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COMPARISON OF PESTICIDE CONCENTRATIONS IN STREAMS AT LOW FLOW IN SIX METROPOLITAN AREAS OF THE UNITED STATES

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Abstract—To examine the effect of urban development on pesticide concentrations in streams under low-flow conditions, water samples were collected at stream sites along an urban land use gradient in six environmentally heterogeneous metropolitan areas of the United States. In all six metropolitan areas, total insecticide concentrations generally increased significantly as urban land cover in the basin increased, regardless of whether the background land cover in the basins was agricultural, forested, or shrub land. In contrast, the response of total herbicide concentrations to urbanization varied with the environmental setting. In the three metropolitan areas with predominantly forested background land cover (Raleigh–Durham, NC, USA; Atlanta, GA, USA; Portland, OR, USA), total herbicide concentrations increased significantly with increasing urban land cover. In contrast, total herbicide concentrations were not significantly related to urban land cover in the three remaining metropolitan areas, where total herbicide concentrations appeared to be strongly influenced by agricultural as well as urban sources (Milwaukee–Green Bay, WI, USA; Dallas–Fort Worth, TX, USA), or by factors not measured in the present study, such as water management (Denver, CO, USA). Pesticide concentrations rarely exceeded benchmarks for protection of aquatic life, although these low-flow concentrations are likely to be lower than at other times, such as during peak pesticide-use periods, storm events, or irrigation discharge. Normalization of pesticide concentrations by the pesticide toxicity index—an index of relative potential toxicity—for fish and cladocerans indicated that the pesticides detected at the highest concentrations (herbicides in five of the six metropolitan areas) were not necessarily the pesticides with the greatest potential to adversely affect aquatic life (typically insecticides such as carbaryl, chlorpyrifos, diazinon, and fipronil).

Keywords—Pesticides Water quality Urbanization Pesticide toxicity index

INTRODUCTION

In 2001, pesticide use in the United States exceeded 544 $\times 10^6$ kg [1]. Although agricultural use accounted for 76% of this total, nonagricultural use was second only to use on corn when compared with agricultural use on individual crops [2]. In streams sampled as part of the U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program, at least one pesticide or degradate was detected in water more than 90% of the time from 1992 to 2001 [2]. Patterns of pesticide occurrence generally corresponded to land use and associated patterns of pesticide use in the basins of the sampled streams. Total pesticide concentrations in urban streams generally were lower than in agricultural streams, but urban streams had more frequent detections and higher concentrations of insecticides [2,3]. Urban streams also have frequent detections of herbicides that are commonly used in nonagricultural applications [2,4–6], often at higher concentrations than in agricultural streams [2,7]. In paired agricultural and urban basins, insecticides constituted a higher proportion of the total pesticide yield (mass of pesticides transported in the stream per year divided by basin area) from urban basins (12–67%, median 29%) than from agricultural basins (1–11%, median 3%) [6]. Regardless of their sources, pesticides in urban and agricultural streams have the potential to harm aquatic life. Of streams sampled in NAWQA studies, 83% of 30 urban streams, 57% of 83 agricultural streams, and 42% of 65 streams in mixed land use basins had pesticide concentrations that exceeded one or more aquatic-life benchmarks [2].

Most studies of pesticide occurrence in urban streams have focused on highly urbanized areas, and little is known about how pesticide occurrence and concentrations are affected by the gradual progression of urban development from low to high density. Moreover, previous studies linking urbanization to water-quality changes tended to focus on environmentally homogeneous regions.

Between 2002 and 2004, the USGS NAWQA Program evaluated the effects of urbanization on stream-water quality and aquatic communities in six environmentally heterogeneous metropolitan areas of the conterminous United States: Raleigh–Durham, North Carolina; Atlanta, Georgia; Milwaukee–Green Bay, Wisconsin; Denver, Colorado; Dallas–Fort Worth, Texas; and Portland, Oregon. The approach called for sampling a large number of sites, ranging from minimally to highly urbanized, in each metropolitan area over a short period of time. Within each metropolitan area, study basins were chosen to both minimize natural variability between basins from factors such as geology, elevation, and climate, and maximize the gradient of urban development covered from minimally to highly developed basins. The present study describes the pesticide results from the stream-water quality component of these six NAWQA urban stream studies. Our objectives are to examine pesticide concentrations in streams under low flow conditions, and their potential aquatic toxicity, in relation to urbanization in different environmental settings.

MATERIALS AND METHODS

The six metropolitan areas studied are herein referred to as study areas. Within each study area, approximately 30 stream

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Table 1. Characteristics of the six metropolitan areas studied in the United States

Study area	Atlanta, Georgia	Raleigh–Durham, North Carolina	Milwaukee–Green Bay, Wisconsin	Denver, Colorado	Dallas–Fort Worth, Texas	Portland, Oregon
Major cities included	Atlanta, Sandy Spring, Marietta	Raleigh, Cary, Greensboro, High Point, Durham, Winston-Salem	Milwaukee, Waukesha, Green Bay, Racine, Oshkosh	Denver, Boulder, Fort Collins, Cheyenne	Dallas, Arlington, Fort Worth	Portland, Vancouver, Beaverton, Salem, Eugene, Springfield, Corvallis
Principal Level III ecoregion[a]	Piedmont	Piedmont	Southeastern Wisconsin Till Plains	Western High Plains	Texas Blackland Prairies	Willamette Valley
Climate	Warm, humid	Warm, humid	Cool, dry winters; moderate summer	Semiarid	Semiarid	Cool, wet winters; warm, dry summers
Mean annual: precipitation (cm)[b]/temperature (°C)[b]	131/16.6	118/15.0	85/7.5	43/8.1	105/18.2	145/11.1
Mean: elevation (m)/slope (%)	249/3.9	172.0/3.2	246/1.4	1,800/5.4	165/1.3	169/7.9
Background land cover	Forest, some agriculture	Forest, some agriculture	Agriculture	Shrub and grassland, some agriculture	Agriculture, some shrub and grassland	Forest, agriculture, shrub and grassland
High base-flow: dates, no. of sites sampled	March 2003, 30	February 2003, 27	May, June 2004, 29	June 2003, 28	May 2004, 24	May 2004, 28
Low base-flow: dates, no. of sites sampled	September 2003, 30	July 2003, 30	August 2004, 30	August 2003, 28	February 2004, 24	August 2004, 28

[a] Level III ecoregions are defined in Omernik [9].
[b] From Daymet (www.daymet.org).

sites were sampled; each stream site is described by its basin (i.e., watershed) characteristics.

Study areas

The six study areas are Atlanta (in north-central Georgia and portions of eastern Alabama); Raleigh–Durham (in north-central North Carolina); Milwaukee–Green Bay (in southeastern Wisconsin); Dallas–Fort Worth (in north-central Texas); Denver (in north-central Colorado and southeastern Wyoming); and Portland (in western Oregon and parts of southwestern Washington). They vary with respect to ecoregion, climate, streamflow characteristics, and *background land cover* (defined here as nonurban land cover), as described in Table 1. Background land cover is an important characteristic because it acts as a surrogate for various nonurban pesticide sources (such as use on crops and orchards and in forestry) in the study areas. Among the six study areas, background land cover (Fig. 1) ranged from predominantly forested (Atlanta, Raleigh–Durham) or shrub land and grassland (Denver) to agriculture (Milwaukee–Green Bay, Dallas–Fort Worth) or mixed (Portland) [8].

Site selection

Within each study area, approximately 30 stream sites were selected to meet two criteria: minimum variability in natural landscape features and maximum gradient in the degree of urbanization represented by the basins. Natural variability among basins within a study area was minimized to reduce the potential for natural factors to confound the interpretation of the chemical response along the urban land use gradient [8]. Geographic Information System-derived data were used to identify candidate basins with similar environmental characteristics within a study area. The U.S. Environmental Protection Agency (U.S. EPA) ecoregions [9] provided a coarse initial framework of relatively homogeneous climate, elevation, soils, geology, and vegetation [10]. Cluster analysis of climate, elevation, slope, soils, vegetation, and geology variables was performed to group the candidate basins on the basis of natural environmental characteristics. A final set of candidate basins was identified from the most similar clusters. Second, sites were selected to cover a gradient of urbanization within the study area. Land cover, infrastructure, and socioeconomic variables were integrated into a multimetric urban intensity index (UII), which was used to characterize the overall degree of urbanization for each potential site within a given study area. A UII value was calculated for each basin as described in McMahon and Cuffney [11]. These UII values were used to select a final group of approximately 30 sites, ranging from minimally to highly urbanized, from the candidate basins.

Sample collection and analysis

Water samples for pesticide analysis were collected twice at each site, once during low base-flow and once during high base-flow conditions, between February 2003 and August 2004. In the hydrology literature, *base flow* often refers only to groundwater contributions; however, use of the term in the present study is not limited to groundwater contributions because urban streams often have many other sources of water at low flow (such as irrigation runoff and washing cars). For the present study, *low base flow* was defined as a period in which, under average climatic conditions, there are few precipitation events; *high base flow* was defined as a period in which, under average climatic conditions, there are more frequent precipitation events and streamflow is derived to a greater degree from recent rain and (or) snow fall. However, samples were not collected during storm events, nor were they necessarily collected during high pesticide use periods. By this approach, samples were collected during conditions expected

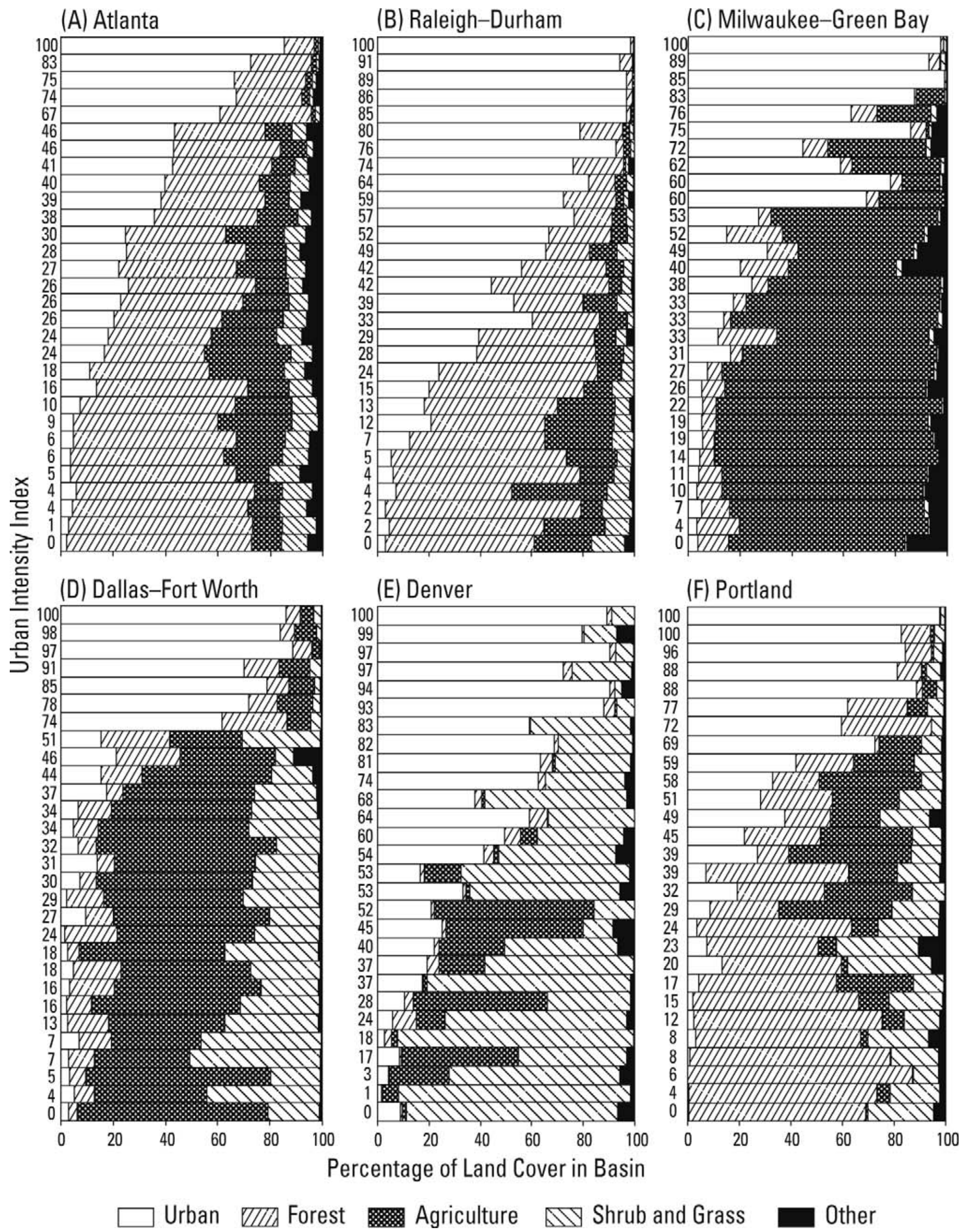

Fig. 1. Basin land cover for sites in the (**A**) Atlanta, Georgia, (**B**) Raleigh–Durham, North Carolina, (**C**) Milwaukee–Green Bay, Wisconsin, (**D**) Dallas–Forth Worth, Texas, (**E**) Denver, Colorado, and (**F**) Portland, Oregon, USA, study areas.

to be relatively stable within each study area (to facilitate comparisons among sites) but were not necessarily collected at times when pesticide concentrations were expected to be highest. In Raleigh–Durham, Milwaukee–Green Bay, and Dallas–Fort Worth, a slightly different set of sites was sampled during low versus high base flow because some sites went dry between the two sampling periods or some sites sampled once were later deemed inappropriate for subsequent sampling of aquatic communities. In these cases, the dropped site was either replaced with a similar site or not replaced. For each metropolitan area, the sampling dates and number of sites sampled are shown in Table 1.

Water samples were collected using depth- and width-integrating techniques and were processed and preserved onsite using standard methods described by the USGS [12] (http://pubs.water.usgs.gov/twri9A). Samples were filtered through a 0.7-μm pore diameter glass-fiber filter in the field to remove suspended particulate matter, and analyzed for 61 pesticide compounds (39 pesticides and 22 degradates [13]) at the USGS National Water-Quality Laboratory in Denver (CO, USA). Compounds were extracted from water samples using C-18 solid-phase extraction columns, then were identified and quantified using capillary-column gas chromatography–mass spectrometry and selected-ion monitoring [14].

Quality control and quality assurance

Concentrations in field blanks were all below laboratory reporting levels. Concentrations in replicate samples generally were consistent with those in the corresponding environmental samples. However, eight compounds (2-chloro-4-isopropylamino-6-amino-s-triazine, 4-chloro-2-methylphenol, desulfinyl fipronil, diazinon, 3,4-dichloroaniline, dieldrin, prometon, and tebuthiuron) had a mean relative percent difference of greater than 10% between the environmental and replicate samples.

For these compounds, the variability in concentrations due to field and laboratory procedures may have been greater than the variability in concentrations between some sites. One compound (2-[(2-ethyl-6-methylphenyl)-amino]-1-propanol) was not detected in a spiked field sample (i.e., false negative in a stream-water sample spiked with known quantities of pesticide analytes) from a single site, indicating that something at the site may have caused incorrect quantitation of this compound; therefore, this compound was dropped from the analysis of environmental samples from the affected site only.

Data analysis

Comparisons were made among study areas to examine the response of pesticide concentrations to urbanization in different environmental settings. The multimetric UII values used for site selection could not be used for comparisons among study areas because the UII for each study area was calculated using a slightly different set of urban variables and because UII values for sites within an individual study area were range-standardized (to range from 1 to 100) for that study area [8]. Therefore, comparisons among study areas were made using a single urban variable—the percentage of urban land cover in the basin. The percentage of urban land cover in the basin is a key variable in the UII for each study area, as indicated by its strong correlation with the basin UII values (Spearman's rank correlation coefficients were 0.98 in Atlanta, Raleigh–Durham, and Milwaukee–Green Bay; 0.97 in Portland; 0.96 in Denver; and 0.87 in Dallas–Fort Worth).

Although most samples were collected during base-flow conditions as designed, approximately 15% of samples were collected during unavoidable or unanticipated elevated streamflow conditions caused by snowmelt, reservoir releases, or localized storm drainage. These samples, which came from sites with a wide range of urban intensities, increased the variability in the data. However, these were not high-leverage points, and they were retained in the data set to maintain coverage over the urban gradient.

Concentrations. Total herbicide and total insecticide concentrations detected in each sample were calculated as the sum of their respective components, with *censored values* (i.e., nondetections expressed as less than the reporting level concentration) set to zero. Spearman's rank correlation analysis was used to assess the strength of the relationships between total herbicide and total insecticide concentrations versus the percentage of urban land cover in the basin. Correlations were considered significant if the p value was ≤ 0.05.

Within each study area, correlations during high versus low base-flow conditions were compared to examine the influence of hydrologic and seasonal variability on the response of pesticide concentrations to urbanization. When different sets of sites were sampled during high versus low base-flow conditions (in Raleigh–Durham, Milwaukee–Green Bay, and Dallas–Fort Worth), Fisher's test for nonoverlapping correlations [15] was used. When the sites sampled during high and low base flow were exactly the same (in Atlanta, Denver, and Portland), the method described by Meng and colleagues [16] for overlapping correlations was used. Correlations during high versus low base-flow conditions were considered significantly different if the p value for Fisher's or Meng's test was less than or equal to 0.05.

Regression models. The data for all six study areas were combined for analysis at a national scale—with high and low base-flow data examined separately—to examine the importance of urbanization relative to environmental characteristics (such as climate, physiography, geology, soils) in explaining patterns observed in total herbicide and total insecticide concentrations. The large sample size when data were combined nationally (n = 166 for high base flow, n = 170 for low base flow), enabled a multiple linear regression approach using log-normal maximum likelihood estimation (MLE) for data with censoring. For samples in which no herbicides or insecticides were detected, the maximum reporting limit for any of the individual compounds in the summed group was used as the reporting limit for that sample [17].

Explanatory variables for the MLE regression were obtained through principal factors analysis. Thirty urban and environmental (climate, soils, topographic, and land cover) variables were log transformed, and principal factors analysis with an oblique promax rotation was used to identify a parsimonious representation of the associations among these 30 variables. Through identification of the last substantial drop in the magnitude of the eigenvalues using the scree test and determination of the most interpretable, hydrologically meaningful combination of higher-loading variables, the first five factors were retained for the MLE regression. Loadings from principal factor analysis are shown in Appendix I (http://dx.doi.org/10.1897/07-276.S1). The first factor (F1, which accounted for 31% of the variability in the original set of 30 explanatory variables) represented urbanization. The second factor (14% of the variability) represented forested land cover and elevation, the third factor (F3; 13% of the variability) slope, the fourth factor (F4; 11% of the variability) soil permeability, and the fifth factor (F5; 8% of the variability) mean annual temperature.

The MLE regression was performed using the censorReg procedure in the statistical software package S-PLUS® 6.1 [18]. An initial model with all five factors was examined to determine whether this five-variable model predicted concentration better than the null model (mean concentration alone). Wald's tests were used to exclude nonsignificant predictors in a backward stepwise manner. Partial likelihood ratio tests comparing the more complex model to the nested simpler one then were used to determine if individual explanatory variables should be retained or excluded; based on these tests, the best regression model was selected and verified for normality and homoscedasticity of the residuals.

Pesticide toxicity index. A pesticide toxicity index (PTI), which represents the potential acute toxicity of pesticide mixtures in a sample by assuming a concentration addition model [19], was calculated for each sample. The PTI combines information on exposure of aquatic biota to pesticides (measured concentrations of pesticides in stream water) with toxicity values (from laboratory bioassays) to produce a relative index value for a sample. A PTI value was computed for each sample of stream water by summing the toxicity quotients for all pesticides detected in the sample, where the toxicity quotient is the measured concentration of a pesticide in a sample divided by the median toxicity concentration (from Munn et al. [19]) for that pesticide in laboratory bioassays. Separate PTI values were computed for fish and cladocerans.

The PTI has several important limitations, as described in Munn et al. [19]. Among the most important are that the PTI approach assumes that toxicity is additive without regard to mode of action, considers acute toxicity only, and does not include all important local species. The PTI does not indicate whether water in a sample is toxic, but it can be used to

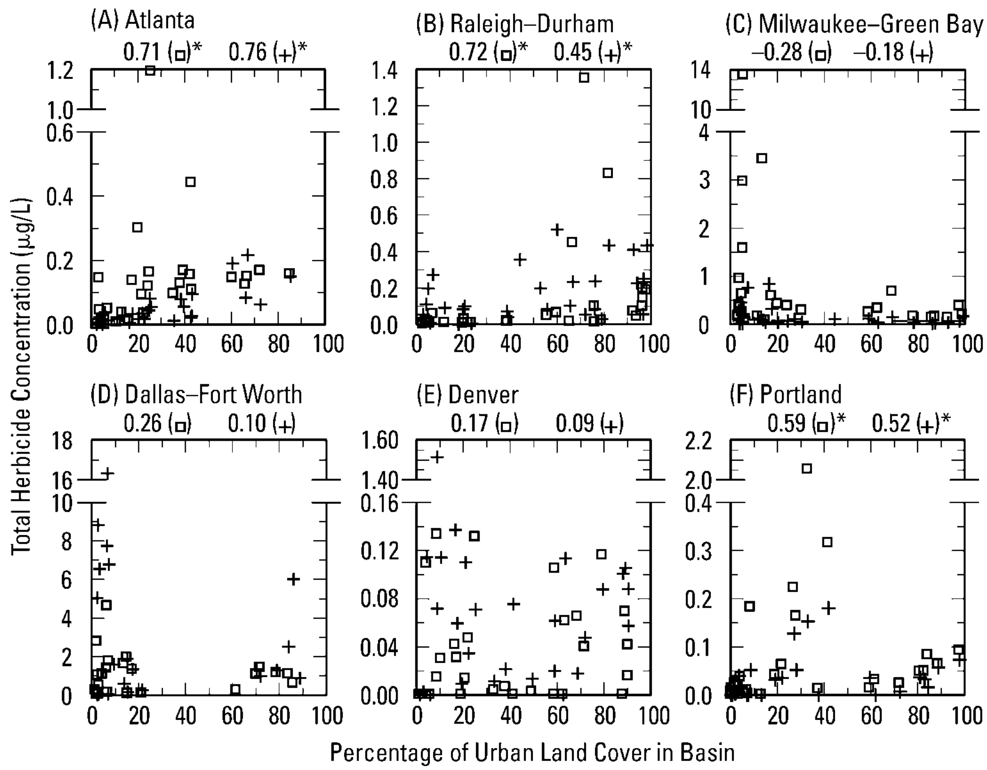

Fig. 2. Total herbicide concentrations at high and low base flow versus urban land cover in the basin (%), for the (**A**) Atlanta, Georgia, (**B**) Raleigh–Durham, North Carolina, (**C**) Milwaukee–Green Bay, Wisconsin, (**D**) Dallas–Forth Worth, Texas, (**E**) Denver, Colorado, and (**F**) Portland, Oregon, USA, study areas. High base flow (□); Low base flow (+). Spearman rank correlation coefficients are shown above each plot; an asterisk indicates that the correlation is significant at the 0.05 level.

compare the relative potential toxicity of different samples or different streams.

Benchmark exceedances. In each study area, concentrations of individual pesticide compounds were compared with water-quality benchmarks in a screening-level assessment of the potential effects of pesticides on aquatic life. The derivation and application of benchmarks, which are based on a combination of U.S. EPA ambient water-quality criteria [20] (http://www.epa.gov/waterscience/criteria/nrwqc-2006.pdf) and aquatic toxicity data from U.S. EPA pesticide risk assessments, are described in Gilliom et al. [2]. One or more aquatic-life benchmarks are available for 34 of the 61 pesticide compounds (32 pesticides and two degradates) analyzed (see Sprague et al. [13] for pesticide benchmark values used in the present study). Acute benchmarks were designed for comparison to instantaneous (maximum) contaminant concentrations, and chronic benchmarks for comparison to mean concentrations over a specific (4–60 d) averaging period [2]. In the present study, however, all benchmarks were compared to pesticide concentrations in individual base-flow samples because too few samples were collected to compute time-averaged concentrations. Although benchmark comparisons are provided as a point of reference, these comparisons have limited utility for assessing potential effects in the sampled streams because the present study sampled infrequently and under low-flow conditions, so would be unlikely to observe peak pesticide concentrations.

RESULTS AND DISCUSSION

Total herbicide concentrations

Total herbicide concentrations significantly increased as urban land cover increased ($\alpha = 0.05$) in Atlanta, Raleigh–Durham, and Portland under both high and low base-flow conditions (Fig. 2A, B, and F). In Atlanta and Raleigh–Durham, these concentration increases generally followed the decrease in forested land cover and the increase in urban land cover (Fig. 1A and B). In Portland, herbicide concentrations were highest at sites with 20 to 50% urban land cover, where the percentage of agriculture in the basins was highest, suggesting mixed agricultural and urban sources at these sites (Fig. 1F); however, the overall increase in herbicide concentrations with increasing urban land cover in Portland was significant.

In contrast, total herbicide concentrations were not significantly correlated with urban land cover ($\alpha = 0.05$) in Milwaukee–Green Bay, Dallas–Fort Worth, and Denver under either high or low base-flow conditions. In Milwaukee–Green Bay and Dallas–Fort Worth, agriculture is an important background land cover in all but the most highly urbanized basins (Fig. 1C and D). In Milwaukee–Green Bay, total herbicide concentrations tended to decrease as urban land cover in the basin increased and as agricultural land cover decreased (Fig. 2C), likely reflecting the influence of agricultural sources on herbicide concentrations. In Dallas–Fort Worth, the pattern observed may reflect the fact that the background land cover includes shrub land as well as agricultural land; total herbicide concentrations were highest in basins with low urban and relatively high agricultural land cover, then decreased sharply as agricultural land cover decreased and shrub land cover (which typically has relatively low herbicide use) increased, and finally increased slightly again as urban land cover increased and both agricultural and shrub land cover decreased in the most urbanized basins (Fig. 2D), at both high and low base flow. If land cover is considered as a surrogate for pesticide sources within the basins, these results suggest that agricultural

Table 2. Multiple linear regression results for total herbicide and total insecticide concentrations from all six study areas in the United States

Base-flow conditions used in model	Regression coefficients[a] Intercept	F1	F2	F3	F4	F5	Scale[b]	No. of samples	No. of censored samples [c]	r_L^2 [d]
Total herbicide concentration										
High	−2.42	—[e]	—	−0.97	−0.73	−0.25	1.40	166	17	41.8
Low	−2.63	—	—	−0.96	−0.64	0.46	1.33	170	15	39.4
Total insecticide concentration										
High	−4.28	0.33	—	—	—	—	1.02	166	70	71.4
Low	−4.03	0.32	—	—	—	—	1.20	170	79	69.7

[a] All regression coefficients shown had a p value ≤ 0.05. F: principal factor.
[b] Scale, estimate of dispersion.
[c] Censored samples: samples with no pesticide detections.
[d] r_L^2 = likelihood coefficient of determination.
[e] Dashes indicate factor not included as a variable in final best-fit model.

sources of herbicides may outweigh urban sources, but both are likely greater than inputs from shrub land and grassland. This interpretation is consistent with previous observations that the most common type of pesticide found is herbicides in agricultural streams, but insecticides in urban streams [2,3]. In Denver, where the predominant background land cover was shrub land (Fig. 1E), total herbicide concentrations did not follow a clear pattern relative to urban land cover (Fig. 2E) or to any nonurban land cover types or landscape variables at either high or low base flow (data not shown, see Sprague et al. [13]), indicating that herbicide concentrations in the Denver basins are influenced by factor(s) not measured in the present study. One possibility may be the extensive water management that occurs in the greater Denver metropolitan area, where a complex network of canals and pipes moves water between different areas for domestic water supply, agricultural irrigation, and power generation [21]. The movement and storage of water in the upstream drainage areas may have disrupted the transport of herbicides to the sampling sites—possibly by retaining water containing herbicides in upstream reservoirs or diverting it out of the stream to another location—resulting in concentrations that, to some degree, were independent of basin-level urban and environmental characteristics [21]. The correlation coefficients at high versus low base flow were not significantly different for any of the six study areas.

When data from all six metropolitan areas were combined and examined at a national level using multiple regression with explanatory variables obtained from factor analysis, factors F3 (slope), F4 (soil permeability), and F5 (mean annual temperature) best described the variability in total herbicide concentrations during high and low base-flow conditions in the basins sampled (Table 2). In both high and low base-flow models, the proportion of variance in total herbicide concentrations explained by the model was approximately 40%, suggesting that other factors not measured in the present study account for most of the variability among concentrations in the streams sampled.

Total insecticide concentrations

Total insecticide concentrations significantly increased with increasing urban land cover ($\alpha = 0.05$) in all six metropolitan study areas (Fig. 3), the only exception being the low base-flow condition in Milwaukee–Green Bay. This contrasts with the response of herbicides, which appeared to vary depending on the background land cover and other factors (such as water management). Urban inputs of insecticides appear to be sufficient to outweigh inputs from sources in agricultural or undeveloped (forest or shrub land) areas. Even in Denver, total insecticide concentrations increased with increasing urbanization (Fig. 3E), whereas there were no clear patterns in total herbicide concentrations with increasing urbanization (Fig. 2E). Because the majority of Denver basins had a disproportionate percentage of urban development close to the sampling site [8], it is possible that pesticides (including insecticides) applied in urban areas were less affected by water management than were pesticides applied in upstream areas.

The correlation of total insecticide concentrations with urban land cover was statistically different during high and low base-flow conditions in only one study area—Dallas–Fort Worth, where the response was stronger during high base-flow conditions (May) than during low base-flow conditions (February), perhaps resulting in part from more frequent, sustained rainfall events in May that contributed to higher rates of runoff.

When data from all six metropolitan areas were combined and examined on a national scale using multiple regression with explanatory variables obtained from factor analysis, F1 (urbanization) alone best described the variability in total insecticide concentrations during both high and low base-flow conditions for the basins sampled (Table 2). The proportion of variance in concentrations explained by both the high and low base-flow models was substantially higher for insecticides (~70%) than for herbicides (~40%). Considered both nationally and by individual study area, total insecticide concentrations in the basins sampled were largely determined by the level of urbanization in the basin.

Background land cover—which acts as a surrogate for pesticide sources in the basin—is key to understanding the different responses of pesticide concentrations to urbanization in the six study areas. Although the actual land use history of the urbanized sites in each study area is unknown, it is reasonable to hypothesize that these basins once resembled the less-urbanized basins in the same study area. In general, conversion of forest or shrub land (where pesticide use tends to be minimal) to urban land would be expected to result in increased pesticide use in the basin. This would be consistent with the increased stream-water concentrations of both herbicides and insecticides observed with increasing urban land cover in Atlanta, Raleigh–Durham, and Portland, where forest and shrub land make up the principal background land cover. On the other hand, conversion of agricultural land (where use of pesticides, especially herbicides, is high) to urban land (where insecticides and some herbicides are applied) would

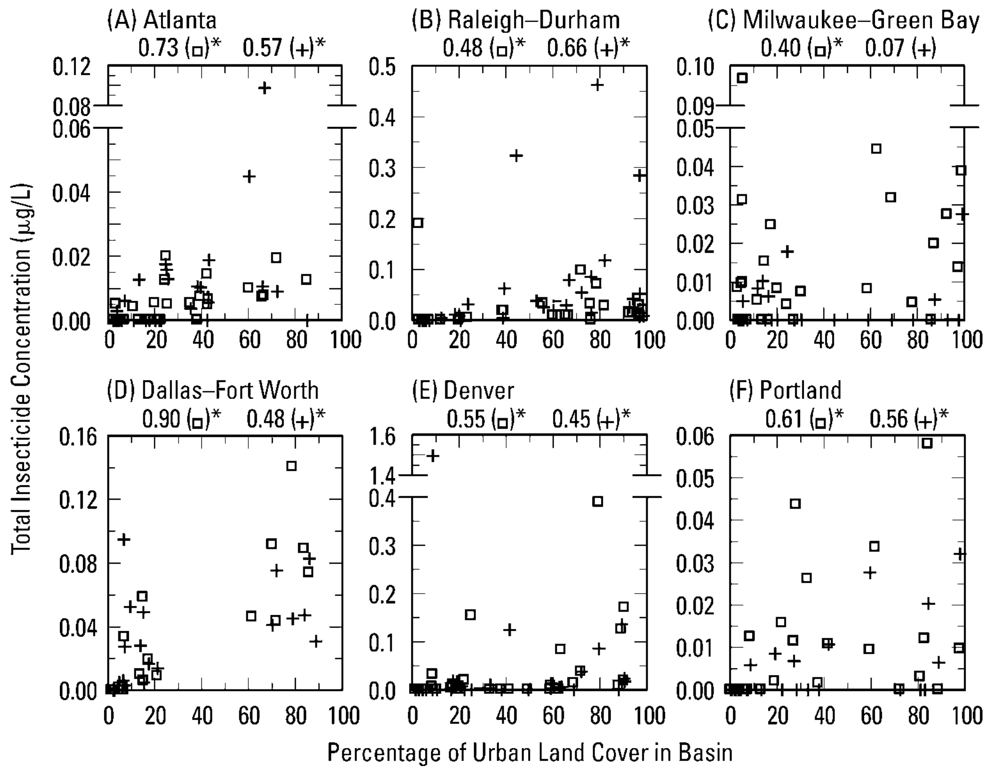

Fig. 3. Total insecticide concentrations at high and low base flow versus urban land cover in the basin (%), for the (**A**) Atlanta, Georgia, (**B**) Raleigh–Durham, North Carolina, (**C**) Milwaukee–Green Bay, Wisconsin, (**D**) Dallas–Forth Worth, Texas, (**E**) Denver, Colorado, and (**F**) Portland, Oregon, USA, study areas. High base flow (□); Low base flow (+). Spearman rank correlation coefficients are shown above each plot; an asterisk indicates that the correlation is significant at the 0.05 level.

not necessarily be expected to increase the total quantity of pesticides applied in the basin, but likely would affect the types of pesticides applied. This would be consistent with observations in Milwaukee–Green Bay and Dallas–Fort Worth, where total insecticides in stream water increased, but total herbicides tended to decrease, as the urban land cover in the study area increased. In Denver, the relation between herbicide concentrations and sources in the basins may have been obscured by the extensive water management occurring in the study area, which may disrupt pesticide transport to streams. However, the positive relation between insecticides and urban land cover (which is disproportionately located near the sampling sites) is consistent with conversion of shrub land and grassland to urban land.

Individual pesticide detections and pesticide toxicity index

Within each study area, mixtures of pesticides were often detected, with some individual pesticides detected at multiple sites. Examples from two study areas show the *pesticide signature*—i.e., concentrations of individual pesticides detected at individual sites in the study area—as a function of urban land cover in the basin under low base-flow conditions. Atlanta (Fig. 4) and Milwaukee–Green Bay (Fig. 5) were selected as examples representing forested and agricultural background land cover, respectively. Both figures show pesticide concentrations in the stream (part A) and after normalization by the PTI for cladocerans and fish (parts B and C). (Figs. 4 and 5 have the same legend, but the *y* axis scales vary.) Similar figures for high base flow and for the other study areas are provided in Sprague et al. [13].

Pesticide signatures reflect the pesticides used within each study area, including both urban and nonurban sources within the individual basins. At high base flow, pesticide signatures for five of the six study areas were dominated by high herbicide concentrations, especially atrazine, simazine, and in some study areas, metolachlor or tebuthiuron. The exception was Denver, whose pesticide signature (not shown) was dominated by insecticides, especially carbaryl, diazinon, and malathion, at both high and low base flow [13]. In the three study areas where the background land cover is predominantly forest and (or) shrub land—Atlanta (Fig. 4A), Raleigh-Durham, and Portland [13]—pesticide concentrations generally were higher at moderately to highly urbanized sites. High base-flow samples were dominated by one or two triazine herbicides, either simazine and (or) atrazine [13], whereas there was a greater variety of pesticides in low base-flow samples. For example, Atlanta's low base-flow sample (Fig. 4A) contained simazine, prometon, and tebuthiuron (all herbicides with substantial nonagricultural uses), atrazine, the herbicide degradate 3,4-dichloroaniline (shown as other herbicides in Fig. 4), and the insecticides carbaryl, diazinon, and fipronil.

Pesticide signatures in the other three study areas did not show a strong relation with urban land cover. In Milwaukee–Green Bay (Fig. 5A) and Dallas–Fort Worth [13]—where the predominant background land cover is agriculture—pesticide concentrations were highest at sites with less than 20% urban land cover, probably resulting from agricultural sources in the less urbanized basins. The herbicides atrazine and (or) metolachlor (which both have high agricultural use) dominated the pesticide signatures under both high and low base-flow conditions. Other pesticides important at one or more sites included the fungicide metalaxyl and insecticides malathion and carbaryl in Milwaukee–Green Bay (Fig. 5A), and the herbicides tebuthiuron and simazine in Dallas–Fort Worth [13].

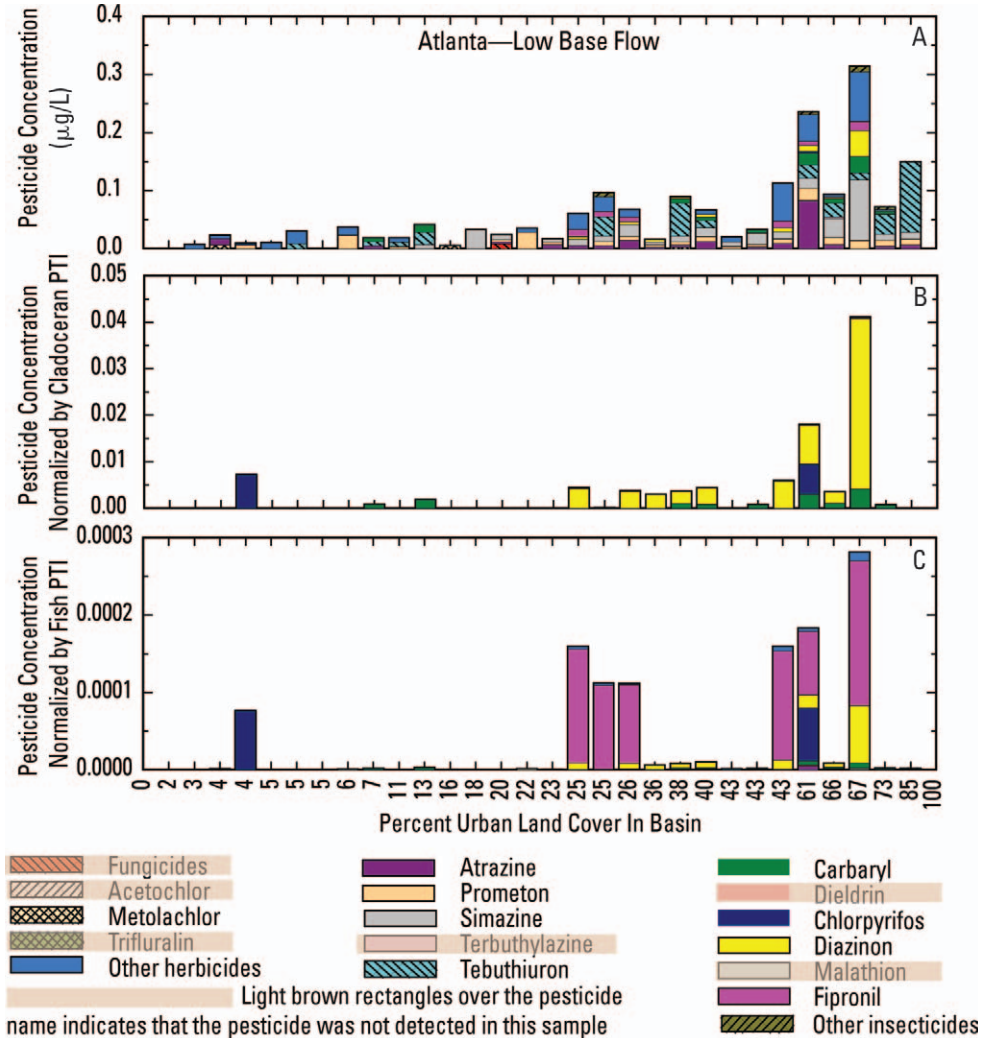

Fig. 4. Pesticide concentrations in stream water in the Atlanta, Georgia, USA, study basins at low base flow, compared to urban land cover in the basin (%). Concentrations are shown (**A**) in micrograms per liter, (**B**) normalized by the cladoceran pesticide toxicity index (PTI), and (**C**) normalized by the fish PTI.

The pesticide signature for Denver [13] was unique in that the predominant pesticides detected were the urban herbicide prometon and the insecticides carbaryl and malathion. At high base flow, these same pesticides were often detected, along with herbicides tebuthiuron, pendimethalin, atrazine, metolachlor, the degradate 3,4-dichloroaniline, and the insecticide diazinon. The highest pesticide concentrations were observed at low base flow at a site with about 9% urban land cover.

When absolute pesticide concentrations were normalized by the PTI, the pesticide signature dramatically changed (parts B and C in Figs. 4 and 5), indicating that the pesticides with the greatest potential to adversely affect cladocerans or fish were not necessarily the pesticides detected at the highest concentrations. Cladocerans, which are arthropod invertebrates, are sensitive to insecticides [22]. In fact, the cladoceran–PTI-normalized plots for all six study areas were dominated by insecticides, especially diazinon, chlorpyrifos, carbaryl, and (or) malathion (Figs. 4B and 5B; [13]). The prevalence of diazinon and chlorpyrifos is somewhat surprising because the sampling period for the present study (2003–2004) occurred during the U.S. EPA's phase-out of all residential uses of diazinon (2001–2004) and most residential uses of chlorpyrifos (2000–2005) (http://www.epa.gov/pesticides/factsheets/chemicals/diazinon-factsheet.htm; http://www.epa.gov/oppsrrd1/REDs/factsheets/chlorpyrifos_fs.htm). Likely urban replacements for diazinon and chlorpyrifos include carbaryl, malathion, imidacloprid, and several pyrethroids (http://www.tdcenvironmental.com/upc031803.pdf). Of these, carbaryl and malathion were common in cladoceran–PTI-normalized plots (part B, Figs. 4 and 5); three pyrethroid insecticides analyzed in filtered water [13] in the present study were not detected (although pyrethroids are likely to partition to sediments, so concentrations would be decreased by filtration); and imidacloprid was not analyzed in the present study.

When normalized by the fish PTI (part C, Figs. 4, 5), the pesticide signature typically differed from both the absolute concentration signature (part A) and the cladoceran–PTI-normalized signature (part B). The fish–PTI-normalized signatures contained the same insecticides that predominated in the cladoceran–PTI-normalized signatures—chlorpyrifos and diazinon, and in some study areas malathion and carbaryl—but additional pesticides also were important. Fipronil (a relatively new insecticide used for structural pest control and on some crops such as rice) appeared in fish-PTI plots for all six study

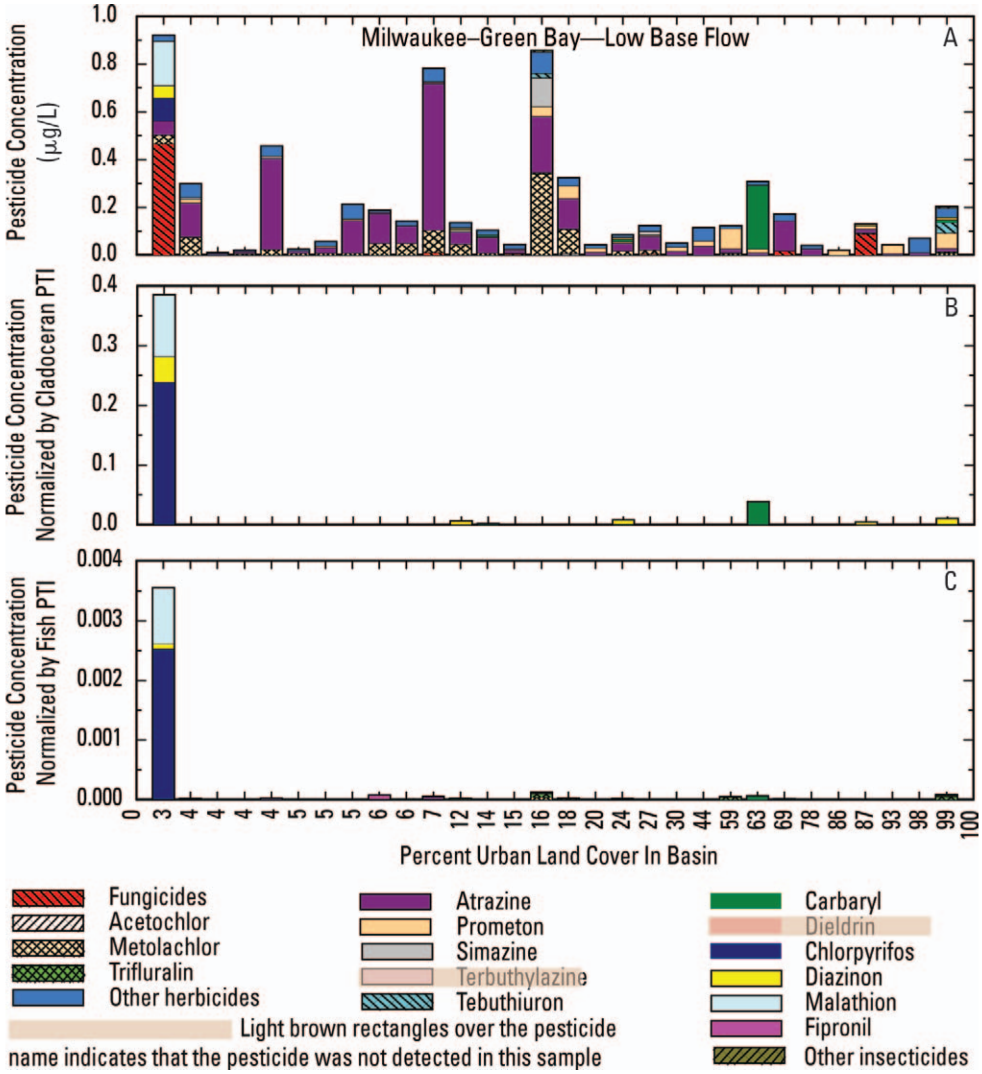

Fig. 5. Pesticide concentrations in stream water in the Milwaukee–Green Bay, Wisconsin, USA, study basins at low base flow, compared to urban land cover in the basin (%). Concentrations are shown (**A**) in micrograms per liter, (**B**) normalized by the cladoceran pesticide toxicity index (PTI), and (**C**) normalized by the fish PTI.

areas, but was especially common in Atlanta (Fig. 4C), Raleigh–Durham, and Dallas–Fort Worth [13]. Other pesticides more important in some fish-PTI plots than in the corresponding concentration plots include the discontinued, but persistent, organochlorine insecticide dieldrin (Dallas–Fort Worth, Raleigh–Durham); the nematocide fenamiphos (Portland); and the herbicides trifluralin (Raleigh–Durham, Portland), atrazine (Atlanta, Fig. 4; Portland), acetochlor (Milwaukee–Green Bay), and pendimethalin (Denver) [13].

Benchmark exceedances

Pesticide concentrations exceeded aquatic-life benchmarks in only four samples, one from each of four sites in three study areas. Concentrations of one or more pesticides exceeded benchmarks at two sites in Raleigh–Durham (acute and chronic benchmarks for diazinon), one site in Denver (chronic benchmarks for malathion), and one site in Milwaukee–Green Bay (chronic benchmarks for malathion; acute and chronic benchmarks for chlorpyrifos). The exceedances occurred at sites located in basins with 3 to 44% urban land cover, and under both low (three samples) and high (one sample) base-flow conditions. Benchmark exceedances at these sites are noteworthy because pesticide concentrations are likely to be lower under the conditions (base flow) sampled in the present study than at other times of the year, such as during peak pesticide-use periods, storm events, or irrigation discharge. For the same reason, the absence of exceedances at other sites does not indicate that benchmark exceedances do not occur at other times. The benchmark exceedance frequencies in the present study are far lower than those observed in broader sampling by the NAWQA program during 1992 to 2001, where over 80% of streams sampled in urban areas had pesticide concentrations in water that exceeded one or more aquatic-life benchmarks [2].

CONCLUSIONS

The response of pesticide concentrations in base flow to urbanization differed for herbicides versus insecticides and by environmental setting. Total insecticide concentrations were significantly related to urbanization in all six metropolitan areas ($\alpha = 0.05$). In contrast, total herbicide concentrations were significantly related to urbanization in only three of six metropolitan areas—those in which forest and shrub land were the predominant background land cover in minimally urbanized basins (Atlanta, GA; Raleigh–Durham, NC; and Portland, OR). In Portland, there was evidence of mixed agricultural and urban sources at sites with 20 to 50% urban land cover; however, the overall increase in herbicide concentrations with increasing urban land cover was significant. In Dallas–Fort Worth, Texas, and Milwaukee–Green Bay, Wisconsin—where agriculture was the predominant background land cover—agricultural sources of herbicides in less urbanized basins likely contributed to the high herbicide concentrations observed in basins with low-to-intermediate urban land cover. And in Denver, Colorado, total herbicide concentrations were not related to urban or agricultural land cover, and therefore appear to be influenced by other factors not measured in the present study. One possibility is that herbicide transport was disrupted by the upstream diversion and storage of water prevalent in the Denver study area; because a disproportionate percentage of urban land cover was located near the sampling sites in this study area, the transport of urban insecticides may have been less affected by water management than herbicides were. In all six study areas, even those where pesticide concentrations were significantly related to urban land cover, there likely were additional (nonurban) sources contributing to the pesticide concentrations measured in streams.

These findings suggest that pollution control practices intended to control insecticide transport in urbanizing areas may be effective when developed nationally, although consideration of local factors likely will improve the outcome. In contrast, pollution control practices intended to control herbicide transport to streams in urbanizing areas may be most effective when developed locally, and may need to be supplemented with additional steps to control agricultural inputs. Moreover, it may be important to consider the effects of local or regional water management (diversion and storage) on pesticide transport when designing and implementing pesticide control practices.

Within a study area, the pesticide signature reflected the pesticides used in the study area, and land use patterns within the individual basins. Normalization of pesticide concentrations by the PTI dramatically changed the pesticide signature, indicating that the pesticides with the greatest potential to adversely affect cladocerans or fish were not necessarily the pesticides detected at the highest concentrations. Herbicides dominated the pesticide signatures in terms of absolute concentrations in five of the six study areas (all except Denver). However, insecticides—especially diazinon, chlorpyrifos, fipronil, and carbaryl—were dominant in pesticide signatures after normalization by the PTI for fish and (or) cladocerans for all six study areas. Additional pesticides that were more important in PTI-normalized signatures than in concentration signatures for one or more study areas included the insecticides malathion and dieldrin and the herbicides trifluralin, acetochlor, and pendimethalin. Measured pesticide concentrations rarely exceeded aquatic-life benchmarks. Because the present study sampled stream water only twice within one year under base-flow conditions, the results described here probably underestimate pesticide occurrence and benchmark exceedance frequencies in these streams at other times, such as during peak pesticide-use periods, storm events, or irrigation discharge.

SUPPORTING INFORMATION

Appendix I. Loadings from principal factor analysis. Found at DOI: 10.1897/07-276.S1 (16 KB PDF).

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