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# Implications of sampling frequency to herbicide conservation effects assessment

E.A. Pappas, C. Huang, and D.L. Bucholtz

**Abstract:** Herbicide losses from agriculture represent potential human health hazards, and are one focus of the Conservation Effects Assessment Project. 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 to 2007 cropping seasons at eight monitoring sites located at the outlets of sub basins ranging in size from 298 to 19,341 ha (736 to 47,793 ac). Herbicide data were analyzed based upon daily sampling, then for 7 possible weekly sampling scenarios, and 14 possible biweekly sampling scenarios. In addition, 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.

**Key words:** atrazine—Conservation Effects Assessment Project (CEAP)—herbicide—maximum contaminant level—water quality

**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 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 US 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 and/or may be on the contaminant candidate list, 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; US Geological Survey 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 Conservation Effects Assessment Project sites, resource constraints, and significant expenses 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, and more than 200,000 residents. The watershed is 281,014 ha (694,400 ac) in size and is studied as part of the Conservation Effects Assessment Project. The herbicides atrazine, simazine, alachlor, acetochlor, metolachlor, and glyphosate are used in the study area, where corn (*Zea mays*) and soybeans (*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

**Elizabeth A. Pappas** is a research hydraulic engineer, **Chi-hua Huang** is a soil scientist and research leader, and **Dennis L. Bucholtz** is a chemist at the National Soil Erosion Research Laboratory, USDA Agricultural Research Service, West Lafayette, Indiana.

**Table 1**
**Characteristics of studied herbicides.**

| Herbicide | Selected common trade names | MCL ($\mu g\ L^{-1}$) | Reference |
|---|---|---|---|
| Atrazine | AAtrex, Bicep II Magnum (with metolachlor) | 3 | USEPA 2006a |
| Simazine | Princep, Sinbar | 4 | USEPA 2006d |
| Acetochlor | Harness, Surpass | NA† | USEPA 2008 |
| Alachlor | Lasso, Lariat (with atrazine) | 2 | USEPA 2006b |
| Metolachlor | Dual, Bicep II Magnum (with atrazine) | 100†‡ | USEPA 1995 |
| Glyphosate | Accord, Roundup | 700 | USEPA 2006c |

† No maximum contaminant level has been established for this chemical as of 2007, but this chemical is on the US Environmental Protection Agency Contaminant candidate list for maximum contaminant level development.

‡ This value represents a health advisory level set by the US Environmental Protection Agency.

**Table 2**
**Experimental watershed characteristics.**

| Site | Area (ha) | Predominant soil types | Land management |
|---|---|---|---|
| XXL | 19,341 | Blount silt loam, Pewamo silty clay, Glynwood loam, Rawson sandy loam, Rensselaer loam, Sebewa sandy loam, Morley silty clay loam | 58% agriculture<br>17% grass/pasture<br>14% forest |
| AXL | 4,303 | Blount silt loam, Pewamo silty clay, Glynwood loam, Rawson sandy loam, Rensselaer loam, Sebewa sandy loam | 78% agriculture<br>14% grass/pasture<br>6% forest |
| ALG | 1,934 | Blount silt loam, Pewamo silty clay, Glynwood loam, Rawson sandy loam, Morley silty clay loam | 77% agriculture<br>16% grass/pasture<br>6% forest |
| BLG | 1,417 | Blount silt loam, Pewamo silty clay, Glynwood loam, Sebewa sandy loam, Rensselaer loam | 83% agriculture<br>12% grass/pasture<br>3% forest |
| CLG | 1,380 | Blount silt loam, Pewamo silty clay, Glynwood loam, Morley silty clay loam | 73% agriculture<br>17% grass/pasture<br>5% forest |
| AME | 298 | Rawson sandy loam, Pewamo silty clay, Morley silty clay loam, Blount silt loam | 79% agriculture<br>15% grass/pasture<br>4% forest |
| BME | 311 | Blount silt loam, Pewamo silty clay, Glynwood loam | 85% agriculture<br>8% grass/pasture<br>6% forest |
| CME | 373 | Glynwood loam, Blount silt loam, Pewamo silty clay | 83% agriculture<br>10% grass/pasture<br>4% forest |

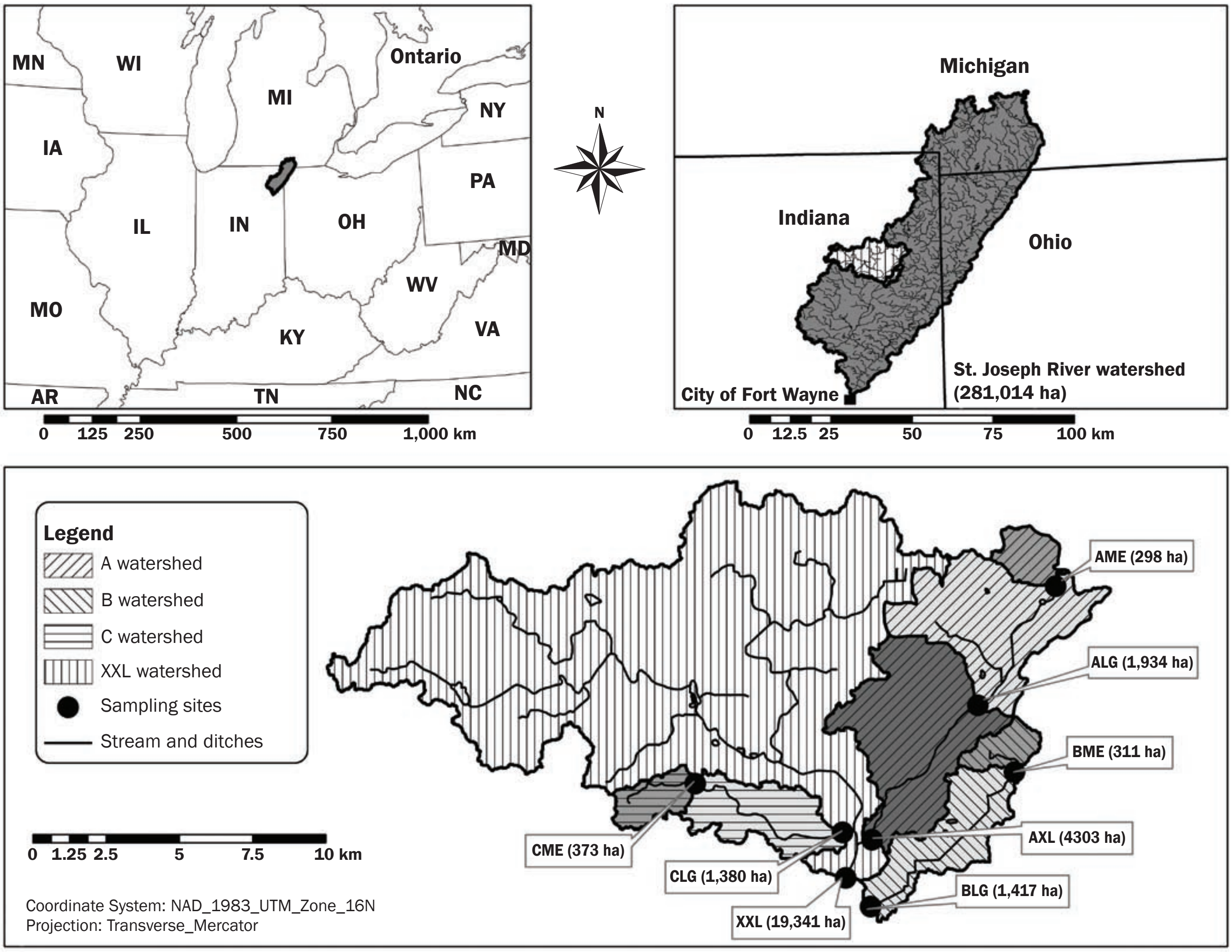
Notes: For the site names, the first letter is a watershed designator (A, B, or C). The following letters represent size (medium [ME], large [LG], or extra large [XL]). One extra extra large watershed was monitored and was referenced using XXL with no A, B, or C designator.

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 soybeans 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 soybeans 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°C (50°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 (figure 1). In addition, a site along the main Cedar Creek channel was moni-

**Figure 1**
Experimental watersheds and monitoring locations.




Note: Watersheds having the same shading are in the same size class.

tored (an extra-extra-large-sized watershed). These nominally represented three "replications" each of medium-sized (298 to 373 ha [736 to 921 ac]) watersheds (monitored at AME, BME, CME) and large-sized (1,380 to 1,934 ha [3,411 to 4,780 ac]) watersheds (monitored at ALG, BLG, CLG), one extra-large-sized (4,303 ha [10,634 ac]) watershed (monitored at AXL), and one extra-extra-large-sized (19,341 ha [47,793 ac]) watershed (monitored at XXL).

***Water Quality Sampling and Analysis.*** Water samples were collected daily for atrazine, simazine, alachlor, acetochlor, metolachlor, and glyphosate analysis at the seven ditch monitoring sites during the 2004 to 2007 cropping seasons (April to November) and at the main channel monitoring site during the 2005 to 2007 cropping seasons. Each 300-mL (10.1-fl oz) daily sample was a composite of six 50-mL (1.69-fl oz) samples taken every four hours, using Isco 6712 autosamplers (Isco Inc., Lincoln, Nebraska). 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 minutes for 30 hours and were composited into 300-mL 90-minute samples.

Within three days of sampling and refrigeration, all samples were filtered by vacuum flask through a nylon membrane (0.45 μm [0.0000117 in]) into glass vials and frozen immediately until analysis could be performed (maximum frozen time of three months). Atrazine, simazine, acetochlor, alachlor, and metolachlor were preconcentrated by solid-phase microextraction according to a modified USEPA method 525.2 described by Rocha et al. (2007) and quantified by gas chromatography with mass spectrometry. In this method, NaCl was added to 7.5-mL (0.25-oz) samples to 83%, and exposed to a solid-phase microextraction fiber coated with 100 μm (0.00394 in) of polydimethylsiloxane for a 40-minute extraction period

**Table 3**
Measured ranges of analytical uncertainty for studied herbicides.

| Herbicide | Measured ranges of analytical uncertainty (μg $L^{-1}$) |
|---|---|
| Atrazine | ±0.84 |
| Simazine | ±1.70 |
| Acetochlor | ±2.11 |
| Alachlor | ±2.48 |
| Metolachlor | ±2.27 |
| Glyphosate | ±3.20 |

with agitation at 40°C (104°F). Afterward, the fiber was directly introduced into the injector of the gas chromatography/mass spectrometry for separation and analysis. An internal standard was used in every sample (terbuthylazine, 10 μg $L^{-1}$), and spiked check samples were run after every nine samples to ensure quality. The detection limit for atrazine, acetochlor, alachlor, and metolachlor was 0.25 μg $L^{-1}$, while the detection limit for simazine was 0.5 μg $L^{-1}$. Glyphosate was quantified by high performance liquid chromatography with post-column derivitization and fluorescence detection, according to USEPA method 547 (USEPA 1990) (detection limit = 2 μg $L^{-1}$).

**Table 4**
Flow-weighted average herbicide concentrations determined by daily + storm sampling.

| | Flow-weighted average concentrations (μg $L^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| Site | Atrazine | Simazine | Acetochlor | Alachlor | Metolachlor | Glyphosate |
| **2004** | | | | | | |
| 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.

***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 $L^{-1}$) 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). Data was collected every day—all seven days of the week. In order to simulate a weekly sampling regime (weekly), calculations were performed using data grouped by weekday. Data collected on Sundays were grouped, data collected on Monday were grouped, etc. To simulate biweekly sampling (biweekly), calculations were performed using data grouped by weekday and by even and odd weeks. Data from even Sundays, odd Sundays, and even Mondays, etc., were grouped together, and this sampling method was repeated for every day of the week for even weeks and for 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 ($\alpha = 0.05$) using the standard deviation of seven randomly selected spike samples distributed over the four-season period. Uncertainty was calculated as the product of the standard deviation and the t-value according to a method performance test described in

USEPA 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

$$C_{ds} - C_e , \quad (1)$$

**Table 5**
**Maximum observed herbicide concentrations from daily + storm sampling 2004 to 2007.**

| | Maximum observed concentrations (µg $L^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| Site | 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.**

| | Site | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | XXL | AXL | ALG | BLG | CLG | AME | BME | CME |
| **Atrazine** | | | | | | | | |
| 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 | | | | | | | | |

Note: NS = not significant.
† Average of 7 possible values.
‡ Average of 14 possible values.

**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.**

| | Site | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | XXL | AXL | ALG | BLG | CLG | AME | BME | CME |
| **Atrazine** | | | | | | | | |
| 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 | | | | | | | | |

Note: NS = not significant.
† Average of 7 possible values.
‡ Average of 14 possible values.

where $C_{ds}$ = the nearest uncertainty boundary of the daily + storm derived herbicide concentration (µg $L^{-1}$), and $C_e$ = the estimated value derived by daily, weekly, or biweekly sampling (µg $L^{-1}$). 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:

$$\beta = \frac{C_{ds} - C_e}{C_{ds}} \times 100 \cdot \quad (2)$$

The standardized root mean square error is defined as

$$E_s = \frac{\sqrt{\frac{\sum_{i=1}^{n} (C_{dsi} - C_{ei})^2}{n}}}{C_{ds}}, \quad (3)$$

where $C_{dsi}$ = the $i^{th}$ daily + storm derived value and $C_{ei}$ = the $i^{th}$ estimated value based on daily, weekly, or biweekly sampling.

## Results and Discussion

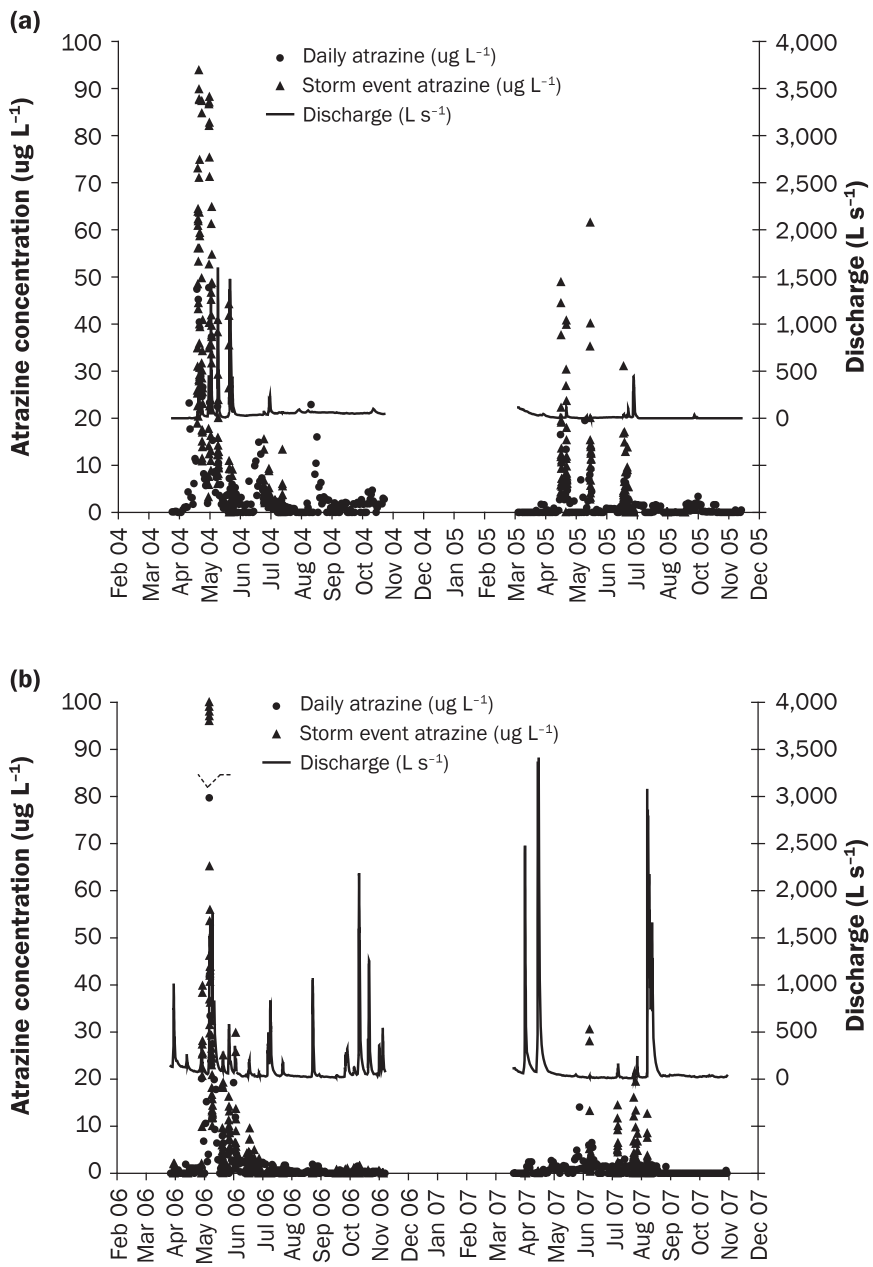
***Temporal Variability of Herbicide Levels.*** Using all available data (daily + storm), seasonal FWA herbicide concentrations and maximum observed herbicide concentrations are given in tables 4 and 5. Flow-weighted average atrazine levels were higher during 2004 and 2006 than during 2005 and 2007. 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 to 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 (figure 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 $L^{-1}$. 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 will 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 to 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 and 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 to be 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 1,400 to 10,980 ha (3,459 to 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. Standardized root mean square error 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

**Figure 2**

**Discharge and atrazine levels measured at BLG: (a) 2004 to 2005; (b) 2006 to 2007.**




not significant for alachlor and glyphosate. Therefore, significant errors in FWA atrazine and metolachlor concentrations can be expected to be 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 to be 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

**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.

| | Site | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | XXL | AXL | ALG | BLG | CLG | AME | BME | CME |
| **Atrazine** | | | | | | | | |
| 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 $E_s$ | NS | NS | NS | NS | NS | NS | NS | NS |
| Weekly $E_s$ | NS | NS | NS | 14.45 | NS | NS | 6.46 | 26.24 |
| Biweekly $E_s$ | 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 $E$ | 30.12 | 6.09 | 35.02 | 53.30 | 39.21 | NS | 69.54 | NS |
| **Glyphosate:** NS | | | | | | | | |

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

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 $E_s$ was also observed in a study that examined sampling frequencies from every 5 minutes (high frequency) to every 360 minutes (low frequency) (King and Harmel 2003).

## Summary and Conclusions

The herbicides atrazine, simazine, acetochlor, alachlor, metolachlor, and glyphosate were monitored in seven agricultural drainage ditches feeding a major drinking water source during the 2004 to 2007 cropping seasons (April to November) and in one natural channel during the 2006 to 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 minutes 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

**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.**

| | Site | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | XXL | AXL | ALG | BLG | CLG | AME | BME | CME |
| **Atrazine** | | | | | | | | |
| 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 | | | | | | | | |

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

biweekly sampling also can not be expected to accurately represent daily + storm based FWA atrazine and metolachlor concentrations and additionally cannot 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.

## Disclaimer

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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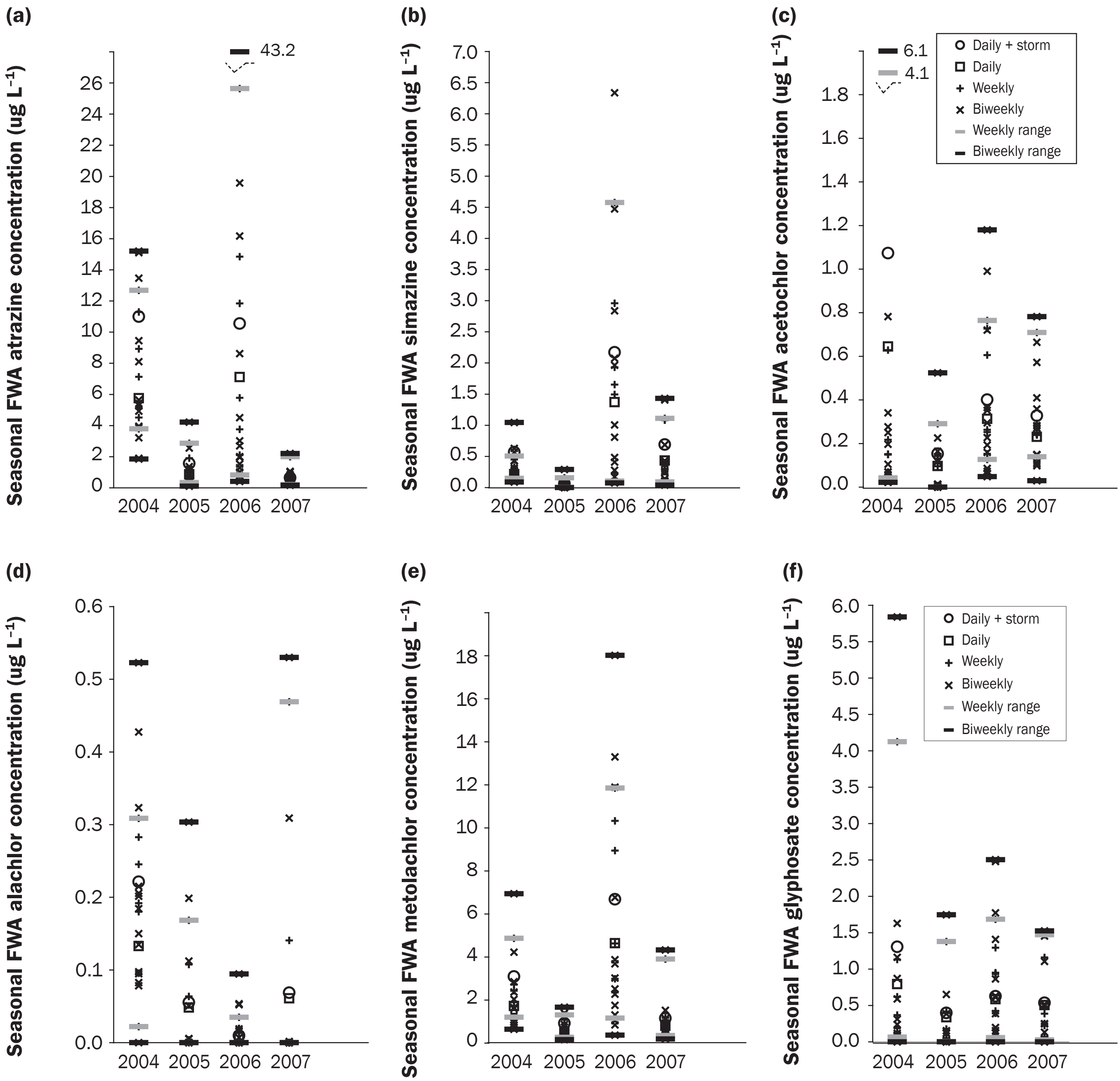
**Figure 3**

**Flow-weighted average (FWA) 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.**





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