2008 Assessment of Atrazine in Des Moines Water Works Source and Finished Waters

The goal of this project was to access the presence of atrazine in the Des Moines Water Works (DMWW) source waters and determine the fate of atrazine in the treatment process at the Fleur and McMullen treatment plants.

The source waters for DMWW, the Raccoon River (RR) and the Des Moines River (DMR), flow through areas of intensive agricultural production where pesticides, herbicides and nitrogen-based fertilizers are extensively used. The Infiltration Gallery (LL) parallels the RR in DMWW Park allowing for naturally filtered RR water to be available as a water source as required.

Atrazine was selected for this study based on its frequency of land application use and its historical detection in the source waters following runoff events. Atrazine, the primary herbicide used to control broadleaf weeds in corn production, is a contaminant of increasing interest. The United States Environmental Protection Agency (USEPA) found humans exposed to atrazine, at concentrations above the drinking water Maximum Contaminant Level (MCL) of 3µg/L, set in 1991, were more prone to numerous serious health conditions. Heart, lung and kidney congestion, damage to the adrenal glands, and cancer are just a few of the health conditions which have been linked to atrazine.

In 1999, DMWW discontinued routine source water monitoring for atrazine and conducted triennial finished water monitoring for compliance with its Public Water Supply Operating permit. The emergence of simple and cost efficient Enzyme-Linked Immunosorbent Assays (ELISA) prompted DMWW to revisit its capability to routinely monitor atrazine in its source and finished waters in 2008.

Samples were analyzed on a weekly basis from April through July using the Abraxis Atrazine ELISA kit. One set of confirmation samples, for quality assurance purposes, was sent to the University Hygienic Labatory (UHL) for analysis. This confirmation analysis consisted of solid-phase extraction (SPE) followed by gas chromatography mass spectrophotometry (GC/MS).

Several conclusions can be drawn from this study: (1) the ELISA kit is a simple, quick and cost efficient method to screen for atrazine occurrences; (2) peak atrazine concentrations corresponded to run off events; (3) early detections of atrazine by ELISA could be used as a indicator as to the amount of carbon required for removal during the treatment process; (4) for compliance purposes, GC/MS remains the method of choice for atrazine; (5) the GC/MS method is atrazine specific; (6) ELISA values may yield positive concentration biases (potential for triazine and atrazine metabolite crossover).

Background

The United States Environmental Protection Agency has estimated atrazine to be the most heavily used herbicide in terms of use per acre in Iowa (Figure 1). Atrazine has been promoted in the agriculture community for the control of competing broadleaf vegetation. Elimination of the broadleaf vegetation competing for corn has resulted in substantial corn crop yields for Iowa

producers. Iowa is ranked first in the nation for corn production producing over 2 billion bushels in 2006 (Allen Baker, USDA). Corn production accounted for 86% of the annual atrazine usage (62 million pounds or >33 lbs/sq mile).

This data allowed Tony Seeman of the Iowa Soybean Association to approximate the annual atrazine application rate in the RR watershed to be > 500,000 lbs. For corn production, Iowa State University recommends atrazine be applied at the rate of 1.5 pounds of active ingredient per acre and not to exceed 3 lbs active ingredient per acre. Iowa State University (1990) determined application rates of atrazine in excess of 1.5 lb/A will result in carryover which could potentially runoff into Iowa waterways.

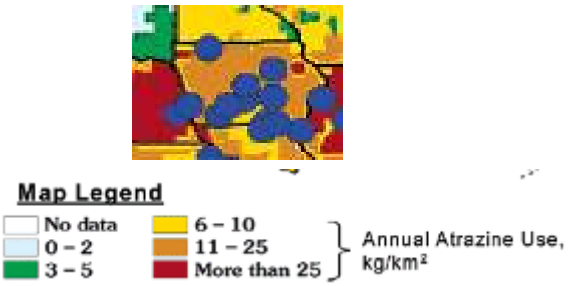

Figure 1. 2003 Annual atrazine use in Iowa

Corn is grown for its use as food, fuel, and fiber. The demand for bio-fuels has ignited a surge in corn production in Iowa within the last five years. Thus, the probability of increased corn production and utilization of pesticides, herbicides, and nitrogen-based fertilizers in the RR watershed is anticipated (Figure 2).

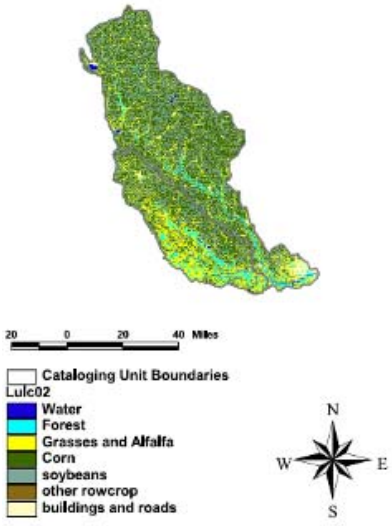

Figure 2. RR watershed land use 2002

Atrazine is applied to the soil at the beginning of the growing season. Atrazine has been found to easily bind to soil particles, be highly soluble and mobile in water, and to have a long half-life.

Following application, atrazine may potentially enter environmental waters by way of runoff or soil infiltration.

Atrazine is the most commonly detected pesticide in drinking water. Historically, atrazine levels vary in concentrations throughout the growing season. The majority of the atrazine detects have routinely been documented in May, post planting, following spring runoff events (2004 USGS study, Scribner and others).

Potential reproductive and developmental health effects have been linked to atrazine exposure. The United States Environmental Protection Agency has found the following health effects linked to short term atrazine exposure over the MCL: heart, lung and kidney congestion, muscle spasms, weight loss, damage to adrenal glands and weight loss. Long term exposure to atrazine exposure over the MCL may potentially cause: cardiovascular damage, retinal and muscle degeneration and cancer (USEPA, *2005 Consumer Fact Sheet on Atrazine*).

The effect of increased agricultural production on water quality in the RR is continually monitored by DMWW. Until 1999, atrazine was one of many contaminants routinely monitored in the Raccoon and Des Moines Rivers by the DMWW laboratory. Routine atrazine monitoring was discontinued in 1999 due to expense and consistent finished water detects less than the MCL. Since 1999 the DMWW has outsourced their finished water samples, every three years, as required for drinking water compliance purposes. Recent development of a simple, quick and cost efficient atrazine screen, ELISA, has made it possible for DMWW to once again investigate atrazine concentrations in its source waters and study the fate of atrazine in its treatment process.

This project, titled the 2008 Assessment of Atrazine in Des Moines Water Works Source and Finished Waters, was designed and conducted by the DMWW laboratory. The purpose of this project was twofold: (1) report the atrazine results gathered throughout the 2008 growing season (2) assess the practicality of instituting a regular testing program utilizing the ELISA assay.

Materials and Methods

Both the Fleur and McMullen treatment plants were included in this study. Select gauging station sites on the RR were also included in the study. Figure 3 correlates the sample sites at both treatment plants and gauging stations with their abbreviation.

Fleur Treatment Plant	
Sample Site	**Sample ID**
Raccoon River	RR
Des Moines River	DMR
Gallery	LL
Filter Effluent	FE
McMullen Treatment Plant	
McMullen Raw	MR
McMullen Filter Effluent	MFE
Crystal Lake	CL
Maffitt Reservoir	MRES
RR Gauging Stations	
North RR at Van Meter	A
Middle RR at Redfield	31
South RR at Redfield	32

Figure 3. Sample site identification

Weekly samples were collected April through July 2008 from both treatment plants and bi-monthly from predetermined gauging station sites on the RR. Samples were analyzed at the DMWW laboratory using the Abraxis ELISA method. A selected set of samples was sent to the UHL for analysis by solid-phase extraction and GC/MS to provide a quality control comparison to the Abraxis ELISA method.

The GC/MS method used by UHL was EPA 525.2. This method required extraction with Dichloromethane and Ethyl Acetate. Equipment for the extraction process included 5 SPEDEX units (model 4790) manufactured by Horizon, C-18 extraction disks, electric pump for the extractor, specialty glassware for the extractor and a concentrator (turbo-vap). Extraction time averaged seven hours for 25 samples on the five SPEDEX units. The manufacturer of the GC/MS and DB5.625 column was Agilent. A mixed standard containing atrazine, simazine, alachlor, metalachlor, desethyl atrazine and acetochlor was used. This mix allowed for the potential detection of additional triazines and atrazine metabolites. The sample run time was approximately 20 minutes per sample. The reporting limit using this method was 0.0001 mg/L. The cost per sample was $150.

The ELISA kits, used by DMWW for this study, were purchased from Abraxis (Warminster, PA). The method allowed paramagnetic particles coated with antibodies to bind with atrazine and related triazines and metabolites in the source waters. (The assays could not differentiate atrazine from other triazines or the atrazine metabolites.) Additional equipment required for analysis included a 60 well magnetic separation system, vortex mixer and a colorimeter able to read at 450 nm. The average analysis time for 25 environmental samples was one and a half hours. The cost per sample was $7.00.

Results and Discussion

Atrazine Occurrence. Historical atrazine data obtained from the Iowa Department of Natural Resource's STORET database indicated that atrazine was typically detected in the RR at Van Meter following the first spring runoff event (figure 4). Small concentrations of atrazine were

detected subsequent to the first runoff event but at concentrations significantly lower (<0.1ppb). This detection pattern suggests atrazine binds to soil particles and is flushed into receiving waters by the first significant spring rain.

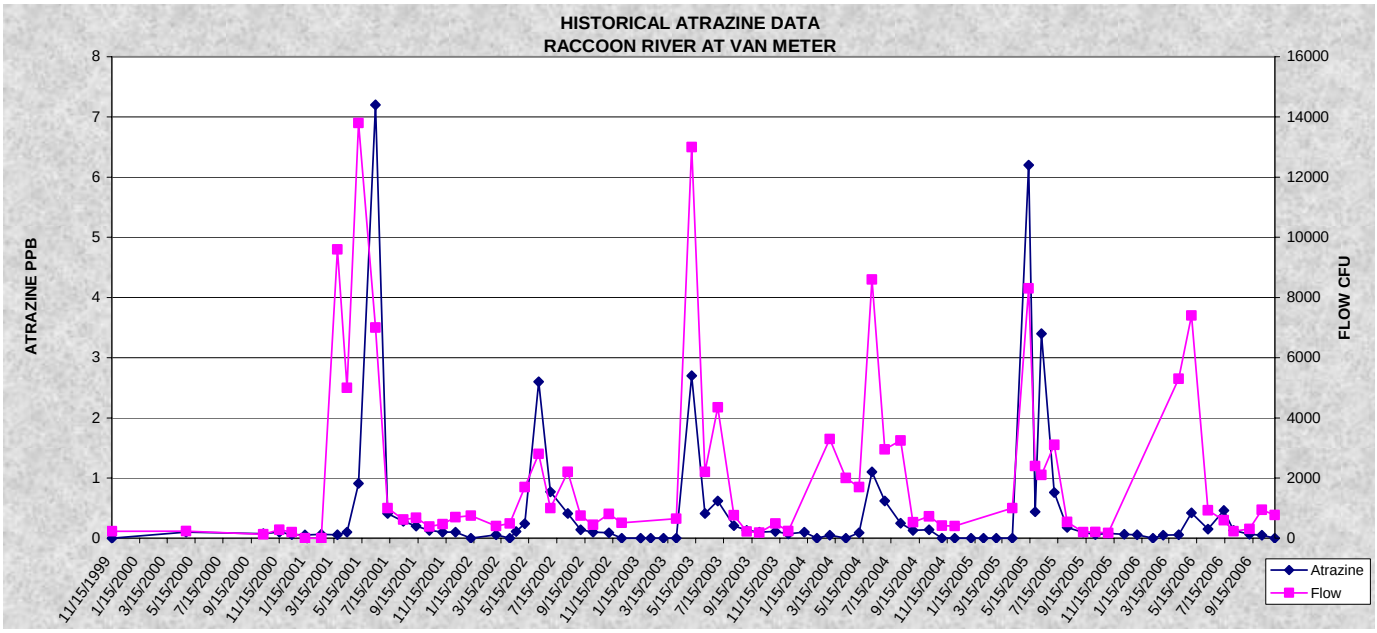

Figure 4. Station ID: 10250002 Raccoon River Upstream of Des Moines at Van Meter

The exception to this finding was during years when extended precipitation occurred. 2008 was an example of one of these atypical years in regards to rainfall. The RR frequently approached "bank full" from March though July. The RR also reached what was described as the "500 year flood stage" in mid June. Figure 5 depicts the RR stage heights during this period. Historically, years with consistently elevated precipitation (abnormally elevated river stages) exhibited significantly lower but consistent atrazine detects. 2008 was one of those years.

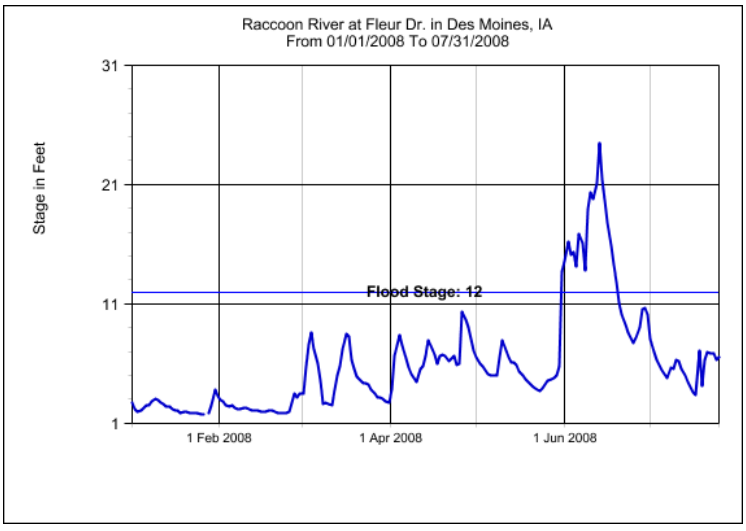

Figure 5: RR Stage Height at Fleur Drive

The relationship between the RR flow and the atrazine concentration detected by ELISA indicated the anticipated historical atrazine flush occurred around June 2, 2008 (Figure 6). Due to the time of year and flood conditions, this detection most likely included some additional triazines (propazine, simazine, cyanazine, hexazinone, metribuzine, prometon, terbutryn) and /or the atrazine metabolites (desethyl atrazine, desisopropyl atrazine) thus yielding a positive bias for atrazine detection with the ELISA screen.

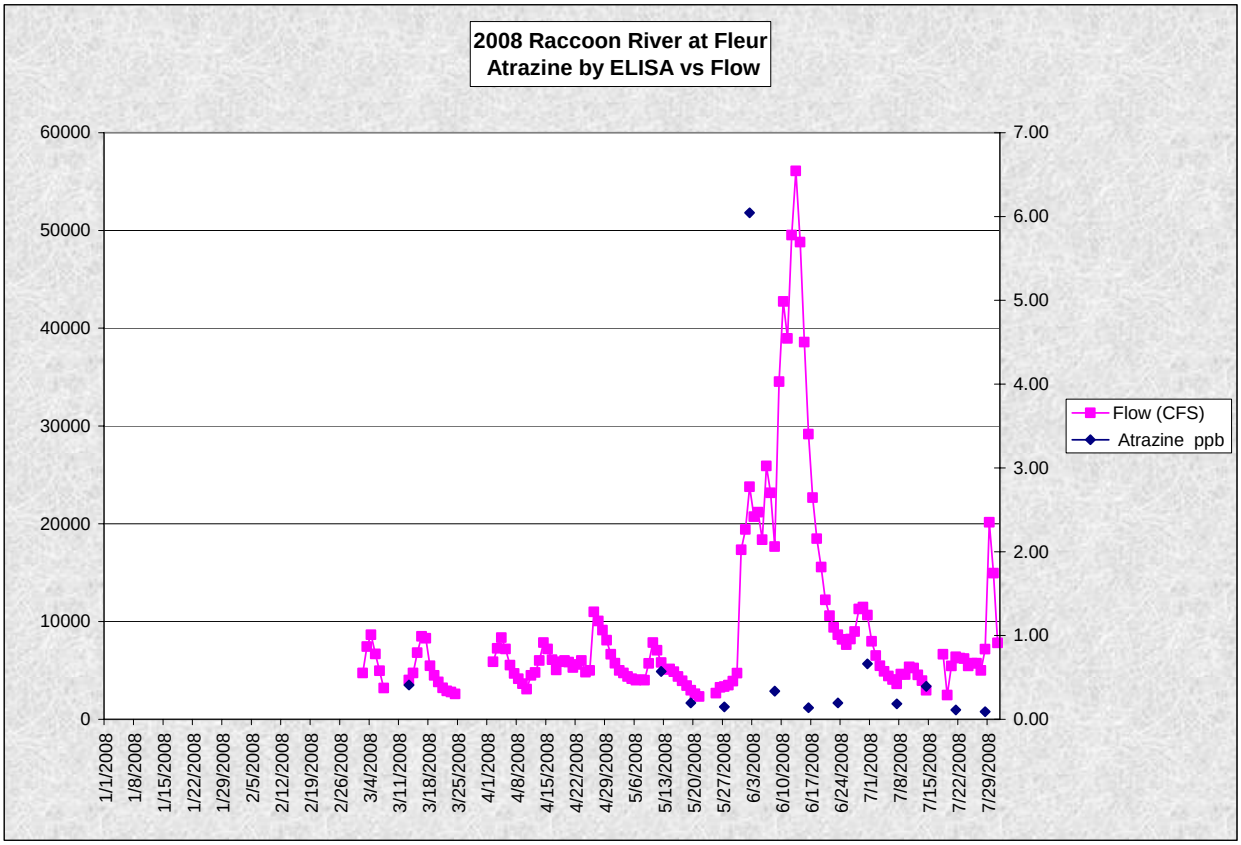

Figure 6. RR flow vs. atrazine ppb detected by Atrazine

Fate of Atrazine in the Treatment Process. Figures 7 and 8 trace the fate of atrazine through the Des Moines Water Works Fleur treatment process during the 2008 sampling period. Atrazine detects in the Raccoon River and Des Moines River were above 3ppb of on June 2nd. The atrazine detects in the Infiltration Gallery were consistently below 0.5 ppb during the entire sampling period. On average atrazine was detected in the rivers and Infiltration Gallery at levels near or below 0.5ppb during the majority of the sampling period. It is speculated that these consistently low detects may be due to the extended precipitation over the course of the study (Figure 8).

Powdered activated carbon is routinely fed to the pre-sedimentation treatment step at the Fleur treatment plant. Powdered activated carbon has been widely accepted by drinking water treatment facilities for removal of pesticides, herbicides, organics and taste and odor causing compounds. Both the Raccoon River and Des Moines River flow through the pre-sedimentation basin during the treatment process at the Fleur treatment plant allowing for atrazine removal (depending of the atrazine/carbon ratio). The Infiltration Gallery by-passes the pre-sedimentation basin and does not come in contact with powdered activated carbon during the treatment process. Therefore, if the Fleur plant were to utilize the Infiltration Gallery as its primary source water, there is a possibility that atrazine might continue through the treatment process and remain in the finished water. Figure 8 illustrates this as shown by detects in the FE (treated) water.

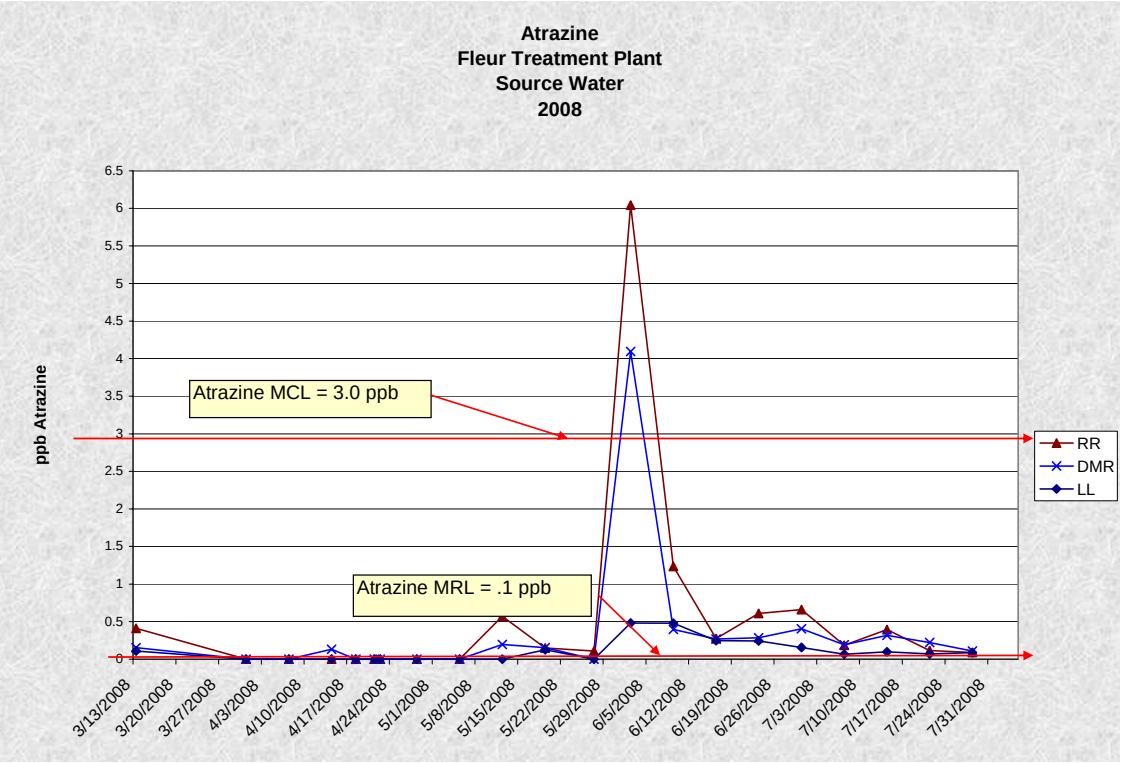

Figure 7. Atrazine levels in the RR, DMR, and LL.

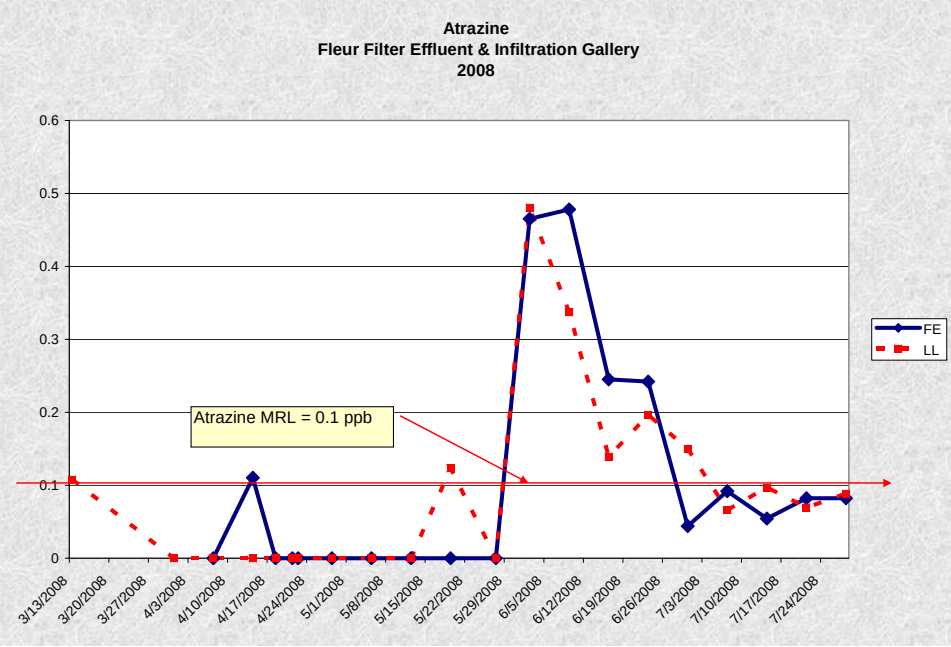

Figure 8. Atrazine detects in the LL and FE by ELISA method

Carbon treatment was not utilized at the McMullen treatment plant at the time of this study. Therefore, it was presumed that any atrazine detect in the source water would carry through the treatment plant (from the raw water through the filter effluent water). Figure 9 substantiates this presumption. Crystal Lake, an additional source for the McMullen treatment facility, was not used as a source during this study due to flood conditions. However, data was collected from Crystal Lake and is presented in Figure 9.

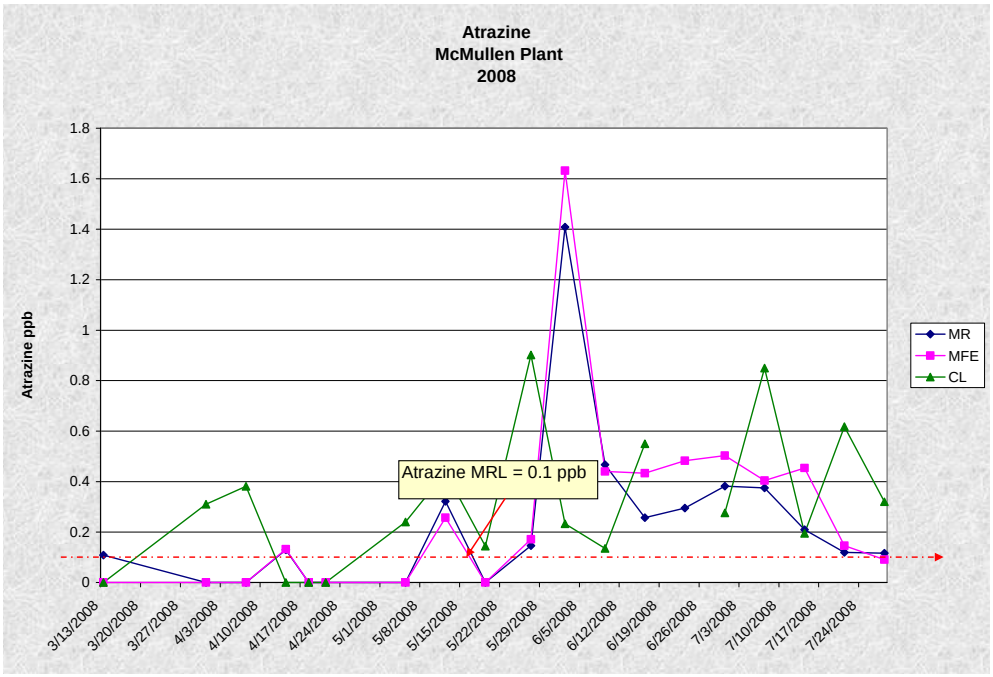

Figure 9. Atrazine Detects during McMullen Treatment Process by ELISA method

Five sites at gauging stations throughout the Raccoon and Boone River watersheds were selected for atrazine detection by the ELISA method. Figure 10 correlates the sample sites in the watersheds with their abbreviations.

Sample Site	Sample ID
A	North RR at Puckerbrush upstream of Van Meter
31	Middle RR at Redfield
32	South RR upstream of confluence with Middle RR
BR03	Boone River at Webster City
BR06	Lyons Creek

Figure 10. Sample Identification

The results of the atrazine detects are presented in Figure 11.

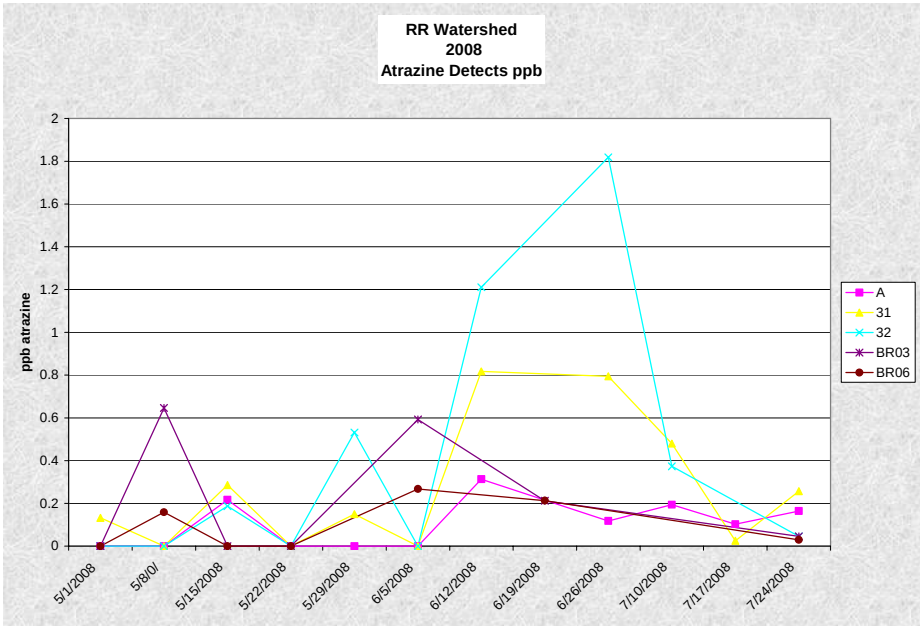

Figure 11. RR gauging station atrazine detects

Atrazine was detected in selected watershed samples up to a concentration of 1.8 ug/L, as shown in Fig. 11. The majority of the watershed samples contained atrazine at concentrations below the MCL of 3 ug/L. Peak levels of the atrazine appeared in late June in the South RR (upstream of the confluence with the Middle RR). These levels corresponded with a significant runoff event following what was described as the "500 year flood stage" in mid June.

Method comparison: GC/MS and ELISA. A brief method and material comparison between the GC/MS and ELISA is summarized in Figure 12.

	ELISA	**GC/MS***
Method	Magnetic particle assay	Extraction process plus GC/MS
Approximate Cost	$10.00 per sample or $350 kit: 50 samples	$150 per sample
Batch	Batch of 25 samples recommended to maximize kit; 2 batches per kit	Batch of 10 samples
Analysis time	1 ½ hours for batch of 25 samples	2 days (7 hour extraction period for 25 samples, (5 extractors used); 20 minute run time per sample or 8 hours for 25 samples)
Sample amount	1mL	1 L
Toxicity	NA	Carcinogens during extraction process
Specificity	Cross reactive	Analyte specific excluding atrazine metabolites
Sensitivity, MRL	0.10 ppb	0.10 ppb
Certified Method	No	Yes

Figure 12. Method Summary

* Information obtained from Sarah May, GC analysis supervisor, at the University of Iowa Hygienic Laboratory

Regarding specificity and accuracy, the ELISA method showed a positive bias in the set of samples collected 6/2/08 (Figure 13). It is presumed that this bias was due to the cross reactivity with other triazines and atrazine metabolites. Water quality during the time of sampling (flood conditions) may have also contributed to this positive bias.

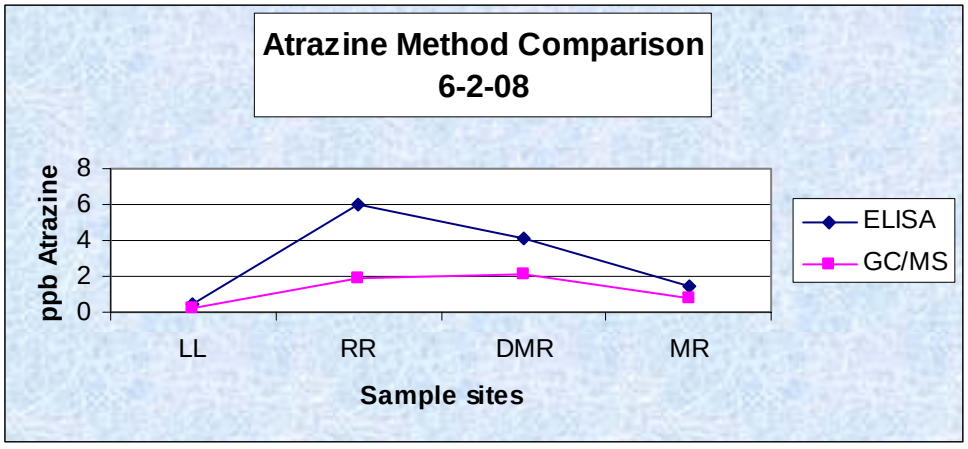

Figure 13. Method Concentration Detects

Figure 14 presents the atrazine concentration of the RR that was detected by GC/MS and how it related to ELISA detection and flow on 6/2/08. The positive atrazine bias of the ELISA method is noticeable.

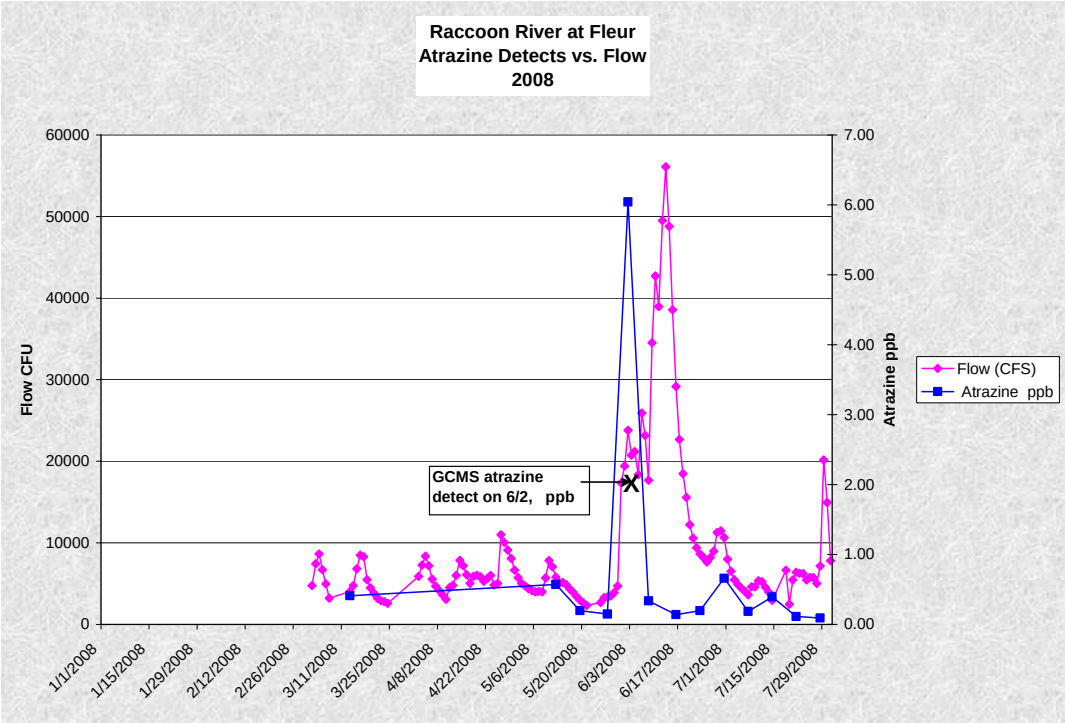

Figure 14. RR GC/MS detection compared to ELISA detection on 6/2/08

Conclusion

Atrazine was detected in the environmental waters throughout the RR watershed and in the source waters for the DMWW. The GC/MS result of 1.9 ppb atrazine on June 2, 2008 quantified the anticipated spring flush of atrazine. The 2008 data supported the hypothesis that atrazine is related to flow. Other than the June 2nd sample, atrazine detects were constantly low throughout the sampling period (<0.5ppb).

Carbon feed has been determined to play a key role in the removal of pesticides, organics, and emerging contaminants during the treatment process (DMWW, *Assessment of Carbon Feed for Removal*, 2004). This study also supported the hypothesis that carbon addition during the treatment process does remove atrazine. Atrazine removal was noted at the Fleur plant (where carbon is routinely fed). However, atrazine removal was not observed when the Infiltration Gallery was used as a source (where carbon is not fed). Atrazine removal was not seen at the McMullen plant (carbon was not utilized during treatment). Utilization of the atrazine ELISA could better enable operators to optimize the amount of activated carbon fed for pesticide removal. The downside is that in order to achieve the cost efficiency of the ELISA kit, a batch of 25 environmental samples must be run together. For this reason, weekly ELISA screening may not prove cost effective for treatment purposes.

The GC/MS method was found to be an expensive, and time consuming method. However, it is analyte (atrazine) specific and provides an opportunity to measure several pesticides during a single run. For regulatory or specificity studies, the GC/MS method would be the preferred method.

The ELISA method was found to be an inexpensive, safe, and quick assay to screen for atrazine. However, this method tended to have positive concentration bias caused by the potential cross-reactivity of other triazines and their metabolites. Therefore, it could not be used for regulatory or specificity monitoring. It could be potentially used for the early detection of atrazine concentrations.

This study suggests, for monetary purposes and efficiency, DMWW continues to outsource their atrazine samples for compliance.