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## **Runoff and Pesticide Discharge from Agricultural Watersheds in NE Indiana**

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**Abstract.** *This paper presents results of monitoring levels of runoff and pesticides from initial sampling of agricultural watersheds in northeastern Indiana. In 2002, four watersheds were monitored in which land-use is predominately row-crop agriculture of corn and soybeans, and they ranged in size from 480 to 10600 acres. Sampling equipment was installed in early spring and was operational at all sites by June 1. Measurements in 2002 were to establish base flow and pollutant levels. Future plans by local personnel are to implement large numbers of BMPs (Best Management Practices) to control herbicide loss on one of the sets of watersheds, then monitor both control and BMP runoff and water quality. We will ultimately observe and monitor 9 watersheds: control large (3500 acres), control medium (770 acres), control small (7 acres), BMP extra large (10600 acres), BMP large (4800 acres), BMP medium (740 acres), BMP small (6 acres), control-2 large (3400 acres), and control-2 medium (920 acres). All medium and larger watershed sampling sites have been actively monitoring base flow and storm events since May 2003. The BMP and control small watersheds have been located and will be instrumented in summer 2003. For the period June – October 2002, measured runoff events ranged from 1 to 4 at the initial four sites. The extra large watershed had the largest number of sampled events (4), and sampled events decreased with decreasing watershed size. Over all sites and events, peak atrazine herbicide concentration measured in runoff water was 66 ppb.*

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**Keywords.** Water quality, watershed, monitoring, runoff, pesticides, herbicides

# **Runoff and Pesticide Discharge from Agricultural Watersheds in NE Indiana**

D.C. Flanagan, S.J. Livingston, C. Huang, E.A. Warnemuende

## **Introduction**

Quality of the water in our streams, rivers and lakes is becoming more important, with increases in population and reductions in available fresh water resources. In many areas of the United States, river water is used by communities to supply drinking water (after appropriate treatment). Growing concerns by these communities and by related agencies are the presence of agricultural chemicals in the river water, potential health risks, treatment costs and other considerations.

The city of Ft. Wayne, Indiana obtains its drinking water supply from the St. Joseph River, which is a tributary of the Maumee River. The entire St. Joseph River watershed is 694,400 acres (2809 km<sup>2</sup>) in size, and extends across northeastern Indiana, southeastern Michigan, and northwestern Ohio (Figure 1). The Ft. Wayne water treatment plant pumps 34 million gallons (129 million liters) of water daily from the river for treatment and use by approximately 200,000 people (SJRWI, 2003a).

From May to August 1995, tap water samples from Ft. Wayne were tested every three days for two common herbicides (atrazine and cyanazine) by a network of environmental groups (Environmental Working Group – EWG). Results for the 14 samples tested were all positive for atrazine, with an average concentration of 3.7 ppb, and a peak concentration of 10.0 ppb, while cyanazine was detected 71% of the time with an average concentration of 1.4 ppb and a peak concentration of 4.8 ppb (Cohen et al., 2003). Since that time, the water treatment plant in Ft. Wayne has purchased water testing equipment that allows the detection of the presence of herbicides in the intake water within a few hours. Operators at the plant can then add more powdered activated carbon to the treatment process to reduce the levels of these chemicals before they reach consumers (City of Ft. Wayne, 2003).

Since the study by the EWG, the Ft. Wayne water treatment facility in cooperation with the St. Joseph River Watershed Initiative has been monitoring the quality of the water at about 20 sites within the St. Joseph watershed for eight months out of the year with weekly grab samples. From 1996 to 1998, their results showed average atrazine concentrations at all the sites ranged from 1.2 to 2.7 ppb, and peak atrazine concentrations ranged from 6.7 to 17.0 ppb; average cyanazine concentration ranged from 0.12 to 0.82 ppb, and peak cyanazine concentration ranged from 1.4 to 5.6 ppb (SJRWI, 2003b).

The current EPA standard for level of atrazine in drinking water is 3.0 ppb on a rolling average annual basis (USEPA, 2002). So while the concentrations of some of the measured grab samples from both tap water and stream sites exceeded 3.0 ppb for atrazine, on a rolling average annual basis the average concentration values would most probably be much lower than the standard. For the stream grab sampling from 1996 to 1998 the average concentrations for atrazine were below the EPA standards. (There is no USEPA standard for cyanazine in drinking water.)

## ***Source Water Protection Initiative***

Local, state, and national stakeholders, however, are still concerned about the presence of even low levels of agricultural herbicides in surface drinking water supplies. A coalition of groups, including the America's Clean Water Foundation and CropLife America has provided national support and direction to local efforts to implement voluntary Best Management Practices (BMP) in watersheds to protect source water. Through these groups' and others' efforts, beginning in 2002 the United States Congress provided new funding to the USDA-Agricultural Research Service to conduct research on watersheds in Ohio and Indiana to examine the transport and fate of agricultural chemicals in these source water supplies, and the impacts of BMP implementation. This work is generally known as the Source Water Protection Initiative (SWPI).

In Ohio, the efforts are focused in the Upper Big Walnut Creek Watershed, located north of Columbus in the counties of Delaware, Morrow, Licking, Knox, and Franklin. Draining over 120,000 acres (485 km<sup>2</sup>), water from this basin fills a reservoir that supplies more than 500,000 people with 72 million gallons (272 million liters) of water daily. In Indiana, efforts are in the already described St. Joseph River Watershed.



**Figure 1.** The St. Joseph River watershed, extending through northeastern Indiana, southeastern Michigan, and northwestern Ohio.

The St. Joseph watershed is largely agricultural (79%), with major crops being corn and soybeans, and minor crops of winter wheat, oats, alfalfa, and pasture. Some livestock producers are present (swine, cattle, poultry, dairy), and there are a few very large operations. Ten percent of the watershed is woodlands and wetlands, while urban areas, farmsteads and other land uses comprise the remaining 11% (SJRWI, 2003a).

The stream in the St. Joseph Watershed that is the largest tributary to the St. Joseph River is Cedar Creek. Cedar Creek drains about 175,000 acres (707 km<sup>2</sup>) in the Indiana counties of DeKalb, Allen, and Noble.

### **Watershed Studies in Tributaries of Cedar Creek**

The USDA-ARS National Soil Erosion Research Laboratory (NSERL) in West Lafayette, Indiana is leading the water quality monitoring, modeling, BMP research and assessment program for the Source

Water Protection Initiative in the St. Joseph River Watershed. Initial efforts in 2002 and 2003 have been in establishment of monitoring stations on pairs of representative watersheds that are tributaries of Cedar Creek. Future work is to monitor and report the impacts of BMP implementation on one set of watersheds, compared to the other (untreated with BMP) control watersheds.

Initial goals were to locate two large watersheds that flowed directly to Cedar Creek that were primarily agricultural and were about of equal size. Then within each of these large watersheds, the plan was to select nested subwatersheds between 500 to 1000 acres (200 to 400 ha), as well as a smaller set of subwatersheds between 5 and 50 acres (2 to 20 ha) in size.

### ***Watershed studies in 2002***

In 2002, two watersheds were selected by the Indiana SWPI cooperators: the Matson Ditch and the Walter-Smith Ditch, both of which discharge to Cedar Creek a few miles southeast of the village of Waterloo (Figure 1). Both of these sites had been included in the previously mentioned grab sample monitoring project, so there was some background information on water quality. Initially according to the local agencies (DeKalb and Allen Counties NRCS, SWCD and SJRWI), each of these watersheds was about 8,000 acres (3,200 ha) in size, with outlets on a single county road only 1.5 miles (2.4 km) apart.

However, upon further evaluation of these two sites with automated watershed delineation software from the Purdue University Department of Agricultural & Biological Engineering (HYMAPS Watershed Delineation Map Interface – <http://pasture.ecn.purdue.edu/~watergen/hymaps>), it became clear that the initial two watersheds were not very similar in size. The Matson Ditch actually drains about 10,600 acres (4300 ha), while the Walter-Smith Ditch only drains about 3,500 acres (1400 ha). At this point, a decision was made to keep the original Matson Ditch very large basin because of the historical monitoring data there, but to select a smaller watershed within in to be used in comparisons with the Walter-Smith Ditch.

The entire Matson Ditch watershed is to be the focus of concentrated efforts to implement BMPs. Initially these will be based upon the CORE 4 conservation practices (CTIC, 2003); however, parts of the research efforts may be in development and testing of new BMPs specifically targeted towards control of agricultural chemicals in surface runoff and tile drainage waters. Water flow, nutrient and pesticide data were collected in 2002 from five watersheds: original Matson (BMP-XL), large Matson (BMP-L), medium Matson (BMP-M), large Walter-Smith (Control-L), medium Walter-Smith (Control-M). Project personnel were unable to locate suitable small watersheds nested within the medium watersheds in 2002.

At the five ditch sites in 2002, automated samplers were installed in April and May, and all were operational by June 1. Weather conditions in spring 2002 were wet and delayed crop plantings and applications of herbicides. Thus, the samplers were operational prior to any runoff occurring from fields sprayed with agricultural chemicals at planting.

### ***Watershed studies in 2003***

SWPI project personnel were informed by the DeKalb County Surveyor's office in early 2003 that the majority of the Walter-Smith Ditch would be cleaned (ditch bottom scooped out) during 2003. Additional large and medium control watersheds were located in spring 2003 on the David-Link Ditch (also known as Swartz Ditch) that drains about 3,400 acres (1,380 ha) south and east of the village of Waterloo (Figure 1), in order to have a control watershed without ditch sediment disturbances.

The same BMP-XL, BMP-L, Control-L and Control-M watersheds used in 2002 have been continued in 2003. The BMP-M watershed in 2002 had basically no runoff, because of a previously unknown tile line upstream of the sampling location cutting off the majority of the flow. Because of this problem, a new BMP-M watershed was located in the upper reach of the Matson Ditch watershed for 2003. The new

second control large and medium watersheds on the David-Link Ditch have also been instrumented in 2003 and have been collecting runoff samples.

Two small watersheds have also been identified, and are being instrumented during the spring and summer of 2003. These are both about 6 acres (2.4 ha) in size, and are located at a site within the Matson Ditch watershed, very close to the project weather station. Drop-box weirs will be used at these small watersheds to provide accurate storm event flow discharge measurements.

**Table 1.** Indiana 2003 SWPI instrumented watersheds and characteristics.

<b>ID</b>	<b>Description &amp; Location</b>	<b>Area (acres)<sup>1</sup></b>	<b>Major Soils<sup>2</sup></b>	<b>Land Use/Cropping<sup>1</sup></b>
BMP-XL	Matson Ditch on CR 39 -very large watershed near Cedar Creek, has historic data, to have BMPs applied beginning in 2003	10634	Blount silt loam, Pewamo silty clay, Glynwood loam, Rawson sandy loam, Rensselaer loam, Sebewa sandy loam	78% Agriculture 14% Grass/Pasture 6% Forest
BMP-L	Matson Ditch on CR 49 – large watershed nested within BMP-XL	4780	Blount silt loam, Pewamo silty clay, Glynwood loam, Rawson sandy loam, Morley silty clay loam	77% Agriculture 16% Grass/Pasture 6% Forest
BMP-M	Matson Ditch North of CR 10 – medium watershed within BMP-L	736	Rawson sandy loam, Pewamo silty clay, Morley silty clay loam, Blount silt loam	79% Agriculture 15% Grass/Pasture 4% Forest
BMP-S	North of 427 near weather station – small watershed within BMP-XL	5.5	Pewamo silty clay, Glynwood loam, Morley silty clay loam	100% Agriculture
CONT-L	Walter-Smith Ditch on CR 39 – large watershed to be used as control #1	3501	Blount silt loam, Pewamo silty clay, Glynwood loam, Sebewa sandy loam, Rensselaer loam	83% Agriculture 12% Grass/Pasture 3% Forest
CONT-M	Walter-Smith Ditch on CR 26 – medium control watershed within CONT-L	768	Blount silt loam, Pewamo silty clay, Glynwood loam	85% Agriculture 8% Grass/Pasture 6% Forest
CONT-S	South of 427, east of weather station site – small wshed. to serve as control near BMP-S	6.7	Glynwood loam, Blount silt loam	100% Agriculture
CONT2-L	David-Link (Swartz) Ditch on CR 37 – large watershed to be used as control #2	3411	Blount silt loam, Pewamo silty clay, Glynwood loam, Morley silty clay loam	73% Agriculture 17% Grass/Pasture 5% Forest
CONT2-M	David-Link (Swartz) Ditch, East of CR 23 – medium control watershed within CONT2-L	921	Glynwood loam, Blount silt loam, Pewamo silty clay	83% Agriculture 10% Grass/Pasture 4% Forest

<sup>1</sup> All areas except two small watersheds obtained from HYMAPS Watershed Delineation Map Interface.

<sup>2</sup> Soil information obtained from DeKalb County Soil Survey (USDA-SCS, 1982).

### ***Monitoring Sites Sampling and Chemical Analyses***

At each of the monitoring sites, an automated sampler (ISCO 6712 Portable Sampler\*, ISCO, Boulder, CO) is used to collect composite samples during base flow and event samples during rising stage storm runoff occurrences.

\* Use of trade names does not constitute an endorsement by USDA-ARS.

Teflon tubing and 350 ml glass bottles are used, and the runoff water samples are kept at approximately 40° F (4° C) until transport from the ISCO samplers. In 2002, samples were taken each week and after every storm event directly to a Ft. Wayne analytical laboratory (Great Lakes Analytical Laboratory) for immediate analysis.

In 2002 for base flows, a sample volume of 50 ml was collected every 4 h, producing a full single bottle every 24 hours. The analyses conducted by the Ft. Wayne lab required 1000 ml of sample, so four bottles (every 4 days) were combined. For runoff events in 2002, the samplers were activated when water level exceeded a set stage, and 300 ml was collected every hour for a total of 20 hours. Again because of the analytical laboratory requirements, four bottles (every 4 hours) were combined.

Great Lakes Analytical Laboratories in Ft. Wayne, IN determined atrazine, simazine, metolachlor, alachlor and acetochlor concentrations in the water samples in 2002. They used USEPA Method #525.2 Modified NPD, a solid-liquid sample extraction followed by analysis with a gas chromatograph spectrometer system. The calculated method detection limit was greater than or equal to 0.25 µg/L for analytes on all analysis dates.

Water sampling procedures in 2003 have changed somewhat because of experience gained in 2002 and also because of new analytical capabilities at the NSERL to determine pesticide concentrations with much smaller sample volumes. For base flow, 50 ml of sample is collected every 4 hours, giving 1 bottle every day with no compositing among days. For runoff events, sampling is initiated based upon a set rate of change in water stage (normally 1.2 inches (3.0 cm) in 2 hours), and 100 ml is collected every 30 minutes (3 samples collected into 1 bottle every 90 minutes) for a total of 30 hours (20 bottles total).

In 2003, the glass sample bottles are being transported to a field lab workspace where subsamples are extracted then frozen for future nutrient and pesticide determinations. Subsamples for total nutrient (N and P) analysis are placed in 60 ml plastic bottles and acidified with sulfuric acid, then the bottles are capped and frozen at 0° F (-18° C). For soluble nutrients, 50 ml subsamples are extracted with a syringe filter (0.45 micron nitrocellulose membrane) then placed in 60 ml plastic bottles, acidified with sulfuric acid, capped, and then frozen. For soluble pesticide analyses, a 45 - 60 ml subsample is poured into 120 ml amber glass bottles, and the bottles are capped and frozen. All frozen subsamples are transported from the field laboratory to the NSERL for subsequent analyses. When time comes for analysis, the frozen samples are thawed in a refrigerator at 40° F (4° C).

Nutrients (N and P) are determined with flow-injection-analysis colorimetry (Lachat Quik Chem Series 8000, Lachat\*, Milwaukee, WI). Inorganic soluble reactive phosphate-P, nitrate-N, and ammonium-N are measured on filtered water samples. Unfiltered water samples are subjected to a mercuric sulfate digestion to solubilize all forms of nitrogen and phosphorus, for subsequent determination of total Kjeldahl Nitrogen and total Phosphorus.

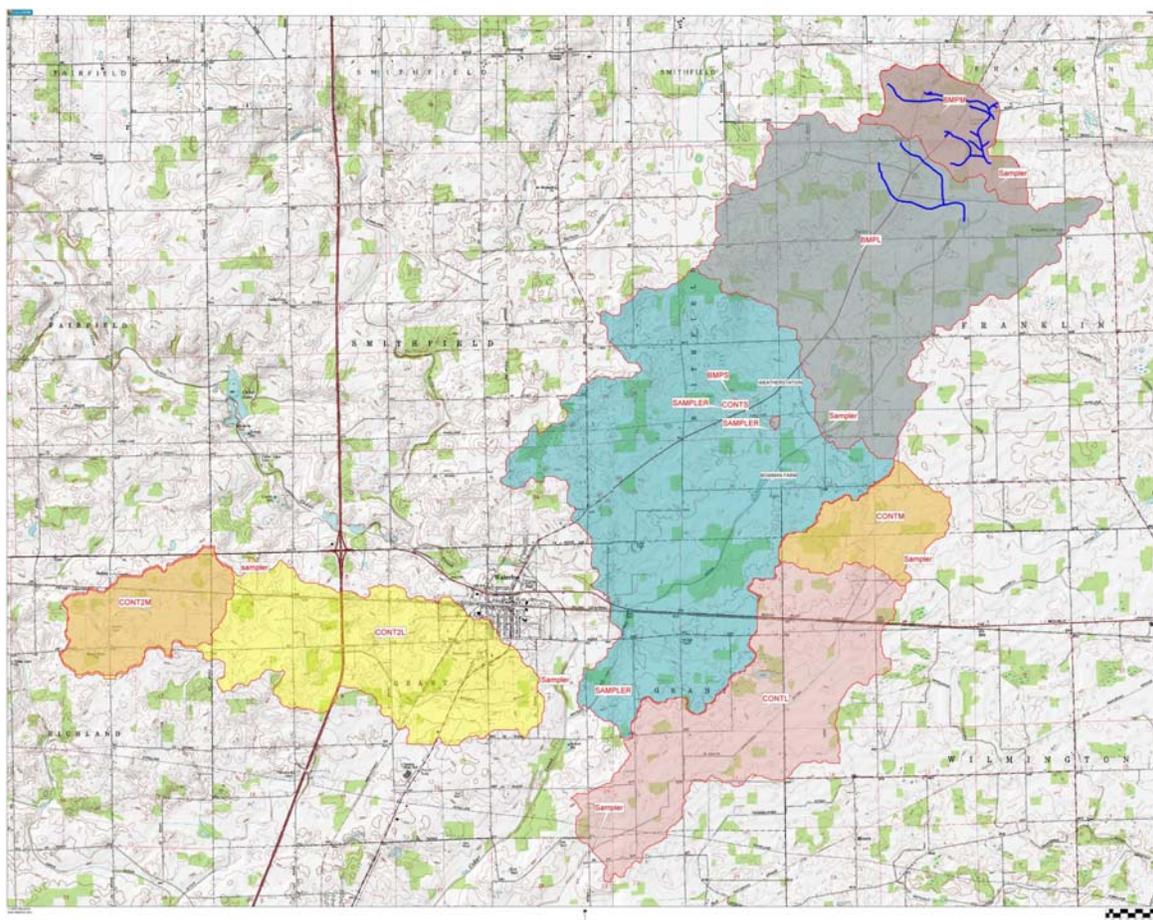
In 2003, herbicide analyses are being conducted at the NSERL using a solid-phase microextraction (SPME) method (Lord and Pawliszyn, 2000) followed by concentration determination with a gas chromatograph mass spectrometer system. Method development process has investigated extraction, chromatographic and mass-spectrometer parameters that will result in the lowest method detection limit. Samples are prepared by saturating with NaCl. Presently, the method outlined in Table 2 reflects current iteration method specifications, and unreplicated analysis indicates that the measurable limit of detection is at or below 1.0 ug/L for all analytes.

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\* Use of trade names does not constitute an endorsement by USDA-ARS.

**Table 2.** NSERL Herbicide Analysis System

Extraction		Chromatography		Spectrometry	
Fiber	100 $\mu$ m PDMS*	Desorption Temp ( $^{\circ}$ C)	270	Ion Trap Temp ( $^{\circ}$ C)	200
Adsorption Temp. ( $^{\circ}$ C)	40	Desorption Time (min)	1	Scan Mode	Electron Ionization
Adsorption Time (min)	30	Oven Temp. ( $^{\circ}$ C)	a	Ion Prep	SIS (Triazines)
Agitation Speed (rpm)	500	Carrier Gas	He		None (chlor)
		Carrier Gas flowrate (ml/min)	1		
*polydimethyl siloxane					
a = 50 $^{\circ}$ C for initial minute; 15 $^{\circ}$ C/min to 150 $^{\circ}$ C					



**Figure 2.** Map of all watersheds near town of Waterloo in DeKalb County, Indiana. (Map from DeLorme\* mapping software)

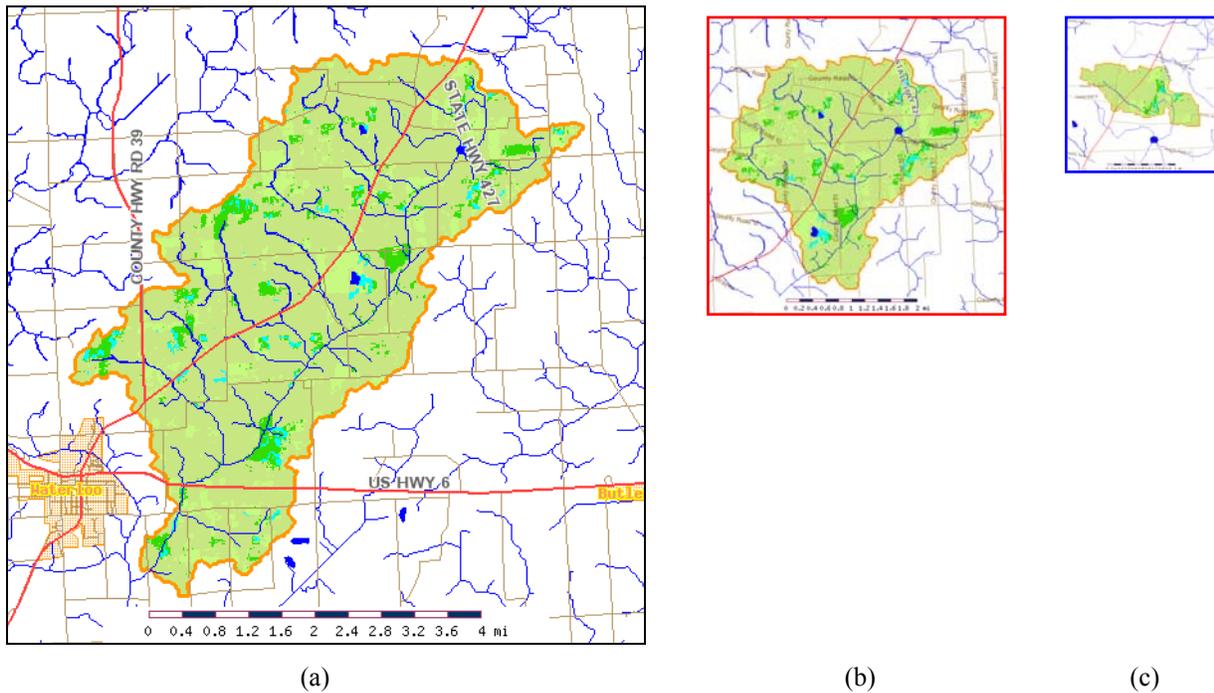
\* Use of trade name does not constitute an endorsement by USDA-ARS.

## Watershed Descriptions

Three sets of nested watersheds are being used in this study. One set of watersheds will be used to examine the impact of implementing Best Management Practices (BMPs) to reduce agricultural chemical losses, and the other two will be used as controls.

### *BMP Watersheds*

The largest watershed currently under study drains approximately 10,600 acres (4289 ha) just to the east of Waterloo, Indiana in DeKalb County (Figure 3). The sampling site is located on the Matson Ditch on DeKalb County Road 37, less than a quarter mile from where the ditch flows into Cedar Creek. A major reason for the selection of this location for monitoring is that grab sample monitoring had been conducted for several years previously here.



**Figure 3.** Extra large BMP watershed (a) near Waterloo, Indiana; stream sampler is located on Matson Ditch at southwestern edge of watershed. Large BMP (b) is in northeastern part of XL watershed. Medium (c) is on northern edge of larger BMP watersheds. (Maps from Purdue University HYMAPS watershed delineation map interface.)

The large BMP watershed is 4780 acres (1934 ha) in the upper reaches of the XL shed, while the medium BMP watershed is 736 acres (298 ha) in size, and is located at the extreme northern edge of the XL. A typical monitoring station for all of the ditch sites of all watersheds (control and BMP) is shown in Figure 4. The stations consist of a wooden platform and enclosure that supports and protects the sampler equipment. A solar panel is used to provide electricity to recharge deep cycle 12-V marine batteries that power the samplers. Plastic tubes that have been placed from the platform to below the water surface contain the Teflon-lined water sampling tubes and depth sensing pressure transducer wires. The ends of the tubes are firmly secured within the stream to steel fenceposts.



(a)



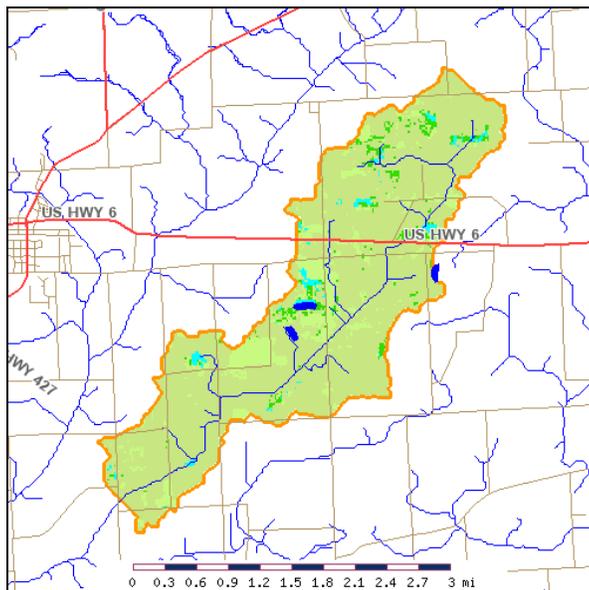
(b)

**Figure 4.** Monitoring site with water extraction tubes in ditch (a) and monitoring station on ditch bank containing sampler and solar panel (b).

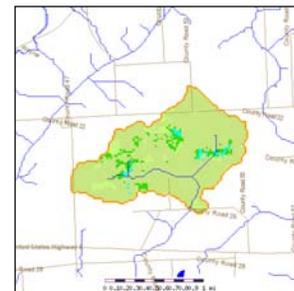
***Control #1 Watersheds***

The initial large control watershed is 3500 acres (1416 ha) in size and is located on the Walter-Smith Ditch, with the automated sampling site off of DeKalb County Road 37. The medium control #1 watershed is about 770 acres (312 ha), and is located at the very northern edge of the large watershed (Figure 5).

In early 2003, the SWPI project staff was informed that the Walter-Smith Ditch was scheduled for maintenance in 2003, which is to include removal of deposited sediment from the bottom of the channel to allow free drainage from some blocked tile. Concern about the impacts of this planned ditch cleaning on channel characteristics, flow discharge and sediment, nutrient and pesticide transport dynamics led the project to locate an additional large control watershed site to also be used in 2003 and beyond. The original large (#1) control watershed will continue to be monitored, and may provide valuable information on the effects of ditch maintenance on contaminant transport.



(a)

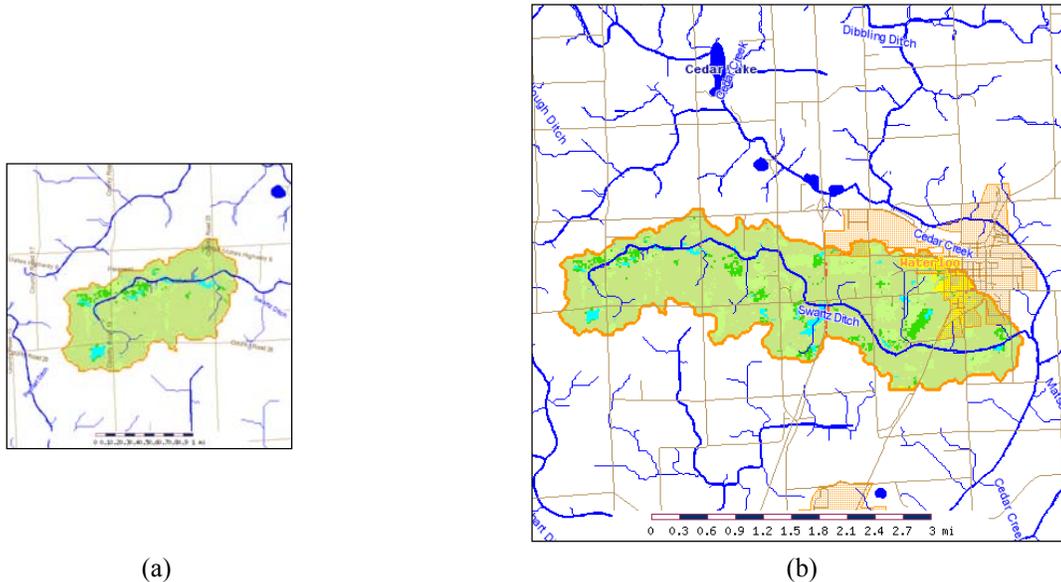


(b)

**Figure 5.** Large (a) and Medium (b) Control #1 watersheds east of Waterloo, Indiana. (Maps from Purdue University HYMAPS watershed delineation map interface.)

### ***Control #2 Watersheds***

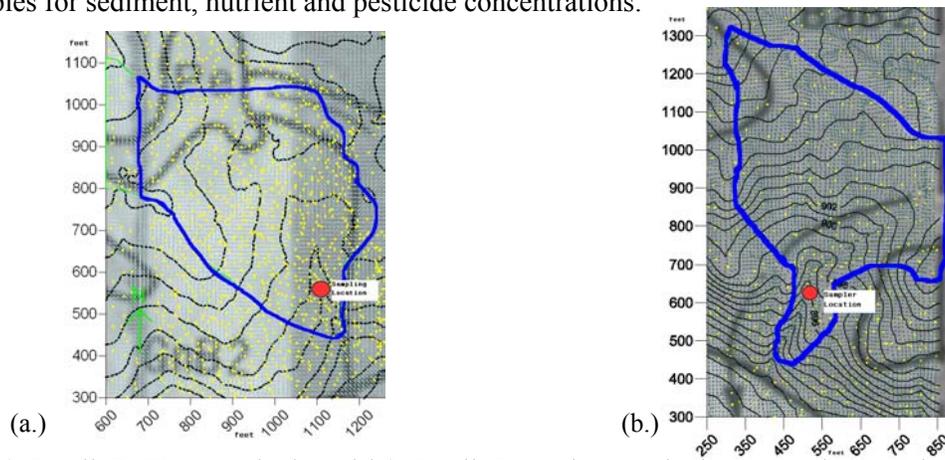
The large control #2 watershed is 3411 acres (1380 ha) in size and is located on a drainage channel locally known as the David-Link Ditch (also known as the Swartz Ditch), with the sampling site on DeKalb County Road 39. The medium control #2 watershed is about 920 acres (372 ha), and located on the western edge of the large watershed (Figure 6).



**Figure 6.** Medium (a) and Large (b) #2 Control watersheds southwest of Waterloo, Indiana. Stream samplers are located on the eastern edge of each watershed. (Maps from Purdue University HYMAPS watershed delineation map interface.)

### ***Small BMP and Control Watersheds***

The sites for the small field watersheds have been selected and are located just off of S.R. 49 near the project automated weather station near the center of the BMP-XL watershed. The target BMP small watershed is 5.5 acres (2.2 ha) in size on Pewamo, Glynwood and Morley soils. The small control watershed is 6.7 acres (2.7 ha) on Blount and Glynwood soils. At each of the sites (Figure 7), a 0.8 ft (0.24 m) deep drop-box weir will be installed for flow measurements and a turbulent point to collect runoff samples for sediment, nutrient and pesticide concentrations.



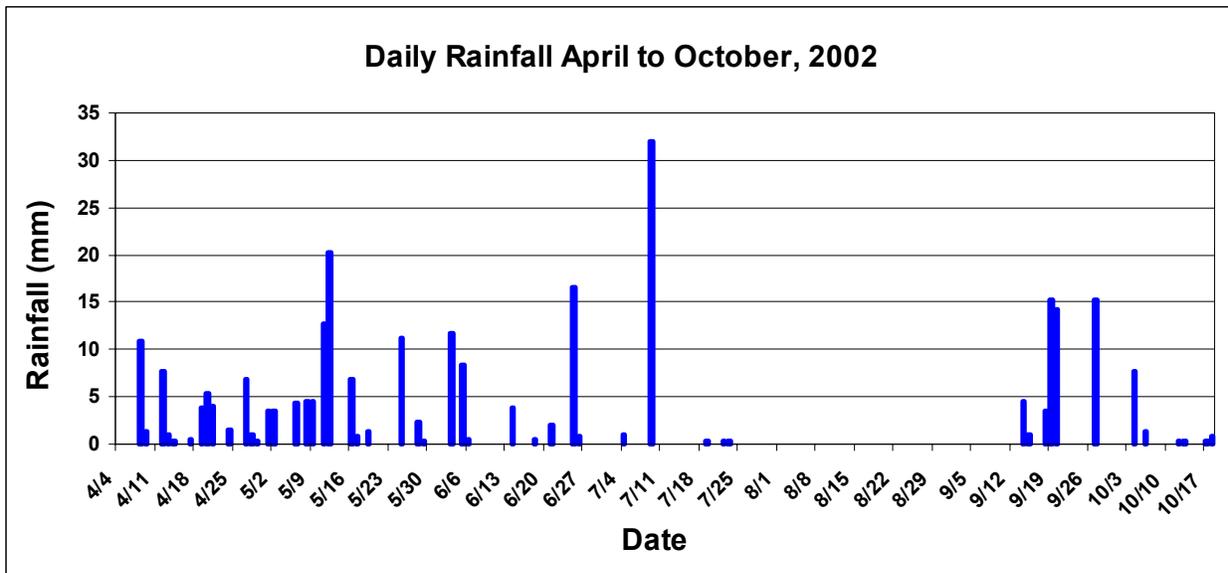
**Figure 7.** a.) Small BMP watershed, and b.) Small Control watershed. Located approximately 2 miles northeast of Waterloo, Indiana.

## Initial Results

Herbicide and nutrient analyses for 2002 are complete. Precipitation and stream flow stage are also available. However, rating curves for each of the stream sites have not yet been completed, so flow discharge rates, nutrient loadings, and herbicide loadings to the stream cannot be computed. Some initial results from 2002 will be presented here.

### *Precipitation*

Daily rainfall measured at the project weather station from April through October 2002 is shown in Figure 8. The weather station equipment failed during August and early September, thus the lack of some data for those times. Due to extremely hot and dry weather during August and September, there were no event runoff samples associated with those times, and base flow sampling at some of the sites could not even be continued because of very low stream levels.

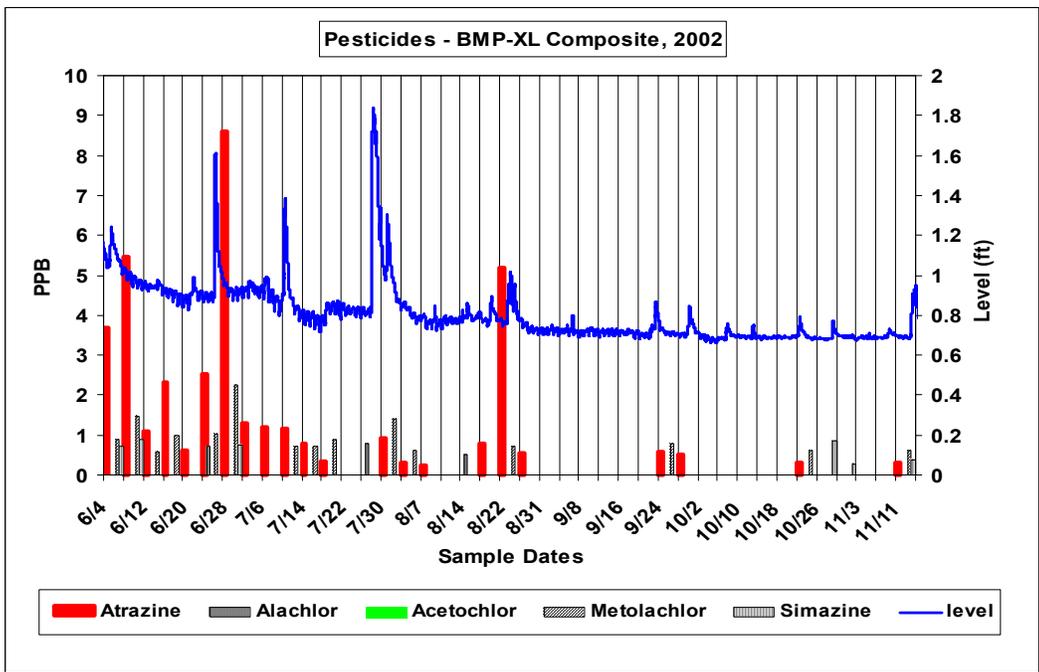


**Figure 8.** Measured daily precipitation from a weather station located in the center of the BMP-XL watershed.

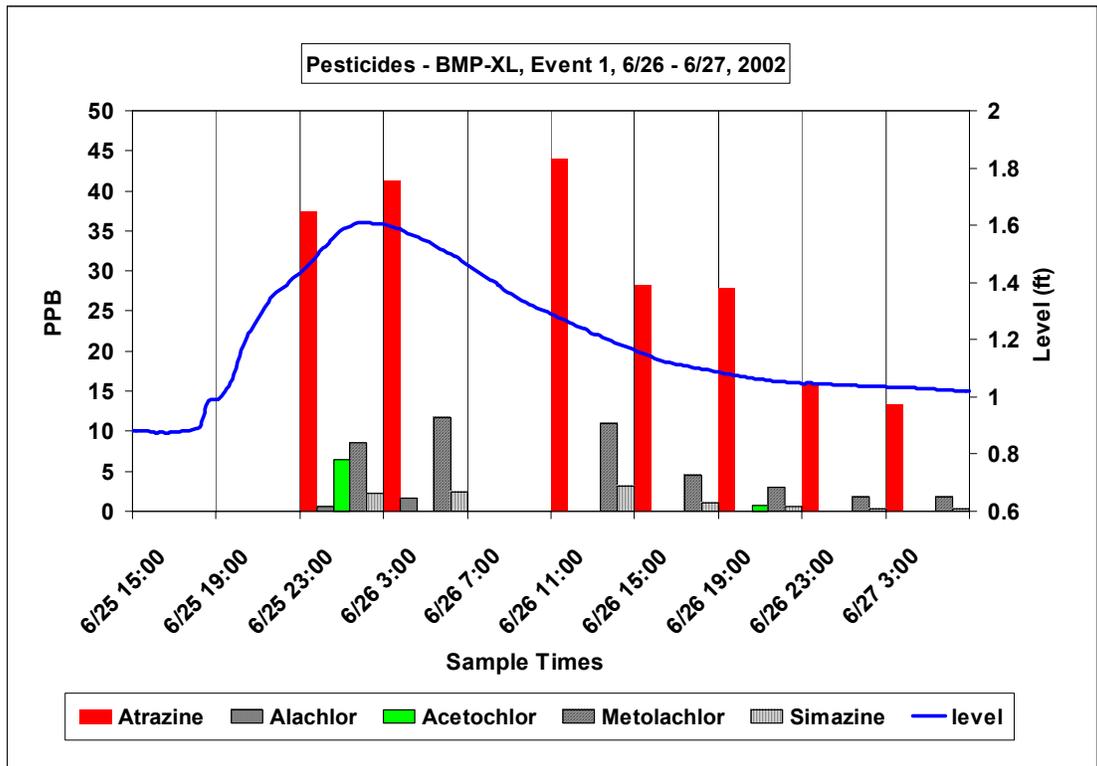
### *Pollutant Concentrations*

As previously described, the water in the glass sampler bottles had to be combined to obtain enough volume for the analytical lab procedures in 2002. Figure 9 shows the herbicide concentrations for the composited (4-day) base flow samples for the Matson-XL watershed from June through November. Results for atrazine, alachlor, acetochlor, metalachlor and simazine are displayed, as well as the stream flow stage.

Highest concentrations from the base flow samples were for atrazine, with a 4-day composite high value of about 8.5 ppb around June 28. The next most prevalent herbicide present was metolachlor, with composite high value of about 2 ppb.



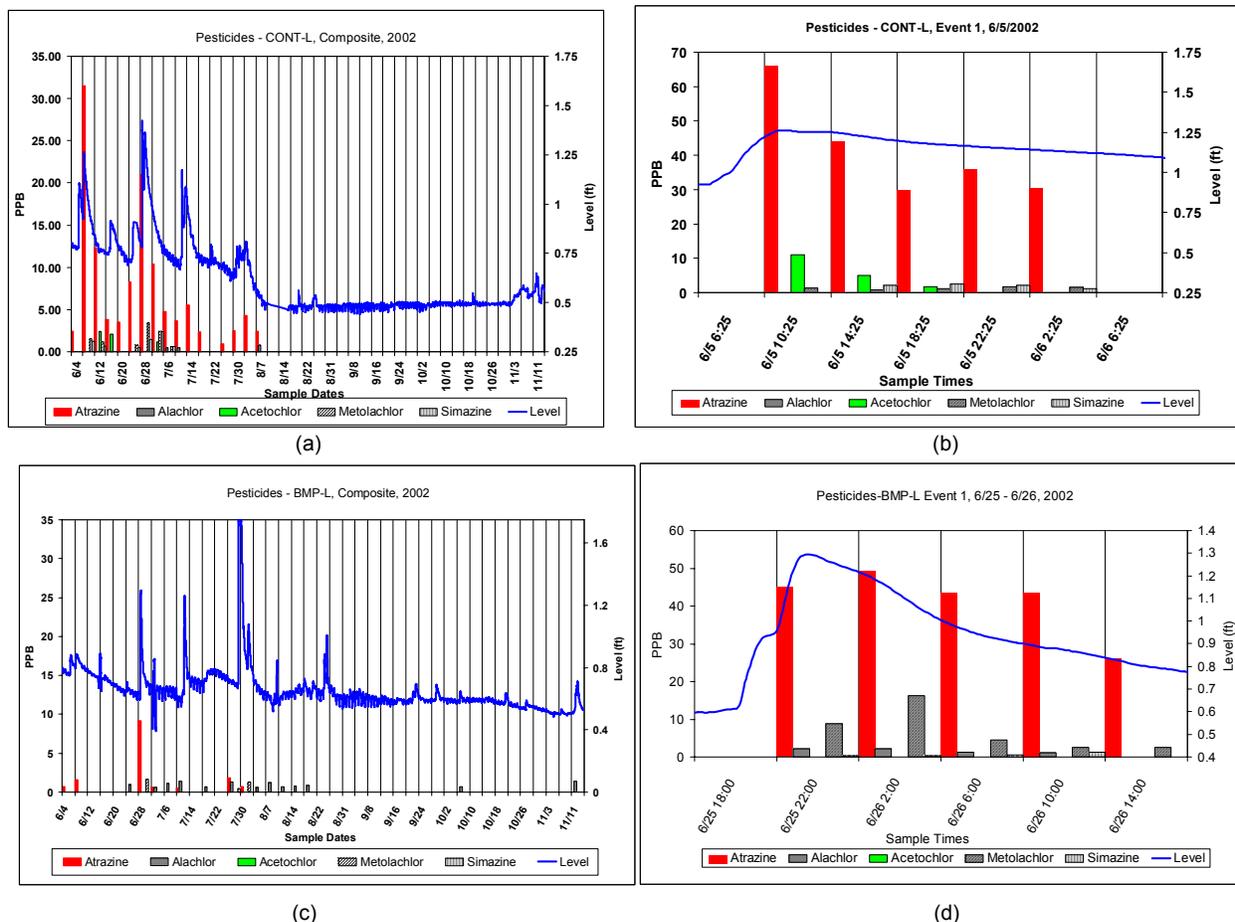
**Figure 9.** Measured water stage and 4-day composite herbicide concentrations from base flow sampling of the XL Matson watershed in 2002.



**Figure 10.** Measured water stage and 4-hour composite herbicide concentrations from storm runoff event flow sampling for the event of June 26-27 of the XL Matson watershed in 2002.

The storm event sampling provided more information on herbicide concentrations associated with rainfall and runoff events. There were 4 runoff events during 2002 that triggered the event sampling on the XL Matson watershed: June 26-27, July 9-10, July 26-27, and July 29. The highest measured concentrations of herbicides were observed in the June 26-27 event (Figure 10). Atrazine concentration (4-hour composite) peaked at about 44 ppb, metolachlor concentration peaked at about 12 ppb, and acetochlor concentration peaked at about 6 ppb. In the second storm event for the XL watershed, measured atrazine concentrations had decreased to less than 8 ppb, and to less than 3 ppb in the third and fourth events.

Results for the baseflow and the initial event sampling for the Control-L and Matson L (BMP-L) watersheds are presented in Figure 11.



**Figure 11.** Measured stage and composite herbicide concentrations from base flow for CONT-L (a) and BMP-L (c), and selected event results for the CONT-L (b) and BMP-L (d) watersheds in 2002.

Base flow measurements for the large control watershed (Figure 11a) show a definite pattern of higher herbicide concentrations earlier in the season, with a high four day composite atrazine concentration of about 32 ppb. All other measured herbicides had concentration levels below 4 ppb, with hardly a trace of them apparent after early July. By contrast, the large BMP watershed base flow measurements did not display as high of stream flow stages in early June, nor as frequent or as high herbicide concentrations – the highest 4-day composite atrazine concentration was only about 9 ppb. The reasons for these differences between the two large watersheds are not known at this time. Some possibilities may be different precipitation patterns and depths, and different amounts of herbicides applied in the two

watersheds. The percentage of area in agriculture is slightly larger for the large control watershed, but the total watershed area is considerably less than the large BMP watershed (Table 1).

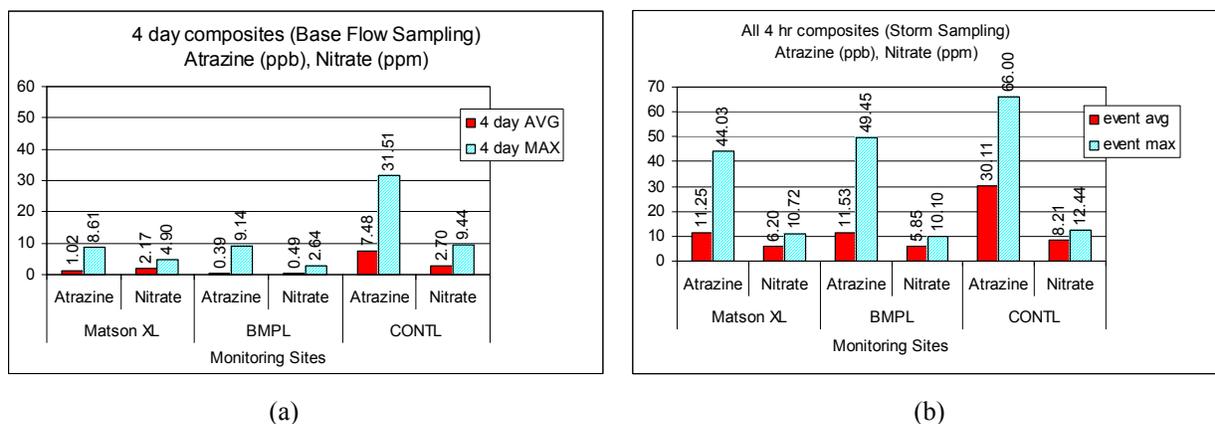
With the runoff event sampling, the large control watershed had only 2 triggered measured events (June 5-6 and June 25-26). The first composite 4-hr sample from the June 5-6 storm event had the highest measured atrazine concentration of 66 ppb (Figure 11b). The other four composite samples for that event had atrazine concentrations ranging from 30 to 44 ppb. Peak acetochlor concentration was 11 ppb, while all other herbicides were below 3 ppb. In the second event on June 25-26, atrazine concentrations for five 4-hr composite samples ranged from 7 to 33 ppb. Acetochlor peak concentration measured in the second storm event was 18 ppb. Only atrazine and acetochlor were detected in the second event.

The large BMP watershed had 4 measured events (June 26-27, July 9-10, July 26-27, and July 28-29). Atrazine concentrations were highest in the first event, with the peak 4-hr composite sample at 49 ppb (Figure 11d). Metolachlor concentration peaked in the first storm event at 16 ppb. Levels of all other herbicides were below 3 ppb in this initial storm (acetochlor was not detected in any event or base flow sampling for this watershed). In the subsequent three storm events, atrazine concentrations were much lower – below 4 ppb in the second storm and below 2.3 ppb in the third and fourth storm events.

The storm event data reveal that the two large watersheds do have similar responses in terms of atrazine concentrations measured in the initial storm events after herbicide application in the watersheds. The differences between the two watersheds may be due to amounts of atrazine applied in the individual basins, types of existing practices in the watersheds, and variations in rainfall patterns falling on the watersheds. The large control watershed had its initial runoff event on June 4, while on this date a significant triggering event did not occur on the large BMP watershed.

At the medium watersheds, atrazine concentrations ranged from 10 to 42 ppb for the Control, and from 0 to 20 for the BMP site. Only a very few samples were obtained from the original BMP-M watershed due to previously mentioned problem of flow being diverted to a tile line upstream of the sampler.

Figure 12 summarizes the results of the atrazine and nitrate-N concentrations measured for the extra large and two large watersheds monitored in 2002. The large control watershed appears to have produced higher levels of atrazine and nitrate-N concentrations than the large BMP or extra large BMP watersheds, especially in the base flow sampling (Figure 12a). In the event sampling (Figure 12b), the nitrate-N concentrations were fairly similar between all three watersheds, though slightly greater for the large control. Event average and peak atrazine concentrations were much greater for the large control watershed than for the BMP-L or BMP-XL watersheds.



**Figure 12.** Base flow sampling (a) and storm event sampling summary for atrazine and nitrate-N concentrations for the Matson XL, BMP-L and Control-L watersheds in 2002.

The reasons for the observed differences between the watersheds in the 2002 data are not known at this time. We are in the process of obtaining detailed information on land use and herbicide applications, which should allow better assessment and modeling of the runoff, sediment, nutrient and pesticide transport processes.

## Summary and Conclusions

Runoff, herbicides and nutrients are being actively measured from watersheds within the St. Joseph River Basin in northeastern Indiana, which is the source of drinking water for the city of Ft. Wayne, Indiana. In 2002, five watersheds ranging in size from 480 acres to 10600 acres were monitored from June through October. Both base flow and storm event sampling were conducted.

Initial results from 2002 showed that the most prevalent herbicide of those measured was atrazine, and the highest concentrations of atrazine were observed during the first large storm runoff events immediately after application. The highest observed atrazine concentration was 66 ppb during a storm runoff event. The large watershed that is slated to be a control (for BMP implementation) had higher observed concentrations of both nitrate-N and atrazine than the other monitored watersheds. Further research is ongoing to continue monitoring of these watersheds, as well as determine land management and agricultural chemical use to assist in determining reasons for differences between the watersheds.

In 2003, a total of 9 watersheds ranging in size from 5.5 to 10600 acres (2.2 to 4289 ha) are being monitored. This project will continue for at least several more years to further monitor pesticide and nutrient losses and the impacts of land management changes on water quality.

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