

ABSTRACT

OU, LING. Impact of Soil Characteristics on Pesticides Sorption and Speciation, Laboratory Studies and Meta-Analysis (Under the direction of Drs. Travis W. Gannon and Grady L. Miller).

Pesticides, which generate billions of dollars in revenue every year, have increased crop production and yield, but they have also caused environmental and health concerns. Pesticide environmental fate and behavior is closely related to soil and environmental conditions. This research investigated edaphic factors that control key pathways of environmental fate, such as sorption and species transformation. Chapter 2 details how edaphic drivers affect monosodium methyl arsenate (MSMA) sorption and species transformation. Laboratory kinetic studies were conducted at varying soil organic carbon (SOC) levels for two soils in incubation. Biphase As removal was found in all SOC levels, with the first phase of incubation controlled by sorption, and the second phase governed by species transformation. Sandy clay loam soil had faster and more extensive As removal than sand. Soils with higher levels of SOC showed decreased As removal and increased species transformation, and SOC levels were linearly correlated to As removal rates in both phases. Dimethylarsinic acid was generated first, but As(V) was the ultimate product. SOC decreased sorption and increased species transformation in all soils, showing that in high SOC conditions there is more risk for As leaching. These results can assist the EPA re-registration decision on the compound in 2019 and guide management practices. In Chapter 3 a meta-analysis determined how soil properties predict atrazine sorption. The research synthesized 48 scientific publications and 378 observations relating to the topic. The synthesis showed that organic carbon (OC) was the most important parameter in predicting atrazine sorption among OC, pH, silt, clay, and

cation exchange capacity (CEC), while other properties improved model fit. Chapter 4 investigates how land use and soil depth affect atrazine and metolachlor sorption. Soil characterization and sorption isotherms were performed and then followed by a model fit of soil properties with sorption parameters. The results indicated sorption depends on compounds, as well as land use and depth. Particularly, sorption was metolachlor > atrazine, turf = forest > cropland at 0 to 5 cm, but not different at 5 to 15 cm. Soil properties were explored in this research as they relate to sorption. Organic C and CEC were the most significant parameters, with OC alone predicting sorption well (atrazine, $R^2 = 0.93$; metolachlor, $R^2 = 0.79$). When sorption models (Freundlich sorption coefficient K_f and sorption distribution coefficient K_d with OC) for atrazine from Chapter 3 and 4 were compared, meta-analysis showed a similar positive trend, but more variation. Models developed in this research can be used in predicting pesticide sorption at a global and regional scale, but with differing levels of accuracy. This knowledge can help evaluate pesticide environmental risks such as leaching and groundwater contamination, and it can help aid the development of best management practices for different soil conditions.

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Impact of Soil Characteristics on Pesticides Sorption and Speciation, Laboratory Studies and
Meta-Analysis

by
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A dissertation submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

Crop Science

Raleigh, North Carolina

2017

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DEDICATION

To LJ, MMM, and SB, who make it as close to home as it can be.

BIOGRAPHY

Ling Ou, born as a second child at the time of severe execution during China's One Child Policy, was returned to her village in a covered bamboo basket with a rock on the other side of a shoulder pole, as an adopted child.

She grew up playing and working on her family farm with rice paddies, tea, vegetables, pigs, chickens, fish ponds, and more. She found enormous joy in rice transplanting, camellia seed picking, and feeding pigs. Though she was a great caretaker for pigs, her parents valued education, and sent her miles away from the village to the best boarding high school in the region. After that, she moved 22 hours away by train to study Resources and Environmental Science at Northwest A&F University, cultivating her deep-rooted passion for nature and the environment.

Her curiosity and sense of adventure led her to Auburn University in Alabama, USA to pursue a Master of Science in Soil and Environmental Science with Dr. Wes Wood. After 2.5 years studying and acquiring some strange threads of a southern accent, she left sweet home Alabama and headed out to Raleigh, NC, where she is earning a Ph.D. studying Environmental Fate of Chemicals with Dr. Travis Gannon.

ACKNOWLEDGMENTS

I am very thankful for my Crop Science major adviser and co-chair Dr. Travis Gannon, who is motivating, energetic, driven, funny, and one of the most hardworking people I have ever known. I know he has prepared me well to take on challenges in the world. I am also indebted to my Soil Science minor chair, Dr. Matt Polizzotto, who possesses amazingly high emotional intelligence as well as intellectual intelligence, a combination I rarely see within one person. He inspires me to go deeper in (soil) depth, and see things in new perspectives. My minor chair in Statistics, Dr. Consuelo Arellano influenced me greatly by those afternoon conversations and magical coding together (mostly from her). I am immensely thankful for her dedication to my research as well as many other peers' research in College of Agriculture and Life Sciences. Her legacy left footprints in many dissertations, theses, papers, and our statistical part of the brain. I want to thank my co-adviser Dr. Grady Miller, who happily joined our committee and made me read a great book, *The Ascent of Man*. He has given me great advice and enlightened me in our interactions. I can not express enough gratitude to my committee member Dr. Dean Hesterberg, who sparked my deep interests for Environmental Soil Chemistry, and how to use the brain and energy more efficiently. He has no idea how many students have a brain crush on him.

Special thanks go to Khalied Ahmed, DJ Mahoney, Dr. Matt Jeffries, Laney McKnight, Scott Brinton, and Patrick Maxwell, for their support through my program. My thanks also go to the entire faculty who taught me classes or let me teach in their classes. The statistics professors Dr. Justin Post and Bill Swallow have impacted me a lot. I also would like to

thank Dr. Dan Bowman, Ms. Angie Barefoot, and Ms. Kathy Kelly for their support during my graduate degree at our department.

I am grateful for my friends, roommates, and officemates who supported me through my Ph.D. degree. I wouldn't have done this without them. Thank you my dear friends Joe and Catherine S., Janny, Molly, Erika, Shannon, Sean, Angel, Wayne, Manal, Maria, Maia, Clara, Lauren, Leah, Evan, Laleh, Ana, Joe, Jacob, Pete, Phi, Liz, Magara, Ashley, Hui, Baljinder, Jess, Ethan, Jason, and many more.

In addition, the world-class facilities at NC State such as the gym and health center helped me be healthy physically and emotionally. NC state police station, legal service, fire station, library, career center, and international student office helped me go thorough challenges and trained me in different aspects. I am especially thankful for the campus policemen and women who drove me in the rain, open building doors for me, and let me beat them up in RAD (Rape Aggression Defense) training; and the fireman who let me put on their 20 kg suits.

Lastly, I have endless thanks to my family; to my mum and all the spirits that supported her and me; to my brother (a real doctor) and soon-to-be sister-in-law, with best wishes for their new chapter of life and career.

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CHAPTER 1. Literature Review

Pesticides

Pesticide applications have been documented for thousands of years, when people used elemental sulfur and poisonous plants to protect their crops (Ranga Rao et al., 2007), but the production and use of pesticides has increased exponentially worldwide since the twentieth century (Miller, 2002). Global revenue for pesticides reached \$40 billion in 2006 and 2007, with herbicides accounting for 40% of sales. In the United States, pesticide revenue was \$12 billion, and herbicides accounted for 50% (Grube et al., 2011). Around 2.3 million tons of pesticides were applied yearly with 40 % as herbicides in 2006 and 2007 worldwide, and more than 0.5 million tons of pesticides were applied in the United States alone (Grube et al., 2011). Pesticides confer benefits of increased yield and productivity, vector disease control, increased quality of food, and miscellaneous functions for landscape management, but pesticide use also has significant environmental health risks (Aktar et al., 2009).

The most commonly used herbicides were glyphosate, atrazine, and metolachlor in 2007 (Grube et al., 2011), among which atrazine and metolachlor were the most commonly detected herbicides in the environment, specifically stream and ground water (Gilliom, 2007). Herbicide usage became increasingly controversial as environmental detection and contamination increased (Jablonowski et al., 2011; Jin-Clark et al., 2008), and environmental fate of multiple herbicides is investigated to better understand how risks can be reduced. Arsenical herbicides have been controversial compounds in the last decade due to their

transformation to more toxic species and potential contamination to groundwater (USEPA, 2016a). Chemical structures of several herbicides are shown (Figure 1).

MSMA

Monosodium methyl arsenate (MSMA), an economical and efficacious herbicide, is used to control grass and broadleaf weeds (Shaner, 2014). MSMA is currently registered to use for golf courses, sod farms, roadsides, and cotton (USEPA, 2016a). It has a very high water solubility K_s of $1,040,000 \text{ mg L}^{-1}$, and high sorption to soil, particularly the Fe and Al hydroxides, with an average K_{oc} of 7000 mL g^{-1} (Shaner, 2014). MSMA is ionizable with pK_a of 4.1 and 9.02, and it has a very long average field half-life of 180 d (Shaner, 2014).

Concerns about the environmental safety of MSMA caused the United States Environmental Protection Agency (EPA) to propose a phase out of MSMA in 2009, and the use of MSMA on athletic fields, parks, residential lawns, forestry, non-bearing fruit and nut trees, and citrus orchards was banned, while the use on other sites previously mentioned (golf courses, sod farms, roadsides, and cotton) was approved after a modification on the 2009 EPA agreement (USEPA, 2016a). Various pathways can convert MSMA into monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenate [As(V)], and arsenite [As(III)], and the EPA was concerned about MSMA transforming into more toxic inorganic arsenical species which contaminates drinking water (USEPA, 2016a). Chapter 2 of this dissertation focuses on investigations of MSMA kinetics of sorption and species transformation.

Atrazine

Atrazine is the second most widely applied and the most widely detected herbicide in the United States and worldwide (Gilliom, 2007; Grube et al., 2011). Atrazine can be applied on corn, sorghum, fallow land, roadsides, sugarcane, macadamia nuts, conifers, and certain turfgrass species. It controls certain grass weeds and many broadleaf weeds. Atrazine is ionizable as a weak base with a pK_a of 1.7. It has a low water solubility of 33 mg L^{-1} , and the average K_{oc} is 100 mL g^{-1} , low to moderate soil sorption. Persistence of atrazine depends on the environment, with averages of 60 d in field, 335 d in water, and 146 to 159 d under laboratory conditions of biological degradation (Shaner, 2014). Atrazine was first applied to corn in 1958, and by 2015 it was applied to 63% of the 39,000,000 ha of corn production in the United States (U.S. Grains Council, 2016). The long history of usage, large hectares of application, and the aforementioned characteristics of atrazine results in movement to off-target areas such as groundwater and surface water (Sherchan and Bachoon, 2011). Due to concerns about potential environmental harm, many European countries banned Atrazine in the 1990s, and the European Union (EU) instituted a continental ban on the chemical in 2004 (Jablonowski et al., 2011). Chapters 3 and 4 of this dissertation focus on Atrazine characteristics elucidated by different research and its comparison to metalachlor.

Metolachlor

Metolachlor is the third most commonly used herbicide in the United States after glyphosate and atrazine (Grube et al., 2011), and it is the third most frequently detected herbicide

following atrazine and deethylatrazine (Gilliom, 2007). Like atrazine, Metolachlor is used to control certain grasses and broadleaf weeds for a variety of plant species including corn, cotton, peanut, pod crops, potato, safflower, sorghum, soybean, nursery and landscape plantings, and certain turfgrass species. Metolachlor is moderately water soluble with a K_s of 488 mg L^{-1} , and moderate sorbed to soil with average K_{oc} of 200 mL g^{-1} . Metolachlor is non-ionizable, and its half-life is 90 to 150 d in field, 70 d in water, and 67 d for microbial degradation (Shaner, 2014). It was used since the 1970s, and its increasing usage and detection in the environment has caused concerns (Gilliom, 2007; Shaner, 2014). Metolachlor was introduced in the fourth chapter of this dissertation to compare with atrazine on sorption because of its similarities in application, detection, and plant species control. Metolachlor is slightly different from atrazine, however, because metolachlor is non-ionizable.

Glyphosate

Herbicidal activity of glyphosate, the most commonly used herbicide in the world and in the United States, was first reported in 1971 (Shaner, 2014). Glyphosate is unique because it is non-selective for plant species, foliar applied, and can be used to control emerged weeds before planting or pre-harvesting certain crops. It is also formulated for POST control of genetically formulated crops, including corn, soybean, cotton, canola, etc. Glyphosate is a weak acid with pK_a of 2.6, 5.6, and 10.3 (Shaner, 2014). The solubility is very high with $15,700 \text{ mg L}^{-1}$, and the average K_{oc} is $24,000 \text{ mL g}^{-1}$, also very high. The persistence is moderate with average field half-life of 47 d (Shaner, 2014). In 2015, the International

Agency for Research on Cancer classified glyphosate as “probably carcinogenic to humans” in group 2A (Guyton et al., 2015). Glyphosate was not further researched in my studies; however, it warranted mentioning here because it frequently appeared in scientific literature and controversial periodical articles.

Environmental Fate and Behavior

Pesticides applied to the environment can dissipate and degrade through pathways that include transformation, transport, and interaction with plants (Arias-Estévez et al., 2008; Cheng, 1990). Transformation processes include biotic and abiotic degradation; transport pathways include volatilization, spray drift, run-off, leaching, and lateral flow. Pesticide-plant interactions include plant uptake, foliar interception and dissipation, and wash-off. Sorption and retention to soil is another key process in the pathways of pesticides (USEPA, 2016b). In this dissertation, mainly two pathways were discussed, sorption and transformation. Sorption strongly influences pesticide environmental fate and behavior among aforementioned processes (Daniel et al., 2002; Gerstl, 2000; Green et al., 1990). Sorption isotherms were performed to approximate sorption capacity, and sorption parameters were expressed as Freundlich sorption coefficients (K_f), sorption coefficients (K_d), and organic carbon sorption coefficients (K_{oc}). Sorption occurs because of Van der Waal’s forces, hydrogen bonding, hydrophobic bonding, electrostatic interactions (charge transfer, ion exchange, or ligand exchange), covalent bonding or combination of these reactions (Bollag et al., 1992). Chemical degradation was also studied in this dissertation,

particularly for MSMA, as it can transform to more toxic inorganic arsenicals, which is a concern to water contamination.

Impacts of Soil Properties

Soil Organic Carbon

Soil organic carbon (SOC) impacts sorption compounds differently. One study showed atrazine and simazine sorption was proportional to SOC content; however, the sorption of glyphosate and aminomethylphosphonic acid (AMPA) decreased with increasing SOC content (Gerritse et al., 1996). Similarly, other research reported that SOC was a predominant factor controlling atrazine (Coquet, 2003; Daniel et al., 2002; Jenks et al., 1998; Pignatello, 1998; Spark and Swift, 2002; Stevenson, 1972; Worrall et al., 2001) and metolachlor sorption (Kodešová et al., 2011; Westra et al., 2015). The least amount of sorption was observed for soils with the most OC for MMA and DMA, but no quantitative studies with various OC content effects on sorption exist in the past literature, and further sorption studies were needed to determine the impact of OC on MSMA (Shimizu et al., 2011a). Based on this knowledge gap, we investigated the impact of different levels of OC on MSMA sorption to soils. The results are reported in Chapter 2. Chapter 3 and 4 show the correlation between OC and sorption using meta-analysis (atrazine) and laboratory studies (atrazine and metolachlor), respectively. It is possible for SOC to act as a sorbent as well as competing for sorption, depending on compounds present. The specific mechanisms were discussed further in the following chapters of this dissertation.

Pesticide degradation is also affected by the SOC source and associated microorganisms (Dickens and Hiltbold, 1967). For MSMA transformation, methylation and demethylation by microorganisms was impacted by SOC (Cullen and Reimer, 1989; Feng et al., 2005; Frankenberger Jr, 2001; Guo et al., 2016; Shimizu et al., 2011b; Yan et al., 2015). Arsenic species transformation is a major concern for management and regulation of MSMA. Transformation of As from its organic forms (e.g. as MSMA) to inorganic forms results in increased As toxicity, but often decreased As mobility and exposure. Unfortunately, there is limited information about how SOC content influences As species transformation. Research in chapter 2 of this dissertation built off prior results (Mahoney et al., 2015b; Matteson et al., 2014) to quantify As transformation rates and phase conversion upon combination of MSMA and soils with different SOC levels.

Other Soil Properties

Other properties such as pH, soil texture, cation exchange capacity (CEC), and Al/Fe content affect pesticide sorption and species transformation in addition to SOC. For instance, some research concluded that clay, iron oxides, and pH value were the key soil parameters affecting the sorption-desorption of atrazine in soil, among which the ratio of clay to OC especially existed relevance (Huang et al., 2013). The sorption of glyphosate and AMPA increased strongly with Fe and Al content of soils, which indicates that glyphosate and AMPA are mainly sorbed by clay minerals, whereas soil organic matter competes for sorption sites and inhibits sorption. One study concluded that K_d of atrazine was related negatively to both silt and CEC ($r^2 = 0.96$) (Daniel et al., 2002), while the other stated that

effective CEC, exchangeable acidity, exchangeable Al, and clay were useful predictive variables for both atrazine mobility and sorption (Johnson and Thomas Sims, 1998). Soil properties such as pH, CEC, and clay were also found to correlate with microbial activity and pesticide degradation (Huang et al., 2000; Kah et al., 2007). These impacts were not further explored in this research.

Study Approaches

Experimental Studies

Studies of environmental fate and behavior of pesticides typically include abiotic degradation (hydrolysis and photolysis), biotic degradation (aerobic and anaerobic) in soil and water, bioconcentration, sorption, and field dissipation studies (USEPA, 2016c). Our laboratory has conducted studies using greenhouse lysimeters (Mahoney et al., 2015a) as well as other field dissipation studies (Mahoney et al., 2015b) to determine the distribution of pesticides. Two types of laboratory studies were chosen for this dissertation, sorption isotherms and kinetics studies of herbicides. The sorption study was chosen because it was a key process for environmental fate while kinetics studies enabled the transformation rates calculation of As in a soil-water systems. All studies mentioned above were integrated to help determine the transport and transformation of pesticides once they enter the environment.

Meta-Analysis Studies

The second chapter includes a meta-analysis relating atrazine sorption to soil properties.

Meta-analysis is defined as “statistical methods for contrasting and combining results from different studies in the hope of identifying patterns among studies, sources of disagreement among those results, or other interesting relationships that may come to light in the context of multiple studies” (Rothman et al., 2008). It is also defined as “a review that is done systematically, following certain criteria, and the results are pooled and analyzed quantitatively” (Walker et al., 2008). Meta-analysis was adopted by medical research in its early stages (Nordmanna et al., 2012; O'Rourke, 2007; Simpson and Pearson, 1904), and later formalized by modern statisticians (Glass, 1976). Meta-analysis can be used to synthesize many individual studies, improve sample size to make inferences about a larger population, improve precision, and increase statistical power. It can also be used to detect differences among studies, provide evidence in regulatory process, and modify practice, and determine if new studies are needed as well as generate new hypothesis for future studies (Berlin and Colditz, 1999; Walker et al., 2008). The major drawbacks of a meta-analysis include unequal quality of data from individual studies, publication bias, and agenda-driven bias (Walker et al., 2008).

Researchers in agriculture and environmental adopted this method from the medical field (Cresswell, 2011; Li et al., 2016). When investigated in 2016, there were “0” results in several data bases (including Agricola, CAB Abstracts, Web of Science, etc.) with search terms “atrazine”, “sorption”, and “meta-analysis”, which indicated that the meta-analysis

approach for atrazine sorption has not been utilized. Whether a universal correlation between atrazine sorption and soil characteristics exist was of great interest; thus, available literature relating to the impact of soil properties on atrazine sorption was compiled and meta-analysis was conducted on this subject. Sampling soils from all over the world and conducting experiments to determine soil characteristics and sorption parameters would be costly and time consuming; however, meta-analysis enables evaluating data over wide spatial and temporal scales to determine how soil characteristics affect sorption, and make a broader scale inference globally. Meta-analysis approach can be potentially applied to other studies of environmental fate and behavior, with different compounds and environmental conditions.

With the background knowledge acquired, three concerning compounds including MSMA, atrazine, and metolachlor were investigated. The key environmental fate processes such as sorption and species transformation were explored for the aforementioned compounds. Edaphic conditions including SOC, pH, CEC, and soil texture were evaluated as how they affect pesticides sorption and degradation. The research in this dissertation identified that SOC was a key parameter impacting both sorption and species transformation. Soil OC increases sorption for some compounds such as atrazine and metolachlor, but decreases sorption for MSMA and the similar compounds. It also increased species transformation for MSMA, and was identified to have a positive relationship with degradation rates for most compounds as prior research stated (Kah et al., 2007).

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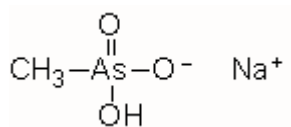
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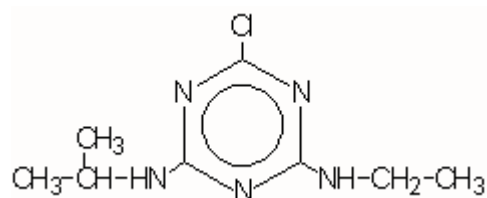
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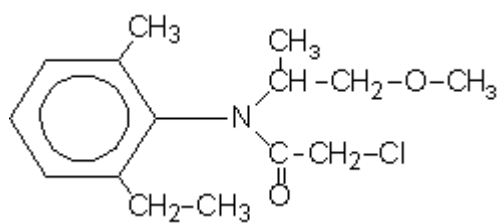
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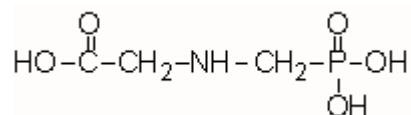
MSMA



Atrazine



Metolachlor



Glyphosate

Figure 1. Chemical structures for MSMA (monosodium methyl arsenate), atrazine, metolachlor, and glyphosate.

Impact of soil organic carbon on MSMA sorption and species transformation

For Submission as a Research Article to *Environmental Science & Technology*

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Abstract

Monosodium methyl arsenate (MSMA), a common arsenical herbicide, is a major contributor of anthropogenic arsenic (As) to the environment. Uncertainty about controls on MSMA fate and the rates and products of MSMA species transformation limits effective MSMA regulation and management. The main objectives of this research were to quantify the kinetics and mechanistic drivers of MSMA species transformation and removal from solution by soil. Laboratory MSMA incubation studies with two soils and varying soil organic carbon (SOC) levels were conducted. Arsenic removal from solution was more extensive and faster in sandy clay loam incubations than sand incubations, but for both systems, As removal was biphasic, with initially fast removal governed by sorption, followed by slower As removal limited by species transformation. Dimethylarsinic acid was the dominant product of species transformation at first, but inorganic As(V) was the ultimate transformation product by experiment ends. SOC decreased As removal and enhanced As species transformation, and SOC content had linear relationships with As removal rates for each soil and reaction phase. These results reveal the importance of edaphic conditions on inorganic As production and overall mobility of As following MSMA use, and such information should be considered in MSMA management and regulatory decisions.

Introduction

Pesticides have been the primary source of anthropogenic As to the environment over the past century in the United States (Onken and Hossner 1996). Inorganic arsenical pesticides, such as lead arsenate, were widely used prior to being banned in 1988 (USEP 1988). Organic arsenical herbicides, including monosodium methyl arsenate (MSMA), disodium methyl arsenate (DSMA), and cacodylic acid, were introduced in the 1950s and are still used today. Prior to 2006, approximately 1,360,777 kg of MSMA or DSMA were used each year (USEPA 2016). MSMA is currently registered for use in cotton and turfgrass (including sod production, golf courses, and roadsides), and its review for reregistration is set to be completed by 2019(OAPTF 2014). However, the Environmental Protection Agency (EPA) has expressed concerns about MSMA use due to As loading to the environment, potential transformation of organic arsenicals to inorganic As species, off-target migration, and subsequent As contamination of groundwater and surface water (USEPA 2016).

After MSMA application, the speciation of As may change, impacting its toxicity and mobility in the environment (Bednar et al. 2002; Feng et al. 2005; Frankenberger Jr 2001; Hiltbold et al. 1974; Tamaki and Frankenberger Jr 1992). Among the four main resultant As species – monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenate [As(V)], and arsenite [As(III)] (Feng et al. 2005; Gao and Burau 1997) – inorganic species As(III) and As(V) are approximately 1-2 orders of magnitudes more toxic than organic species DMA and MMA(U.S. Department of Health and Human Services. 2007), but the organic species are generally less well retained by soil minerals than the inorganic species (Lafferty and Loeppert 2005). Previous research has shown that MMA and DMA demethylated to

inorganic species during a one-year aerobic soil incubation, with the majority of the transformation occurring during the first month (Shimizu et al. 2011a). However, kinetics of As species transformation remain understudied, limiting the ability to accurately quantify As-based risks to human and environmental health following MSMA use (Feng et al. 2005). Specific edaphic factors, particularly soil organic carbon (SOC) content, are often metrics by which pesticide environmental fate is characterized. However, there is a lack of understanding on how SOC may influence the mobility and transformation of MSMA-derived As. Some research has indicated that increased SOC can decrease MMA and DMA sorption to soils, but no clear correlation between SOC content and As sorption has been documented (Shimizu et al. 2011b). Another study concluded that soil substrate composition significantly influenced As mobility and speciation in percolate water following MSMA application; however, although clay content was seen as a driving factor on As downward leaching potential, the presence of SOC (peat) did not significantly change As retention in soils (Feng et al. 2005). Similarly, in one study, As species transformation was enhanced by SOC content (Dickens and Hiltbold 1967), whereas in another study, addition of cellulose depressed the species transformation of organic arsenicals (Gao and Bureau 1997). Given these apparently contradictory findings, research is needed to discern the effect of SOC on As sorption and species transformation within soils.

The objectives of this research were to 1) quantify the kinetics of MSMA species transformation and removal from solution by two soils, and 2) systematically determine the effect of SOC on As sorption and species transformation potential. Aerobic incubation experiments were conducted to examine the timing and mechanistic drivers on MSMA-

derived As cycling within soil-water systems, and results here provide insights for how and where MSMA can be used safely without adversely affecting human and environmental health.

Materials and Methods

Experimental Procedure

A laboratory incubation experiment was conducted with two soils with contrasting textures: Candor sand (sandy, kaolinitic, thermic Grossarenic Kandiodults) and Cecil sandy clay loam (Fine, kaolinitic, thermic Typic Kanhapludults) (Table 1). The Candor sand had 88, 9, and 3% sand, silt, and clay, respectively, a pH of 6.8, and 0.84% SOC. The Cecil sandy clay loam had 48, 24, and 28% sand, silt, and clay respectively, a pH of 5.4, and 2.21% SOC. The citrate-bicarbonate-dithionite (CBD) extractable Fe and As is shown at the same table. Soils were air-dried, ground, and sieved through a 2-mm mesh. Sphagnum peat (SOC source, 49.18% OC, Premier Horticulture, Quakertown, PA) was hydrated using a 1:20 ratio (by weight) of peat:deionized water in volumetric flasks. Following hydration, peat solutions were stirred on an orbital shaker. The pH of the peat solutions was adjusted to the native soil pH with 1 N potassium hydroxide (KOH), and this pH adjustment was repeated daily for two weeks until pH equilibrated. The experiment was a $4 \times 2 \times 10$ full factorial design with four SOC levels, two soil textures, 10 sampling times, and three replications. Sphagnum peat solution (0, 1.25, 2.5, and 5% added OC by weight) was transferred to 50 mL light-impermeable centrifuge tubes (Greiner Bio-One) using a pipette, while a magnetic stirring bar was constantly moving to keep the solution homogenized. Water was added to the centrifuge tubes to bring the total volume of solution to 20 mL. After transferring peat, 5 g of

air-dried sand or sandy clay loam was placed in each centrifuge tube. All centrifuge tubes were capped, thoroughly mixed, and placed on a horizontal shaker to equilibrate for 48 h. After reaching equilibrium, the soil solution was spiked with MSMA (Chem Service, 99.0% purity) to reach concentrations of $1,054 \mu\text{g L}^{-1}$ As, chosen based on typical field application rates. Bottles were hand shaken vigorously for 60 s, and the incubation was started by placing all samples on a horizontal shaker. The laboratory had constant room temperature of 23°C .

Samples were collected at 30 min, 12 h, 1, 3, 5, 7, 10, 14, 21, and 28 d after MSMA addition. At each sampling time, tubes were centrifuged, and 20 mL syringes were used to collect aqueous samples. Samples were filtered (25 mm with $0.2 \mu\text{m}$ nylon membrane, VWR International; needles, BD PrecisionGlide, $1.2 \text{ mm} \times 40 \text{ mm}$) and collected into VACUETTE sampling tubes (9 mL, Greiner Bio-One). Samples were stored in a refrigerator at 4°C before analyses. At each sampling time, pH was measured, and dissolved oxygen (DO) was monitored with a Foxy-R probe and NeoFox spectrophotometer (Ocean Optics). The DO ranged from 5.9 - 8.6 ppm (Figure S1), indicating that the incubation environment stayed aerobic throughout the experiments. pH values remained relatively constant for all treatments during the experiments, at 6.8 – 7.2 for the sand incubations and 5.4 – 5.8 for the sandy clay loam incubations (Figure S2), values in between the pK_a values of MSMA (4.1 and 9.02) (Senseman and Armbrust 2007).

Sample Analyses

The VACUETTE tubes with filtered liquid samples were subsampled into three different tubes/vials to measure total dissolved As, dissolved As species, and dissolved organic carbon

(DOC). Samples for total As were acidified using 2% nitric acid and analyzed using inductively coupled plasma-mass spectrometry (ICP-MS, detection limit for As of $0.1077 \mu\text{g L}^{-1}$) in the University of North Carolina, Biomarker Mass Spectrometry Facility (Chapel Hill, NC). Concentrations of dissolved As species were measured using high-performance liquid chromatography coupled with ICP-MS in the same facility, and the four dominant As species – MMA, DMA, As(V), and As(III) – were quantified. Comparison between the total dissolved As and the summation of the four dominant species demonstrated 80-120% recovery of total As during speciation analysis. Dissolved organic carbon (detection limit: 0.5 mg L^{-1}) was analyzed as total non-purgeable organic carbon on a Shimadzu TOC-V analyzer (Shimadzu Corporation, Japan) in the Environmental and Agricultural Testing Service Laboratory at North Carolina State University (Raleigh, NC).

Statistical Analyses

Data analyses were performed using SAS 9.4 (Cary, NC). Analysis of variance was conducted for response variables including total dissolved As and As species of MMA, DMA, As(V) and As(III), with the explanatory variables of time, soil texture, and SOC. Regression analyses of time and total dissolved As were performed by SigmaPlot 12.5 (SyStat Software Inc. Chicago, Illinois), and the piecewise linear regression functions (Vieth 1989) with different separation points were used to model the temporal trends of total dissolved As. Rates of As removal from liquid to solid phases were calculated based on the slopes of the piecewise linear regression fits in SAS.

Results and Discussion

Arsenic Removal from Solution

Throughout the 28-d experiments, 81-95% of total As was removed from solution in the sand incubations, and 98-99% of the As was removed in the sandy clay loam incubations (Figure 1). Arsenic removal occurred much faster in the sandy clay loam incubations compared to the sand incubations. For instance, after 12 h, 73-88% of introduced As was removed by the sandy clay loam, but only 9-20% of the As was removed by the sand. In addition, it took 21-28 days for the sand to remove 90% of the As, whereas the sandy clay loam only took 3-5 days. Greater As removal in the sandy clay loam system was likely due to the higher clay content of the sandy clay loam, which had higher specific surface area and Fe/Al/Mn (hydr)oxides to which As could readily adsorb (Akkari et al. 1986; Dickens and Hiltbold 1967; Feng et al. 2005; Shimizu et al. 2011b).

Arsenic removal in both soil systems was biphasic, with initially fast removal, followed by slower As removal from solution (Figure 1), consistent with previous research (Fuller et al. 1993; Raven et al. 1998; Shimizu et al. 2009; Shimizu et al. 2011b). Piecewise linear regression was used to define the temporal domains and rates of As removal for each soil system (Figure 1 and Table 2). Arsenic removal kinetic separation points were observed at 9 ± 1 d for the sand incubations and 65 ± 7 min for the sandy clay loam incubations, and across the two kinetic domains, the As removal rate decreased 3-35 times in the sand system and 2,325-6,350 times in the sandy clay loam system (Table 2). Arsenic removal was 214-326 times faster in the sandy clay loam incubations than the sand incubations within the first kinetic domain, but removal was slightly faster in the sand incubations within the second

kinetic domain. The biphasic nature of As removal from solution could be attributed to 1) sorption sites being quickly filled with As species at the beginning of the experiments, followed by slowing sorption due to fewer available sorption sites, 2) transition to diffusion-dominated controls on As sorption into the interiors of soil aggregates or sorption sites of different reactivity, and/or 3) sorption affinity changing as MMA was converted to other As species with a differing affinities for soil mineral surfaces (Fuller et al. 1993; O'reilly et al. 2001; Shimizu et al. 2011b), as discussed below.

Arsenic Species Transformation

Species transformation impacted the fate of As during the 28-day soil incubations. In solution, MSMA($K_s \sim 1,040,000 \text{ mg L}^{-1}$) readily dissociates to MMA, which represented the sole As species observed at the initiation of the experiments (Figures 2 and 3). Throughout the incubation experiments, dissolved MMA concentrations progressively decreased by 93-99% in the sand incubations and 99% in the sandy clay loam incubations, while DMA, As(V), and As(III) concentrations increased. The sum concentrations of transformed As species [DMA, As(V), and As(III)] peaked around day 5 across all soil treatments, after which concentrations declined (Figures 2 and 3). In general, DMA was the predominant transformation product for the first 14 d, with its concentrations peaking around 5 d. Although total As concentrations were low at the latter stages of the incubations, As(V) became the dominant species of transformation in most treatments, and it peaked in concentration around 21 d (Figures 2, 3, S3 and S4). As(III) was detected at low concentrations (Figures 2 and 3), but its relative contribution to the total As speciation was important only in the latter stages of some sandy clay loam treatments (Figure S4).

Prior research using 70-day laboratory incubations (Gao and Bureau 1997), one-year laboratory incubations (Shimizu et al. 2011a), and 8-week greenhouse lysimeter studies (Mahoney et al. 2015) has identified As(V) as the predominant product of As species transformation following MSMA or MMA introduction to soils, in agreement with our end-of-experiment results. However, our study also reveals the importance of As-species intermediaries, as well as the influence of edaphic conditions on the timing and extent of As(V) production and the overall mobility of As. MMA sorption and biologically controlled methylation to DMA and demethylation to As(V) remove it from solution, and this species transformation governs the overall sorption affinity of As, with increased methyl content generally associated with decreased sorption (Lafferty and Loeppert 2005; Shimizu et al. 2011a). Therefore, DMA production increased the concentrations of As transformation products in the first 5 d of all incubation treatments, whereas decreasing concentrations of DMA and other As transformation products after 5 days of incubation might be attributed to production of inorganic As species, which possess a higher sorption affinity to soils. Observations of As(III) within the sandy clay loam incubations may be a consequence of As release/transformation in reducing soil microsites, given that the bulk systems remained aerobic (Figure S1). Finally, it is also important to note that the aqueous As species distributions may differ from the solid-phase distributions, due to As sorption affinity differences associated with different As species, soil textures, and SOC levels (Lafferty and Loeppert 2005).

Effect of SOC on As Removal from Solution and Species Transformation

For both soils, overall As removal from solution was lessened as SOC increased, and this inverse relationship of SOC content and As removal was more pronounced in the sand incubations than the sandy clay loam incubations (Figure 1). For instance, at day 5 (when As transformation product concentrations were at a maximum), 56, 44, 36, and 27% of the total As was removed from solution in incubations with 0, 1.25, 2.5, and 5% SOC added to sand, respectively; for the sandy clay loam incubations, 95, 93, 90, and 89% of the initial As was removed with 0, 1.25, 2.5, and 5% SOC additions, respectively. These results agree with previous research, which showed that increasing SOC decreased inorganic As sorption to iron oxides, soils, and sediments (Bauer and Blodau 2006; Grafe et al. 2002; Harvey et al. 2002; Kalbitz and Wennrich 1998). However, our results differed from other research, in that peat did not significantly change As sorption in soil (Feng et al. 2005) or no clear correlation between OC content and MMA and DMA sorption was observed (Shimizu et al. 2011b). Although total As removal decreased with increasing SOC, SOC effects on removal rates varied between the two temporal kinetic domains for each soil. In the first domain, as SOC increased, the As removal rate decreased linearly (Figure 4, a and c). Compared to the 0% SOC treatment, 1.25, 2.5, and 5% SOC treatments decreased the As removal rates by 17, 39, and 46% in the sand incubations and 20, 24, and 28% in sandy clay loam incubations, respectively (Table 2). However, in the second kinetic domain, the As removal rates increased as SOC increased (Figure 4, b and d). Compared to the 0% SOC treatment, 1.25, 2.5, and 5% SOC treatments increased the As removal rates by 196, 400, and 307% in the

sand incubations and 58, 75, and 118% in the sandy clay loam incubations, respectively (Table 2).

Finally, in addition to impacting the amount and rates of total As removal from solution, SOC additions also induced more As species transformation throughout each stage of the incubations with both soils (Figure 2 and 3). For instance, at day 5, when the maximum concentrations of transformed As species were observed in all incubations, the sum of the species of DMA, As(V), and As(III) in solution was 44, 78, 148, and 156 $\mu\text{g L}^{-1}$ for the sand incubations (Figure 2, a-d), and 21, 25, 38, and 67 $\mu\text{g L}^{-1}$ for the sandy clay loam incubations (Figure 3, a-d), for 0, 1.25, 2.5, and 5% SOC treatments, respectively. Increasing SOC was also associated with a higher As(V) concentrations, especially at later incubation times. At day 21, As(V) concentrations peaked to 0, 2, 53, and 217 $\mu\text{g L}^{-1}$ in the sand incubations (Figure 2, e-h), and 3, 2, 21, and 22 $\mu\text{g L}^{-1}$ in the sandy clay loam incubations (Figure 3, e-h), for 0, 1.25, 2.5, and 5% SOC treatments, respectively.

Processes Governing As Cycling and Removal from Solution

Both abiotic and biotic processes controlled As cycling and removal from solution. Arsenic sorption, the main abiotic process governing As removal throughout the experiments, was impacted by SOC, soil texture, and As species transformation. Increasing SOC decreased sorption, which could be due to 1) organic carbon competition for As binding sites on soil minerals, 2) soluble complexation of As to DOC (perhaps through bridged As-Fe-DOC complexes), preventing As sorption (Liu et al. 2011), and/or 3) SOC-induced changes to redox chemistry influencing sorbent surfaces and As speciation (Wang and Mulligan 2006). Our data show that DOC increased with SOC additions (Figure S5), supporting competition

or soluble complexation models as the key SOC-based factors maintaining As in solution. In contrast, although redox reactions and pH are important factors impacting As sorption (Bauer and Blodau 2006; Lafferty and Loeppert 2005; Wang and Mulligan 2006), data collected showed that DO and pH had minimal variation across our incubation times (Figures S1 and S2), and therefore these confounding variables are less likely to have caused the SOC-driven sorption differences observed in our experiments. In addition to SOC content, soil texture also played an important role in sorption, as As removal in the sand incubations was less compared to removal in the sandy clay loam incubations. Finally, species transformation also influenced sorption by changing the sorption affinity of As species, with sorption of MMA and DMA less extensive than sorption of As(V) and As(III) (Lafferty and Loeppert 2005). Besides sorption, microbially mediated As methylation and demethylation (Cullen and Reimer 1989; Feng et al. 2005; Frankenberger Jr 2001; Shimizu et al. 2011a; Yan et al. 2015) also influenced As cycling and removal from solution in our experiments. The amount of SOC available for microorganisms might have had a direct effect on transformation rates, as previous research (Dickens and Hiltbold 1967) suggested. The magnitude and extent of As species transformation are dependent on substrate, with peat amendments to soils stimulating faster transformation of MMA (Feng et al. 2005). Although some research has found that cellulose supplementation depresses As demethylation rates, the specific carbon source may have a significant effect (Gao and Burau 1997). In our experiments, since more As was in the solution with higher SOC, there was more accessible As for microorganisms, which likely allowed for higher rates of As species transformation. Along these lines, there was more

species transformation in the sand incubations as compared to the sandy clay loam incubations, probably due to lower sorption of As onto the sand.

The abiotic sorption and biotic species transformation processes co-occurred in the soil-water systems, influencing each other and the biphasic pattern of As removal observed in our experiments. In the first portions of the incubations, As concentration profiles were driven by sorption of MMA, with specific removal rates governed by soil texture and SOC content. However, as the experiments progressed, species transformation played a larger role in influencing As concentrations, ultimately converting As to As(V) and resulting in continued but slower As removal from solution due to the enhanced sorption affinity of As(V) over organic As species. Thus, SOC decreased As removal rates within the first kinetic domain by limiting sorption, but because the second domain was driven by species transformation, incubations with higher As concentrations in solution (e.g. due to higher SOC or low-surface-area sandy soil) enabled greater microbially induced As species transformation and higher As removal rates.

Environmental Implications

Prior research has demonstrated that upon MSMA application to agricultural soils, As is tightly bound within the soil-plant-water system (Mahoney et al. 2015; Matteson et al. 2014), but uncertainty about the drivers, rates and products of MSMA species transformation has limited effective management of the commonly used herbicide. Our research revealed that 81-99% of As was removed from solution during 28-day MSMA incubations with sand or sandy clay loam. Biphasic removal of As from solution was due to a confluence of abiotic sorption and biotic species transformation processes, with the rates and products of species

transformation depending on soil type and organic carbon content. In general, increasing SOC content decreased the amount of total As removed by soil and increased production of As(V) in solution. These results raise concerns with use of MSMA in sandy and high-SOC soils, as such conditions increase the the overall mobility of As and promote transformation of MSMA to more toxic inorganic As species. Accordingly, such factors should be taken into consideration on MSMA labeling and regulatory/reregistration decisions in order to meet the goal of sustainable and environmentally-responsible MSMA use.

ASSOCIATED CONTENT

Supporting Information

Associated content in support of the main manuscript includes five figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGEMENTS

We thank Dr. Dean Hesterberg for providing peat hydration methods, Longshaokan Wang and Kaitlyn Hamlett for providing statistical assistance, and Pete Cable and Guillermo

Ramirez for analytical assistance. This research was funded by the NC State University Center for Turfgrass Environmental Research and Education.

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Figures and Tables

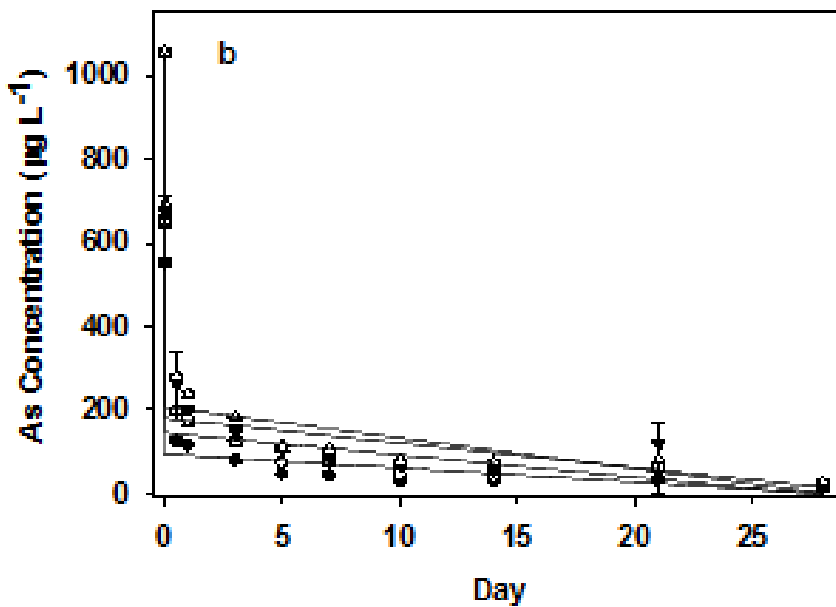
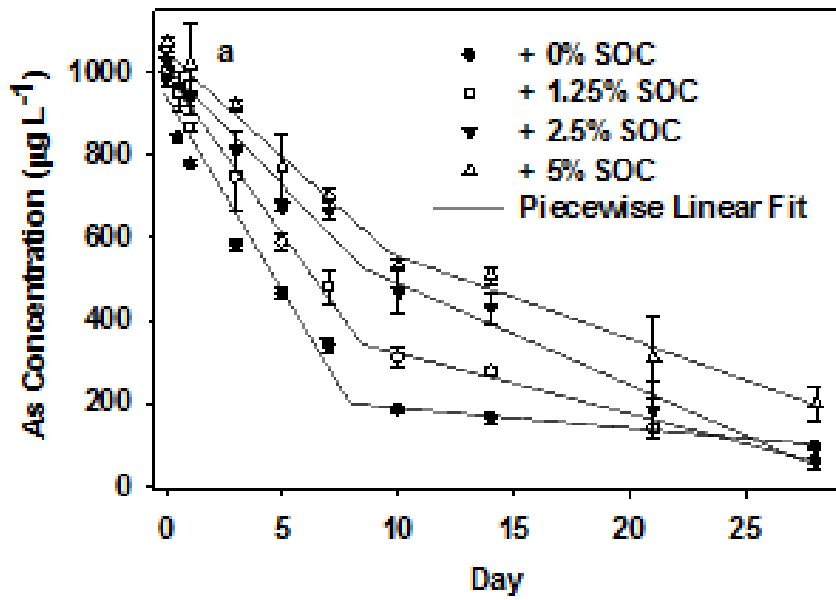


Figure 1. The temporal trend of total dissolved As concentrations for (a) Candor sand and (b) Cecil sandy clay loam, given addition of 0, 1.25, 2.5, or 5% soil organic carbon (SOC) as peat. Error bars represent standard deviation of triplicate samples, and lines represent piecewise linear regression fits of the observed data.

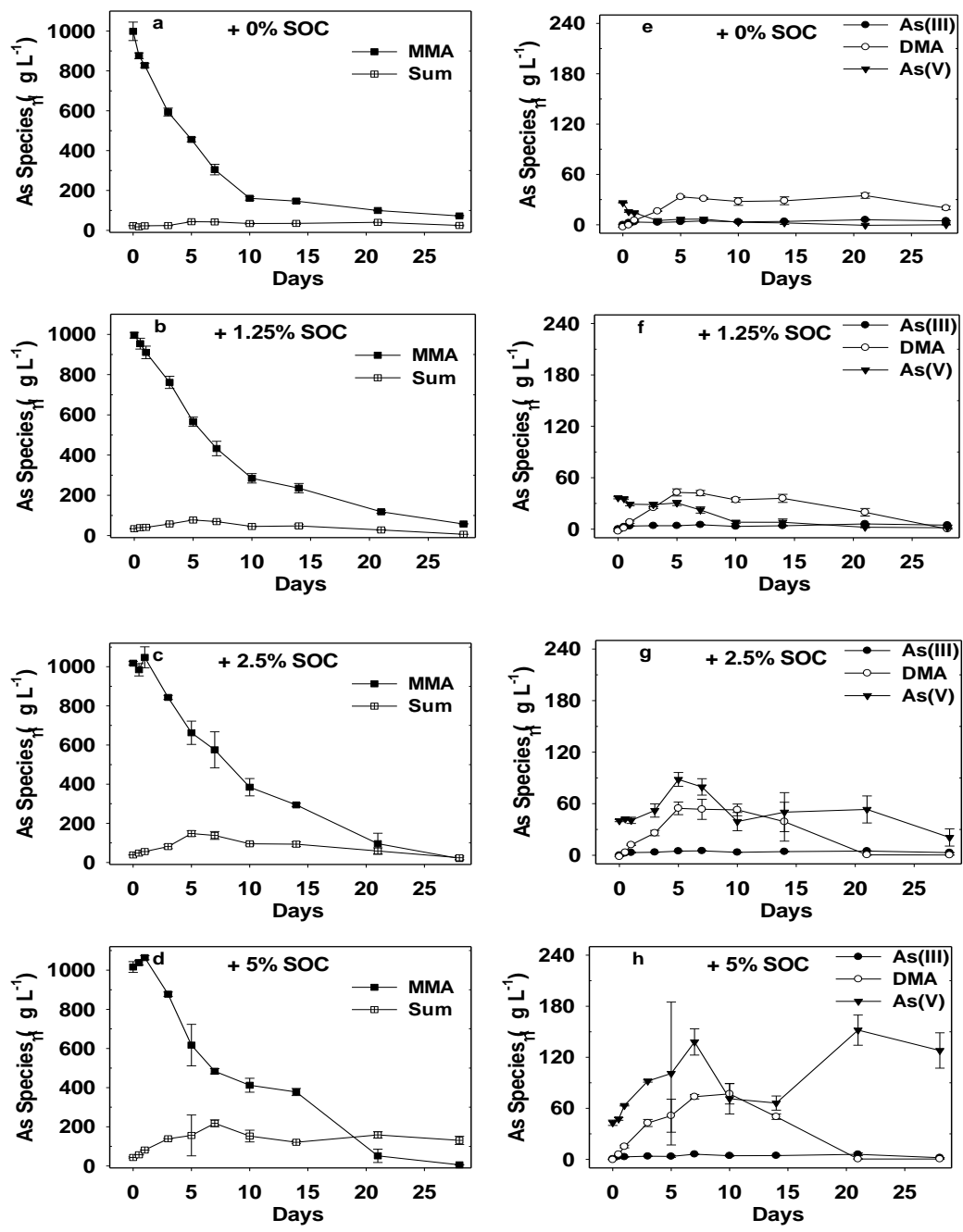


Figure 2. Dissolved As species concentrations as a function of time for Candor sand and different SOC additions. (a-d) Concentrations of monomethylarsonic acid (MMA) and the sum of transformed As species [As(III), dimethylarsinic acid (DMA), and As(V)]. (e-h) Concentrations of As(III), DMA, and As(V). Error bars represent standard deviation of triplicate samples.

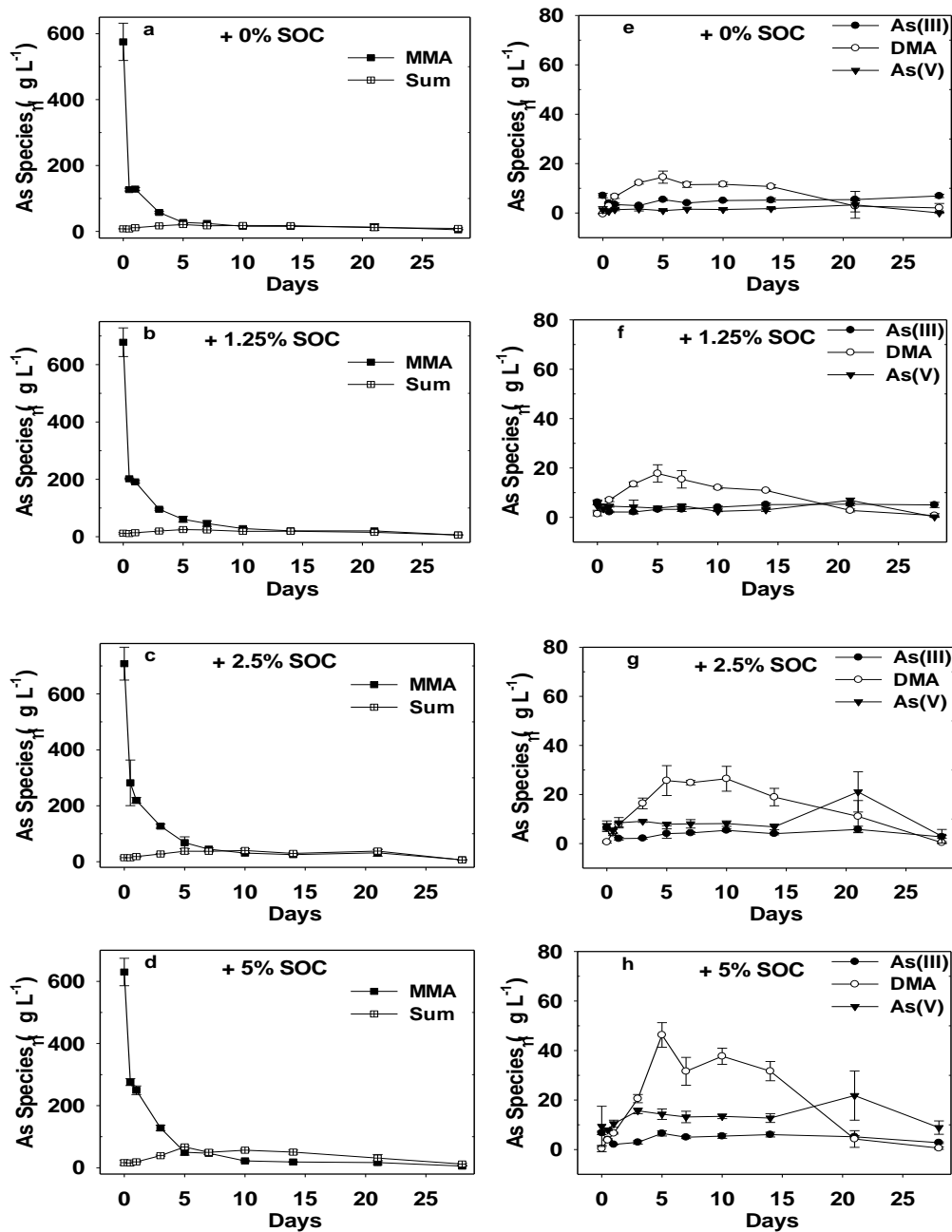


Figure 3. Dissolved As species concentrations as a function of time for Cecil sandy clay loam and different SOC additions. (a-d) Concentrations of monomethylarsonic acid (MMA) and the sum of transformed As species [As(III), dimethylarsinic acid (DMA), and As(V)]. (e-h) Concentrations of As(III), DMA, and As(V). Error bars represent standard deviation of triplicate samples.

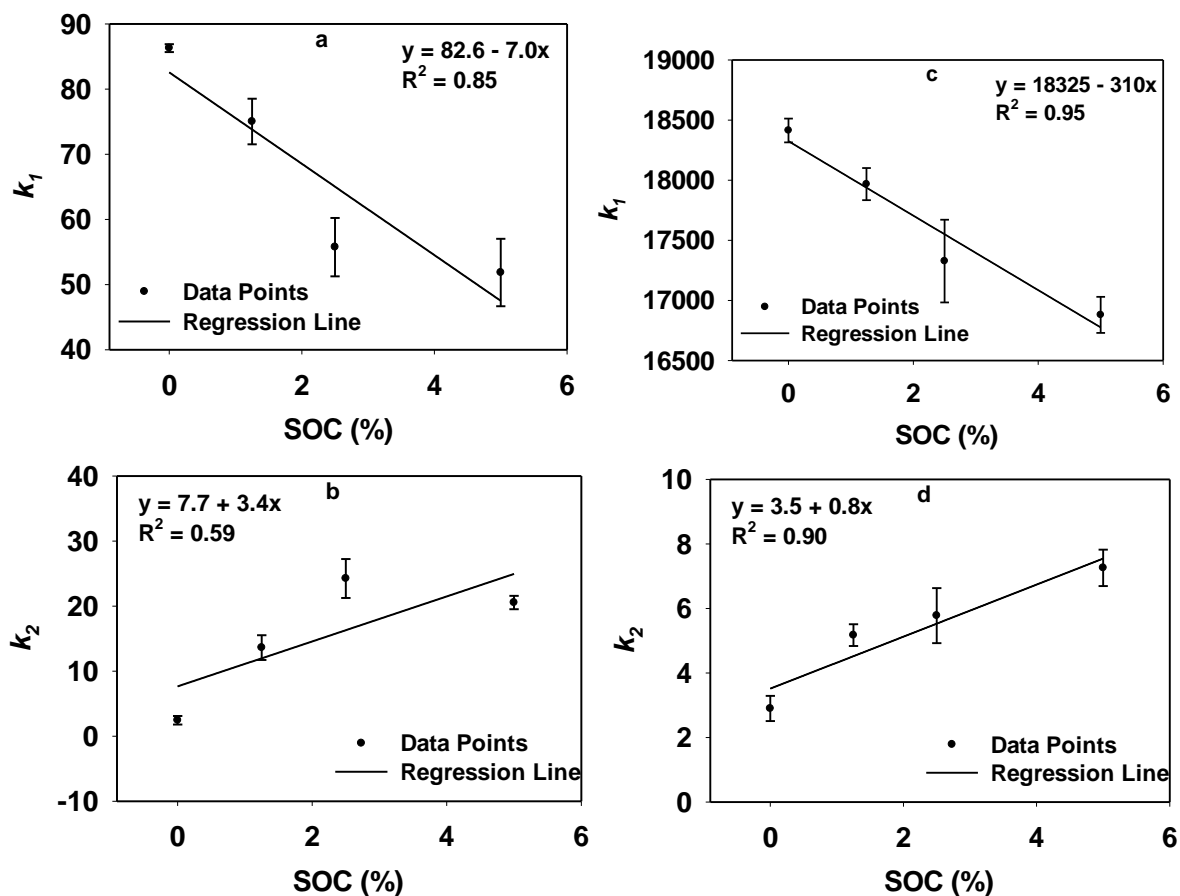


Figure 4. Arsenic removal rates as a function of SOC (%) content for (a-b) Candor sand and (c-d) Cecil sandy clay loam incubations. Top panels represent the first kinetic domain of As removal (k_1), dominated by MMA sorption. Bottom panels represent the second kinetic domain of As removal (k_2), impacted by As species transformation. k_1 and k_2 are the negative slope of the piecewise linear fits shown in Figure 1. Error bars in data points represent standard deviation of rates calculated from triplicate samples. The equation shows the linear regression fit with R^2 as the coefficient of determination.

Table 1. Chemical and physical properties of soils used in incubation experiments.

Soil Series	Soil texture				Extractable elements ^b			
	Sand	Silt	Clay	Class	pH	SOC ^a	Fe	As
	------(%)-----					(%)	-----(mg kg^{-1})---	
Candor	88	9	3	sand	6.8	0.84	2,951	3
Cecil	48	24	28	sandy clay loam	5.4	2.21	12,510	13

^aSOC: soil organic carbon.

^bCitrate-bicarbonate-dithionite (CBD) extraction

Table 2. Arsenic removal rates and kinetic domain separation points for Candor sand and Cecil sandy clay loam incubations, given different additions of soil organic carbon.

SOC ^b (%)	As Removal Rate ^a		Separation Point ^d (d)	R ^{2e}
	Domain 1 (k_1) ^c -----($\mu\text{g L}^{-1} \text{d}^{-1}$)-----	Domain 2 (k_2) ^c		
Candor (sand)				
0	86.3±0.6	2.4±0.7	7.97	0.976
1.25	75.0±3.5	13.6±1.9	8.45	0.994
2.5	55.8±4.5	24.3±3.0	8.60	0.989
5	51.8±5.2	20.6±1.0	9.69	0.990
Cecil (sandy clay loam)				
0	18,414.4±99.1	2.9±0.4	0.04	0.995
1.25	17,968.3±133.4	5.2±0.3	0.05	0.989
2.5	17,327.3±344.2	5.8±0.8	0.05	0.979
5	16,879.6±150.2	7.3±0.6	0.05	0.982

^aThe rate equals the negative slope of the regression line in Figure 1.

^bSOC is the abbreviation for soil organic carbon.

^cTwo domains were observed for both soils, with rates k_1 and k_2 .

^dSeparation point is where the linear pieces connect.

^eThe R² is the coefficient of determination, showing the goodness of model fit.

The supporting information for
CHAPTER 2. Impact of soil organic carbon on MSMA sorption and
species transformation

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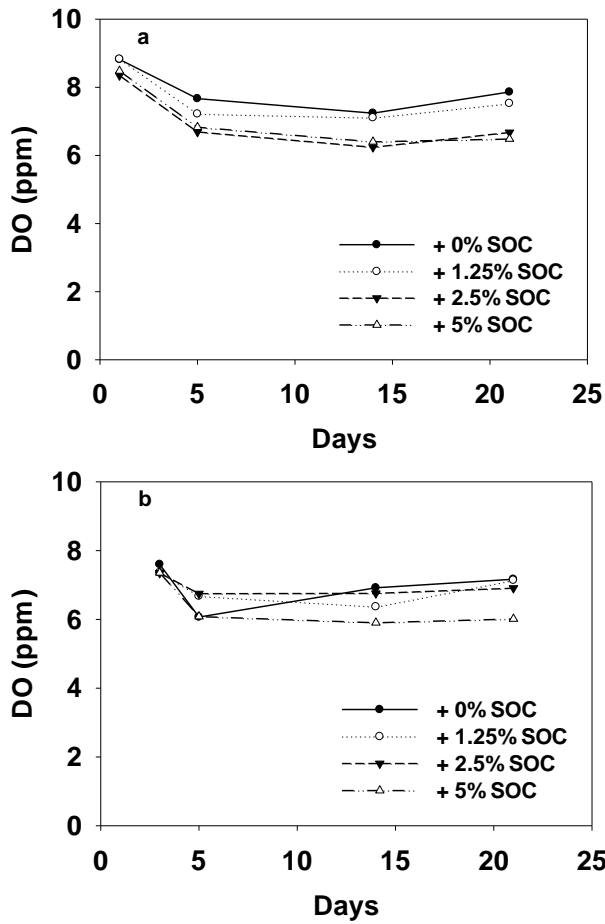


Figure S1. The temporal trend of DO (dissolved oxygen) in (a) Candor sand and (b) Cecil sandy clay loam incubations, with different soil organic carbon (SOC) additions. The reference DO in the laboratory atmosphere ranged from 8.6-9.3 ppm.

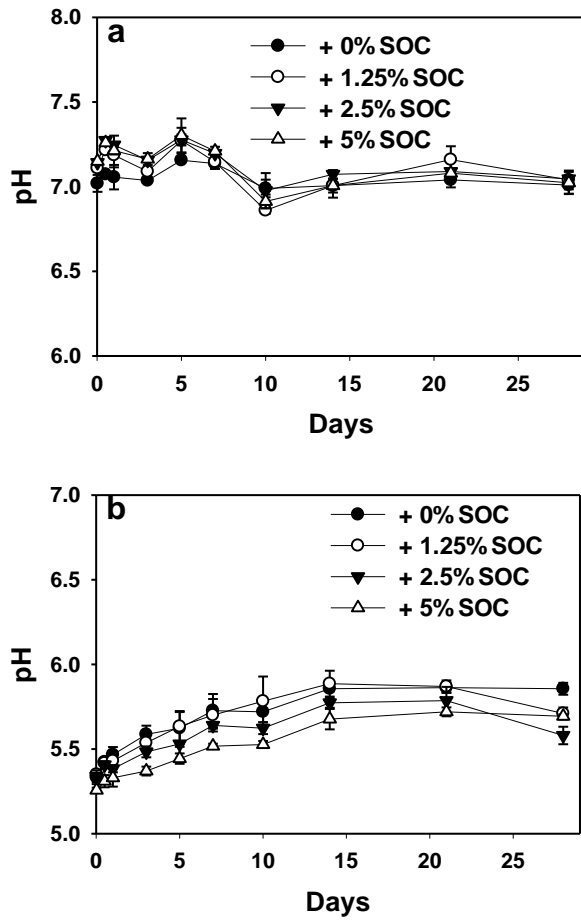


Figure S2. The temporal trend of pH in Candor sand (a) and Cecil sandy clay loam (b) incubations, with different soil organic carbon (SOC) additions. Error bars represent standard deviation of triplicate samples.

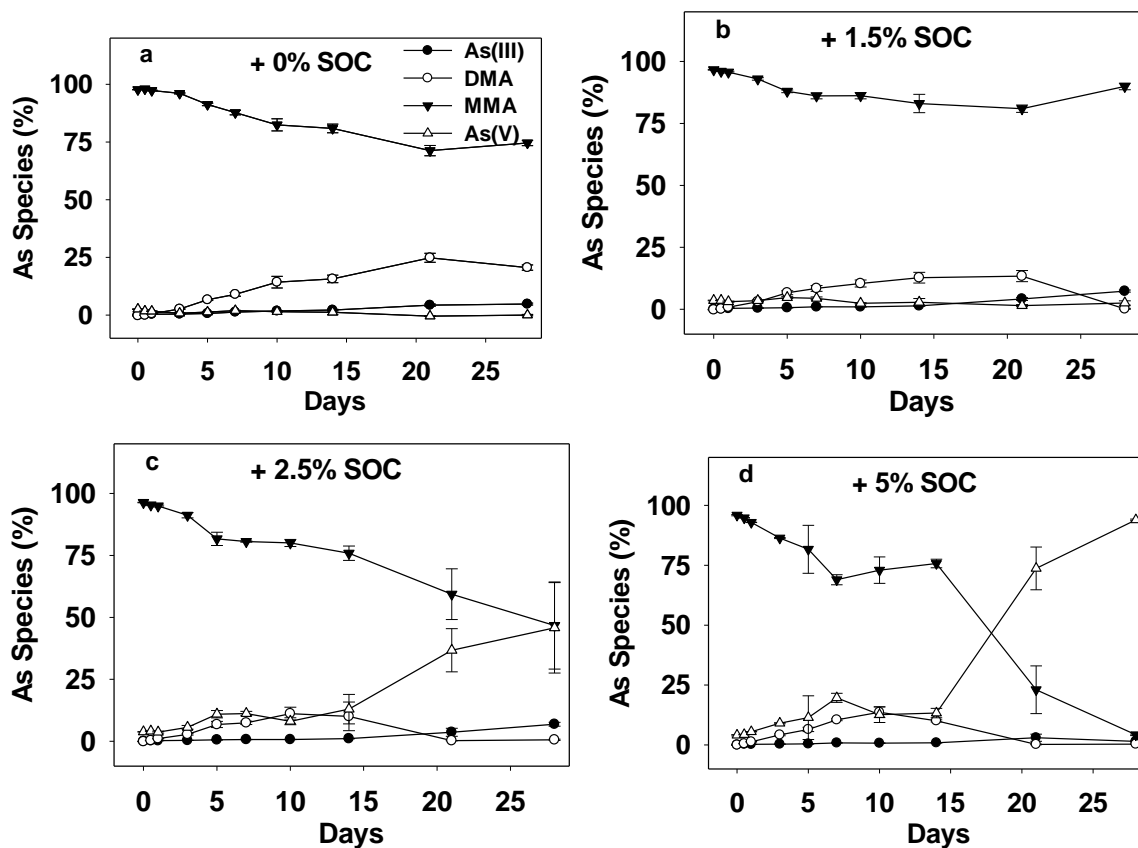


Figure S3. The temporal trend of dissolved As species composition (%) in Candor sand incubations, with different soil organic carbon (SOC) additions: (a) 0% SOC, (b) 1.25% SOC, (c) 2.5% SOC, and (d) 5% SOC. Error bars represent standard deviation of triplicate samples.

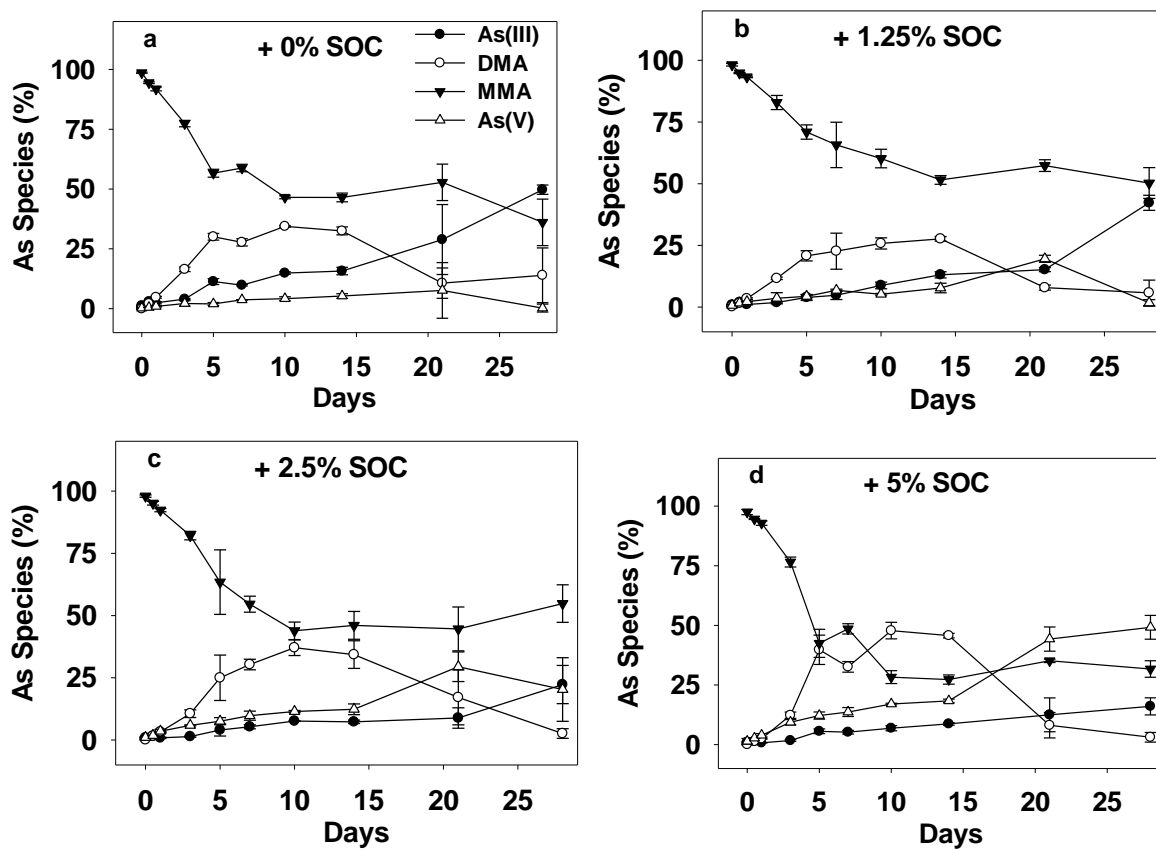


Figure S4. The temporal trend of dissolved As species composition (%) in Cecil sandy clay loam incubations, with different soil organic carbon (SOC) additions: (a) 0% SOC, (b) 1.25% SOC, (c) 2.5% SOC, and (d) 5% SOC. Error bars represent standard deviation of triplicate samples.

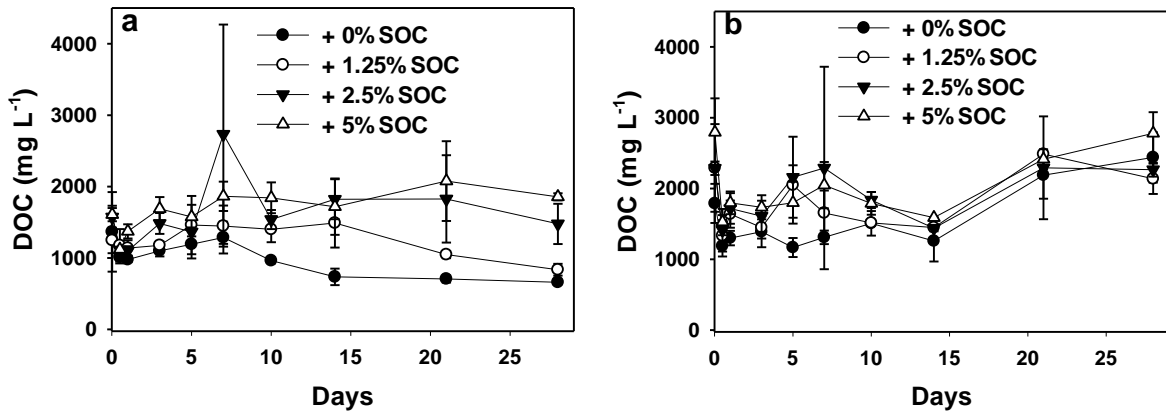


Figure S5. The temporal trend of dissolved organic carbon (DOC) concentrations in (a) Candor sand and (b) Cecil sandy clay loam incubations, with, with different soil organic carbon (SOC) additions. Error bars represent standard deviation of triplicate samples.

CHAPTER 3. Predicting Atrazine Sorption from Soil Properties: A Meta-Analysis

For submission as a technical report to Journal of Environmental Quality

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Abbreviation List

AIC, Akaike's information criterion; CEC, cation exchange capacity; C_p , Mallows's C_p ; CV, coefficient of variation; N or n, number of observations; NA, not available; N miss, number of missing observations; K_d , sorption distribution coefficient; K_f , Freundlich distribution coefficient; K_{oc} , soil organic carbon sorption coefficient; OC, organic carbon; P, P value; r, Pearson correlation coefficient; R^2 , coefficient of determination; SE, standard error

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Core Ideas:

- Meta-analysis was used to determine what soil properties affect atrazine sorption
- Organic carbon had the highest correlation with atrazine soil sorption
- Other properties (texture, depth, pH, cation exchange capacity) improved model fit
- The meta-analysis models showed similar trends with experimental study models
- Meta-analysis models had more variation than experimental study models

Abstract

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is one of the most widely used herbicides worldwide and groundwater contamination is of great concern, especially in certain soil and environmental conditions. Sorption of atrazine to soils plays an essential role in atrazine environmental fate and behavior. A quantitative meta-analysis was conducted to characterize soil properties and land use affect atrazine sorption. The meta-analysis synthesized this effect via models built using 378 previous observations published from 1985 - 2015. A supplemental experimental study was conducted to characterize atrazine sorption and was compared to meta-analysis results. The meta-analysis indicated that organic carbon (OC) was the most important parameter to estimate atrazine sorption, followed by pH, soil depth, silt, and clay, while cation exchange capacity (CEC) was not significant. Meta-analysis and experimental study models were developed between OC and Freundlich sorption coefficient (K_f) and sorption distribution coefficient (K_d). The meta-analysis models followed similar trends compared to experimental study models, but with large variation ($R^2 = 0.20$ and 0.24 for K_f and K_d , respectively). Organic carbon was highly correlated with K_f and K_d in experimental study models ($R^2 = 0.93$ and 0.92 , respectively), indicating that this parameter accurately predicts sorption within a region. Models developed in this research via meta-analysis may be used to predict atrazine sorption for a general trend globally, but more accurate prediction requires specific regional establishments of models through experimental study.

Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), the second most widely applied herbicide in the world, was registered in the United States in 1959 for broadleaf and grass weeds control (Shaner, 2014). It is an efficacious and economical option (Hong-Jian and JIANG, 2010; Huang et al., 2003), applied in various specialty crops, roadside, conifers, to some established turfgrass stands, and over extensive agronomic crops such as corn, sorghum, and sugarcane (Shaner, 2014). Notably, corn was grown on 36,000,000 ha in the United States in 2015 (USDA, 2017), and 60 - 70% of this acreage was treated with atrazine (Armel et al., 2003; Mitchell, 2014). However, atrazine is mobile and yet persistent in the environment, which is due in part to its nature as a weak base with a pK_a of 1.7, water solubility of 33 mg L^{-1} , and its half-life of 335 d in water, 146 – 159 d under laboratory conditions in loam soil, and 60 d under field conditions on average (Shaner, 2014). Its long use history, extensive application, and its aforementioned characteristics result in movement to and detection in off-target areas such as groundwater and surface water (Sherchan and Bachoon, 2011).

Atrazine is the most frequently detected pesticides in freshwater sources in the United States, and it is observed in the majority of drinking water treatment plants (Benotti et al., 2008; Gilliom et al., 2006). Concerns over drinking water contamination led to severe restrictions and countrywide bans in European countries such as Germany and Italy in 1991, followed by a continental ban from the European Union in 2004 (Jablonowski et al., 2011). Atrazine has been detected in rainwater (Bossi et al., 2002; Brun et al., 2008; Goolsby et al., 1997; Sanusi

et al., 2000), fog, ambient air, arctic ice, and seawater (Chernyak et al., 1996; Glotfelty et al., 1987). It disrupts hormones that regulate ovulation of fish and amphibians (Rohr and McCoy, 2010; Solomon et al., 2008), and it is toxic to aquatic organisms (Botelho et al., 2012; Hincapié et al., 2005), frogs (Hayes et al., 2002), and humans (Rayner and Fenton, 2011). Due to atrazine's toxicity and frequent detection, its use remains controversial. Therefore, improved prediction of the environmental fate of atrazine can help inform management decisions.

The environmental fate and behavior of atrazine is governed by many processes, including sorption, degradation, and transport among others (Arias-Estévez et al., 2008; Cheng, 1990). Sorption influences atrazine's environmental fate and off-target transport because it controls solution concentrations to a greater extent than other processes (Daniel et al., 2002; Gerstl, 2000; Green et al., 1990). Sorption is one of the most important input parameters for models predicting pesticide environmental fate, including models such as GLEMAS (Groundwater Loading Effects of Agricultural Management Systems), LEACHM (Leaching Estimation and Chemistry Model), PRZM (Pesticide Root Zone Model), and HYDRUS (Carsel et al., 1985; Dann et al., 2006; Sakaliene et al., 2007). Because accuracy of sorption parameters can be more important than model selection in simulating pesticide leaching (Sakaliene et al., 2007), our research investigated what parameters affect sorption at a global and regional scale.

As previously reported, sorption is affected by pesticide physicochemical properties, as well as soil characteristics (Hall et al., 2015). Previous studies demonstrate that organic matter content is a key indicator of atrazine sorption behavior, with other properties contributing.

For instance, Capriel et al. (1985) reported 90% of the atrazine was sorbed by the organic fraction compared to 10% by the mineral fraction. Jenks et al. (1998) revealed that soil organic matter was a good predictor of atrazine sorption ($r^2 = 0.98$), followed by soil pH ($r^2 = 0.82$), while Daniel et al. (2002) found that Freundlich sorption coefficient (K_f) was related positively and negatively to OC and silt ($r^2 = 0.93$), respectively. If sorption can be accurately predicted based on soil properties, they would serve as valuable model inputs in predicting leaching and groundwater contamination.

Soils heterogeneity presents challenges to assessing factors governing pesticide sorption (Daniel et al., 2002). Previous research on soil characteristics correlating to atrazine sorption parameters has treated soils from relatively small geographic regions, and research characterizing a range of soils from a global scale remains limited (Huang et al., 2013).

Therefore, the available literature concerning soil properties association on atrazine sorption was compiled and meta-analysis was conducted. The specific objectives were to: 1) conduct a meta-analysis of available literature to quantify, in a global context, the correlation between soil properties with atrazine sorption and 2) compare laboratory-generated experimental study models to meta-analysis models for atrazine sorption. This research will enhance our understanding of using soil properties to predict atrazine sorption globally and regionally and may be used to devise best management practices for certain soil conditions.

Materials and Methods

Literature Research and Data Extraction for Meta-Analysis

There were two phases for selecting refereed scientific publications for inclusion. Phase one utilized CAB (Commonwealth Agricultural Bureaux) abstracts with the following search criteria: key words as “atrazine”, “sorption” or “adsorption”, and “soil properties” or “soil characteristics” or “soil organic matter”, year published as 1985 – 2015, and language as English, which resulted in 132 publications. Explanatory variables including organic carbon (OC), pH, cation exchange capacity (CEC), soil texture (sand, silt, and clay), land use, and soil depth were extracted from publications. In previous research, the three sorption parameters have been commonly used to approximate sorption capacity of atrazine with predominantly Freundlich model fits (Boivin et al., 2005; Briceño et al., 2008; Daniel et al., 2002), including K_f , distribution coefficient (K_d), and soil organic carbon sorption coefficient (K_{oc}). The K_f parameter is an empirical constant of the Freundlich model expressing soil sorbent capacity for a given range of pesticide concentrations (Boivin et al., 2005). The Freundlich sorption equation is

$$q = K_f c^n \quad [1]$$

where q is sorbed concentration, c is the equilibrated concentration, and n is constant for the Freundlich model. As for K_d , the equation is

$$K_d = dq/dc \quad [2]$$

Where dq and dc is the derivative of q and c , respectively. K_d is a parameter determined using different approaches in the literature, some with specific concentrations including 1 mg L^{-1} (Kookana et al., 2008), 5 mg L^{-1} (Beck and Jones, 1996), and 10 mg L^{-1} (Barriuso et al.,

1992), some with average K_d values over a range of different concentrations (Alekseeva et al., 2006), and still others with a linear fit for calculation, assuming n equals one (Ben-Hur et al., 2003; Tyess et al., 2006). The calculation of K_{oc} is presented below

$$K_{oc} = K_d/OC \quad [3]$$

Phase two began with refining search criteria to exclude publications that did not include pertinent soil and sorption parameters including K_f , K_d , or K_{oc} among the aforementioned 132 publications. Also, publication that used the Langmuir model (1 paper) instead of the Freundlich model was eliminated. In total, 373 observations were extracted from 48 publications. Soil sample collection locations covering six continents and publication information (author, year, number of soils used in the publication, land use, experimental replicates, soil depth, measured variables, and measured responses) are shown in Figure 1 and Table 1.

Data Preprocessing

Data analyses were performed using SAS 9.4 (SAS Institute, 2014). Standard error and confidence interval information were not available for all observations, thus they were removed and only mean values were included to achieve a consistent data format. Soil depth range data were converted to average soil depth (for instance, 0 - 30 cm converted to 15 cm). In addition, if the publication did not include replicate information, this was set as one. Histograms of key explanatory and response variables were made and data beyond the top 5% quantile were removed as outliers since the histogram displayed a positive skew.

Statistical Analyses

A linear mixed model was used to assess the relationship between response variables and explanatory variables using the equation:

$$Y = X\beta + Z\gamma + \varepsilon \quad [4]$$

where Y is the known vector of observations (such as K_f and K_d); X and Z are known design matrices relating to β and γ ; β is an unknown vector of fixed effects (such as land use, depth, OC, pH, CEC, and texture) and γ is an unknown vector of random effects (such as author and year of publication); ε is unknown vector of random error. Number of replicates was used as a weighting coefficient in the model. Precision was expressed through the number of replicates, with higher weight assigned to studies with greater number of replicates. Since clay, silt, and sand sum 100%, the third component is a linear combination of the other two; therefore, only clay and silt were used in the analysis, due to the application of compositional data analysis (Aitchison, 1986). Since there was a large quantity of missing data, interactions were not analyzed to avoid false estimation, decreased statistical power, and loss of information (Dong and Peng, 2013). Pearson correlation coefficients ($\alpha = 0.01$) were generated between K_f and K_d with select soil properties including OC, pH, CEC, soil depth, clay, and silt. K_{oc} was not included since it was calculated by K_d/OC .

Laboratory Experiment

In addition to the meta-analysis, six soils with two depths (0 - 5 and 5 - 15 cm) were collected from three different land uses including turfgrass, cropland, and forest in North

Carolina. Soil characterization and sorption isotherm experiments were conducted. Soil OC was analyzed using a Shimadzu Total Organic Carbon/Total Dissolved Nitrogen analyzer, while sorption isotherm experiments were conducted according to methods modified from previous research (Daniel et al., 2002; Müller et al., 2012; Sparks, 2003). Five g soil and 25 mL 0.01 M CaCl₂ solution were added in centrifuge tubes to shake for 24 h at 200 rpm at room temperature, to ease colloid flocculation and equilibrate. Initial atrazine analyte concentrations were 0, 0.5, 1, 2, 5, and 10 mg L⁻¹. The mixtures of soil, water, and analyte were shaken at room temperature for 24 h at 200 rpm, centrifuged at 3750 rpm for 15 min, and filtered (25 mm syringe filter and 0.45 µm nylon filter). The filtered solution was analyzed using high performance liquid chromatograph-diode array detector-mass spectroscopy (HPLC-DAD-MS). The C₁₈ HPLC column (Poroshell 120 EC-C18, 4.6×75 mm, 2.7 micron; Agilent Technologies) was used with the wavelength of 220 nm. Sorption parameter calculations were performed in a similar manner with meta-analysis.

Results

Explanatory Analysis

A summary of explanatory and response variables including number of observations (N), minimum, maximum, mean, median, number of missing observations (N miss), variance, standard error (SE), and coefficient of variation (CV) are presented in Table 2. The minimum and maximum values reveal a wide range in the data for each variable. For instance, OC and pH range from 0.02 to 5.97% and 4.09 to 8.70, respectively. Similarly, response variables K_f and K_d range from 0.19 to 11.76 and 0.06 to 5.78, respectively. The variance indicates large

variations among the data. The wide range of soil properties and sorption parameter values show data heterogeneity, and afford the ability to make inference applicable to a wide range of soils.

Model Selection

Pearson statistics for select soil characteristics with response variables K_f and K_d are shown (Table 3). These data reveal that OC, pH, depth, and texture had the most significant correlation with sorption. Organic carbon was positively correlated with K_f ($r = 0.44$; $P < 0.0001$), while pH was negatively correlated with K_f ($r = -0.27$, $P = 0.0006$). Several soil properties including OC ($r = 0.49$, $P < 0.0001$), soil depth ($r = -0.46$, $P < 0.0001$), clay ($r = 0.23$, $P = 0.0027$), and silt ($r = 0.39$, $P < 0.0001$) were correlated with K_d . These soil properties were selected as terms in the linear mixed models described below.

Linear mixed models were fit for soil characteristics (those with $P < 0.01$ for r) and response variables K_f and K_d (Table 4). For each response variable, the first model included all variables which met the aforementioned criteria; the subsequent model removed the variable with the largest P-value from the last model, and continued iteratively until only one variable remained in the model. Table 4 shows the variables used in each response, the P-value, N used in a given model, model equation, and Akaike's Information Criterion (AIC) value, which was used to determine fit for each model with smaller AIC values indicating a better fit compared to larger values. For K_f , two models were selected; one with OC and pH, and another with OC only. These two models had similar AIC values and N. For K_d , four models were selected with combinations of OC, depth, silt, and clay. Model 2 with OC, depth, and silt has the smallest AIC value. Including land use as a determinant for K_f , K_d , and K_{oc} was

explored; however, it was not significant in any model ($P = 0.7244, 0.1852, \text{ and } 0.7146$, respectively).

Laboratory Study

Table 5 displays results from the experimental study including OC, sorption isotherm parameters (K_f , K_d , and K_{oc} ; K_d was calculated at 1 mg L^{-1} , while K_{oc} was calculated as previously described), constant n , and coefficient of determination R^2 for Freundlich fit. The equation for Freundlich fit referred to previously stated. Organic carbon, K_f , and K_d ranged from $0.29 - 3.51\%$, $1.9 - 6.2$, and $1.7 - 4.6$, respectively. The constant n indicated nonlinearity for the majority of the soils and R^2 demonstrated good fit for the Freundlich model.

Meta-Analysis Model versus Experimental Data

From the Pearson correlation coefficients and meta-analysis model selection, OC was the most significant soil property to predict K_f and K_d ; therefore, models from meta-analysis and experimental study including OC alone and response variables K_f and K_d were compared. The meta-analysis model determined using a linear mixed model was $K_f = 1.0 + 0.9OC$ ($R^2 = 0.20, P < 0.0001, N = 155$), while the fit for experimental data was $K_f = 1.5 + 1.4OC$. ($R^2 = 0.93, P < 0.0001, N = 12$) (Figure 2). The meta-analysis model showed the same positive relationship between K_f and OC; however, it underestimated K_f compared to the experimental study. The individual experimental data points fell within the range of meta-analysis data points, but exhibited less variation and demonstrated a good linear fit. As for K_d , the meta-analysis model and the experimental study models were also compared (Figure

3). Similar to K_f , the meta-analysis model had a similar positive trend for K_d but underestimated it with experimental study. The individual points were also within the scatter of meta-analysis data points with less variation ($R^2 = 0.92$).

Discussion

Correlation of Soil Properties with Atrazine Sorption Parameters within Meta-Analysis

Organic Carbon From the meta-analysis, OC was the dominant property governing atrazine sorption. Among all the properties, OC has the highest absolute value of r for K_f and K_d with $P < 0.0001$ (Table 3). Finding of OC to be a most important factor agreed with previous studies (Coquet, 2003; Daniel et al., 2002; Jenks et al., 1998; Pignatello, 1998; Spark and Swift, 2002; Stevenson, 1972; Worrall et al., 2001). The strong correlation of OC content and atrazine sorption is due to a variety of highly retentive functional groups found in soil organic matter, such as hydrophobic, hydrophilic, and free radicals (Huang et al., 2013). While some have reported that sorption depends more on total OC content rather than soil organic matter characteristics (Boivin et al., 2005), other research indicated that OC characteristics such as aromaticity can vary among different fractions and offer differing sorption capacities (Ahmad et al., 2001; Ding et al., 2002). Still other research indicated that aliphatic group and conformational arrangement of organic materials play important roles (Piccolo et al., 1998). This present study indicates that the amount of OC was closely correlated with sorption capacity, but it cannot address how various OC fractions and composition may affect sorption behavior.

pH Following OC, K_f was influenced most by soil pH ($r = -0.27$; $p = 0.0006$), indicating that increasing pH decreased K_f . Others have also reported a negative correlation between pH and K_f ($r = -0.577$; $p < 0.05$) (Huang et al., 2013) and K_d (McGlamery and Slife, 1966). Research by Jenks et al. (1998), not only corroborated this relationship, but also produced a multiple regression analysis showing that sorption can be predicted by pH ($R^2 = 0.82$) following organic matter content. When pH increases, atrazine tends to dissociate from a weak base form (protonated) to a conjugate acid (neutral) form, which might reduce sorption to soil surfaces. It is likely that the ionic bonding between protonated atrazine molecule amino groups and humic acid functional groups decreased as soil pH increased (Huang et al., 2013; McGlamery and Slife, 1966). In addition, this pH-dependent relationship can be explained by decreased van der Waal forces, hydrogen bonds, and decreased sorption via SiOH groups (Boivin et al., 2005; Frissel, 1961; McGlamery and Slife, 1966).

Depth Soil depth correlated with K_d ($r = -0.46$; $p < 0.001$) but not K_f ($r = -0.04$, $P = 0.6310$) in meta-analysis. Other research reported that increasing depth reduced K_f (Daniel et al., 2002). Depth may be confounded with other soil properties, since it had a significant correlation with most of the included soil properties (OC, $r = -0.40$, $P < 0.0001$, $n = 272$; pH, $r = -0.22$, $P = 0.0008$, $n = 235$; clay, $r = -0.17$, $P = 0.0081$, $n = 230$; silt, $r = -0.46$, $P < 0.0001$, $n = 212$, data not shown). Previous research has similarly shown that soil properties such as organic matter and pH vary with depth (Barriuso et al., 1992; Fierer et al., 2003; Gannon et al., 2013) and may overshadow its effect. In addition, a potential limitation of our meta-analysis was that the depth was averaged over a range (for instance, 0 - 30 cm as 15 cm); since researchers collected soils at different depth ranges, the information obtained from the

average could be compromised, because part of information may be lost during the conversion. Also, depths were difficult to compare across heterogeneous soils in a global geographic scale, but might be more applicable to soils in specific regions.

Texture In the meta-analysis, clay ($r = 0.23$, $P = 0.0027$, $n = 169$) and silt ($r = 0.39$, $P < 0.0001$, $n = 157$) content had a significant correlation with K_d but not K_f . The addition of texture to the model generally enhanced fit, indicated by the lower AIC values (Table 4). Previous research has shown that clay was a key parameter for characterizing atrazine soil sorption (Daniel et al., 2002; Hiller et al., 2008; Huang et al., 2013; Johnson and Thomas Sims, 1998; Mueller and Banks, 1991; Sakaliene et al., 2007; Spark and Swift, 2002; Walker et al., 1994), while others have found atrazine sorption was not correlated with clay content (Dousset et al., 1994; Oliveira et al., 2001). Some study found that clay did not affect sorption until the ratio of clay:OC was $> 30:1$ (Karickhoff, 1984), and clay fraction is more effective than other properties due to its association with OC (Wang and Keller, 2009). Other research showed that the sorption depended on the type of clay, and the expandable clay such as smectite and vermiculite had more sorption capacity than non-expandable clays such as illite or kaolinite (Park et al., 2004). The effect of silt has not been as extensively researched as that of clay. One study reported silt was responsible for 1.2% of atrazine sorption in soils (Jenks et al., 1998), while another concluded that K_d was negatively correlated to silt (Daniel et al., 2002). However, silt was selected multiple times in the meta-analysis models (Table 4), and the specific reason warranted further investigation.

Cation Exchange Capacity According to the meta-analysis, CEC did not correlate with atrazine soil sorption (K_f : $r = 0.13$, $P = 0.1917$; K_d : $r = 0.28$, $P = 0.0486$). In other research, a combination of OC and CEC produced the low C_p (2.33; Mallows' C_p , indicating good fit, the smaller the better fit) and high R^2 value (0.99) (Jenks et al., 1998), indicating the best model. Further, CEC may confound with characteristics such as OC and clay content since generally high OC and clay content corresponded to a high CEC. In this meta-analysis, CEC and clay were highly correlated ($r = 0.41$, $P < 0.0001$, $n = 105$). Since atrazine is an ionizable compound ($pK_a = 1.7$), the molecular form ionizes to become a cation at a lower pH as it approaches its pK_a . This implies CEC can have more effect at certain pH ranges when atrazine is at a different ionization state. This suggests that CEC may not be the main factor to predict sorption, but it could affect sorption.

Land Use Land use collected in the meta-analysis and experimental data included cropland, turf, forest, and NA (not available, Table 1). Land use did not significantly affect atrazine sorption in the meta-analysis. There were large variations for land use worldwide. Even the same land use category may be very different depending on geography and topography. In addition, different plant species and land history can be found within a category; for instance, wheat – sorghum and sugarcane were included for cropland in one publication, and the ages of the land use ranged from 11 to 56 yr old (Barriuso et al., 1992). Therefore, land use effect may not be as apparent on a global scale. In addition, land use could be a confounded variable as it affects OC and pH. Previous research has indicated that from cropland to forest, OC increased and pH decreased in general (Islam and Weil, 2000; Laganiere et al., 2010).

Differences between K_d and K_f One possible explanation of the different correlation of soil properties between K_d and K_f is that there were more observations for K_d than K_f in general in the meta-analysis (other than CEC, Table 3). Due to the sample size effect, it may have been easier to detect significance with more observations (Sullivan and Feinn, 2012). In addition, K_d has typically been determined for a linear fit at a lower and specific concentration other than a wide range compared to K_f , which could contribute to the difference as well. Further, data collected for K_f and K_d were from different sources with various soils and experimentation, which could also impact the correlation of soil properties to sorption parameters.

Limitations One challenge was that there was little data for CEC (N miss =197) and land use (N miss = 170). In addition, it is important to note that statistical significance does not imply scientific or environmental significance (Wasserstein and Lazar, 2016). For example, although we did not find statistical significance on CEC or land use, they may still be significant factors influencing atrazine sorption approximated by K_f , K_d , and K_{oc} . Land use for experimental study on a regional scale is not further discussed in this paper.

Comparison between Meta-Analysis and Experimental Study Models

Meta-analysis and experimental study models of K_f and K_d with OC had similar trends; however, meta-analysis underestimated K_f and K_d values and it was more variable compared to experimental study, which may be due in part to soil variation, experimental variation, and other driving factors. Soils included in meta-analysis models were part of experiments conducted in different climatic regions, whereas soil for experimental study models was collected in North Carolina. The ranges of soil properties and sorption parameters were

different. For example, the meta-analysis and experimental study OC ranged from 0.02 to 5.97% and 0.29 to 3.51%, respectively. In addition, research methodology has changed during the 30 years of atrazine sorption. Data contributing to meta-analysis models were acquired from different experiments using different methodologies and over a long period of time, but the experimental study model research was conducted by four researchers at NC State University. Various OC analyses, sorption isotherms, and atrazine concentration gradients were utilized in the studies collected for meta-analysis and may have increased variability in determining atrazine sorption. Further, other soil properties were not included in the models for comparison, which lowered AIC values when incorporating into models. Other factors such as iron oxides and ratio of clay to total OC have also been suggested as important parameters to correlate with atrazine sorption parameters (Huang et al., 2013).

Implications The models created through meta-analysis can be important input in environmental fate models to help identify soil profiles which may be more susceptible for leaching and runoff, thus preventing environmental contamination. Soil properties can be incorporated into leaching models to help predict sorption parameter and develop soil management tools for improved environmental safety during atrazine applications. Meta-analysis models have a broad scope of application, but site-specific research is still needed for more accurate sorption prediction due to the heterogeneity of soils. This study also revealed the possibility that OC alone can satisfactorily predict sorption for regional experimental study. The smaller scale, similar soil composition, and consistent experimentation of the experimental study models can result a strong correlation between OC and atrazine sorption. More compounds with different physicochemical properties should be

researched, in addition to different regions and soils, which further assist predicting sorption and environmental fate of pesticides using soil properties.

Conclusion

In the meta-analysis, publications have been collected from the past 30 years worldwide relating to soil properties correlating to atrazine sorption with wide range and high variability. Organic carbon was the most important property controlling atrazine sorption for both meta-analysis and experimental study. Other soil properties such as pH, depth, clay, and silt also showed significant correlation in the meta-analysis with improved model fit, while Land use and CEC were not statistically significant. Linear mixed models were developed for response variables K_f and K_d , respectively as meta-analysis models. In addition, a set of soils collected at North Carolina was used for sorption isotherm experiments as well as soil characterization, with experimental study models developed. The meta-analysis models with explanatory variable OC and response variables K_f and K_d were used to compare to experimental study models. The meta-analysis models had similar trends with experimental study models, but underestimated K_f and K_d ; in addition, the meta-analysis models also had more variation and poorer fit. These differences may be due to soil and experimental variation, as well as other driving factors not incorporated into the models. Both of meta-analysis and experimental study approaches can complement each other for pesticides risk assessment, to meet the goal of environmentally-responsible chemical usage.

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Figures and Tables

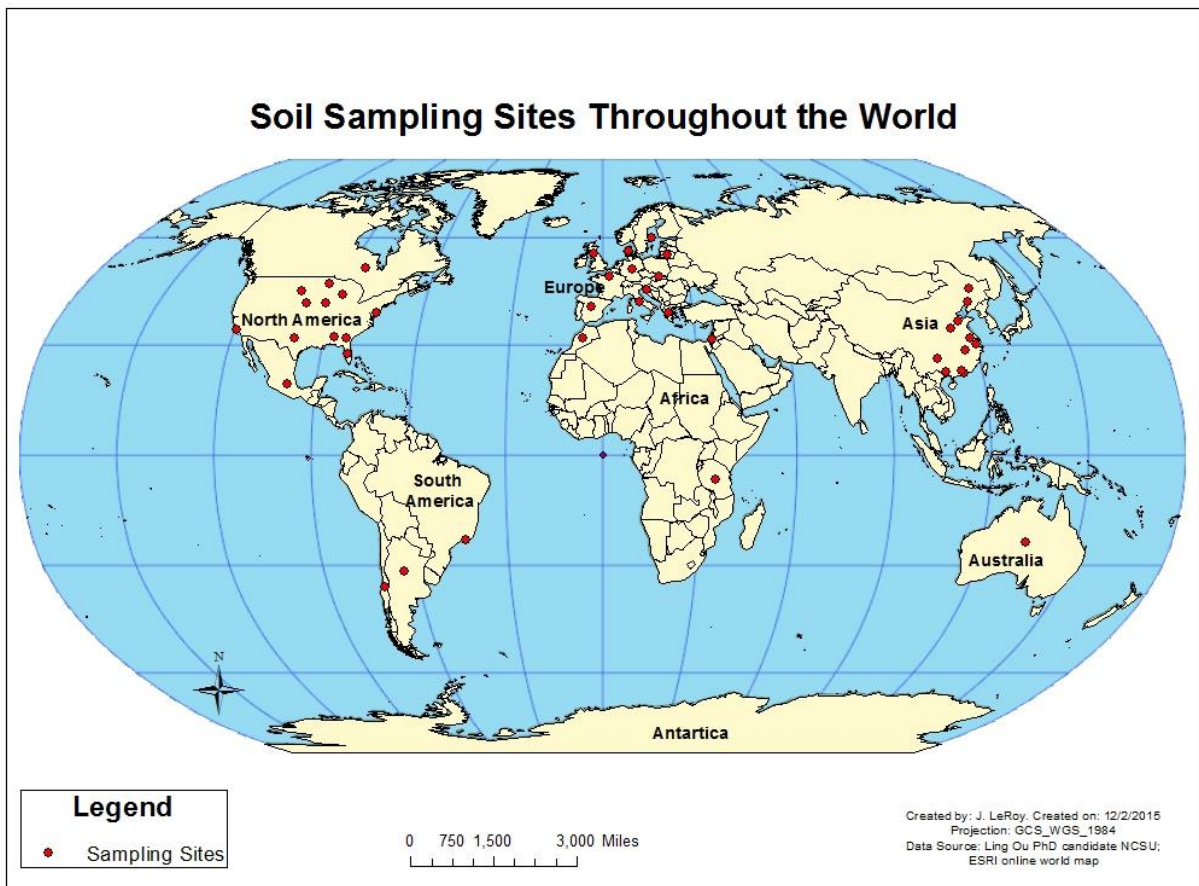


Figure 1. World map showing study locations used in meta-analysis.

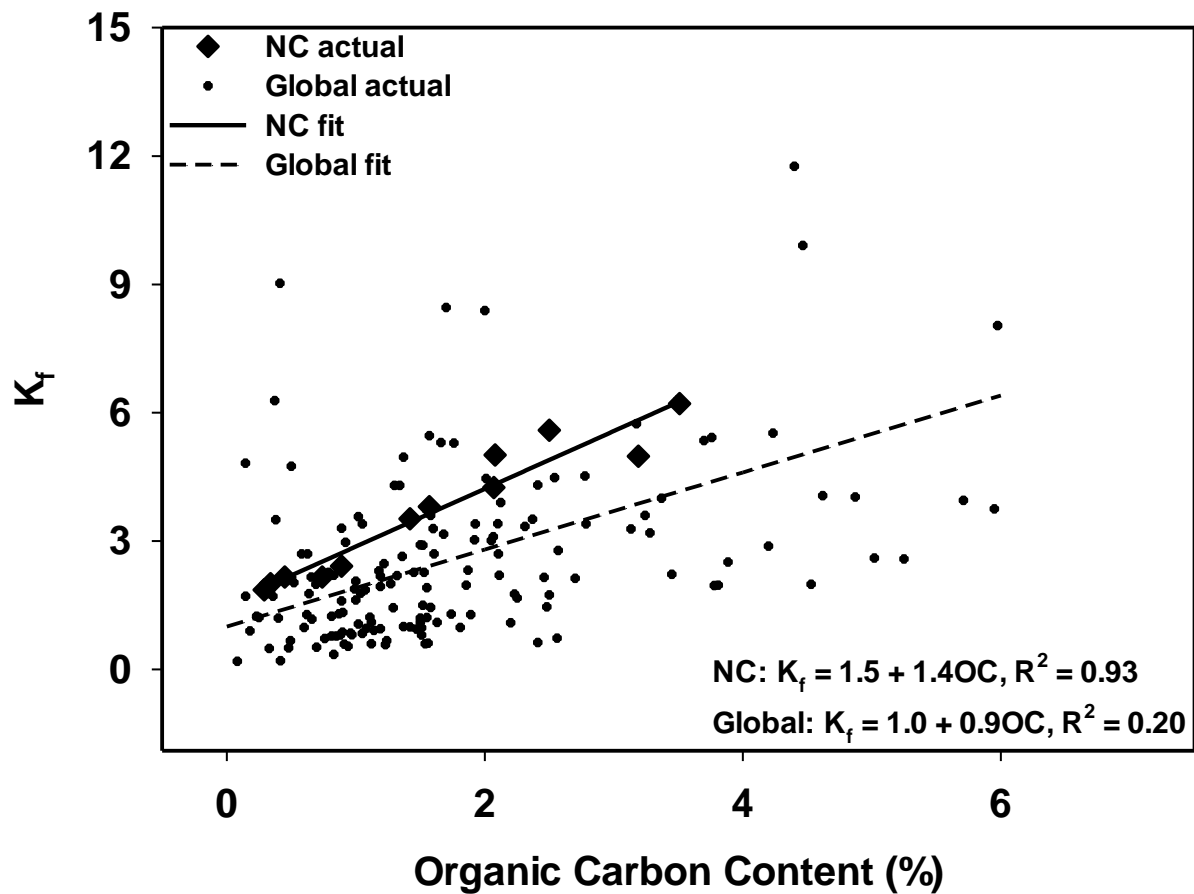


Figure 2. Freundlich sorption coefficient (K_f) as a function of organic carbon content (OC, %) for meta-analysis and North Carolina experimental data.

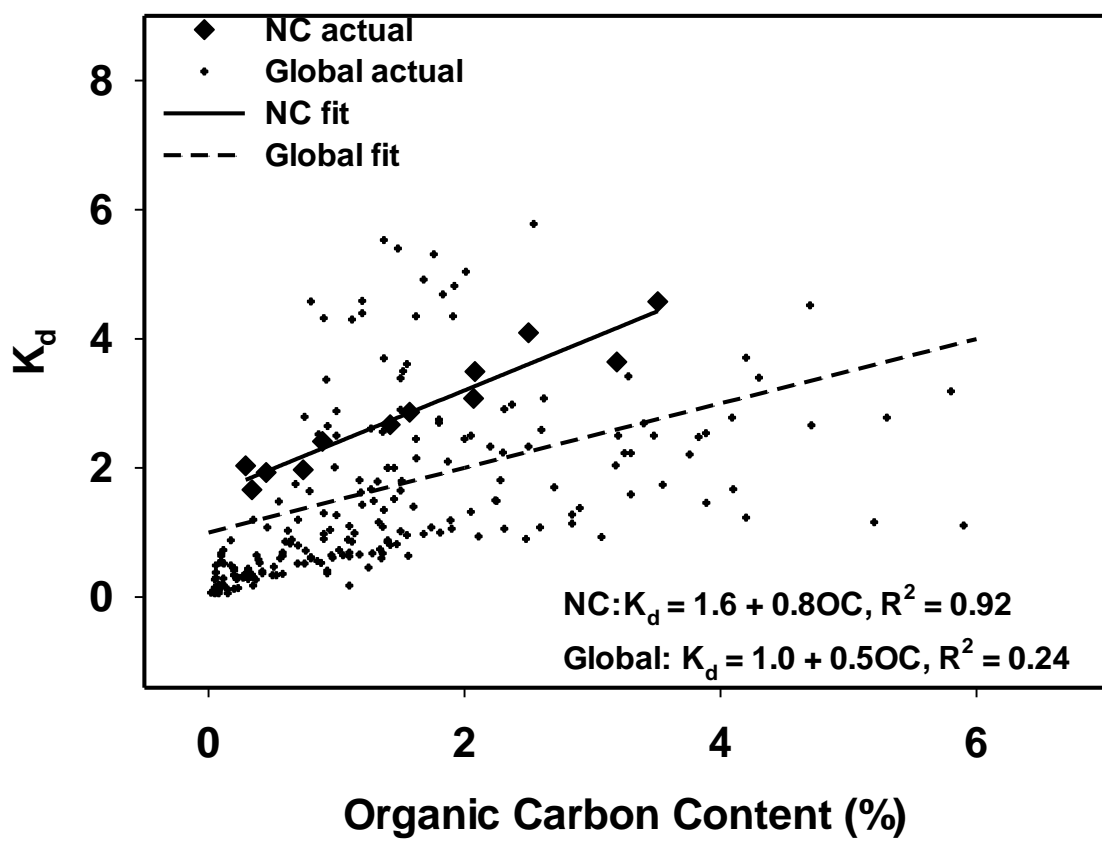


Figure 3. Sorption distribution coefficient (K_d) as a function of organic carbon content (OC, %) for meta-analysis and North Carolina experimental data.

Table 1. Publications included in meta-analysis, with author, year, number of soil types used in the study, land use, replicates of experiments, soil depth, measured variables, and measured responses.

No	Authors/Year Published	Soils No	Land use	Reps [†]	Depth (cm)	Measured variables	Measured response
1	(Jenks et al., 1998)	2	Cropland	3	0-60	SOC [‡] , pH, CEC [§] , Texture	K _f [¶]
2	(Bedmar et al., 2011)	4	Cropland	3	0-41	SOC, pH, CEC, Texture	K _f
3	(Boivin et al., 2005)	13	NA [#]	NA	0-15	SOC, pH, CEC, Texture	K _f
4	(Barriuso et al., 1992)	17	Turf/Cropland/ Woods	NA	0-40	SOC, pH, CEC	K _d ^{††} , K _{oc} ^{‡‡}
5	(Alekseeva et al., 2006)	1	NA	NA	0-20	SOC, pH, CEC, Clay	K _f , K _d , K _{oc}
6	(Prado et al., 2014)	2	NA	NA	20-40	SOC, pH, CEC, Texture	K _d , K _{oc}
7	(Ben-Hur et al., 2003; Kookana et al., 2008)	3	Cropland	3	NA	SOC, pH, CEC, Texture	K _f , K _d , K _{oc}
8	(Beck and Jones, 1996)	1	Cropland	3	NA	SOC, pH	K _d , K _{oc}
9	(Kookana et al., 2008)	31	NA	NA	0-170	SOC, pH, Texture	K _d , K _{oc}
10	(Ling et al., 2006)	10	NA	3	0-15	SOC, pH, Texture	K _f , K _d , K _{oc}
11	(Gerritse et al., 1996)	2	Woods	2	0-20	SOC, pH	K _d , K _{oc}
12	(Wang and Keller, 2009)	5	Cropland	2	0-15	SOC, pH, CEC, Texture	K _f , K _d , K _{oc}
13	(Bolan and Baskaran, 1996)	5	Turf	3	0-20	SOC, pH, CEC, Texture	K _f
14	(Baskaran et al., 1996)	32	Turf	3	0-70	SOC	K _d , K _{oc}
15	(Daniel et al., 2002)	12	Cropland	3	0-40	SOC, pH, CEC, Texture	K _f , K _d , K _{oc}
16	(Spark and Swift, 2002)	5	Cropland/Turf/ Woods	3	NA	SOC, pH	K _d , K _{oc}
17	(Muller et al., 2007)	3	Turf	3	0-10	SOC, pH, CEC, Texture	K _f , K _d , K _{oc}
18	(Drori et al., 2008)	4	Woods	3	3-30	SOC, pH, CEC, Clay	K _f
19	(Mechrafi et al., 2001)	7	NA	3	NA	SOC, pH, Texture	K _f
20	(Hiller et al., 2008)	6	NA	2	0-20	SOC, pH, Texture	K _f
21	(Abate et al., 2004)	1	NA	2	0-20	SOC, pH, Texture	K _f
22	(Park et al., 2004)	5	NA	3	NA	SOC, pH, CEC, Texture	K _f , K _d , K _{oc}
23	(Sakaliene et al., 2007)	7	Cropland	3	0-20	SOC, pH, Texture	K _d , K _{oc}

Table 1. Continued.

24	(Huang et al., 2013)	15	NA	3	0-20	SOC, pH, CEC, Texture	K _f
25	(Mueller and Banks, 1991)	3	NA	4	0-10	SOC, pH, CEC, Texture	K _f
26	(Dousset et al., 1994)	3	Cropland	3	0-30	SOC, pH, Texture	K _f
27	(Stipičević et al., 2009)	2	Turf	NA	0-1410	SOC, pH, Clay	K _f
28	(Nkedi-Kizza et al., 2006)	5	NA	3	0-30	SOC, pH, Texture	K _f
29	(Celis et al., 1998)	1	Cropland	3	0-20	SOC, pH, CEC, Texture	K _f
30	(Krutz et al., 2003)	2	Turf/Cropland	4	0-5	SOC, pH, CEC, Texture	K _f , K _d , K _{oc}
31	(Coquet, 2003)	14	Cropland	3	0-20	SOC, pH, Texture	K _f , K _d , K _{oc}
32	(Yang et al., 2003)	6	NA	2	NA	SOC, pH, CEC, Texture	K _f
33	(Rochette and Koskinen, 1998)	3	NA	NA	NA	SOC, pH, Texture	K _f
34	(Yang et al., 2009)	5	NA	3	10-20	SOC, pH, CEC, Texture	K _f
35	(Drori et al., 2006)	2	Woods	3	3-30	SOC, pH, CEC, Texture	K _f
36	(Rodriguez-Cruz et al., 2006)	5	NA	2	0-30	SOC, pH, CEC, Texture	K _f
37	(Borggaard and Streibig, 1988)	11	NA	NA	0-150	SOC, Clay	K _d , K _{oc}
38	(Briceño et al., 2008)	1	NA	3	0-20	SOC, pH, Texture	K _f
39	(Tyess et al., 2006)	10	Cropland/Turf/NA	NA	NA	SOC, pH, CEC, Texture	K _d , K _{oc}
40	(Rodriguez-Cruz et al., 2004)	5	Turf	2	NA	SOC, pH, Texture	K _f
41	(Shapir and Mandelbaum, 1997)	10	Cropland	NA	0-400	SOC, Texture	K _d , K _{oc}
42	(Johnson and Thomas Sims, 1998)	24	Cropland	3	0-232	SOC, pH, Texture	K _d , K _{oc}
43	(Walker et al., 1994)	12	Cropland	NA	0-10	SOC, pH, Texture	K _d , K _{oc}
44	(Locke et al., 2002)	3	NA	3	0-10	SOC, pH, CEC, Clay	K _d , K _{oc}
45	(Farenhorst et al., 2001)	1	Cropland	3	0-15	SOC, pH, CEC, Texture	K _f
46	(Fingler et al., 2004)	6	NA	2	NA	SOC, pH, CEC, Texture	K _f
47	(Seybold et al., 1994)	39	NA	3	0-180	SOC, pH, Texture	K _d , K _{oc}

Table 1. Continued.

48	(González-Pradas et al., 1994)	7	NA	2	NA	SOC, pH, CEC	K_f
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† Reps, replications.

‡ SOC, soil organic carbon.

§ CEC, cation exchange capacity.

¶ K_f, Freundlich sorption coefficient.

NA, not available.

†† K_d, sorption distribution coefficient.

‡‡ K_{oc}, soil organic carbon sorption coefficient.

Table 2. Summary of variables used in the meta-analysis.

Variable[†]	N[‡]	Min.	Max.	Mean	Median	N miss[§]	Variance	SE[¶]	CV[#]
OC^{††}	322	0.02	5.97	1.51	1.19	0	1.72	0.07	87.01
pH	285	4.09	8.70	6.34	6.10	37	1.47	0.07	19.12
Clay	268	0.10	75.00	22.91	20.04	54	304.66	1.07	76.19
Silt	249	0.10	83.80	25.20	21.10	73	369.58	1.22	76.29
Sand	249	0.70	99.70	51.72	50.00	73	871.81	1.87	57.09
CEC^{‡‡}	125	1.90	145.40	18.44	15.20	197	334.51	1.64	99.16
Soil depth	272	2.50	132.00	24.61	10.00	50	766.77	1.68	112.51
K_f^{§§}	155	0.19	11.76	2.55	2.03	167	3.88	0.16	77.28
K_d^{¶¶}	216	0.06	5.78	1.48	1.03	106	1.73	0.09	88.82
K_{oc}^{##}	216	16.36	844.83	158.12	107.07	106	22359.34	10.17	94.57

† For the min., max., mean, and median of variables in this table, the unit of OC, clay, silt, and sand are %; the unit of CEC is cmol kg⁻¹; the unit of soil depth is cm.

‡ N, number of observations.

§ N miss, number of missing observations.

¶ SE, standard error.

CV, coefficient of variation.

†† OC, organic carbon content.

‡‡ CEC, cation exchange capacity.

§§ K_f, Freundlich sorption coefficient.

¶¶ K_d, sorption distribution coefficient.

K_{oc}, soil organic carbon sorption coefficient.

Table 3. Pearson correlation coefficients (r) statistics for K_f and K_d , compared to soil properties determining atrazine sorption, in meta-analysis.

Sorption Parameter	Pearson Statistics	OC [†]	pH	CEC [‡]	Soil Depth	Clay	Silt
K_f [§]	r [¶]	0.44	-0.27	0.13	-0.04	0.14	0.08
	P [#]	<.0001	0.0006	0.1917	0.6301	0.0919	0.3666
	n ^{††}	155	155	100	118	148	141
K_d ^{‡‡}	r	0.49	0.11	0.28	-0.46	0.23	0.39
	P	<.0001	0.1476	0.0486	<.0001	0.0027	<.0001
	n	216	180	51	197	169	157

† OC, organic carbon content, with the unit %.

‡ CEC, cation exchange capacity, with the unit of cmol kg^{-1} .

§ K_f , Freundlich sorption coefficient.

¶ r, Pearson correlation coefficient.

P, P value.

†† n, number of observations.

‡‡ K_d , sorption distribution coefficient.

Table 4. Model equations selected through linear mixed model, with response variables of K_f and K_d .

Response	No	Variable [†]	P Value	N [‡]	Model Equation	AIC [§] Value
K_f [¶]	1	OC [#] pH	<0.0001 0.0135	155	$K_f = 2.57 + 0.91OC - 0.23pH$	494.6
	2	OC	<0.0001	155	$K_f = 0.99 + 0.93OC$	497.8
K_d ^{††}	1	OC Depth Silt Clay	<0.0001 0.1367 0.1973 0.2716	143	$K_d = 0.34 + 0.82OC - 0.003Depth + 0.006Silt + 0.006Clay$	341.8
	2	OC Depth Silt	<0.0001 0.1782 0.1356	143	$K_d = 0.46 + 0.82OC - 0.003Depth + 0.007Silt$	334.4
	3	OC Silt	<0.0001 0.0389	157	$K_d = 0.36 + 0.85OC + 0.009Silt$	374.0
	4	OC	<0.0001	216	$K_d = 1.02 + 0.54OC$	546.1

[†] Units for variables: OC, silt, and clay, %; depth, cm.

[‡] N, number of observations used in the model.

[§] AIC, Akaike's information criteria.

[¶] K_f , Freundlich sorption coefficient.

[#] OC, organic carbon content.

^{††} K_d , sorption distribution coefficient.

Table 5. Organic carbon (OC) and Freundlich sorption isotherm parameters for atrazine of 12 North Carolina soils.

Soil	Land use	Region	Depth	OC [†]	K _d [‡]	K _{oc} [§]	K _f [¶]	n [#]	R ^{2††}
			cm	%	--(mg kg ⁻¹)(mg L ⁻¹) ⁻ⁿ --				
1	Turf	Coastal plain	0-5	2.08	3.50	168.03	5.10	0.69	0.998
2	Turf	Coastal plain	5-15	0.34	1.66	488.58	2.00	0.83	0.991
3	Turf	Piedmont	0-5	3.19	3.64	114.19	4.98	0.73	0.996
4	Turf	Piedmont	5-15	1.42	2.67	187.97	3.52	0.76	0.997
5	Crop	Coastal plain	0-5	2.07	3.08	148.70	4.25	0.73	0.996
6	Crop	Coastal plain	5-15	1.57	2.86	182.25	3.80	0.75	0.997
7	Crop	Piedmont	0-5	0.74	1.97	266.29	2.16	0.91	0.990
8	Crop	Piedmont	5-15	0.45	1.93	428.76	2.17	0.89	0.996
9	Forest	Coastal plain	0-5	2.5	4.10	163.84	5.59	0.73	0.994
10	Forest	Coastal plain	5-15	0.29	2.03	700.82	1.86	1.09	0.965
11	Forest	Piedmont	0-5	3.51	4.58	130.42	6.21	0.74	0.998
12	Forest	Piedmont	5-15	0.89	2.41	270.89	2.41	1.00	0.987

† OC, organic carbon content.

‡ K_d, sorption distribution coefficient, calculated at 1 mg L⁻¹ equilibrated concentration.

§ K_{oc}, soil organic carbon sorption coefficient.

¶ K_f, Freundlich sorption coefficient.

n, constant for the Freundlich sorption model equation.

†† R², coefficient of determination for Freundlich sorption isotherm model.

CHAPTER 4. Land use and depth effect on atrazine and metolachlor sorption

For Submission as a Research Article to Weed Science

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Abstract

Soil sorption is a key factor determining herbicide environmental fate and behavior. It differs by compound, and sorption of individual compounds differs in various environmental and soil conditions. The overall goal of this research was to systematically compare the effect of land use and soil properties on sorption of atrazine (ionizable) and metolachlor (non-ionizable), which were chosen for frequent detection in drinking water and their difference in ionizability. Sorption isotherm experiments were conducted for soils from three land uses including turf, cropland, and forest at two depths (0 to 5 and 5 to 15 cm). Soil sorption ranked metolachlor > atrazine, and turf = forest > cropland at 0 to 5 cm but they were similar at 5 to 15 cm. Among considered variables: soil organic carbon (SOC), pH, cation exchange capacity (CEC), clay, and silt, OC and CEC were consistently positively correlated with the Freundlich sorption coefficient (K_f) and sorption coefficient (K_d), indicating the most influential soil properties. Organic carbon alone predicted sorption (K_f) well for atrazine ($R^2 = 0.93$) and metolachlor ($R^2 = 0.79$). Collectively, this research provides new insights that

herbicide sorption depends on compounds as well as land use and soil depth, and sorption can be predicted by soil properties at a regional scale. This knowledge can be utilized to better assess pesticide environmental fate and improve efficacy.

Nomenclature: Atrazine; Metolachlor.

Keywords: Adsorption, organic carbon, sorption coefficient, soil depth.

Introduction

Atrazine is the second most widely applied herbicide active ingredient following glyphosate, while metolachlor is the third in the United States in 2007 (Grube et al. 2011). They both are used for broadleaf and grass control, and applied in agronomic and specialty crops, conifers, and turf (Shaner 2014). Physicochemical properties of these two herbicides are provided (Table 1). Atrazine is an ionizable weak base (pK_a 1.7) while metolachlor is non-ionizable. The difference in ionizability is one of the reasons these two compounds were selected. The half-life of atrazine and metolachlor are 45 – 335 d and 8 – 124 d, respectively (Shaner 2014). The water solubility is low to moderate with 33 and 488 mg L⁻¹ for atrazine and metolachlor, respectively. According to Gilliom (2007) atrazine and metolachlor are among the most frequently detected pesticides in groundwater and surface water in United States, and are detected in 90 and 80% of samples, respectively which is due to frequent long term usage, low to moderate water solubility, and long persistence as discussed above (Benotti et al. 2008; Gilliom et al. 2006).

Soil sorption is a key process to predict pesticide environmental fate and behavior, as it regulates the amount of a compound that remains in soil solution, which may be subject to off-target transfer routes such as leaching into groundwater (Daniel et al. 2002; Gerstl 2000; Green et al. 1990). Sorption depends on compound properties as well as soil types and environmental conditions. Prior research compared the sorption of different pesticides as affected by soil and environmental factors, such as acetochlor, atrazine, and metolachlor for surface and subsurface soils (Bedmar et al. 2011), simazine and metolachlor from a

chronosequence of turfgrass systems (Gannon et al. 2013), and atrazine and metribuzin correlating to soil properties (Daniel et al. 2002); however, land use effect on pesticide sorption has not been elucidated. Land use has potential importance because pesticides such as atrazine and metolachlor may behave differently at different land uses due to varying physicochemical properties, and this knowledge can help guide best management practices to reduce off-target herbicide transport, such as application timing and rates at different soil conditions.

The impact of soil properties on pesticide sorption has been investigated; however, conflicting results exist. Gerritse et al. (1996) concluded atrazine sorption was correlated to organic carbon (OC) content and was not impacted significantly by other soil properties, while (Spark and Swift (2002) indicated OC and clay mineral content influenced sorption. Other research stated that clay fractions were more important than other soil constituents and atrazine showed soil texture dependence (Wang and Keller 2009). In addition, pH was considered an important factor, in addition to OC and mineral fraction according to prior research (Stipičević et al. 2009), and cation exchange capacity (CEC) has been reported to be a useful variable (Bedmar et al. 2011; Johnson and Thomas Sims 1998). As for metolachlor, one study found that OC ($r = 0.886$), silt ($r = 0.628$), and sand ($r = -0.519$) had strong correlations with K_d (Westra et al. 2015), whereas another study reported pH ($r = -0.608$), CEC ($r = 0.574$), and OC ($r = 0.836$) were correlated with K_f (Kodešová et al. 2011). However, a separate study found that CEC ($r = 0.81$) was the only significant soil property with regards to K_d , and other properties such as total carbon, clay content, and soil pH produced the best model to predict K_d (Si et al. 2009). The aforementioned research implies

that the soil heterogeneity as well as different physicochemical properties in compounds may result in different significant soil properties impacting pesticide sorption, and there is a need for a systematic analysis of sorption across soils of various types and systems.

The objectives of this research were to: 1) characterize atrazine and metolachlor soil sorption at surface and subsurface soils collected from various land uses; 2) determine how soil properties affect soil sorption for both herbicides, and use statistical modeling to predict sorption. This research can help identify leaching potentials at different land uses and depths for different herbicides, and provides potential useful models to predict sorption according to soil properties in North Carolina and similar regions. This research also provides evidence that the same herbicide may behave differently across different systems, which should be taken into consideration when registering herbicides.

Materials and Methods

Soils. Six soils of surface (0 to 5 cm) and subsurface (5 to 15 cm) depths were sampled from three different land uses including established turfgrass, cropland, and forest in North Carolina in 2015 (Figure 1). The soils of turfgrass were sampled from Lochmere Golf Club in Cary, NC (35.73°N, 78.78°W) and Porters Neck Country Club in Wilmington, NC (34.29°N, 77.76°W), established in 1985 and 1991, respectively. Samples were also collected at the adjacent forest sites. Cropland soils were sampled from Upper Piedmont Research Station in Reidsville, NC (36.38°N, 79.69°W) with 30 years of no tillage treatment and Upper Coastal Plain Research Station in Rocky Mount, NC (35.89°N, 77.68°W) with 15 years of no tillage treatment (area between strip tilled sections). After sampling, soils were air dried and

sieved (2 mm) before characterization. Soil texture analysis was performed using a hydrometer method (Bouyoucos 1962; Klute 1986). The organic carbon analysis was conducted using Shimadzu Total Organic Carbon/Total Dissolved Nitrogen analyzer with the Model TOC-VCPN. The pH and CEC testing were conducted using standard methods (Mehlich 1984).

Sorption Isotherm Experiment. Technical grade atrazine (99.1% purity) and metolachlor (98.2% purity) (Sigma-Aldrich, 3300 S 2nd St, St. Louis, MO 63118) were dissolved in acetonitrile for standard solutions. The sorption isotherm experiments were performed according to previously published methods (Daniel et al. 2002; Müller et al. 2012; Sparks 2003). Five g soil and 25 mL 0.01 M CaCl₂ solution were added to centrifuge tubes and shaken 24 h at 200 rpm at room temperature to alleviate colloid flocculation and to equilibrate. Initial analyte atrazine and metolachlor concentrations were 0, 0.5, 1, 2, 5, and 10 mg L⁻¹. The range was determined based on values from aforementioned literature and theoretical concentration of the herbicide in the top layer (0 to 5 cm) of the field soil calculated by application rates (0.67 to 1.38 mg L⁻¹ for one single application). The mixtures of soil, water, and analyte in unique containers were shaken at room temperature for 24 h at 200 rpm, centrifuged at 3,750 rpm for 15 min, and filtered (25 mm syringe filter followed by 0.45 µm nylon filter). Previous research determined that 24 h is sufficient for reaching equilibrium of atrazine sorption (Daniel et al. 2002; Huang et al. 2013).

The filtered solution was analyzed using high performance liquid chromatography-diode array detector (HPLC-DAD). The C₁₈ HPLC column (Poroshell 120 EC-C18, 4.6 by 75 mm, 2.7 micron; Agilent Technologies) was used with 220 nm as detected wavelength. The

mobile phase was acetonitrile and water 65:35 and 60:40 by vol with 0.1% formic acid, respectively, for atrazine and metolachlor. Injection parameters for atrazine were: 10 μL injection volume, 0.8 mL min^{-1} flow rate, 30° C column temperature with 1.45 min as retention time and 20 μL injection volume, 1 mL min^{-1} flow rate, 25° C as column temperature and 2.60 min retention time for metolachlor. The limit of detection was 0.5 mg L^{-1} , and the limit of quantification was 1 mg L^{-1} for both compounds.

Calculations. Based on concentration of analyte in aqueous solution (c), sorbed concentration (q) was calculated assuming no additional analyte lost during the 24 h of incubation due to long very long vhalf-life of atrazine. Sorption isotherms were made for both herbicides using q as a function of c for all 12 soils. Subsequently, Freundlich sorption isotherm models were fit using the equation:

$$q = K_f c^n \quad [1]$$

where K_f is Freundlich sorption coefficient, and n is constant for the Freundlich model.

Sorption coefficient K_d , the slope of sorbed concentration to the aqueous concentration, was calculated as:

$$K_d = dq/dc = K_f n c^{n-1} \quad [2]$$

where dq and dc are the derivatives for q and c. We

defined the sorption coefficient at 1 mg L^{-1} , thus

$$K_d = K_f n \quad [3]$$

Soil organic carbon sorption coefficient (K_{oc}) was calculated as:

$$K_{oc} = K_d/OC\% \quad [4]$$

Statistical Analyses. Statistical analyses were performed using SAS 9.4 (SAS Institute 2014). Regions were considered blocks, whereas treatment (land use, depth, and herbicide) effects on K_f were explored through general linear model and mean separations were conducted. Pearson correlation coefficients were generated through CORR model between sorption parameters (K_f and K_d) and soil properties, such as OC, pH, CEC, clay, and silt. Due to the application of compositional data analysis, sand was not included in the analysis as clay, silt, and sand sum 100% (Aitchison, 1986). Stepwise model selection in REG model was used to select models using soil properties to predict atrazine and metolachlor sorption. Significance level was set at 0.05 for all the analyses except otherwise stated.

Results and Discussion

Soil Properties. Land use, region, soil depth, and soil properties including texture (sand, silt, and clay), OC, pH, and CEC are shown in Table 2. The 12 soils were comprised of three land uses by two regions by two depths. Soil textures of the collected soils included sand, sandy loam, loamy sand, loam, and clay loam. Organic carbon ranged from 0.29 to 3.51%; pH ranged from 4.8 to 6.5; CEC had a range from 3.2 to 18.3 cmol kg^{-1} . The highest OC was from the forest soil in piedmont area at 0 to 5 cm, and the lowest from 5 to 15 cm forest soil in coastal plain. Organic carbon at 0 to 5 cm was 2.2 to 6.1, 1.3 to 1.6, and 3.9 to 8.6 times of that at 5 to 15 cm, for turf, crop, and forest, respectively. The properties described above showed variability of soils collected.

Sorption Isotherms. Freundlich sorption isotherms were performed for herbicides for land uses, regions, and soil depths (Figure 2). In addition, sorption parameters of 12 sampled soils were shown for atrazine and metolachlor (Table 3). For atrazine, K_f ranged from 1.9 to 6.2,

with the highest and lowest value corresponding to forest piedmont at 0 to 5 cm and forest coastal at 5 to 15 cm, respectively; K_d ranged from 1.7 to 4.6, higher than previously reported values of 0.2 to 2.5 (Shaner 2014); K_{oc} ranged from 114.2 to 700.8, higher than the average value of 100 (Table 1) (Shaner 2014). The n in the table was less than 1.0 for all soils other than two of them, showing nonlinearity in sorption. The R^2 was above 0.99 for most soils indicating excellent fit for Freundlich sorption isotherms. As for metolachlor, K_f ranged from 2.5 to 10.2, with the maximum for turf in coastal plain at 0 to 5 cm, and minimum for forest in coastal plain at 5 to 15 cm; K_d ranged from 2.3 to 7.6, higher compared to 0.11 to 2.16 as previously reported (Shaner 2014); K_{oc} ranged from 180.2 to 780.4, also higher than the average value of 200 (Table 1) from prior research (Shaner 2014). The higher sorption parameters from this research can be the result of a higher OC content and different soil composition compared to previously reports. All n values were less than 1.0, and all R^2 values were above 0.99 other than one soil, which demonstrated nonlinearity as well as good fit for the model.

Herbicide. Main effect of herbicide was significant ($P = 0.0023$) and results are presented accordingly (Table 4). Mean separation for main effect of herbicides on K_f analysis showed a significant difference for metolachlor and atrazine, with metolachlor (5.6) 51% higher compared to atrazine (3.7) according to Fisher's protected least significant difference, when averaged over land uses and depths. The sorption isotherm figures also showed consistent higher sorption of metolachlor compared to atrazine (Figure 2, a-f). Bedmar et al. (2011) reported higher sorption of metolachlor (16.5 to 29.2) than atrazine (4.8 to 12.3), but with higher K_f values compared to our research. The higher K_f values may be due to different soil

properties, such as 4.4% OC content included in the prior research. Since leaching potential is governed by sorption, atrazine may have higher leaching potential than metolachlor under similar soil conditions.

Land Use. Land use main effect on soil sorption was not significant ($P = 0.0889$), but the interaction effect with soil depth was significant ($P = 0.0133$). For atrazine at surface, forest had similar sorption to turf, and turf similar to cropland, but forest had higher sorption than cropland; land use was not different at subsurface. For metolachlor, forest had similar sorption with turf and higher than cropland at surface while land use effect was not significant at subsurface (Table 5). When the sorption isotherm figure panels were compared across land use, 0 to 5 cm turf (Figure 2, a, b; solid fill) and forest (Figure 2, e, f; solid fill) had higher sorption than the same cropland depth (Figure 2, c, d; solid fill). This could be due to the accumulation of organic matter at the surface of turf and forest through clipping deposition and leaf accumulation, whereas biomass of cropland was harvested every year. The subsurface might be affected less because of less organic matter accumulation. Previous research has shown organic matter accumulation in turf systems; one study indicated organic matter increased in a chronosequence of turfgrass systems from 1 to 99 years (Gannon et al. 2013), and another study showed carbon sequestration rate as $1 \text{ t ha}^{-1} \text{ yr}^{-1}$ in a turf setting (Qian and Follett 2002). However, as grassland changed to cropland, 34% SOC lost in 10 years (Jiao et al. 2009), 43% SOC lost in 12 years (Evrendilek et al. 2004) due to anthropogenic activities, disturbance, and aggregate turnover (Six et al. 1998). From forest to cropland, the carbon pool of 0 to 20 cm changed from 56,480 to 32,636 kg ha^{-1} (Evrendilek et al. 2004), and in total 20 to 50% of SOC lost through erosion (Eswaran et al. 1993). The

aforementioned research collectively indicates varying OC content difference across land uses may be the primary reasons for different sorption behavior.

Soil Depth. The main effect of depth was significant ($P < 0.0001$). As for interaction effect separated by herbicides, surface soil had higher sorption than subsurface for atrazine in forest, but similar in turf and cropland; for metolachlor, surface soil had higher sorption than subsurface for forest and turf, but not for cropland (Table 5). The sorption isotherms also showed that depth effect was more significant in turf (Figure 2, a, b) and forest (Figure 2, e, f) compared to cropland (Figure 2, c, d), with surface $>$ subsurface. Agricultural management practices such as tillage in cropland can disturb soil up to 40 cm as some studies have shown (Angers and Eriksen-Hamel 2008; Laganiere et al. 2010), which may explain why depth did not impact cropland K_f . The OC difference among depths was a major soil property which impacted sorption. According to previous publications, OC differed across soil depths at different land uses. Comparing 0 to 6 with 6 to 12 cm of forest, OC decreased 50%, comparing 0 to 10 cm with 10 to 20 cm of grassland, 13% OC decreased, whereas 0 to 24% OC decreased comparing 0 to 10 cm with 10 to 20 cm in cropland for different crops such as wheat-soybean and cane (Barriuso et al. 1992). Gannon et al. (2013) reported OC decreased up to 94% from 0 to 5 cm compared to 5 to 15 cm in turf systems, and OC decreased 34% in native pine. In this research, OC decreased from 0 to 5 cm as compared to 5 to 15 cm, ranging from 55 to 84, 24 to 39, and 75 to 88% for turf, cropland, and forest, respectively.

Soil Properties. Pearson correlation coefficient statistics for K_f and K_d with selected soil properties are shown for atrazine and metolachlor (Table 6). For atrazine, the table showed that OC and CEC were strongly correlated with K_f (OC: $r = 0.96$, $P < 0.0001$; CEC: $r = 0.83$,

$P = 0.0008$) and K_d (OC: $r = 0.96$, $P < 0.0001$; CEC: $r = 0.89$, $P = 0.0001$). Similar trends were observed for metolachlor, as OC and CEC were the significant soil properties for K_f (OC: $r = 0.89$, $P = 0.0001$; CEC: $r = 0.76$, $P = 0.0042$) and K_d (OC: $r = 0.92$, $P < 0.0001$; CEC: $r = 0.85$, $P = 0.0005$). Organic carbon and CEC showed dominant effects for K_f and K_d , which agreed with previous research (OC: $r = 0.66$ to 0.96 ; CEC: $r = 0.82$ to 0.99 for simazine and metolachlor, with significance at 1% level) (Gannon et al. 2013). Other research also showed significant correlations between K_f and OC ($r = 0.80$ to 0.88) and CEC ($r = 0.47$ to 0.57) for atrazine and metolachlor (Bedmar et al. 2011). There was no significant correlation of pH with sorption parameters in this study, possibly due to a relatively narrow range of pH values. In addition, the pH values of the soils were distant from the pK_a of atrazine (1.7), and not relevant to the non-ionizable herbicide, metolachlor.

Stepwise model selection was performed for response variables K_f and K_d , with soil properties for atrazine and metolachlor (Table 7 and 8). For each variable in each model, P-value was also given, indicating the proportion of a certain property accounted in the model. The stepwise models included variables which had P values > 0.15 (Beal 2005). Model equations were shown for every stepwise model for K_f and K_d , respectively. The R^2 implies how well the model predicts true values, while C_p value (Mallows' C_p statistic) assesses the fit of a regression model. The larger the R^2 value, the better prediction of the model; the smaller the C_p value, the more precise a fit. Among the soil properties, OC, pH, and silt were fit for K_f of atrazine, whereas OC, CEC, and silt were fit for K_d through stepwise model selection. As for metolachlor, OC and silt were selected in the model for K_f , and OC, silt, and CEC for K_d through the same selection process in the program. Similarly, OC, silt, and CEC

were chosen for sorption of atrazine in the models for one study (Daniel et al. 2002), while OM, CEC, and pH were chosen for simazine and metolachlor for one (Gannon et al. 2013), and OC only for atrazine and metolachlor for the other study (Bedmar et al. 2011). The equations were not universal, but dependent on soils collected in each individual experiment. Organic carbon had a dominant impact on sorption parameters, indicated by the r values (Tables 6, 7, and 8), R^2 values of all first stepwise models including only OC (Table 7 and 8), and P values of OC (Table 6, 7, and 8). Thus, the response variable K_f was plotted as a function of OC for each herbicide (Figure 3). Both models showed good fit (atrazine, $R^2 = 0.93$; metolachlor, $R^2 = 0.79$), with atrazine an even stronger correlation. Other research indicated that in certain regions (General Alvarado, Argentina), the R^2 was 0.83 for atrazine and 0.74 for metolachlor; but for another region (Tres Arroyos, Argentina), it was 0.93 for atrazine, and 0.97 for metolachlor (Bedmar et al. 2011) indicating ability to predict K_f from OC is likely region specific. It is promising, however, to use OC for sorption prediction at a regional scale once the correlation is established.

This research compared soil sorption at different land uses and depths for atrazine and metolachlor. The findings show metolachlor had higher sorption than atrazine within selected soils, indicating it may be less apt to leach. In terms of land use, turf and forest had higher sorption than cropland at 0 to 5 cm, which implies the environmental risk of off-target herbicide transport differs at various land uses, and is potentially highest for cropland, among systems compared within this research. The depth effect was significant greater with surface compared to subsurface for turf and forest, but not for cropland. This suggests that depth needs to be taken into consideration when assessing mobility of compounds for different land

uses. The leaching and groundwater contamination potential depends on the herbicide as well as land use and soil depth. Pearson correlation analysis and stepwise model selection indicated OC as the key soil property predicting sorption for both herbicides; other properties such as pH, CEC, and silt were important as well, and they were selected to predict sorption. Though OC alone predicted sorption (K_f) well for both herbicides, the atrazine model had less variation compared to metolachlor. Organic carbon can be used as a model input for risk assessment of herbicides with different accuracies for different compounds. Model selection can be determined by soil properties that are available and can be region specific. Future research should focus on assessing soil sorption for additional land use sites and include additional herbicides with a broader range of physicochemical properties.

Acknowledgments

The authors thank Jessica LeRoy Hicks for making the North Carolina map, Dr. Matt Jeffries, Dr. David Jordan, and Patrick Maxwell for assistance with soil sampling, and Khalied Ahmed for residue analyses. This research was funded by NC State University Center for Turfgrass Environmental Research and Education.

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Figures and Tables

Table 1. Physicochemical properties of atrazine and metolachlor.^{a,b}

Property	Atrazine	Metolachlor
Ionizability (pK_a)	1.7 (Weak Base)	Non-Ionizable
Water solubility (mg L⁻¹)	33 (22 °C)	488 (20 °C)
Vapor Pressure (Pa)	3.87×10 ⁻⁵ (25 °C)	1.73×10 ⁻³ (20 °C)
Longevity (DT₅₀, days)	45-335	8-124
K_{oc} (mL g⁻¹)	100	200
K_d (mL g⁻¹)	0.20-2.46	0.11-2.16
K_{ow}(25 °C)	481	794

^a Abbreviations: K_{oc}, soil organic carbon sorption coefficient; K_{ow}, octanol-water partition coefficient.

^b Shaner 2014

Table 2. Select properties of soils used in this study.^a

Land use	Region	Depth	Sand	Silt	Clay	OC	pH	CEC
		cm	-----%-----					cmol kg ⁻¹
Turf	Coastal plain	0-5	89	10	1	2.08	6.3	10.1
Turf	Coastal plain	5-15	91	8	1	0.34	6.5	3.2
Turf	Piedmont	0-5	46	43	11	3.19	5.3	8.3
Turf	Piedmont	5-15	34	49	17	1.42	6.0	9.4
Crop	Coastal plain	0-5	53	43	3	2.07	6.1	10
Crop	Coastal plain	5-15	51	41	8	1.57	6.2	8.7
Crop	Piedmont	0-5	64	26	10	0.74	5.1	3.5
Crop	Piedmont	5-15	66	24	10	0.45	5.0	3.2
Forest	Coastal plain	0-5	80	14	6	2.50	6.5	16.1
Forest	Coastal plain	5-15	74	11	15	0.29	4.8	5.1
Forest	Piedmont	0-5	34	45	21	3.51	6.1	18.3
Forest	Piedmont	5-15	33	40	27	0.89	5.6	11.7

^a Abbreviations: OC, organic carbon; CEC, cation exchange capacity.

Table 3. Freundlich sorption isotherm parameters for atrazine and metolachlor.^a

Soil	Atrazine					Metolachlor				
	K _d	K _{oc}	K _f	n	R ²	K _d	K _{oc}	K _f	n	R ²
	mg ^{1-1/n} L ^{1/n} kg ⁻¹					mg ^{1-1/n} L ^{1/n} kg ⁻¹				
Turf Coastal 1	3.5	168.0	5.1	0.69	0.998	6.9	329.6	10.2	0.67	0.999
Turf Coastal 2	1.7	488.6	2.0	0.83	0.991	2.2	643.0	2.6	0.83	0.998
Turf Piedmont 1	3.6	114.2	5.0	0.73	0.996	5.7	180.2	7.8	0.74	0.997
Turf Piedmont 2	2.7	188.0	3.5	0.76	0.997	3.6	250.1	4.5	0.79	0.998
Crop Coastal 1	3.1	148.7	4.2	0.73	0.996	4.6	221.6	6.6	0.70	0.995
Crop Coastal 2	2.9	182.3	3.8	0.75	0.997	3.7	238.6	4.9	0.77	0.995
Crop Piedmont 1	2.0	266.3	2.2	0.91	0.990	2.6	347.8	3.2	0.80	0.998
Crop Piedmont 2	1.9	428.8	2.2	0.89	0.996	2.4	533.1	3.1	0.78	0.999
Forest Coastal 1	4.1	163.8	5.6	0.73	0.994	6.3	253.9	8.8	0.72	0.994
Forest Coastal 2	2.0	700.8	1.9	1.09	0.965	2.3	780.4	2.5	0.91	0.997
Forest Piedmont 1	4.6	130.4	6.2	0.74	0.998	7.6	217.4	9.1	0.84	0.984
Forest Piedmont 2	2.4	270.9	2.4	1.00	0.987	3.8	428.4	4.0	0.96	0.996

^a Abbreviations: K_f, Freundlich sorption coefficient; K_d, sorption distribution coefficient (determined at 1 mg L⁻¹); K_{oc}, soil organic carbon sorption coefficient; n, constant for the Freundlich sorption model equation; R², coefficient of determination.

Table 4. ANOVA table with explanatory variables including land use, herbicide, and depth and Freundlich sorption coefficient (K_f) as response variable.

Source of variation	P Value^a
Land use	0.0889
Herbicide	0.0023**
Land use × Herbicide	0.6871
Depth	<.0001***
Land use × Depth	0.0133*
Herbicide × Depth	0.0794
Land use × Herbicide × Depth	0.6162

^a *, **, and *** are used to indicate statistical significance at the 0.05, 0.01, and 0.001 probability levels, respectively.

Table 5. Mean separation for interaction effects of land use by depth on Freundlich sorption coefficient (K_f).

Land Use	Depth	----- K_f^a -----	
		Atrazine	Metolachlor
Turf	0-5	5.0 ab	9.0 a
Cropland	0-5	3.2 bc	4.9 b
Forest	0-5	5.9 a	8.9 a
Turf	5-15	2.8 bc	3.6 b
Cropland	5-15	3.0 bc	4.0 b
Forest	5-15	2.1 c	3.2 b

^a Within an herbicide, means followed by a common letter are not significantly different according to Fisher's Protected LSD ($P = 0.05$).

Table 6. Pearson correlation statistics for sorption parameters of atrazine and metolachlor, compared to select soil properties, observation number n = 12.

Sorption parameter	Pearson statistics	OC ¹	pH	CEC [‡]	Clay	Silt
-----Atrazine-----						
K_f	<i>r</i>	0.96	0.53	0.83	-0.09	0.28
	P	<0.0001	0.0733	0.0008	0.7926	0.3743
K_d	<i>r</i>	0.96	0.45	0.89	0.07	0.31
	P	<.0001	0.1441	0.0001	0.8367	0.3291
-----Metolachlor-----						
K_f	<i>r</i>	0.89	0.51	0.76	-0.17	0.12
	P	0.0001	0.091	0.0042	0.5954	0.7173
K_d	<i>r</i>	0.92	0.48	0.85	0.01	0.20
	P	<0.0001	0.1164	0.0005	0.9635	0.5256

^a Abbreviations: OC, organic carbon; CEC, cation exchange capacity; K_f, Freundlich sorption coefficient; r, Pearson correlation coefficient; P, P value; K_d, sorption distribution coefficient.

Table 7. Model equations selected through stepwise regression for atrazine, with response variables of sorption parameters and explanatory variables of soil properties.^a

Response	Stepwise	Variable	P-value	Model Equation	R ²	C(p)
K_f	1	OC	<0.0001	$K_f = 1.52 + 1.35OC$	0.92	18.22
	2	OC pH	<0.0001 0.0362	$K_f = -1.17 + 1.25OC + 0.49pH$	0.95	9.69
	3	OC pH Silt	<0.0001 0.0530 0.1006	$K_f = -0.48 + 1.34OC + 0.41pH - 0.01 \text{ Silt}$	0.97	6.97
K_d	1	OC	<0.0001	$K_d = 1.58 + 0.81OC$	0.92	69.74
	2	OC CEC	<0.0001 0.0032	$K_d = 1.34 + 0.57OC + 0.07CEC$	0.97	22.17
	3	OC CEC Silt	<0.0001 0.0003 0.0091	$K_d = 1.50 + 0.62OC + 0.07CEC - 0.01\text{Silt}$	0.99	7.44

^aAbbreviations: R², coefficient of determination; C_p; Mallows's C_p, to assess the fit of a model, the smaller the C_p value, the better the model fit; K_f; Freundlich sorption coefficient; OC, organic carbon; K_d; sorption distribution coefficient; CEC; cation exchange capacity.

Table 8. Model equations selected through stepwise regression for metolachlor, with response variables of sorption parameters and explanatory variables of soil properties.^a

Response	Stepwise	Variable	P-value	Model equation	R ²	C _p
K_f	1	OC	0.0001	$K_f = 2.06 + 2.23 \text{ OC}$	0.79	4.43
	2	OC Silt	< 0.0001 0.0232	$K_f = 3.22 + 2.61 \text{ OC} - 0.06 \text{ Silt}$	0.89	0.80
K_d	1	OC	< 0.0001	$K_d = 1.76 + 1.60 \text{ OC}$	0.85	6.54
	2	OC Silt	< 0.0001 0.0614	$K_d = 2.36 + 1.79\text{OC} - 0.03 \text{ Silt}$	0.90	3.65
	3	OC	0.0005	$K_d = 1.90 + 1.34\text{OC} + 0.13 \text{ CEC} - 0.03 \text{ Silt}$	0.94	1.27
		CEC Silt	0.0326 0.0241			

^aAbbreviations: R², coefficient of determination; C_p; Mallows's C_p, to assess the fit of a model, the smaller the C_p value, the better the model fit); K_f; Freundlich sorption coefficient; OC, organic carbon; K_d; sorption distribution coefficient; CEC; cation exchange capacity.

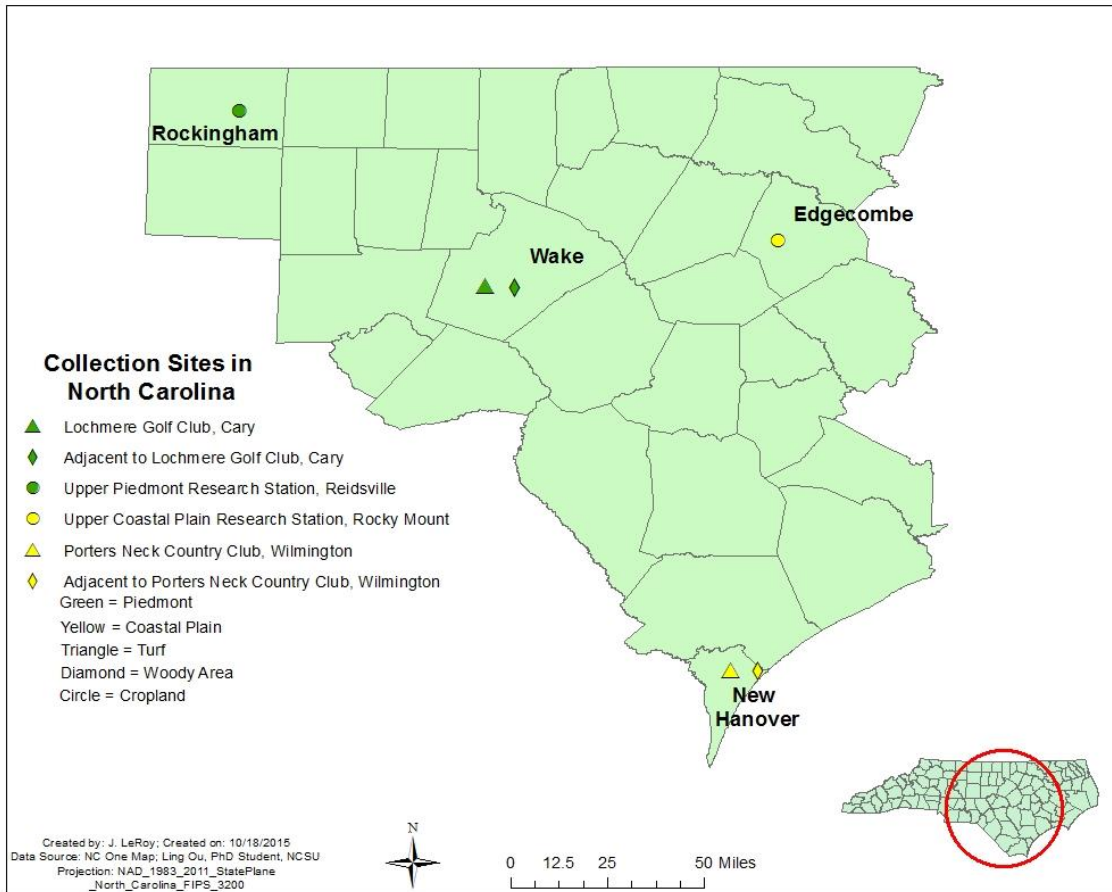


Figure 1. Sampling locations in North Carolina for determining how soil characteristics and land use affect atrazine sorption.

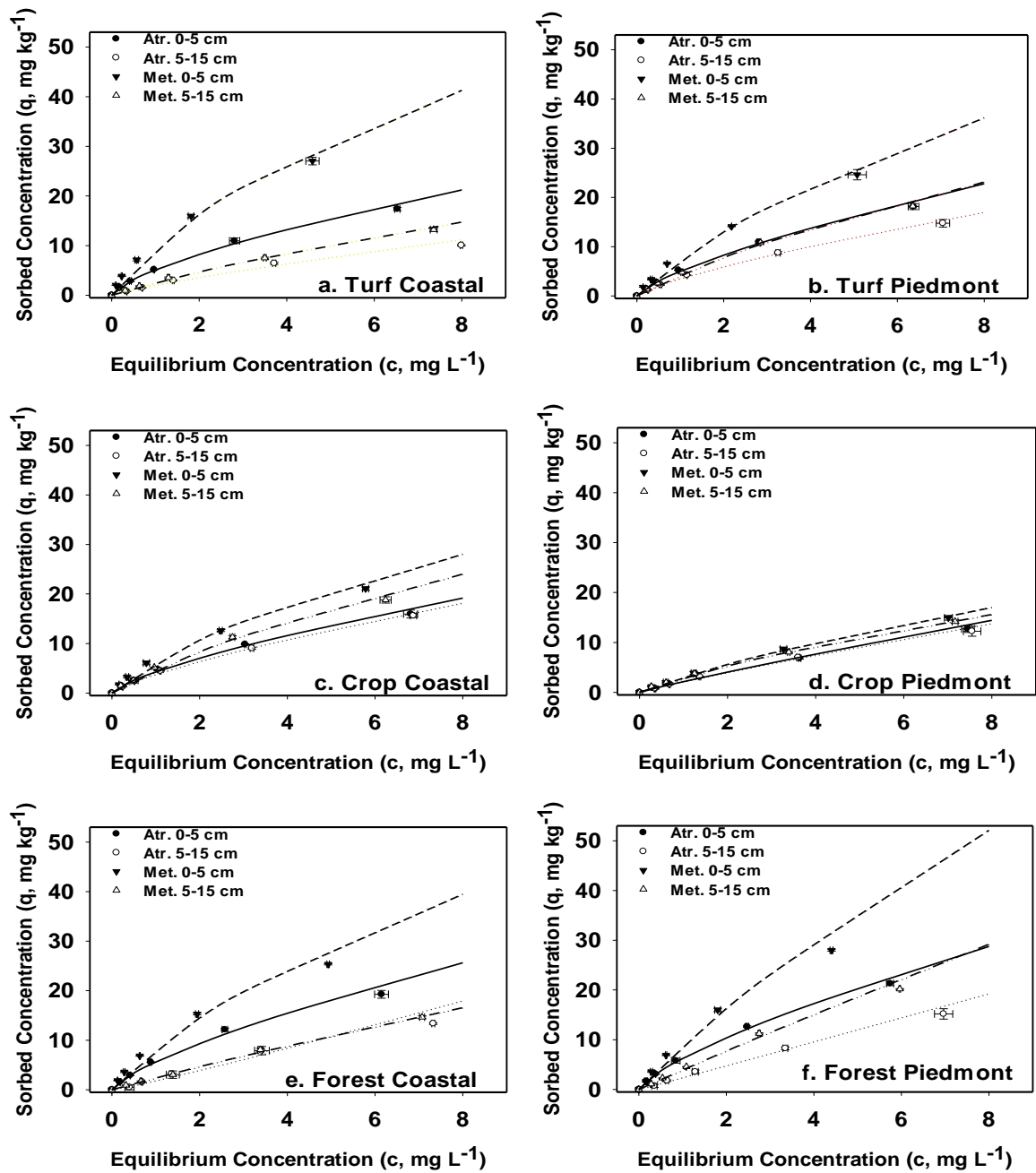


Figure 2. Sorption isotherms of 12 soils for atrazine (Atr.) and metolachlor (Met.), a, b, c, d; and e, f show turf, cropland, and forest respectively; a, c, and e were sampled from coastal plain region, while b, d, and e were sampled from piedmont region in North Carolina. Error bars show standard deviation of triplicate samples.

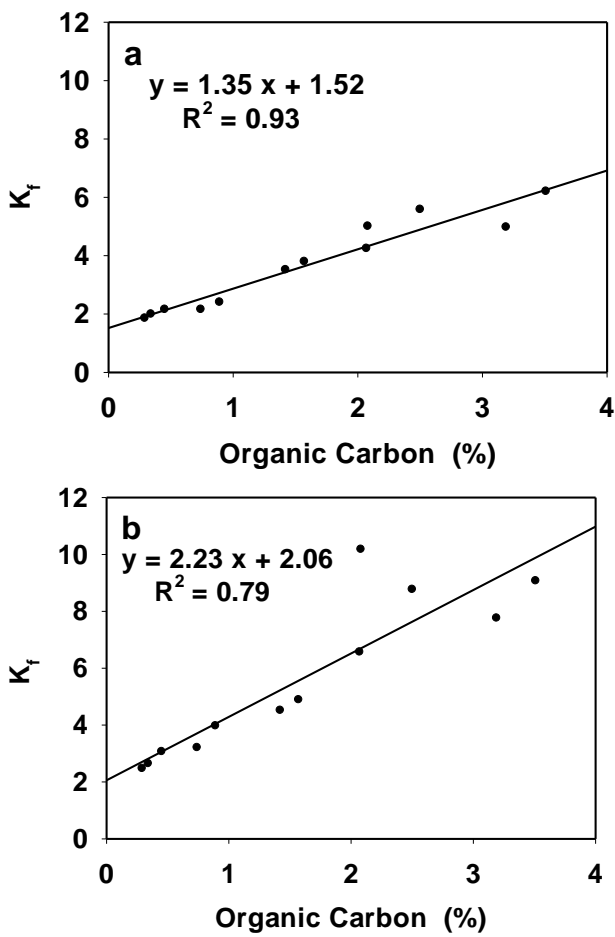


Figure 3. Regression model of Freundlich sorption coefficient (K_f) as a function of organic carbon (%) for atrazine (a), and for metolachlor (b).

CHAPTER 5. Conclusion

To achieve the goal of balancing chemical usage and environmental health, the research investigated on how soil properties impact environmental fate and behavior of pesticides, including controversial compounds MSMA (monosodium methyl arsenate), atrazine, and metolachlor, through experimental and meta-analysis studies. Soil organic carbon (SOC), 0.5 – 5% fraction of mineral soil, was identified to play an important role in sorption and species transformation of herbicides. SOC was linearly positively correlated to sorption of atrazine ($R^2 = 0.93$) and metolachlor ($R^2 = 0.79$) via sorption isotherm studies, positively correlated to atrazine in meta-analysis, while it decreased sorption for MSMA in a kinetics study during the 28 days of incubation. SOC also increased species transformation in the MSMA incubation study and the presence of more toxic inorganic arsenical species. Other soil properties such as soil texture, pH, and CEC (cation exchange capacity) also affect herbicide environmental fate. They impacted kinetics of sorption and species transformation, and improved models when using soil properties predicting sorption parameters. The impact of soil properties on sorption demonstrated further in different land uses and soil depths. Reregistration decisions of these compounds (labeling of application rates, timings, restrictions, etc.) and management practices should take soil properties especially SOC into consideration. In addition, different compounds should evaluate differently in terms of how SOC and other soil properties' impact, since they may have opposite effect or very distinct influence. Taking soil properties such as SOC into consideration as well as compounds

difference when evaluating pesticide environmental fate and behavior will help reach the goal of balancing pesticides usage and a healthy environment.