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OCCURENCE OF HERBICIDES IN CENTRAL INDIANA STREAMS

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ABSTRACT. Agricultural chemicals, such as pesticides and herbicides, play an important role in agricultural operations to control unwanted pests and maximize crop yield. However, these chemicals may also threaten aquatic life. The abundance of agricultural chemicals, specifically atrazine and metolachlor, was measured in eighteen headwater streams of the Upper White River Watershed (UWRW) of central Indiana. Sites were selected to represent a range of agriculture activity within the watershed. Sites were sampled seasonally over one year (N=4) to assess temporal variation in herbicide abundance and the influence of physiochemical factors. Pearson correlation coefficients were used to assess independent variables influencing stream herbicide concentrations. All sites had measurable concentrations of atrazine and metolachlor during June 2010 sampling; no herbicides were above the detection limit in August; only two sites had measureable concentrations of metolachlor in November; and, one site had measurable concentrations of atrazine and metolachlor in May. These data indicate concentrations of atrazine and metolachlor in central Indiana streams are temporally variable, being highest in late spring. Concentrations measured were comparable to other studies in agricultural areas and frequently exceeded concentrations known to have adverse effects on aquatic organisms.

Keywords: Agriculture, herbicides, streams

Freshwater is a valuable resource to both surrounding ecosystems and human activities. Streams play an important role linking terrestrial ecosystems to downstream ecosystems because they assist in energy and nutrient exchange among adjacent terrestrial, atmospheric, and downstream ecosystems (Likens et al. 1974). In addition, they provide fundamental resources including drinking water, sanitation, and flood control. Freshwater ecosystems also provide habitat for a variety of flora and fauna that can improve or maintain water quality (Meyer et al. 2007). Since terrestrial and aquatic ecosystems are fundamentally linked, agricultural activities can influence the integrity of receiving waters within a watershed.

Agricultural activities can influence water quality and the organisms that depend on freshwater habitats in a number of ways. For example, agricultural activities can inflate erosion rates, especially after rain events, increasing sediments entering waterways (Al-Kaisi 2009). This sediment runoff is one of the leading impairments to streams and rivers in the United States (Miller et al. 2011). Increased sediment in turn provides more surface area for pathogens and yields light limitation to autotrophic organisms (Matson et al. 1978; Vidon et al. 2008). Agricultural activity can also increase nutrient concentrations, primarily as nitrogen and phosphorus, resulting in algal blooms and subsequent eutrophication (Paerl 1997). Eutrophication decreases dissolved oxygen concentrations threatening fish and reducing diversity of other aquatic organisms (Nixon 1995). Decades of research have highlighted adverse effects of sediment and nutrients associated with agricultural activity on freshwater ecosystems (Wolman 1967; Paerl 1997; Turner et al. 2003; Schoonover et al. 2006; Miller et al. 2011). However, agricultural activity can also influence freshwater ecosystems via introduction of herbicides and pesticides and less is known about the potential effects of these contaminants on freshwater integrity.

Herbicides, in particular atrazine and metolachlor, are commonly used in central Indiana and the Midwestern United States (Fenelon et al. 1996; Pratt et al. 1997; Fenelon 1998; Fuhrer et al. 1999; USGS 2011) but comprehensive data on concentrations and effects are lacking (Thurman et al. 1992; Crawford 1995). According to 2007 United States Census data, 64% of Indiana is classified as cropland (United States Department

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of Agriculture 2009). Indiana also lies within the Mississippi River Watershed yielding agricultural inputs draining into the Mississippi River and subsequently the Gulf of Mexico. Historically, the Gulf of Mexico has experienced hypoxic areas partly due to the increased nutrient loading from nonpoint sources within the Midwest (Ongley 1996; Kanwar et al. 2005). It is likely that other agricultural contaminants, like herbicides and pesticides are also being transported to downstream ecosystems.

Abundance of herbicides and pesticides, especially atrazine and metolachlor, can differ substantially with regards to individual studies conducted. In studies conducted in Midwestern streams, atrazine, a pre-emergence herbicide, can reach concentrations exceeding 1 mg/L in nonpoint sources (agricultural runoff), and up to 40 μg/L in precipitation (Hayes et al. 2002). Atrazine can also persist in streams at high concentrations for weeks (Pratt et al. 1997). Metolachlor can reach concentrations as high as 138 μg/L in surface waters, with increases in concentration primarily associated with runoff events in agricultural areas (Rivard 2003; Extoxnet 2000a). Another study performed in Illinois over eight years (1992–2000), measured atrazine concentrations as high as 49 μg/L and metolachlor at 8.2 μg/L in freshwaters draining agricultural areas (David et al. 2003).

Amount of precipitation, terrain, soil characteristics, and type of tillage system may all influence export of agricultural chemicals into receiving waters (Kalkhoff et al. 2003; Miller et al. 2011). Soil physical and chemical characteristics can foster chemical degradation as well as transport to ground water and receiving streams. For example, as the permeability of soil increases, ground water infiltration and movement into streams also increases (Burkart et al. 1999; Kalkhoff et al. 2003). In contrast, when soil permeability is low, agricultural chemicals are more likely to be retained on the landscape and enter freshwater primarily during runoff events (Burkart et al. 1999; Kalkhoff et al. 2003). Runoff events frequently introduce higher concentrations of contaminants into receiving waters (Burkart et al. 1999; Kalkhoff et al. 2003). Type of tillage system used in the surrounding agricultural fields can also affect the abundance of herbicides and pesticides in receiving waters. Conventional tillage and crop harvesting exposes the ground to the elements, increasing the rate of erosion and resulting in greater runoff of herbicides and pesticides to receiving streams (Miller et al. 2011).

Once in the freshwater ecosystem, pesticides and herbicides may have adverse effects on aquatic organisms. Atrazine is considered to be lethal to invertebrates at concentrations ranging from 6–22 mg/L (Mayer et al. 1986; Pratt 1997) and from 0.8–2.7 mg/L for fishes (Mayer et al. 1986; Pratt 1997). Even though agricultural chemicals may not be lethal at environmentally-relevant concentrations, sub-lethal effects on organismal growth, reproduction, or behavior may also occur (Fleeger et al. 2003). For example, atrazine can act as an endocrine disrupter in frogs at 1 μg/L (Hayes et al. 2002). Herbicides can also alter the behavior of lobsters and crayfish by impairing their ability to locate food sources (Wolf and Moore 2002; Cook et al. 2008).

Criteria used to determine how a chemical may influence water quality include toxicity, persistence, degradates, and environmental fate (Ongley 1996). Further, effects at the organism or ecosystem level are usually considered to be an early warning indicator of potential human health impacts (Ongley 1996). However, many times these criteria are established using isolated samples not representative of spatial and temporal variability in ecosystem contaminants or target aquatic communities. To protect water resources, more comprehensive research is needed to assess the distribution and concentrations of agricultural chemicals in central Indiana freshwaters.

METHODS

Study sites.—Sampling was conducted in the Upper White River Watershed (UWRW) of central Indiana (Figure 1). The UWRW covers 2,720 square miles across 16 counties with a gradient of agricultural activities (UWRWA 2010). The UWRW supplies 85% of the surface water needed for human use in Indianapolis and central Indiana (Crawford 1995). Within the UWRW, 17 headwater stream sites were selected for sampling, representing a range of agricultural activity (Table 1). One site in another nearby watershed (Sugar Creek) was also sampled for a total of 18 sites. Sites were sampled seasonally over one year (N=4) in June, August, and November 2010 and May 2011.

Water sampling.—At each sampling event, two filtered water samples were collected at each site. All water samples were collected using a rinsed 60 mm syringe placed in the

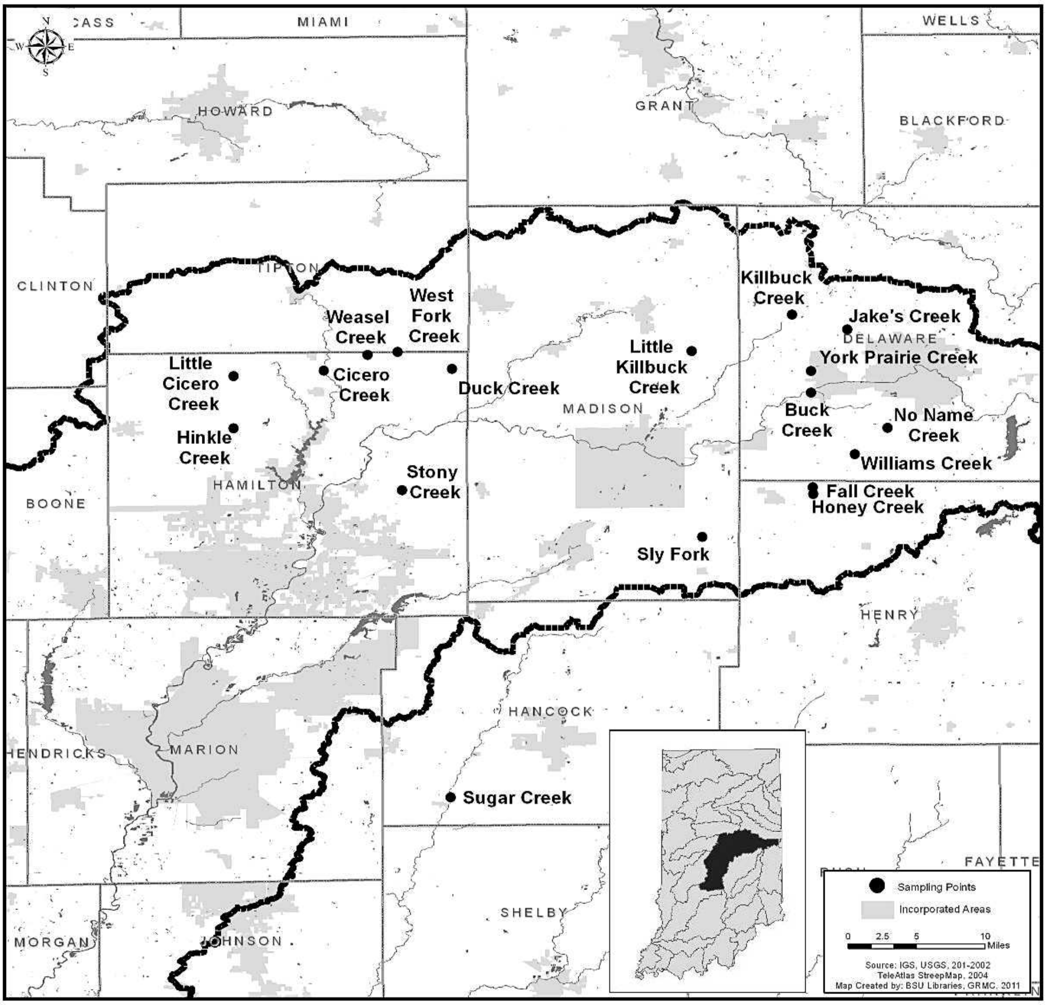

Figure 1.—The Upper White River Watershed (UWRW) in central Indiana with sampling locations (black circles). Surrounding land use is identified within the watershed.

Table 1.—Mean site physiochemical characteristics values for June, August, and November 2010 and May 2011 with standard deviation in parenthesis.

Site	Width (m)	Mean depth (m)	Mean velocity (m/s)	Discharge (m^3/s)	Temperature (C°)	pH	Specific Conductivity (µS/cm)	Total Dissolved Solids (g/L)	DO (% sat)	DO (mg/L)	Salinity (ppt)	% Organic Matter
Buck Creek	20.13 (3.04)	0.30 (0.12)	0.55 (0.27)	3.71 (2.78)	15.96 (4.53)	9.33 (0.28)	661.30 (134.25)	0.42 (0.09)	99.78 (7.60)	11.40 (1.66)	0.34 (0.07)	1.52 0.92)
Cicero Creek	15.00 (2.58)	0.54 (0.20)	0.36 (0.15)	3.14 (2.17)	17.39 (5.71)	8.18 (1.85)	538.90 (101.82)	0.34 (0.07)	99.00 (15.69)	11.07 (2.90)	0.28 (0.06)	1.13 (0.22)
Duck Creek	12.53 (2.49)	0.44 (0.27)	0.33 (0.11)	1.84 (1.20)	17.03 (4.93)	8.75 (0.22)	768.78 (331.33)	0.48 (0.19)	79.35 (14.76)	9.04 (2.97)	0.39 (0.16)	2.66 (1.83)
Fall Creek	1.80 (1.24)	0.31 (0.23)	0.06 (0.08)	0.07 (0.12)	12.76 (9.44)	6.88 (4.59)	492.45 (332.73)	0.32 (0.21)	77.43 (52.17)	7.83 (5.46)	0.26 (0.17)	2.07 (1.47)
Hinkle Creek	2.23 (1.10)	0.27 (0.18)	0.16 (0.17)	0.17 (0.23)	16.09 (6.88)	8.87 (0.71)	596.63 (128.78)	0.38 (0.08)	89.85 (45.47)	10.34 (6.16)	0.30 (0.07)	0.95 (0.33)
Honey Creek	4.83 (1.02)	0.14 (0.06)	0.23 (0.22)	0.21 (0.24)	16.23 (3.11)	9.06 (0.09)	661.85 (127.78)	0.40 (0.07)	109.30 (10.26)	11.92 (2.93)	0.33 (0.05)	0.59 (0.19)
Jake's Creek	5.63 (2.41)	0.33 (0.22)	0.25 (0.24)	0.96 (1.59)	17.29 (5.17)	8.82 (0.34)	422.30 (297.19)	0.27 (0.19)	72.43 (9.41)	8.17 (1.91)	0.22 (0.15)	2.20 (1.58)
Killbuck Creek	9.60 (1.55)	0.39 (0.22)	0.18 (0.12)	0.79 (0.78)	16.33 (4.51)	8.80 (0.38)	700.08 (126.05)	0.45 (0.08)	77.40 (8.44)	8.87 (1.99)	0.36 (0.07)	2.54 (1.19)
Little Cicero Creek	7.93 (1.18)	0.33 (0.05)	0.20 (0.14)	0.59 (0.50)	17.38 (5.98)	9.04 (0.35)	635.18 (121.50)	0.41 (0.08)	97.03 (20.85)	10.91 (3.46)	0.33 (0.07)	3.19 (2.87)
Little Killbuck	4.60 (1.25)	0.24 (0.14)	0.08 (0.09)	0.16 (0.24)	14.41 (4.48)	8.52 (0.64)	613.23 (124.69)	0.39 (0.08)	69.43 (10.33)	8.36 (2.59)	0.32 (0.07)	2.66 (2.04)
No Name Creek	3.35 (0.62)	0.28 (0.12)	0.14 (0.15)	0.19 (0.23)	15.33 (3.69)	9.23 (0.35)	676.10 (113.95)	0.43 (0.07)	97.05 (14.39)	11.49 (3.58)	0.35 (0.06)	1.41 (0.43)
Sly Fork	6.95 (2.28)	0.36 (0.15)	0.15 (0.08)	0.48 (0.46)	17.59 (4.01)	9.03 (0.25)	675.75 (93.43)	0.44 (0.04)	105.68 (16.26)	11.63 (1.83)	0.36 (0.04)	4.65 (3.09)
Stony Creek	4.40 (1.71)	0.25 (0.13)	0.37 (0.28)	0.44 (0.44)	17.04 (4.83)	8.78 (0.40)	594.53 (130.18)	0.38 (0.08)	102.60 (15.01)	11.60 (3.23)	0.31 (0.07)	1.72 (1.58)
Sugar Creek	15.30 (9.83)	0.58 (0.15)	0.34 (0.22)	4.51 (5.88)	18.42 (5.88)	9.28 (0.35)	587.30 (136.08)	0.38 (0.09)	110.25 (16.26)	12.02 (2.42)	0.30 (0.07)	1.14 (0.39)
Weasel Creek	2.40 (0.70)	0.41 (0.34)	0.09 (0.03)	0.11 (0.10)	16.21 (6.35)	8.88 (0.20)	643.30 (118.93)	0.41 (0.08)	77.38 (49.94)	9.39 (7.12)	0.33 (0.06)	5.27 (2.43)
West Fork	5.53 (2.36)	0.58 (0.06)	0.03 (0.01)	0.16 (0.21)	16.44 (6.10)	8.79 (0.50)	596.20 (119.95)	0.38 (0.08)	72.25 (35.59)	8.67 (5.08)	0.31 (0.06)	11.72 (5.07)
Williams Creek	6.68 (1.49)	0.17 (0.09)	0.22 (0.19)	0.37 (0.47)	15.68 (4.34)	9.12 (0.12)	629.00 (87.40)	0.40 (0.06)	95.28 (12.46)	10.77 (3.11)	0.33 (0.05)	1.07 (0.72)
York Prairie Creek	5.08 (0.81)	0.33 (0.32)	0.35 (0.16)	0.43 (0.21)	16.46 (4.17)	9.02 (0.50)	744.70 (116.04)	0.48 (0.07)	79.73 (6.49)	9.01 (1.24)	0.39 (0.06)	1.85 (1.91)

thalweg of each stream and subsequently filtered through a glass fiber filter (Whatman GF/F; 0.6 μm nominal pore size) into acid-washed sample bottles. The first filtered water sample was collected into a 1000 mL amber glass bottle containing preservative, which was then analyzed within 24h for 33 specific herbicides at the Indiana State Department of Health Analytical Laboratory, Indianapolis, using liquid chromatography followed by mass spectrometry (ISDH SOP: 525.2 SVOC). Herbicides analyzed included atrazine (detection limit=0.20 μg/L), metolachlor (0.15 μg/L), simazine (0.15 μg/L), acetochlor (0.16 μg/L), alachlor (0.12 μg/L), hexachlorocycolpentadiene (0.044 μg/L), propachlor (0.075 μg/L), desethylatrazine (0.062 μg/L), trifluralin (0.054 μg/L), desisopropylatrazine (0.54 μg/L), hexachlorobenzene (0.10 μg/L), clomazone (0.072 μg/L), pentachlorophenol (0.59 μg/L), lindane (0.098 μg/L), terbufos (0.083 μg/L), heptachlor (0.11 μg/L), chlorpyrifos (0.088 μg/L), cyanazine (0.40 μg/L), aldrin (0.11 μg/L), pendimethalin (0.13 μg/L), heptachlor epoxide (0.094 μg/L), oxychlordane (0.030 μg/L), gamma-Chlordane (0.068 μg/L), alpha-Chlordane (0.090 μg/L), trans-Nonachlor (0.060 μg/L), dieldrin (0.11 μg/L), endrin (0.23 μg/L), cis-Nonachlor (0.067 μg/L), p,p'-DDT (0.10 μg/L), bis (2-ethylhexyl) adipate (0.020 μg/L), methoxychlor (0.32 μg/L), bis (2-ethylhexyl) phthalate (0.090 μg/L), and benzo[a]pyrene (0.13 μg/L). Three additional 1000 mL amber glass bottles were collected, at a randomly chosen site, during each sampling event to be used for matrix assessments in analytical procedures. The second filtered water sample was collected into a 125 mL acid-washed Nalgene bottle and frozen within 8 h for subsequent analysis of cations (ammonium, calcium, lithium, magnesium, potassium, sodium) and anions (bromide, chloride, nitrate, nitrite, phosphate, sulfate) using ion chromatography (DIONEX, ICS-3000).

Sediment sampling.—In addition to water samples, sediment was also collected at each sampling site by collecting a composite sample, along an established transect, of the top 5–10 cm of sediment and placing into a 120 mL specimen cup. Sediment was transported on ice to the laboratory, and subsequently dried (60°C). Once dried, each sample was then further processed to determine percent organic matter. Three sub-samples were taken from each sediment sample and weighed, followed by combustion in a Barnstead Thermolyne© FB 1400 muffle furnace for at least 2 h followed by measurement of ash weight. Sediment % organic matter for each sampling event was calculated as the mean of the three sub-samples.

Ancillary variables.—Stream physiochemical and channel characteristics were also measured at each location and sampling period. Water quality parameters were measured using a Hydrolab© minisonde equipped with a Luminescent Dissolved Oxygen (LDO) sensor, temperature probe, conductivity sensor, and pH sensor. Stream discharge, mean depth, velocity, and wetted width were measured using a Marsh McBirney flow meter.

Statistics.—Differences in herbicide concentrations among seasons and sites were assessed using analysis of variance (ANOVA). Factors influencing measured herbicide concentrations were analyzed using Bonferroni-corrected Pearson correlation statistics.

RESULTS

Physiochemical characteristics.—The 18 sites selected for this study represented a range of headwater streams with variation among average width (1.80–20.13 m), depth (0.17–0.58), velocity (0.03–0.28), and discharge (0.07–4.51 m/s) (Table 1). In addition, specific conductivity (422–769 μS/cm), dissolved oxygen (7.83–12.02 mg/L), and percent organic matter (0.59–11.72%) also varied among sites. Temperature (12.76–18.42 C °), pH (8.18–9.33), and salinity (0.26–0.39 ppt) were the least variable characteristics among sites.

Sugar Creek had the highest mean discharge (4.51 m^3/s) and DO (110%; 12.02) of all sampling sites; whereas, Fall Creek and Weasel Creek had the lowest mean discharge (0.07 m^3/s; 0.11 m^3/s, respectively). West Fork had 2× benthic organic matter in sediment relative to Weasel Creek (11.72% compared to 5.27%). Specific conductivity varied significantly across the four sampling events (standard deviation was >87 for all sites), while variation in salinity was lower (standard deviation <0.15).

Herbicide concentrations.—Across all sampling periods, only four herbicides were at or above the detection limits including atrazine, metolachlor, acetochlor, and simazine. Herbicides which were not detected during any sampling event included hexachlorocycolpentadiene, propachlor, desethylatrazine, trifluralin, desisopropylatrazine, hexachlorobenzene, clomazone, pentachlorophenol, lindane, terbufos,

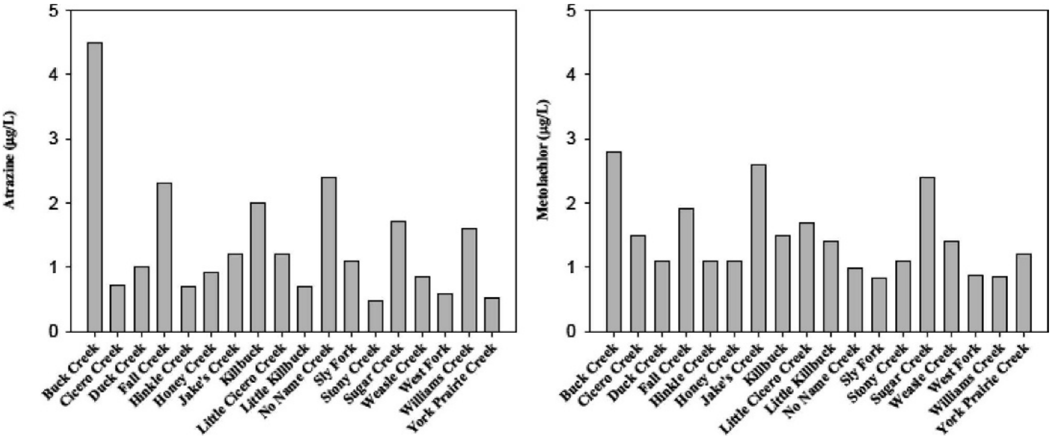

Figure 2.—Concentrations (µg/L) of atrazine and metolachlor for June 2010 sampling.

heptachlor, chlorpyrifos, cyanazine, aldrin, pendimethalin, heptachlor epoxide, oxychlordane, gamma-Chlordane, alpha-chlordane, trans -Nonachlor, dieldrin, endrin, cis-Nonachlor, p,p'-DDT, bis (2-ethylhexyl) adipate, methoxychlor, bis (2-ethylhexyl) phthalate, and benzo[-a]pyrene. In the June 2010 sampling, atrazine (0.52–4.5 µg/L) and metolachlor (0.86–2.8 µg/L) were found detected at all sites (Figure 2). Acetochlor was detected at 10 sites (56%

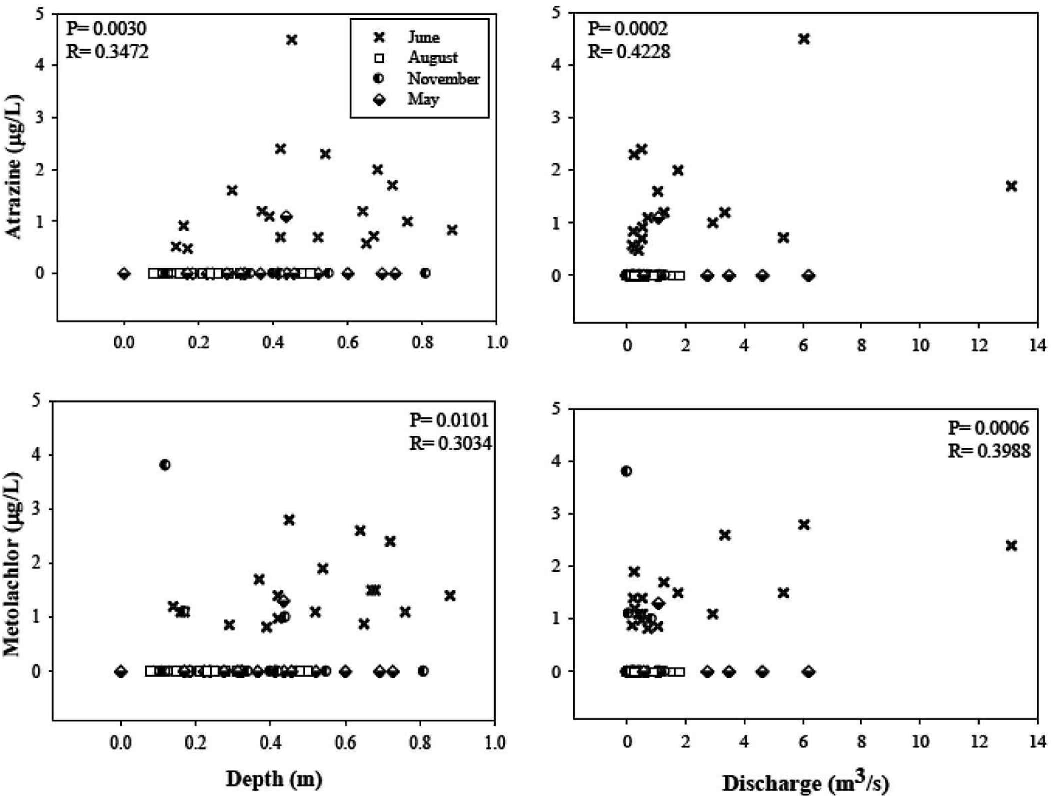

Figure 3.—The relationship between stream discharge and depth with atrazine and metolachlor concentrations for all sampling events. Pearson Correlation statistics noted.

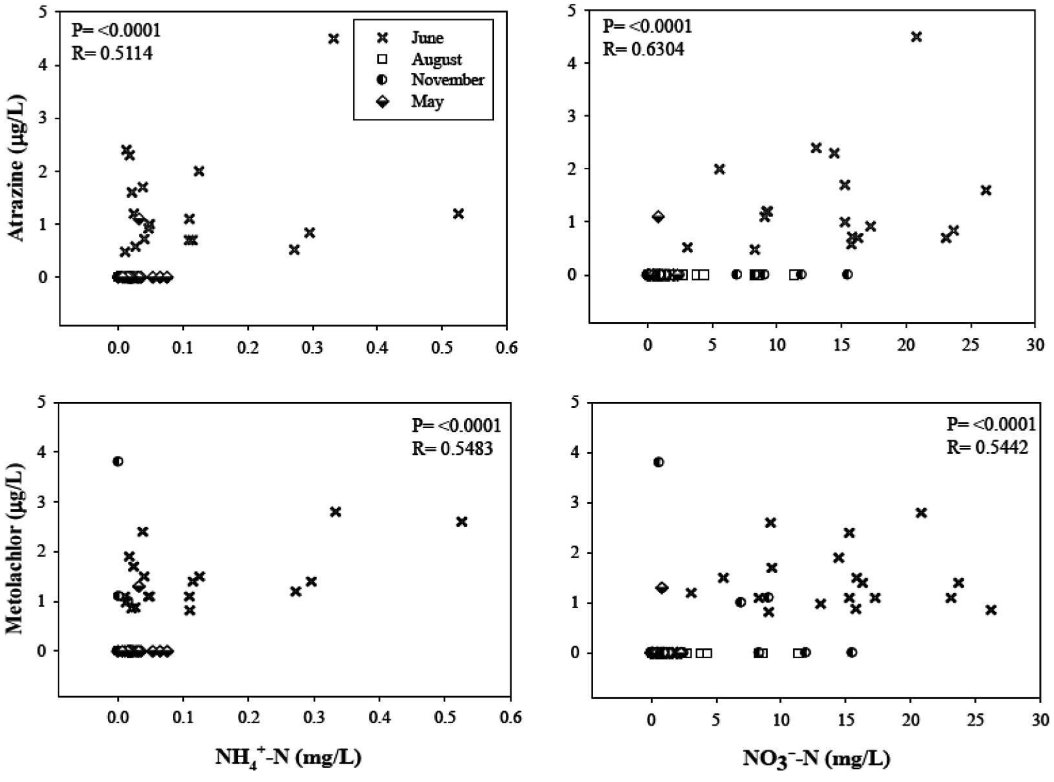

Figure 4.—The relationship between ammonium (NH_4^+-N) and nitrate (NO_3^--N) with atrazine and metolachlor concentrations for all sampling events. Pearson Correlation statistics noted.

detection frequency; 0.68–2.1 µg/L) during the June sampling event and simazine was detected at 1 site (0.05% detection frequency; 0.92 µg/L) only during the June sampling event. The highest concentration of atrazine was also found during the June sampling event (4.5 µg/L) and was measured at Buck Creek, which was characterized by both urban and agricultural inputs. The August 2010 sampling event yielded concentrations that were below detection limits for all herbicides tested. In November 2010, all herbicides were below detection limits except for metolachlor. Little Killbuck (3.8 µg/L) and Stony Creek (1.1 µg/L) had metolachlor concentrations above detection limits. Across all sites and sampling events, the highest concentration of metolachlor was measured at Little Killbuck in November 2010. In May 2011, only one site, Stony Creek, had any herbicides that were above detection limits with measureable concentrations of atrazine (1.1 µg/L) and metolachlor (1.3 µg/L).

Factors influencing herbicide concentrations.—Depth and discharge were positively correlated with both atrazine ($R=0.3472$ $p=0.0030$; $R=0.4228$ $p=0.0002$, respectively) and metolachlor concentrations ($R=0.3034$ $p=0.0101$; $R=0.3988$ $p=0.006$, respectively; Figure 3). Dissolved nutrient concentrations were also correlated with herbicide concentrations. Specifically, nitrate (NO_3^--N) and ammonium (NH_4^+-N) were positively correlated with atrazine ($R=0.6304$ $p=<0.0001$; $R=0.5114$ $p=<0.0001$, respectively) and metolachlor concentration ($R=0.5442$ $p=<0.0001$; $R=0.5483$ $p=<0.0001$, respectively; Figure 4). Temperature, pH, dissolved phosphate concentrations and sediment percent organic matter were not correlated with herbicide concentrations across sites ($p>0.1$).

DISCUSSION

Herbicide concentrations found in this study were comparable to other studies conducted within the United States. Specifically, Fenelon (1998) measured atrazine concentrations between 0.04–>10 µg/L and metolachlor concentrations between 0.005–10 µg/L in streams.

Similarly, David et al. (2003) measured atrazine concentrations between 0–17 μg/L and metolachlor between 0–3.4 μg/L in Illinois streams influenced by agriculture.

Although concentrations measured in this study were comparable to previous studies, metolachlor concentrations were higher than atrazine for 71% of the sampling sites across all sampling events, inconsistent with previous studies. Atrazine is thought to be more widely used in the United States, relative to metolachlor and previous studies of freshwater have yielded higher atrazine concentrations, relative to metolachlor. These higher metolachlor concentrations may either be due to higher usage rates or variability in sample collection timing (Thurman et al. 1992; David et al. 2003). However, one previous study conducted in Illinois, Iowa and Minnesota, found herbicide concentrations above detection limits even during base-flow conditions (Kalkhoff et al. 2003). This was not supported in our study as no herbicides were found above detection limits during the August sampling.

Higher concentrations of herbicides typically occur after high-flow conditions, particularly in spring (Thurman et al. 1992). These data support this observation as the greatest concentrations of herbicides were measured during the June 2010 sampling period. However, lower concentrations were measured in early spring (May) indicating a delay in herbicide runoff following early spring runoff. Land use and agricultural practices can also influence the abundance of pesticides and herbicides in streams (Fenelon 1998; David 2003).

Herbicide concentrations as low as 1 μg/L can have non-lethal effects on aquatic life (Hayes et al. 2002). These effects can range from being an endocrine disruptor to changing the behavior of a particular organism (Hayes et al. 2002; Wolf and Moore 2002; Cook et al. 2008). In this study, atrazine and metolachlor concentrations were measured at these effective concentrations in 58% and 81% of samples, respectively. Continued study of the abundance of herbicides in these streams is needed to identify periods of time of greatest concern.

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