

Stream Transport of Herbicides and Metabolites in a Tile-Drained, Agricultural Watershed

Mark B. David,* Lowell E. Gentry, Karen M. Starks, and Richard A. Cooke

ABSTRACT

The occurrence of metabolites of many commonly used herbicides in streams has not been studied extensively in tile-drained watersheds. We collected water samples throughout the Upper Embarras River watershed [92% corn, *Zea mays* L., and soybean, *Glycine max* (L.) Merr.] in east-central Illinois from March 1999 through September 2000 to study the occurrence of atrazine [2-chloro-4-ethylamino-6-isopropylamino-s-triazine], metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(methoxy-1-methylethyl) acetamide], alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl) acetamide], acetochlor [2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl) acetamide], and their metabolites. River water samples were collected from three subwatersheds of varying tile density (2.8–5.3 km tile km⁻²) and from the outlet (United States Geological Survey [USGS] gage site). Near-record-low totals for stream flow occurred during the study, and nearly all flow was from tiles. Concentrations of atrazine at the USGS gage site peaked at 15 and 17 µg L⁻¹ in 1999 and 2000, respectively, and metolachlor at 2.7 and 3.2 µg L⁻¹; this was during the first significant flow event following herbicide applications. Metabolites of the chloroacetanilide herbicides were detected more often than the parent compounds (evaluated during May to July each year, when tiles were flowing), with metolachlor ethanesulfonic acid [2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoethanesulfonic acid] detected most often (>90% from all sites), and metolachlor oxanilic acid [2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoacetic acid] second (40–100% of samples at the four sites). When summed, the median concentration of the three chloroacetanilide parent compounds (acetochlor, alachlor, and metolachlor) at the USGS gage site was 3.4 µg L⁻¹, whereas it was 4.3 µg L⁻¹ for the six metabolites. These data confirm the importance of studying chloroacetanilide metabolites, along with parent compounds, in tile-drained watersheds.

ILLINOIS' AGRICULTURAL SOILS are some of the most productive in the world, with corn and soybean the two major crops in the state. To achieve desirable economic yields that meet the increasing market demand for more food worldwide, the use of herbicides and other agrochemicals is a critical component of current production systems. The most commonly used herbicides in the USA before 1995 were atrazine, cyanazine [2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropionitrile], metolachlor, and alachlor (Meyer and Thurman, 1996; Battaglin and Goolsby, 1999). Since

1994, however, acetochlor has replaced alachlor in the U.S. Midwest for corn weed control (Battaglin and Goolsby, 1999) and was detected in surface waters during the year it was first used (Kolpin et al., 1996a). Each of these herbicides has been found in the Mississippi River as it nears the Gulf of Mexico, demonstrating their movement into rivers and subsequent transport downstream (Clark and Goolsby, 2000).

Studies of rivers in the Midwest have shown that quite often the highest concentrations of herbicides are measured during the first significant streamflow increase (runoff event) after herbicide applications (Thurman et al., 1991; Scribner et al., 1994; Gentry et al., 2000). Therefore, many studies have focused sampling on the first streamflow event in late spring to early summer. From samples collected in 1989 through 1990, USGS studies showed that atrazine and alachlor were the primary herbicides in storm runoff in the Midwest and that concentrations were frequently above drinking water standards (Scribner et al., 1994). Battaglin and Goolsby (1999) and Scribner et al. (2000a) used sampling from the first large event following applications to examine whether changes in herbicide use were reflected in concentrations in Midwestern rivers. They indicated that both the decrease in alachlor use and increase in acetochlor were reflected in river concentrations, but that for other herbicides (metolachlor, cyanazine, and atrazine), changes in river concentrations could not be attributed solely to use patterns (Battaglin and Goolsby, 1999; Scribner et al., 2000a).

Clark and Goolsby (1999) evaluated acetochlor in streams to determine the movement of this new herbicide in more detail. They found that most of the acetochlor measured in the Mississippi River was from subbasins draining Illinois, Iowa, and Indiana, although only 2% of the samples exceeded the 2 µg L⁻¹ standard for drinking water (78% of the 375 samples collected at 32 stream sites contained detectable concentrations). Clark and Goolsby (1999) indicated that overall, acetochlor behaved like other acetanilide herbicides, with less persistence than triazine herbicides, which was consistent with previous studies comparing acetanilides with triazines (Larson et al., 1997; Clark and Goolsby, 1999).

Subsurface (tile) drainage is commonly and extensively used in Illinois to artificially drain fields and allow production agriculture. Agrochemicals can move through soil profiles to tile lines, where they are carried directly into surface waters. This has been shown to contribute large amounts of N to various watersheds in

M.B. David, L.E. Gentry, and K.M. Starks, University of Illinois, Department of Natural Resources and Environmental Sciences, W-503 Turner Hall, 1102 South Goodwin Avenue, Urbana, IL 61801. R.A. Cooke, University of Illinois, Department of Agricultural Engineering, 332J AESB, 1304 West Pennsylvania Avenue, Urbana, IL 61801. L.E. Gentry, current address: University of California, Environmental Studies, 1156 High Street, Santa Cruz, CA 95064. Received 9 July 2002. *Corresponding author (mbdavid@uiuc.edu).

Published in J. Environ. Qual. 32:1790–1801 (2003).

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677 S. Segoe Rd., Madison, WI 53711 USA

Abbreviations: DEA, deethylatrazine; DIA, deisopropylatrazine; ESA, ethanesulfonic acid; GC, gas chromatography; HPLC, high-performance liquid chromatography; MS, mass spectrometry; OA, oxanilic acid; USGS, United States Geological Survey.

the Midwest (e.g., Kladivko et al., 1991; David et al., 1997; Gentry et al., 1998), particularly during high rainfall events. Recent studies have also shown that tiles can transport large amounts and high concentrations of P through preferential flow processes (i.e., where solutes are transported through only a small portion of the soil volume) (Gaynor and Findlay, 1995; Gächter et al., 1998; Stamm et al., 1998). In areas with low livestock intensities and extensive tile drainage, such as east-central Illinois, tile transport of P can be as important or more important than surface transport (Xue et al., 1998). Pesticide transport in tiles may also be as important as surface runoff in extensively tile-drained watersheds of Illinois.

Although the movement of nitrate is well known in tile-drainage waters (and P is just becoming known), pesticides have not been as well studied (Flury, 1996). Kladivko et al. (1991) demonstrated on experimental farms that preferential flow to tile lines could quickly cause the movement of small amounts of pesticides from soils into tile lines. Buhler et al. (1993) pointed out that herbicide movement in subsurface drainage from agricultural land is still not well understood despite a large body of information on herbicides in the environment. Gentry et al. (2000) showed that herbicides (atrazine and metolachlor) can be rapidly transported through soils to tile drains and surface waters in central Illinois. Gaynor et al. (1995, 2001) have also shown the importance of both surface and subsurface transport of herbicides, and how alterations in one can change the other.

Donald et al. (1998) examined herbicide distribution and variability across a small watershed in Missouri, and observed that there are few published studies on herbicide concentrations and variability in surface waters at this scale (7250 ha). Fenelon and Moore (1998) studied the transport of herbicides in the Sugar Creek watershed in Indiana that had extensive tile drainage. They observed that tile-drainage patterns of atrazine and atrazine metabolites in the watershed were similar to seasonal trends in Sugar Creek.

Metabolites of pesticides are now known to be important contaminants of both ground water and surface water (Kalkhoff et al., 1998; Kolpin et al., 1996b, 2000, 2001; Scribner et al., 2000b), and in many studies the metabolites have been found at higher concentrations than the parent compounds. This was known previously for triazine herbicides, but has only recently been shown for chloroacetanilide herbicides (parent compounds are acetochlor, alachlor, and metolachlor). Thurman et al. (1996) found that the median concentration of an alachlor metabolite (alachlor ethanesulfonic acid [ESA], 2-[(2,6-diethylphenyl) (methoxymethyl)amino]-2-oxoethanesulfonic acid) exceeded the median concentration of alachlor in rivers and reservoirs of the Midwest. Kalkhoff et al. (1998) determined that several metabolites of chloroacetanilide herbicides were common in Iowa surface waters and ground waters, and were found more frequently and at higher concentrations than the parent compounds (80% of the mass in surface waters consisted of metabolites). Kolpin et al. (2000) showed that most

of an herbicide's measured concentration was in the form of metabolites in Iowa ground water. Kalkhoff et al. (1998) suggest the reason chloroacetanilide herbicides were so infrequently found in previous studies was because the metabolites were not determined.

Phillips et al. (1999) evaluated metolachlor and its metabolites in both tile drainage and stream runoff in New York. They observed that two metabolites of metolachlor (metolachlor ESA and metolachlor oxanilic acid [OA]) were 200 to 1800 times higher in concentrations than the parent compound in tile drainage. In the stream they evaluated, metolachlor ESA was 2 to 45 times higher in concentration than metolachlor, although concentrations of both were much less than in tile-drainage water. In fine-textured soils, Phillips et al. (1999) found that the transport of metolachlor ESA was greater than metolachlor OA. Aga and Thurman (2001) reported that both alachlor ESA and metolachlor ESA were transported at higher concentrations and to deeper soil depths as compared with their parent compounds. Tauler et al. (2000) found that the major source of alachlor ESA in outflows from reservoirs in the Midwest was related to the spring flush and seasonal runoff, with ground water a source. These studies suggest that ground water may be a much more important source of chloroacetanilide metabolites than their parent compounds, and we would expect surface waters in heavily tile-drained watersheds to reflect this.

Chlorinated atrazine metabolites (primarily deethylatrazine [DEA], 2-amino-4-chloro-6-isopropylamino-*s*-triazine, and deisopropylatrazine [DIA], 2-amino-4-chloro-6-ethylamino-*s*-triazine) are known to be common contaminants of surface and ground waters in the Midwest (Thurman et al., 1992; Burkart and Kolpin, 1993; Kolpin et al., 1995, 1996b; Barrett, 1996). However, Lerch et al. (1998) reported that hydroxylated atrazine metabolites can also be important, demonstrating that the number of herbicide metabolites being detected is continually increasing. For example, cyanazine degradates were recently observed to be more prevalent than the parent compound in ground water across Iowa (Kolpin et al., 2001).

In this study, we collected water samples and measured herbicides (triazines and chloroacetanilides) in river waters to obtain concentrations throughout the Upper Embarras River watershed, Illinois, and to estimate herbicide loads (in subwatersheds with variable subsurface drainage densities and the overall watershed). The specific objectives of our study were to (i) report herbicide concentrations and loadings in the river of an agricultural watershed at several locations across a range of tile-drainage densities, focusing on the period when tile drainage occurs; (ii) evaluate the importance of tile drainage versus surface runoff in contributing to herbicide concentrations and loads during various flow events in each subwatershed; and (iii) examine the occurrence and concentrations of both parent compounds and metabolites of the studied herbicides.

MATERIALS AND METHODS

Field Sampling and Monitoring

Four instrumented sampling sites in the Upper Embarras River watershed were used in this study. This watershed has been previously described (David et al., 1997) and has been the focus of detailed studies on N and P export (Xue et al., 1998). It is 92% row-cropped in corn and soybean agriculture (typical of the Midwest) and is extensively tile-drained. The primary sampling site was located at the USGS streamflow gaging station (Embarras River near Camargo, IL; Station no. 03343400), the outlet of the 48 173-ha watershed. Three subwatershed sites were selected from detailed geographic information system tile maps of the Upper Embarras River watershed (David et al., 2002). These sites were equipped with flow monitoring devices at points that represent subwatersheds with low (S2, 2.8 km tile km⁻²), medium (S3, 4.35 km tile km⁻²), and high (S1, 5.3 km tile km⁻²) tile-drainage densities. Corresponding watershed areas were 9300, 3100, and 2939 ha for low-, medium-, and high-tile-drainage subwatersheds. Each of these three sites was equipped with an Isco (Lincoln, NE) Model 2900 water sampler that allowed for flow-proportional sampling. The normal sampling line into the Isco sampler was replaced with Teflon tubing, and special Isco bases allowed

the use of glass sampling containers. In addition to these four sites, 13 other sampling locations were established in the watershed to obtain grab samples from all branches and subwatersheds (Fig. 1). Samples from these locations were collected monthly from March 1999 through August 2000. For the USGS gage site on the Embarras River, samples were collected daily to weekly to monthly, depending on flow, from 29 Mar. 1999 through 12 Sept. 2000, for a total of 71 samples for herbicide analysis. During the largest flow events, samples were collected twice a day at this site.

The grab samples were collected in precleaned 120- or 500-mL glass bottles with Teflon-lined caps by submerging the bottle in the middle of the river or in an area with rapid flow. Several bottles were used to provide samples for each of the laboratories conducting herbicide analyses. All bottles were cleaned using a machine washing procedure followed by heating in a muffle furnace (475°C for 4 h). Field samples were immediately placed in a closed cooler with ice packs and returned to the laboratory for analysis.

Glass bottles (precleaned 375 mL) from Isco automatic samplers were collected no more than one day following an event, with samples placed in a cooler following removal from the Isco sampler. While samples were in the Isco sampler they were shaded and in the dark. All glass bottles used in the Isco

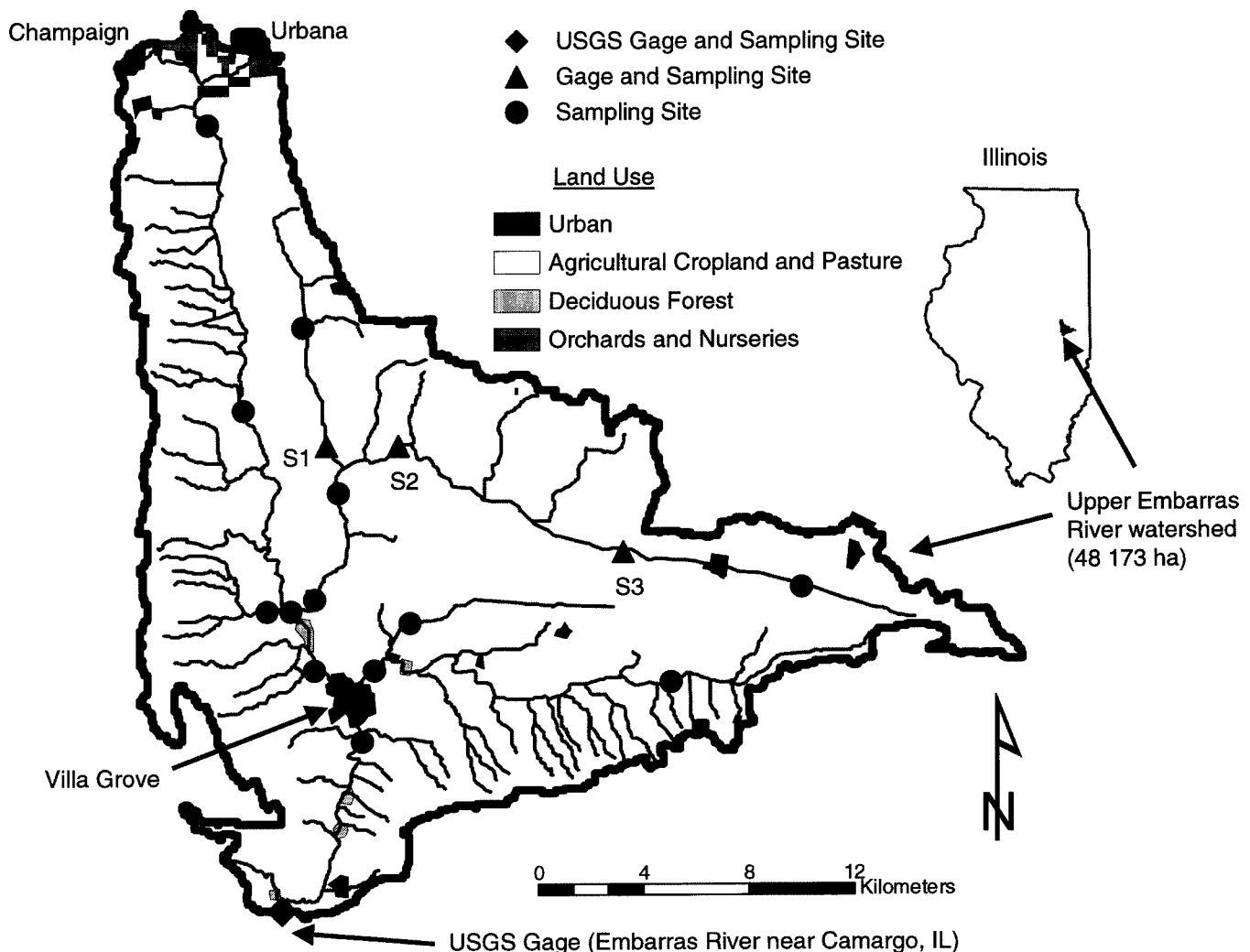


Fig. 1. Map of land use and sampling locations in the Upper Embarras River watershed showing high- (S1), medium- (S3), and low-density (S2) tile subwatershed sites, and the United States Geological Survey (USGS) gage site (outlet of watershed).

water samplers were precleaned as described above for the grab samples. A full quality assurance–quality control (QA–QC) program was used for all sampling and analysis. For the sampling component, this included field duplicates and travel blanks with each set of samples.

Three monitoring sites were established in sections of the watershed with varying drain density as detailed previously. Each site was equipped with a data logger, which was connected to a Starflow meter (Unidata Australia, O'Connor, Western Australia) and an Isco sampler. The Starflow used an ultrasonic Doppler technique and recorded water velocity, depth, and temperature at 15-min intervals (Unidata Australia, 1996). A wireless weather station was also installed to measure rainfall at each site. The flow rate and total flow amounts were computed based on channel profiles from surveying data.

Laboratory Analysis

Laboratory analysis was divided among three laboratories, each determining different analytes. Immunoassay techniques were used on all samples as a screening tool to determine when more detailed analyses should be conducted. Both atrazine and metolachlor were determined using immunoassays (van Emon et al., 1989) in the Department of Natural Resources and Environmental Sciences at the University of Illinois. Samples were filtered through 0.45- μm Gelman acrodisc filters (Pall Corporation, Ann Arbor, MI) into 3-mL glass vials with Teflon caps, and were then analyzed using atrazine and metolachlor kits from Strategic Diagnostics (Newark, DE). The quantitation limit was 0.1 $\mu\text{g L}^{-1}$ for both atrazine and metolachlor using this technique. Holding times were less than 7 d.

More detailed analyses of herbicides in samples were conducted at the Waste Management and Research Center (WMRC), Champaign, Illinois. Each sample was disk-extracted (47-mm Empore high-performance SDB-XC extraction disks; 3M, St. Paul, MN) and analyzed for atrazine, DEA, DIA, cyanazine, acetochlor, alachlor, metolachlor, pendimethalin [(*N*-1-ethylpropyl)-2,6-dinitro-3,4-xylidine], and trifluralin (α,α,α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine) by gas chromatography–mass spectrometry (GC–MS). The quantitation limits were 0.5 $\mu\text{g L}^{-1}$ in 1999 and 0.4 $\mu\text{g L}^{-1}$ in 2000 for each of these compounds.

Samples were also shipped to the USGS Organic Geochemistry Research Laboratory in Lawrence, Kansas, for determination of alachlor, metolachlor, and acetochlor metabolites. These included ESA and OA forms of these three herbicides. For samples collected before 23 May 2000, all analyses were analyzed by high-performance liquid chromatography (HPLC) with diode-array detection (DAD) with a quantitation limit of 0.2 $\mu\text{g L}^{-1}$, and following that date by liquid chromatography–mass spectrometry with a quantitation limit of 0.05 $\mu\text{g L}^{-1}$ (Zimmerman et al., 2000; Hostetler and Thurman, 2000). For the samples collected before 23 May 2000, confirmation of alachlor ESA and acetochlor ESA [2-(2-ethyl-6-methylphenyl) (ethoxymethyl)amino-2-oxoethanesulfonic acid] by HPLC was not possible by HPLC–MS (Kalkhoff et al., 1998; E.M. Thurman, personal communication, 2003).

The QA–QC program for all analyses included field and analytical duplicates, spikes, travel blanks, and calibration QC samples. During the project a total of 500 water samples were collected (not counting QA–QC samples), and all were analyzed using the immunoassay techniques. Of the 500 samples, 87 were then analyzed by the Waste Management and Research Center, and 70 of those by the USGS laboratory.

We used immunoassay concentrations and stream flow to

choose samples for detailed metabolite analysis (metabolite analysis was limited due to cost). Because of the low river flows throughout much of the study period with corresponding low immunoassay concentrations, metabolite analysis was only obtained during late March through June 1999, and May through July 2000. This is when tiles were flowing in the watershed. Therefore, our results concerning chloroacetanilide herbicide metabolites only apply to the tile-flow period during each year of the study. No metabolite analysis was conducted during the intervening low-flow period.

Comparison of Herbicide Analysis Techniques

Immunoassays were used on all samples as a screening tool to identify samples for further analysis and to provide a larger data set to examine the sources and movement of herbicides in the watershed. A comparison of immunoassay and GC–MS atrazine concentrations indicated that the immunoassay routinely overestimated this herbicide, although the response was linear ($r^2 = 0.96$, $n = 62$). The equation was:

$$\text{GC–MS atrazine} = \text{immunoassay atrazine} \times 0.5366 \quad [1]$$

When all GC–MS triazines (atrazine, DEA, DIA) were compared with immunoassay concentrations there was a better agreement at concentrations below 5 $\mu\text{g L}^{-1}$, but little change above that concentration because the parent compound dominated at high concentrations.

For metolachlor, immunoassays were closer to GC–MS concentrations overall, but there was considerable scatter and the r^2 of the regression line was 0.76 ($n = 61$). The equation was:

$$\text{GC–MS metolachlor} = 0.4364 + (\text{immunoassay metolachlor} \times 0.5589) \quad [2]$$

Comparing immunoassay metolachlor with the sum of acetochlor and metolachlor by GC–MS did not improve the relationship, demonstrating that the immunoassay is probably not detecting acetochlor.

The relationship observed between immunoassay and GC–MS atrazine is well known (Aga and Thurman, 1993), and is in part due to cross-reactivity by both organic and inorganic compounds as well as metabolites of atrazine. Aga and Thurman (1993) used a solid-phase extraction procedure to remove much of the interfering compounds. However, our linear relationship between the methods was quite strong and most of the variation was explained. Therefore, all immunoassay results reported in this paper have been corrected using the relationships shown above.

Detection Frequencies

The analytical detection limits for the parent compounds (0.5 $\mu\text{g L}^{-1}$) were greater than their degradation productions (either 0.2 or 0.05 $\mu\text{g L}^{-1}$), so raw data would not be appropriate when comparing frequencies. Therefore, we used a common detection threshold of 0.5 $\mu\text{g L}^{-1}$ to assess the frequency of detection for all chloroacetanilide compounds, similar to the approach used by Kalkhoff et al. (1998). However, data above the appropriate detection limits were used in all other analyses.

Recent Herbicide Use in Illinois

Herbicide use in Illinois has changed greatly during the last 10 yr. In the early 1990s, atrazine, cyanazine, metolachlor, and alachlor were the most-applied herbicides, with smaller

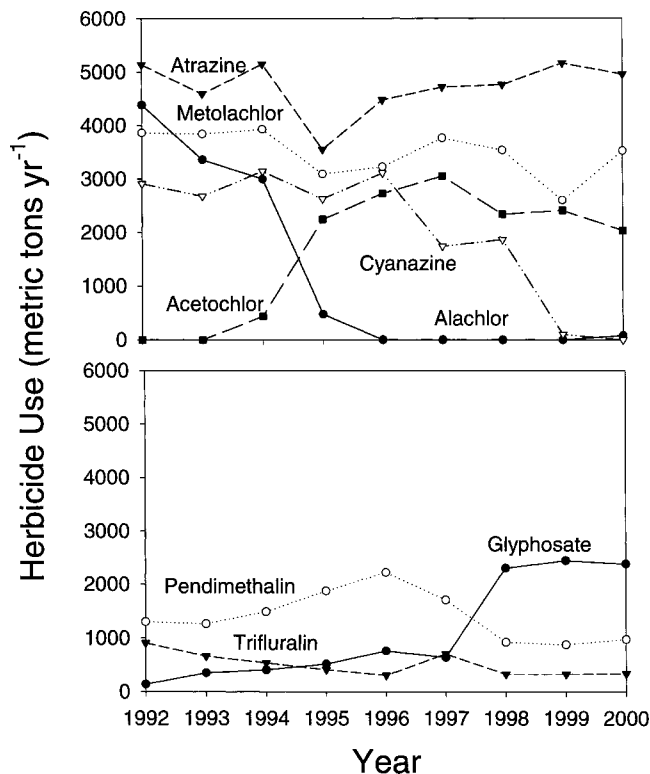


Fig. 2. Herbicide use in Illinois from 1992 through 2000 (USDA National Agricultural Statistics Service, 2002).

amounts of pendimethalin and trifluralin (Fig. 2). However, following the approval of acetochlor in 1993 (with first applications in 1994), alachlor quickly was phased out so that by 1996 alachlor was not used in Illinois, and acetochlor use was nearly 3000 metric tons yr^{-1} . Cyanazine use also decreased through this time period, and was not used in 1999 or 2000. The other major change was with glyphosate [*N*-(phosphonomethyl)glycine], which increased greatly in use in 1998 through 2000. Therefore, during 1999 and 2000, the major herbicides in use in Illinois were (in order of metric tons of active ingredient) atrazine, metolachlor, acetochlor, glyphosate, pendimethalin, and trifluralin.

RESULTS AND DISCUSSION

Embarras River Flow

The 1999 and 2000 water years had less flow than average, with the only large events at the USGS-gaged outlet of the Upper Embarras River watershed during January and February 1999, before herbicide applications. From 1973 through 1998, yearly flow averaged 169 million $\text{m}^3 \text{yr}^{-1}$ for the Upper Embarras River watershed. Yearly flows were 132 and 51.6 million $\text{m}^3 \text{yr}^{-1}$ for the 1999 and 2000 water years, with 2000 having the lowest flow recorded during the last 28 yr (even less than the drought years of the 1980s). Therefore, our results must be placed in the context of much-lower-than-normal flow in this watershed.

During the late spring through early summer period when we would expect herbicide transport to be greatest, there were only two flow events each in 1999 and 2000. These events produced flow rates of 15 to 25 $\text{m}^3 \text{s}^{-1}$, considerably less than the 50 to 150 $\text{m}^3 \text{s}^{-1}$ flow

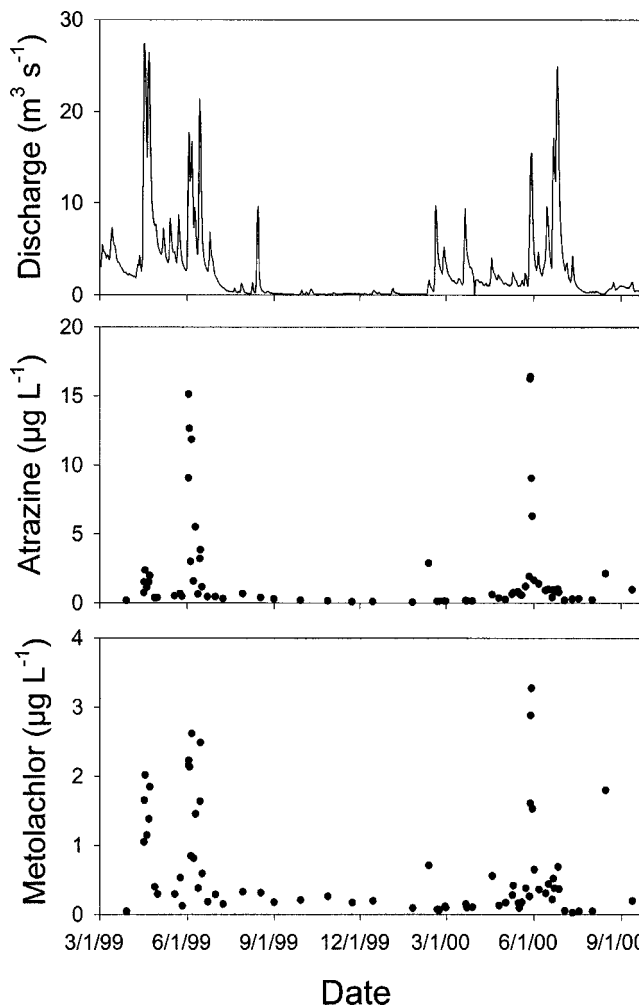


Fig. 3. Discharge and concentrations of atrazine and metolachlor (corrected immunoassay) in surface water at the United States Geological Survey (USGS) gage site on the Embarras River from 1 Mar. 1999 through 1 Oct. 2000.

events that typically occur once or twice each water year. This lack of flow events greatly limited our ability to examine a range of events where we would have expected surface runoff and tile drainage to vary as contributors to river flow. Because rainfall intensities were always less than infiltration rates during the study period, we assumed all events during the project sampling period were driven by tile-drainage flow alone, except for the event that began on 24 June 2000 at subwatershed S3, where there was some surface runoff. However, our Isco sampler failed at this site during this time period (a weekend), and no samples were obtained. Therefore, all of our analysis of herbicide data is for events driven by tile flow, and we could not separate the effects of surface runoff versus tile drainage.

Immunoassay Herbicide Results

The largest flow in the Embarras River at the USGS gage site was during April 1999, before application of herbicides (Fig. 3). No extremely large flows ($>50 \text{ m}^3 \text{ s}^{-1}$) based on flow patterns during the last 30 yr occurred from late April 1999 through the summer of 2000. How-

ever, the first 10 to 20 m³ s⁻¹ storm event that occurred during late May through June each year did have the greatest concentration of herbicides as measured by immunoassay atrazine and metolachlor. Concentrations of atrazine at the USGS gage site peaked at 15 and 17 µg L⁻¹ in 1999 and 2000, respectively, and metolachlor at 2.7 and 3.2 µg L⁻¹. As observed in other rivers of the Midwest (Thurman et al., 1991), the spring flush led to the highest concentrations of herbicides measured during the project.

Each of the subwatersheds responded in a similar manner (data not shown). Highest concentrations of immunoassay atrazine and metolachlor occurred during these early events following applications. The highest concentrations did vary greatly among the subwatersheds, and this was probably due to differences in rainfall intensity. We measured different rainfall amounts and increases in flow among the subwatersheds for each event, which no doubt greatly affected the herbicide concentrations. All subwatersheds had much greater immunoassay atrazine and metolachlor concentrations than the overall watershed, with atrazine concentrations reaching a maximum of 49 µg L⁻¹ at S2 on 23 May 2000. However, this was well before the large flow event that began on 27 May.

On 23 May 2000, atrazine concentrations were variable throughout the watershed (0.5–49 µg L⁻¹). At this point herbicide applications were probably completed by all farmers, but there had only been some small rain events that led to low-tile-flow events. Concentration of atrazine upstream of S3 was 6.4 µg L⁻¹, but increased to 49 µg L⁻¹ at S2. Other branches of the river all had relatively low atrazine concentrations (<8 µg L⁻¹). The highest concentration in the main branch on this date was below Villa Grove (46 µg L⁻¹); at the USGS gage the concentration was low (1.2 µg L⁻¹). With only low flow occurring, this pattern indicates that atrazine had entered the river along some branches, but was not yet leaving the watershed. With the large flow events on 27 to 28 May, however, this changed. Concentration of atrazine at S1 reached a high of 38 µg L⁻¹ on 27 May, whereas the upstream sites from S2 decreased to about 4.6 µg L⁻¹. On 28 May the river concentration at the USGS gage site peaked with the peak in flow at 17 µg L⁻¹ (Fig. 3). Together this pattern of atrazine concentrations shows variable movement into the branches during low flow, and a flushing of the herbicide during the first event following applications.

The pattern of metolachlor concentrations and movement in streams throughout the watershed during this period were similar to atrazine (although concentrations were much lower), with variable concentrations in the watershed (0.5–2.5 µg L⁻¹) before the large flow events on 27 to 28 May, and then highest concentrations at the watershed outlet during 28 and 29 May. Concentrations measured at the USGS gage site were 2.9 µg L⁻¹ on 28 May, and 3.2 µg L⁻¹ on 29 May.

The largest event during spring through early summer (May through July) of the two-year period occurred on 26 June 2000 at the USGS gage site, but both the atrazine and metolachlor concentrations were only 1.0 µg

L⁻¹, and concentrations of both herbicides were less at all other sampling sites in the watershed. Even in a dry year, events that occur after the initial flush apparently do not cause parent compound concentrations to increase much. However, metabolite concentrations during these events will be discussed below.

Herbicide Parent Compound and Metabolite Concentrations

Detection Frequency

Frequency of detection (by GC–MS, liquid chromatography–diode-array detection, and HPLC–MS) was summarized to obtain an indication of how often both the parent compounds and metabolites of the herbicides commonly applied in Illinois were found. However, only selected samples (based on immunoassay concentrations and flow considerations) were analyzed, nearly all during the period of the year when tiles were flowing. Atrazine was detected in 60 to 75% of the samples at each of the four sites, DEA 20 to 50%, and DIA from 0 to about 15%. Therefore, for this heavily applied herbicide, the parent compound was detected in many more samples than the metabolites DIA and DEA. Other herbicides, such as trifluralin, cyanazine, and pendimethalin, were not detected in any samples (other than one sample with cyanazine), suggesting that they sorb strongly to soil particles and did not move through soils into tiles. There is also the possibility that these herbicides were not used recently in this watershed (e.g., cyanazine). However, given the large amounts used in Illinois on corn and soybean, there is no reason to think they were not used in similar amounts in our study watershed.

The chloroacetanilide herbicides had different patterns than the triazines and other compounds. Acetochlor and metolachlor were both detected in many samples, ranging from 0 to 50% of samples for acetochlor, and 50 to nearly 80% of samples for metolachlor (Fig. 4). Metabolites were found at about the same frequency as the parent compounds, with metolachlor ESA detected most often (>80% from all sites). Acetochlor ESA and acetochlor OA (2-[(2-ethyl-6-methylphenyl)(ethoxymethyl)-amino]-2-oxoacetic acid) were detected in about half of the samples. Alachlor and alachlor ESA were also detected in a few samples, which is interesting since this herbicide has not been used since 1995. However, the number of detections was much less than for the currently used metolachlor and acetochlor, and alachlor OA (2-[(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoacetic acid) was not detected in any samples. For chloroacetanilide herbicides, these results demonstrate that the metabolites are generally present in water samples in the watershed where they are applied during the periods when tile drains were active (April or May into July in 1999 and 2000).

Atrazine

The median concentration of atrazine by immunoassay for all samples was about 0.3 µg L⁻¹, but many

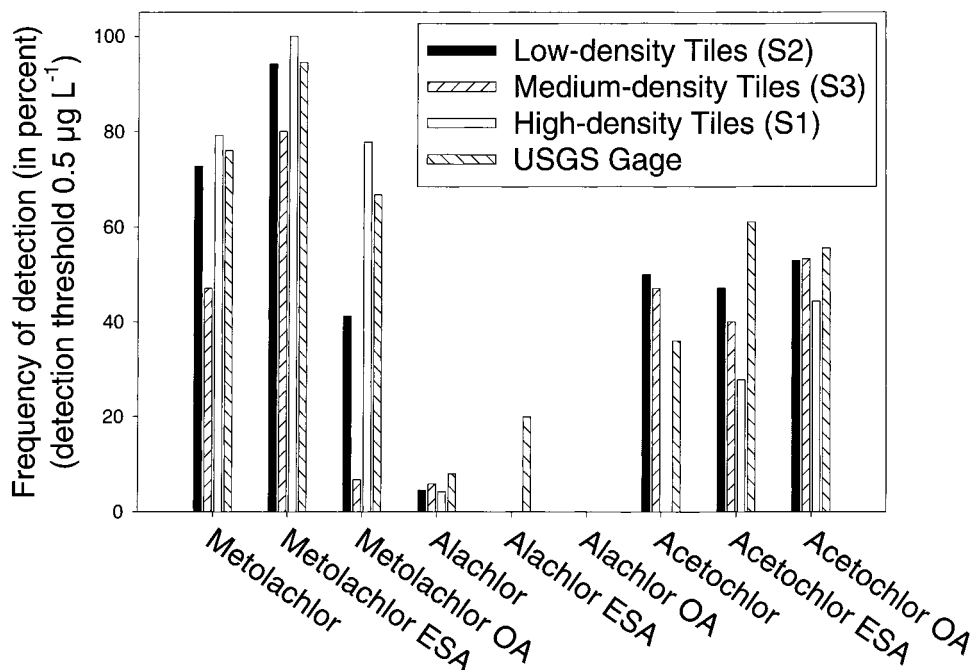


Fig. 4. Detection rates of chloroacetanilide herbicides and their sulfonic and oxanilic metabolites. Data from March to June 1999 and May through July 2000, the period of tile flow in the Upper Embarras River watershed. ESA, ethanesulfonic acid; OA, oxanilic acid.

samples were well beyond the 90th percentile (Fig. 5a). When analyzed by GC-MS, the median concentration was $5 \mu\text{g L}^{-1}$ (Fig. 5b), primarily because we chose samples for this analysis based on the concentration by immunoassay (higher concentrations were analyzed by GC-MS). When viewed by subwatershed and at the USGS gage site, median concentrations were all similar, ranging from 0.3 to $0.7 \mu\text{g L}^{-1}$ (Fig. 6). However, as discussed previously, high atrazine concentrations were observed during the first flow event following April and early May applications.

The two atrazine metabolites were measured at generally low concentrations when detected, with median concentrations of 0.8 and $1 \mu\text{g L}^{-1}$ for DIA and DEA, respectively (Fig. 5b). Therefore, during this study these metabolites were about 25% of the concentration of the parent compound.

Chloroacetanilides

Metolachlor was found at much lower concentrations than atrazine (Fig. 5a). The median concentration was $0.6 \mu\text{g L}^{-1}$ for all 500 samples analyzed by immunoassay, but was measured as high as $8.2 \mu\text{g L}^{-1}$. There was no trend among the subwatersheds, and the USGS gage site had similar median concentrations (Fig. 6). When analyzed by GC-MS, each of the parent chloroacetanilide compounds had a similar median concentration of just more than $1 \mu\text{g L}^{-1}$ for all samples, although acetochlor and metolachlor had much higher concentrations measured than alachlor (Fig. 7a). When detected, the metabolites (OA and ESA) for each of the chloroacetanilides had different concentrations (Fig. 7b). Alachlor ESA and OA had the lowest median concentrations, ranging from 0.1 to $0.25 \mu\text{g L}^{-1}$, with no concentrations above $0.6 \mu\text{g L}^{-1}$.

Acetochlor had the next highest median concentrations of 0.5 to $0.7 \mu\text{g L}^{-1}$ for the ESA and OA metabolites, respectively, with individual samples as high as $6 \mu\text{g L}^{-1}$. Metolachlor ESA had by far the highest median concentration, however, of $2 \mu\text{g L}^{-1}$, and metolachlor OA and acetochlor OA had similar median concentrations ($0.6 \mu\text{g L}^{-1}$). Again, similar to acetochlor metabolites, many samples had metolachlor ESA concentrations of more than $2 \mu\text{g L}^{-1}$.

The median value of the sum of the three chloroacetanilide parent compounds was $3.4 \mu\text{g L}^{-1}$, whereas it was $4.3 \mu\text{g L}^{-1}$ for the sum of the six metabolites. Kalkhoff et al. (1998) measured values of 0.13 and $6.4 \mu\text{g L}^{-1}$ for the same parent compounds and metabolites in surface waters of Iowa in 1996, and observed a pattern of $\text{ESA} > \text{OA} > \text{parent compounds}$. Our pattern of concentrations differed among the three herbicides, with parent compounds $>$ metabolites for acetochlor and alachlor, but $\text{ESA} > \text{parent compound} > \text{OA}$ for metolachlor. Our results support the importance and persistence of chloroacetanilide metabolites as discussed by Kalkhoff et al. (1998), but the concentrations of metabolites were not as high as in their study. There are several possible reasons for this difference, including size of the rivers, amount of tile drainage, sampling periods, and runoff. We sampled three subwatersheds and the outlet of the overall watershed that were small in size, whereas the Kalkhoff et al. (1998) study included major river sampling sites in eastern Iowa. A large part of the watershed that they sampled was also not tile-drained, which may alter breakdown and transport of herbicides. Finally, we sampled during two low-stream-flow years, which may have greatly affected transport of these herbicides. The dry conditions may have caused a slower breakdown of the parent material as well. Our results do

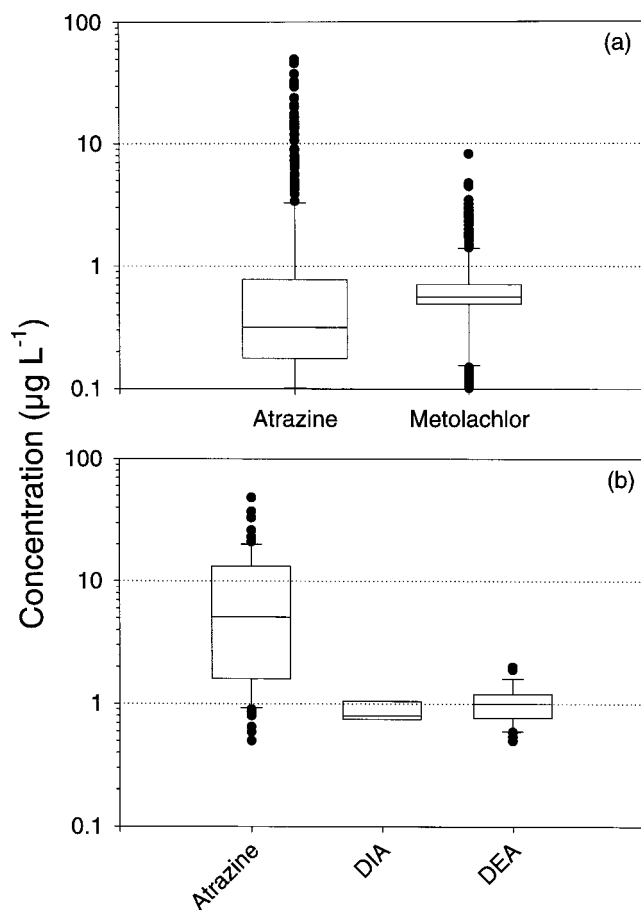


Fig. 5. Concentrations of (a) atrazine and metolachlor (corrected immunoassay) and (b) gas chromatography–mass spectrometry (GC–MS) atrazine, deisopropylatrazine (DIA), and deethylatrazine (DEA) for all surface water samples collected in the Upper Embarras River watershed from 1 Mar. 1999 through 1 Oct. 2000. Box plot shows median (line in center of box), 25th and 75th percentiles (bottom and top of box, respectively), 10th and 90th percentiles (bottom and top error bars, respectively), and values < 10th percentile and > 90th percentile (solid circles below and above error bars, respectively).

point out that significant herbicide concentrations of chloroacetanilide parent and metabolite compounds can move into streams of central Illinois through tile flow alone (no surface runoff).

Ratios of metolachlor ESA to metolachlor (SAM) and metolachlor ESA to metolachlor OA (SAO) can also be used to examine the fate of metolachlor (Phillips et al., 1999). The mean SAM and SAO ratios for the USGS gage site were 3.0 (range of 0.7–6.7) and 3.5 (range of 1.0–9.4), respectively, with mean SAM ratios of 1.3 to 2.1 for the subwatershed sites (S1, S2, and S3) and mean SAO ratios of 2.4 to 4.1. Phillips et al. (1999) measured wider SAM ratios ranging from 2 to 45 in the Canajoharie Creek in New York, with much higher ratios in the two tile drains sampled (approximately 1200). Their SAO ratios in tile drains (range of 1.7 to 5) were similar to our river ratios, and they only detected metolachlor OA in one surface water sample (SAO ratios in the Canajoharie Creek were therefore not calculated). Our surface water samples had a similar SAO

ratio as Phillips et al. (1999) observed in tiles, which again indicates that stream flow was dominated by tile water during the May through July period each year when these compounds were measured. Both metolachlor ESA and OA formation is thought to occur when water has significant contact time with the soil, which should occur during tile drainage (Phillips et al., 1999) compared with surface runoff. However, our SAM ratios were similar to Phillips et al. (1999) surface water samples, not their tile samples. We measured much higher concentrations of metolachlor in our samples, compared with Phillips et al. (1999), which could reflect less sorption in our soils compared with the New York watershed.

When examined by site, some interesting patterns were identified for the chloroacetanilide metabolites. At the USGS gage site, metolachlor and its metabolites were the dominant chloroacetanilide herbicide (Fig. 8). Metolachlor ESA concentrations were remarkably constant throughout tile-flow period, ranging from 1.2 to 3.9 $\mu\text{g L}^{-1}$ at this site during late March to June 1999 and May through July 2000. There was no relationship of this metabolite to flow during these periods. It appears that metolachlor ESA is a common metabolite that is present at relatively high concentrations in the river during the tile-flow period each spring and early summer. Among the subwatersheds, there was no apparent pattern with tile density for the chloroacetanilides or their metabolites (data not shown). The S3 site (medium tile density) had lower median concentrations of metolachlor and ESA and OA metabolites compared with the other subwatersheds. This difference could result from application rates of the herbicides in the subwatersheds.

Herbicide Loads

Load calculations were made for the entire Upper Embarras River watershed using data from the USGS gage site and the medium- and high-density subwatersheds. An estimated 27 Mg of atrazine, 13.5 Mg of metolachlor, and 12.6 Mg of acetochlor were applied in 1999 and 2000 to the watershed on corn. These were estimated by using the application rates and the percent of crop they are applied to from state summaries, because more detailed information was not available. The area of the watershed and percent in corn was taken from David et al. (1997). An estimated 138 and 65 kg of atrazine was exported from the watershed during the 1999 and 2000 water years, respectively (1999 water year estimate only began in March, when data collection was initiated). This was 0.5 and 0.2% of the amount applied each year for 1999 and 2000, respectively, and was much lower than rates observed for the Mississippi River basin but similar to what Gentry et al. (2000) measured in tile drainage from a field in the Upper Embarras River watershed (0.5% of amount applied during 1997). Clark and Goolsby (2000) estimated that 2% of the atrazine applied in the Mississippi River basin from 1991 to 1997 entered the Gulf of Mexico. They also determined that most of the herbicide load occurred during May to Au-

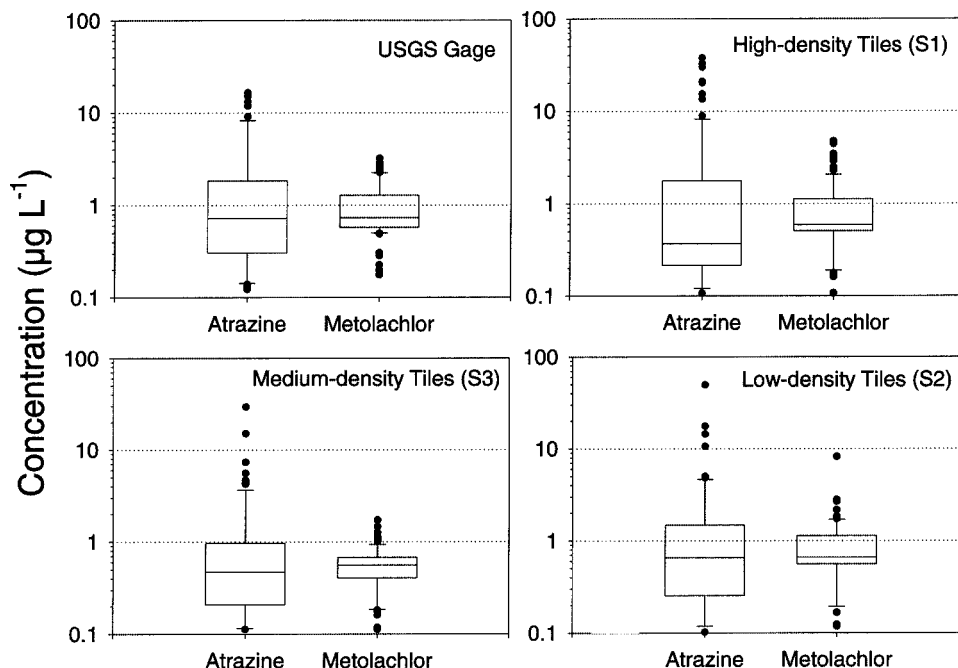


Fig. 6. Concentrations of surface water atrazine and metolachlor (corrected immunoassay) by site in the Upper Embarras River watershed for samples collected from 1 Mar. 1999 through 1 Oct. 2000. Box plot shows median (line in center of box), 25th and 75th percentiles (bottom and top of box, respectively), 10th and 90th percentiles (bottom and top error bars, respectively), and values < 10th percentile and > 90th percentile (solid circles below and above error bars, respectively).

gust, peaking in June. We also estimated that most of the atrazine was discharged during May through July (105 and 58 kg for the 1999 and 2000 water years, respectively, 76 and 89% of the yearly sum). Due to the below-normal hydrologic conditions during this study, it is not surprising that atrazine losses were small. However, atrazine is often thought to be lost primarily through surface runoff (Ng and Clegg, 1997); our losses were from tile drainage only. Gaynor et al. (1995, 2001) found approximately equal losses from tile and surface transport, but indicated that hydrology and application methods can affect losses. The lack of large flow events that are typical during most springs in our watershed no doubt limited atrazine losses, but did show that losses (although a small percentage of application amounts) can occur only through tile transport into streams.

Metolachlor ESA was the dominant chloroacetanilide herbicide residual compound in the river at the USGS gage site during May and June (tile-flow period) in both 1999 and 2000 (Fig. 9). It was 53 and 62% of summed metolachlor compounds in 1999 and 2000, respectively. Metolachlor OA loads were similar to metolachlor during both years in the May to June period. Clark and Goolsby (2000) determined that the percentage of chloroacetanilide herbicides that was exported from the Mississippi River basin was generally much less than 1% of the applied amount, much less than atrazine. Our results are somewhat different than Kalkhoff et al. (1998) and Phillips et al. (1999), because we did not find the level of dominance of chloroacetanilides metabolites that were measured in their studies, as discussed previously using the metolachlor ESA to metolachlor and metolachlor OA ratios.

The subwatersheds with gaged flows (S1 and S3) did

differ in herbicide loads, following the same patterns as concentration data presented previously (Fig. 9). The high-density subwatershed (S1) had estimated metolachlor ESA losses of about 3.1 g ha^{-1} during May through June each year, whereas the medium-density subwatershed (S3) had much lower losses of only 0.8 g ha^{-1} . Metolachlor OA export was generally less than the parent compound at both subwatershed sites (with the exception of S1 in 2000), demonstrating either that metolachlor ESA and OA move through soils into tile lines and into the river system differently or that the metolachlor OA formation rate or its persistence was less than the ESA form.

CONCLUSIONS

We sampled the Upper Embarras River watershed for herbicides during two dry springs with low stream flow (compared with historical data). Rainfall intensities and soil infiltration rates suggested that during the sampling period there was only one rainfall event that generated some surface runoff, and that was only in a portion of the watershed. Therefore, the herbicide concentrations that were observed were almost entirely due to subsurface tile flow throughout the sampling period. Due to the lack of storms causing large flow events, we were not able to evaluate the influence of surface runoff on herbicide transport and concentrations. The varying density of tiles among the subwatersheds studied did not influence concentrations of herbicides during the study, which may have been due to the low rainfall and stream flow observed. Because tile-drainage capacity was never exceeded, we did not observe a difference in

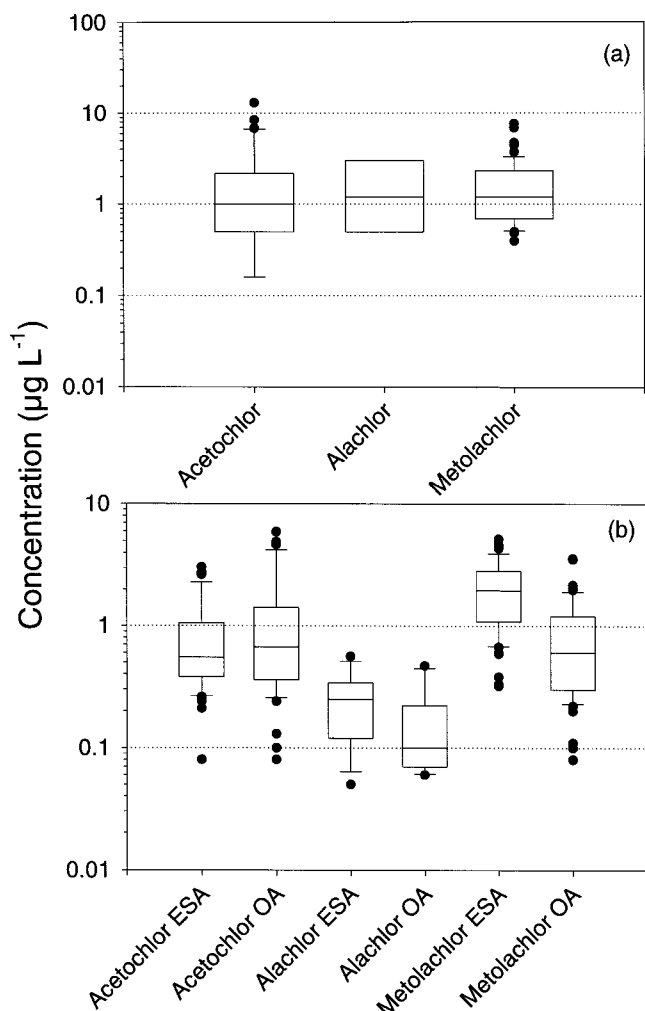


Fig. 7. Concentrations of chloroacetanilide (a) herbicides and (b) their metabolites for all surface water samples collected in the Upper Embarras River watershed. Data from March to June 1999 and May through July 2000, the period of tile flow in the watershed. ESA, ethanesulfonic acid; OA, oxanilic acid. Box plot shows median (line in center of box), 25th and 75th percentiles (bottom and top of box, respectively), 10th and 90th percentiles (bottom and top error bars, respectively), and values < 10th percentile and > 90th percentile (solid circles below and above error bars, respectively).

herbicide concentrations due to varying drainage densities.

Atrazine was found in streams throughout the watershed and peaked in concentration during the first flow event each year in late May to early June. Similar to previous studies in the Midwest, we observed a spring flush that transported the greatest concentrations of atrazine from the watershed. Atrazine metabolites DIA and DEA were detected in many samples, but were generally much lower in concentration than the parent compound. On a mass basis, <0.5% of the applied atrazine was exported from the watershed.

For the chloroacetanilide herbicides (alachlor, metolachlor, and acetochlor), metabolites were detected in many samples during late spring and early summer (during periods of no tile flow and low stream flow, metabolites were not analyzed), particularly metolachlor ESA,

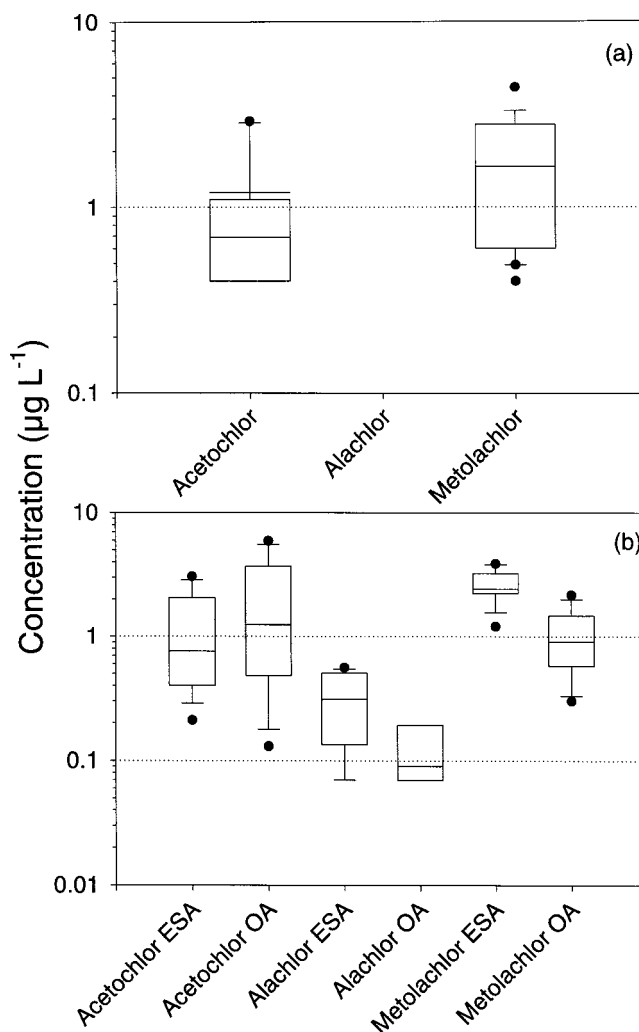


Fig. 8. Concentrations of chloroacetanilide (a) herbicides and (b) their metabolites for surface water samples collected at the United States Geological Survey (USGS) gage site in the Upper Embarras River watershed. Data from March to June 1999 and May through July 2000, the period of tile flow in the watershed. ESA, ethanesulfonic acid; OA, oxanilic acid. Box plot shows median (line in center of box), 25th and 75th percentiles (bottom and top of box, respectively), 10th and 90th percentiles (bottom and top error bars, respectively), and values < 10th percentile and > 90th percentile (solid circles below and above error bars, respectively).

which was found in nearly all samples analyzed for this compound. The summed median concentration of the six metabolites was greater than the sum of the three parent compounds, demonstrating the importance of analyzing both types of compounds. These metabolites have only recently been investigated and detected in surface waters, and there are no drinking water standards established for them. One metabolite that should be further studied is metolachlor ESA, which was found at concentrations of 1.2 to 3.9 $\mu\text{g L}^{-1}$. Concentrations of this metabolite did not appear to vary with flow. Whether chronic exposure to this chemical in combination with other herbicides causes adverse effects on aquatic ecosystems or human health is unknown.

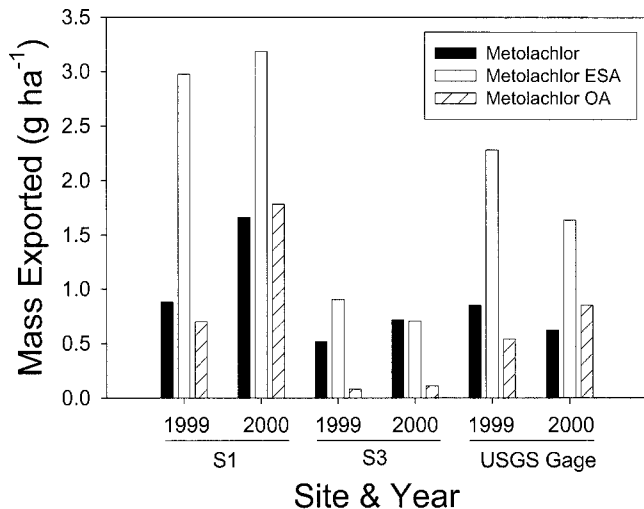


Fig. 9. Export of metolachlor, metolachlor ethanesulfonic acid (ESA), and metolachlor oxanilic acid (OA) from subwatersheds S1, S3, and the United States Geological Survey (USGS) gage site in the Upper Embarras River watershed summed for the two months of May and June in 1999 and 2000.

ACKNOWLEDGMENTS

Financial support in part was provided by the Illinois Waste Management and Research Center (WMRC) of the Illinois Department of Natural Resources. We thank Marvin Piwoni, Dan McGinness, Monte Wilcoxon, Brad Daniels, and Teresa Chow at WMRC for their assistance in the analysis of herbicides in this study. The USGS Organic Geochemistry Research Laboratory in Lawrence, KS is also thanked for the chloroacetanilide herbicide metabolites, particularly Betty Scribner. Jennifer Benson and Christy Davidson assisted with field sampling and laboratory analysis during the project and are thanked. Finally, we thank the three farmers who allowed access to the subwatershed sites used in the study.

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