Surface Water Sampling Project

Impact of pesticides on streams in smaller Wisconsin watersheds

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Wisconsin Department of Agriculture, Trade and Consumer Protection

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DATCP Surface Water Sampling Project

Project Summary:

Between April and September 2008, The Department of Agriculture, Trade and Consumer Protection (DATCP) conducted a Surface Water Sampling project to document the impact pesticide use was having on several streams in smaller watersheds in Wisconsin. As part of this project, surface water samples were collected monthly from ten streams in Wisconsin.

The streams selected for this project included ten streams that are a part of the Department of Natural Resources' (WDNR's) "wadeable" stream sampling project. Streams were selected predominately based on a having a high percentage of agricultural land in each watershed. Samples were collected by WDNR staff, and submitted to DATCP's Bureau of Laboratory Services (BLS) for analysis of seven widely used pesticides, plus nine breakdown products, for a total of sixteen compounds.

A total of 59 surface water samples were collected as a part of this project. Of those samples, the most frequently detected compound was metolachlor ethanesulfonic acid (ESA), a breakdown product of the widely used pesticide metolachlor, which was quantified in 95% of all the samples collected. The second most commonly quantified compound was alachlor ESA, which was quantified in 56% of all samples collected, followed by metolachlor oxanilic acid (OA) in 36% of all samples and acetochlor ESA in 24% of all samples.

Other pesticides detected include acetochlor, acetochlor OA, alachlor, alachlor OA atrazine, dimethanamid, metolachlor, and simazine. These other pesticides and their breakdown products were detected only in the June or July sampling events, which is during or after the main pesticide application season.

Project Design

The goal of this project was to document what impact pesticide use was having on surface water quality in Wisconsin. Specifically, surface water samples were colleted prior to the traditional pesticide application season (April), during the main application season (May, June, July), and after the pesticide application season was over (August and September). This strategy was employed to provide an indication of how the timing of pesticide application is related to surface water quality.

A total of ten perennial surface water streams were selected for this project (Figure 1). To simplify the sampling effort, the streams selected for sampling included ten of the streams that are currently being sampled by WDNR staff on a monthly basis as a part of their Non LTT (Long Term Trend) wadeable stream monitoring project.

The ten streams sampled for this project were also selected based on the percentage of agricultural land present within the individual drainage basins (Table 1). The percentage of agricultural land within the watersheds ranged from 76.2 percent to 33.8 percent. While the percentage of row type agriculture (corn, soybeans) is not specified, the watersheds selected are generally in the southern 1/3 of Wisconsin, where row crop agriculture predominates. Consideration was also given to the size of the watershed, with the largest watershed being 289 square miles, and the smallest watershed being only 86.2 square miles.

Stream	Agric. (%)	Watershed (sq. mi.)	Watershed	DNR Region
Grand River	76.2	62.0	Upper Fox/Wolf	NER
De Nevue Creek	74.5	99.4	Upper Fox/Wolf	NER
Ahnapee River	70.6	135.6	Lake Shore	NER
Little River	58.5	210.3	Lower Fox/ Upper Green Bay	NER
Little Platte River	75.7	154.9	West	SCR
Yahara River	72.5	112.6	East	SCR
Grant River	71.0	106.1	West	SCR
Rush River	42.9	289.6	Lower Chippewa	WCR
Mukwonago River	37.4	86.2	Inland	SER
Four Mile	33.8	214.0	Central Wisconsin	WCR

Table 1. Selected Streams and Watershed Information

Samples were collected by or under the supervision of WDNR field staff from several different WDNR regions (Table 1). Water samples were collected at the same time and on the same schedule as those collected by WDNR as a part of their wadeable stream monitoring project, which was roughly one sampling event per month, during the third week of the month. The schedule was not exact due to conflicts the sampling team experienced with other program responsibilities, although with only one exception, each stream was sampled once a month approximately four weeks after the previous sample.

The goal of the WDNR's sampling protocol is to collect water samples in an unbiased fashion with respect to flow, weather, and other factors. All samples were collected in free flowing, well-mixed areas of the streams generally between the hours of 8 a.m. and 2 p.m.

Surface water samples were collected by filling the two 1-liter amber glass sampling jars from each sampling station, placing the bottles in an ice-filled shipping cooler, and shipping the samples to BLS using an overnight deliver service or having the samples hand delivered to BLS.

Surface water samples were analyzed for the pesticides and metabolites presented on Table 2.

Figure 1. Stream Sampling Locations

This analytical list includes primarily corn herbicides, including seven widely used pesticides, plus nine breakdown products (metabolites), for a total of sixteen compounds. In addition to the 16 compounds, the DATCP laboratory is capable of detecting and reporting other pesticides that may be present in the water samples not on the list (e.g. dimethanamid). Only those compounds quantified above the "Limit of Detection" will be considered in following discussions.

Analyte	Limit of Detection	Unit
Acetochlor	0.1	ug/L
Acetochlor ESA	0.1	ug/L
Acetochlor OA	0.1	ug/L
Alachlor	0.15	ug/L
Alachlor ESA	0.1	ug/L
Alachlor OA	0.1	ug/L
Atrazine	0.15	ug/L
Atrazine (diamino)	0.5	ug/L
Atrazine (de-ethyl)	0.3	ug/L
Atrazine (deisopropyl)	0.3	ug/L
Cyanazine	0.5	ug/L
Dimethanamid*	0.5	ug/L
Metolachlor ESA	0.1	ug/L
Metolachlor OA	0.1	ug/L
Metribuzin	0.5	ug/L
Simazine	0.15	ug/L

*dimethanamid was not included in the original laboratory analytical list.

Table 2. Analytical Parameters and Laboratory Limit of Detection

2008 Weather Conditions/ Agrichemical Application Timing

Before the results of the Surface Water Sampling Project are presented, it is appropriate to discuss two issues that likely impact the results of this investigation, namely pesticide application timing and weather conditions in 2008.

A majority of the herbicides are applied early in the growing season in Wisconsin, which can include applications from as early as late April, but most herbicides are applied in late May and early June, with some (rescue treatments) being applied as late as July. This does not include late season burn-down applications of glyphosphate, which generally occur in August through September. The spring of 2008 was not exceptional in that regard, with most crops being planted on time or nearly on time.

Beginning June 7th and ending on June 13th, 2008, the southern (approximately) 1/3 of Wisconsin experienced unusually high rainfall (Figure 2). Of the ten streams sampled as a part of this investigation, six were within the flooded portion of the state.

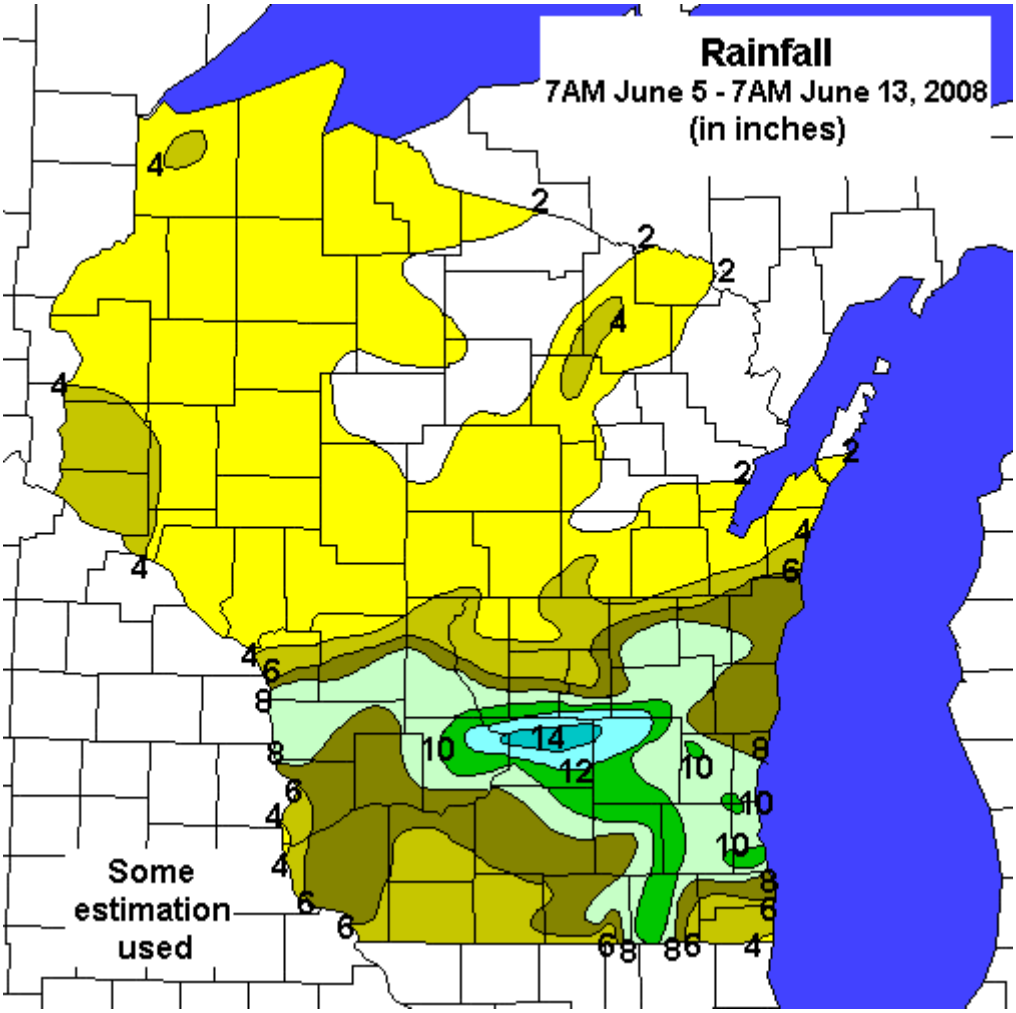

Figure 2. Rainfall in Wisconsin June 7 – June 13, 2008 (From National Weather Service)

Even though the flood of June represents a single storm event observed at most of the streams sampled, it was not the only storm event that impacted the stage of the rivers during this investigation. Rather, the 2008 growing season had many rain events in addition to the flooding event of June. Stream hydrographs, where available, show the effects of several smaller rainfall events on the surface water streams as well, although not with the significance of the June flood event.

SAMPLE RESULTS

Grand River

The sampling location for the Grand River (Figure 1) is located in southwestern Green Lake County. The Grand River flows primarily east to west, discharging into the Fox River at Buffalo Lake in Montello. The watershed of the Grand River has the highest percentage of land in agriculture of the streams sampled, with 76.2 percent of its 62.0 square miles being in agriculture. The only sampling event missed in the surface water sampling effort was in the Grand River, the result of a miscommunication between DATCP and the DNR sampler. No April 2008 sample was therefore collected.

According to the National Weather Service, the drainage basin for the Grand River received approximately 13 inches of rain during the June flood event. This is the most precipitation measured in any of the sampling streams in this project. Unfortunately, the United States Geological Survey (USGS) has no gauging station on the Grand River, so no information is available on what stage the river was at during any of the sampling events. However, it can be assumed that the Grand River was in flood stage during the June 10th sampling event, since the June flood event came between June 7th and June 13th.

A total of 10 different pesticide compounds were quantified in the Grand River during the course of this investigation (Appendix A). Of those, two (metolachlor ESA and alachlor ESA) were quantified in each of the five sampling events. Additionally, metolachlor OA was quantified in four of five sampling events. These three compounds, metolachlor ESA, alachlor ESA, and metolachlor OA, appear to be in the Grand River independent of the application season or river stage. Therefore, we consider these compounds to be in the Grand River as a result of base flow, or groundwater discharging into the Grand River. Furthermore, based on a survey of rural private drinking water wells across Wisconsin completed in 2007, metolachlor ESA and alachlor ESA were the two most commonly detected pesticide compounds in potable wells across Wisconsin (DATCP, 2008).

With the exception of metolachlor ESA, the concentration of the pesticides quantified in the Grand River are all very low, less than 0.64 ug/L. The concentration of metolachlor

ESA ranges from 0.292 ug/L during the June flood event to 1.35 ug/L in the May sampling event.

The remaining five compounds (atrazine, metolachlor, acetochlor, dimethanamid, and alachlor) were quantified in the sample collected on June 10, 2008. It is believed that these compounds entered the Grand River as overland flow from the June storm event. The concentration of these parent pesticides ranged from 0.192 ug/L (alachlor) to 1.45 ug/L (dimethanamid) and 1.44 ug/L (metolachlor).

Little Platte River

The Little Platte River is located in southwestern Grant County (Figure 1). The Little Platte River flows primarily to the southwest, discharging into the Platte River, which discharges into the Mississippi River. The watershed of the Little Platte River has the second highest percentage of land in agriculture of the streams sampled, with 75.7 percent of its 154.9 square miles being in agriculture.

According to the National Weather Service, the drainage basin for the Grand River received approximately 8 inches of rain during the June flood event. There is no USGS gauging station along the Little Platte River. However, there is a gauging station on the Platte River near Rockville, which is the adjacent drainage basin approximately five miles from the Little Platte River. A hydrograph was prepared using the data collected from the Platte River and is presented in Appendix B. The hydrograph shows that water sample collected on June 16th was collected when the area was recovering from the flood event that reached its peak on June 12th. The rest of the surface water samples were collected when the area was experiencing normal flow conditions.

A total of 7 different pesticide compounds were quantified in the Little Platte River during the course of this investigation (Appendix A). Of those, two (metolachlor ESA and alachlor ESA) were quantified in each of the six sampling events. Since these pesticide breakdown products are present in the in the Little Platte River independent of the pesticide application season, we consider these compounds to be in the Little Platte River as a result of base flow, or groundwater discharging into the Little Platte River.

The concentration of metolachlor ESA is considerably higher than the concentration of alachlor ESA, with the concentration of metolachlor ESA in the water ranging from 0.999 ug/L to 1.52 ug/L. The concentration of alachlor ESA ranges from a 0.106 ug/L during the June flood event to 0.267 ug/L in the August sampling event.

Four of the remaining five compounds (atrazine, metolachlor, metolachlor OA, acetochlor OA) were quantified in only the sample collected on June 16, 2008. Acetochlor ESA was quantified in the June and July sampling events. It is likely that these five compounds entered the Little Platte as overland flow following the June storm event. The concentration of these parent pesticides ranged from 0.119 ug/L (acetochlor OA) to 0.343 ug/L (metolachlor).

De Nevue Creek

The sampling location for De Nevue Creek (Figure 1) is located in central Fond du Lac County. De Nevue Creek flows to the north, discharging into Lake Winnebago at Fond du Lac. The watershed of De Nevue Creek has the third highest percentage of land in agriculture of the streams sampled, with 74.5 percent of its 99 square miles being in agriculture. The drainage basin of De Nevue Creek received approximately 10 inches of rain during the June flood event. Unfortunately, there is no USGS gauging station on De Nevue Creek that tracks river stage, so no information is available as to what level the river was at during any of the sampling events.

A total of four different pesticide compounds were quantified in De Nevue Creek during the course of this investigation (Appendix A). Of these, metolachlor ESA was quantified in five of the six sampling events. Since the metolachlor ESA is present in the sampling events apparently independent of the pesticide application season, it is considered to be a part of base flow, or groundwater discharge in De Nevue Creek.

Three other pesticide compounds quantified, including metolachlor, metolachlor OA, and atrazine, are present in only the June sampling event (metolachlor) or the June and July sampling event (metolachlor OA and atrazine). The presence of these compounds is likely related to the timing of the pesticide application.

Yahara River

The sampling location for the Yahara River (Figure 1) is located in on the north side of Madison in Dane County. The Yahara River is sampled at the Highway 113 Bridge, immediately below Cherokee Lake. The watershed of the Yahara River is approximately 73 percent in agriculture, with a drainage basin of 112 square miles. The Yahara River watershed received between 8 and 10 inches of rain during the June storm event. There is a USGS gauging station on the Yahara River in nearby Windsor, Wisconsin, approximately five miles upstream of where the samples were collected for this project.

A hydrograph was prepared using the data collected at the Windsor gauging station and is presented in Appendix B. The hydrograph shows that the sample collected on June 17th was collected when the river was recovering from the flood event that reached its peak on June 9th. The hydrograph shows that the rest of the surface water samples collected from the Yahara River were collected when the area was experiencing normal flow conditions

A total of nine different pesticide compounds were quantified in the Yahara River during this investigation. Of these, four, including alachlor ESA, acetochlor ESA, metolachlor ESA, and metolachlor OA were quantified in six of six (alachlor ESA and metolachlor ESA) or five of six (acetochlor ESA and metolachlor OA) sampling events. The concentration of acetochlor ESA, metolachlor ESA, and metolachlor OA are all fairly low, with concentrations ranging from less than the detection limit (0.010 ug/L) to a high of 0.565 ug/L, 0.713 ug/L, and 0.281 ug/L for acetochlor ESA, metolachlor ESA and

metolachlor OA, respectively. However, the concentration of alachlor ESA is quite variable, with concentrations ranging from between 0.409 ug/L and 1.61 ug/L. All of these compounds are considered likely to be a part of base flow discharge into the Yahara River.

The remaining five pesticide compounds quantified in the Yahara River, including acetochlor OA, atrazine, simazine, acetochlor, and metolachlor, are present in only the June sampling event (atrazine, simazine and acetochlor) or the June and July sampling event (acetochlor OA and metolachlor). It is likely that these compounds entered the Yahara River as overland flow during and after the June storm event.

The presence of atrazine in the Yahara River is somewhat disturbing, as greater than approximately 95 percent of the Yahara River watershed upstream for the sampling location is in an atrazine prohibition area.

Little River

The sampling location for the Little River is located in eastern Oconto County (Figure 1). The Little River flows to the southwest, discharging into the Oconto River, which subsequently discharges into Green Bay at Oconto. The watershed of the Little River has 58.5 percent of its 210 square miles being in agriculture. No USGS gauging station is present along the Little River.

A total of three different pesticide compounds were quantified in the Little River during the course of this investigation (Appendix A). Of these, metolachlor ESA was quantified in all six sampling events at a concentration of up to 0.322 ug/L. The metolachlor ESA is considered to be a part of base flow, or groundwater discharge into the Little River.

The two other pesticide compounds quantified in the Little River at very low concentrations include metolachlor OA (0.15 ug/L) and atrazine (0.15 ug/L), are present in only the July sampling event. It is likely that these compounds entered the Little River as overland flow from normal precipitation during July.

Ahnapee River

The sampling location for the Ahnapee River (Figure 1) is located on the county line between Door and Kewaunee Counties in northeastern Wisconsin. The Ahnapee River flows to southeast, discharging into Lake Michigan at Algoma. The watershed of the Ahnapee River has the third highest percentage of land in agriculture of the streams sampled for this investigation, with 70.6 percent of its 135.6 square miles being in agriculture. The drainage basin of the Ahnapee River received only approximately 2 inches of rain during the June flood event. There is no USGS gauging station on the Ahnapee River, so no information is available as to what stage the river was at during any of the sampling events.

A total of four different pesticide compounds were quantified in the Ahnapee River during the course of this investigation (Appendix A). Of these, metolachlor ESA was quantified in all six sampling events, and is considered to be a part of base flow, or groundwater discharge into the Ahnapee River. The concentration of metolachlor ranges from 0.171 ug/L to 0.454 ug/L.

The three other pesticide compounds quantified, including metolachlor, metolachlor OA, and atrazine, are present only in the June sampling event (metolachlor at 0.426 ug/L) or the June and July sampling event (metolachlor OA and atrazine). It is likely that these compounds entered the Ahnapee River as overland flow from normal precipitation during June and July.

Grant River

The sampling location for the Grant River (Figure 1) is located in west central Grant County. The Grant River flows to the south, discharging into the Mississippi River near Petosi. Approximately 71 percent of the 107 square mile watershed upstream of the sampling point on the Grant River is in agriculture. According to the National Weather Service, between 6 and 8 inches of rain fell in the drainage basin of the Grant River between June 7th and June 13th.

The USGS has a gauging station on the Grant River located approximately 8 mile downstream from the surface water sampling point location. Using this data, a hydrograph was prepared and is included as Appendix B of this report. The hydrograph shows that the sample collected on June 16th was collected approximately 2 days after the main flood event along the Grant River had passed, and the flood water had mostly receded. It also shows that the July 15th sampling event took place approximately three days after the river responded to a storm even that was significantly smaller than the June event. Three of the remaining four sampling events took place when the river was a base flow conditions. No discharge data are available for the April 17, 2008 sampling event.

A total of five different pesticide compounds were quantified in the Grant River during the course of this investigation (Appendix A). Of these, alachlor ESA and metolachlor ESA were quantified in all six sampling events. The concentration of metolachlor ESA ranges from between 0.574 ug/L and 0.729 ug/L, and the concentration of alachlor ESA ranges from between 0.152 ug/L to 0.262 ug/L. Since these two compounds are present in the sampling events prior to and after the main pesticide application season, they are considered to be a part of base flow, or groundwater discharge in the Grant River.

The three other pesticide compounds quantified, including acetochlor ESA, acetochlor OA, and atrazine, are present in only the June sampling event (atrazine and acetochlor OA) or the June and July sampling event (acetochlor ESA). It is likely that these compounds entered as overland flow during the large June storm event and possibly the small July storm event. The concentration of these compounds are very low, with acetochlor ESA being quantified at a concentration of up to 0.229 ug/L, and atrazine and acetochlor OA at a concentration of 0.183 ug/L and 0.12 ug/L, respectively.

Rush River

The sampling location for the Rush River is located in south central Pierce County (Figure 1). The Rush River flows to the south, discharging into the Mississippi River at Maiden Rock. Approximately 43 percent of the 290 square mile drainage basin is in agriculture. According to the National Weather Service, the drainage basin for the Rush River received over four inches of rain during the June flood event.

The USGS has a gauging station on the Rush River that is located adjacent to the surface water sampling point location. Using the data collected by USGS, a hydrograph was prepared and is included as Appendix C of this report. The hydrograph shows that the sample collected on June 11th was collected on a day where the river was responding to a minor rainfall event, but a day prior to the main June storm event. It also shows that the April 8, 2008 sampling event was collected when the river was responding to a minor rainfall event. The other samples were collected when base flow conditions prevailed.

The Rush River is unique among the ten rivers sampled for this project because metolachlor ESA and alachlor ESA were only quantified in four of six and three of six sampling events, respectively. While still the most frequently detected compounds, it is difficult to say that they are the result of groundwater discharging into the Rush River. The concentration of these two pesticide metabolites are also uniformly very low, with the concentration of alachlor ESA never exceeding 0.136 ug/L, and the concentration of metolachlor ESA never exceeding 0.112 ug/L.

The remaining five pesticide compounds quantified in the Rush River, including acetochlor ESA, atrazine, acetochlor OA, metolachlor, and acetochlor are only present in the June sampling event, with the exception of acetochlor ESA, which is also quantified in the April sampling event. Of all these compounds, only atrazine and metolachlor were quantified at a concentration greater than 0.30 ug/L, with atrazine being quantified at a concentration of 0.877 and metolachlor at 0.591.

Mukwonago River

The sampling location for the Mukwonago River is located in south central Waukesha County immediately upstream from the Lower Phantom Lake. The Mukwonago River drainage basin is the second smallest in this sampling set (86.2 square miles) , and it also has the next to lowest percentage of land in its drainage basin in agriculture (37 percent).

The USGS has a gauging station on the Mukwonago River. Using the data provided by the USGS, a hydrograph was prepared and is included in Appendix B of this report. The hydrograph shows that the sample collected on June 11th and was collected when the Mukwonago River was in flood stage. It also indicates that the sample collected on May 8th was collected when the Mukwanago River was beginning to show the effects of a

much smaller storm event. The remaining samples were collected when the River was in or near base flow conditions.

Only one pesticide metabolite was quantified in the samples collected from the Mukwonago River. Metolachlor ESA was quantified at very low concentrations, ranging from a 0.106 ug/L to 0.176 ug/L, in each of the samples collect from the Mukwonago River. We consider the low concentrations of metolachlor ESA as base flow, the result of groundwater discharging into Mukwonago River.

Four Mile Creek

The sampling location for the Four Mile Creek is located in southeastern Wood County in Wisconsin's Central Sand area. The drainage basin of Four Mile Creek is the second largest of all the surface water streams sampled, with 214 square miles, but has the lowest percentage of its drainage basin in agriculture (33.8 percent). The sample point for Four Mile Creek is less than 1-mile from Nepco Lake, which discharges into the Wisconsin River to the west.

A total of four pesticide compounds were quantified in each of the six sampling events collected from Four Mile Creek, including alachlor ESA, alachlor OA, metolachlor ESA, and metolachlor OA. Since all four pesticide compounds were quantified in all sampling events, it is concluded that all four of these compounds entered the Four Mile Creek as base flow. The concentration of alachlor ESA decreased throughout the sampling effort from a high of 2.43 ug/L (May) to a low of 1.57 ug/L (September). However, the concentration of alachlor ESA is considerably above the concentration of alachlor ESA in any of the other streams sampled for this project.

The concentration of the remaining three pesticide compounds were very steady throughout the sampling effort, with the average concentration of metolachlor ESA being 0.82 ug/L, the average concentration of metolachlor OA being 0.58 ug/L, and the average concentration of alachlor OA being 0.30 ug/L. Four Mile Creek is the only surface water stream where alachlor OA was quantified.

With the exception of the Mukwanago River, Four Mile Creek is the only surface water stream that did not show evidence of direct impact of pesticides due to application timing and/or the June rain event. Rather, it appears that the pesticides quantified in both of these surface water streams is due only to groundwater discharge into the stream.

Discussion: Drinking Water and Surface Water Standards

As originally stated, the purpose of this investigation was to document the impact pesticide use was having on several streams in smaller watersheds in Wisconsin. That being said, it is clear that the use of pesticides has impacted local surface water streams to at least some degree.

However, to characterize that impact, we compared the concentration of pesticides that were quantified to existing (or calculated) environmental water quality standards, namely the Wis. Admin Code NR 140 Enforcement Standard for drinking water, and surface water "secondary values" calculated using Wis. Admin Code NR 105. Table 2 presents the maximum concentration of any pesticide quantified in any stream sample, as well as when and where the sample was collected. Please note that the secondary values presented are not formally promulgated water quality criteria because the toxicological database does not meet the minimum database requirements as specified in Wis. Admin. Code NR 105. The numbers used here are for comparative purposes only.

Compound	Maximum Concentration	Location	Sample Date	NR 140 ES	Secondary Surface Water Standards*
Acetochlor	0.321 ug/L	Grand River	6/10/2008	None	4.0 ug/L
Acetochlor ESA	0.565 ug/L	Yahara River	6/17/2008	None	Not Calculated
Acetochlor OA	0.744 ug/L	Yahara River	6/17/2008	None	Not Calculated
Alachlor	0.192 ug/L	Grand River	6/10/2008	2.0 ug/L	79 ug/L
Alachlor ESA	2.43 ug/L	Four Mile Creek	4/22/2008	20 ug/L	Not Calculated
Alachlor OA	0.446 ug/L	Four Mile Creek	4/22/2008	None	Not Calculated
Atrazine	1.04 ug/L	Grand River	6/10/2008	3.0 ug/L	65 ug/L
Dimethanamid	1.45 ug/L	Grand River	6/10/2008	None	18 ug/L
Metolachlor	1.44 ug/L	Grand River	6/17/2008	15 ug/L	77 ug/L
Metolachlor ESA	1.52 ug/L	Little Platte	6/16/2008	None	Not Calculated
Metolachlor OA	0.778 ug/L	Four Mile Creek	4/22/2008	None	Not Calculated
Simazine	0.444 ug/L	Yahara River	6/17/2008	4.0 ug/L	Not Calculated

* Chronic Exposure, Cold Water Fishery

Table 2. Drinking Water and Surface Water (Secondary) Standards

Of the pesticides and pesticide metabolites quantified in the investigation, only atrazine was quantified at a concentration approaching its Wis. Admin Code NR 140 Enforcement Standard (NR 140 ES). The concentration of atrazine in the Grand River during the June sampling event was quantified to be 1.04 ug/L, which is approximately 35 percent of the NR 140 ES of 3.0 ug/L. This was the only sampling event (June 10, 2008) when atrazine was quantified in the Grand River. In fact, all of the parent pesticides quantified in this investigation in any stream, including alachlor, acetochlor, atrazine, dimethanamid, metolachlor, and simazine were quantified in either the June or July sampling events. These sampling events were also completed shortly after the pesticides would have been applied to the agricultural fields in the drainage basins.

While the above discussion compares the concentration of the quantified pesticides to their respective NR 140 ES's, it is critical to note that these are drinking water standards, and none of the surface water streams included in the sampling effort are used to supply drinking water for human consumption. We only included these numbers for discussion purposes.

Table 2 also presents the Wis. Admin Code NR 105 (NR 105) surface water "secondary values". The most conservative secondary value calculated is for the chronic effects of these compounds in cold water fisheries. Similar to the drinking water discussion, not all of the streams in the sampling program are cold water fisheries. We simply chose the "chronic exposure, cold water fishery" to make the most conservative estimate of water quality as possible.

Only two compounds were quantified during this investigation at concentration of greater than approximately 1 percent of their calculated NR 105 surface water secondary values. Acetochlor and dimethanamid were both quantified at a concentration approximately 8 percent of the surface water secondary value. Similar to the drinking water discussion, both of these pesticides were quantified in the Grand River in the June sampling event.

Conclusions:

Pesticide metabolites were present at low concentrations in all of the streams sampled during this investigation independent of the "pesticide application season" or the hydrologic stage of the river. Consistent with other researchers, then, (Phillips *et al*, 2000) we believe that the pesticide metabolites quantified in the streams before and after the pesticide application season are probably the result of the movement of pesticides into groundwater and their subsequent discharge to the rivers as base flow. In total, metolachlor ESA was quantified in 95% of all the samples collected, and alachlor ESA was quantified in 56% of all samples collected.

Not coincidentally, the two pesticide metabolites quantified most frequently (metolachlor ESA and alachlor ESA) were also the two most commonly detected pesticide compounds quantified in drinking water wells across Wisconsin, according to the *2008 Agricultural Chemicals In Wisconsin Groundwater* Survey completed by DATCP (DATCP, 2008). In that investigation, alachlor ESA and metolachlor ESA were quantified in a proportion estimate of 21.6 %.

Finally, parent pesticides (non-metabolites) were quantified in the streams only during the June and July sampling events, or soon after a majority of the pesticides were applied.

References Cited

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