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Trends in Concentrations and Use of Agricultural Herbicides for Corn Belt Rivers, 1996−2006

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Trends in the concentrations and agricultural use of four herbicides (atrazine, acetochlor, metolachlor, and alachlor) were evaluated for major rivers of the Corn Belt for two partially overlapping time periods: 1996−2002 and 2000−2006. Trends were analyzed for 11 sites on the mainstems and selected tributaries in the Ohio, Upper Mississippi, and Missouri River Basins. Concentration trends were determined using a parametric regression model designed for analyzing seasonal variability, flow-related variability, and trends in pesticide concentrations (SEAWAVE-Q). The SEAWAVE-Q model accounts for the effect of changing flow conditions in order to separate changes caused by hydrologic conditions from changes caused by other factors, such as pesticide use. Most of the trends in atrazine and acetochlor concentrations for both time periods were relatively small and nonsignificant, but metolachlor and alachlor were dominated by varying magnitudes of concentration downtrends. Overall, with trends expressed as a percent change per year, trends in herbicide concentrations were consistent with trends in agricultural use; 84 of 88 comparisons for different sites, herbicides, and time periods showed no significant difference between concentration trends and agricultural use trends. Results indicate that decreasing use appears to have been the primary cause for the concentration downtrends during 1996−2006 and that, while there is some evidence that nonuse management factors may have reduced concentrations in some rivers, reliably evaluating the influence of these factors on pesticides in large streams and rivers will require improved, basin-specific information on both management practices and use over time.

Introduction

The use of pesticides has a long history and is constantly changing in response to such factors as regulations, market forces, and the development of new pesticides and genetically engineered crops. Pesticide use on agricultural crops began in the United States in the late 1800s, accelerated during the late 1940s, and has continued to constantly evolve to the present time (*1*). The annual use of pesticides in the U.S. was about 230 million kilograms in the 1930s, increased to nearly 460 million kilograms by the late 1940s, peaked at nearly 700 million kilograms in the late 1970s, and was relatively steady at about 540 million kilograms during the 1990s (*2*). Although total use, in terms of mass applied, has been relatively constant during the past 10−20 years, major changes have occurred in the use of many individual pesticides, as some have been reduced or phased out and others have been introduced. Evaluation of the effects of these changes in use on trends in pesticide concentrations in streams, as well as the possible influences of other changes, such as in management practices or streamflow conditions, is vital to understanding and managing the potential water-quality effects of pesticides, which are frequently present in streams that drain agricultural areas, sometimes at concentrations greater than water-quality benchmarks for aquatic life (*3, 4*).

Assessment of trends in pesticide concentrations in streamwater is difficult because there are few streams with long-term records of concentrations, most such streams have had data gaps and sporadic sampling intensities over time, and concentrations of many pesticides have high proportions of nondetections, resulting in highly censored data sets. Battaglin and Goolsby (*5*) evaluated changes in Corn Belt herbicides by comparing concentrations and yields for single peak-season samples for 1989 and 1990 (two consecutive postapplication samplings), to 1994 and 1995 (two consecutive postapplication samplings), for 53 streams. For most of the herbicides evaluated, the medians of concentrations and yields were generally higher during 1989/90 compared to 1994/95, whereas regional use estimates for most of the herbicides did not follow that pattern. Their study was limited in depth of interpretation by the lack of substantial time-series data for concentrations and streamflow over a continuous period of time, combined with a lack of basin-specific use estimates. The present study improves the reliability and explanatory power of trend analysis by analyzing time-series data that represent the complete annual cycle of concentrations and streamflow over multiple years and evaluating the trends in relation to estimated use over time in individual basins. As background for this paper, Sullivan and others (*6*) comparatively evaluated several statistical methods for analyzing trends in pesticide concentrations and tested them by application to Corn Belt streams with a wide range of watershed sizes and settings. For analysis of trends with adjustment for streamflow, a parametric regression model specifically designed for analyzing seasonal variability and trends in pesticide concentrations (*7*) was found best suited for evaluating concentration trends in relation to changes in use and other management factors.

The purposes of this paper are to (1) assess recent (1996−2006) trends in the concentrations and annual agricultural use of four of the most commonly occurring herbicides—atrazine, acetochlor, alachlor, and metolachlor—in major rivers in the Corn Belt, an agricultural region dominated by corn and soybean production and which accounts for the majority of national herbicide use, and (2) compare concentration and use trends to evaluate their concordance and

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FIGURE 1. Locations of pesticide sampling sites and associated watersheds.

TABLE 1. Sampling Sites Analyzed for Herbicide Trends

map name	U.S. Geological Survey station no.	site name	drainage area (km^2)	percent land use: cropland	pasture	urban	undeveloped
		Ohio River Basin					
OHIO-CA	03303280	Ohio River at Cannelton Dam at Cannelton, IN	250,000	13	19	3.8	62
WABASH	03378500	Wabash River at New Harmony, IN	75,800	59	18	3.4	18
OHIO-GRCH	03612500	Ohio River at Dam 53 near Grand Chain, IL	527,000	22	20	3.4	52
		Upper Mississippi River Basin					
MSSP-CL	05420500	Mississippi River at Clinton, IA	239,000	34	19	1.8	40
IOWA-WAP	05465500	Iowa River at Wapello, IA	32,400	73	6.1	8.6	11
ILLI-VC	05586100	Illinois River at Valley City, IL	69,200	66	4.6	15	14
MSSP-GR	05587455	Mississippi River below Grafton, IL	447,000	48	18	2.8	13
		Missouri River Basin					
MIZZ-OM	06610000	Missouri River at Omaha, NE	831,000	19	50	0.3	20
PLATTE	06805500	Platte River at Louisville, NE	221,000	21	1.3	3.4	73
MIZZ-HE	06934500	Missouri River at Hermann, MO	1,350,000	23	51	0.7	19
		Combined Upper Mississippi and Missouri River Basins					
MSSP-TH	07022000	Mississippi River at Thebes, IL	1,840,000	30	12	1.3	21

whether differences may indicate influences of agricultural management practices other than those that affect overall annual use intensity in a watershed.

Trends are analyzed for 11 sites on major rivers in the Ohio River Basin, the Upper Mississippi River Basin, and the Missouri River Basin (Figure 1; Table 1). These sites are among 201 sites selected nationally that have adequate pesticide data for trend analysis (*8*). They are a subset of 31 Corn Belt sites analyzed for trends by Sullivan and others (*6*), who showed that most of 11 pesticides assessed in 31 Corn Belt streams and rivers were dominated by concentration downtrends during all or part of 1996−2006.

In this paper, concentration trends for 11 of the 31 Corn Belt sites with the largest drainage areas, and thus most reliable use estimates, are evaluated for the selected herbicides in relation to estimated trends in agricultural use in their watersheds. Focusing on widely used and commonly detected herbicides, and analyzing concentrations for large rivers that were sampled for many years over a wide range of hydrologic conditions and times of year, should provide the best chance of determining large-scale concentration trends and reliably relating concentration trends to use trends or other potential factors.

Atrazine, acetochlor, alachlor, and metolachlor all have moderate to high water solubility and relatively low soil-adsorption coefficients, resulting in relatively similar and high mobility in water and moderate to strong potential for transport from fields by surface runoff, primarily in the dissolved phase (*6*). Overall, the relatively high mobilities, combined with half-lives of much less than a year, indicate that stream concentrations of these herbicides should respond to year-to-year changes in use and not be much affected by use in past years. Agricultural use of these herbicides in the Corn Belt during 1996−2006 generally decreased for metolachlor and alachlor, in response to the introduction of acetochlor and S-metolachlor (*6*), and stayed relatively constant for atrazine and acetochlor (Figure 2).

Materials and Methods

Sample Collection and Chemical Analysis. Sampling frequencies varied by site and among some years, but the typical frequencies were one to four samples per month during the growing season and once a month or once every other month during other times of the year.

Flow-weighted, depth-, and width-integrated water samples for the analysis of pesticides were collected and processed following standard U.S. Geological Survey (USGS) methods (*9*−*11*). Filtered water samples were analyzed for pesticides at the USGS National Water Quality Laboratory in Denver, Colorado using gas chromatography/mass spectrometry (GCMS) with selected-ion monitoring (*12, 13*). All detections conclusively identified are quantified (*12*) and

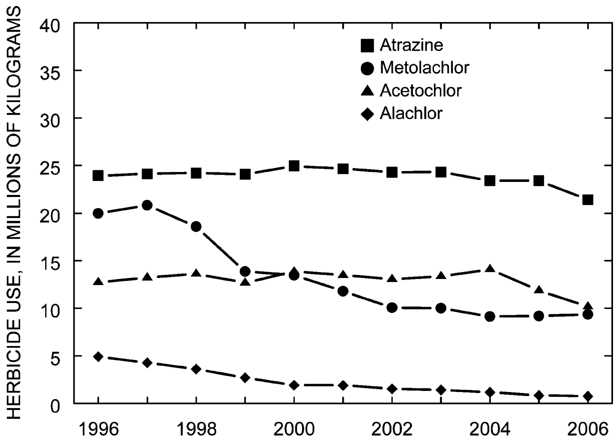

FIGURE 2. Total agricultural use of selected herbicides in the Corn Belt, 1996−2006 (total for states of South Dakota, Nebraska, Kansas, Minnesota, Iowa, Missouri, Illinois, Indiana, and Ohio).

nondetections are reported as less than a reporting level, which varied over time (*14*). See Martin (*8*) for additional information on data reporting procedures. It is important for trend analysis to ensure that the censoring level ("less-than" value assigned to nondetections) and precision (significant digits for quantified values) are consistent through time and to compensate for changes in recovery (bias) of the analytical method (*15*).

To prevent bias in the fitted concentration trends due to serial correlation or to changes in recovery, rounding, and reporting levels, pesticide concentration data were prepared for trend analysis by (see ref *8*): (a) removing samples collected more frequently than weekly to avoid serial correlation (if more than one sample per calendar week, the sample closest to noon Wednesday was retained); (b) adjusting the quantified concentrations (detections) to 100% recovery to compensate for temporal changes in recovery; (c) rounding the recovery-adjusted concentrations to a consistent level of precision; (d) censoring all recovery-adjusted and rounded concentration values that are less than the maximum value of the long-term method detection level (LT-MDL); and (e) treating concentration values for all routine nondetections as less than the maximum value of the LT-MDL.

Statistical Analysis of Concentration Trends. Concentration trends were evaluated using a parametric regression model designed for analyzing seasonal variability and trends in pesticide concentrations (*7*), modified for additional adjustment for streamflow (*6*), and referred to as SEAWAVE-Q. The SEAWAVE-Q model is expressed as

$$\log C(t) = \gamma_0 + \gamma_1 W(t) + \gamma_2 \mathrm{LTFA}(t) + \gamma_3 \mathrm{MTFA}(t) + \gamma_4 \mathrm{STFA}(t) + \gamma_5 t + \eta(t) \quad (1)$$

where log $C(t)$ denotes the base-10 logarithm of pesticide concentration, in micrograms per liter; t is decimal time, in years, with respect to an arbitrary time origin; $W(t)$ is a seasonal wave; LTFA, MTFA, and STFA denote long-term, midterm, and short-term flow anomalies; γ_0, $\gamma_1 - \gamma_5$ are regression coefficients; and $\eta(t)$ is the model error, assumed to consist of independent normal random variables with mean zero and constant variance. The seasonal wave is a periodic function of time with a period of one year, specifically designed to mimic the behavior of pesticide concentrations as observed at each site in response to seasonal application rates, basin accumulation, and removal from processes such as degradation and runoff (*7*).

The flow variables (LTFA, MTFA, and STFA) were included in the SEAWAVE-Q model to account for flow-related variability in pesticide concentrations, which may disguise or alter trends caused by other factors, such as changes in pesticide use. The variables are computed using log-transformed daily flow, $X(t) = \log Q(t)$, where $Q(t)$ is daily mean flow, in cubic meters per second, for the USGS gaging station corresponding with each site (Table 1; data from USGS National Water Information System http://waterdata.usgs.gov/nwis). The first flow variable represents long-term flow variability and is defined as

$$\mathrm{LTFA}(t) = X_A(t) - X_* \quad (2)$$

where LTFA is the long-term flow anomaly (dimensionless); $X_A(t) = \mathrm{Ave}\{X(u),\ t - 1 < u \le t\}$ is the average of log-transformed daily flow for 1 year up to and including time t; and X_* is the average of log-transformed daily flow for the trend analysis period. LTFA can affect pesticide concentrations in different ways and to different degrees depending on the type of pesticide, the size of the basin being analyzed, the climatic and hydrologic properties of the basin, and the degree of streamflow regulation. For example, for a large basin with substantial nonagricultural runoff, higher-than-normal annual flow conditions (as indicated by a positive value for LTFA) may lead to decreased pesticide concentrations because of more dilution from nonagricultural runoff. The second flow variable represents midterm (month-to-month) flow variability and is defined as

$$\mathrm{MTFA}(t) = X_M(t) - X_A(t) \quad (3)$$

where MTFA is the midterm flow anomaly (dimensionless) and $X_M(t) = \mathrm{Ave}\{X(u),\ t - {}^1/_{12} < u \le t\}$ is the average of log-transformed daily flow for ${}^1/_{12}$ of a year (about 1 month) up to and including time t. MTFA, like LTFA, can affect pesticide concentrations in different ways depending on the site or pesticide being considered. The third flow variable represents short-term (day-to-day) streamflow variability and is defined as

$$\mathrm{STFA}(t) = X(t) - X_M(t) \quad (4)$$

where STFA is the short-term flow anomaly (dimensionless). Large positive values of STFA and associated increases in pesticide concentrations tend to occur near the beginning of a substantial rainfall-runoff event, whereas negative values of STFA and associated decreases in pesticide concentrations tend to occur after the event passes.

The regression coefficients and associated p-values and confidence bounds for eq 1 were estimated using maximum likelihood estimation with censored data. The best seasonal wave for each site-pesticide combination was selected using an automatic selection criterion (*7*).

Because flow variables are included in the model, the concentration trend obtained using eq 1 is interpreted as a trend in flow-adjusted concentration. Subtracting the seasonal wave and flow variables from both sides of eq 1 yields

$$\log \mathrm{FAC}(t) = \gamma_0 + \gamma_5 t + \eta(t) \quad (5)$$

where

$$\mathrm{FAC}(t) = \frac{C(t)}{10^{\gamma_1 W(t) + \gamma_2 \mathrm{LTFA}(t) + \gamma_3 \mathrm{MTFA}(t) + \gamma_4 \mathrm{STFA}(t)}} \quad (6)$$

is the flow-adjusted concentration. The flow-adjusted concentration trend is defined as the change in flow-adjusted concentration, in percent per year (pct/yr), and is given by $100(10^{\gamma_5} - 1)$. Hereinafter, the flow-adjusted concentration trend will be referred to more compactly as a concentration trend.

Approximations of average annual pesticide fluxes are used later to help interpret the trends. The flux estimates were obtained using the fitted daily concentrations from the SEAWAVE-Q model along with observed daily flows. The fitted daily log-transformed concentrations were untransformed, multiplied by a bias correction factor based on a log-normal distribution ($\exp\{(2.3s)^2/2\}$, where s is the estimated error standard deviation), multiplied by the daily flows (with the appropriate conversion factor), and aggregated to obtain annual flux estimates.

Statistical Analysis of Agricultural Use Trends. Annual estimates of agricultural use for 1996−2006 for each pesticide/site combination were developed using annual pesticide use estimates for individual crops for multicounty areas referred to as "Crop Reporting Districts" (CRDs) (proprietary data, DMRKynetec, Inc., St.Louis, Missouri) and county-level annual harvested acres of individual crops from either the U.S. Department of Agriculture Census of Agriculture (*16*) or annual survey data for major crops. The CRD-level use estimates for each crop were disaggregated to county-level use estimates by dividing the mass of a pesticide applied to a crop by the acres of that crop in the CRD to yield a rate per harvested acre. This rate was then multiplied by harvested crop acreages in each county to obtain county-level use. Annual pesticide use for each individual watershed was calculated as a weighted sum of county-level use estimates for all counties contained in or overlapping the watershed. The weight for a county was equal to the proportion of cropland in the county that was contained in the watershed, and was obtained using GIS to overlay mapped land cover with digital maps of drainage basins and county boundaries (*17*−*19*). The annual pesticide use for each watershed was divided by the watershed area to obtain estimated annual use intensity (kg/yr/km^2). Use estimates are expected to increase in reliability with watershed area and extent of agricultural land because (1) survey data are regional estimates that may not accurately reflect application rates in smaller areas, and (2) county-level variability in crop data is smoothed out for large watersheds.

Trends in agricultural use for each pesticide-site combination were obtained by regressing log-transformed annual use intensity versus the year,

$$\log U(t) = \beta_0 + \beta_1 t + \varepsilon(t) \tag{7}$$

where $U(t)$ is the estimate of pesticide use intensity (kg/yr/km^2) for the study site for year t; β_0 and β_1 are regression parameters; and $\varepsilon(t)$ is the error, assumed to consist of independent normal random variables with mean zero and constant variance. Unlike eq 1, there was only one value per year used to fit eq 7. For comparison to the estimated concentration trends, the use trend was expressed as a percent change per year, $100(10^{\beta 1} - 1)$.

Trend-Analysis Periods and Sampling Frequencies. The sampling interval 1996−2006 was selected for analyzing trends because most sites had sparse data before 1996 and available data extended to the end of 2006 at the time of preparation for this study. Initially, trends were evaluated for the entire interval. Model residuals, however, indicated that most trends tended to occur primarily within shorter timeframes, either from the mid 1990s to the early 2000s, or in some cases during 2000−2006. Furthermore, in some cases there appeared to be changes in the seasonal concentration patterns from the mid- to late 1990s to the early to mid-2000s (presumably from changes in seasonal use patterns), making the selection of a single seasonal wave for 1996−2006 problematic. Therefore, trends were analyzed separately for partially overlapping early and late time periods: 1996−2002 and 2000−2006. The sample sizes and censoring rates for the 11 sites and both trend analysis periods are given in Supporting Information (SI) Table S1.

Interpretation of Results. For interpreting results, a trend in either concentration or use is defined as significant if the 2-sided p-value of the trend slope is less than 0.10, or equivalently, if 90% confidence bounds on the trend slope do not overlap with zero. When comparing concentration and use trends for a particular site, the trends are defined as significantly different if 90% confidence bounds for the two trends do not overlap. Because the confidence bounds on the use and concentration trends are individual, as opposed to joint, confidence bounds, there is up to a 20% chance that the slopes of the use and concentration trends are the same even if the confidence bounds do not overlap. Therefore, a significant difference should not be interpreted as definitive proof of a difference, but rather an indicator that use and concentration trends may be different enough to warrant further investigation of potential causes for the difference. Examples illustrating the concentration and use data and model output are given in SI Figure S1.

Results and Discussion

Overview of Trends. Overall, trends in concentrations of the herbicides analyzed closely corresponded to trends in agricultural use (Figure 3); 84 of 88 site/herbicide combinations for both time periods had concentration and use trends that were not significantly different (as indicated by overlapping 90% confidence bounds). The majority of use and concentration trends for atrazine and acetochlor for both time periods were small and nonsignificant. Metolachlor and alachlor were dominated by downtrends, especially during 1996−2002, when most of the downtrends in both use and concentration were significant.

With few exceptions, trends were concordant among tributary and downstream basin outlet sites, supporting the reasonableness of estimated trend directions and magnitudes. For the Ohio River Basin, more of the herbicide flux for the outlet site (OHIO-GRCH) was contributed by the intensively farmed WABASH subbasin than the less intensively farmed OHIO-CA subbasin, despite the much lower streamflow contribution of WABASH compared to OHIO-CA. Both subbasins provided a substantial contribution to the flux for the outlet site and concentration trends for the outlet site generally were bracketed by the trends for the two subbasins, with the possible exception of alachlor (for which the trends were highly uncertain). For the Upper Mississippi River Basin, like the Ohio Basin, the intensively farmed tributary subbasins (IOWA-WAP and ILLI-VC) provided proportionally more herbicide flux in relation to streamflow than the upstream subbasin (MSSP-CL). All three subbasins provided a substantial portion of the flux for the outlet basin (MSSP-GR) and the concentration trends for the outlet basin generally were bracketed by the trends for the three subbasins, with the possible exception of alachlor (for which the trends were highly uncertain). For the Missouri River Basin, the PLATTE subbasin provided proportionally more herbicide flux in relation to streamflow than the upstream subbasin (MIZZ-OM). Although a substantial portion of the fluxes for the outlet basin (MIZZ-HE) were from sources downstream of the two subbasins, concentration trends for MIZZ-HE were bracketed by trends for the two subbasins. For the downstream Mississippi River mainstem site (MSSP-TH), both upstream basins (MSSP-GR and MIZZ-HE) provided substantial portions of both streamflow and herbicide flux. There is only a small fraction of the downstream drainage that is not contained in the two upstream basins and trends for MSSP-TH were bracketed by the trends at the two upstream sites.

Concentration and Use Trends for Individual Herbicides. Evaluation of concentration and use trends for the individual

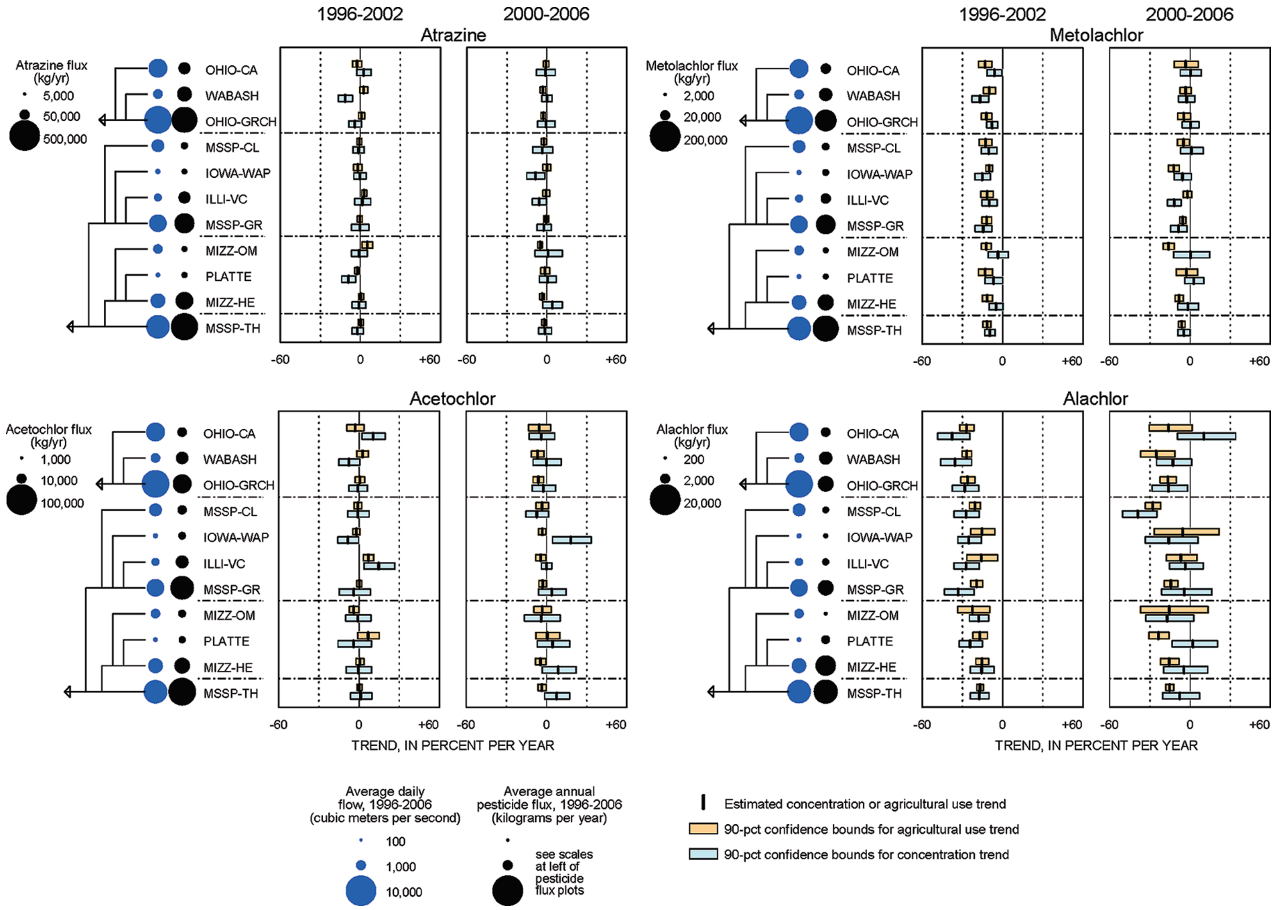

FIGURE 3. Average annual fluxes, agricultural use trends, and concentration trends for atrazine, acetochlor, metolachlor, alachlor.

herbicides provides insight into how changes in agricultural use affected concentrations for individual drainage basins and whether factors other than changes in agricultural use may have influenced some of the trends.

Atrazine. Use intensity for all of the sites was stable during 1996−2002 and stable to slightly decreasing during 2000−2006. The concentration trends (or lack thereof) were generally consistent with use trends. For 21 of 22 site comparisons over both time periods, there were no significant differences between the concentration and use trends. However, there were highly significant downtrends in atrazine concentration for WABASH ($p < 0.001$) and PLATTE ($p = 0.008$) during 1996−2002 and a significant downtrend for IOWA-WAP ($p = 0.07$), during 2000−2006, and confidence bounds for those trends did not overlap with (for WABASH) or barely overlapped with (for PLATTE and IOWA-WAP) confidence bounds for the use trends. These findings suggest the possibility that changes in agricultural management practices, other than decreasing use, may have contributed to the significant downtrends for these primarily agricultural tributary sites. Agricultural management practices, such as no-application buffer strips along streams, vegetative buffer strips around fields, improved labeling and outreach programs, and increased conservation tillage have been shown to be effective in certain situations to reduce local pesticide runoff (*20*). The degree and timing of implementation of these changes in the WABASH, PLATTE, and IOWA-WAP basins, and why significant downtrends were not evident in other basins with similar agricultural settings, are potential topics for further investigation.

Acetochlor. Like atrazine, acetochlor concentration trends were generally consistent with use trends; 21 of 22 comparisons indicated no significant difference between concentration and use trends. However, unlike atrazine, there were indications of concentration uptrends for a few sites. In particular, significant acetochlor concentration uptrends occurred for OHIO-CA ($p = 0.034$) and ILLI-VC ($p = 0.024$) during 1996−2002 and for IOWA-WAP ($p = 0.025$) during 2000−2006. Although changes other than increasing use may be causing concentrations to increase in these basins, the uptrends for OHIO-CA and ILLI-VC during 1996−2002 also may have been caused, at least in part, by use uptrends in the two basins, as indicated by the overlapping confidence limits. The concentration uptrend for IOWA-WAP during the latter time interval, despite apparently stable use, provides indication of a potential cause unrelated to watershed use intensity or of an inaccurate estimate of the use trend. Improved information on changes in acetochlor use and agricultural management practices in these basins is required to determine the likely cause for the increasing concentrations. Widespread changes in agricultural practices (other than use) would be expected to affect acetochlor and atrazine in a similar manner. However, there were no concordant uptrends in atrazine concentration, suggesting the possibility that acetochlor use may have increased faster than estimated in these watersheds.

Metolachlor. Compared to atrazine and acetochlor, metolachlor had more widespread and stronger downtrends in use during 1996−2002, and then weaker downtrends in use, generally similar to acetochlor, during 2000−2006. During 1996−2002, all concentration and use trends for metolachlor were downward, all 11 use downtrends and 8 of 11 concentration downtrends were significant, and there were no significant differences between the concentration and use trends. Thus, there is no indication that the concentration downtrends during this time were caused by anything other than use downtrends. During 2000−2006, similar to atrazine and acetochlor, mostly small downtrends in metolachlor use were accompanied by relatively small and mostly nonsignificant concentration trends in mixed directions. The only significant difference between use and concentration trends was for ILLI-VC, where a significant concentration downtrend occurred during 2000−2006 despite stable use. Again, as for atrazine, further investigation is required to determine if and why concentrations may be decreasing faster than use for ILLI-VC.

Alachlor. Alachlor has a general pattern of use trends similar to metolachlor, with strong downtrends at all sites during 1996−2002 and still dominant, but somewhat weaker downtrends during 2000−2006. The magnitudes of the estimated downtrends in alachlor use, however, are substantially greater than the metolachlor downtrends. During 1996−2002, both concentration and use trends for alachlor all were downward, all were significant, and none of the concentration and use trends were significantly different. Therefore, like metolachlor, the alachlor results provide no indication that the concentration downtrends during this time were caused by anything other than use downtrends. During 2000−2006, concentration trends were also downward at most sites, consistent with use downtrends, but all but two were not significant. The lack of significant trends may be due in large part to the high degree of censored data for 2000−2006, and associated wide confidence intervals on the alachlor concentration trends.

Implications. Combined results for the four herbicides lead to two primary implications:

(1) Reduced annual use appears to be the primary cause of the concentration downtrends in major rivers of the Corn Belt during 1996−2006, and results indicate that reductions in alachlor and metolachlor use, which accompanied the introduction of acetochlor and S-metolachlor in the mid-1990s, effectively reduced river concentrations. Multiyear concentration downtrends generally corresponded to similar magnitude use downtrends in the watersheds. Out of 26 significant downtrends in concentration, 22 were accompanied by a significant and similar downtrend in use.

(2) Four significant concentration downtrends (three for atrazine and one for metolachlor) that were accompanied by small and nonsignificant use downtrends (concentration and use trends were significantly different for two cases) suggest the possibility that agricultural management factors (other than those that affect annual use in a watershed) may have caused concentrations to decrease faster than use in some basins. In addition, the frequently found lack of significant differences between concentration and use trends does not imply that agricultural management practices had no effect. There may be impacts that were not distinguishable given the uncertainty in the concentration and use trends, or there may have been little or no change in management practices during the analysis period of this study. Many studies have shown varying degrees of effectiveness of field-scale practices for reducing pesticide runoff from agricultural land (*20*), but little is known about the long-term, large-scale effects of these practices on major rivers that are simultaneously affected by many different management practices and transport pathways. The possible influences of changes in agricultural management practices on large streams and rivers will be difficult to assess and distinguish from effects of changing use without detailed, basin specific information on both management practices and use over time.

The implications of this study regarding the dominant importance of use in controlling concentration trends, and the less certain—and more difficult to assess—possible effects of changing management practices, also likely apply to other pesticides that have generally similar physical and chemical properties and to other rivers within the Corn Belt region or relatively similar hydrologic environments. Markedly different pesticides, such as hydrophobic pesticides with long half-lives or extremely short-lived pesticides, may show different results, and small streams as well as rivers in substantially different hydrologic settings, such as irrigated agricultural areas, may also have different responses.

Acknowledgments

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Supporting Information Available

Table S1 of sample sizes and percent censored data for sites, analysis periods, and herbicides analyzed. Figure S1 showing measured metolachlor and alachlor concentrations, SEAWAVE-Q model-simulated concentrations, and estimated agricultural use intensity for PLATTE site. This material is available free of charge via the Internet at http://pubs.acs.org.

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