Implications of Sampling Frequency to Herbicide Conservation Effects Assessment

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ABSTRACT

Herbicide losses from agriculture represent potential human health hazards, and are one focus of the Conservation Effects Assessment Project (CEAP). Since frequent herbicide sampling can be rigorous and expensive, it is desirable to determine expected uncertainties associated with reduced sampling frequencies. Atrazine, simazine, alachlor, acetochlor, metolachlor, and glyphosate were monitored in tile-fed drainage ditches. Water samples were collected during the 2004-2007 cropping seasons at 8 monitoring sites located at the outlets of sub basins ranging in size from 298-19,341 ha (736-47,793 ac). Herbicide data were analyzed based upon daily sampling, then for 7 possible weekly sampling scenarios, and 14 possible biweekly sampling scenaios. Additionally, the value of sampling more intensively during runoff events was evaluated. Statistical analyses indicate the need for management practices to reduce atrazine and metolachlor loading to drainage water can best be assessed in these drainage networks using daily sampling in conjunction with a more intensive sampling regime during storm events, while sampling frequency had little impact on observed levels of other herbicides. This indicates that biweekly sampling may be sufficient for monitoring of some herbicides, allowing for reduced analytical costs.

Keywords: Conservation Effects Assessment Project (CEAP), Water quality, herbicide, atrazine, maximum contaminant level

INTRODUCTION

In the United States, many municipalities rely on surface waters as sources of domestic water supply. This water is treated by the water utility and distributed to residents as potable water. Where largely agricultural watersheds drain to surface waters that serve as drinking water sources, the transport of agriculturally applied herbicides, such as atrazine [2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine], simazine [6-chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine], alachlor [2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide], acetochlor [2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl) acetamide], metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide], and glyphosate [N-(phosphonomethyl)glycine], into the water supply represents a potential risk to human health, as well as a cost to municipalities for removal. One objective of the Conservation Effects Assessment Project (CEAP) is to evaluate the potential for voluntary best management practices to reduce herbicide loading to drinking water sources. It is hoped that this would allow municipalities to reduce the treatment costs associated with these herbicides while maintaining acceptable levels in drinking water.

The United States Environmental Protection Agency (USEPA) regulates the amount of some herbicides allowable in drinking water by setting maximum contaminant levels (MCLs). Those which do not yet have an established MCL may have a health advisory level (HAL) and / or may be on the contaminant candidate list (CCL), slated for future MCL development. Common trade names and drinking water limits of all studied herbicides are listed in Table 1.

Previous studies have found herbicides to be frequently detected in surface waters in regions where they are used (Kalkhoff et al., 2003), with levels sometimes significantly higher than MCL (Shipitalo et al., 1997; Johnson and Baker, 1982, 1984; USGS, 1993). Concentrations of some herbicides in surface water have been observed to be a highly seasonal phenomenon, with greatest losses occurring during the first runoff events following application (Thurman et al., 1991; Battaglin et al., 2005). Temporal variability in herbicide concentrations in surface water systems should be considered in establishing a sampling protocol. Much of the existing research on the prevalence of herbicides in finished and unfinished drinking water is based upon weekly or biweekly sampling (Richards et al., 1995; Graziano et al., 2006). More intensive monitoring for the purpose of conservation effects assessment is desirable, but the resources required for this should be carefully weighed against other needs of the project. Sampling parameters, including timing and frequency, affect both analysis costs and data quality (Novotny and Olem, 1994). Given that there are a large number of monitored CEAP sites, resource constraints, and significant expense associated with herbicide monitoring, it is important to evaluate the importance of each analyte and uncertainties associated with decreasing intensity of sampling.

The primary objectives of this study were to evaluate levels of atrazine, simazine, alachlor, acetochlor, metolachlor, and glyphosate in a set of surface drainage ditches under the current conservation practices, to determine whether daily, weekly, or biweekly sampling can be expected to represent herbicide levels as observed using a daily sampling with more intensive sampling during storm events.

MATERIALS AND METHODS

Site Description

The St. Joseph River watershed is a largely agricultural watershed that provides the drinking water supply for the City of Fort Wayne, Indiana (USA) and more than 200,000 residents. It is 281,014 ha (694,400 ac) in size and is studied as part of the CEAP. The herbicides atrazine, simazine, alachlor, acetochlor, metolachlor, and glyphosate are used in the study area, where corn (*Zea mays*) and soybean (*Glycine max (L.) Merr.)* grown in annual rotation is common. Most of the corn in the region receives some level of pre-emergent atrazine application, often with metolachlor or other herbicides, or in the case of an increasing fraction of glyphosate tolerant corn, post-emergent glyphosate with or without other herbicides. Almost all of the soybean in the region are glyphosate tolerant and receive post-emergent glyphosate application. Fort Wayne tap water has a history of contamination by atrazine, simazine, metolachlor, acetochlor, and alachlor, with average atrazine levels greater than MCL during the months of May and June, 1995 (Cohen et al. 2003), and today requires extensive treatment in order to meet the safe drinking water MCL.

The study region was located in northeastern Indiana within the Cedar Creek sub-basin of the St. Joseph River watershed. Cedar Creek is the largest tributary of the St. Joseph River, and represents about 25% of the St. Joseph River drainage area. Predominant soils are Blount silt loams (fine, illitic, mesic, Aeric Epiaqualfs), Pewamo silty clays (fine, mixed, active, mesic Typic Argiaquolls) and Glynwood loams (fine, illitic, mesic Aquic Hapludalfs). Approximately 80% of the land area within the studied basins is agricultural, with the majority cropped to corn and soybean in annual rotation (Table 2). The area receives an average of 93 cm (36.6 in) of precipitation annually, and the average temperature is 10 ^{o}C (50 ^{o}F). Most of this land would be too wet to farm without the use of artificial drainage systems. Nearly all fields in the study area are drained by a network of subsurface drainage tile (usually located about 1 m (3.3 ft) deep), to drainage ditches. Field drainage is then conveyed from the ditches to natural waterways. Direct entry of surface runoff into ditches is impeded in most locations due to reverse grade caused by either excavated soil from ditch construction or dredged sediment left on ditch banks during routine ditch maintenance. As a result, it is thought that the majority of ditch base flow is contributed by natural subsurface flow and tile drains. However, surface tile inlets are common in field depressions and surface runoff entering these may constitute a significant percentage of total "tile" flow. Instrumentation was installed in 2006 in order to monitor this.

Seven sampling locations were selected for daily water quality monitoring in three tile-fed ditches draining watersheds A, B, and C (Fig 1). Additionally, a site along the main Cedar Creek channel was monitored (XXL). These nominally represented three "replications" each of medium (ME)-sized (298-373 ha (736-921 ac)) and large (LG)-sized (1380-1934 ha (3411-4780 ac)) watersheds, one extra-large (XL)-sized (4303 ha (10,634 ac)) watershed, and an extra-extra-large (XXL)-sized watershed (19,341 ha (47,793 ac)).

Water Quality Sampling and Analysis

Water samples were collected daily for atrazine, simazine, alachlor, acetochlor, metolachlor, and glyphosate analysis at the 7 ditch monitoring sites during the 2004-7 cropping seasons (April – November), and at the main channel monitoring site during the 2005-7 cropping seasons. Each 300-mL (10.1-fl oz) daily sample was a composite of 6 50-mL (1.69-fl oz) samples taken every 4 h, using ISCO 6712 autosamplers (ISCO, Inc., Lincoln, NE)*. Samples were immediately refrigerated until processing. Hydrologic and climatologic data were collected on 10-min intervals. Sharp rises in ditch discharge during or after rainfall were recorded as runoff events. During runoff events, samples were taken more frequently. Aliquots of 100 mL (3.4 fl oz) were pulled every 30-min for 30 hours, and composited into 300-mL 90-min samples.

Within 3 days of sampling and refrigeration, all samples were filtered by vacuum flask through a nylon membrane (0.45 μm) into glass vials, and frozen immediately until analysis could be performed (max frozen time = 3 months). Atrazine, simazine, acetochlor, alachlor, and metolachlor were preconcentrated by solid-phase microextraction (SPME) according to a modified EPA method 525.2 described by Rocha et al. (2007), and quantified by gas chromatography (GC) with mass spectrometry (MS). In this method, NaCl was added to 7.5-mL samples to 83%, and exposed to a SPME fiber coated with 100 μm of polydimethylsiloxane for 40-min extraction period with agitation at 40 °C. Afterward, the fiber was directly introduced into the injector of the GC/MS for separation and analysis. An internal standard was used in every sample (terbuthylazine, 10 μg/L), and spiked check samples were run after every 9 samples to ensure quality. The detection limit for atrazine, acetochlor, alachlor, and metolachlor was 0.25 μg/L, while the detection limit for simazine was 0.5 μg/L. Glyphosate was quantified by high performance liquid chromatography with post-column derivitization and fluorescence detection, according to EPA method 547 (USEPA, 1990) (detection limit = 2 μg/L).

Calculations

Seasonal Flow-weighted average (FWA) concentrations were determined at each site by summing the following by cropping season: herbicide concentration of each sample (μg/L) multiplied by the discharge during the time span represented by the sample (L), and then dividing by the total seasonal discharge. For the purposes of these calculations, concentrations determined to be below detection limit were assumed to be zero.

These calculations were performed using daily sampling with more intensive sampling during storm events (Daily+Storm), and the results were assumed to be the "true" values. For the daily sampling regime (Daily), these calculations were performed using daily sampling data (1 sample per day). In order to simulate a weekly sampling regime (Weekly), these calculations were performed using only data collected on a Sunday, or a Monday… for all seven days of the week, such that seven possible outcomes representing Weekly sampling on each day of the week resulted. To simulate biweekly sampling (Biweekly), these calculations were performed using only data collected on an odd Sunday, or an odd Monday… for every day of the week and for both even and odd weeks. This resulted in 14 possible outcomes representing Biweekly sampling on each day of the week on even and odd weeks.

Statistical Analysis

Percent bias (β) was determined to indicate the tendency of the studied sampling frequencies to over or under estimate Daily+Storm herbicide levels. In addition, standardized root mean square error (E_s) was determined to represent the expected accuracy of FWA herbicide concentrations obtained using various sampling frequencies, as compared to the Daily+Storm derived value.

First, analytical uncertainty was calculated for each analyte by performing a Student's t-test (α=0.05) using the standard deviation (σ) of 7 randomly selected spike samples distributed over the 4 season period. Uncertainty was calculated as the product of σ and the t-value according to a method performance test described in EPA method 525.2 (USEPA, 1990). These uncertainty ranges are given in Table 3. Daily, Weekly, and Biweekly derived estimated herbicide levels were determined to be not significantly different from the Daily+Storm derived herbicide level if the estimated value was within the uncertainty range of the Daily+Storm derived value. If the difference was significant, then the "error" was calculated as: C_{ds}-C_e , where C_{ds} = the nearest uncertainty boundary of the Daily+Storm derived herbicide concentration (μg/L), and C_e = the estimated value derived by Daily, Weekly, or Biweekly sampling (μg/L). The nearest uncertainty boundary was chosen over the “true” Daily+Storm value in this calculation in order to maintain continuity between the insignificant errors, which were assigned a zero value, and the errors where the estimated value was just outside the uncertainty boundary.

Bias was determined according to the following equation:

$$\beta = \frac{C_{ds} - C_e}{C_{ds}} \times 100$$

The standardized root mean square error is defined as:

$$E_s = \frac{\sqrt{\dfrac{\sum_{i=1}^{n}(C_{dsi} - C_{ei})^2}{n}}}{C_{ds}}$$

where: C_{dsi} *= the* i^{th} *Daily+Storm derived value*
C_{ei} *= the* i^{th} *estimated value based on Daily, Weekly, or Biweekly sampling*

RESULTS AND DISCUSSION

Temporal Variability of Herbicide Levels

Using all available data (Daily+Storm), seasonal FWA herbicide concentrations and maximum observed herbicide concentrations are given in Tables 4 and 5. FWA atrazine levels were higher during 2004 and 2006 than during 2005 and 2007. This can be largely attributed to differences in the seasonal hydrology. Figure 2 illustrates the discharge and atrazine concentrations observed at the BLG site over the cropping seasons of 2004-2007. In 2004, rainfall did not occur during early April, and so most of the planting and associated herbicide applications occurred then. During the period that immediately followed, spikes in discharge indicating runoff events occurred frequently. Associated with these events, high atrazine concentrations were observed (Fig 2). In 2005, runoff events also occurred during the period following planting, but were much lesser in magnitude than 2004 and resulted in lower magnitude storm related atrazine losses. Similar to 2004, frequent higher magnitude runoff events occurred during and after the mid-April time of typical planting in 2006. The associated atrazine concentrations were observed as high as 417 μg/L. It can be observed in Figure 2 that runoff events of notable magnitude occurred prior to mid April in 2006, indicating probable high moisture conditions at the time that most fields were planted. This may account for the very high atrazine concentrations observed during early May. In 2007, two high magnitude runoff events occurred in April, delaying planting of most fields until May. The next runoff events following did not occur until late May and early June, and were very low in magnitude. As a result, the associated atrazine losses were comparatively minimal. Atrazine losses were in all cases associated with the first few runoff events following planting, regardless of runoff event magnitude, and declined throughout the season.

Frequency of Sampling

It is expected that decreasing sampling frequency will increase the range of the deviation of FWA concentration values with respect to values calculated using Daily+ Storm sampling, and therefore result in increasing E_s values. Atrazine FWA concentrations calculated from Daily+Storm, as well as Daily, Weekly, and Biweekly sampling, are shown in Figure 3. By eliminating intensive storm sampling from our data set and using only Daily samples, we lowered the observed FWA concentration of every herbicide during every cropping season. This is also indicated by consistently positive bias in Daily estimated FWAs (Tables 6-9). Daily bias was not significant for simazine, acetochlor, alachlor, and glyphosate, and was infrequently significant for metolachlor. Bias in Daily observed atrazine levels tended to be significantly positive for 2004 and 2006, when major runoff events occurred during May, and infrequently significant for the cropping seasons of 2005 and 2007, when no major May runoff events occurred. Likewise, the corresponding Daily E_s tended to be insignificant for simazine, acetochlor, especially during cropping seasons when major runoff events occurred during May, while atrazine and metolachlor had significant E_s at some sites during every cropping season except for 2007. No significant differences in Alachlor or glyphosate were observed. Significant errors in FWA atrazine and metolachlor concentrations can be expected associated with Daily sampling versus the Daily+Storm regime, and this is especially notable during wet seasons. An intensive storm sampling regime was also found to be of significant importance in a study of nutrient and sediment losses from watersheds 1400-10,980 ha (3459-2,133,217 ac) (Robertson and Roerish, 1999).

By sampling Weekly, observed FWA concentrations incurred generally higher E_s values than Daily sampling, and both positive and negative bias was observed. However, it can be observed in Figure 3 that bias is not symmetrical. This is because estimated FWA values are bound by zero (100% positive bias), whereas estimated FWA values with negative bias is theoretically not bound. However, Weekly sampling generated more randomly distributed bias than Daily sampling, since the possibility of excluding a disproportionate number of days having lower herbicide concentrations exists with Weekly and Biweekly sampling, but not with Daily sampling, which only excludes the typically higher concentration and discharge Storm samples. Decreasing the sampling frequency from Daily to Weekly decreased measurement accuracy, as indicated by higher E_s values. E_s values were significant at one or more sites for atrazine and metolachlor during every cropping season, whereas Weekly E_s was significant less often for simazine and acetochlor, and not significant for alachlor and glyphosate. Therefore, significant errors in FWA atrazine and metolachlor concentrations can be expected associated with Weekly sampling, and significant errors in simazine and acetochlor concentrations during cropping seasons when conditions are more favorable for herbicide transport can be expected associated with Weekly sampling.

Further decreasing sampling frequency to Biweekly generated the highest and most often significant E_s values for atrazine and metolachlor overall, with values sometimes greater than 100%. Large Biweekly E_s values were also observed for simazine and acetochlor. It can therefore be determined that FWA atrazine and metolachlor concentrations observed by Biweekly sampling do not describe FWA concentrations observed using the Daily+Storm method in this case. The same statement can be made for simazine and acetochlor for the seasons when major runoff events occurred during May. No significant errors were detected for alachlor and glyphosate, and bias was distributed similarly to the Weekly scenario. A negative correlation between sampling frequency and standardized root mean square error was also observed in a study that examined sampling frequencies from every 5 min (high frequency) to every 360 min (low frequency) (King and Harmel, 2003).

CONCLUSIONS

The herbicides atrazine, simazine, acetochlor, alachlor, metolachlor, and glyphosate were monitored in 7 agricultural drainage ditches feeding a major drinking water source during the 2004 - 2007 cropping seasons (April – November), and in one natural channel during the 2006 – 2007 cropping seasons. Water samples were collected daily at monitoring sites located at the outlets of sub basins ranging from 298 to 19,341 ha (736 to 47,793 ac), and every 90 min during runoff producing rainfall events. Cropping season FWA herbicide concentrations were higher when major runoff events occurred during May than when no major runoff events occurred during May.

Eliminating storm event sampling resulted in significant decreases in calculated FWA atrazine concentrations in most cases. Likewise, observed levels of acetochlor and metolachlor were significantly decreased some of the time (usually during seasons having major May runoff events). Observed levels of simazine, alachlor, and glyphosate were not significantly different between Daily and Daily+Storm sampling regimes. As sampling frequency was further reduced from Daily to Weekly and Biweekly, decreases in accuracy, indicated by increasing E_s values, were observed. Weekly or Biweekly sampling also can not be expected to accurately represent Daily+Storm based FWA atrazine and metolachlor concentrations, and additioanally can not be expected to accurately represent Daily+Storm based FWA simazine and acetochlor concentrations during seasons when significant runoff events occur during May. In this and similar agricultural drainage networks, the need for conservation practices to reduce atrazine and metolachlor, and during seasons when major runoff events occur during May, simazine and acetochlor levels in surface water can best be evaluated using the Daily+Storm sampling regime, while Daily, Weekly, or Biweekly sampling regime is acceptable for simazine and acetochlor during seasons when major runoff events do not occur in May. Observed FWA alachlor and glyphosate levels were not significantly impacted by sampling frequency.

*Mention of a trade name, proprietary product, or specific equipment does not constitute a guarantee or warranty by the USDA or the Soil and Water Conservation Society and does not imply its approval to the exclusion of other products that may be suitable.

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Table 1. Characteristics of studied herbicides.

Herbicide	Selected Common Trade Names	MCL (μg/L)	Reference
Atrazine	AAtrex, Bicep II Magnum (with metolachlor)	3	USEPA, 2006a
Simazine	Princep, Sinbar	4	USEPA, 2006b
Acetochlor	Harness, Surpass	N/A[†]	USEPA, 2007
Alachlor	Lasso, Lariat (with atrazine)	2	USEPA, 2006c
Metolachlor	Dual, Bicep II Magnum (with atrazine)	100[†‡]	USEPA, 1995
Glyphosate	Accord, Roundup	700	USEPA, 2006d

[†]No maximum contaminant level has been established for this chemical as of 2007, but this chemical is on the USEPA Contaminant Candidate List (CCL), for MCL development.

[†]This value represents a Health Advisory Level set by the USEPA.

Table 2. Experimental watershed characteristics.

Site	Area (ha)	Predominant Soil Types	Land Management
XXL	19341	Blount silt loam, Pewamo silty clay, Glynwood loam, Rawson sandy loam, Rensselaer loam, Sebewa sandy loam, Morley silty clay loam	58% Agriculture 17% Grass/Pasture 14% Forest
AXL	4303	Blount silt loam, Pewamo silty clay, Glynwood loam, Rawson sandy loam, Rensselaer loam, Sebewa sandy loam	78% Agriculture 14% Grass/Pasture 6% Forest
ALG	1934	Blount silt loam, Pewamo silty clay, Glynwood loam, Rawson sandy loam, Morley silty clay loam	77% Agriculture 16% Grass/Pasture 6% Forest
BLG	1417	Blount silt loam, Pewamo silty clay, Glynwood loam, Sebewa sandy loam, Rensselaer loam	83% Agriculture 12% Grass/Pasture 3% Forest
CLG	1380	Blount silt loam, Pewamo silty clay, Glynwood loam, Morley silty clay loam	73% Agriculture 17% Grass/Pasture 5% Forest
AME	298	Rawson sandy loam, Pewamo silty clay, Morley silty clay loam, Blount silt loam	79% Agriculture 15% Grass/Pasture 4% Forest
BME	311	Blount silt loam, Pewamo silty clay, Glynwood loam	85% Agriculture 8% Grass/Pasture 6% Forest
CME	373	Glynwood loam, Blount silt loam, Pewamo silty clay	83% Agriculture 10% Grass/Pasture 4% Forest

Table 3. Measured ranges of analytical uncertainty for studied herbicides (μg/L).

Atrazine	Simazine	Acetochlor	Alachlor	Metolachlor	Glyphosate
+/- 0.84	+/- 1.70	+/- 2.11	+/- 2.48	+/- 2.27	+/-3.20

Table 4. Flow-weighted average herbicide concentrations determined by Daily+Storm sampling.

Flow –Weighted Average Concentrations (μg/L)						
2004						
Site	Atrazine	Simazine	Acetochlor	Alachlor	Metolachlor	Glyphosate
XXL	NA	NA	NA	NA	NA	NA
AXL	5.6	2.0	0.7	0.2[†]	1.8	0.4[†]
ALG	4.8	0.4[†]	0.9	0.2[†]	1.2	0.1[†]
BLG	11.0	0.6	1.1	0.2[†]	3.1	1.3[†]
CLG	3.0	0.1[†]	0.4	0.2[†]	1.2	0.2[†]
AME	1.7	0.0[†]	0.4	0.2[†]	0.9	0.1[†]
BME	21.8	1.5	0.4	0.4	9.5	0.4[†]
CME	3.1	0.9	0.6	0.4	0.6	0.7[†]
2005						
XXL	1.3	0.2[†]	0.1	0.0[†]	1.0	0.3[†]
AXL	0.9	0.2[†]	0.0[†]	0.1[†]	0.7	0.3[†]
ALG	0.3	0.0[†]	0.0[†]	0.1[†]	0.3	0.1[†]
BLG	1.6	0.1[†]	0.2[†]	0.1[†]	0.9	0.4[†]
CLG	4.1	0.0[†]	0.0[†]	0.0[†]	9.1	0.2[†]
AME	0.2[†]	0.1[†]	0.0[†]	0.0[†]	0.3	0.2[†]
BME	0.9	0.1[†]	0.0[†]	0.1[†]	0.4	0.1[†]
CME	0.2[†]	0.0[†]	0.0[†]	0.0[†]	0.2[†]	0.0[†]
2006						
XXL	4.8	0.4[†]	1.2	0.0[†]	1.4	0.1[†]
AXL	3.2	0.5	0.3	0.0[†]	1.4	0.3[†]
ALG	3.5	0.3[†]	0.5	0.1[†]	1.2	0.1[†]
BLG	10.6	2.2	0.4	0.0[†]	6.7	0.6[†]
CLG	4.9	1.0	2.2	0.0[†]	3.0	0.0[†]
AME	0.8	0.0[†]	0.1[†]	0.0[†]	0.2[†]	0.0[†]
BME	10.1	1.2	0.3	0.0[†]	9.1	0.2[†]
CME	10.0	3.1	7.1	0.0[†]	0.8	0.0[†]
2007						
XXL	0.6	0.3[†]	0.1[†]	0.0[†]	0.5	0.2[†]
AXL	0.5	0.7	0.0[†]	0.0[†]	0.4	0.7[†]
ALG	0.3	0.4[†]	0.1[†]	0.0[†]	0.3	0.1[†]
BLG	0.7	0.7	0.3	0.1[†]	1.2	0.5[†]
CLG	0.3	0.0[†]	0.0[†]	0.0[†]	0.3	0.4[†]
AME	0.3	0.0[†]	0.1[†]	0.0[†]	0.5	0.1[†]
BME	0.6	1.7	0.2[†]	0.0[†]	0.4	0.2[†]
CME	0.2[†]	0.0[†]	0.2[†]	0.0[†]	0.1[†]	0.2[†]

[†]Flow-weighted average value is below single sample detection limit.

Table 5. Maximum observed herbicide concentrations from Daily + Storm sampling 2004-2007.

Site	Maximum Observed Concentrations (μg/L)					
	Atrazine	Simazine	Acetochlor	Alachlor	Metolachlor	Glyphosate
XXL	37.7	7.9	9.6	2.6	22.5	24.5
AXL	69.2	22.7	48.6	10.6	23.1	68.7
ALG	79.2	12.9	52.5	5.4	16.8	48.8
BLG	417.0	23.7	33.3	1.9	180.6	117.3
CLG	91.2	13.8	33.1	4.0	344.2	61.0
AME	42.1	7.7	21.1	2.6	32.8	22.6
BME	155.1	38.2	5.2	4.3	69.7	240.4
CME	152.0	44.9	74.6	4.3	11.2	12.1

Table 6. Percent bias and percent standardized root mean square error (E_s) associated with various sampling frequencies and all studied herbicides in drainage water from the study watersheds during 2004.

	2004							
Atrazine	XXL	AXL	ALG	BLG	CLG	AME	BME	CME
Daily Bias	N/A	13.43	11.79	40.00	10.72	NS	39.69	NS
Weekly Bias†	N/A	11.06	12.38	26.69	4.24	7.27	-2.44	6.25
Biweekly Bias‡	N/A	8.11	13.76	32.76	10.45	10.43	11.10	8.01
Daily E_s	N/A	13.43	11.79	40.00	10.72	NS	39.69	NS
Weekly E_s	N/A	18.84	20.72	35.93	8.09	11.71	42.93	23.84
Biweekly E_s	N/A	27.04	32.70	47.76	16.48	17.13	73.15	34.69
Simazine								
Daily Bias	N/A	NS	NS	NS	NS	NS	NS	NS
Weekly Bias†	N/A	-34.24	NS	NS	NS	NS	-4.30	NS
Biweekly Bias‡	N/A	-39.46	NS	NS	NS	NS	-8.65	-3.37
Daily E_s	N/A	NS	NS	NS	NS	NS	NS	NS
Weekly E_s	N/A	173.55	NS	NS	NS	NS	23.74	NS
Biweekly E_s	N/A	292.87	NS	NS	NS	NS	40.17	37.58
Acetochlor								
Daily Bias	N/A	NS	NS	NS	NS	NS	NS	NS
Weekly Bias†	N/A	NS	NS	-3.89	NS	NS	NS	NS
Biweekly Bias‡	N/A	NS	NS	-6.61	NS	NS	NS	NS
Daily E_s	N/A	NS	NS	NS	NS	NS	NS	NS
Weekly E_s	N/A	NS	NS	30.50	NS	NS	NS	NS
Biweekly E_s	N/A	NS	NS	73.31	NS	NS	NS	NS
Alachlor NS								
Metolachlor								
Daily Bias	N/A	NS	NS	NS	NS	NS	25.46	NS
Weekly Bias†	N/A	NS	NS	NS	NS	NS	-1.81	NS
Biweekly Bias‡	N/A	NS	NS	-1.46	NS	NS	5.29	NS
Daily E_s	N/A	NS	NS	NS	NS	NS	25.46	NS
Weekly E_s	N/A	NS	NS	NS	NS	NS	26.94	NS
Biweekly E_s	N/A	NS	NS	13.69	NS	NS	45.30	NS
Glyphosate NS								

† Represents the average of 7 possible values.
‡Represents the average of 14 possible values.
NS = not significant

Table 7. Percent bias and percent standardized root mean square error (E_s) associated with various sampling frequencies and all studied herbicides in drainage water from the study watersheds during 2005.

	2005							
Atrazine	XXL	AXL	ALG	BLG	CLG	AME	BME	CME
Daily Bias	NS	NS	NS	NS	13.38	NS	NS	NS
Weekly Bias†	NS	NS	NS	10.04	11.70	NS	-13.07	NS
Biweekly Bias‡	NS	NS	NS	8.58	14.75	NS	-13.02	-0.84
Daily E_s	NS	NS	NS	NS	13.38	NS	NS	NS
Weekly E_s	8.69	NS	NS	20.24	55.05	NS	59.77	NS
Biweekly E_s	24.23	NS	NS	37.17	82.16	NS	81.92	18.03
Simazine NS								
Acetochlor NS								
Alachlor NS								
Metolachlor								
Daily Bias	NS	NS	NS	NS	1.56	NS	NS	NS
Daily Bias	NS	NS	NS	NS	10.00	NS	NS	NS
Weekly Bias†	NS	NS	NS	NS	12.05	NS	NS	NS
Biweekly Bias‡	NS	NS	NS	NS	1.56	NS	NS	NS
Daily E_s	NS	NS	NS	NS	72.69	NS	NS	NS
Weekly E_s	16.32	NS	NS	NS	121.05	NS	NS	NS
Glyphosate NS								

† Represents the average of 7 possible values.

‡Represents the average of 14 possible values.

NS = not significant

Table 8. Percent bias and percent standardized root mean square error (E_s) associated with various sampling frequencies and all studied herbicides in drainage water from the study watersheds during 2006.

	2006							
Atrazine	XXL	AXL	ALG	BLG	CLG	AME	BME	CME
Daily Bias	19.47	NS	NS	24.63	5.63	NS	25.11	33.75
Weekly Bias†	3.89	2.18	4.60	12.98	8.17	-1.25	-12.35	26.33
Biweekly Bias‡	14.06	0.83	2.24	25.46	16.72	-7.43	17.64	43.42
Daily E_s	19.47	NS	NS	24.63	5.63	NS	25.11	33.75
Weekly E_s	49.97	31.44	41.84	71.87	29.40	6.72	74.14	50.47
Biweekly E_s	72.72	65.19	83.08	105.00	59.46	41.80	96.37	72.38
Simazine								
Daily Bias	NS	NS	NS	NS	NS	NS	NS	NS
Weekly Bias†	NS	NS	NS	1.40	NS	NS	-0.99	18.11
Biweekly Bias‡	NS	NS	NS	-0.01	-0.47	NS	-1.89	23.62
Daily Es	NS	NS	NS	NS	NS	NS	NS	NS
Weekly Es	NS	NS	NS	14.45	NS	NS	6.46	26.24
Biweekly Es	NS	NS	NS	32.64	4.66	NS	17.38	37.04
Acetochlor								
Daily Bias	NS	NS	NS	NS	NS	NS	NS	6.71
Weekly Bias†	NS	NS	NS	NS	-1.40	NS	NS	13.71
Biweekly Bias‡	NS	NS	NS	NS	-5.34	NS	NS	27.17
Daily E_s	NS	NS	NS	NS	NS	NS	NS	6.71
Weekly E_s	NS	NS	NS	NS	7.33	NS	NS	34.24
Biweekly E_s	28.35	NS	NS	NS	39.60	NS	NS	72.74
Alachlor NS								
Metolachlor								
Daily Bias	NS	NS	NS	NS	NS	NS	14.55	NS
Weekly Bias†	NS	NS	NS	7.61	-0.66	NS	-0.44	NS
Biweekly Bias‡	NS	-0.62	-3.18	12.04	-1.38	NS	21.41	NS
Daily E_s	NS	NS	NS	NS	NS	NS	14.55	NS
Weekly E_s	NS	NS	NS	29.45	12.01	NS	48.67	NS
Biweekly E_s	30.12	6.09	35.02	53.30	39.21	NS	69.54	NS
Glyphosate NS								

† Represents the average of 7 possible values.
‡Represents the average of 14 possible values.
NS = not significant

Table 9. Percent bias and percent standardized root mean square error (E_s) associated with various sampling frequencies and all studied herbicides in drainage water from the study watersheds during 2007.

	2007							
Atrazine	XXL	AXL	ALG	BLG	CLG	AME	BME	CME
Daily Bias	NS	NS	NS	NS	NS	NS	NS	NS
Weekly Bias†	NS	NS	NS	-4.88	NS	NS	NS	NS
Biweekly Bias‡	NS	NS	NS	-3.39	NS	NS	-0.17	-0.26
Daily E_s	NS	NS	NS	NS	NS	NS	NS	NS
Weekly E_s	NS	NS	NS	29.55	NS	NS	NS	NS
Biweekly E_s	16.77	NS	NS	29.04	NS	NS	1.61	4.66
Simazine NS								
Acetochlor NS								
Alachlor NS								
Metolachlor								
Daily Bias	NS	NS	NS	NS	NS	NS	NS	NS
Weekly Bias†	NS	NS	NS	-2.01	NS	NS	NS	NS
Biweekly Bias‡	NS	NS	NS	-1.88	NS	NS	0.05	NS
Daily E_s	NS	NS	NS	NS	NS	NS	NS	NS
Weekly E_s	NS	NS	NS	15.79	NS	NS	NS	NS
Biweekly E_s	NS	NS	NS	20.84	NS	NS	0.20	NS
Glyphosate NS								

† Represents the average of 7 possible values.

‡Represents the average of 14 possible values.

NS = not significant

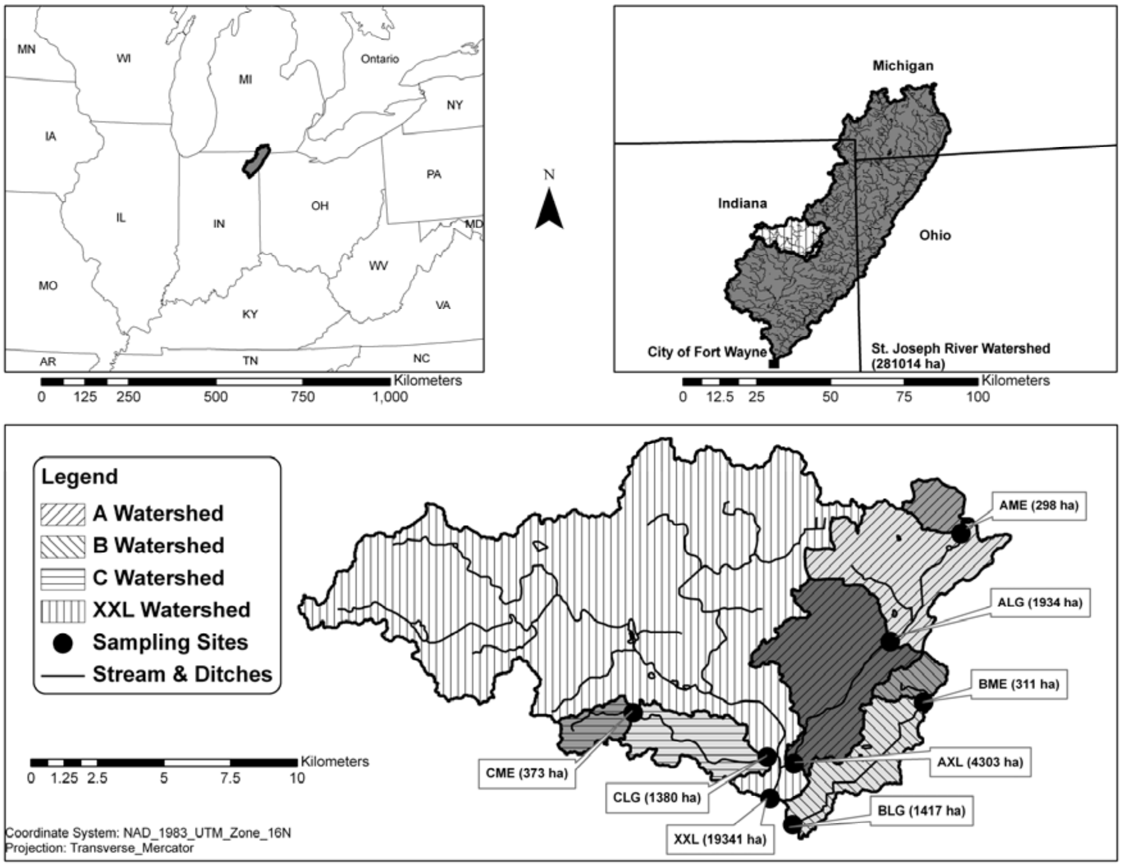


Figure 1. Experimental watersheds and monitoring locations. Watersheds having the same shading are in the same size class.

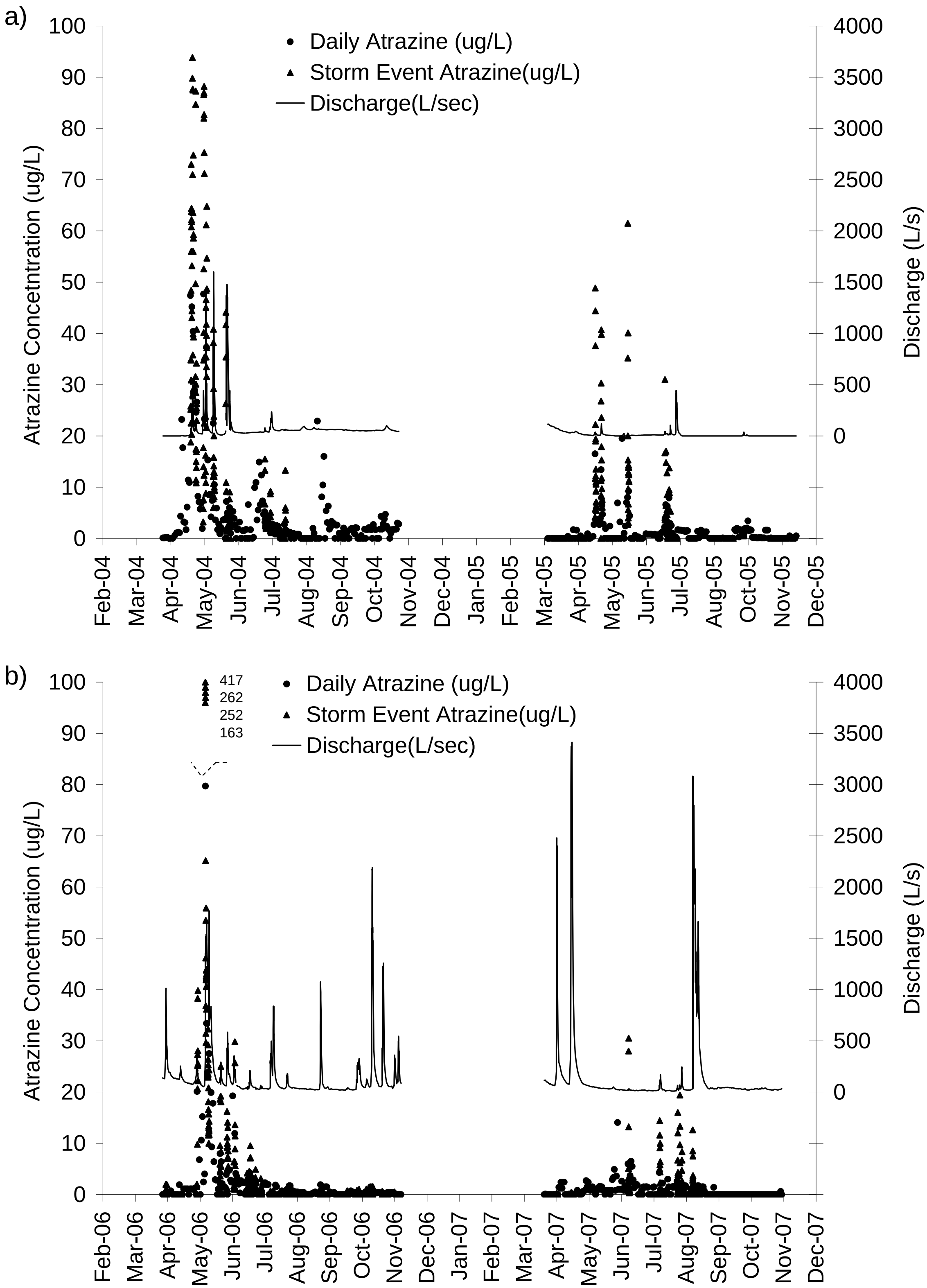
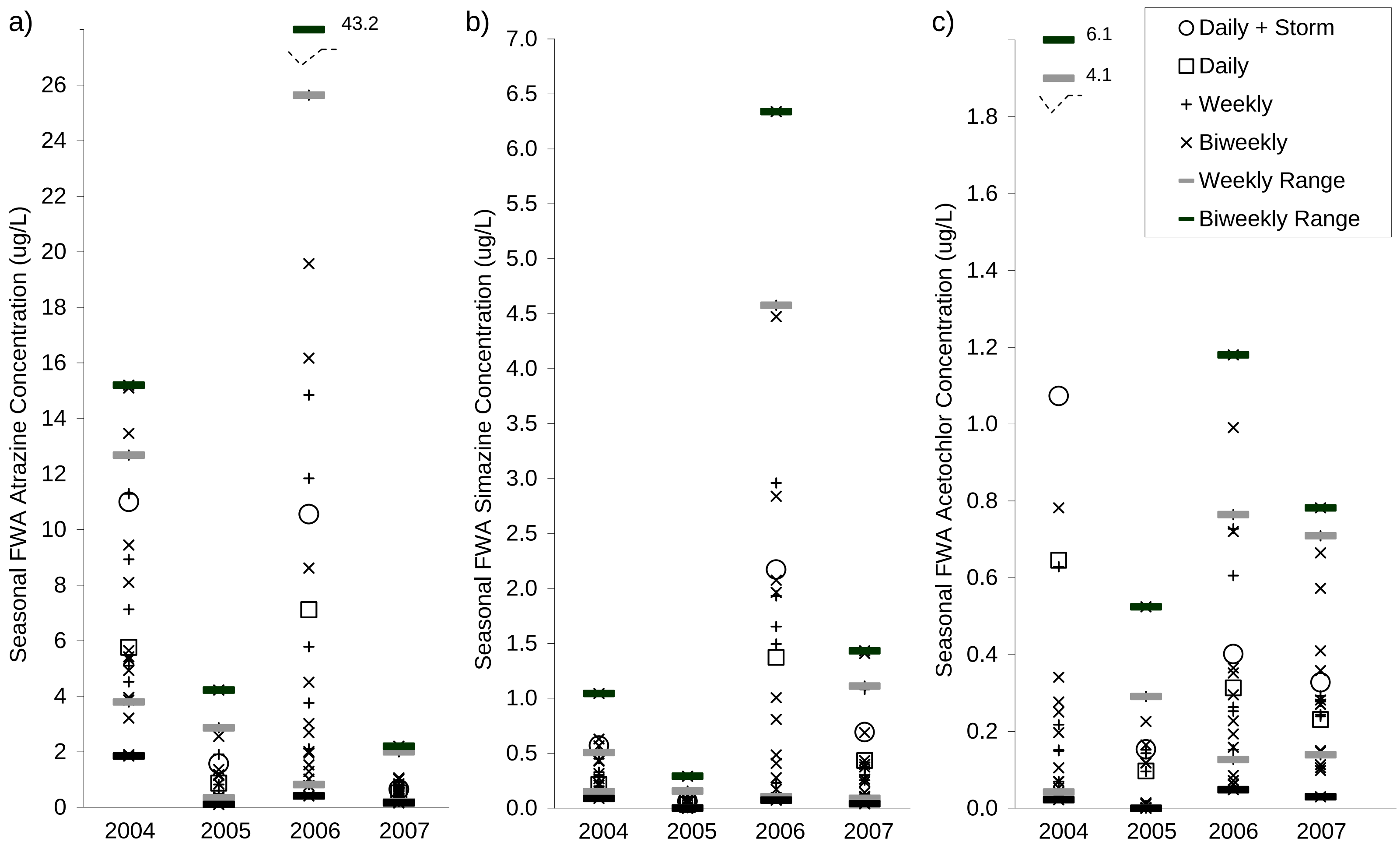


Figure 2. Discharge and atrazine levels measured at BLG: a) 2004-2005, b) 2006-2007.



a)
43.2
Seasonal FWA Atrazine Concentration (ug/L)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
2004
2005
2006
2007
b)
Seasonal FWA Simazine Concentration (ug/L)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
2004
2005
2006
2007
c)
6.1
4.1
Seasonal FWA Acetochlor Concentration (ug/L)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2004
2005
2006
2007
Daily + Storm
Daily
Weekly
Biweekly
Weekly Range
Biweekly Range

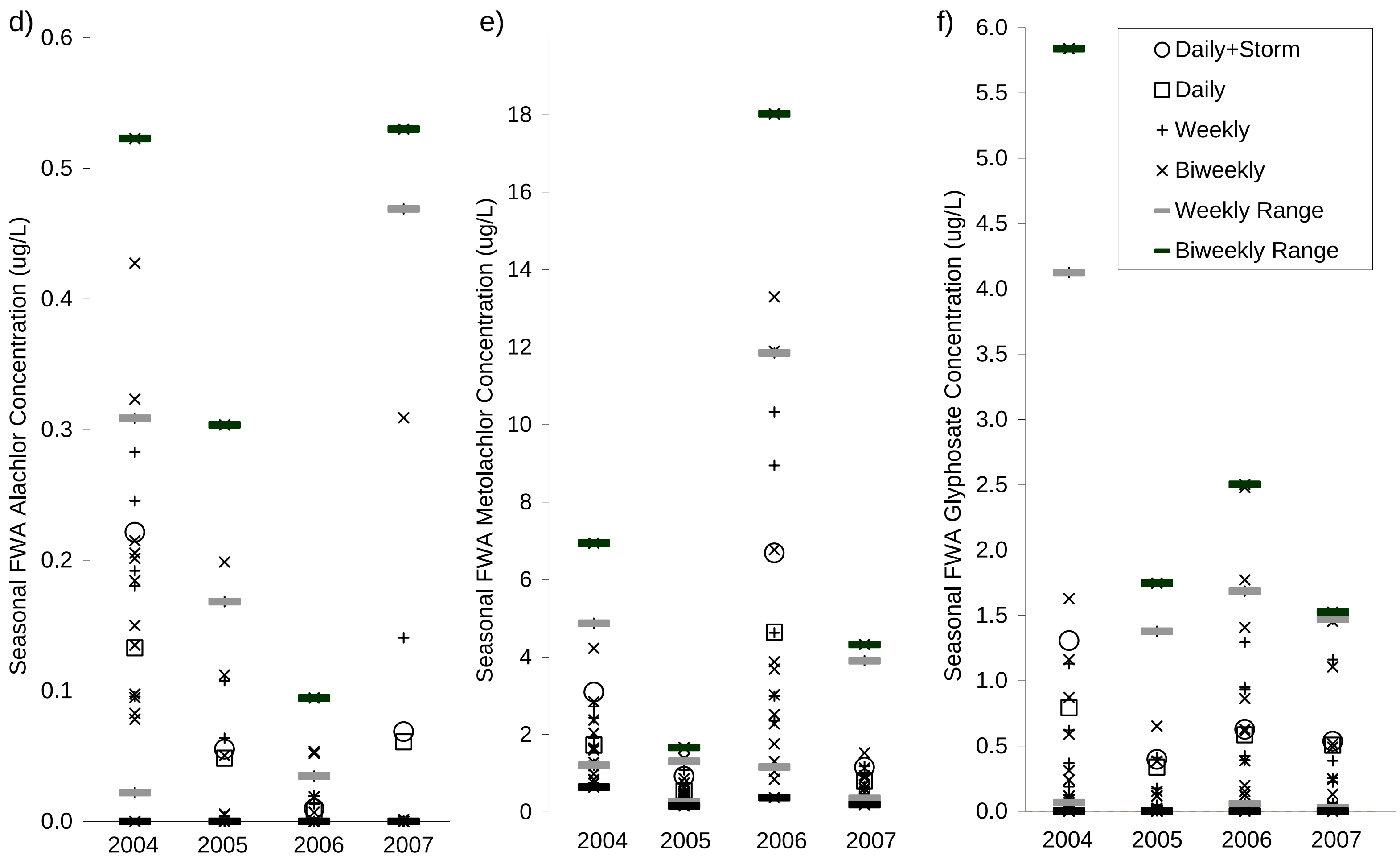


Figure 3. Flow-weighted average concentrations of a) atrazine, b) simazine c) acetochlor d) alachlor e) metolachlor and f) glyphosate at BLG as calculated from Daily+Storm, Daily, Weekly, and Biweekly sampling