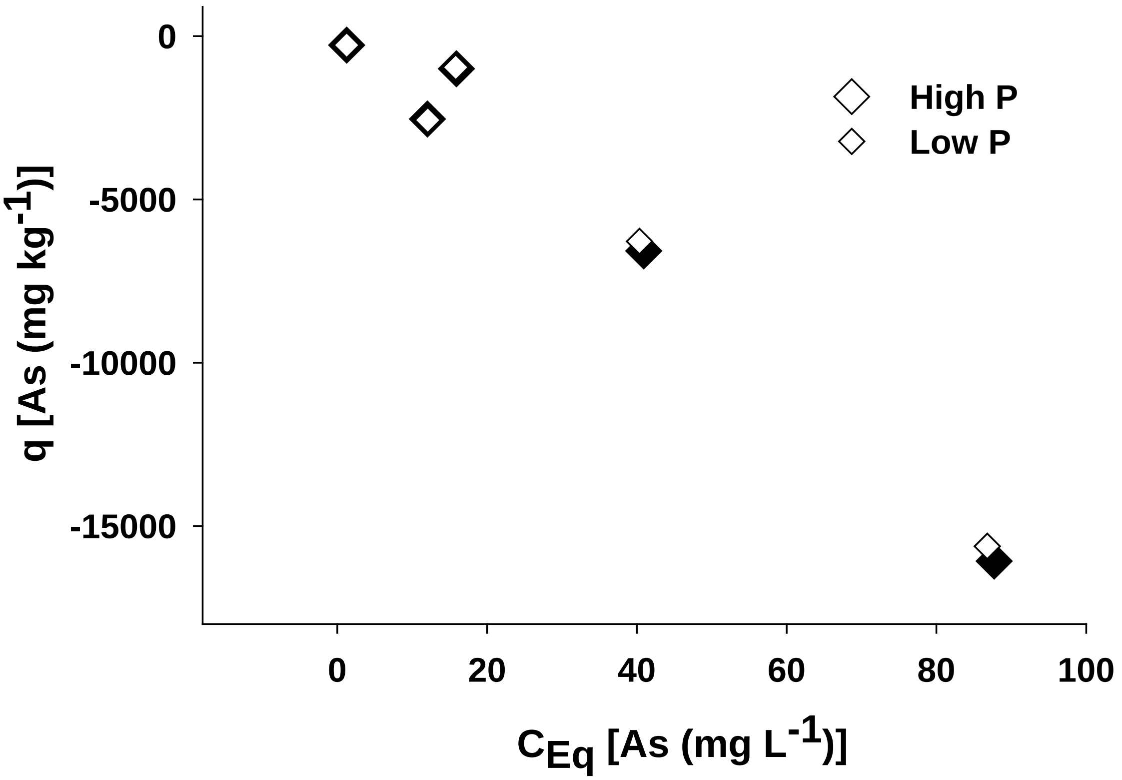

Figure 10. Relationship between sorbed arsenic concentration (q) and equilibrium arsenic concentration (C_{Eq}) from added MSMA in high and low phosphorus (P) soils.

References

Barrow, N.J. 1974. On the displacement of adsorbed anions from soil: 2. Displacement of phosphate by arsenate. Soil Sci. 117:28-33.

Calace, N., A. Di Muro, E. Nardi, B.M. Petronio and M. Poetroletti. 2002. Adsorption isotherms for describing heavy-metal retention in paper mill sludges. Ind. Eng. Chem. Res. 41:5491-5497.

Dickens, R., and A.E. Hiltbold. 1967. Movement and persistence of methanearsonates in soil. Weeds 15(4):209-304.

Garbarino, J., A.J. Bednar, D.W. Rutherford, R.S. Beyer, and R.L. Wershaw. 2003. Environmental fate of roxarsone in poultry litter. I. degradation of roxarsone during composting. Environ. Sci. Technol. 37:1509-1514.

Hingston, F.J. 1981. A review of anion adsorption. P. 51-90. *In* M.A. Anderson and A.J. Rubin (ed.) Adsorption of inorganics at solid-liquid interfaces. Ann Arbor Sci. Publ., Ann Arbor, MI.

Jackson, B.P., J.C. Seaman, and P.M. Bertsch. 2006. Fate of arsenic compounds in poultry litter upon land application. Chemosphere. 65: 2028-2034.

Kuo, S. 1996. Phosphorous. *In* Methods of Soil Analysis Part 3: Chemical methods. Sparks, D.L. (ed.) Soil Sci. Soc. of America. Madison,WI.

Liu, F., A. De Cristofaro, and A. Violante. 2001. Effect of pH phosphate and oxalate on the adsorption/desorption of arsenate on/from goethite. Soil Sci. 166:197–208.

Livesey, N.T., and P.M. Huang. 1981. Adsorption of arsenate by soils and its relation to selected chemical properties and anions. Soil Sci. 131:88–94.

Manning, B.A., and S. Goldberg. 1996. Modeling competitive sorption of arsenate with phosphate and molybdate on oxide minerals. Environ. Sci. Technol. 31:2005-2011.

Markis, K.C., J. Salazar, S. Quazi, S.S. Andra, D. Sarkar, S.B. Bach, and R. Dutta. 2008. Controlling the fate of roxarsone and inorganic arsenic in poultry litter. J. Environ. Qual. 37(3):963-971.

McDonald, M., K. R. Byre, D.M. Miller, and E.G. Edward. 2009. Broiler-litter application history and soil depths effects on arsenic sorption. Soil Sci. 174(12): 661-675.

Peryea, F.J. 1991. Phosphate-induced release of arsenic from soils contaminated with lead arsenate. Soil Sci. Soc. Am. J. 55:1301–1306

Roy, W.R., J.J. Hassett, and R.A. Griffin. 1986. Competitive coefficient for the adsorption of arsenate, molybdate, and phosphate mixtures by soils. Soil Sci. Soc. Am. J. 50:1176–1182.

Rutherford, D., A.J. Bednar, J.R. Garbarino, R. Needdham, K.W. Staver, and R.L. Wershaw. 2003. Environmental fate of roxarsone in poultry litter. Part II. Mobility of arsenic in soils amended with poultry litter. Environ. Sci. Technol. 37:1515-1520.

Sadiq, M. 1997. Arsenic chemistry in soils: An overview of thermodynamic predictions and field observations. Water Air Soil Pollut. 93:117–136.

Smith, E., R. Naidu, and A.M. Alston. 2002. Chemistry of Inorganic Arsenic in Soils II. Effect of Phosphorus, Sodium, and Calcium on Arsenic Sorption. J. Environ. Qual. 31:557-563.

Sposito, G.. 1982. On the use of Langmuir equation in the interpretation of “adsorption” phenomena: The “two surface” Langmuir equation. Soil Sci. Soc. Am. J. 46:1147-1152.

United States Department of Agriculture-Natural Resources Conservation Service (USDA-NRCS), 2007. Soil Survey Laboratory Methods Manual [Online]. Available at ftp://ftp-fc.sc.egov.usda.gov/NSSC/Lab_Methods_Manual/SSIR42_2004_view.pdf (verified 20 January 2009).

US Environmental Protection Agency (US-EPA), 2007. Method 3051a- Microwave assisted acid digestion of sediments, sludges, soils and oils [Online]. Available at http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/3051a.pdf (verified 14 January 2009).

Violante, A., and M. Pigna. 2002. Competitive sorption of arsenate and phosphate on different clay minerals and soils. Soil. Sci. Am. J. 66:1788-1796.

Woolson, E.A., J.H. Axely, and P.C. Kearney. 1973. The chemistry and phytotoxicity of arsenic in soils: Effect of time and phosphorus. Soil Sci. Am. Proc. 37:254–259.

Zhongqui, He, W. Honeycutt, I. A. Tazisong, Z. N. Senwo, and D. Zang. 2009. Nitrogen and phosphorus accumulation in pasture soil from repeated poultry litter application. Communications in Soil Sci. and Plant Anal. 40: 587-598.