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IMPACT OF CONCENTRATED FLOW PATHWAYS ON THE MOVEMENT OF ATRAZINE, METOLACHLOR AND IMIDACLOPRID THROUGH AGRICULTURAL FIELDS

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Abstract

Riparian buffers are an important component of watershed management strategies aimed at improving water quality. These buffers are installed as best management practices (BMPs) to reduce runoff pollution from agricultural fields by diffusing surface runoff and allowing the water to percolate through the soil. They are well-documented to effectively mitigate nutrients and pesticides in agricultural runoff under ideal conditions. However, previous studies have shown that the performance of vegetated buffers can be undermined by the development of concentrated flow pathways (CFPs) that bypass the vegetation, limiting water quality benefits. To better understand the occurrence and potential effects of the presence of CFPs on the transport of pesticides from agricultural fields to nearby streams, soil samples were collected within CFPs and in adjacent areas outside of the CFPs in agricultural fields in Klingerstown, Pennsylvania. A total of nine sites representing various agricultural land uses, with two hay fields, two pasture fields and five cropland were studied. Soil samples were collected at a 0-2 cm depth to characterize pesticide concentrations in each of four categories of transport: CFPs within the field; non concentrated areas within the field; non concentrated areas in the associated riparian buffer zone (if present at the site); and, CFPs within the buffer. Samples were extracted using the QuEChERS (Quick, Easy, Cheap, Safe, Effective, Rugged, and Safe) solid phase extraction method for three pesticides of interest: atrazine, metolachlor, and imidacloprid, then analyzed using LC-MS.

Concentrations of each of the analytes of interest in soil were compared within each site to understand differences within and outside of CFPs. This analysis showed that soils with highest concentrations of pesticides varied as a function of land use. Overall, the highest concentrations of atrazine, metolachlor, and imidacloprid in soil were found in one cropped study site: 3.4 ug/kg, 127 ug/kg, and 2085 ug/kg respectively. The lowest concentrations were found in the pasture and hay fields and were present in the samples below analytical method detection limits.

The results of this study provided insights into the potential effects that CFPs may have on field-scale pesticide fate and transport, with two patterns emerging as dominant. Concentrations were found to either be mitigated or enhanced in CFPs of the field relative to the upslope non-concentrated flow areas of the field, with concentrations either decreasing or

increasing along flow paths from the field to the stream. The sites that generally fell within the first pattern were cropland fields that have historically received all three pesticides as inputs. For those fields, the highest concentrations of each pesticide were generally found in the non-concentrated flow areas in the field itself, with concentrations lower in the CFPs in the field and lowest in the non-concentrated flow areas in te buffer. These results suggest that as the pesticides are transported across the field, they are mitigated prior to reaching the stream. In contrast, for the pasture and hay field sites, concentrations were generally were higher in the samples collected from the CFPs of the field locations than the non-concentrated flow areas of the field locations. This shift in trends demonstrated the impact of pesticide usage in upgradient cropland fields.

Overall, the pesticide concentrations were consistently higher in the row cropland than the pasture and hay fields, and the patterns were generally consistent with land management (i.e., pesticide application history). For example, imidacloprid is often introduced to agricultural fields as a coating on corn and soybean seeds. It is not directly introduced into pasture and hay fields unless an imidacloprid-containing pesticide is applied by the farmer. The results of this study found that imidacloprid was nearly always absent from non-concentrated flow areas of the field samples collected in the pasture and hay fields, but that it was present in some of the CFPs of the fields. In these cases, the CFPs of the field were a result of CFPs starting in the upgradient cropland that contained imidacloprid. Therefore, the concentrations increased rather than decreased in the CFPs, suggesting that the presence of CFPs in these cases facilitates the transport of imidacloprid to the nearby streams.

The results of this study highlight the importance of the underlying factors that caused the CFP to develop in determining which of the roles the CFP will play in pesticide transport (i.e., mitigation or enhancement). The majority of the CFPs identified in the study area appeared to be either erosional or groundwater driven. Erosional channels were likely caused from different factors, including biological (e.g., cattle crossings), anthropogenic (e.g., tractor usage) and topographical (e.g., swales). Many of the CFPs documented as part of this study appeared to have developed due to the presence of springs, with frequent movement of groundwater that originated from upgradient locations through the CFPs. In these cases, CFPs likely facilitated transport of pesticides that had not been applied in the adjacent field, but rather had been applied at upgradient fields and had leached into groundwater. For CFPs that were driven by biological and anthropogenic factors, pesticide concentrations decreased along the flow pathway, suggesting that pesticide concentrations were mitigated along the flow path as runoff traveled to a nearby stream.

Overall, this study demonstrated that the role of CFPs in off-site pesticide loss is associated with a variety of factors, including: land use and land management practices, natural landscape factors, and pesticide physiochemical properties. The understanding of how these CFPs affect the transport of pesticides can help guide efforts to minimize pesticide loadings to local waterways. Specifically, CFPs appear to be important to pesticide transport in an agricultural setting and should be mitigated. Additionally, promoting awareness of the persistence of pesticides in agricultural soils could lead to farmers improving land management practices and local environmentalists modifying and utilizing different BMPs to reduce water-borne pesticide transport and improve soil health.

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Section 1: Introduction

The degraded water quality of the Chesapeake Bay and its tributaries has been a major concern in the Mid-Atlantic region of the eastern United States since the 1960s. In 2016, the Chesapeake Bay Foundation stated that the water quality had improved from a grade of D+ to a C-, but is still in need of improvement (CBF, 2016). With agriculture being a dominant source of excess nutrients and sediment to the Chesapeake Bay, states within the Bay watershed are focusing on reducing agricultural sources of these contaminants. The EPA has given the Commonwealth of Pennsylvania a 2025 deadline to reduce the total maximum daily load (TMDL) of nitrogen by 34 million pounds, phosphorus by 0.7 million pounds and sediment by 531 million pounds (Phase 2019). The 2015 evaluation to the Commonwealth it determined that Pennsylvania would meet its mid-term goal of reducing phosphorus, but would not meet nitrogen or sediment goals (Agriculture 2016).

Further water quality improvement depends on the increased adoption of agricultural best management practices (BMPs). Considered one of the most effective BMPs, riparian buffers have been shown to reduce nutrients, sediments, and other chemicals from entering adjacent waterways by as much as 99% (Liu et al., 2017). Riparian buffers are generally composed of grass, shrubs and trees and function by filtering water runoff from upslope agricultural areas before the water enters a waterway (Lowrance et al., 1997). Buffers defined by the Natural Resource Conservation Service (NRCS) as "an area predominantly trees and/or shrubs located adjacent to and up-gradient from watercourses or water bodies"((NRCS), 2010). These buffers promote infiltration, deposit of sediments and increase uptake of nutrients in plants. Although the main focus of the riparian buffers is to reduce nutrients and sediment in surface runoff from agricultural fields in order for the Commonwealth of Pennsylvania to comply with the Chesapeake Bay TMDL, agricultural pesticides are another type of contaminant to humans and the aquatic ecosystem that may be mitigated through the implementation of riparian buffers (Reungsang et al., 2005).

Environmental concerns regarding pesticide use began in the 1960's when the use of a common pesticide, DDT, was linked the decline of the bald eagle population (Grier, 1982). This pesticide entered waterways where it was bioaccumulated by fish. Consumption of the fish by birds caused their eggs to become fragile and ultimately break. Usage restrictions on DDT have helped restore the once endangered bald eagle population (Smith et al., 2016). Even with the banning of DDT in 1972, other pesticides are still causing environmental and human health concerns today. For example, atrazine is a commonly used herbicide in the United States. In the United States alone, approximately 34,000 metric tons (37,479 tons) was applied in 2007 (Shelley et al., 2012). With a half-life that can be as long as 16 years, atrazine persists in the waterbodies and groundwater and poses a long-term risk to human and aquatic health (Salazar-Ledesma et al., 2018). Studies of long-term exposure in population groups such as female farmers have shown increased occurrences of ovarian and breast cancer (Huang et al., 2014). Studies on rainbow trout have shown that atrazine has an effect on their immune system, which can have a drastic impact on the population (Shelley et al., 2012).

Metolachlor, which is commonly applied with atrazine to cropland fields, is another pesticide of interest. Metolachlor also targets pre- and post- emergent plants and has been detected in streams at concentrations that are known to cause negative impacts on ecosystem health. Studies have shown that metolachlor can have a negative impact to the oyster population by effecting reproduction process of the oyster. (Mai et al., 2014). This is significant to the Chesapeake Bay because oysters are a high economic return (Lipton, 2019). Also, it has been documented that metolachlor can be fatal to other species such as rainbow trout (*Oncrhynchus mykiss*) and scuds (*Daphina magna)* (Wan et al., 2006). Additionally, metolachlor poses potential human health risks, with documented cases of metolachlor found in drinking water (Li et al., 2018). If metolachlor is ingested, it can affect the function of the liver (Hartnett et al., 2013).

Recently, the pesticide industry has started to move away from more traditional methods of pesticide application (e.g., spraying) and towards a coating directly on the plant seeds. Quantities of the new class of pesticides, known as neonicotinoids (e.g., imidacloprid), introduced into the agricultural environment have experienced recent, drastic increase in the past 5 years alone. In 2011 in the United States, approximately 79-100% of corn plantings and up to 44% of soybean plantings were with neonicotinoid-coated seeds (Tooker et al., 2017). The novelty of neonicotinoids is that they are highly water soluble and are designed to be taken up by crops, such that the plant itself contains the pesticide. This has been linked to the honeybee decline, and also to the decline of other desirable predators in agricultural fields (Dively et al., 2015). However, only a small portion (≤20 %) of the imidacloprid mass introduced into fields can be accounted for by plant uptake, suggesting that is binds tightly to the soil or is highly mobile in the environment (Alford and Krupke, 2017) . It has been found that imidacloprid is common in groundwater (Wettstein et al., 2016). If contaminated groundwater enters the stream, it can have a negative impact on the macroinvertebrate population (Roessink et al., 2013). Therefore, adoption of BMPs that can be used to mitigate pesticide loss to nearby streams is desirable (Reungsang et al., 2005).

As the Commonwealth of Pennsylvania continues to promote new agricultural BMPs for meeting the Chesapeake Bay water quality restoration goals, widespread adoption of riparian buffers is anticipated on farms with streams that run through or border them. Riparian buffers are known to reduce the transport of pesticides by as much as 79-94% (Reungsang et al., 2005). However, the effectiveness of riparian buffers is also known to vary widely, with reported removal rates as low as 0% and as high as 99% (Liu et al., 2017) for nutrients and sediment. Additionally, the contracts under which riparian buffers are implemented in Pennsylvania tend to be long averaging 15 years. Very little long-term data exist and therefore the performance of riparian buffers for extended periods of time is not well understood. However, some data suggest that after approximately a decade, buffers may actually begin to act as a source of contaminants, such as phosphorus, if the biogeochemical capacity of the buffer is exceeded (Dodd et al., 2018).

The development and occurrence of concentrated flow pathways (CFPs), can affect the way surface runoff moves across the field, through a riparian buffer, and ultimately to the stream. As CFPs facilitate surface runoff bypass through buffers, they reduce the quantity of water treated by the buffer and diminish the water quality benefits that are obtained by the buffer. In several case study watersheds, the presence of CFPs was shown to reduce the amount of runoff treated by the buffer by as much as 22-78% (Wallace et al., 2018). The CFPs can be formed from animals, natural topographical influences, and by field equipment such as tractors (Wallace et al., 2018). A concentrated flow pathway can be seen in Fig.1-1. Although the occurrence of CFPs in agricultural landscapes has been documented, the effects of CFPs in transporting pollutants to surface waters has received limited attention (Wallace et al., 2018).

Figure 1-1: Example of a concentrated flow pathway in an agricultural field

The purpose of this study is to determine whether CFPs are important to pesticide losses in runoff and whether they undermine the effectiveness of buffers. This was inferred through soil sampling various agricultural settings, such as hay, crop and pasture fields, and differences in pesticide concentrations between the CFP soils and surrounding soils. The study area is located in a small headwater region of the Mahantango Creek watershed in Northumberland County, Pennsylvania. Pesticide concentrations within the CFPs of the field, non-concentrated flow areas of the field, non-concentrated flow areas of the buffer and CFPs the buffer will be investigated by collecting soil samples in each of these locations and analyzing them for three pesticides of interest: atrazine, metolachlor, and imidacloprid. It is anticipated that the study findings will improve our scientific understanding of how atrazine, metolachlor and imidacloprid travel in agricultural systems. Ultimately, the study aims to help landowners and policymaker’s adopt land management practices that are likely to be most effective in reducing the transport of pesticides from agricultural fields and into local waterways.

Section 2 Literature Review

2.1 Introduction

Pesticides are commonly used in agricultural fields throughout the world to help reduce competition from weeds and to reduce predatory insects. The most common application method is for pesticides to be sprayed directly onto the cropped area. After application, pesticides may be sorbed onto the soil, volatilize, leach through the soil profile, be uptaken by crops, and/or transported in surface runoff to nearby aquatic ecosystems. Their presence in the environment is a concern for human health, soil health and non-target species, such as honeybees and fish. The pesticides of interest for this study are atrazine, metolachlor, and imidacloprid.

2.2 Pesticide usage and impacts to human and ecosystem health:

Pesticides are used by farmers to reduce the competition of weeds with cash crops. Pesticides can sorb to organic carbon in the soil, building up over time with repeated additions every year, and can have a negative impact on the microorganisms in the soil. A decrease in microorganisms in the soil can cause crop development and productivity to decrease (Aktar et al., 2009). Herbicides such as Round-Up ®, with the active ingredient glyphosate, can have negative effects on mycorrhizal fungi. These fungi aid plant growth by increasing nutrient uptake from the soil and thus reducing the crop's production value. Finally, pesticides can have an effect on non-target species such as honeybees (Aktar et al., 2009). Each of the pesticides selected as part of this study have known impacts on human or ecological health.

2.2.1 Atrazine

Atrazine is one of the most commonly used pesticides in the United States. In 2007, approximately 34,000 metric tons were applied to agricultural fields throughout the US (Shelley et al., 2012). This herbicide is mainly applied to corn fields and is used to reduce broadleaf and grass weeds (Rohr et al., 2018). The application attempts to reduce competition and increase corn crop yields.

Farmers that are in increased contact with these pesticides can be at risk. Atrazine has been linked to affecting the Caco-2 cells in the intestinal track (Cragin et al., 2011; Olejnik et al., 2010), which affects digestion by impacting the intestinal track and stomach lining (Olejnik et al., 2010). Atrazine has also been found in drinking water supplies and because of its known human health risks, the Environmental Protection Agency (EPA) establishing a drinking water standard of 3 µg/L. For women, some of the risks of exposure to atrazine in drinking water are menstrual irregularity and an increase of infertile ovulatory cycles (Cragin et al., 2011). Atrazine can also have an impact on aquatic species such as fish and amphibians.

The aquatic ecosystem health impacts of atrazine are well documented for sensitive aquatic organisms. Shelley et al. (2012) conducted an exposure study of juvenile rainbow trout to water containing atrazine. The study lasted for four days, and then the specimens were tested for any abnormalities. It was concluded that even non-lethal concentrations of atrazine (18 µg/L) could have an effect on the trout's overall health. The juvenile trout's immune system and metabolism were both affected during the study (Shelley et al., 2012). Atrazine is also known to have negative effects on amphibians such as frogs. Metamorphosis has been observed to be either delayed or increased, immune function was reduced and altered sex hormone concentration levels due to atrazine were observed (Rohr et al., 2018). Leopard Frogs (*Rana popiens)* were found to be affected even at low concentrations (≥ 0.1 mg/L). The exposure caused underdeveloped testicular tubes and germ cells in the larva stage (Hayes et al., 2003).

2.2.2 Metolachlor

Metolachlor, like atrazine, is a commonly used herbicide that targets pre- and post-emergent broadleaf species in corn fields (Jaikaew et al., 2015). Metolachlor is often found in samples from water bodies such as streams. It was found that 60% of samples collected from the Mississippi River Basin contained metolachlor (Rebich et al., 2004). If ingested, metolachlor can affect an individual's liver function. A study concluded that exposure to 0.005 mg/L over a 72 hr period can reduce the cell cycle rates. (Hartnett et al., 2013).

Metolachlor is also known to impact aquatic ecosystems, with oyster populations that are exposed to atrazine experiencing altered development. Metolachlor contaminated water can also lead to the degradation of oyster sperm, which can increase the risk of infertility and thus lower the population (Mai et al., 2014). Metoalcholor has also been detected in drinking water supplies. In Guangxi, China, water samples were collected from groundwater as well as tap water. These samples contained 11 commonly used herbicides that are used in sugar cane production. The metoalcholor that was found in the collected samples was between 0.089 and 1.031 µg/L (Li et al., 2018).

2.2.3 Imidacloprid

Imidacloprid is a neonicotinoid insecticide that disrupts the nervous system of insects (Lima et al., 2017). Imidacloprid can be applied to agricultural by fields in various methods. Typically, it is coated on crop seeds or can be sprayed directly on the plant (Roessink et al., 2013). The usage of imidacloprid is to increase crop yields that can be reduced by pest insects (Zhang et al., 2015). With the various application rates and the chemical properties of imidacloprid, various non-target species can be affected by the insecticide.

Since imidacloprid is generally introduced to agricultural fields below the soil surface on the seed itself, it has been found in greater amounts in subsurface flow than surface runoff (McTish, 2019). For streams that are groundwater-fed, imidacloprid may affect macroinvertebrate populations. In a study understanding how imidacloprid affects mayfly (*Cloeon dipterum*) and caddisfly (*Limnephilidae*) nymphs, it was found that imidacloprid can have a negative impact on the species. With exposure of imidacloprid for 28 days, it was found *Cloeon dipterum* were affected with the lethal mean concentration (LC_{50}) of 0.195µg/L (Roessink et al., 2013). It was also concluded, through an exposure duration of 96 hrs, that the LC_{50} was 26.3 and 25.7µg/L for *Cloeon dipterum* and *Limnephilidae* nymphs respectively (Roessink et al., 2013).

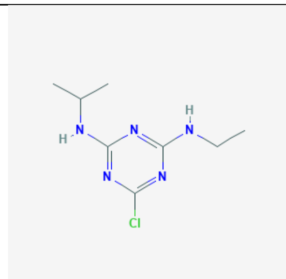
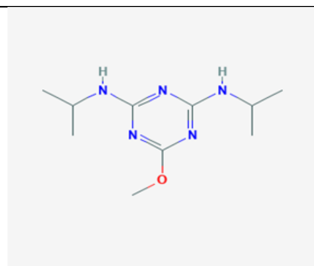
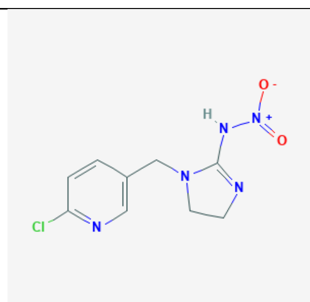
Imidacloprid can also have an adverse effect on soil macroinvertebrates. The cause of this is the application process of spraying or the planting of coated seeds. In a study that spiked imidacloprid into the soil at various concentrations and then examined five different macroinvertebrates (earthworms (*Eisenia andrei*), enchytraeids (*Enchytraeus crypticus*), collembola (*Folsomia candida*), oribatid mites (*Oppia nitens*) and isopods (*Porcellio scaber*)), it was concluded that imidacloprid had different effects on each species. LC_{50} concentrations for the most sensitive species *Eisenia andrei* and *Folsomia candida* were found to be 0.2 and 0.77 mg/kg dry soil respectively. *Enchytraeus crypticu, Oppia nitens and Porcellio scaber* had a higher tolerance and had LC_{50} concentrations of >30, 360 and 76 mg/kg dry soil respectively. With the mortality of these macroinvertebrates, soil health could be reduced, which would result in a reduction of crop yield (Lima et al., 2017).

Honeybee (Apis mellifera) can also be impacted by the usage of imidacloprid. A study which provided either treated or untreated imidacloprid pollen substitute to Apis mellifera colonies found that doses of containing 20-100 µg/kg of imidacloprid did not affect forging or other normal activity. However, hives with higher rates led to a reduction of the colony surviving the winter months. The reason for this is colonies that had greater concentrations had greater replacements of the queen due to premature death, in result lowers the amount of worker bees and causes a reduction of honey production (Dively et al., 2015). It was concluded that the scenarios of high concentrations may not be encountered in a real world scenario (5µg/kg). However, it was noted that long term exposure should be examined. A study that investigated direct exposure to a bee concluded that the LC_{50} for a 24 hr period was 0.018 µg per bee. This direct exposure could be a result of a spray drift scenario and can be detrimental to the population of Apis mellifera (Iwasa et al., 2004).

2.3 Physico-chemical properties of pesticides

After pesticides are applied to cropland, their fate and transport are determined by the coupling of biogeochemical and hydrologic processes. The physcio-chemical parameters of the compounds of interest govern their partitioning between soil organic carbon and water, movement through the soil profile via leaching, volatilization to the atmosphere, mobility in surface runoff, and degradation by biotic and abiotic factors. The parameters that are most relevant for understanding the environmental fate, transport, and persistence of atrazine, metolachlor, and imidacloprid includes first-order degradation rate (i.e., half-lives), organic carbon partition coefficient (K_{OC}), aqueous solubility, and vapor pressure (Table 2-1).

Table 2-1: Characteristics of pesticides a = PubChem©. b = California Department of Pesticide Regulation

Pesticide	Structure[a]	Half-Life in Soil (days)[b]	K_{oc} (L/kg)[b]	Lof KOW	Aqueous Solubility (mg/L)[b]	Vapor Pressure (mm Hg at 20°C)[b]
Atrazine		146	25-155	2.61[a]	33	$3*10^{-7}$
Metolachlor		114	22-1023	3.13[a]	530	$1.3*10^{-5}$
Imidacloprid		27-229	132-310	3.7[b]	514	$1.0*10^{-7}$

2.4 Pesticide Transport

After, pesticides are introduced into agricultural fields; they can then be transported via surface runoff, infiltrate through the soil profile, leach to groundwater, be taken up by crops, and volatilize (Fig. 2-1). Surface runoff begins as sheet flow, but may concentrate as it flows over the field, developing concentrated flow pathways that can bypass riparian buffers and directly enter the stream. The importance of each of these pathways varies for each pesticide of interest.

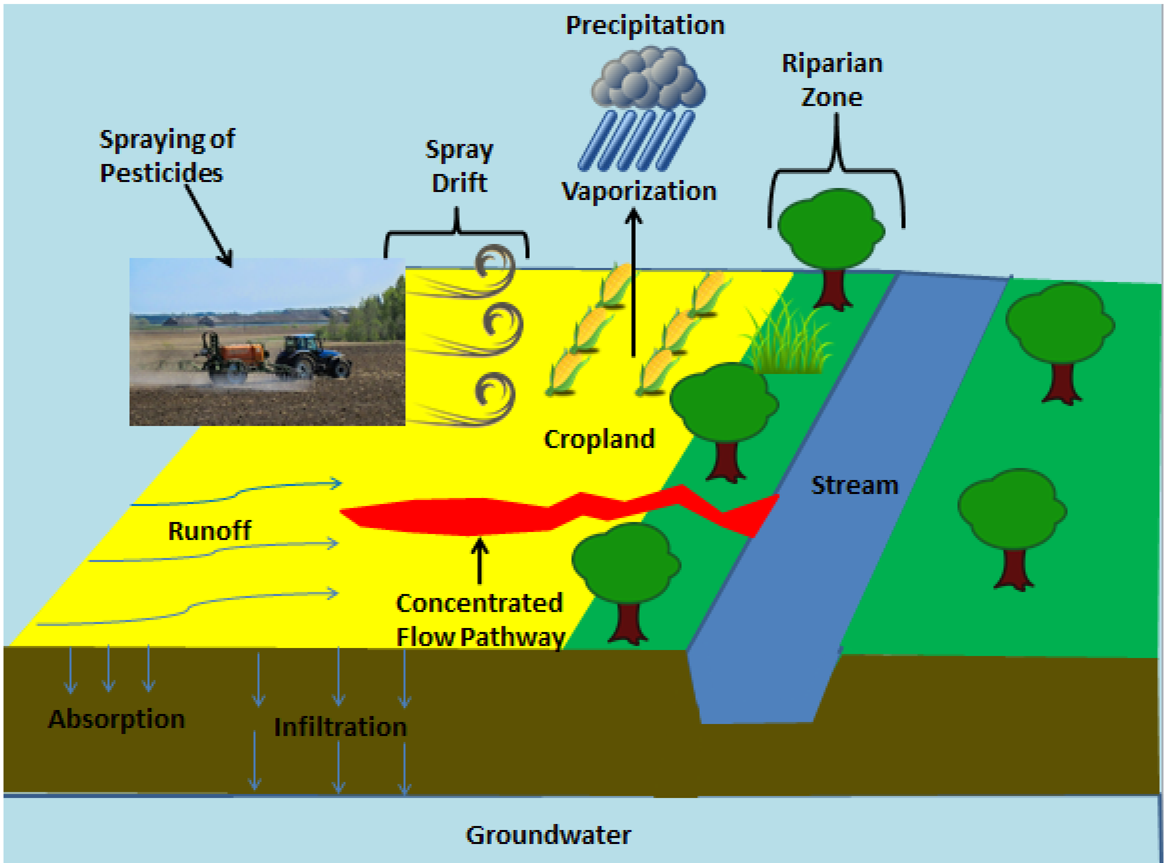


Figure 2-1: Pesticide cycle in the environment

2.4.1 Leaching

When rainfall events occur at rates below the saturated hydraulic conductivity of the soil and the soil is not saturated, water infiltrates into the soil profile. Pesticides present at the soil surface can be mobilized and transported with the water front as it moves through the soil profile. If the pesticide has not completely degraded when it leaves the vadose zone, then it enters the underlying groundwater. The soil drainage class affects how quickly water leaches through the soil profile, and the physico-chemical properties affect how much of the pesticide makes its way through the vadose zone. Soils with high organic carbon content tend to act as more effective biogeochemical filters, sorbing organic pollutants, such as pesticides, as they move through the soil profile. However, if the soil is sufficiently deep and the half-life of the pesticide is sufficiently short, then the pesticide will likely have degraded prior to reaching groundwater.

The presence of macropore flow can affect the movement of water and contaminants through the soil, reducing the opportunity for contaminants to sorb to soil organic matter and thereby leach at higher rates through the soil than if only matrix flow occurred (Rosenbom et al., 2016). Landscapes that have fractured clays soils allow leaching to occur at even a higher rate than in sandy soils (Rosenbom et al., 2016). The macroporous channels inside the fractured clay allow pesticide-contaminated water to percolate further down into the profile from the soil surface (Rosenbom et al., 2016).

In a previous study conducted in the Mahantango Creek Watershed, atrazine was found in groundwater wells likely due to the dense cropland in the area, in which approximately 2 kg/ha on average atrazine are applied. It was found that wells that were in pasture land had lower concentrations (1 mg/L) than cropland wells (5 mg/L) (Pionke and Glotfelty, 1990), potentially due to differences in the application of atrazine on the pasture fields than the cropland fields. In another study in Delaware examined the contamination of groundwater with atrazine and metolachlor, it was found that atrazine concentrations were greater (≤19 mg/L) than metolachlor (not detected) in groundwater samples (Ritter et al., 1994). Ritter et al. (1994) speculated that the reason for these differences was due to differences in sorption to the loam soil, with metolachlor having higher K_{OC} values (Table 2-1) (Ritter et al., 1994) and therefore sorbing more to the soil organic carbon than the atrazine. Imidacloprid has been found to be present more prevalently in shallow subsurface flow compared to surface runoff (McTish, 2019), suggesting that leaching may be an important pathway for imidacloprid.

2.4.2 Spray Drift

Pesticides are typically sprayed directly onto the soil surface and/or the plant itself. The application rates and application area of pesticides can be affected by meteorological conditions such as wind speed and direction. Spray drift is defined as the "downwind movement of airborne spray droplets beyond the intended area of application originating from aerial or ground-based spraying operations" (Stephenson et al., 2007). Monitoring results of a watershed in California found that spray drift is responsible for 24% of the pesticides reaching water bodies , while others have reported that spray drift can result in as much as 20-82% of the applied pesticides leaving the targeted area (Maybank et al., 2012; Ravier et al., 2005). The levels of pesticides in water impacted by spray drift can be more detrimental than pesticides entering receiving water bodies through surface runoff pathways. In one study that examined toxicity of the larval stages of mayflies to pesticide presence, it was concluded that the concentrations due to spray drift were higher and more toxic than concentrations due to surface runoff (Dabrowski et al., 2005). This can be due to the pesticides not being sorb to soil and instead being directly added to the stream. However, vegetative areas such as wind rows and riparian buffers can reduce spray drift from entering nearby water bodies (Zhang et al., 2018).

2.4.3 Surface Runoff

Pesticides applied above ground are vulnerable to be transported from the field during surface runoff events. When this occurs, the water can enter the local stream and have a negative impact on the aquatic ecosystem and drinking water supplies. The transport of atrazine and metolachor with surface runoff are well-documented. For example, in a silt loam soil in Louisiana, pesticides losses via surface runoff were 0.75-1.49 kg/ha for atrazine and 0.95-1.91 kg/ha for metolachlor. These losses were 5.2-10.8% and 3.7-8%, respectively, of the amounts of atrazine and metolachlor applied (Southwick et al., 2003). There is little knowledge of how surface runoff affects the transport of imidacloprid. However, a recent field-scale study suggests that subsurface flow was a more important transport pathway for neonicotinoid pesticides compared to surface runoff. The cause of this can be due to the incorporation of the seeds in the soil, which moves the pesticide-laden coating away from surface runoff generation (McTish, 2019) . Further studies need to be conducted to investigate surface runoff loss of imidacloprid, particularly for spray application methods.

CFPs can be common in various agricultural settings. For instance a study that examined 389 agricultural fields in Illinois found that typically the average per field had between 0 and 17 CFPs. Of the fields studied, approximately 70% were drained by CFPs. The main determinants of CFPs formation are the soil properties, such as soil erodibility factors, material make-up and slope of the area (Shrestha et al., 2018). Additionally, CFPs often form based on the topography of the area. Swales act as narrow valleys and cause water to concentrate and flow rapidly to the adjacent stream. Due to this, sediment can accumulate and create berms and furrows. This can prevent water entering riparian buffer areas and create CFPs, which would cause water to bypass and or undermine the buffer (Wallace et al., 2018). It was found that the area effectively buffered in some watersheds within the Chesapeake Bay was potentially reduced by up to 78% due to CFPs (Wallace et al., 2018).

2.4.4 Sediment-Bound Transport

Pesticides can also be transported bound to sediment that becomes mobilized due to erosion and can enter nearby streams during surface runoff events. Fields with steep slopes increase the amount of erosion that can occur, making pesticides applied to these areas more likely to be transported. Erosion also depends on land use and the soil type (Yang et al., 2016), as well as the intensity of the rainfall event, with erosion increasing during intense rainfall events (Yang et al., 2016).

Land management practices, including the type of equipment utilized on fields, can also influence erosional processes. In the agricultural environment farmers predominately use tractors to do daily tasks (i.e., spray herbicides and fertilizers). The compaction from tractor wheels can have a significant impact on the infiltration of water. A study that observed the effects of wheel traffic concluded that soils that did not have any wheel traffic had a 36.3% lower runoff rate than a highly trafficked soil (Li et al., 2007). The reason for this was due to the compaction of the soil. Micro and macropores are decreased when soils are compacted, reducing the infiltration of rain water (Li et al., 2007). Additionally, soils with greater bulk density generate a lower amount of sediment loss (Jepsen et al., 1997).Therefore, agricultural practices that increase the bulk density of soils, such as equipment traffic, are more likely to facilitate sediment-bound transport of contaminants, such as pesticides.

The amount of sediment loss can be due to the occurrence of CFPs in the field. In a study that investigated CFPs in controlled plots found that 61-78% of the loss from the plots were due to the erosion rills (X. J. Zhang et al., 2018). It was also found that sediment amounts were based on the amount of CFPs. If new CFPs formed during a rainfall events, sediment levels would increase, than if there was already a stable network of CFPs (X. J. Zhang et al., 2018). Another controlled study concluded similar results that developments of CFPs do increase sediment loss (He et al., 2017). It was also concluded that more erosion occurs during high rainfall events and the runoff velocity is reduced when new CFPs are formed (He et al., 2017).

2.5 Riparian Buffers

Best management practices (BMPs) are used to help prevent sediment, nutrients and chemicals from entering adjacent waterways. The BMP that is the current main focus to reduce runoff pollutants is the installment of riparian buffers. These buffers consist of vegetation that separates agricultural fields from streams. These buffers have been known to reduce pesticides from entering the stream from runoff and erosion. As much as 94% atrazine reduction can occur depending on the plant mass available and the soil pore size (Reungsang et al., 2005). In a field plot study investigating the removal efficiency of atrazine and metolachlor, it was concluded that grass buffer strip reduced pesticide emission by 40-95% (Caron et al., 2010). In scenarios in which imidacloprid is transported via surface runoff it was concluded that grassed buffer strips and riparian buffer soils will absorb more then to cropland soils(Satkowski et al., 2018). Although, riparian buffers can reduce the impact of pesticides from entering streams, concentrated flow pathways have an effect on the reduction rate of riparian buffers.

2.6 Concentrated Flow Pathways

The hindrance of the CFPs has been examined based on measurements from modeling and surface flow of pesticides. In one study the amount of pesticides that would wash with the runoff from fruit orchards was investigated. It was found that CFPs can reduce the efficiency of riparian buffer strips and BMPs should have more of a focus on CFPs (Stehle et al., 2016). Another study investigated the nitrate removal of riparian buffers. It was concluded that riparian zones can reduce nitrates from water; however CFPs hinder the natural performance because they bypass these buffer zones (P. J. Wigington et al., 2003).

2.7 Conclusion

Pesticides have been proven to have adverse effects on the environment. They have been linked to the hindrance of fish populations, human digestive systems and inadvertent effects on non-target species such as honey bees. Due to their chemical properties can be mobile and enter adjacent water ways or infiltrate into the groundwater. BMPs are used to reduce the amount of pesticides transported by sediment dispersal via runoff. However, CFPs from agricultural fields have been shown to bypass BMP areas and reduce their effectiveness. There have been, apparently, few studies investigating the role of CFPs in influencing transport of pollutants. This knowledge gap can be investigated by conducting a field study designed to elucidate how pesticides travel through agricultural fields via CFPs.

Section 3: Goals/Hypothesis/Tasks

This reconnaissance study was designed to indicate the role that CFPs can play in the movement of pesticides across fields via surface runoff. Field-scale soil sampling campaigns were conducted at nine agricultural fields at a Long-Term Agroecosystem Research site in Pennsylvania to investigate how pesticide concentrations changed along flow paths from the field to a nearby stream. The pesticides of interest included atrazine, metolachlor, and imidacloprid. The soil concentrations of each of the pesticides of interest were compared within each site from up to four locations: the field itself, CFPs within the field, the buffer zone, and CFPs within the buffer zone. The results were used to identify the potential role that CFPs can play in altering the transport of pesticides from agricultural fields to nearby streams. Findings will help inform future modeling and field investigations and will be used to inform field-scale best management practices likely to be most effective in reducing pesticide transport to surface water.

Goal:

The goal of this research is to develop an improved understanding of field-scale pesticide transport and the potential role of CFPs in altering pesticide movement to nearby streams.

Hypotheses:

The land use in the study site and origin of CFPs will affect whether pesticides are present at higher or lower concentrations in the CFPs compared to the surrounding areas within the field at the study site.

- Part 1: For pesticides that are applied within a crop field (non-concentrated flow areas of the field), concentrations are expected to be lower in CFPs (CFPs of the field) than in areas that experience sheet flow.
- Part 2: For pesticides that are not used in the study site field (e.g., pasture or hay fields) but were applied in an upgradient crop field, concentrations are expected to be elevated, relative to non-concentrated flow areas of the field, in CFPs (CFPs of the field) that originate in the upgradient field (non-concentrated flow areas of the field) (see Fig 3.1).

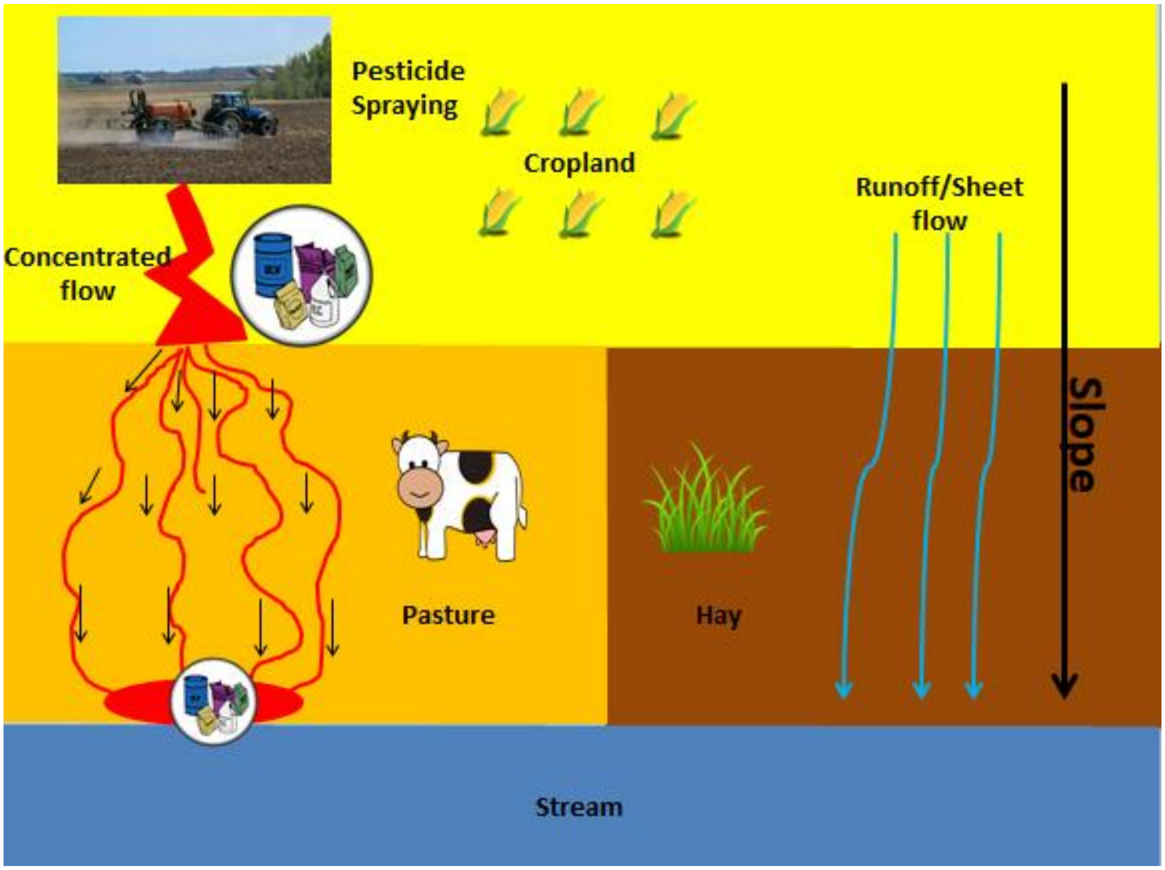


Figure 3-1: Transport of pesticides from an upgradient corn field that received pesticide applications to downgradient pasture and hay fields that did not receive pesticide applications

Research questions:

1. How do anthropogenic factors, such as land use and land management (i.e., pesticide application amounts, type, timing, and location) affect pesticide concentrations within an agricultural field?
2. How does the distribution of pesticides across a field vary by the physico-chemical properties of three pesticides of interest: atrazine, metolachlor, and imidacloprid?
3. How do the types of concentrated flow pathway (i.e., topographical, animal-driven, or natural spring) affect pesticide concentrations within an agricultural field?

Tasks:

1. Document number and type of CFPs within each studied field.
2. Collect soil samples from CFPs, non-concentrated flow areas and adjacent riparian buffers.
3. Analyze samples for atrazine, metolachlor and imidacloprid.
4. Use geographic information system (GIS) to identify areas of flow accumulation and compare those to the CFPs documented in Task 1.

The concentrations of pesticides in the Mahantango Creek watershed have not been previously investigated. The results of this study will be used to inform future sampling campaigns and modeling research. Additionally, they will be used to inform the adoption of BMPs that are most likely to effectively reduce pesticide transport to adjacent waterways.

Section 4: Methodology

4.1 Introduction

To answer the research questions above, a sub-watershed located in Schuylkill County Pennsylvania was selected as the study site. This area is part of the USDA's Long-Term Agroecosystem Research network. As a result, strong relationships with farmers have formed and enabled ready access to land throughout the sub-watershed. The sub-basin is characterized by land use and specific properties were chosen based on permission of the land owner. At the site, CFPs were identified and soil samples were collected from the CFPs, the fields and riparian buffers were taken. Soil samples were taken back to the USDA Agricultural Research Service (ARS) lab in University Park, PA for analysis of pesticide concentrations.

4.2General Overview and Flow Chart of Methodology

Fig. 4-1 represents the organization of the four phases that will occur to understand the effects of CFPs on pesticide transport. Phase one of the flow chart is the field studies section. The first step is the identification of land uses. These land uses were identified by looking at aerial imagery and characterizing the land uses as crop, hay or pasture fields. Next, landowners were contacted to ask for permission to access the property. Then, once at the field site, CFPs were first determined and global positioning system (GPS) coordinates taken to identify the location and of the CFPs. The final step was collecting the soil samples in the CFPs, in the field and the riparian buffer.

The second phase of the research was to analyze the soil samples and GPS coordinates that were collected. The first step of this process was to prep the soil samples for extraction process. Next, the soil samples were extracted and the solutions were analyzed for pesticide concentrations. Also, the GPS coordinates were transcribed onto (GIS) software to identify the lengths of the CFPs and other possible measurements.

The third phase is where the data that was analyzed in phase two is interpreted. The data trend that is found will help understand if CFPs affect pesticide transport in an agricultural setting.

The final fourth phase presents the conclusion of the findings. This phase interprets the findings of the third phase and suggests possible environmental strategies to improve water quality.

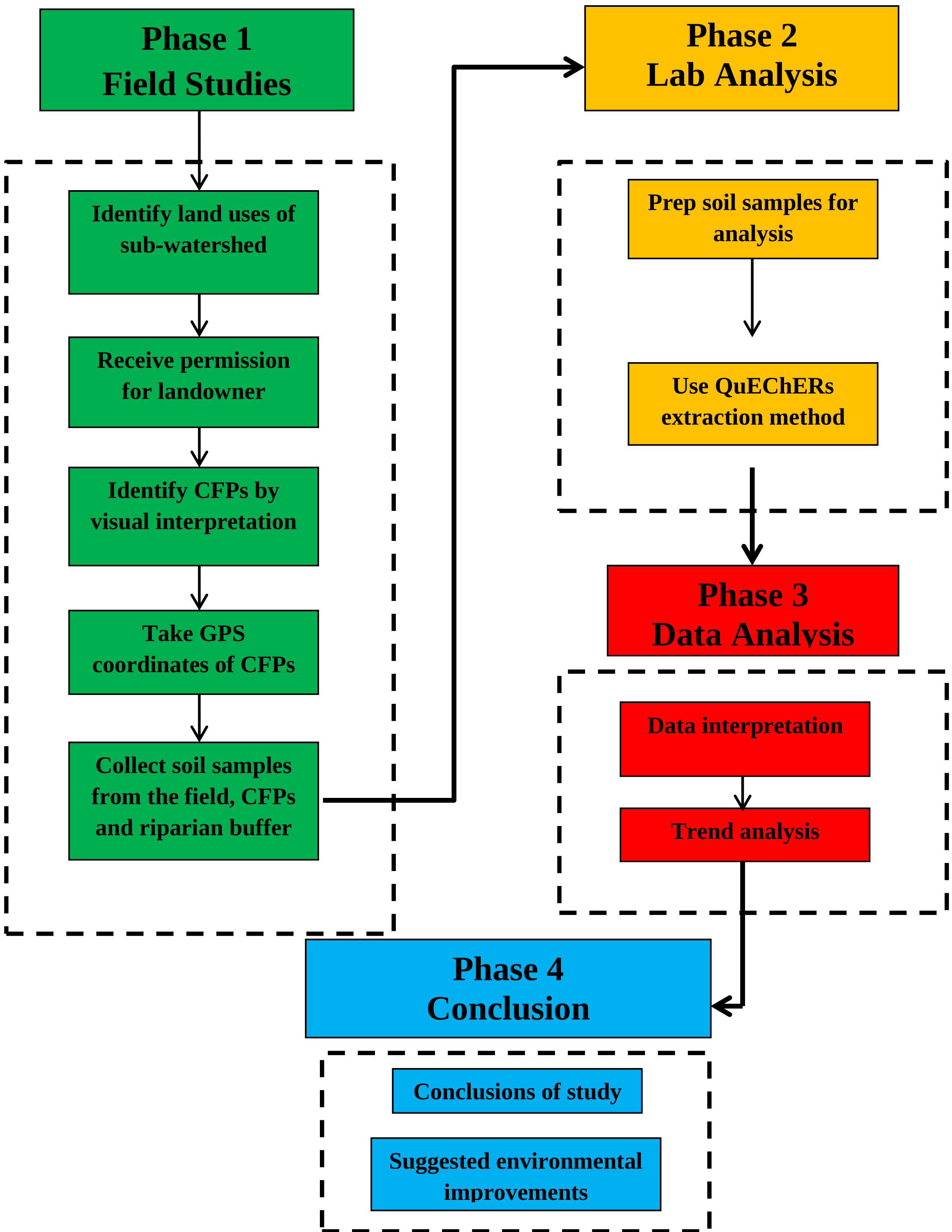


Figure 4-1 Methodology Flowchart for understanding the impact of concentrated flow pathways (CFPs) CFPs on pesticide transport.

4.3 Description of field site

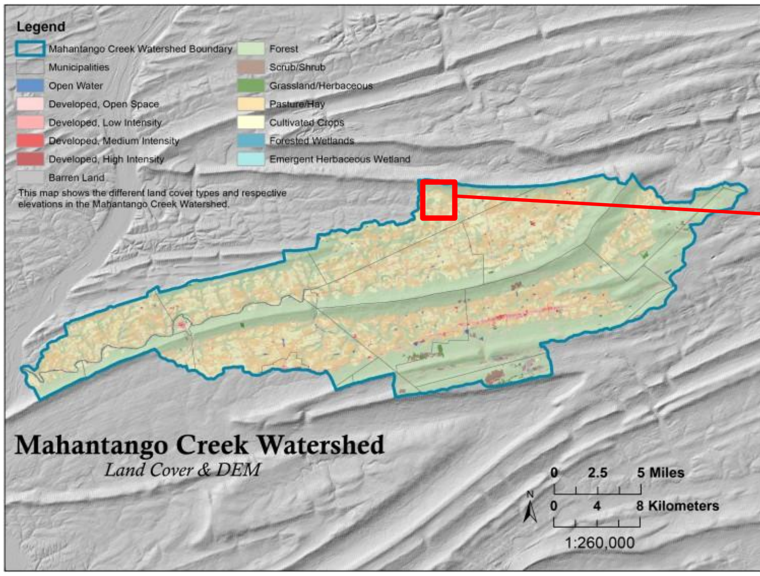


Figure 4-2: Illustration of land use in Mahantango Creek Watershed Source: USDA ARS

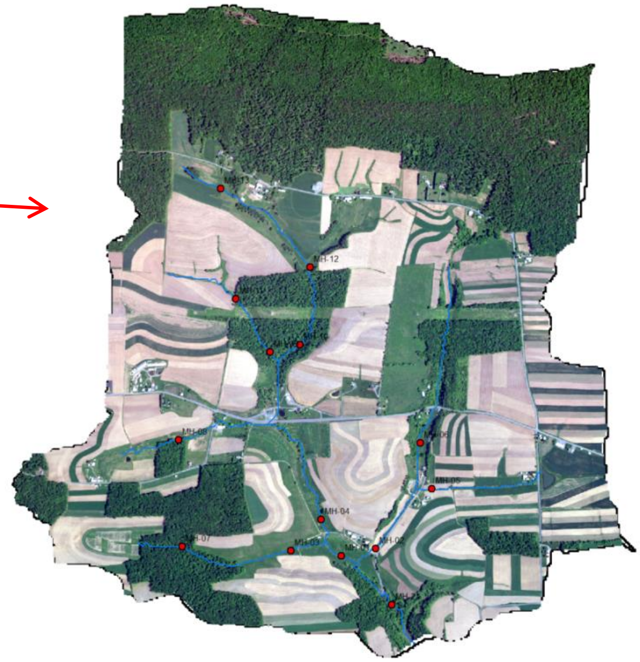


Figure 4-3: Illustration of study area Source USDA ARS Red dots show representative fields sampled as part of this research Source USDA-ARS

The study area that was chosen was a sub-watershed of the Mahantango Creek watershed. Fig. 4-2 illustrates the topography and landscape of the entire watershed. The area highlighted in red is the sub-watershed that was the focus area for this study. This sub-watershed is comprised of agricultural fields such as 57% crop, 8% pasture fields (Pionke and Glotfelty, 1990). The crops that are grown in this area are mainly corn and soybeans for animal consumption. Fig. 4-3 illustrates the sub-watershed in which the red marks were possible locations for this study. For confidentiality of the famers not all marks were tested for this study.

The most commonly adopted BMPs in the study watershed are contour farming, strip cropping and conservation tillage. Riparian buffers are sparse within the sub-basin and none were planted. Areas that do have riparian buffers exist, but are generally due to land of low crop productivity. The streams that are located near the farms are classified as a warm water fishery. This is due to the low water levels as well as high water temperatures caused by unshaded stream channels.

The topography of the area is mainly rolling hillslopes, which is common in the ridge and valley region of Pennsylvania. The area also contains many springs that occur within the cropland. There are a few dwellings in the sub-basin, which are typically farm houses that use septic systems for sewage disposal.

In total, there were nine sites that were selected for this research project. The nine sites were characterized as two hay, five row crop, and two pasture sites. The sites were identified from a previous project and for clarity the same identifications are used (Hirt, 2016). Each site is identified as Mahantango (MH) followed by the field number (Table 4-1). The dominant soil series for the cropland were Calvin (Loamy-skeletal, mixed, active, mesic Typic Dystrudepts) and Klinesville (Loamy-skeletal, mixed, active, mesic Lithic Dystrudepts) with an average 12% slope. Pasture and hay fields soil types differed from site to site and the pasture had an average slope of 14%, while the hay fields had an average slope of 16% (Table 4-1). Any features that could have an impact on the development of CFPs were documented during site visits. The CFPs were characterized as erosional, biological, topographical and sub-surface driven (e.g., springs). Land management of application of the pesticide was also obtained. The sampling period was during a one-month period in the spring season, from May-June 2018. However, the application reference is 2017 data due to the 2018 census not being completed. More detailed site descriptions and land application are provided in Appendix I.

Table 4-1: Land use and soil characteristics of study site (Web Soil Survey)

Site	Land Use	Soil Series
MH 2	Cropland	Calvin-Klinesville
MH 3	Hay	Weikert
MH 4	Pasture	Albrights
MH 5	Cropland	Watson
MH 6	Cropland	Calvin-Klinesville
MH 8	Cropland	Calvin-Klinesville
MH 11	Cropland	Albrights
MH 12	Pasture	Albrights
MH 13	Hay	Shelmadine

4.4 Materials/Equipment

4.4.1 Collection of Samples

Upon surveying each field, CFPs were determined by identification of channelization within the field. Also, it should be noted that any identified springs were considered CFPs. Soil samples were collected inside the CFP at the base of the flow path, which was located just before the CFP entered the riparian buffer or the stream (Fig. 4-4). The non-concentrated flow areas of the field and the non-concentrated flow areas of the buffer were sampled using a zig-zag pattern (Fig. 4-4) to collect a representative sample of the field, ensuring that no samples were collected within any CFPs. This was done on both the left and right side of the streams. Orientation was based on the position when viewing up stream. For example, for the left side of the stream there would be one aggregate of the non-concentrated flow areas of the field, one aggregate of the CFPs of the field, one aggregate of the non-concentrated flow areas of the buffer and if present one aggregate of CFPs the buffer.

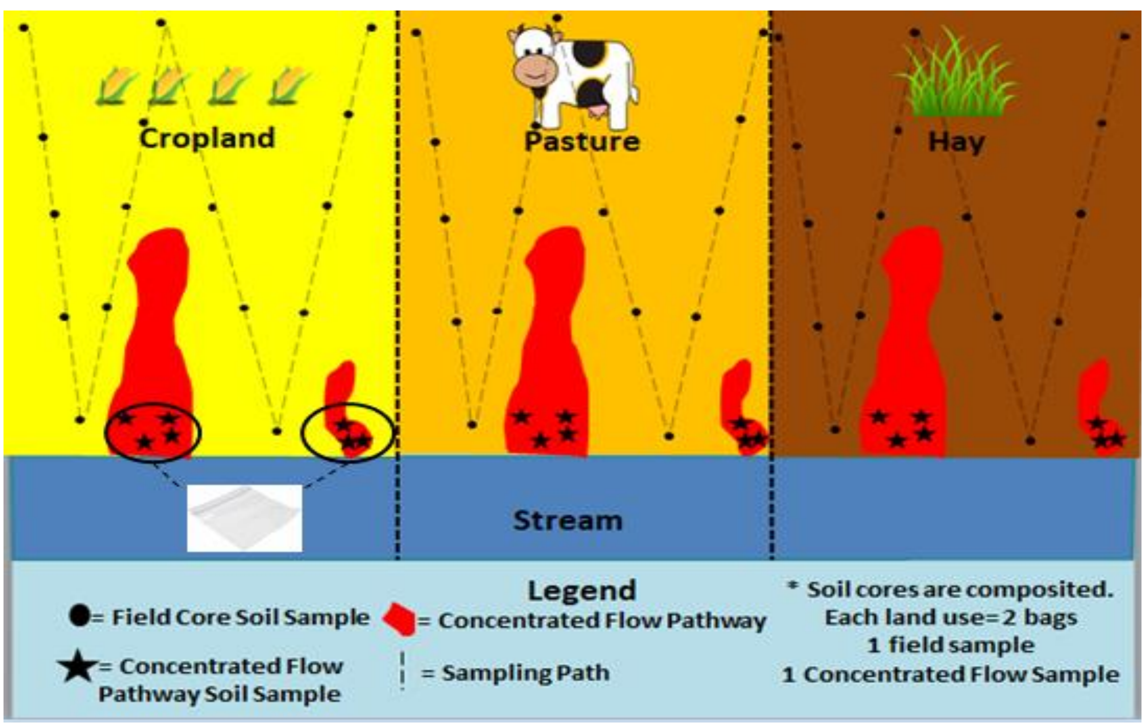


Figure 4-4 Sampling Strategy. The dotted line and the black circles are the zig zag pattern and the collected field soil samples respectively. The red areas are CFPs and samples taken within them are indicated by a dark star.

Soil probes were used to collect all soil samples. To reduce contamination, 95% ethanol was used to wash probes in between field sites and different areas of the field. Sterile nitrile gloves were also used during sampling and were changed each time the soil probes were sanitized to reduce cross contamination. Each composite sample consisted of fifteen to twenty 0-2 cm depth cores samples and these core samples were composited into plastic Ziploc® bags. The bags were properly labeled and stored in backpacks with ice packs. During transport back to campus, the ZipLlock® bags were kept inside a cooler and upon arrival at the University, placed in a Thermmax© freezer at -17°C until analysis preparation began.

4.5 Analysis of Samples

Analysis of the samples began by lyophilizing the samples using a Virtis 35XL (SP Scientific, Gardiner, NY) to less than 1% moisture, over a 3-day drying cycle (Fig. 4-5). Next, the dried samples were ground until all aggregates were pulverized and then sifted through a 2 mm sieve. The soil were bagged, labeled and frozen until ready for the QuEChERS ("Quick, Easy, Cheap, Effective, Rugged, Safe") extraction procedure.

The QuEChERS method first uses 7.5 g soil sample, which is extracted by adding the soil to 10 mL of 1% acetic acid in acetonitrile, 1.5 g anhydrous sodium acetate and 6 g magnesium sulfate into a 50 mL centrifuge tube. This is then vortexed for 30 sec. and centrifuged at 3000 rpm for 5 min at 20°C. Next, the 10 mL of clear solution above compacted soil was added to a 15 mL centrifuge tube that contains 1.2 g of magnesium sulfate, 400 mg of PSA and vortexed for 30 sec. The mixture was centrifuged at 3000 rpm for 5 min at 20°C. Finally, 200 µL of extract is added to a 1ml vial containing 300 µL of acetonitrile, and 500 µL of 8mM ammonium formate buffer.

The following methodology was provided by Dr. Kyle Elkin (5/9/2019)

"Analysis and quantification of the three pesticides in soil samples were done using a high-resolution accurate mass (HRAM) Q Exactive mass spectrometer (Thermo-Fisher Scientific, Bremen, Germany), interfaced with an ICS-5000+ chromatography system (Thermo-Fisher Dionex, Sunnyvale, CA) via a heated electrospray injection (HESI) source. Ten µL of sample was injected onto a 2.1x100 mm, 3µm Hypersil Gold aQ column (Thermo-Fisher Scientific, San Jose, CA) and eluted using 0.1% formic acid and 4 mM ammonium formate in water (A) and Methanol (B) under the following linear gradient: 88%A:12%B at 0 min, 100% B at 9 min with a 2 minute hold, followed by a 3 min equilibration at 88%A:12%B. The flow rate during the elution was 0.3 mL/min. The mass range for the mass spectrometer was set from 80 to 1100 m/z with a resolution of 70,000 and operated in data dependent MS2 mode for all analytes in the predefined inclusion list. The ddMS2 mode used a resolution of 35000 and used normalized collision energies of 20, 40, and 60 electron volts. The percent recoveries for all of the analytes were determined using the standard addition method, and were found to be greater than 90%. The calibration range for each of the analytes was 0.1 to 100 µg/L."

Each of the three pesticides that were analyzed had an instrument limit of detection (LOD) of 0.01 µg/L and a limit of quantification (LOQ) of 0.1 µg/L (signal to noise ratio of 10 over background). This translates to a dry soil detection limit of 0.02 µg/kg and a quantification limit of 0.2 µg/kg. The concentrations from the LC-MS were given in µg/L and using fig.4-5 the concentrations were converted to µg/kg.

$$\frac{0.075X\ ug\ A}{7.5\ g\ soil} = \frac{0.01X\ ug\ A}{g\ soil} \text{ or } \frac{10*X\ \mu g\ A}{kg\ soil}$$

Figure 4-5 Where X µg A is the concentration of pesticide A in µg/L

There were three sites (MH 2, MH11, MH13) which incorporated a different sampling strategy. Instead of compositing all CFPs into a bag they were separated individually. Each sample went through the same processing procedure and then final concentrations were averaged together. Averaging was done by taking the sum of the concentrations and dividing by the total number of the CFPs sampled at the site. This included samples that contained concentrations below the quantification limit of 0.2 µg/kg but above the detection limit of 0.02 µg/kg. This sampling process was done in the beginning of the sampling period and due to time constraints, the sampling was changed to the process previously explained.

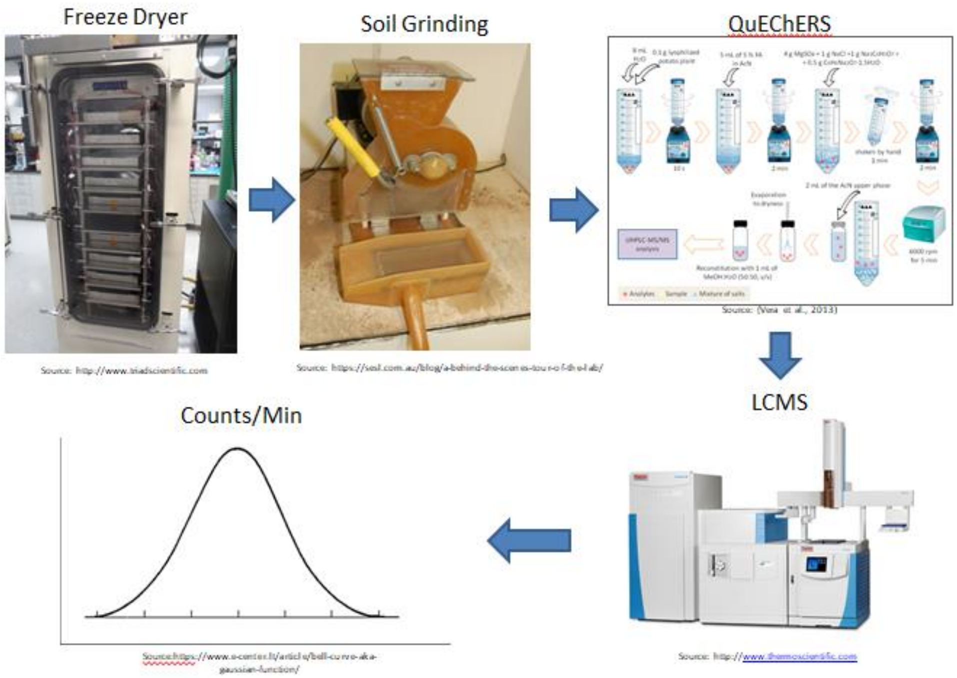


Figure 4-6 Step by step analysis of samples a=Triad Scientific© b= SESL Australia© c= Vera et al., 2010 d= ThermoFisher Scientific © e=E-Center ©

4.6 Data Analysis and Interpretation

The concentrations of the pesticides were first aggregated together based on being a non-CFP or a CFP for each land use. It should be noted that due to low numbers of samples, pasture and hay fields were tested together to provide a stronger output value. Additionally, none of the pesticides of interest were directly applied to the pasture and hay fields, so this grouping essentially allowed areas where pesticides were applied (i.e., crop fields)_to be compared to areas where the pesticides were not applied (pasture and hay fields). These values were analyzed by conducting a "Two Sample T-test" using Minitab© software. Equal variance was not assumed during the analyses and a confidence interval of 95% was used. Box plots were created using MATLAB© to illustrate the range values of each pesticide for non-CFP and CFPs for each landuse. Based on the analysis findings, an investigation of the trends of each specific site followed.

The concentrations of each pesticide are illustrated as bar charts for each land use, with each of the concentrations normalized to the concentration in the non-concentrated flow areas of the field samples, which were collected from areas of the field where the downslope movement of water was assumed to occur via sheet flow.. Samples collected from other locations at the site (i.e., CFPs of the field, non-concentrated flow areas of the buffer, and non-concentrated flow areas of the field) were compared to the non-concentrated flow areas of the field concentration to determine whether concentrations increased or decreased along the flow path to the stream. The percentages located above the respective bars are comparative percentages based on the field concentration as a reference.. When concentrations were present below the method limit of quantification, a value equal to LOQ/2 (0.1 µg/kg) was used to calculate the percent differences compared to the in-field baseline. The results are depicted such that each land use is a different color: cropland, pasture and hay fields are represented as yellow, orange and brown respectively, while CFPs are represented as red bars. The blue dotted line is used to represent the stream that divides the sampling sites into two sides (A and B). A visual illustration of each field is given in Appendix I.

Hydrus© software was also used to understand possible concentrations and leaching depth for one year based on a modeling perspective. Modeling was only conducted at one crop site (MH 6) which had similar characteristics to the other sampled sites, such as soil type (Table 4-1), acreage and slope. Table 4-2 provides the assumed depth and soil characteristics based on soil horizons. Table 4-3 provides the assumptions made for model process and Table 4-4 provides chemical information that was used for solute inputs. (The assumptions and conclusions were collectively done in Dr. Jack Watson's, spring 2019 Soils 502 class.)

Table 4-2 Residual soil water content (Qr), saturated soil water content (Qs), organic carbon content (OC), and soil water retention function (N) were obtained from Web Soil Survey.

Soil Type	Depth (cm)	Qr	Qs	OC	N
Silt Loam	0-20	0.0405	0.4295	0.0203	1.3827
Silt Loam	20-46	0.0369	0.3707	0.0147	1.3882
Silt Loam	46-115	0.04626	0.3733	0.0233	1.3116

Table 4-3 Assumptions for Hydrus© variables

Lowest Koc values were used to calculate K_d coefficients
Application methods were at a constant rate
No runoff
Groundwater depth of 20ft (610 cm)
Constant water flux of -0.33 cm/day (US Climate Data©)
Dispersivity factor of 10
Chemicals are not in equilibrium
Bound Condition=100

Table 4-4 Chemical information. Used low Kd values for worst case scenario. a= PubChem©

Material	***Fractional Organic Matter Content***	***Organic Carbon***	K_{oc}^{a}	K_{d}^{a}
Solute *1 Atrazine*				
1	0.013	0.0065	26	0.169
2	0.003	0.0015	26	0.039
3	0.001	0.0005	26	0.013
Solute 2 Metolachlor				
1	0.013	0.0065	22	0.143
2	0.003	0.0015	22	0.033
3	0.001	0.0005	22	0.011
Solute 3 Imidacloprid				
1	0.013	0.0065	132	0.858
2	0.003	0.0015	132	0.198
3	0.001	0.0005	132	0.066

Section 5: Results and Discussion

5.1Introduction:

A total of nine different field sites, five cropland, two hay, and two pasture fields, were selected as study sites in the Mahantango Creek watershed. A detailed description of each field is provided in the Appendix I. Here, the trends of pesticide concentrations were summarized by comparing concentrations in the CFPs to the surrounding soil and downgadient riparian zone, if one was present at the site. The results are organized by land use to highlight the patterns that emerged across the study sites.

5.2 Statistics

Based on the Minitab© results (Table 5-1) it is concluded that the majority of the comparisons conducted of the non-concentrated areas and the CFPs in the different landuses were statistically similar for each pesticide due to the p values being greater than .05. However, atrazine in the cropland setting was the only scenario where the difference of the non-concentrated flow areas and the CFPs were statistically different. The reason for this could be due to atrazine priesting longer in non-concentrated flow areas than in CFPs. Box plots that show the ranges of each pesticide for each landuse can be seen below. Due to the concentrations being aggregated together were typically similar, an investigation of specific site trends was conducted.

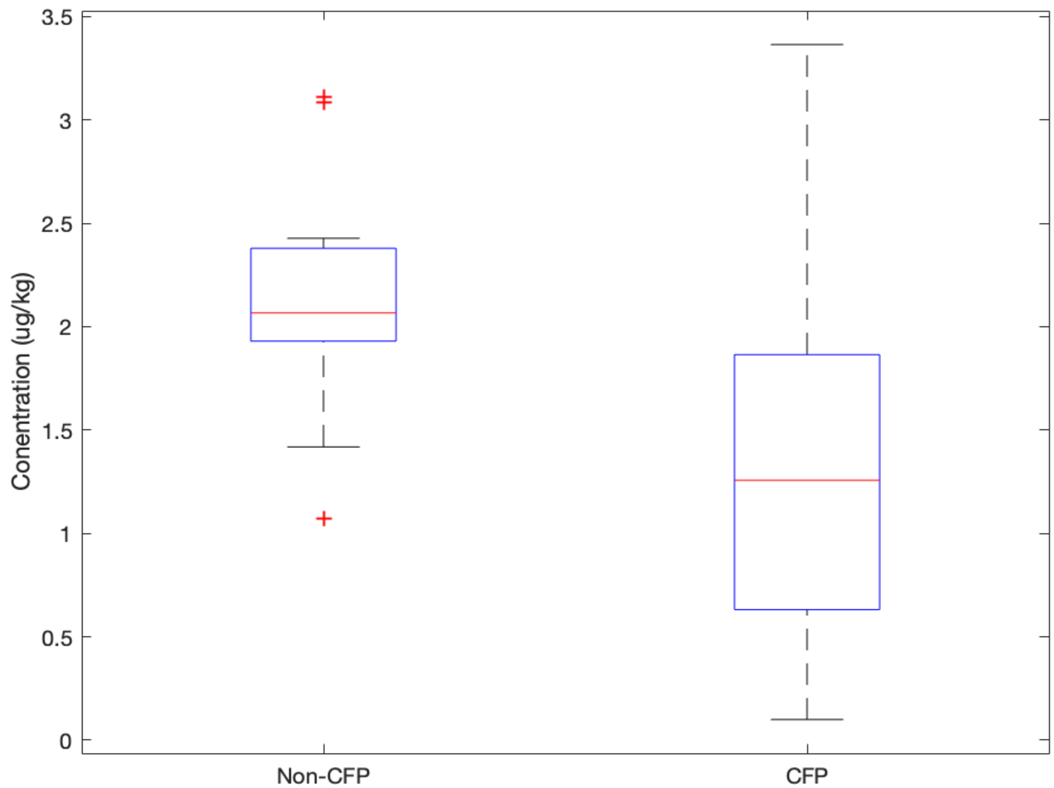


Figure 5-1 illustrates the box and whisker plot of atrazine in a cropland setting. The central line shows the median, and the bottom and top edges of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers. The '+' symbol indicates each individual outlier.

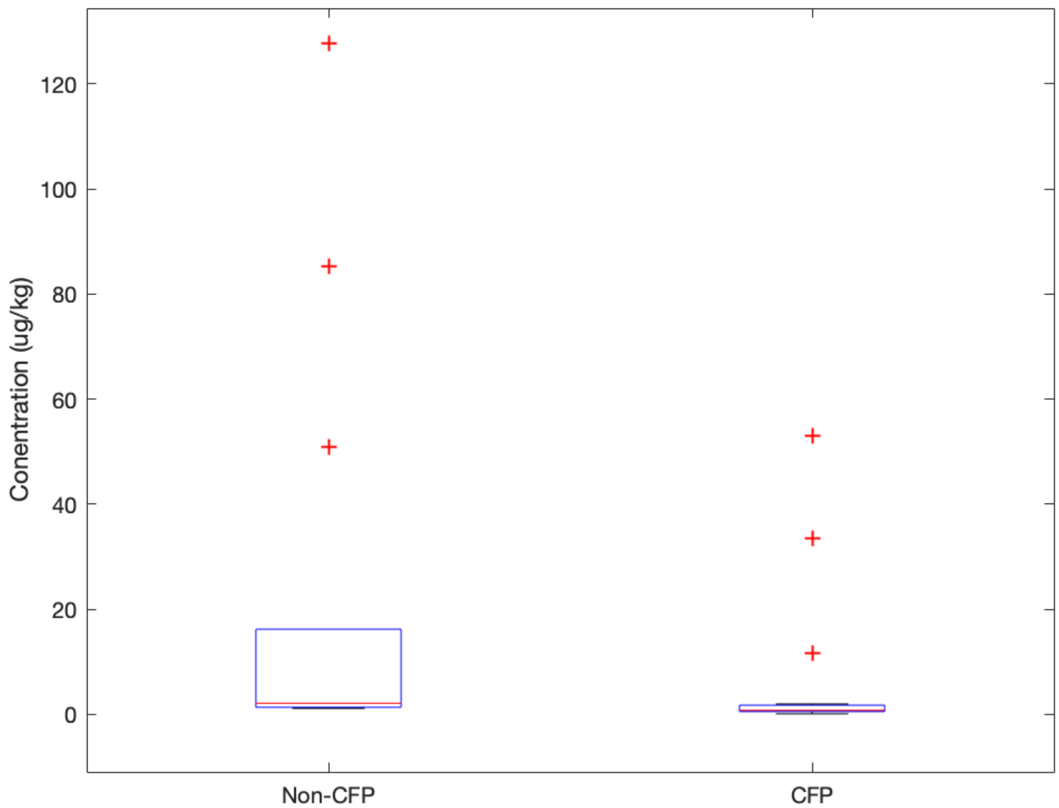


Figure 5-2 Illustrates the box and whisker plot of metolachlor in a cropland setting. The central line shows the median, and the bottom and top edges of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers. The '+' symbol indicates each individual outlier.

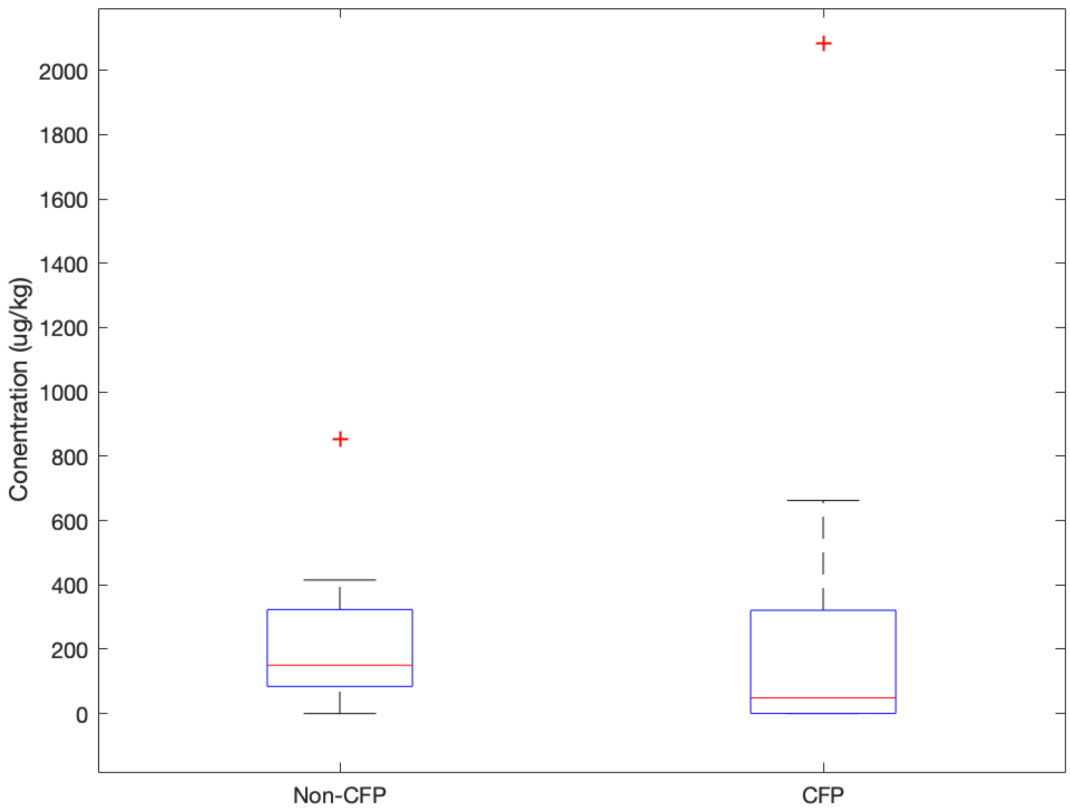


Figure5-3 Illustrates the box and whisker plot of imidacloprid in a cropland setting. . The central line shows the median, and the bottom and top edges of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers. The '+' symbol indicates each individual outlier.

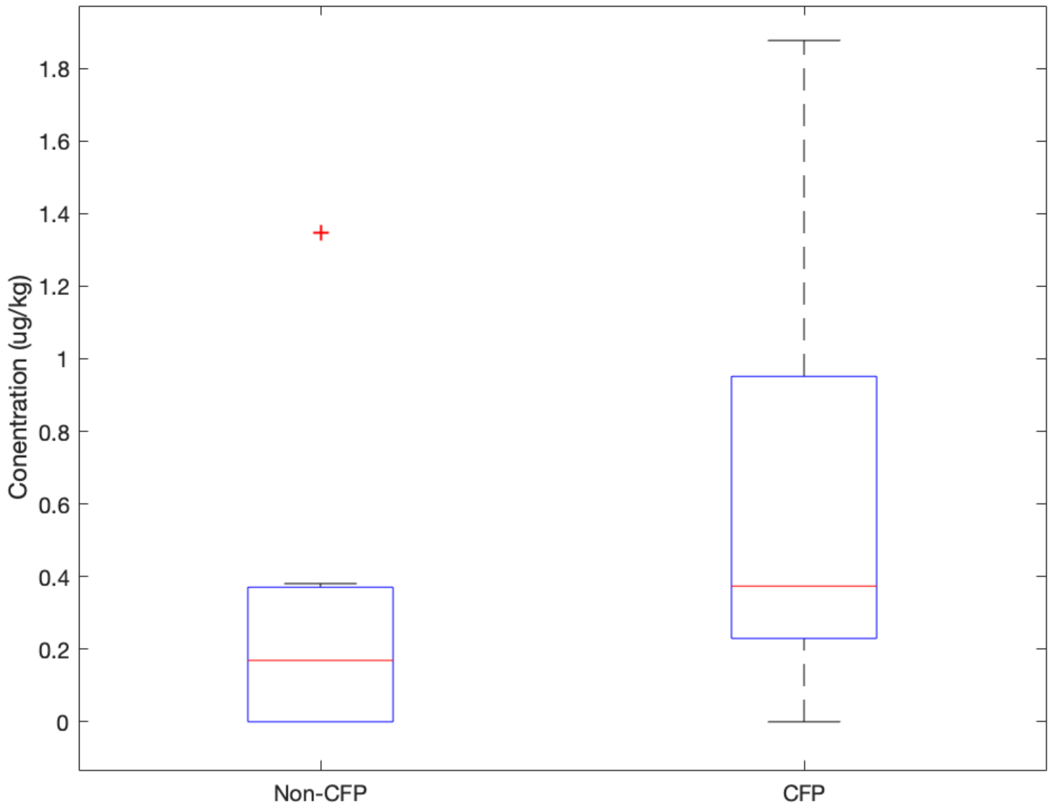


Figure 5-4 Illustrates the box and whisker plot of atrazine in a pasture/hay setting . The central line shows the median, and the bottom and top edges of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers. The '+' symbol indicates each individual outlier.

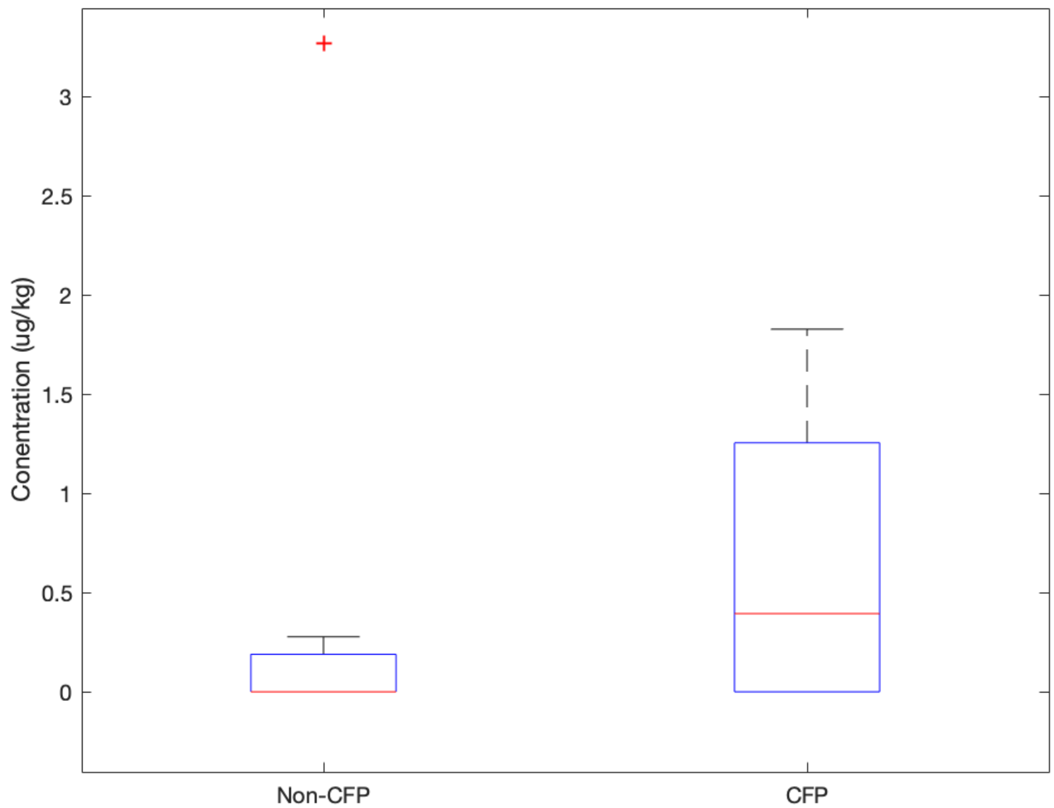


Figure 5-5 illustrates the box and whisker plot of metolachlor in a pasture/hay setting. . The central line shows the median, and the bottom and top edges of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers. The '+' symbol indicates each individual outlier.

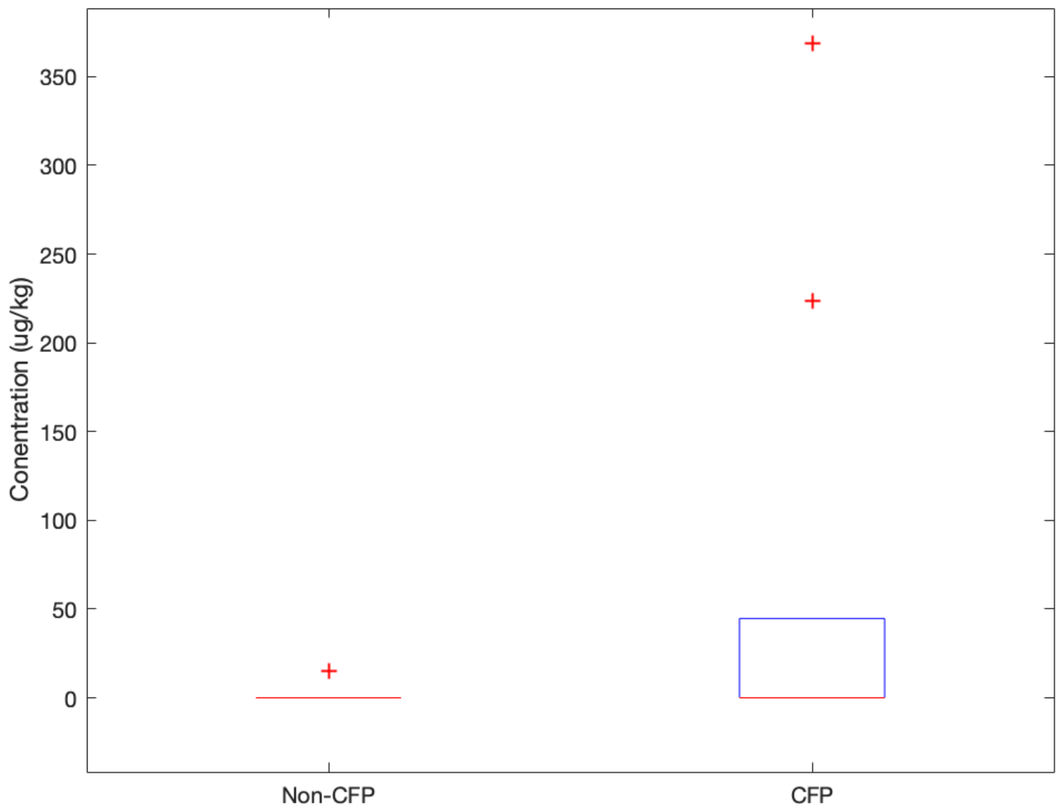


Figure5-6 illustrates the box and whisker plot of imidacloprid in a pasture/hay setting. The central line shows the median, and the bottom and top edges of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers. The '+' symbol indicates each individual outlier.

Table 5-1 Results of Two Sample T Test when comparing Non CFPs to CFPs with a 95%confidence interval

Crop Field	p value	Standard Deviation		Mean	
		Non CFP	CFP	Non CFP	CFP
Atrazine	0.012	2.126	1.381	0.563	0.934
Metolachlor	0.207	22.1	6.5	40.7	14.5
Imidacloprid	0.892	223	511	235	254
Pasture/Hay					
Atrazine	0.226	0.451	0.557	0.303	0.609
Metolachlor	0.685	1.14	0.752	0.46	0.651
Imidacloprid	0.161	5.25	128	1.86	64

5.3 Corn Fields:

In general, the CFPs started in the corn fields, and therefore atrazine and metolachlor were applied directly to the CFPs. In contrast, imidacloprid is coated on the seeds, so unless a seed is planted in a CFP, no imidacloprid is directly applied to the CFP. All of the fields had crop residue and are typically no till, with the exception of MH 6. The characterizations of the CFPs in the corn fields were typically erosional and were created by repeated tractor use and exposure of vulnerable soil to rainfall. A total of 28 samples from the cropland sites, with 8 CFPs of the field samples, 9 non-concentrated flow areas of the field samples, 2 CFPs the buffer samples, and 9 non-concentrated flow areas of the buffer samples were collected.

5.3.1 Atrazine

The atrazine concentrations found within the corn fields ranged from 0.27 to 3.37μg/kg (Fig.5-7). All of the measured concentrations were above the method LOQ for each of three pesticides. The common trend that emerged from comparing soil samples collected within the non-concentrated flow areas of the field to CFPs of the field was that concentrations in the CFPs of the field were lower than non-concentrated flow areas of the field (Fig 5-8 through5-11). The concentrations were likely found to be higher in the non-concentrated flow areas of the field because areas outside of CFPs experience surface runoff via sheet flow for which flow velocities are lower compared to the CFPs. Surface runoff via sheet flow carries less sediment than concentrated flow; causing atrazine to remain on the field rather than mobilized in surface runoff (Germany, 2018). However, when concentrated flow occurs, sediment-bound atrazine is likely mobilized from within the CFPs of the field themselves or drainage from the non-concentrated flow areas of the field to the CFPs of the field, likely resulting in the lower concentrations in the soil within the CFPs of the field compared to the non-concentrated flow areas of the field.

Some exceptions to this trend were observed at sites MH 2 and MH 11. As shown in Fig. 5-7 (MH 2), side A contained a higher concentration in the CFPs than the field (i.e., CFPs of the field concentrations were higher than non-concentrated flow areas of the field concentrations). This was likely due to the presence of a culvert that brought stormwater from side B to side A, enabling the CFPs of the field to have elevated atrazine concentrations on side A relative to the non-concentrated flow areas of the field samples on side A. The other discrepancy can be seen at

MH 11 Fig. 5-11 side B, which had similar concentrations in the field, CFPs and the buffer. The reason for this is likely due to the CFPs at that site being characterized as springs. Flow from these springs likely contained elevated levels of atrazine from upgradient fields and were not erosional features in the landscape. Therefore, soils in the CFPs were able to maintain similar levels of atrazine compared to the rest of the site.

For the study sites that contained riparian buffer zones (MH 2, MH 5, MH 6, MH 8), atrazine concentrations were found to be lower in the (non-concentrated flow areas of the buffer sample) than the upgradient (non-concentrated flow areas of the field sample), with concentrations reduced by as much as 91% in the buffer compared to the field. Of the sites with buffer zones, two of them had CFPs that originated in the cropland field and bypassed the buffers (MH 2 and MH 8). At these sites, the concentrations in the CFPs the buffer were overall greater than the non-concentrated flow areas of the buffer. However, for the remainder of the sites with riparian buffer zones, the concentrations in the non-concentrated flow areas of the buffer samples were lower than the samples collected in the non-concentrated flow areas of the field. This provides evidence that the buffer is able to effectively reduce atrazine that is from in runoff from an adjacent field when the flow through the buffer is not short-circuited. However, it also provides evidence that CFPs compromise the integrity of buffers and are less effective in reducing pesticides through CFPs, suggesting that the presence of CFPs in riparian buffers can lower the ability of the buffer to reduce surface runoff quantity and quality.

One site (MH 2) contained an area on the edge of the field that was deemed a wetland area (see Appendix I) that was comprised of dense vegetation and hydric soil. The concentration of atrazine was found to be similar (< 10% higher) in the wetland than the upgradient field, and > 80% higher than the CFPs of the field and non-concentrated flow areas of the buffer samples. Atrazine is degraded via microbial activity, which is faster under aerobic conditions compared to anaerobic conditions (Accinelli et al., 2001). The wetland likely experienced prolonged periods of anoxic conditions, causing atrazine degradation to be reduced and potentially increase over time as more surface runoff and sediment-bound atrazine entered the wetland.

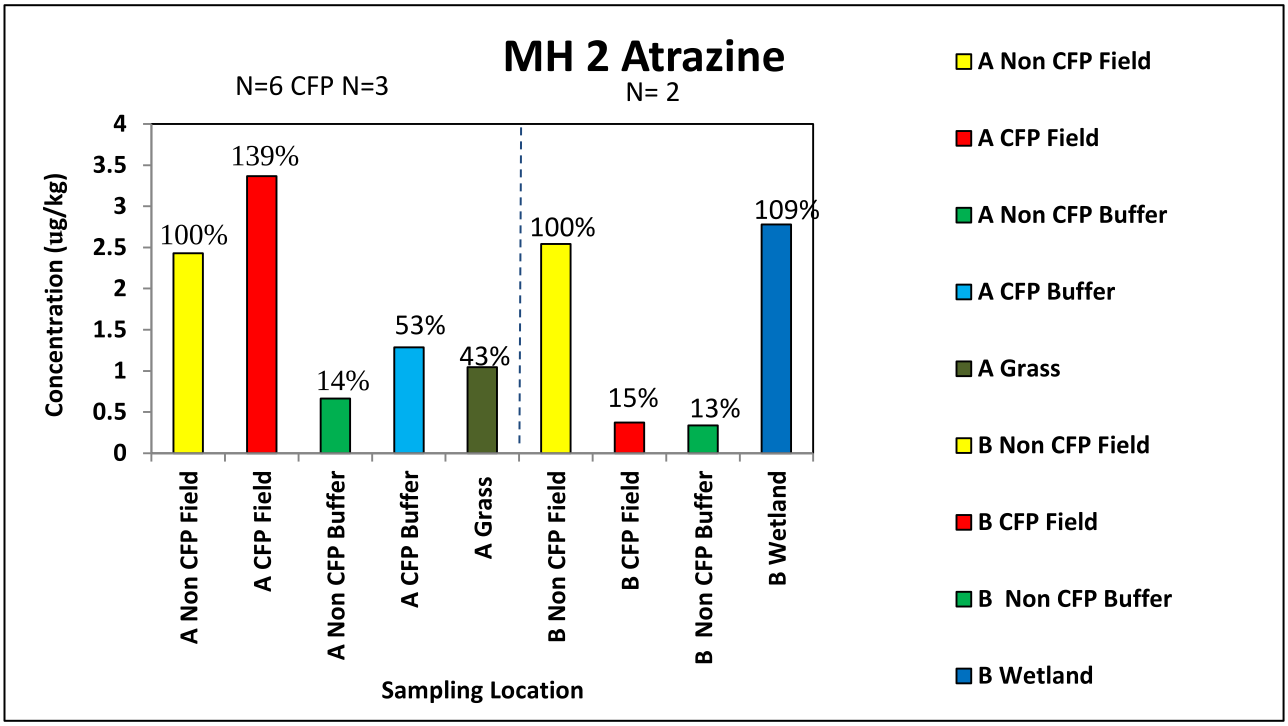


Figure 5-7 Atrazine concentrations in composite soil samples collected in non-concentrated flow path areas and concentrated flow path areas at field site MH 2. Percentage values are referenced to non-concentrated flow areas of the field concentrations for each field. N represents the number of CFPs

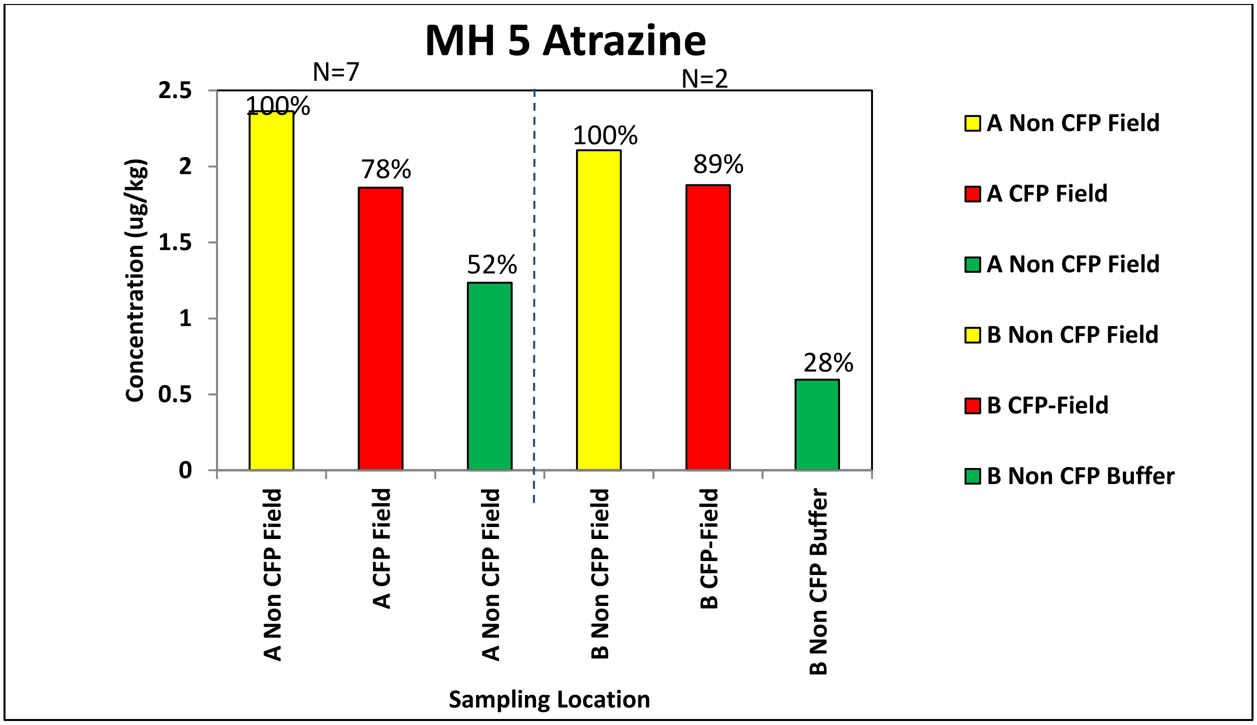


Figure 5-8 Atrazine concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 5. Sides A and B denote field locations on the left and right sides of the stream.

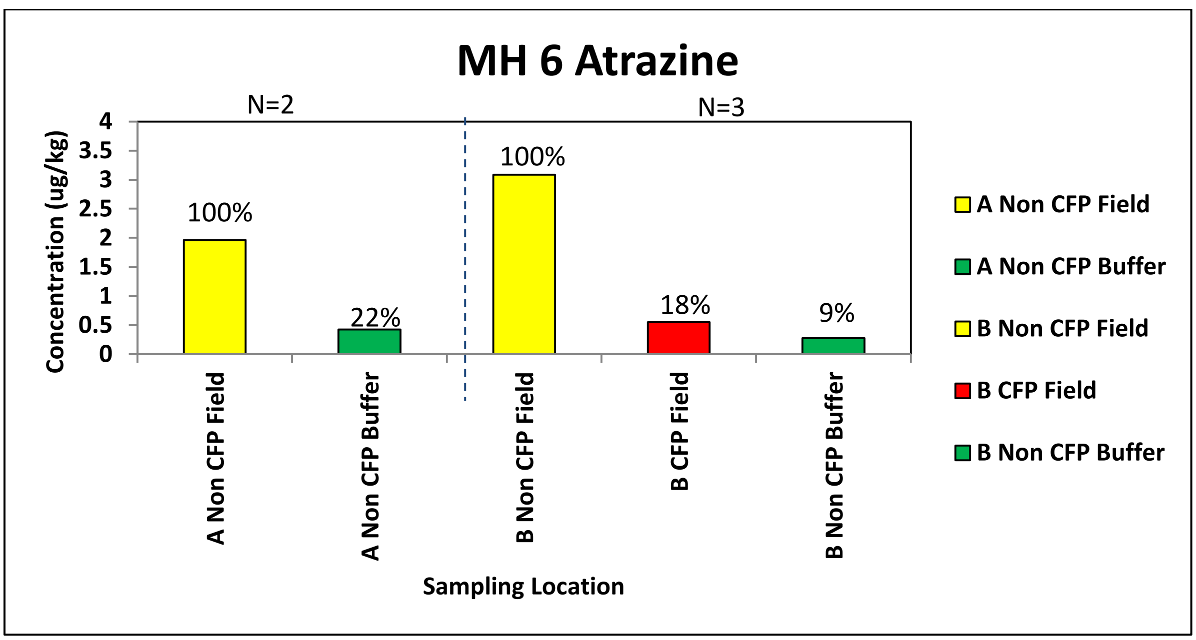


Figure 5-9 Atrazine concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 6. Sides A and B denote field locations on the left and right sides of the stream.

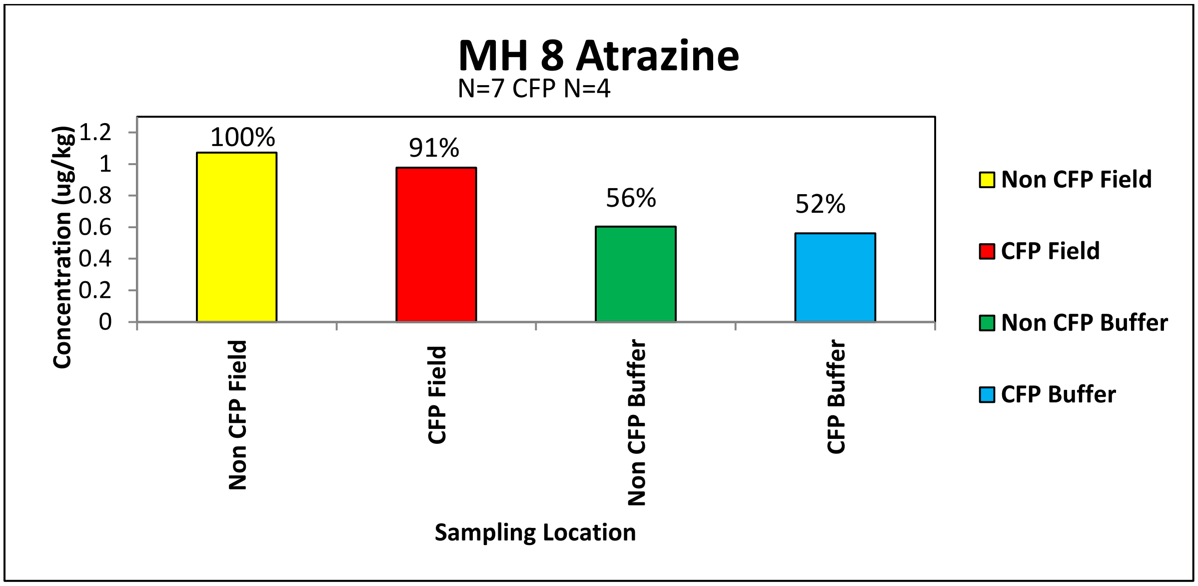


Figure 5-10 Atrazine concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 8.

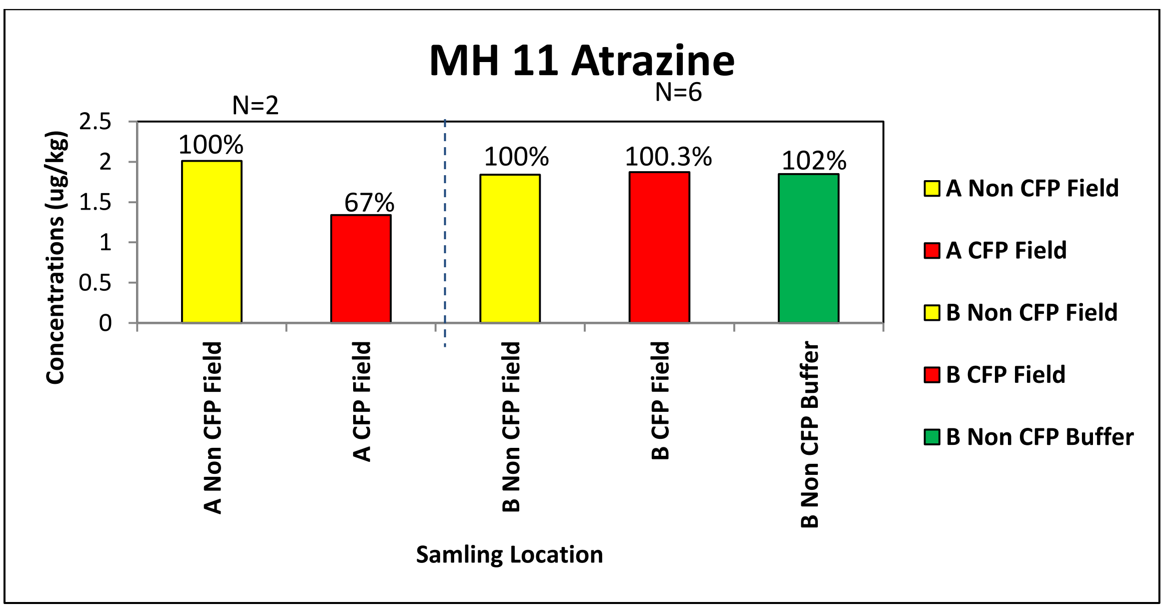


Figure 5-11 Atrazine concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 11. Sides A and B denote field locations on the left and right sides of the stream.

5.3.2 Metolachlor

The metolachlor concentrations found within the cropped fields ranged from <LOQ to 127.82 µg/kg and as low as<LOQ. All of the concentrations were present above the method LOQ except for one at MH 6. The overall trend observed for metolachlor in cropland fields was that it was present at higher concentrations in the non-concentrated flow areas of the field samples than in the CFPs of the field samples. These results are similar to those observed for atrazine in cropland fields. Concentrations generally were reduced in the CFPs of the field samples by 33-86% relative to the non-concentrated flow areas of the field samples, and within the buffer zone, metolachlor concentrations were typically58 -100% lower compared to the non-concentrated flow areas of the field samples.

The transport behavior for metolachlor, as suggested by the soil samples collected for this research, appears to be similar to atrazine. This is likely because the two pesticides are typically applied together and they have similar physcio-chemical properties (Table 2-1). Since their sorption coefficients and half-lives are on the same order of magnitude and environmentally relevant aqueous concentrations are well below the aqueous solubility limit, the observed similar transport patterns are consistent with expectations.

For areas that contained buffer zones (MH 2, MH 5, MH 6, and MH 8), metolachlor concentrations were found to be lower in the buffer than the upgradient cornfield. As with atrazine, CFPs may be hindering the buffer performance. Another reason is that the buffers typically did not have dense vegetation and consisted of mainly shrubs. However, there was one site (MH 11 side B) where the buffer zone was mainly of grass. At this location, the amount of metolachlor was greater than the upgradient field. The reason for this is that the dense vegetative area was able to capture more of the metolachlor bound sediment that was being transported by CFPs characterized as springs.

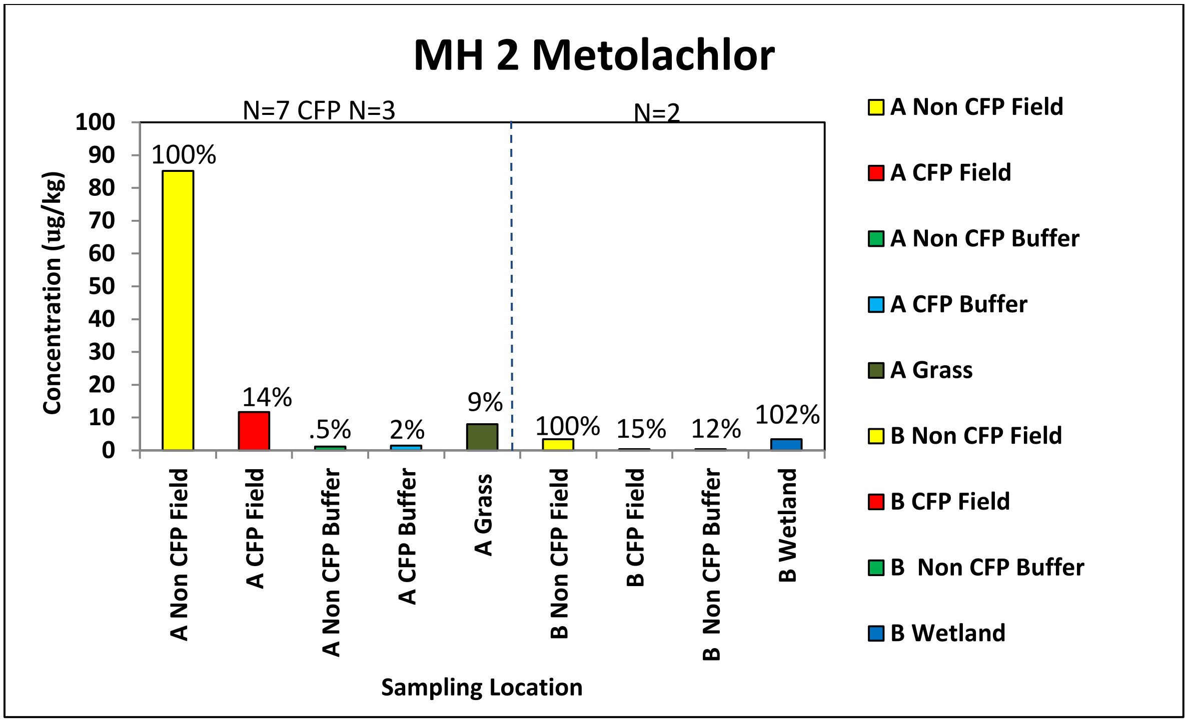


Figure 5-12 Metolachlor concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 2. Sides A and B denote field locations on the left and right sides of the stream.

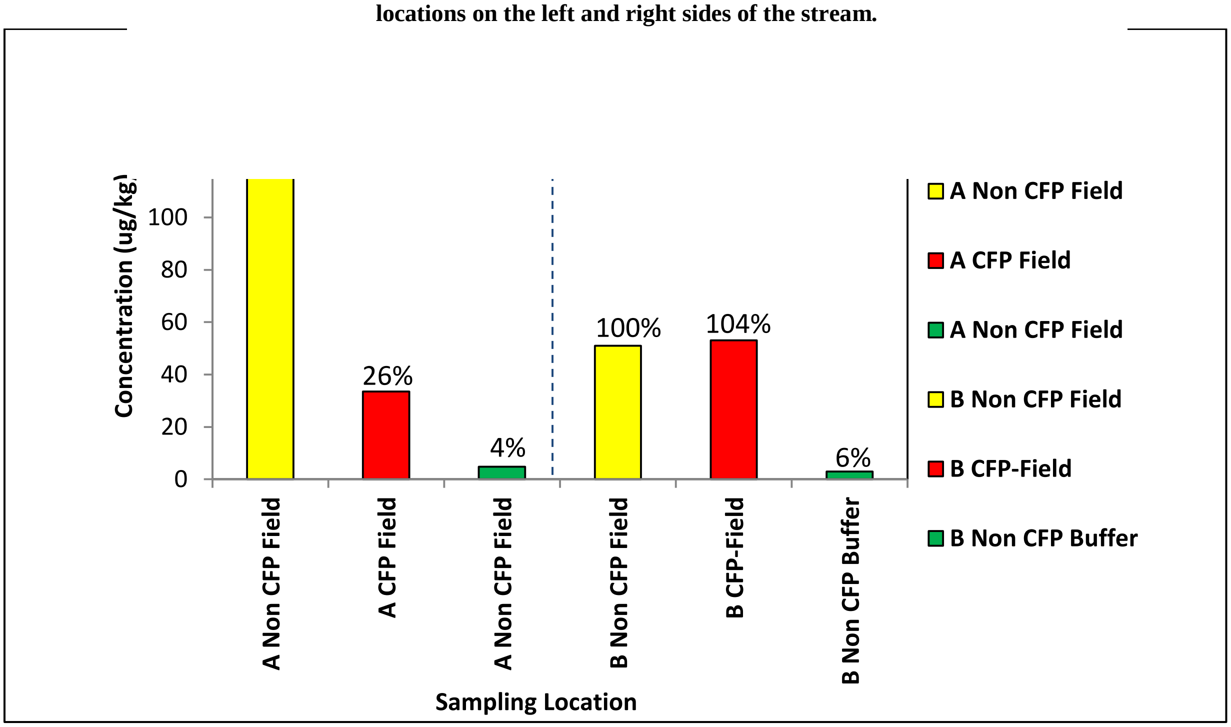


Figure 5-13 Metolachlor concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 5. Sides A and B denote field locations on the left and right sides of the stream.

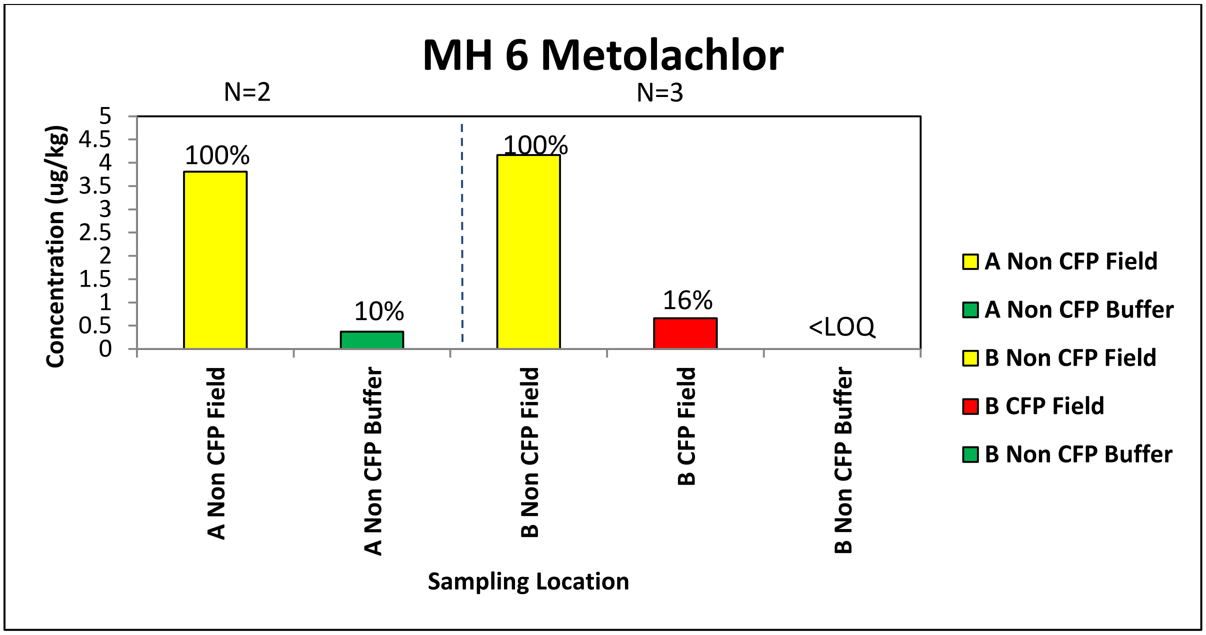


Figure 5-14 Metolachlor concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 6. Sides A and B denote field locations on the left and right sides of the stream.

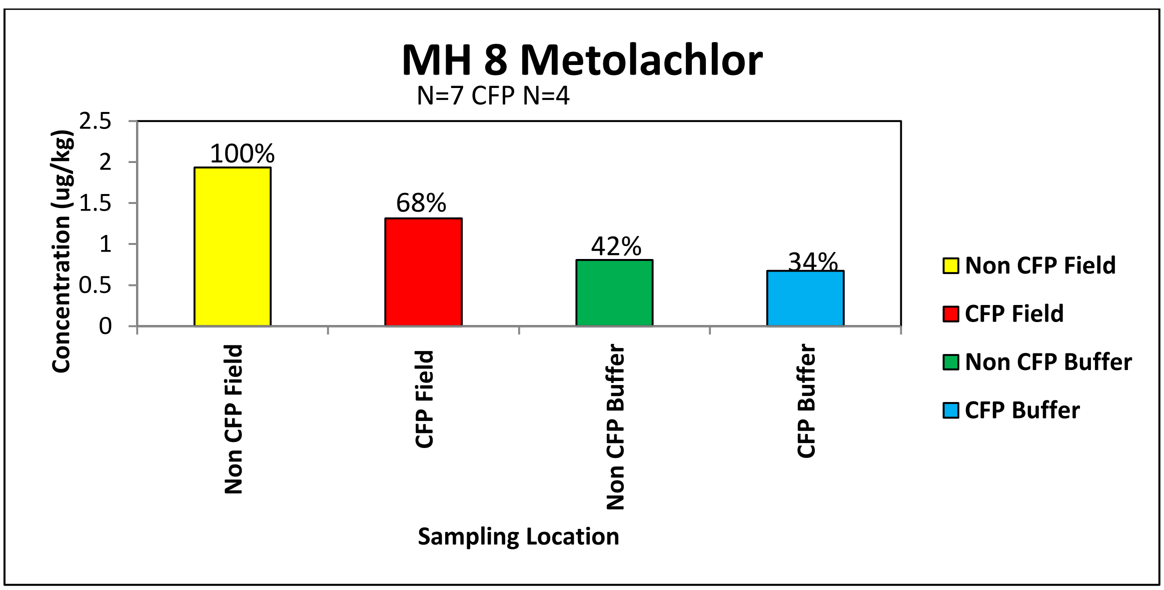
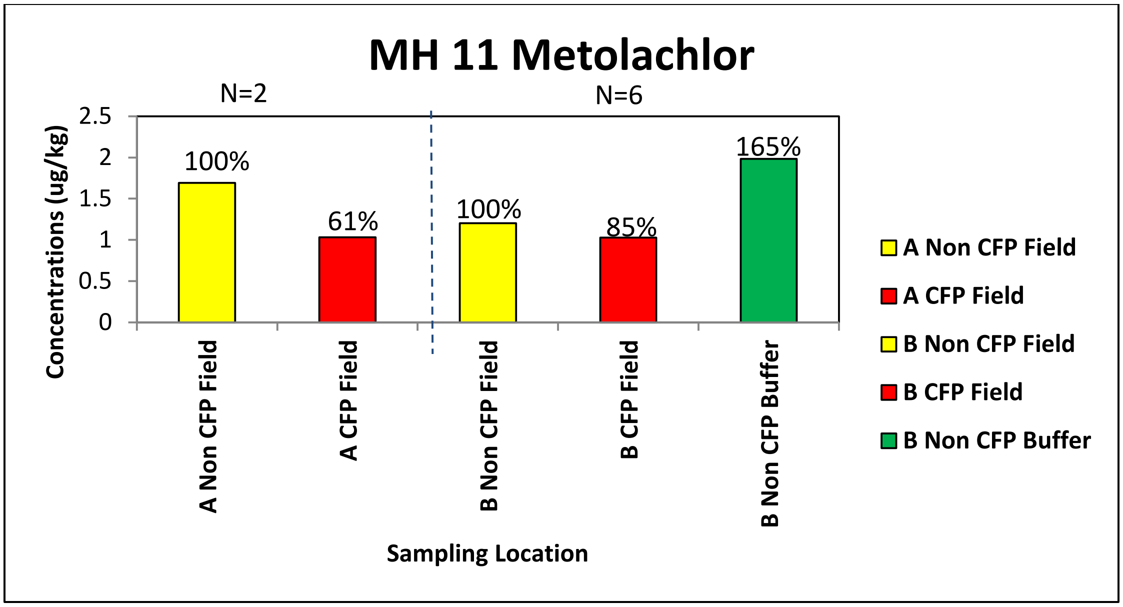


Figure 5-15 Metolachlor concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 8.



26 Figure 5-16 Metolachlor concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 11. Sides A and B denote field locations on the left and right sides of the stream.

5.3.3 Imidacloprid

The imidacloprid concentrations found within the corn fields ranged from <LOQ to 587.99µg/kg. Nearly 30% of the sampled concentrations were < LOQ. The concentrations of imidacloprid were typically found to be higher in the non-concentrated flow areas of the field samples compared to the CFPs of the field samples by 9-100% (Figs. 5-17 through 5-20). There was one exception at site MH 8 (Fig. 5-20) where the CFPs of the field had a concentration that was several orders of magnitude greater compared to the non-concentrated flow areas of the field sample. The reason for this is that many of the CFPs that were sampled at this site were springs. Since imidacloprid has a higher aqueous solubility and a relatively low organic carbon partition coefficient (Table 2-1), it is highly mobile and may be transported from other upgradient fields that have been planted with neonicotinoid-coated seeds. This site also had the highest concentration of imidacloprid, which may be due to recent planting.

The concentrations of imidacloprid were generally low in the riparian buffer samples. Concentrations in the CFPs the buffer and non-concentrated flow areas of the buffer samples were generally 52-100% and 45-100% lower, respectively, than the non-concentrated flow areas of the field samples. This is likely due to subsurface flow rather than surface runoff being a relatively more dominant transport pathway for imidacloprid compared to atrazine and metolachlor. It is unlikely that imidacloprid was bound to sediment that was transported during surface runoff, and therefore it would not be expected to be deposited in sediment trapped by buffer vegetation if was applied to the seed directly before planting. There was one location (MH 2, side A; Fig 5-17) where the concentrations were relatively high inside the buffers compared to the other sites. This may be due to a rain event that occurred within two days prior to the sampling event. The few CFPs that were springs and experienced sheet flow on side A of the site likely facilitated transport of imidacloprid during the storm event, such that the imidacloprid had recently reached the buffer, resulting in elevated levels in the grass buffer on side A of MH 2.

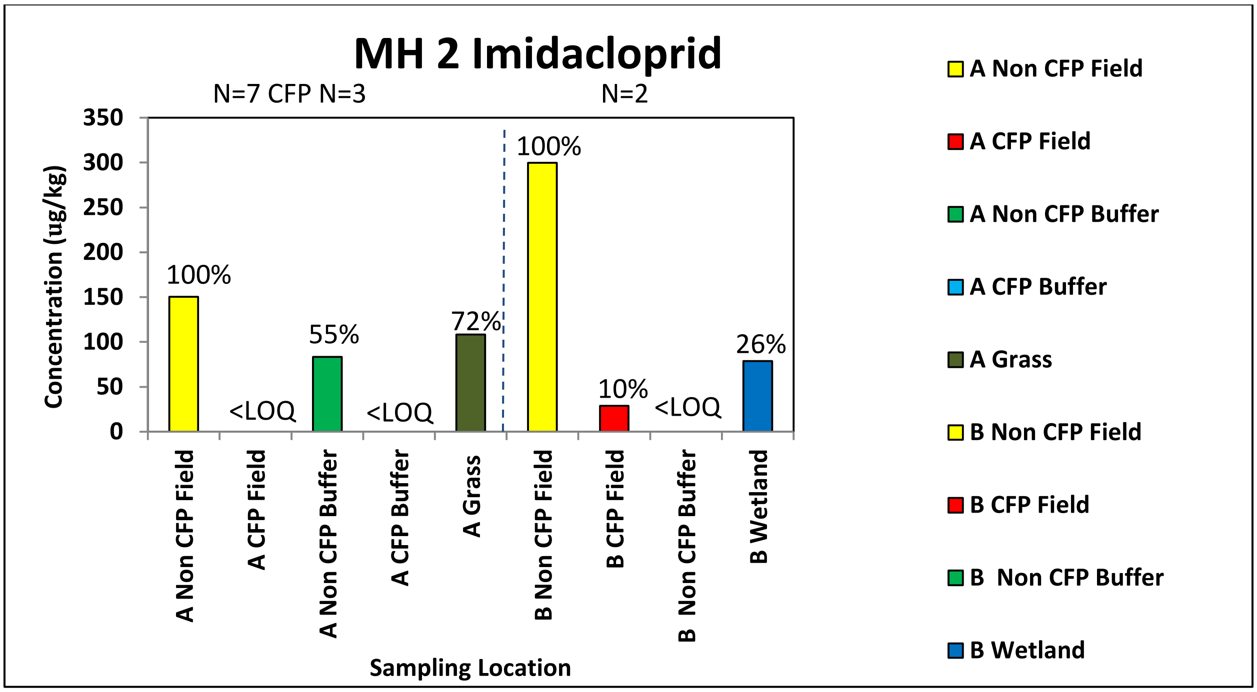


Figure 5-17 Imidacloprid concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 2. Sides A and B denote field locations on the left and right sides of the stream.

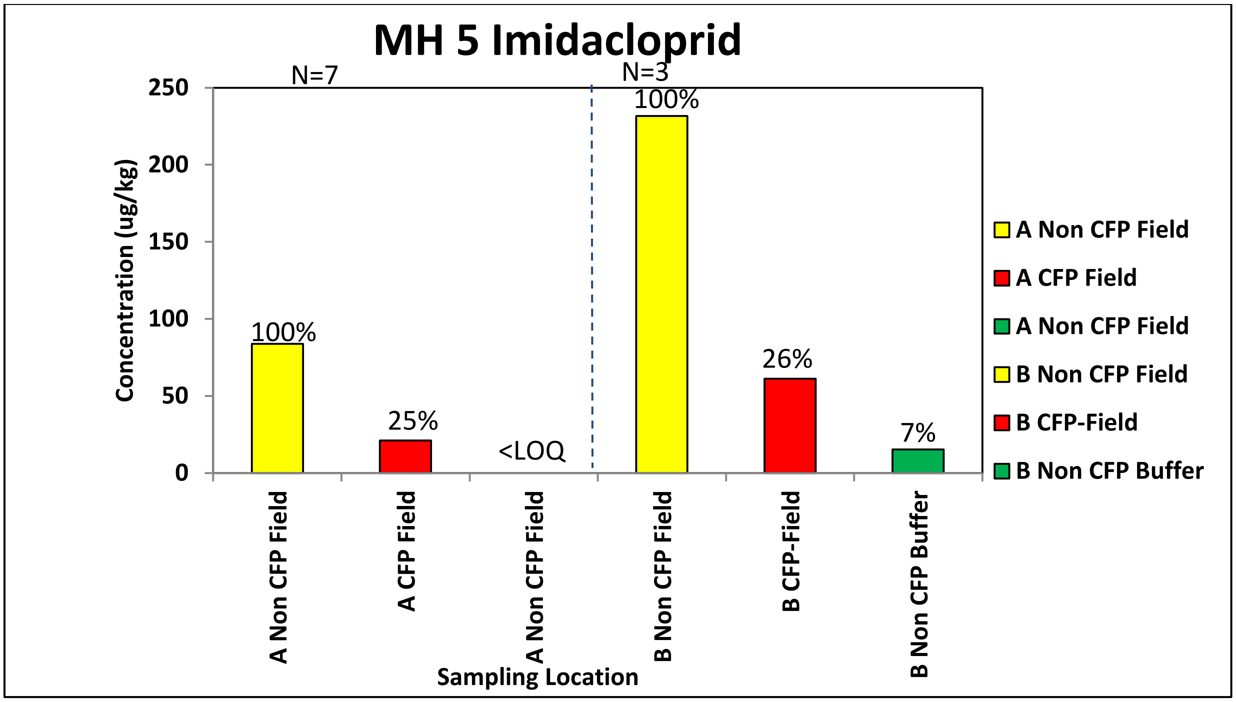


Figure 5-18 Imidacloprid concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 5. Sides A and B denote field locations on the left and right sides of the stream.

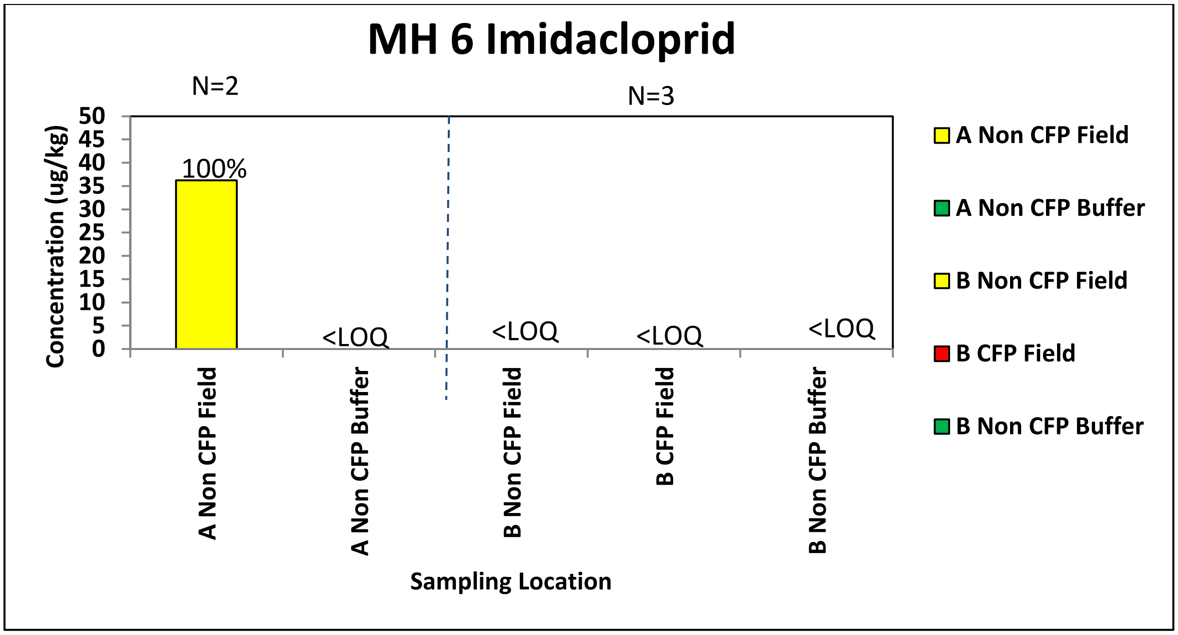


Figure 5-19 Imidacloprid concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 6. Sides A and B denote field locations on the left and right sides of the stream.

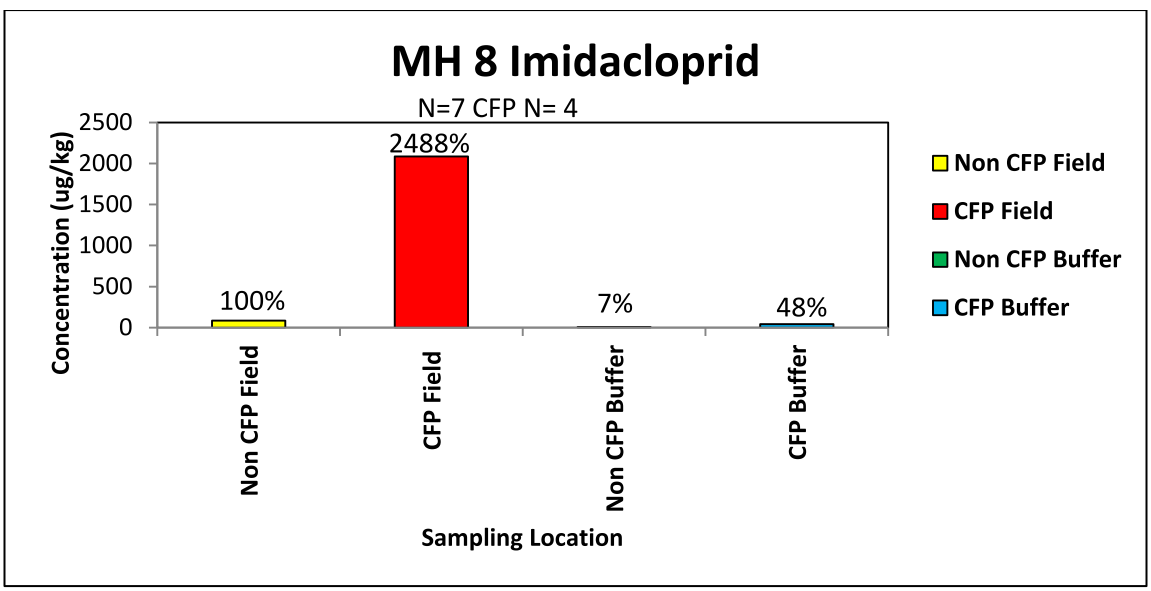


Figure 5-20 Imidacloprid concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 8. Sides A and B denote field locations on the left and right sides of the stream.

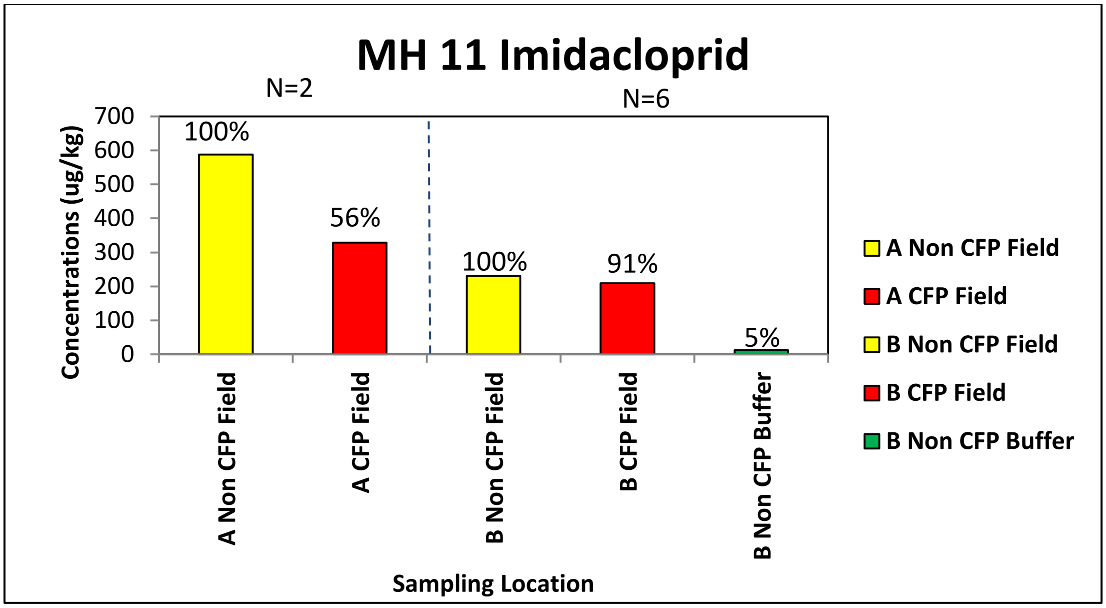


Figure 5-21 Imidacloprid concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 11. Sides A and B denote field locations on the left and right sides of the stream.

5.4 Pasture Fields

A total of 8 samples from the pasture sites, with 4 CFPs of the field samples, 4 non-concentrated flow areas of the field samples were sampled. The CFPs that were present in the pasture fields would typically start in an upgradient cornfield and the CFP would disperse back into sheet flow when entering the pasture field (Fig. 5-22). The fields were not treated with any pesticide; thus, the only source of the pollutants is from upgradient cropland fields (see Appendix I for pesticide application information for each field site). The dominant characterizations of CFPs were biological (repeated cattle movement) and groundwater driven (i.e., springs). The results were affected by multiple high rainfall events that occurred during sampling time period.

5.4.1 Atrazine

Atrazine concentrations observed within the pasture sites ranged from below the LOQ to approximately 0.4µg/kg. These concentrations are approximately an order of magnitude lower than the atrazine concentrations observed in the cropland fields. The results from the two pasture sites varied, with no clear pattern emerging. Site-specific differences that resulted in non-consistent trend are discussed below.

At MH 4 (Fig. 5-23), the concentrations of atrazine were less than the LOQ in both the CFPs of the field and non-concentrated flow areas of the field samples. On side B, atrazine was present at a higher in the CFPs of the field sample than the non-concentrated flow areas of the field sample by approximately 30%. The low concentrations on side A are likely due to no atrazine applied within the field itself and no immediately upgradient sources of atrazine that could enter the CFP, which was characterized as a seep (see Appendix I). On side B, atrazine was likely transported by runoff from an immediately upgradient cropland fields to which atrazine had been applied. The night prior to sampling, a 5 cm rainfall event occurred, which likely mobilized atrazine and resulted in detectable levels in the non-concentrated flow areas of the field and CFPs of the field samples despite no atrazine being applied directly to the pasture field itself. The CFPs on side B were characterized as old stream channels and compaction trails from cattle and were therefore driven by erosional processes that mobilized upgradient sources of pesticides that became deposited in the CFP that were present in the pasture fields. At MH 12 (Fig. 5-24) the concentrations of atrazine were higher in the non-concentrated flow areas of the field samples than in the CFPs of the field samples, which may be attributed to: (i) more frequent activation of sheet flow pathways, enhancing the atrazine concentrations in the portions of the field that received upgradient runoff as sheet flow; or (ii) erosional processes occurring within the CFPs, which continually remove atrazine after it is deposited from upgradient fields during subsequent storm events.

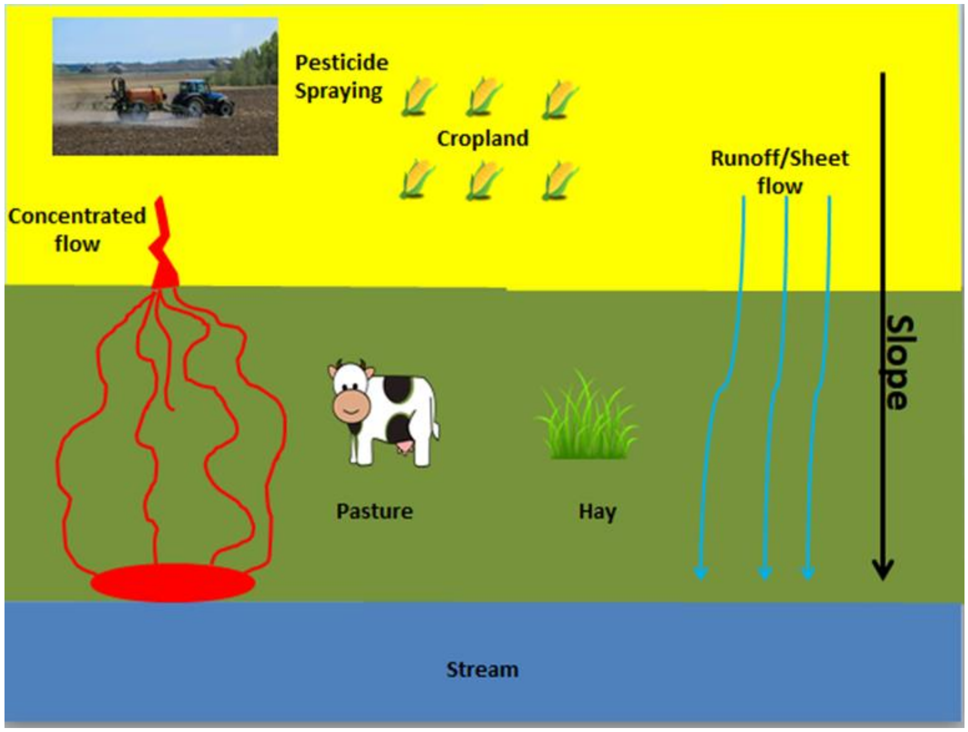


Figure 5-22 Observations of the behavior of CFPs entering Pasture/Hay fields

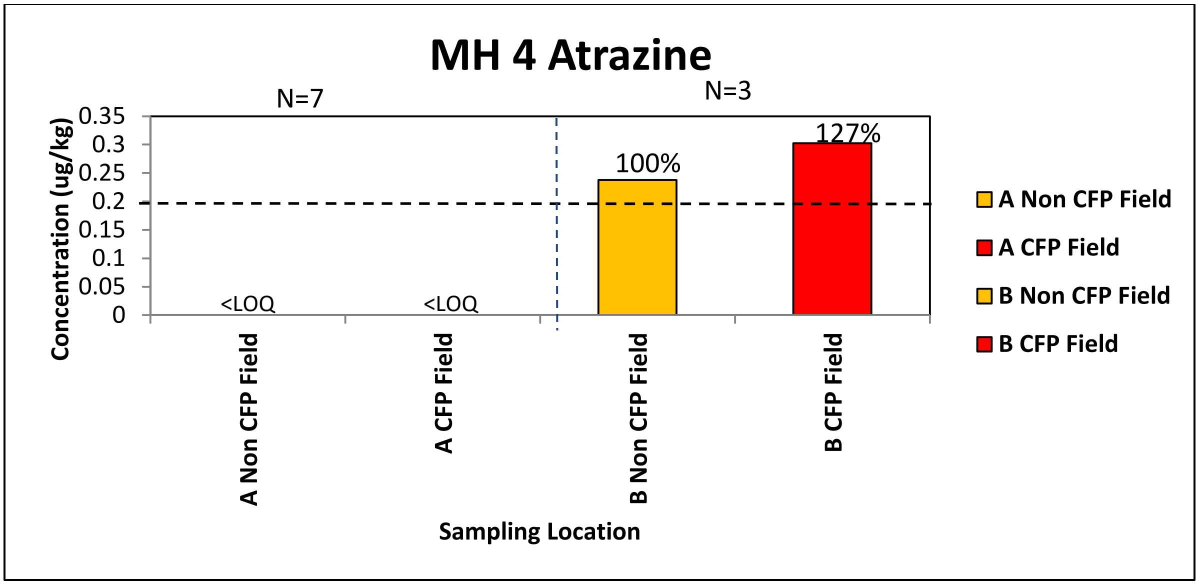


Figure 5-23 Atrazine concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 4. Sides A and B denote field locations on the left and right sides of the stream.

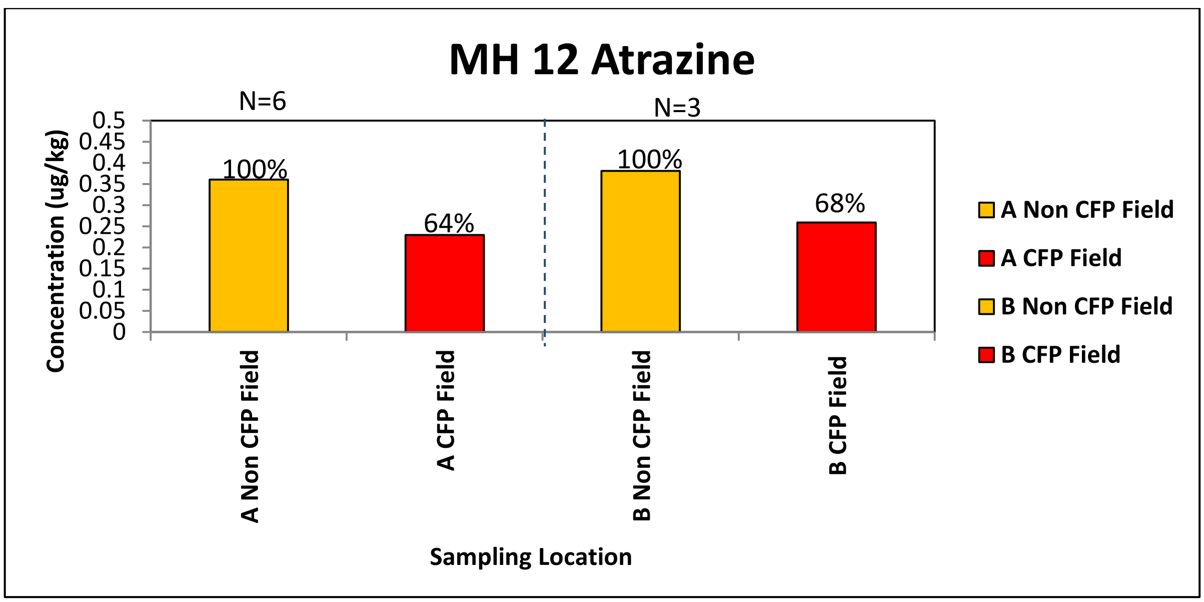


Figure 5-24 Atrazine concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 12. Sides A and B denote field locations on the left and right sides of the stream.

5.4.2 Metolachlor

Unlike atrazine, nearly all of the metolachlor concentrations were below the LOQ. The only sample from the pasture sites that had a quantifiable level of metolachlor was the non-concentrated flow areas of the field sample collected from side B of site MH 4 (Fig. 5-25). This was likely due to runoff from the immediately upgradient cropland field, which may have had a recent application of metolachlor. This is consistent with the presence of atrazine at side B of site MH 4. The lower detection of metolachlor could be due to a somewhat higher sorption coefficient (see Table 2-1) that could have resulted in lower mobility of metolachlor relative to atrazine.

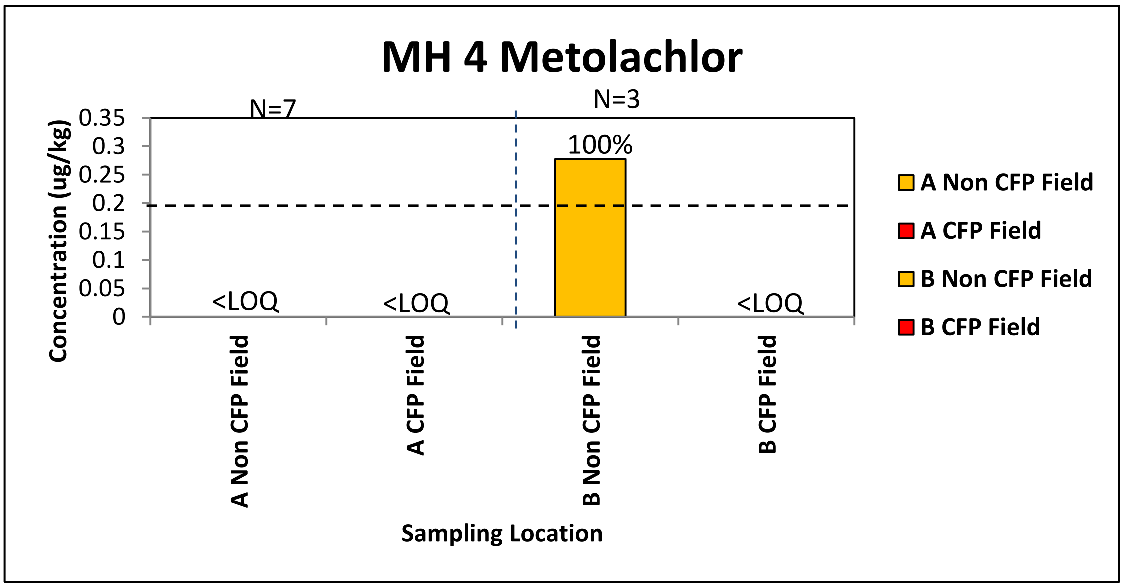


Figure 5-25 Metolachlor concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 4. Sides A and B denote field locations on the left and right sides of the stream.

5.4.3 Imidacloprid

Imidacloprid was only present at a quantifiable concentration in one sample collected in the pasture sites (MH 12, side B; Fig. 5-26). At site MH 12, side B had higher concentrations in the CFP then the field. Consistent with observations for atrazine and metolachlor, the imidacloprid likely came from an adjacent cropland field that had been sprayed with imidacloprid (see Appendix I). Since imidacloprid is thought to be the most mobile of the three pesticides, it is likely that it was transported during the rainfall event that occurred the night before sampling. The observed concentration is comparable (on the same order of magnitude) to the concentrations observed for imidacloprid in the cropland fields, providing further evidence to support this likely transport pathway. This rainfall event could also explain the absence of imidacloprid at MH 4, as it may have been mobilized during the event and if no additional imidacloprid was transported into the pasture field, then it would likely be present at concentrations too low to be quantifiable.

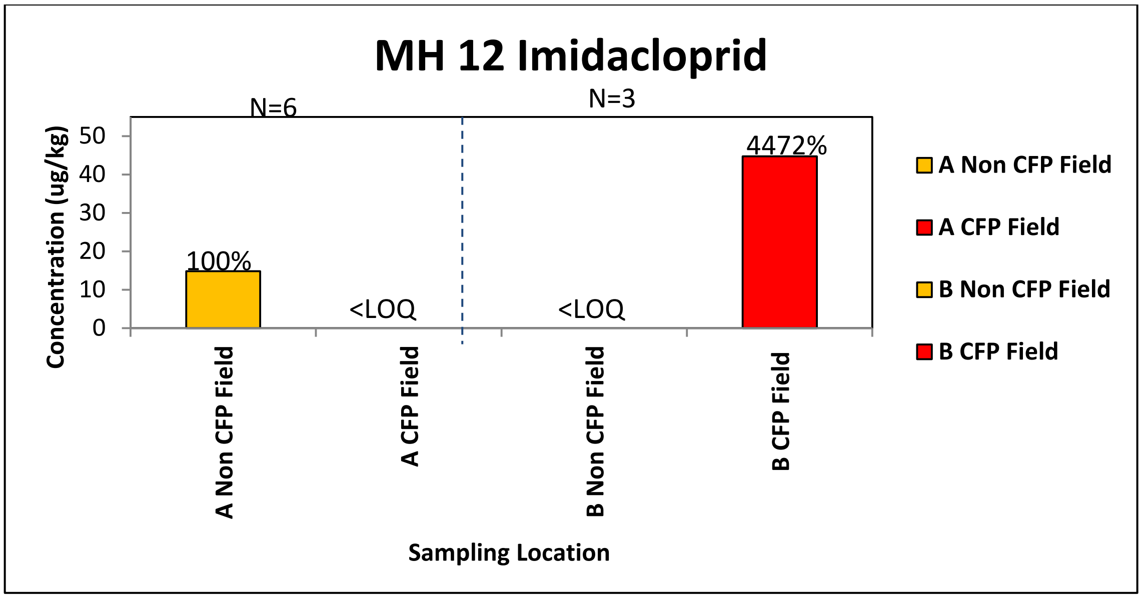


Figure 5-26 Imidacloprid concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 12. Sides A and B denote field locations on the left and right sides of the stream.

5.5 Hay Fields

A total of 8 samples from the hay sites, with 4 CFPs of the field samples, 4 non-concentrated flow areas of the field samples. The patterns observed in the hay fields were similar to the pasture. The topographical features were similar; with CFPs starting in an upgradient crop field and dispersing in several directions when entering the hay field (Fig. 5-22). The cause of this dispersal is due to the transition of vegetation that occurs on the edge of the fields and also by other biological factors, such as rodent trails that was observed at the hay sites. These rodent trails cause small CFPs to form. It was observed that these dispersed CFPs would combine to form the CFPs that were located next to the stream bank.

5.5.1 Atrazine

Atrazine was found in the hay fields (MH 3 and MH 13) at concentrations ranging from below the LOQ to 1.35ug/kg. 50% of samples had concentrations below the LOQ, limiting the identification of patterns along the flow paths.

At site MH 3 (Fig 5-27), which was downgradient of corn fields, concentrations in the CFPs of the field samples were higher than the non-concentrated flow areas of the field samples, which did not have quantifiable concentrations. This is likely due to transport through CFPs that start in the upgradient crop field and then disperse in multiple directions when entering the hay field. It was observed that these dispersed CFPs would regather in the CFPs that were located next to the stream bank, causing the higher concentration of atrazine in the CFPs.

Site MH 13 (Fig. 5-28) did not have quantifiable concentrations on side B. There was no upgradient corn field, so no sources of atrazine were present. However, side A was located next to a cornfield and did contain quantifiable concentrations of atrazine. There are two potential reasons for this. First, the field sampled could have been contaminated from spray drift when the farmer was applying to the adjacent crop field. Secondly, this farm could have been sprayed in this area to create a new cropland field. These may explain why atrazine was higher in the non-concentrated flow areas of the field sample than the CFPs of the field sample.

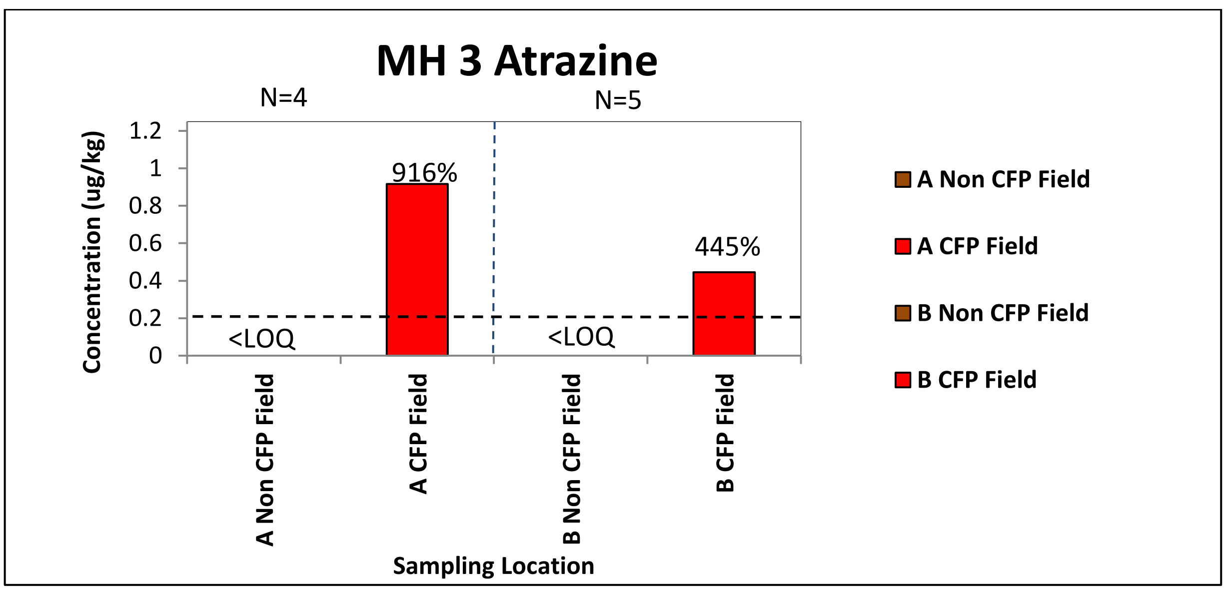


Figure 5-27 Atrazine concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 3. Sides A and B denote field locations on the left and right sides of the stream.

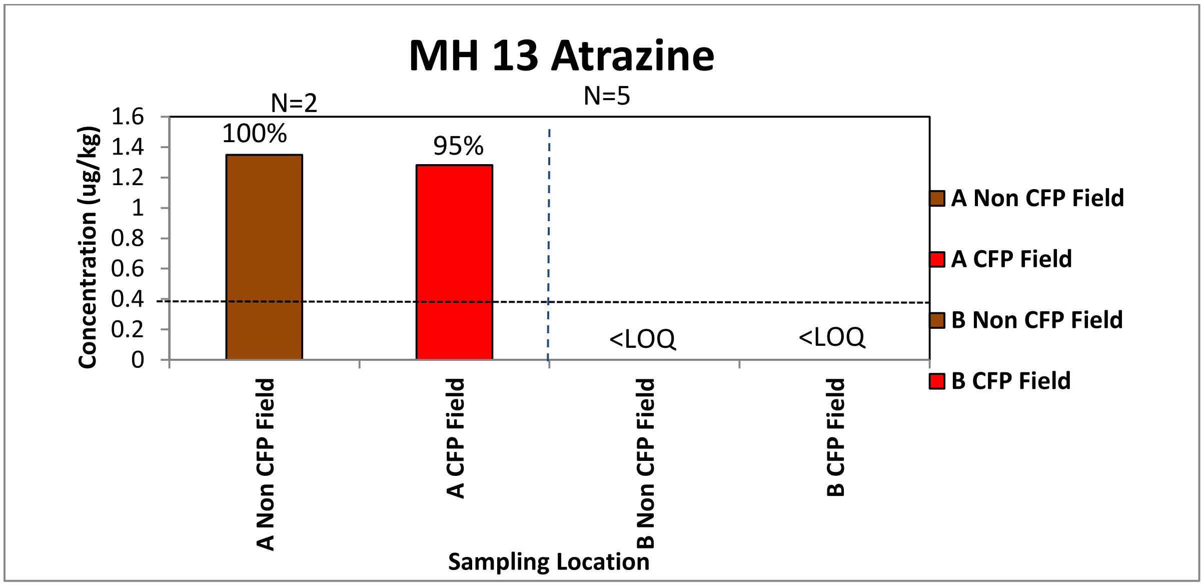


Figure 5-28 Atrazine concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 13. Sides A and B denote field locations on the left and right sides of the stream.

5.5.2 Metolachlor

For both hay field sites, metolachlor portrayed similar trends as atrazine. Site MH 3 (Fig. 5-29) had higher concentrations in the CFPs of the field samples than the non-concentrated flow areas of the field samples (< 1 ug/kg in the CFPs of the field samples and below the LOQ in the non-concentrated flow areas of the field samples). These concentration values could have been affected by the 5 cm rainfall event facilitating transport from upgradient corn fields into the CFPs, enabling them to be present at quantifiable concentrations during the sampling event. At side A of MH 13 (Fig. 5-30), metolachlor was present at higher concentrations in the non-concentrated flow areas of the field sample than the CFPs of the field sample and was present below the LOQ on side B. This followed similar trends observed at this site for atrazine, and could be due to spray drift of atrazine and metolachlor likely applied to areas being converted to cropland that were adjacent to side A of site MH 13. No cropland was adjacent to side B, and therefore no sources of metolachlor affected side B.

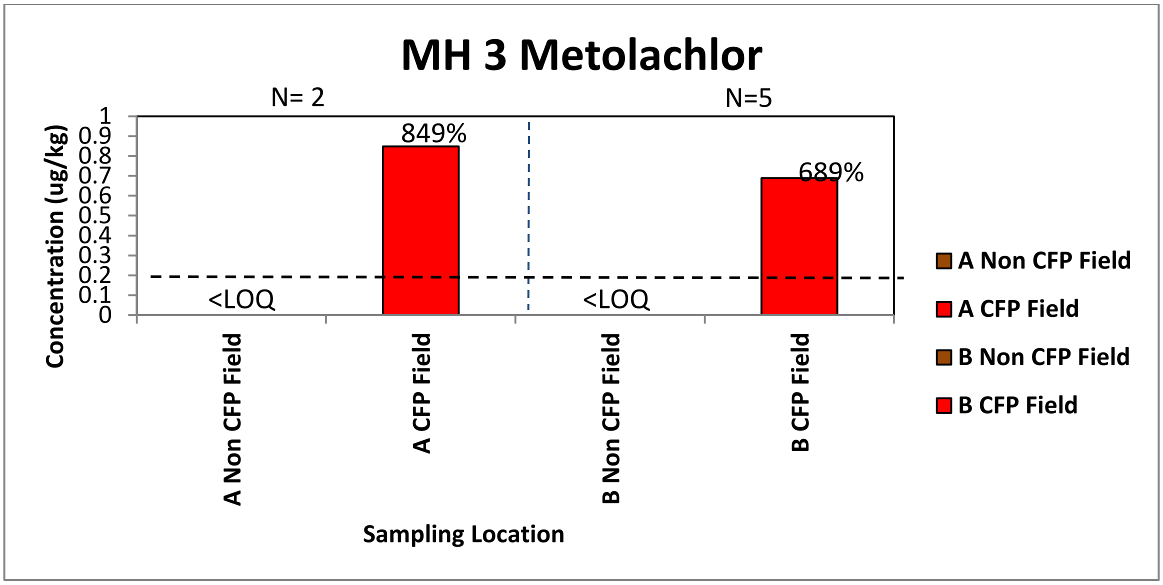


Figure 5-29 Metolachlor concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 3. Sides A and B denote field locations on the left and right sides of the stream.

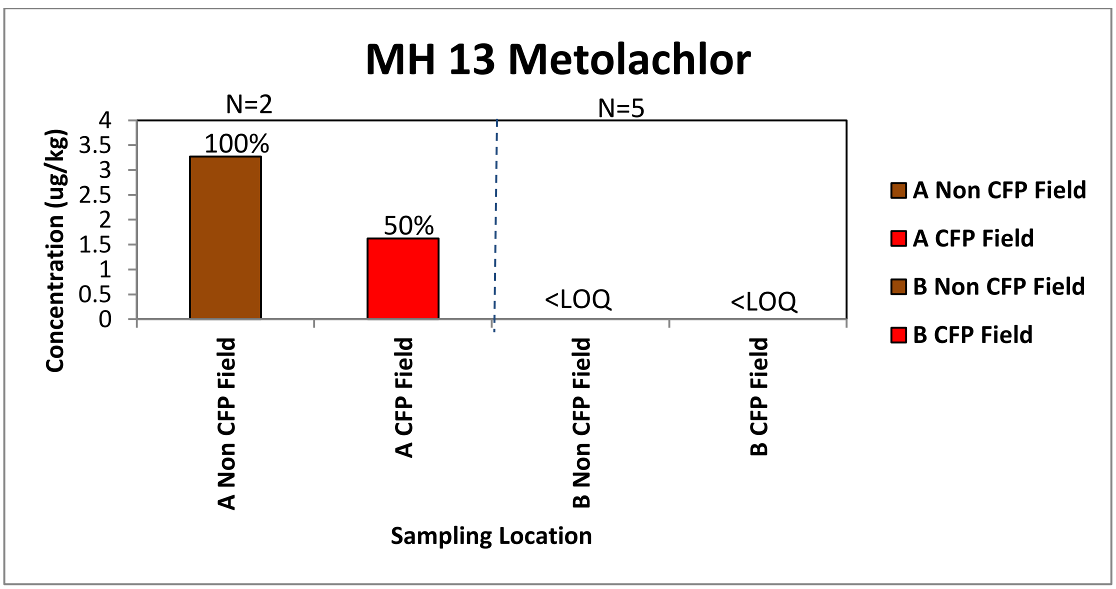


Figure 5-30 Metolachlor concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 13. Sides A and B denote field locations on the left and right sides of the stream.

5.5.3 Imidacloprid

There was only one hay site that had quantifiable concentrations of imidacloprid, which was MH 3 (Fig. 5-31). This site was bordered by cropland and appeared to contribute to the presence of atrazine and metolachlor to the CFPs of the field samples. Therefore, it is consistent with atrazine and metolachlor observations to also find concentrations of imidacloprid present above the LOQ. It should be noted that these concentrations were comparable to some of the cropland that were sampled (Figs 5-17, 5-18 5-20, 5-21). Similar to the observations made at MH 3 for atrazine and metolachlor, imidacloprid was present below the LOQ in the non-concentrated flow areas of the field samples.

Again, consistent with the observations for atrazine and metolachlor, MH 13 had no quantifiable concentrations of imidacloprid in the CFPs of the field samples, likely due to no adjacent crop field. Atrazine and metolachlor were detected in the non-concentrated flow areas of the field samples while metolachlor was not. It is likely that atrazine and metolachlor were applied to kill grass that was being converted to a crop field, but since no corn had been planted yet, there was no source of imidacloprid to enter the field prior to the time of sampling.

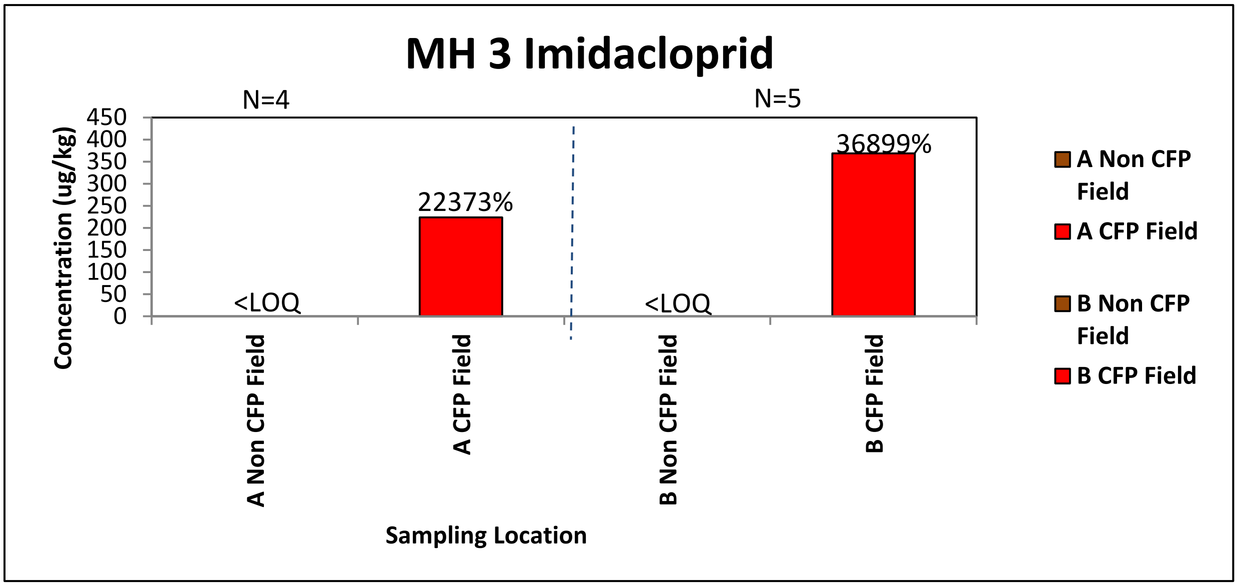


Figure 5-31 Imidacloprid concentrations in soils collected from non-concentrated flow path areas and concentrated flow path areas at field site MH 3. Sides A and B denote field locations on the left and right sides of the stream.

5.6 Concentration Trends across the WE-38 watershed:

Concentrations of each pesticide varied across the different land uses (Table 5-2). Cropland typically had larger concentrations than hay and pasture fields. The reason for this is due to direct application of the pesticide, either from spraying or from seed planting. The pasture and hay fields typically had higher concentrations in the CFPs, which as noted is due to the upgradient cropland having CFPs that entered the fields. In the areas that concentrations were higher in the field, could be result of sheet flow or spray drift. The concentrations that were found for imidacloprid can be fatal to macroinvertebrates (earthworms (*Eisenia andrei*), enchytraeids (*Enchytraeus crypticus*), collembola (*Folsomia candida*), oribatid mites (*Oppia nitens*) and isopods (*Porcellio scaber*)) (Lima et al., 2017). The soil concentrations for atrazine and metolachlor were similar to a field study in Connecticut where soil samples were collected. Samples were collected between two to fifteen months after the application. The range of atrazine and metolachlor was 57.6-236 µg/kg dry soil and 37.2-510 µg/kg dry soil, respectively (Pignatello and Huang, 1991). The tested pesticides are generally higher, but this can be due to the soil characteristics, weather patterns and application rates.

Table 5-2: Concentrations of sampled sites. Yellow, Brown and Orange are Cropland, Hay and Pasture fields respectively.

Location	Concentration(µg/kg)		
	Atrazine	Metolachlor	Imidacloprid
MH 2 A non-concentrated flow areas of the field	2.54	3.37	299.65
MH 2 A CFPs of the field	0.37	0.40	28.96
MH 2 A non-concentrated flow areas of the buffer	0.34	0.40	<LOQ
MH2 A Wetland	2.78	3.42	78.73
MH 2 B non-concentrated flow areas of the field	2.43	85.22	150.28
MH 2 B CFPs of the field	3.37	11.65	<LOQ
MH2 B non-concentrated flow areas of the buffer	0.66	1.11	83.27
MH2 B CFPs the buffer	1.29	1.48	<LOQ
MH2 B Grass	1.04	7.99	108.48
MH 5 A non-concentrated flow areas of the field	2.11	50.95	231.71
MH 5 A CFPs of the field	1.88	53.03	61.18
MH 5 A non-concentrated flow areas of the buffer	0.60	3.03	15.23
MH 5 B non-concentrated flow areas of the field	2.36	127.82	83.81
MH 5 B CFPs of the field	1.86	33.50	21.01
MH 5 B non-concentrated flow areas of the buffer	1.23	4.75	<LOQ
MH 6 A non-concentrated flow areas of the field	3.09	4.17	<LOQ
MH 6 A non-concentrated flow areas of the buffer	0.55	0.66	<LOQ
MH 6 B non-concentrated flow areas of the field	0.27	<LOQ	<LOQ
MH 6 B CFPs of the field	1.96	3.81	36.25
MH 6 B non-concentrated flow areas of the buffer	0.42	0.37	<LOQ
MH 8 A non-concentrated flow areas of the field	1.07	1.93	83.81
MH 8 A CFPs of the field	0.98	1.31	2085.26
MH 8 A non-concentrated flow areas of the buffer	0.60	0.81	6.03
MH 8 B CFPs the buffer	0.56	0.67	40.20
MH 11 A non-concentrated flow areas of the field	1.84	1.20	230.89
MH 11 A CFPs of the field	1.87	1.03	209.16
MH 11 A non-concentrated flow areas of the buffer	1.85	1.98	12.43
MH 11 B non-concentrated flow areas of the field	2.01	1.69	587.99
MH 11 B CFPs of the field	1.34	1.03	328.91
MH 4 A non-concentrated flow areas of the field	0.24	0.28	<LOD
MH 4 A CFPs of the field	0.30	<LOQ	<LOD
MH 4 B non-concentrated flow areas of the field	<LOQ	<LOQ	<LOD
MH 4 B CFPs of the field	<LOQ	<LOQ	<LOD
MH 12 A non-concentrated flow areas of the field	0.38	<LOQ	14.85
MH 12 A CFPs of the field	0.26	<LOQ	<LOQ
MH 12 B non-concentrated flow areas of the field	0.36	<LOQ	<LOQ
MH 12 B CFPs of the field	0.23	<LOQ	44.72
MH 3 A non-concentrated flow areas of the field	<LOQ	<LOQ	<LOQ
MH 3 A CFPs of the field	0.92	0.85	223.77
MH 3 B non-concentrated flow areas of the field	<LOQ	<LOQ	<LOQ
MH 3 B CFPs of the field	0.44	0.69	368.99
MH 13 A non-concentrated flow areas of the field	<LOQ	<LOQ	<LOD
MH 13 A CFPs of the field	<LOQ	<LOQ	<LOD
MH 13 B non-concentrated flow areas of the field	1.35	3.27	<LOD
MH13 B CFPs of the field	1.28	1.63	<LOD

5.7 Hydrus Modeling Results

The results from the Hydrus model illustrate that concentrations of atrazine, metolachlor and imidacloprid would not reach groundwater within a one-year period (Fig 5-32). The reason for this is that the pesticides would either bond tightly to the soil particles or degrade before reaching the groundwater. The concentrations that were found during the modeling process are values that represent a one-time application of pesticides at a concentration of 100 µ/L. This value was chosen because the modeled concentrations would represent a percentage of the applied pesticide. It was concluded that quantifiable concentrations of pesticides could be found within the soil profile a year after application. Atrazine tended to slowly seep into the soil profile over the year period. Unlike atrazine, both metolachlor and imidacloprid stayed on the surface for a longer time period. This could be due to the degradation rates and the K_{oc} values. With approximate concentrations of 0.275 mg/cm^3 of atrazine and metolachlor and 600 mg/cm^3 of imidacloprid applied during each application process in WE-38 the concentrations that were modeled were higher than what was sampled. There could be multiple reasons for this, such as weather patterns, the actual K_d of the pesticide, the degradation rate of the pesticide and infiltration rate. This model, however, can be utilized to understand concentration trends throughout a soil profile under simplistic conditions.

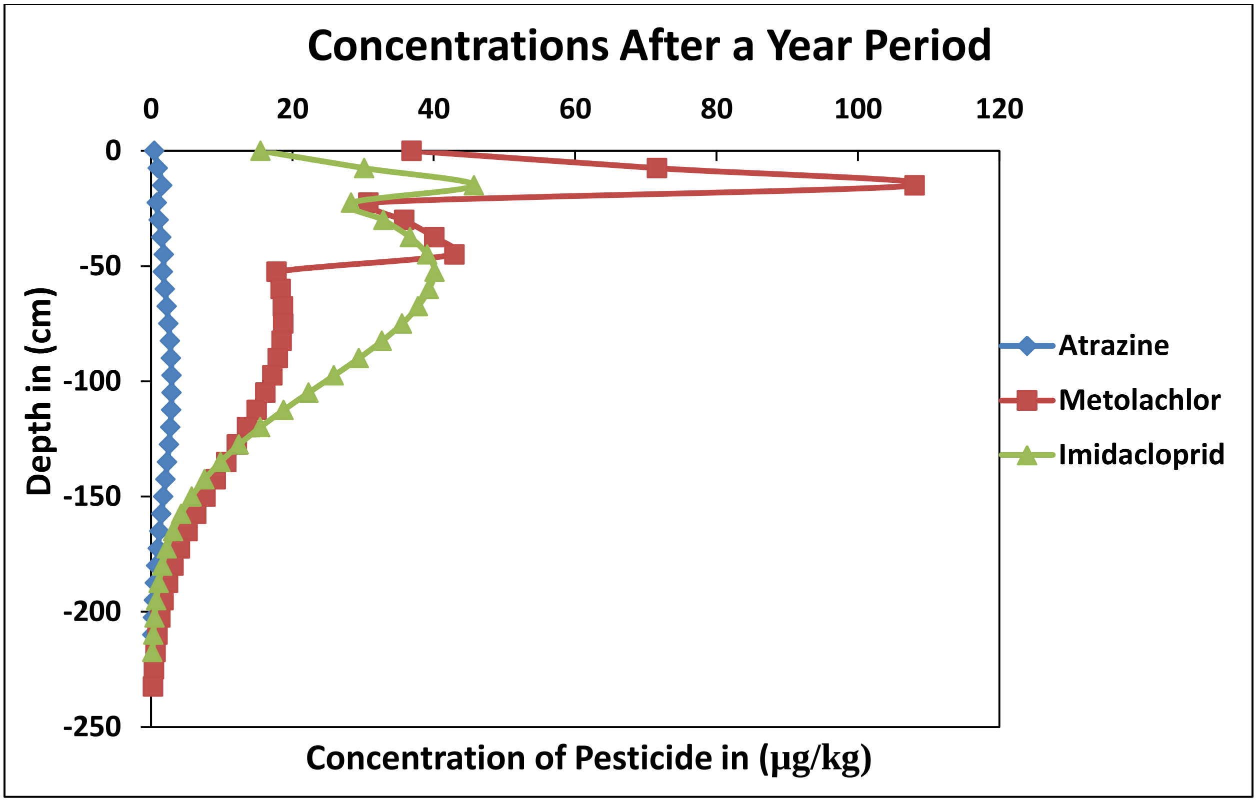


Figure 5-32 Hydrus atrazine concentrations for a one year period.

5.8 Possible Confounding Issues

During the investigation of how CFPs affect pesticide transport, there were several possible errors identified. One possible error is due to the timing of the sampling period. The sampling period occurred in a time period which the region had record rainfall amounts. This could have diluted concentrations to where they were not quantifiable or resulted in an unusual amount of mobilization into the study sites from upgradient fields that had received pesticide applications that differed from those that the study sites had received. The high amounts of rainfall could have also delayed pesticide application to a later date. This would result in early sampling periods, measuring residue concentrations from the year prior (Appendix I). Another possible error could be cross contamination from soil sampling and grinding of the samples. Although we took care to reduce this source of error by rinsing the sampling probes with ethanol and changing nitrile gloves between samples, there could have been instances where the soil probe was not properly cleaned, resulting in cross-contamination. Also, when there was grinding of the samples, an air hose was used to clean out any sediment from the previous sample. If there was any sediment that was left in the grinder could have been mixed into the sample. Lastly, the QuEChERS method may not have been able to extract all of the pesticides in the soil sample. Although this method has been reported to be effective for pesticides, it is possible that the soil at the study sites had a sufficiently high clay content to reduce the extraction efficiency of the QuEChERS method.

5.9 Future Studies

Based on the methods and findings of this project, it is suggested that future studies should investigate these trends to a greater detail. To narrow the range of sampling, one of each type of each agricultural practice should be examined. This would allow all samples to be taken within one day and reduce the variability of storm events that could have an impact on the concentrations as noted earlier. Also, an understanding of the amounts and the timing of pesticide spraying should be more accurately noted. With this information along taking water samples of the fields runoff, can create a better understanding of the transport of the pesticides. Another suggestion could be using a controlled plot to test the effects of CFPs has on the transport of pesticides. Similar to the controlled plot by (X. J. Zhang et al., 2018), could plant various vegetation, apply know concentrations of pesticides and, water amounts to plot. This closed system would provide results that are not based on natural patterns that could affect the concentrations trends as it did in this study.

5.10 Summary:

5.10.1 Corn Fields:

The general trend that was observed in the cornfields was that concentrated flow paths had lower concentrations of pesticides than the surrounding field. This is most likely due to erosional processes in the concentrated flow paths washing out the pesticides. The pesticides bound to the sediment would then be deposited into the stream adjacent to the field. However, when buffers were present between the corn fields and the stream, the concentrations in the buffer (non-concentrated flow areas of the buffer samples) were generally lower than the concentrations in the field (non-concentrated flow areas of the field samples) The exception to this general pattern was the detection of imidacloprid in CFPs of the field samples that were the result of groundwater springs, which tended to enhance the transport of imidacloprid. Overall, these results suggest that surface runoff is a relatively more important transport pathway for atrazine and metolachlor while subsurface flow is a relatively more important transport pathway for imidacloprid.

5.10.2 Hay and Pasture Fields:

Similar patterns were observed for pesticides in both hay and pasture field sites. For the most part, pesticides were present at higher in the CFPs of the field samples than the non-concentrated flow areas of the field. This is likely due to no direct application of pesticides to these field sites. However, the pesticides that were found at these sites were likely due to transport via groundwater springs (into CFPs of the field samples) or surface runoff via sheet flow and concentrated flow from upgradient fields that had received pesticide applications Also, another important factor that influenced the results at these sites was the timing of sampling. The reason for this is due to rain events, which could have either enhanced transport from upgradient fields or washed out residues on the soils where pesticides had previously been deposited, either increasing or decreasing, respectively, the pesticide concentrations at the time of sampling.

5.10.3 Types of Concentrated Flows

The field sites at WE-38 had different types of concentrated flows such as topographical, springs, biological and erosional pathways. Each flow type affects the transport of pesticides differently. Topographically-driven CFPs were identified by noting swales. Usually, these areas had grass strips, which reduced erosion. The springs identified at the study sites were found to have the possibility of transporting pesticides from upgradient areas outside of the sampled site. These springs were observed to have increased concentrations of pesticides compared to the topographically-driven CFPs. Biological features, such as cow and rodent paths, can be a direct path from a source to an adjacent field. Additionally, erosional paths were found the most often in cropland and can change from year to year. These paths can be caused by tractor ruts or from loose soil dislodged by rainfall.

Section 6.0 Conclusions:

The Chesapeake Bay's water quality has been degraded due to runoff from agricultural fields in the Susquehanna River watershed. The current main focus is restricting nitrogen and phosphorus losses from sedimentation and runoff. However, pesticides can also be bound to soil sediments and be mobilized during surface runoff events. This research sought to understand field-scale pesticide transport and the potential role of CFPs in altering pesticide movement to nearby streams. Soil samples were collected along flow paths in agricultural fields to create a comparison of concentrations of atrazine, metolachlor and imidacloprid to the non-concentrated flow areas of the field, CFP R, non-concentrated flow areas of the buffer and CFPs the buffer. The study site selected for this project was a sub-watershed of the Mahantango Creek watershed, which is a Long-Term Agroecosystem Research site. Soil cores representing the top 0-2 cm of the soil profile were analyzed for atrazine, metolachlor, and imidacloprid. This research found that land use and the types of CFPs present at a field site affected the patterns observed for each of the pesticides.

For each land use, CFPs had different effects on the transport of pesticides. In cropland, concentrations in the CFPs were typically lower than the adjacent field, whereas in hay and pasture fields, concentrations were generally higher in the CFPs than the field. This was likely due to differences in where the pesticides were applied and the role in which CFPs played in transporting them from their sources. In the cropland, atrazine and metolachlor were applied across the entire fields, including to any CFPs present at the site. Therefore, the general trend was for concentrations to decrease along the flow path to the stream, with concentrations in the buffers generally lower than the CFPs, which were lower than the concentrations in the field (non-concentrated flow areas of the field samples). However, for the hay and pasture fields, CFPs had higher concentrations because they were downgradient of cropland. The CFPs that had formed in the upgradient cropland dispersed when entering the hay and pasture study site fields. The result is that the fields tended to have lower concentrations because there was no pesticide application to the field, whereas the CFPs facilitated transport from locations where pesticides were applied, resulting in elevated concentrations in the CFPs of the field samples relative to the non-concentrated flow areas of the field samples. The pasture and hay field scenarios provide an understanding of how the transport of pesticides can travel from field to field and ultimately to the stream.

The relative importance of surface runoff versus subsurface flow transport pathways appeared to be similar for atrazine and metolachlor but different for imidacloprid. The reason for this can be due to the application methods for each pesticide. Atrazine and metolachlor are typically applied as sprays directly to the soil surface. If a rain event occurred after application then any surface runoff would be contaminated with atrazine and metolachlor. Imidacloprid being coated on the seeds and having a high aqueous solubility can be easily transported to subsurface flows. Given the findings of this research, several suggestions could be made to landowners to reduce the impact of CFPs transporting pesticides to the stream. For topographical features such as swales, grass waterways could be planted to reduce the erosional transport of sediment-bound pesticides. It is also suggested that to reduce groundwater contamination, applications should be planned to not occur directly before a rainfall event. This would give the pesticide time to sorb to soil sediments, reducing the amount available for transport in soil solution, which could be easily leached to the groundwater. Biological factors such as cow paths could be reduced if the farmer alternates routes or applies rocks to walking paths. This would decrease compaction and increase water absorption, which would then lower potential channelization from high water velocity. Erosional CFPs were typically found in a crop field that did not have a cover crop. With the farmer utilizing a cover crop would reduce erosion of loose sediment. Also, it would be suggested to the farmer tractor usage should be reduced and driving patterns should be altered to reduce compaction to the soil. Both cases would reduce the likelihood of CFP formation.

It is suggested that further studies should investigate how riparian buffers affect the concentrations of pesticides delivered by CFPs. Based on the findings of this study it is possible that CFPs could undermine the performance of the riparian buffers. Investigation of the management practices that cause sheet flow to converge and form CFPs would be helping in the decision of what land practices should be adopted to reduce the likelihood that flow convergence will occur. Also, investigation of how different soil types alter the concentrations of pesticides should be conducted. This understanding could change the rate of application of the pesticide and reduce the amount that is available to leach to groundwater.

In summary, CFPs do affect the transport of pesticides in an agricultural setting, but the specific roles can be site specific and depend on both natural and anthropogenic factors. Overall this research generalized these factors and provided an enhanced understanding of how CFPs affect the water quality in an agricultural setting.

Appendix

Appendix I Site descriptions

MH2

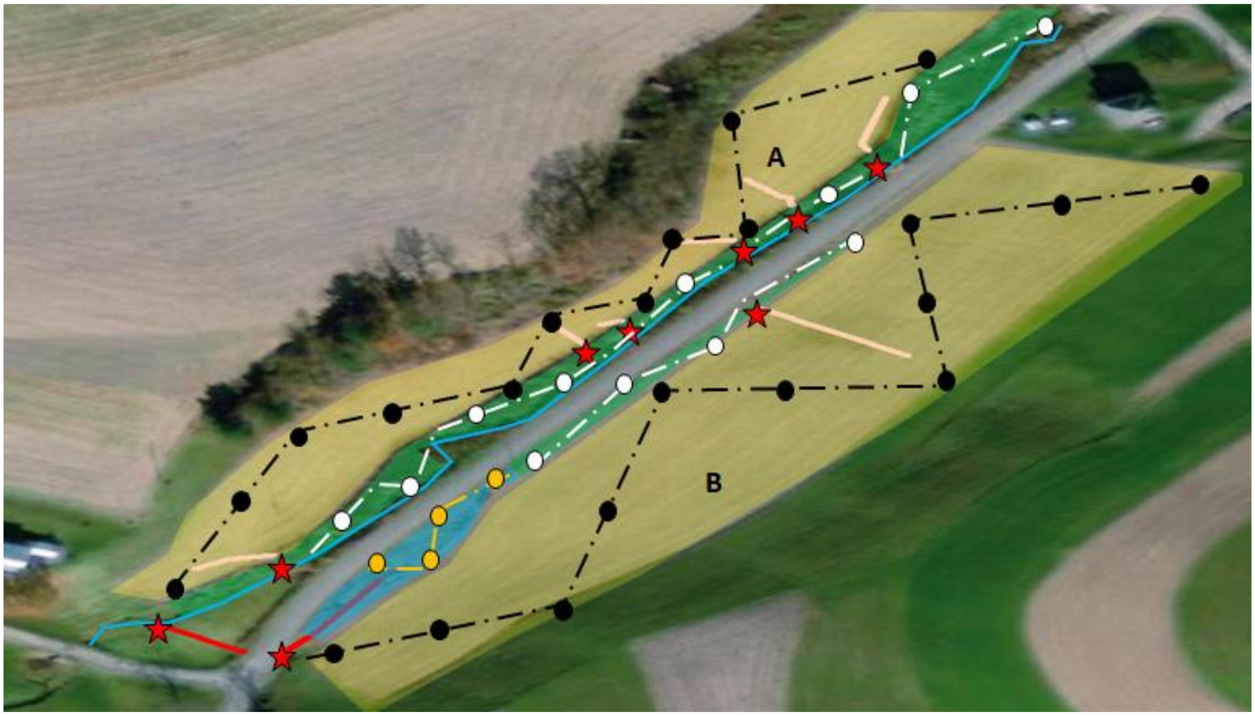


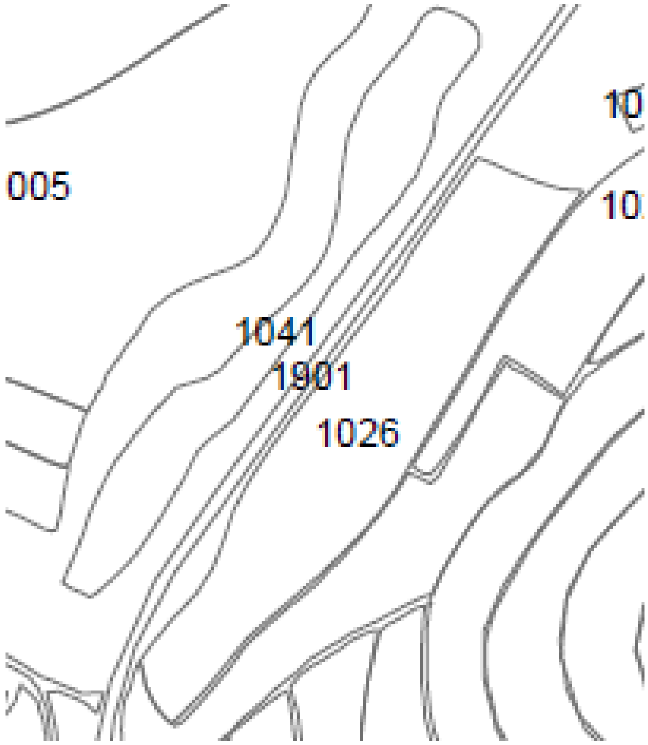
Figure was created using Google Earth© and Arc GIS© software

Label	Description
(yellow)	Cropland
(green)	Buffer
(blue)	Wetland
(black line)	Sampling Path In Field
(gray line)	Sampling Path in Buffer
(orange line)	Sampling Path in Wetland
(black dot)	Soil Sample in Field
(white dot)	Soil Sample in Buffer
(orange dot)	Soil Sample in Wetland
(tan line)	CFP
(red line)	Culvert
(red star)	CFP Sample in Field
(blue line)	Stream

MH 2 side A is a crop field which was sampled on two different days (4/21/18 and 5/10/2018). The reason for this is due to loss of daylight on 4/21 and only the field composite sample was collected. On 5/10 the CFPs and buffer samples were collected and should also be noted that it was after a rain event. The buffer is located between the field and the stream. The dominant soil type was a Calvin-Klinesville profile, had an approximate slope of 12%, and an area of 3 acres. Side B had six CFPs and was characterized as two springs and four erosional. The culvert that drained Side A was counted as a CFP and was composited with the other CFPs of that side. This can cause elevated concentrations of the CFPs on side B. Due to the topography of this site it is assumed that sheet flow also occurs.

MH 2 side B is a crop field which during the time of sampling (4/21/18) contained the reminiscence of the past years corn debris. The dominant soil type was a Calvin-Klinesville profile that had an approximate 12% slope and had an area of 3.2 acres. Side A had two of CFPs that were all documented erosional and could be caused by exposed soil to rainfall events and the compaction of continuous tractor use. There was a riparian zone that divided the field edge from the adjacent road and formed a channel that leads to a wetland area. This wetland area drained to a culvert pipe which went under the road to the B side of MH 2. Due to the topography of this site it is assumed that sheet flow also occurs.

Fields	**Description**	**Tillage**	**Pesticide (17)**	**Method**	**Active Ingredients (%)**
1026	Sampled Corn Side A	No Till	Poncho 250 Seed Treatment, Brawl ATZ, Instigate, Paraquate	Herbicides and Manure applied together Water carrier Applied 10 Gallons/ Acre	Clothianidin(48), Atrazine(33) S-Metoloachlor (26.1), Rimsulfuron (4.17) Mesotrione(41.67), Paraquatre(43.2)
1041	Sample Corn Side B	No Till	Poncho 250Seed Treatment, Brawl ATZ, Instigate, Paraquate	Herbicides and Manure applied together Water carrier Applied 10 Gallons/ Acre	Clothianidin(48), Atrazine(33) S-Metoloachlor (26.1), Rimsulfuron (4.17) Mesotrione(41.67), Paraquatre(43.2)


005
1041
1901
1026

MH5

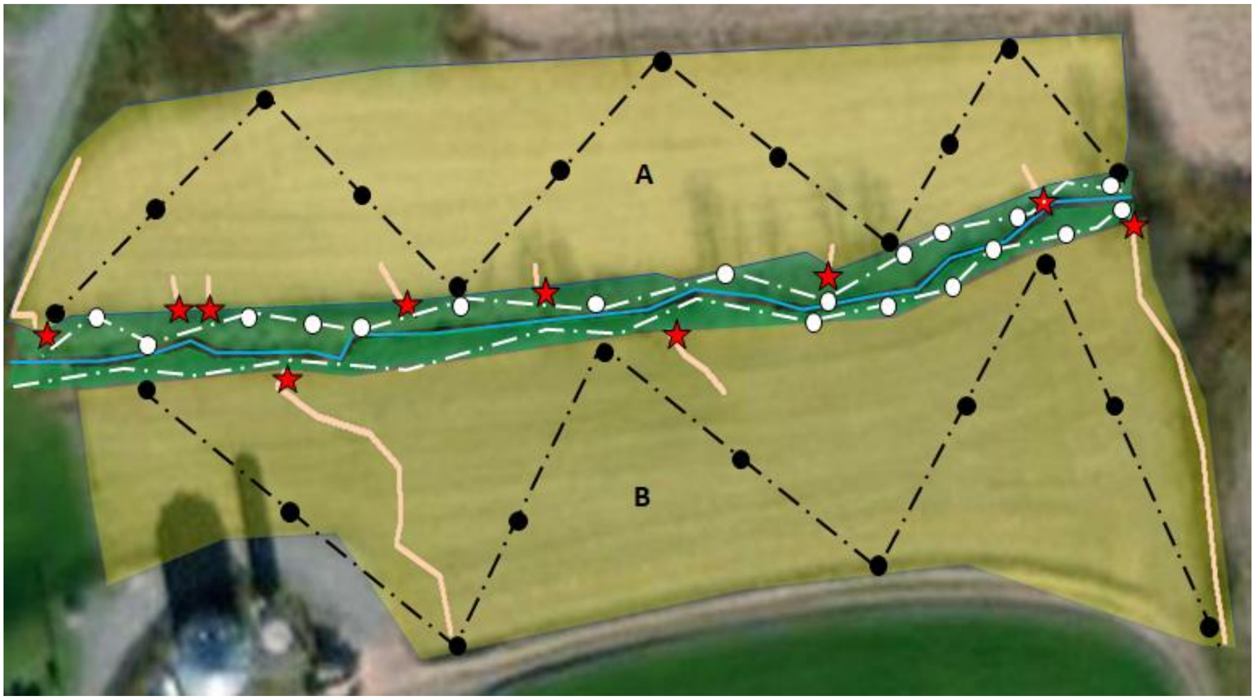


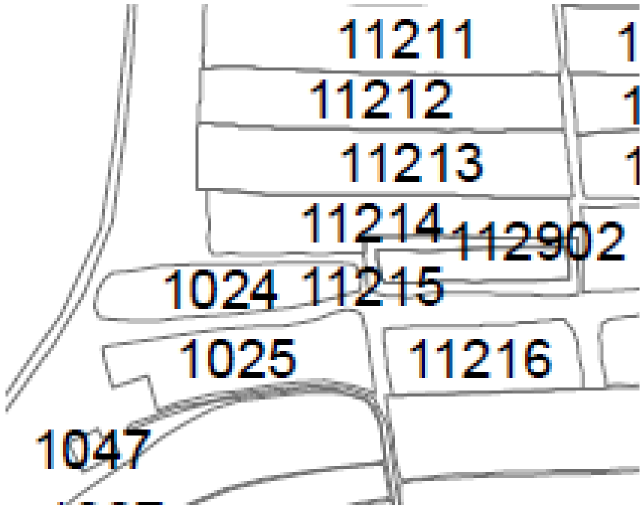
Figure was created using Google Earth© and Arc GIS© software

Label	Description
	Cropland
	Buffer
	Sampling Path In Field
	Sampling Path in Buffer
	Soil Sample in Field
	Soil Sample in Buffer
	CFP
	CFP Sample in Field
	Stream

MH5 side A is a crop field that was sampled on 5/10/18 and contained debris from the previous year's crop. Sampling was done recently after a rain event. The dominant soil type is a Watson soil series a slope of approximately 12% and the total area was 1.1 acre. There were seven FPs identified. These CFPs were characterized as erosional and were caused by the continuous use of tractors that compacts the soil which will increase the water velocity thus increasing the erosion of the soil. Another factor that could generate the CFPs is the absence of cover crops. With the soil being exposed, rainfall impact can cause the eroding of soil and channelization to occur in extreme cases.

MH5 side B is a crop field that was sampled on 5/10/18 and contained debris from the previous year's crop. Sampling was done recently after a rain event. The dominant soil type is a Watson soil series, a slope of approximately 12% and a total area of one acre. There were three CFPs identified. These CFPs were characterized as erosional and were caused by the continuous use of tractors that compacts the soil which will increase the water velocity thus increasing the erosion of the soil. Another factor that could generate the CFPs is the absence of cover crops. With the soil being exposed, rainfall impact can cause the eroding of soil and channelization to occur in extreme cases.

Fields	**Description**	**Tillage**	**Pesticide (17)**	**Method**	**Active Ingredients (%)**
1024	Sample Corn A	No Till	Poncho 250Seed Treatment, Brawl ATZ, Instigate , Paraquate	Herbicieds and Manure applied togther Water carrier Applied 10 Gallons/ Acre	Clothianidin(48), Atrazine(33) S-Metoloachlor (26.1), Rimsulfuron (4.17) Mesotrione(41.67), Paraquatre(43.2)
11214	Crop Side A	No Till	Poncho 250Seed Treatment,Lexar		Clothianidin(48), S-metolachlor (19) Atrazine (18.61) Atrazine related compounds (.39),
11215	Crop Side A	No Till	Poncho 250Seed Treatment,Lexar		Clothianidin(48), S-metolachlor (19) Atrazine (18.61) Atrazine related compounds (.39),
11213	Barley Side A	No Till	Quilt		Azoxystrobin(7) Propiconazole (11.7)
1025	Sample Corn B	No Till	Poncho 250Seed Treatment, Brawl ATZ, Instigate , Paraquate	Herbicieds and Manure applied togther Water carrier Applied 10 Gallons/ Acre	Clothianidin(48), Atrazine(33) S-Metoloachlor (26.1), Rimsulfuron (4.17) Mesotrione(41.67), Paraquatre(43.2)
11216	Crop Side B	No Till	Poncho 250Seed Treatment,Lexar		Clothianidin(48), S-metolachlor (19) Atrazine (18.61) Atrazine related compounds (.39),


11211
11212
11213
11214
112902
1024
11215
1025
11216
1047

MH6

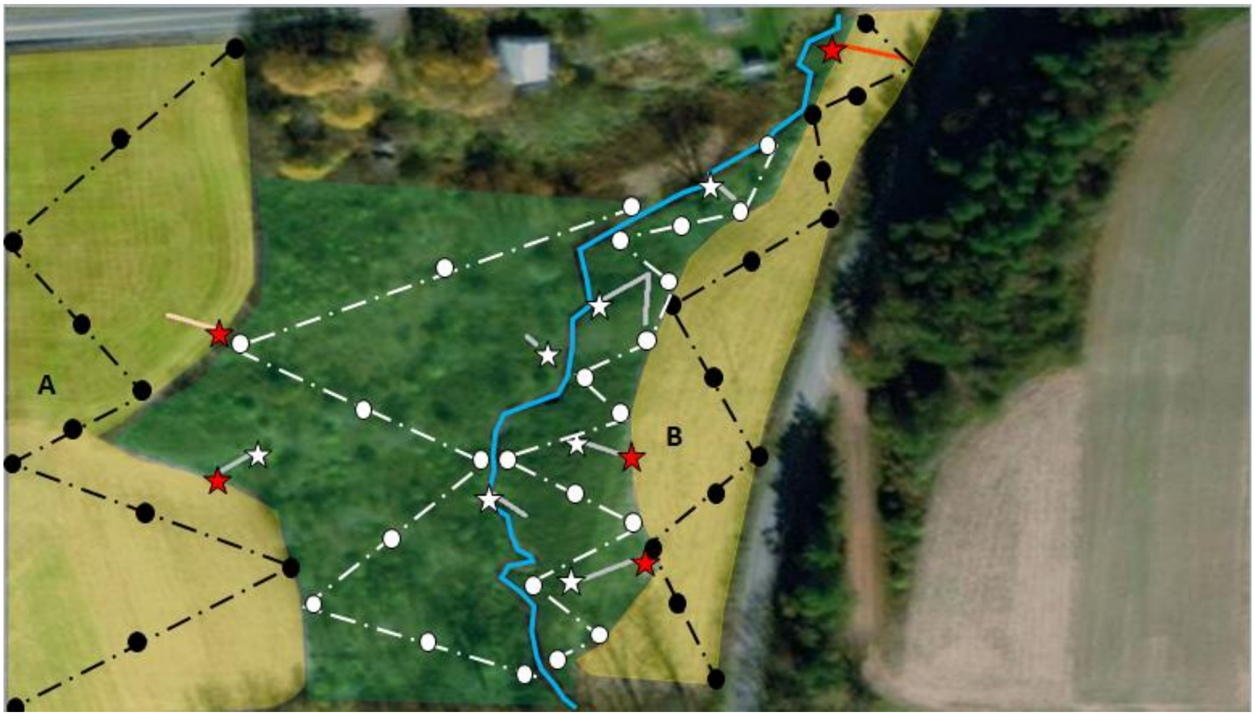


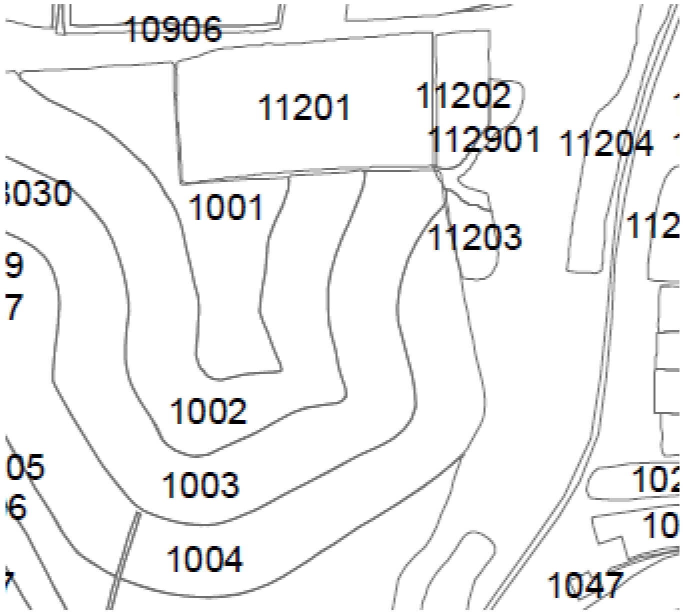
Figure was created using Google Earth© and Arc GIS© software

Label	Description
(yellow)	Cropland
(green)	Buffer
(black line)	Sampling Path In Field
(gray line)	Sampling Path in Buffer
●	Soil Sample in Field
○	Soil Sample in Buffer
(orange line)	CFP
(red line)	Culvert
★ (red)	CFP Sample in Field
☆	CFP Sample in Riparian Buffer
(blue line)	Stream

MH6 was a crop field that was sampled on 5/10/18 and contained debris from the previous year's crop. On side A the main soil type was also a calvin-klinesville soil series that had an approximate slope of 17% and was 3.3 acres. The buffer was documented as a successional buffer which contains grasses shrubs and trees. It is not believed to be a planted buffer and has been established because of the slope being to step for farming practices. There were two CFPs found on Side A .Manure was noted at the site when sampling was conducted.

On side B the main soil type was a calvin-klinesville soil series had an approximate slope of 12% and area of 1.9 acres. This site was sampled after a rain event occurred. There was 3 CFPs and were characterized as erosional and springs. The buffer on side A was a successional area where the farmer most likely did not farm because of the soil being highly saturated. There were signs of biological factors from groundhogs. It was observed that the groundhog tunnels, when downslope of CFPs could create a direct link from the CFP to the stream. The water would enter the hole and would flow to the exit hole which was sometimes next to the stream. This was the only tiled field, which enabled some of the CFPs to drain to the buffer area due to the creation of a plow furrow. When CFPs did enter the buffer, they diffused in several directions.

Fields	Description	Tillage	Pesticide (17)	Method	Active Ingredients (%)
11202	Crop Sample Side A	Chisel Plow Finishing Harrow	Poncho 250Seed Treatment,Lexar	Spray	Clothianidin(48), S-metolachlor (19) Atrazine (18.61) Atrazine related compounds (.39),
11201	Crop Sample A	Chisel Plow Finishing Harrow	Poncho 250Seed Treatment,Lexar	Spray	Clothianidin(48), S-metolachlor (19) Atrazine (18.61) Atrazine related compounds (.39),
1001	Crop Side A		Poncho 250Seed Treatment, Brawl ATZ, Instigate , Paraquate	Spray	Clothianidin(48), Atrazine(33) S-Metoloachlor (26.1), Rimsulfuron (4.17) Mesotrione(41.67), Paraquatre(43.2)
1002	Crop Side A		April-Round Up, Sharpen, Metribuzin, Gaucho Seed treatement July-Thunder master, Credit Extra	Spray	Glyphosate(48.8),Metibuzin(75),Imdacloprid, Glyphosate (22) Imaethapyr (1.8), Glyphosate NH4 salt (17.85%) Glyphosate K salt (16.26%)
1003	Crop Side A		Poncho 250Seed Treatment, Brawl ATZ, Instigate , Paraquate	Spray	Clothianidin(48), Atrazine(33) S-Metoloachlor (26.1), Rimsulfuron (4.17) Mesotrione(41.67), Paraquatre(43.2)
11201	Crop Sample A	Chisel Plow Finishing Harrow	Poncho 250Seed Treatment,Lexar	Spray	Clothianidin(48), S-metolachlor (19) Atrazine (18.61) Atrazine related compounds (.39),
11204	Crop Sampled B	No Till	Poncho 250Seed Treatment,Lexar	Spray	Clothianidin(48), S-metolachlor (19) Atrazine (18.61) Atrazine related compounds (.39),


10906
11201
11202
112901
11204
1001
11203
1002
1003
1004
1047

MH 8

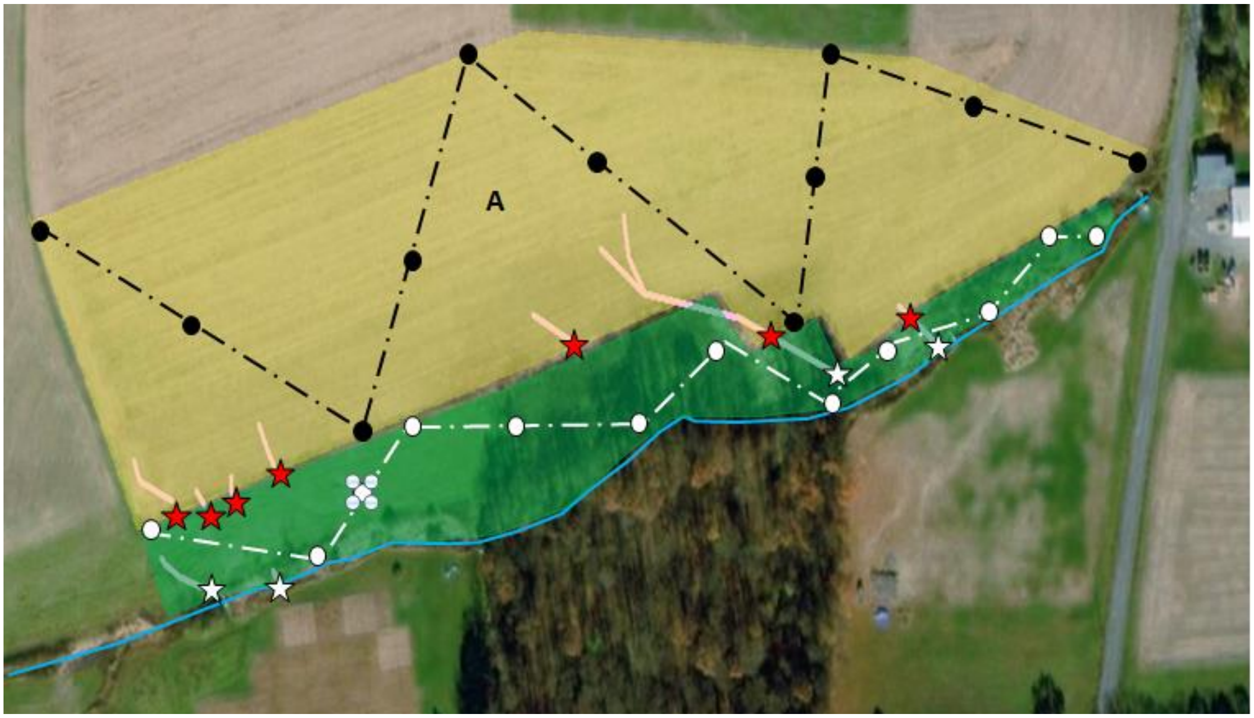
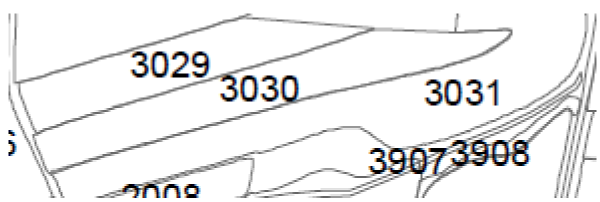


Figure was created using Google Earth© and Arc GIS© software

Label	Description
(yellow)	Cropland
(green)	Buffer
—	Sampling Path In Field
—	Sampling Path in Buffer
●	Soil Sample in Field
○	Soil Sample in Buffer
—	CFP
★	CFP Sample in Field
☆	CFP Sample in Riparian Buffer
—	Stream

MH8 was a crop field that was sampled on 5/18/2018 and did have plant debris from the previous year. The main soil type was a calvin-klinesville soil series with an approximate slope of 15% and area of 4.2 acres. There was seven CFPs and were characterized as seep and erosional flow pathways. Sampling was done recently after a rain event. The springs were considerably larger than other springs found in WE38. The buffer area was composed of a grass area where it is believed that the farmer uses for hay, and eventually transfers to a successional buffer zone. There was CFPs located throughout the buffer and were characterized as springs.

Fields	Description	Tillage	Pesticide (17)	Method	Active Ingredients (%)
3031	Crop field sampled	no till	none		
3030	Crop field	no till	Seed Treatment(Poncho, Warroir (3oz/ac)) Sharpen (1oz/ac), Credit Extra (1.5 QT/ac), Metribuzin (4oz/Ac), Atrazine(1Qt/Ac), Roundup Power Max 1Pt/Ac, Status 5oz/ac Priaxor 4oz-Ac	applied may-June Sharpen, credit and metribuzi sparyed preplant all together	Clothianidin(48),dimethylcyclopropanecarboxylate Glyphosate NH4 salt (17.85%) Glyphosate K salt (16.26%), Metribuzin(75),Atrazine(42.12),Glyphosate(48.8), sodium salt of diflufenzopyr (17.7), sodium salf of dicamba(44), fluxapyroxad(14.33%) pyraclostrobin (25.58)



MH 11

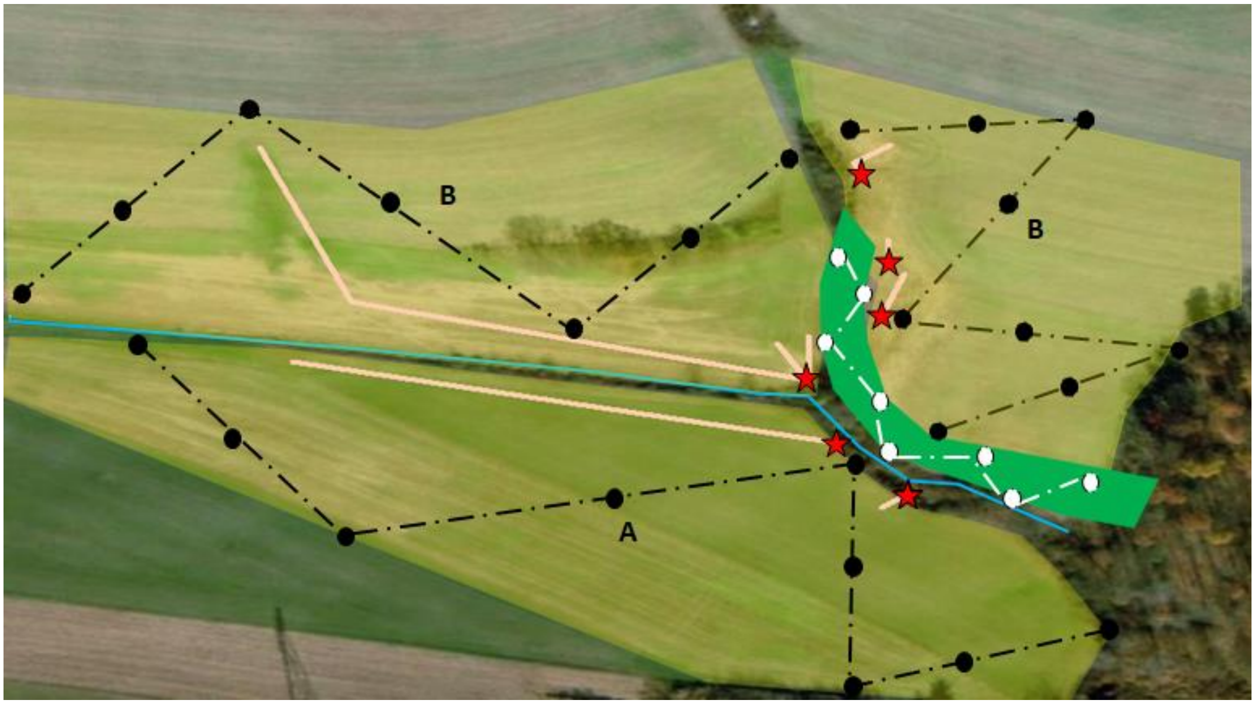


Figure was created using Google Earth© and Arc GIS© software

Label	Description
	Cropland
	Buffer
	Sampling Path In Field
	Sampling Path in Buffer
	Soil Sample in Field
	Soil Sample in Buffer
	CFP
	CFP Sample in Field
	CFP Sample in Riparian Buffer
	Stream

MH11 was a crop field that was sampled on 4/21/2018 and had debris from the previous year's crop. The dominate soil type was an Albrights soil series, had an approximate slope of 8% (B left) and 12% (B right) and a total area of 7.9 acres. There was six cfps and were characterized as erosional and seep pathways. The erosional pathways were created from continuous tractor use, exposed soil and topographical features. The topographical feature was a swale, in which the farmer had installed a grassed waterway to reduce erosion. However, there was erosional channelization that formed directly after the grassed waterway. The buffer was a grassed area and was followed by a small successional buffer approximately 10 ft in width from the stream bank. (B right) was compiled of many springs while (B left) was dominated by erosional pathways. The left side of the site had an approximate slope of 8% and contained two CFPs that were documented as erosional flow paths.

Fields	**Description**	**Tillage**	**Pesticide (17)**	**Method**	**Active Ingredients (%)**
16024	sampled Side A	no till	Poncho 250 seed treatment Acuron (2.5 Qt/ac)	Spray	Clothianidin(48), S-Metolachlor (23.4) Atrazine (10.93) Mesotrione (2.6) Bicylopyrone (.65)
16021	sample Side B	no till	Poncho 250 seed treatment Acuron (2.5 Qt/ac)	Spray	Clothianidin(48), S-Metolachlor (23.4) Atrazine (10.93) Mesotrione (2.6) Bicylopyrone (.65)
16018	Sample Side B	no till	Poncho 250 seed treatment Acuron (2.5 Qt/ac)	Spray	Clothianidin(48), S-Metolachlor (23.4) Atrazine (10.93) Mesotrione (2.6) Bicylopyrone (.65)
16022	Sample Crop Side B	no till	Poncho 250 seed treatment Acuron (2.5 Qt/ac)	Spray	Clothianidin(48), S-Metolachlor (23.4) Atrazine (10.93) Mesotrione (2.6) Bicylopyrone (.65)
16913	Grass strip	no till		Spray	
16019	Side B	no till	seed treated with Gaucho, Authority First (4oz/ac), Round Up (1qt/ac)	Spray	Imidacloprid(600g/L),Sulfetnrazone (62.1) Cloransulam (7.9)Glyphosate (41)

MH 4

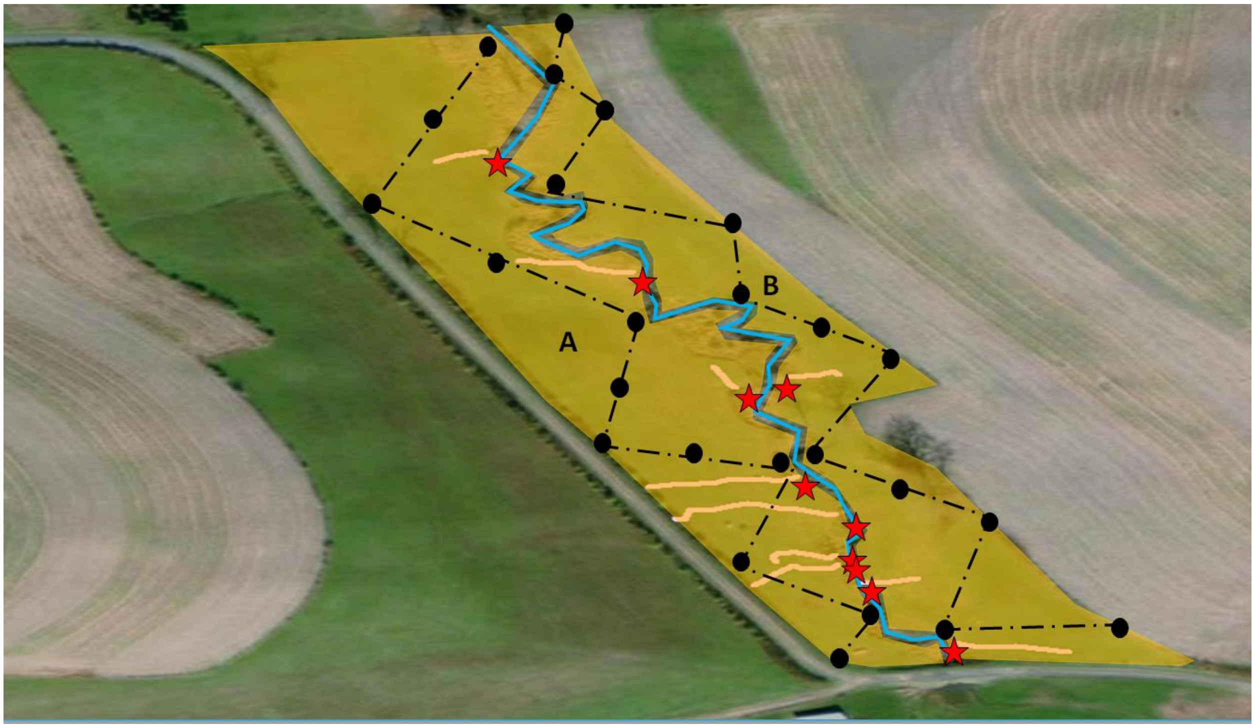


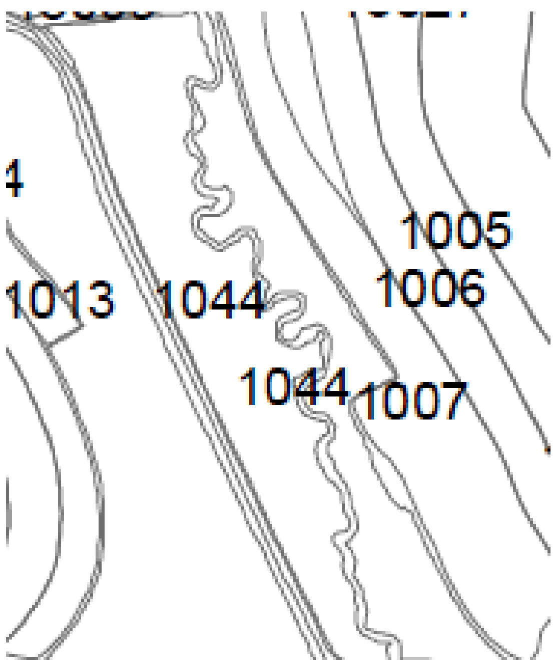
Figure was created using Google Earth© and Arc GIS© software

Label	Description
	Pasture
	Stream
	Sampling Path In Field
	Soil Sample in Field
	CFP
	CFP Sample in Field

MH 4 is a pasture field that was sampled on 5/24/2018 and occurred after a 2in rainfall event. Side A had an approximate slope of 19% and an area of 3 acres. There were a total of seven CFPs and were characterized only a springs. The area was over saturated and due to cattle in the field at the time of sampling, the soil was all mud.

MH 4 is a pasture field that was sampled on 5/24/2018 and occurred after a 2in rainfall event. The dominate soil type of side B is an Albrights soil, had an approximate 10% slope and an area of 3.9 acres. There was a total of three CFPs and were characterized only as erosional pathways. Upgradient of the field was a crop field, by which some CFPs started and ended at the stream bank. The other CFPs were observe as depression areas from old stream channels.

Fields	**Description**	**Tillage**	**Pesticide (17)**	**Active Ingredients**
1044	Pasture	None		
1007	No Till	Poncho 250Seed Treatment, Brawl ATZ, Instigate , Paraquate	Herbicieds and Manure applied togther Water carrier Applied10 gallons/ Acre	Clothianidin(48), Atrazine(33) S-Metoloachlor (26.1), Rimsulfuron (4.17) Mesotrione(41.67), Paraquatre(43.2)



Pasture Fields

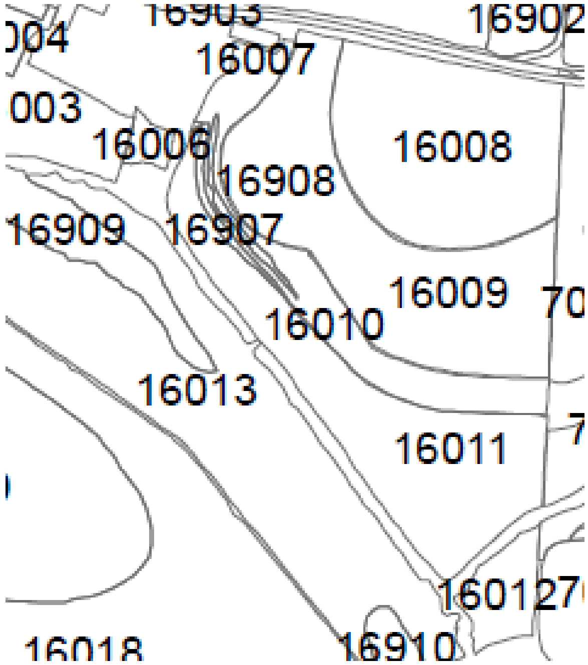
MH12

Figure was created using Google Earth© and Arc GIS© software

Label	Description
	Pasture
	Stream
	Sampling Path In Field
	Soil Sample in Field
	CFP
	CFP Sample in Field

MH12 was sampled on 5/3/2018 and was down gradient of a hay area on the northeast side followed by a crop area on the south end. There was a total of six CFPs on the A side and three CFPs on the B side. The dominant soil type is an Albright soil series and the areas were 2.4 and 4.4 acres for side A and B respectively. It seemed that sheet flow was common and the CFPs occurred close to the stream bank. Manure was found as well as fertilizer application.

Fields	Description	Tillage	Pesticide (17)	Method	Active Ingredients (%)
16013	Sample Pasture Side A	no till	Distinct (5oz/ac)		sodium salt of diflufenzopyr (21.3), sodium salf of dicamba(55)
16019	Side A (Crop)	no till	seed treated with Gaucho, Authority First (4oz/ac), Round Up (1qt/ac)		Imidacloprid(600g/L),Sulfet nrazone (62.1) Cloransulam (7.9)Glyphosate (41)
16018	Side A Crop	no till	Ponch 250 seed treatment Acuron(2.5qt/ac)		Clothianidin(48), S-Metolachlor (23.4) Atrazine (10.93) Mesotrione (2.6) Bicylopyrone (.65)
16011	Side B Sampled Pasture	no till	Distinct (5oz/ac)		sodium salt of diflufenzopyr (21.3), sodium salf of dicamba(55)


16903
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16018

MH3

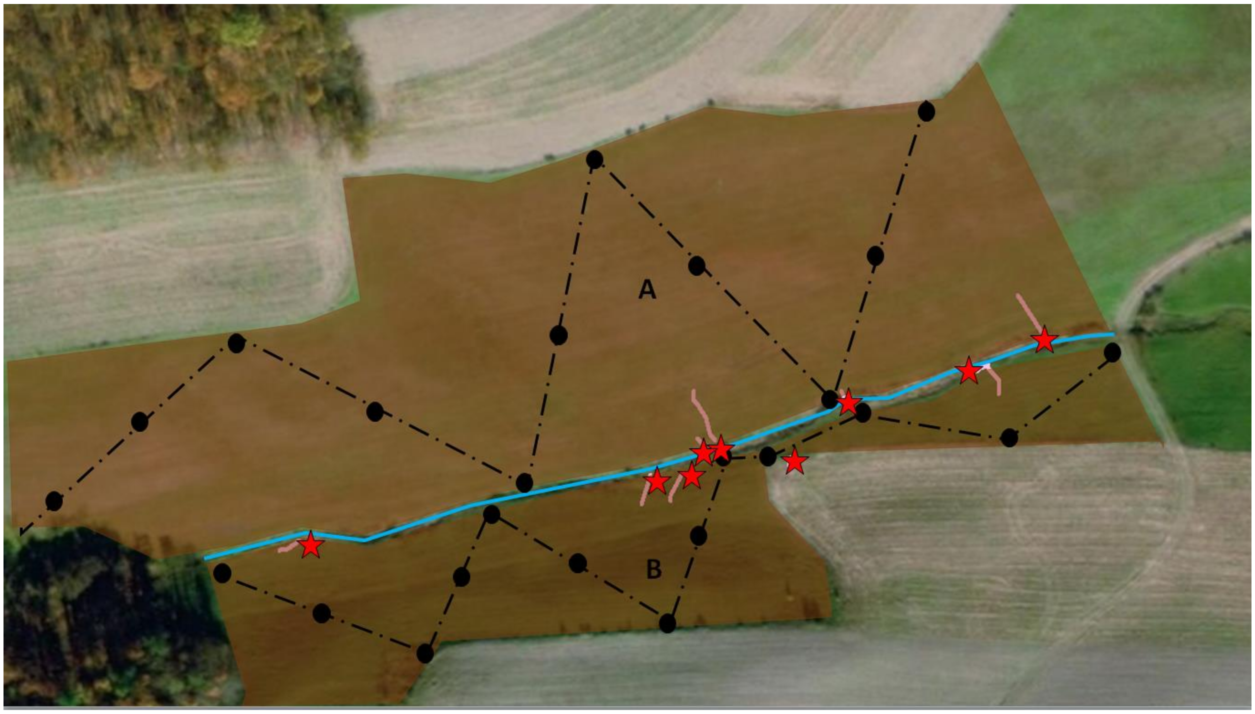
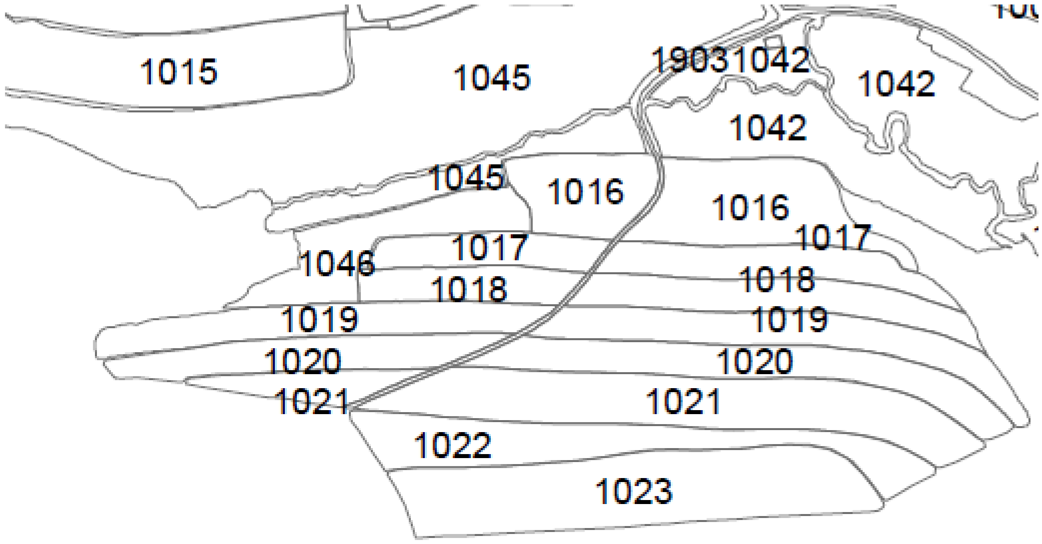


Figure was created using Google Earth© and Arc GIS© software

Label	Description
	Hay
	Stream
	Sampling Path In Field
	Soil Sample in Field
	CFP
	CFP Sample in Field

Both sides of MH 3 were hay fields that were downgradient of corn fields. The dominate soil type was a Weikert soil profile and the approximate slopes were 24% (Side A) and 22% (Side B). In side A there were a total of four CFPs and side B had five CFPs. The CFPs were characterized as erosional and were found around the stream. The main reason for this is due to the dense grasses, which was difficult to locate and fallow the paths. This area had numerous mice paths which in time can turn into concentrated flow pathways in time.

Fields	Description	Tillage	Pesticide (17)	Method	Active Ingredients (%)
1045	Sampled Hayfield	No Till	None		
1009	Cornfield Side A	No Till	Poncho 250Seed Treatment, Brawl ATZ, Instigate , Paraquate	Herbicieds and Manure applied togther Water carrier Applied 10 Gallons/ Acre	Clothianidin(48), Atrazine(33) S-Metoloachlor (26.1), Rimsulfuron (4.17) Mesotrione(41.67), Paraquatre(43.2)
1015	Cornfield Side A	No Till	April-Round Up Sharpen Metribuzin Gaucho Seed treatement July-Thunder master Credit Extra	Spray	Glyphosate(48.8),Metibuzin(75),Imdacloprid, Glyphosate (22) Imaethapyr (1.8), Glyphosate NH4 salt (17.85%) Glyphosate K salt (16.26%)
1046	Sampled Hayfield Side B		None	Spray	
1016	Cornfield Side B	No Till	April-Round Up, Sharpen, Metribuzin, Gaucho Seed treatement July-Thunder master, Credit Extra	Spray	Glyphosate,Metibuzin,Imdacloprid (600g/L), Glyphosate (22) Imaethapyr (1.8), Glyphosate NH4 salt (17.85%) Glyphosate K salt (16.26%)



MH13

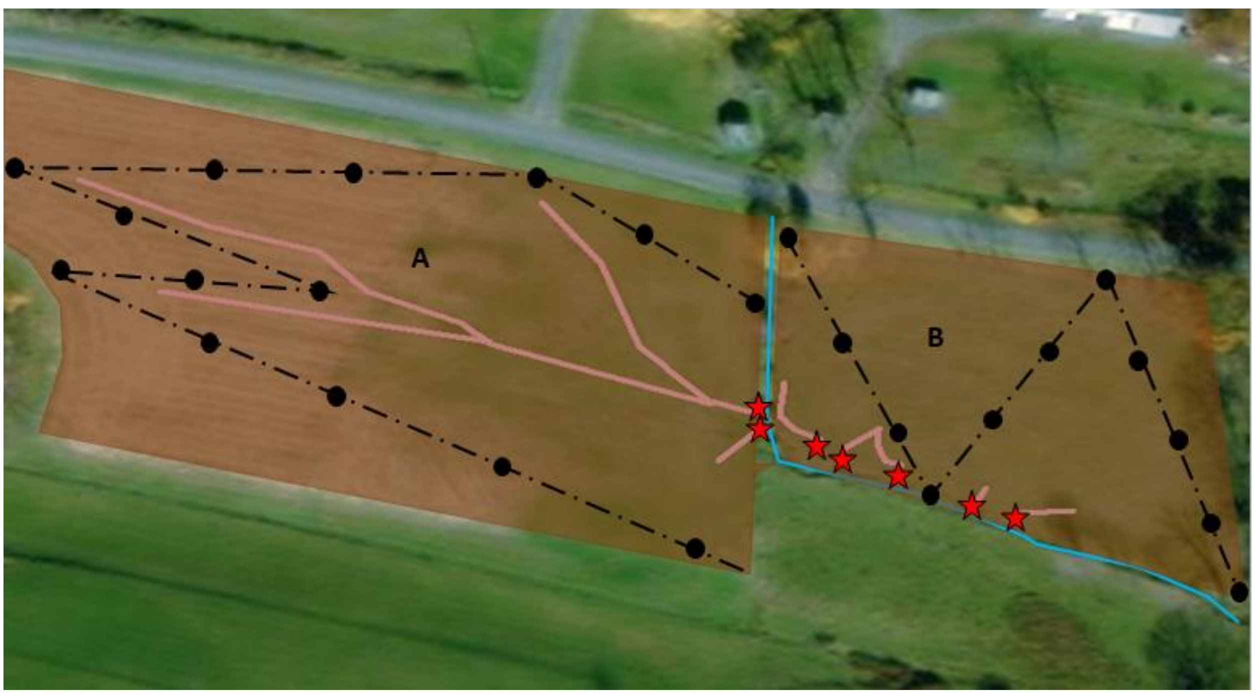


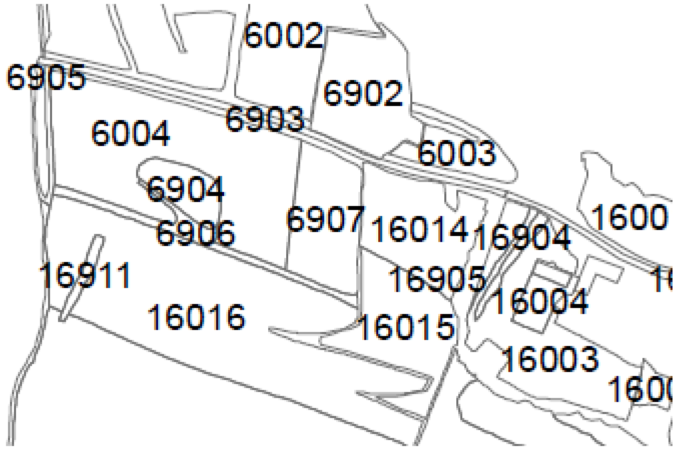
Figure was created using Google Earth© and Arc GIS© software

Label	Description
(brown fill)	Hay
(blue line)	Stream
(black line)	Sampling Path In Field
(black dot)	Soil Sample in Field
(tan line)	CFP
(red star)	CFP Sample in Field

MH 13 Side A is also a hay field which was sampled on 4/21/18. The dominant soil type was a Shelmandine profile, had an approximate 6% slope and had an area of 1.7 acres. Side B had two CFPs and was characterized as micro-ditches. These micro-ditches were installed to increase drainage of the adjacent corn field

MH 13 side B is a hay field which the date of sampling occurred on 4/21/18. The dominant soil type was a Shelmadine profile, had an approximate 10% slope and an area of 1.3 acres. Side B had five CFPs and were characterized as erosional. The CFPs typically formed near the stream bank. The longest CFP could have been caused from continuous use of a tractor. This side had no crop field upgradient and it appeared that sheet flow was predominant at the site.

Field ID	Description	Tillage	Pesticide	Active Ingredients
16905	Sample A (Hay)			
6004	Crop Side A (W)	no till	Poncho 250 seed treatment Acuron (2.5 Qt/ac)	Clothianidin(48), S-Metolachlor (23.4) Atrazine (10.93) Mesotrione (2.6) Bicylopyrone (.65)


6002
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6003
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16014
16904
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Vita.

Joseph Chandler
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Skills:

GIS and Autocad software	Electrofishing experience and Water Quality Testing
Data Analysis using Microsoft Excel and Mintab	Experience with Campbell Scientific Dataloggeres and Isco Samplers
Macroinvertebrate Sampling and Biotic Index Experience	Strong communication and people skills

Education:
- Master Degree: Biorenewable Systems (PSU) (2019)
- Impact of concentrated flow pathways on the movement of pesticides through the various agricultural fields Environmental Resource Management (PSU) (Water Option) – B.S. December 2016
  - Minors: Wildlife and Fisheries
  - Certifications/Affiliations **-** Wetland Professional in Training Certification

Publications:
- Coauthor: Continuous Hydrologic and Water Quality Monitoring of Vernal Ponds (JOVE)

Honors/Awards:
- 2015 Agricultural Sciences Scholarship
- Wegmans Scholarship (2012-2016)

Experience/Employment:

Natural Resources Engineering and Protection Lab, Department Agricultural and Biological Engineering, Penn State University (2014-2016)
- Implemented Atrazine test throughout Susquehanna Watershed
- Responsible for designing testing system and delineation of watersheds
- Performed field work, identifying possible outlet areas, water collection, soil drainage patterns

Wegmans Food Markets, State College, PA (2011-Present)

Front End Coordinator
- Develop and train cashiers to help develop great customer service skills
- Manage front end operation with cashiers and other Front End Coordinators.
- Assist Front End Managers to create an organized department
- Assist customers with any problems or questions with their purchases.

Cheese/Seafood Departments
- Provide customer service and advice on a perishable foods
- Communicate and coordinate a steady supply of products for customers
- Practicing safe food handling and sanitation procedures
- Consult with customers on where and how the product was made or caught

Volunteering:

Spring Creek Stream Restoration, PA Fish and Boat Commission, Trout Unlimited, and Clearwater Conservancy (2010)
- Strengthened team building and communication skills
- Installed stream bank structures
- Acquired skills to maintain a fresh water fishery

Purple Loosestrife Control (2010-2015)
- Practiced accurate population counts skills and protocol
- Used accepted biocontrol methods to treat an invasive species and translated results to audiences

References

References can be available upon request