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Temporal Changes in Surface-Water Insecticide Concentrations after the Phaseout of Diazinon and Chlorpyrifos

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The recent (late 2001) federally mandated phaseout of diazinon and chlorpyrifos insecticide use in outdoor urban settings has resulted in a rapid decline in concentrations of these insecticides in urban streams and rivers in the northeastern and midwestern United States. Assessment of temporal insecticide trends at 20 sites showed that significant step decreases in diazinon concentrations occurred at 90% of the sites after the phaseout, with concentrations generally decreasing by over 50% in summer samples. Chlorpyrifos concentrations showed significant step decreases in at least 1 season at 3 of the 4 sites with sufficient data for analysis. The decrease in diazinon concentrations in response to the phaseout resulted in a decline in the frequency of concentrations exceeding the acute invertebrate water-quality benchmark of 0.1 μg/L from 10% of pre-phaseout summer samples to fewer than 1% of post-phaseout summer samples. Although some studies have indicated an increase in concentrations of carbaryl in response to the organophosphorous phaseout, carbaryl concentrations only increased at 1 site after the phaseout. A full assessment of the effect of the phaseout of diazinon and chlorpyrifos on surface water will require data on other insecticides used to replace these compounds.

Introduction

In late 2000, the United States Environmental Protection Agency (USEPA) and the manufacturers of organophosphorous insecticides reached an agreement that curtailed the use of diazinon and chlorpyrifos in urban settings (*1*−*3*). The agreement resulted in the phaseout of diazinon for residential outdoor use, through a mandated 25-percent decrease in production in 2002 and a 50-percent decrease in production in 2003 (*1*, *2*, *4*). All sales of diazinon to retailers had ceased by August 2003, and, by December 2004, registration and sales for residential outdoor uses of diazinon had ended. Retail sales of chlorpyrifos for most home outdoor uses ended in December 2001, and application rates were lowered for remaining uses (*3*, *5*). The USEPA anticipated that the phaseout would result in a decrease in chlorpyrifos and diazinon stream concentrations (*2*, *4*, *5*).

The phaseout of diazinon and chlorpyrifos resulted in decreasing sales at some home improvement and garden supply stores, and an attendant increase in sales of alternative compounds. Diazinon sales from large home-improvement stores in King County, Washington decreased by 50% in 2002 (*6*), whereas sales of carbaryl increased tenfold that year. A study of insecticide sales in the San Francisco area indicated that sales of diazinon and chlorpyrifos for home use decreased and that sales of pyrethroid insecticides increased between 2000 and 2003 (*7*).

Assessments of temporal trends of diazinon, chlorpyrifos, and carbaryl have been limited to studies in Texas and the Pacific Northwest. The detection frequency of diazinon decreased from 100% to 45% and average growing-season concentration declined from 0.32 to 0.04 μg/L between 2001 and 2004 in 70 streams in Denton, Texas (*8*); the percentage of sites with detectable concentrations of chlorpyrifos decreased from 68 to 11% from 2001 to 2002 at these sites (*9*). A study at two urban streams in the Pacific Northwest found that diazinon concentrations in these streams before the phaseout (1999 and earlier) were greater than those in 2001−2002 (*6*), whereas carbaryl concentrations in these streams increased.

National (*10*, *11*) and regional (*12*−*16*) studies in the United States have identified diazinon, chlorpyrifos, and carbaryl as some of the most frequently detected pesticides in urban streams, suggesting that changes in the concentrations of these insecticides should be observable on a regional basis. Diazinon and chlorpyrifos were detected in more than 25% of samples collected from urban streams across the United States during 1992−2001, reflecting the common use of these compounds in residential settings. Diazinon is highly toxic to freshwater aquatic invertebrates (*2*, *4*), and concentrations of diazinon in urban streams can exceed levels indicative of potential adverse effects on wildlife. For example, the 1992−2001 national study indicated that diazinon concentrations exceeded an acute invertebrate aquatic-life benchmark (0.10 μg/L) in at least 1 sample from 57% of urban streams sampled, whereas chlorpyrifos exceeded this benchmark (0.05 μg/L) in at least 1 sample from 30% of those streams, and carbaryl exceeded this benchmark (2.55 μg/L) in at least 1 sample from fewer than 25% of the streams (*10*). Any decrease in diazinon and chlorpyrifos concentrations in response to the phaseout would be expected to decrease the ecological effects of these insecticides on aquatic life. However, if concentrations of other insecticides increased after the phaseout, the overall effect on aquatic life may not change.

This paper analyzes recent (1993−2004) temporal trends in concentrations of diazinon and chlorpyrifos in 20 streams throughout the northeastern and midwestern United States in response to the recent phaseout of outdoor residential uses of these insecticides. This assessment does not give a complete indication of the changes in the occurrence of all insecticides in streams after the phaseout because pyrethroids and many other insecticides used as replacements for diazinon and chlorpyrifos were not analyzed. However, this paper does assess temporal changes in carbaryl to indicate whether changes in diazinon and chlorpyrifos concentrations are correlated with changes in concentrations of another urban-use insecticide whose sales have not been subject to a phaseout.

Materials and Methods

Pesticide samples were collected periodically from 20 selected streams and rivers (Supporting Information Table 1) in the

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northeastern and midwestern United States from 1992 to 2004 as part of the U.S. Geological Survey (USGS) National Water Quality Assessment program. The 20 sites met two criteria necessary for determination of diazinon temporal trends: (1) at least 20% of all the samples collected at each site had detectable concentrations of diazinon, and (2) at least 20 samples were collected before and 20 samples were collected after October 1, 2001. Of these 20 sites, 16 sites met these criteria for determining carbaryl trends, and three met these criteria for determining chlorpyrifos trends; an additional site with a chlorpyrifos detection frequency of 18% was included in the chlorpyrifos trend determination. The sampling frequency at each site varied but included at least 6 samples per year collected bimonthly. Overall, urban applications were likely the predominant source of insecticides detected in the streams, due to the elevated population density (greater than 200 per km^2) at most of the sites (Supporting Information Table 1).

Sample Collection and Analysis. Standard width- and depth-integrated techniques were used along with trace organic collection protocols (*17*). Samples were passed through a 0.7-μm baked glass-fiber filter, collected in 1-L amber glass bottles, chilled to 4 °C, and shipped overnight to the USGS National Water Quality Laboratory (NWQL) in Denver, CO for analysis. Concentrations of carbaryl, chlorpyrifos, and diazinon were measured at the NWQL by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected ion monitoring (*18*).

Determinations of carbaryl concentrations by the analytical method used in this study may be more variable than those for diazinon and chlorpyrifos, so that it may be harder to detect temporal changes in carbaryl than in the other two compounds. Method development data indicate that carbaryl has a higher variability in method performance than either chlorpyrifos or diazinon (*18*). Field spike data indicate median recoveries are similar among these compounds (ranging from 88% for diazinon to 99% for carbaryl), but that relative standard deviations are higher for carbaryl (63%) than for chlorpyrifos and diazinon (25 and 19%, respectively) (*19*). Field replicate data are similar among these analytes, however: relative median standard deviations for field replicates range from 8 to 12% for carbaryl, 9 to 13% for chlorpyrifos, and 2.9 to 9.4% for diazinon (*20*).

Chlorpyrifos was detected in 1 of 134 blank samples collected and carbaryl was detected in none of the blank samples. Seven of eight diazinon blank detections were associated with samples collected at 2 sites within a short period; data at these 2 sites within this period were censored to account for these blank detections, and were not used in trend calculations. The long-term method detection level (LT-MDL) ranged from 0.003 μg/L for chlorpyrifos and diazinon to 0.021 μg/L for carbaryl. Confirmed detections below the LT-MDL are considered as estimated values (*18*), and were treated the same as concentrations reported above the LT-MDL in all statistical analysis and computations. For computational purposes, nondetected concentrations were set to less than the lowest estimated concentration; the statistical results were not affected by the use of this value for nondetections.

Data Analysis. The seasonal step-trend analysis was the primary method used to assess temporal trends in this study (*21*); this analysis involved performing a nonparametric rank-sum test on pesticide concentrations for the period before and after October 1, 2001 (pre-phaseout and post-phaseout periods, respectively). Step trends were evaluated for 3 seasons: summer (Jun−Sep), fall−winter (Oct−Jan), and winter−spring (Feb−May), and correspond to the seasonal variability in pesticide concentrations. Step-trend analysis was performed only on seasons in which at least 6 samples were collected in each of the pre- and post-phaseout periods. The step-trend analysis indicates the significance of the pre-phaseout and post-phaseout concentration comparison; this method was supplemented with the Hodges−Lehman estimator (*21*) which was used to indicate the magnitude of the concentration difference between the pre- and post-phaseout periods. The Hodges−Lehman estimator is a nonparametric method, which is the median of all pairwise differences between two independent groups (in this case, insecticide concentrations from before and after the phaseout), calculated on a seasonal basis. The percent difference in concentration between the 2 periods was calculated for each season by dividing the Hodges−Lehman estimator by the median concentration for the pre-phaseout period.

The Seasonal Kendall test (*22*) was also used at 8 sites with adequate data to confirm results indicated by the step-trend analysis, and generally focused on the period from October 1998 through September 2004—a time span that includes an equal number of years before and after the diazinon phaseout. The number of seasons used in the analysis (4−12) was chosen to maximize the number of possible within-season statistical comparisons. No flow adjustment was used in trend analyses because the concentrations were not strongly correlated with discharge (Supporting Information Figure 1). General relations between concentrations and time or discharge were evaluated through the locally weighted scatterplot smoothing (LOWESS) procedure (*23*). Statistical tests for temporal trends were considered significant for *p*-values less than or equal to 0.10, although most significant trends reported had *p*-values of less than 0.05.

Results

Temporal Trends in Pesticide Concentrations 1994−2004. Plots of concentration over time at site VA1 show decreased concentrations since 2000−2001 for diazinon and chlorpyrifos (Figure 1); plots of 15 of the 20 sites included in the trend analysis show a similar decrease in diazinon concentration since 2000−2001. Plots for chlorpyrifos at site VA1 (Figure 1) and the 3 other sites (NJ2, OH1, and OH2) with sufficient data for trends assessment show similar decreases beginning in 2000. These plots indicate that the decrease in diazinon and chlorpyrifos concentrations began as early as 2000, suggesting that the decline may have preceded the start of the phaseout in late 2001. By contrast, plots of carbaryl over time at site VA1 (Figure 1) and the 15 other sites with sufficient data for carbaryl trends assessment indicated no consistent decrease or increase around the phaseout period.

Diazinon. The step-trend analysis showed a significant decrease ($p < 0.05$) in diazinon concentrations after the phaseout (in October 2001) in 18 (90%) of the 20 streams in at least 1 season, confirming that the phaseout resulted in a significant decrease in diazinon concentrations in streams. The concentration decreases were most prevalent during the summer and in watersheds with high population density (Figure 2). Significant decreases in diazinon concentrations occurred during the summer at 14 (70%, Figure 3) of the 20 sites, during the winter−spring at 7 (35%) of the 20 sites, and during the fall−winter at 4 (27%) of the 15 sites with sufficient data (Figure 2). No site had any season with a significant step increase in diazinon concentrations.

Seasonal decreases in diazinon concentrations after the phaseout, as indicated by the Hodges−Lehmann estimator, ranged from around 10% to about 90% for the 16 sites with sufficient data. The greatest decrease was found for summer samples, which had a median decrease of 63% for the 14 sites with sufficient data for calculation of the Hodges−Lehmann estimator; decreases in this season generally ranged from 50 to 85%. The percent decrease for the other 2 seasons generally ranged from 30 to 70%.

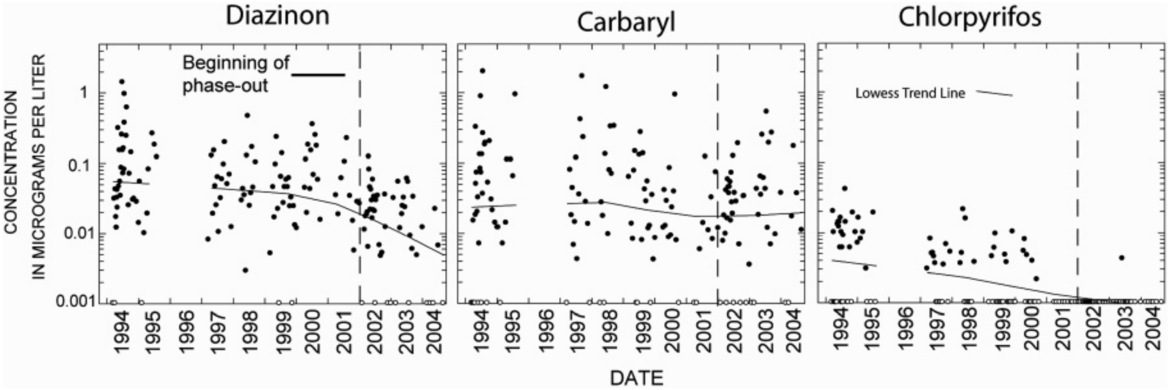

FIGURE 1. Temporal trends in concentrations of diazinon, carbaryl, and chlorpyrifos at Site VA1, 1994–2004. LOWESS trend line (solid line) denotes general temporal trend. Dashed line denotes beginning of phaseout period for diazinon and chlorpyrifos. Nondetected values are shown as open circles plotted at 0.001 μg/L .

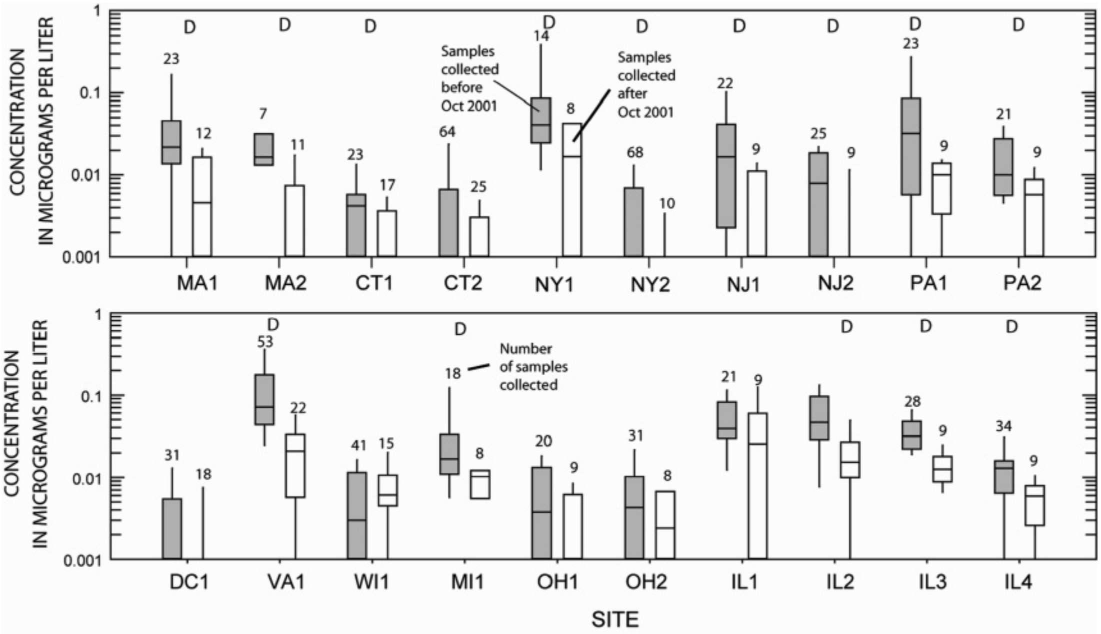

FIGURE 2. Concentrations of diazinon in summer (June–September) streamwater samples from the 20 sites in the northeastern and midwestern United States, 1994–2001 (before 2001 phaseout) and 2002–2004 (since phaseout). Box plots depict seasonal distribution of concentrations, with top whisker equal to 90% of concentrations, bar at the top of box equal to the 75th percentile, bar at the middle of the box equal to the 50th percentile, bar at the bottom of the box equal to the 25th percentile, and bottom whisker equal to the 10th percentile. Shaded box indicates the concentration range for samples collected before the phaseout of diazinon (samples collected before October 1, 2001) and the unshaded box represents the concentration range for samples collected after the phaseout of diazinon (samples collected after October 1, 2001). A 'D' above the paired boxplots indicates a significant ($p < 0.05$) step-trend decrease for summer samples between the pre- and post-phaseout periods for that site. Sites are described in Supporting Information Table 1.

Results of the Seasonal Kendall test results were similar to those for step-trend results. The Seasonal Kendall tests based on 1998–2004 data indicate that diazinon concentrations decreased significantly by 20–40% at 6 of the 8 sites with sufficient data for analysis (Figure 4). Four of these sites had a step decrease in diazinon concentrations for 2 or more seasons, and a significant step decrease was found in 1 of the 3 seasons at the other 2 sites. Although the Seasonal Kendall test for site MA1 indicated a decrease of around 10%, this change was not statistically significant (Figure 4); however, the step-trend analysis indicated a significant decrease in summer sample diazinon concentrations at this site. Both the Seasonal Kendall and step-trend results indicated no significant change in diazinon concentrations at site OH2.

Comparison of Seasonal Kendall estimates for a series of incrementally increasing periods (1998–2004, 1997–2004, 1996–2004, and 1995–2004) confirms that much of the decrease occurred during the latter part of the data record. Estimates of decreases in diazinon concentrations for these 4 periods at 2 sites (VA1 and IL4) indicate that, as additional years before 1998 are included in the Seasonal Kendall test, its power to discern the effect of the 2001 phaseout of diazinon use is gradually diminished (Supporting Information Figure 2). The lack of trends, or the decreasing strength of trends, with increased time periods confirms that the changes in pesticide concentrations detected by the step-trend tests occurred over only a few years, contemporaneous with the diazinon phaseout, and did not reflect decreases in diazinon use beyond 3 years before the phaseout.

Chlorpyrifos and Carbaryl. The phaseout of chlorpyrifos use beginning in 2001 resulted in significant step decreases in concentration at 3 of the 4 sites (NJ2, VA1, OH1) with sufficient data for analysis. These 3 sites had significant step decreases in chlorpyrifos concentration during the summer, and 2 of these sites (NJ2, VA1) had significant decreases in the winter–spring; VA1 also had a significant decrease in the

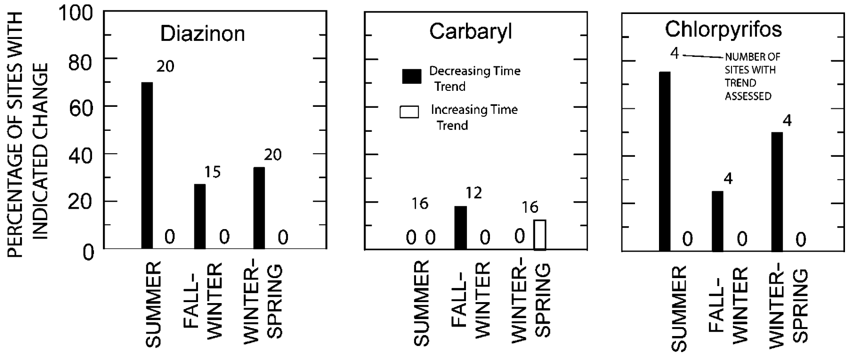

FIGURE 3. Percentages of sites with a significant step-trend increase or decrease in pesticide concentration, by season, in 3 years before, and 3 years after the phaseout of diazinon sales in October 2001 (summer represents June–September, fall–winter represents October–January, and winter–spring represents February–May). A zero (0) denotes that no sites had a significant trend. All trends are significant at the 0.05 level except for the winter–spring decrease for diazinon (3 of 7 sites have a *p*-value of <0.10) and the winter–spring decrease trend for chlorpyrifos (1 of 3 sites had a *p*-value of <0.10).

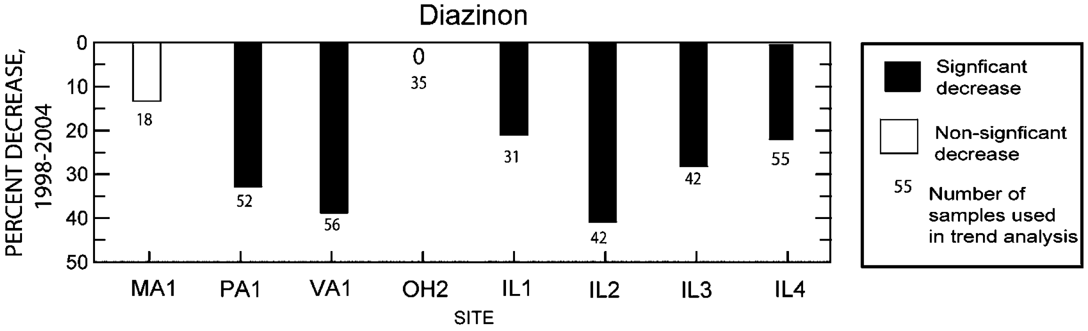

FIGURE 4. Percent change in diazinon concentration, 1998–2004, using Seasonal Kendall trend test at the 8 sites with sufficient data for trends test. A zero (0) denotes a non-significant percent change less than 5%. No sites had a significant increase in diazinon concentration. Analysis for all sites used 12 seasons, except for MA1 (4 seasons) and OH2 and IL1 (6 seasons). All trends are significant at the 0.05 level except for IL4, which is significant at the 0.10 level.

fall–winter season (Figure 3). The detection rate for chlorpyrifos in samples collected before October 2001 at these 3 sites ranged from 23 to 45%; after October 2001, the percent detections ranged from 2 to 8%. The decline in percent detection for site OH2 was less (23 to 15%) between the 2 periods, which is consistent with the lack of a significant Seasonal Kendall trend at this site. Hodges–Lehmann estimates of percent change by season reflect these changes in detection frequency at sites NJ2 and VA1 (percent change at site OH1 could not be calculated), as chlorpyrifos concentration decreased by nearly 100% at these sites in all seasons with significant step decreases.

Carbaryl, whose use was not curtailed during the 1992–2004 study period, showed a significant step trend at very few sites (Figure 3). Significant changes in carbaryl concentrations were not found in any of the 16 sites with adequate data for assessment of summer trends for carbaryl, and few (less than 20%) of the sites had an increasing or decreasing trend in the 2 other seasons.

Discussion

Analysis of diazinon data at 20 sites indicate that, as anticipated by the USEPA (*4*), concentrations of diazinon rapidly decreased in streams in the northeastern and midwestern United States in response to the phaseout of residential uses of this insecticide beginning in late 2001. These results are similar to those found in Texas (*8*) and the Pacific Northwest (*6*), which also indicated a rapid decrease in diazinon concentrations in response to the phaseout. The significant decline in chlorpyrifos concentrations observed in most of the 4 streams in this region after the chlorpyrifos phaseout is also consistent with trends found in Texas (*9*). These results show that phasing out commonly used urban pesticides can result in rapid declines in stream pesticide concentrations throughout the United States, and that these declines may predate the official start of the phaseout.

Decreases in diazinon and chlorpyrifos concentration were greatest in highly urbanized watersheds; for example, all 6 of the sites with summer diazinon decreases over 80% had population densities greater than 400 per km^2, and agricultural land use less than 40% (Supporting Information Figure 3). The only 2 sites with significant decreases in chlorpyrifos for 2 or more seasons (sites NJ2 and VA1) are also highly urbanized (population density greater than 1000 km^2 and agricultural land use less than 5%).

By contrast, diazinon and chlorpyrifos concentrations did not decrease as much at the 2 agricultural sites. Neither of the 2 sites (OH1 and OH2) with low population density (less than 60 per km^2) and high agricultural land use (greater than 85%) had a significant summer decrease in diazinon concentrations (Supporting Information Figure 3); site OH2 had no season with a significant diazinon decrease, and site OH1 had just 1 season with a significant diazinon decrease. Both these sites also had sufficient data for chlorpyrifos trend assessment. Although site OH2 had no significant decrease for any of the 3 seasons, site OH1 had a significant decrease in chlorpyrifos concentrations for 1 season. Trends in diazinon and chlorpyrifos concentrations in agricultural streams could only be determined for a few sites because these compounds are not frequently detected in agricultural watersheds in the northeast and midwest. The low number of agricultural streams available for trends assessment makes it difficult to extrapolate these findings to other agricultural sites; thus, further assessment of diazinon and chlorpyrifos concentrations in agricultural streams in other regions will be required to accurately assess changes in stream insecticide concentrations due to changes in agricultural use of these compounds.

The decrease in diazinon concentrations after the start of the phaseout resulted in a large decline in the frequency of concentrations exceeding the acute invertebrate water-quality benchmark (*10*) of 0.1 μg/L. (The acute invertebrate water-quality benchmark was used because it represented the lowest benchmark concentration of any of the aquatic-life benchmarks available). Ten percent (58 of 579) of summer samples collected among all sites before October 2001 had a concentration greater than 0.1 μg/L. After this date, less than 1% (1 of 235 samples) had a concentration greater than 0.1 μg/L (with one exception, none of the samples exceeded this water quality benchmark for chlorpyrifos). These results indicate that the decline in diazinon concentrations have probably resulted in a lessening of ecological effects from diazinon in streams in the region.

The lack of significant increases in carbaryl concentrations, particularly during the summer, strongly indicates that carbaryl concentrations in the northeastern United States did not increase as diazinon concentrations decreased, unlike those reported in the Pacific Northwest (*6*). Although the higher variability in analytical method performance for carbaryl compared to diazinon and chlorpyrifos may make it more difficult to demonstrate temporal changes in carbaryl concentrations, the results reported in the Pacific Northwest (*6*) showing an increase in carbaryl concentrations over time indicate that this method can be used to evaluate time trends. The changes in carbaryl concentrations reported in the Pacific Northwest study rely on U.S. Geological Survey NAWQA data that were generated by the same analytical method and laboratory used in this study; thus, although the analytical method is more variable for carbaryl than the other two compounds, it nonetheless is sufficient to indicate major changes in carbaryl concentrations. Despite the similar decrease in diazinon concentrations in the Pacific Northwest and the sites included in this study, concentrations of carbaryl in the northeast and midwest did not change in response to the diazinon phaseout, indicating that there may be important regional differences in the response of stream insecticide concentrations to the diazinon and chlorpyrifos phaseout.

The lack of an increase in carbaryl concentrations should not be extrapolated to other insecticides. Use of pyrethroid insecticides has expanded in response to the phaseout (*7*), and pyrethroids have been found to be a major contributor to toxicity in urban streams in California (*24*). A full assessment of the effect of the phaseout of diazinon and chlorpyrifos on surface water quality will require assessment of insecticides used to replace these compounds, as well as their potential effects on aquatic life and sources of drinking water. At present, few studies are available of the most common replacement insecticides (including imidacloprid, fipronil, and pyrethroids) in urban settings, and most of these insecticides are not included in current long-term monitoring.

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Supporting Information Available

Summary data on the sites included in the study (Supporting Information Table 1), plots of diazinon concentration with discharge at 4 sites (Supporting Information Figure 1), Seasonal Kendall results for differing time periods at 2 sites (Supporting Information Figure 2), and a plot of population density and percent agricultural land use for the sites, with symbols coded to percent changes for diazinon summer concentrations (Supporting Information Figure 3). This material is available free of charge via the Internet at http://pubs.acs.org

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