Groundwater

Pesticides in Groundwater of the United States: Decadal-Scale Changes, 1993–2011

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Abstract

The national occurrence of 83 pesticide compounds in groundwater of the United States and decadal-scale changes in concentrations for 35 compounds were assessed for the 20-year period from 1993–2011. Samples were collected from 1271 wells in 58 nationally distributed well networks. Networks consisted of shallow (mostly monitoring) wells in agricultural and urban land-use areas and deeper (mostly domestic and public supply) wells in major aquifers in mixed land-use areas. Wells were sampled once during 1993–2001 and once during 2002–2011. Pesticides were frequently detected (53% of all samples), but concentrations seldom exceeded human-health benchmarks (1.8% of all samples). The five most frequently detected pesticide compounds—atrazine, deethylatrazine, simazine, metolachlor, and prometon—each had statistically significant ($p < 0.1$) changes in concentrations between decades in one or more categories of well networks nationally aggregated by land use. For agricultural networks, concentrations of atrazine, metolachlor, and prometon decreased from the first decade to the second decade. For urban networks, deethylatrazine concentrations increased and prometon concentrations decreased. For major aquifers, concentrations of deethylatrazine and simazine increased. The directions of concentration changes for individual well networks generally were consistent with changes determined from nationally aggregated data. Altogether, 36 of the 58 individual well networks had statistically significant changes in concentrations of one or more pesticides between decades, with the majority of changes attributed to the five most frequently detected pesticide compounds. The magnitudes of median decadal-scale concentration changes were small—ranging from −0.09 to 0.03 µg/L—and were 35- to 230,000-fold less than human-health benchmarks.

Introduction

This study by the U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program provides a comprehensive analysis of pesticide occurrence and decadal-scale changes in pesticide concentrations in groundwater of the United States. Pesticides released into the environment for agricultural and nonagricultural purposes can contaminate groundwater, a vital and potentially vulnerable source of drinking water.

In 2007, about 390 million kilograms of active ingredients of conventional pesticides, including herbicides, insecticides, and fungicides, were used in the United States (Grube et al. 2011). Agriculture accounted for 80% of total national use of conventional pesticides; nonagricultural uses accounted for the remaining 20% (Grube et al. 2011; Grey et al. 2012). In 2011, nearly half of the population of the United States obtained their drinking water from groundwater (U.S. Environmental Protection Agency (USEPA) 2012b, 2013) much of it from aquifers overlain by land uses where pesticides are applied. The extent to which applied pesticides reach groundwater is governed by factors such as (1) land-management practices; (2) attenuation processes and chemical or biological degradation; and (3) hydrogeochemical conditions such as depth to water, thickness of the unsaturated zone, amount of recharge, hydraulic conductivity, and redox conditions (Schlosser et al. 2002; Kolpin et al. 2004; Murray and McCray 2005; Close and Skinner 2012; Stackelberg et al. 2012; USGS 2013a).

In the first decade of NAWQA studies (1993–2001), the occurrence of 83 pesticide compounds—73 of which are not currently regulated in drinking water by the U.S. Environmental Protection Agency (USEPA)—was assessed in groundwater based on samples from about 5000 wells. Occurrence data were evaluated as a function of land use, crop type, agricultural use intensity, and other factors such as the physical and chemical properties of the pesticides. Findings revealed the widespread occurrence of pesticides in groundwater, although concentrations infrequently exceeded human-health benchmarks (Gilliom et al. 2006). Subsequent analyses reinforced these findings for private domestic wells (DeSimone 2009) and public-supply wells (Toccalino et al. 2010). Although

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complicated by differences in study design, contaminants analyzed, and detection limits, these findings generally also were consistent with the USEPA National Survey of Pesticides in drinking water wells (USEPA 1990) and with results from other countries, including New Zealand (Close and Skinner 2012), Norway (Haarstad and Ludvigsen 2007), and a pan-European study including 23 countries (Loos et al. 2010).

Temporal changes in pesticide concentrations in groundwater were not extensively characterized during the first decade of NAWQA studies because monitoring had not yet covered a long enough period of time to assess such changes in most locations (Gilliom et al. 2006). Long-term consistent data, however, are essential for tracking long-term water-quality responses to changes in pesticide use and land-management practices (Fogg and LaBolle 2006; Gilliom et al. 2006; Bexfield 2008). To date, the most extensive analysis of changes in pesticide concentrations in groundwater over time in the United States was conducted by Bexfield (2008). Findings from 362 wells revealed that three of the most frequently detected pesticides—atrazine, deethylatrazine, and prometon—decreased in concentration from 1993–1995 to 2001–2003, but did not change in detection frequency (Bexfield 2008). Several other countries have national groundwater quality programs that are designed, at least in part, to examine long-term changes in groundwater quality. There is great diversity in program designs because of differences in program objectives, sizes of the countries, and diversity of aquifer types, but a review of nine programs indicates that different approaches can achieve similar goals (Rosen and Lapham 2008).

This study builds upon (1) the previous assessment of the occurrence of pesticides in the Nation's streams and groundwater during 1993–2001 by Gilliom et al. (2006) by adding a second decade of data and (2) the previous assessment of temporal changes in pesticide concentrations by Bexfield (2008) by evaluating decadal-scale changes in pesticide concentrations using a larger dataset and updated statistical methods. Our objectives were to assess (1) the occurrence of 83 pesticide compounds in groundwater from 1271 wells sampled over two decades and (2) changes in concentrations for 35 pesticide compounds between the first decade (1993–2001) and the second decade (2002–2011) of study. We also explored information about changes in national agricultural pesticide use as a possible explanatory variable for changes in pesticide concentrations in agricultural well networks, although it was outside the scope of this study to comprehensively investigate the factors that lead to changes in concentrations.

Methods

Sampling Design

This study is based on two samples collected approximately one decade apart from 1271 wells located in 58 nationally distributed well networks (Figure 1). Each well network contained 11 to 30 wells (Table S1). Table 1 (see "Human-Health Benchmark Exceedances" section below) shows the number of wells sampled by land use and well type. The wells withdraw water from parts of 23 regionally extensive principal aquifers that account for 76% of the estimated withdrawals of groundwater used for public drinking-water supply in the United States (Maupin and Barber 2005).

Two main types of well networks—land-use studies and major aquifer studies—were sampled. Land-use studies were designed to indicate the influence of specific land uses—primarily agricultural and urban—on shallow groundwater quality. Major aquifer studies, also referred to herein as mixed land-use networks, were designed to broadly characterize the quality of deeper aquifers or aquifer systems that are major current or future sources of drinking water, and reflect the effects of a variety of land uses and groundwater ages on water quality (Gilliom et al. 2006; Rosen and Lapham 2008).

Only those wells that were sampled during both Decade 1 and Decade 2 of the NAWQA Program were included in this study. As a result, this study included fewer wells than the 5000 wells included in the assessment of pesticides from the first decade (Gilliom et al. 2006). Program reductions during Decade 2 required a reduction in geographic coverage, and a shift to regional-scale analyses conducted in selected principal aquifers (Rowe et al. 2010). Wells were selected in (1) principal aquifer systems that have high use for drinking water and are representative of major aquifer lithologies and (2) recently recharged groundwater upgradient of these principal aquifers in a nationally representative range of hydrologic and land-use settings.

Sample Collection and Analysis

One untreated groundwater sample was collected from each of the 1271 wells during 1993–2001 (Decade 1) and one sample was collected from the same wells during 2002–2011 (Decade 2), for a total of 2542 samples. Each sample was analyzed for as many as 83 pesticide compounds, including 75 pesticides and 8 pesticide degradates (Table S2). The timespan between network resampling ranged from about 7 to 14 years (Table S1), with a median of 9.0 years. Typically, wells were resampled during the same season to help avoid the effects of seasonal variations on groundwater quality. Only networks with 10 or more wells sampled in each decade were included in this analysis to improve the validity of statistical comparisons between networks, consistent with previous studies (Bexfield 2008; Lindsey and Rupert 2012).

All samples were collected and analyzed using nationally consistent protocols (Koterba et al. 1995; Gilliom et al. 2006; USGS variously dated) in order to yield samples representative of environmental conditions and consistent among study areas nationwide. All samples were collected at the wellhead, before any treatment or blending, by USGS personnel. Samples were filtered through 0.7-µm baked glass-fiber filters into amber-colored glass bottles in the field and were

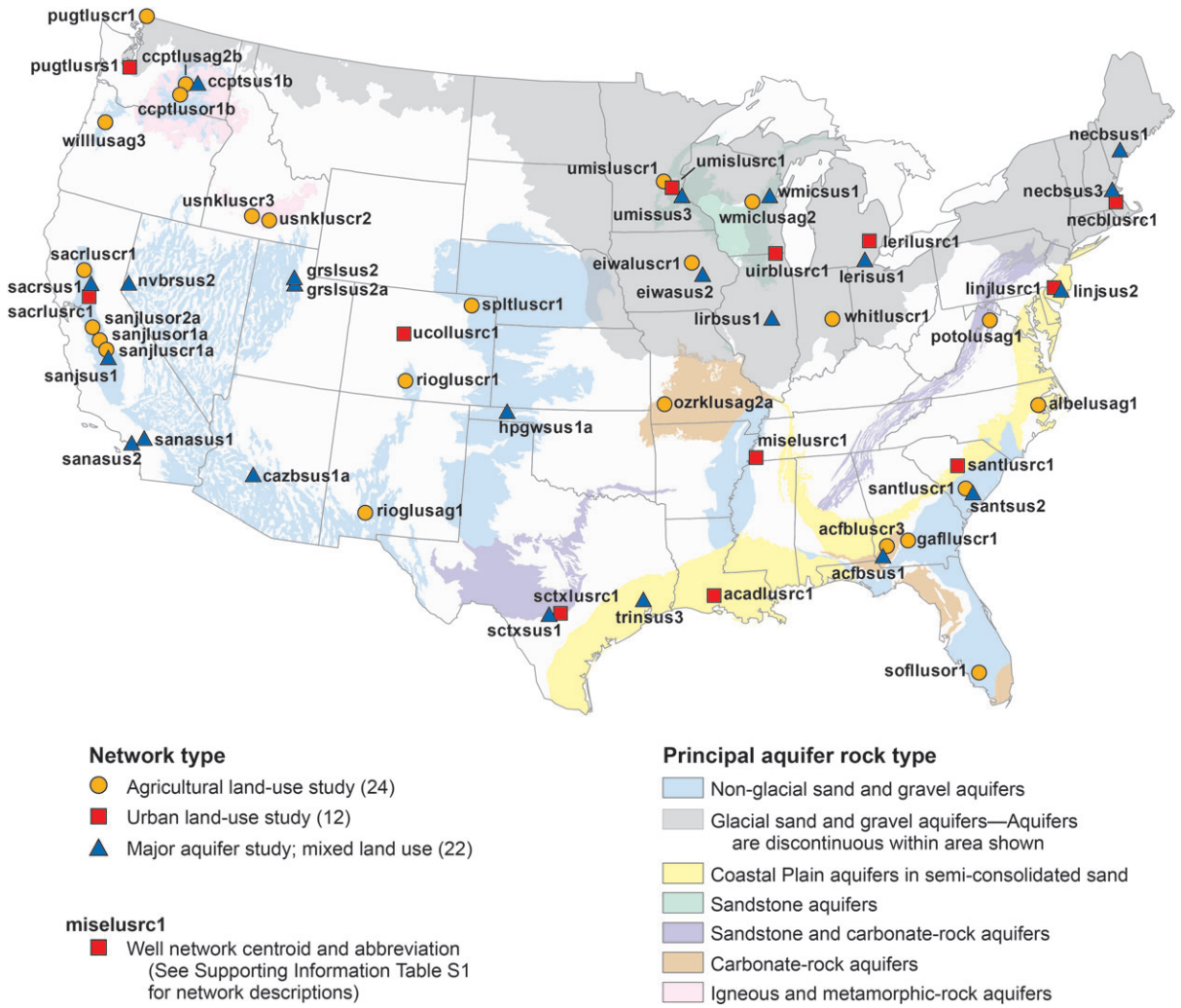

Figure 1. Locations of 58 well networks sampled for pesticide compounds by the USGS National Water-Quality Assessment Program, 1993–2011. Principal aquifers were grouped according to lithology into rock-type categories using classifications in the National Atlas (Miller 2000).

immediately chilled. Samples were analyzed within 7 days at the USGS National Water-Quality Laboratory (NWQL) in Denver, Colorado by gas chromatography/mass spectrometry (GC/MS) (Zaugg et al. 1995) or by high-performance liquid chromatography (HPLC) (Werner et al. 1996; Furlong et al. 2001) (Table S2). Quality-control samples (field blanks, replicates, and field matrix spikes) were collected to ensure that sample collection and handling procedures did not introduce contamination to water-quality samples (Appendix S1).

Data Sources

Water-quality data for 83 pesticides and ancillary data associated with the 1271 wells were retrieved from the NAWQA Data Warehouse database (USGS 2013b) in July and August 2012. Estimates of annual agricultural pesticide use for 1992–2009 were obtained from Stone (2013), using the "EPest-low" version of the estimates. Estimates of nonagricultural pesticide use for 1999–2001 were obtained from Kiely et al. (2004). For 2000–2007, with the exception of diuron and 2,4-dichlorophenoxyacetic acid (2,4-D), nonagricultural pesticide use estimates were prepared by the USEPA using unpublished proprietary data (T.M. Kiely, written communication, 2009). For diuron and 2,4-D, estimates of nonagricultural pesticide use for 2003–2007 were obtained from Grube et al. (2011).

Human-Health Benchmarks

For the purposes of placing study findings in the context of human health, concentrations of 10 pesticides that are regulated by USEPA in drinking water under the Safe Drinking Water Act were compared to maximum contaminant levels (MCLs) obtained from USEPA (2012a), and concentrations of 63 unregulated pesticides were compared to USGS health-based screening levels (HBSLs) obtained from the HBSL website (Toccalino et al. 2012). MCLs and HBSLs were current as of February 2013, and were not available for 10 pesticides (Table S2).

Pesticide concentrations were normalized to human-health benchmarks by computing Benchmark Quotient (BQ) values, which are ratios of contaminant

concentrations to MCLs or HBSLs, when available. Except for dieldrin, all analytical reporting levels were less than human-health benchmarks (Table S2), indicating that the low reporting levels achieved by the NWQL were adequate for detecting concentrations of potential human-health concern. Dieldrin, however, may be present at a concentration greater than its benchmark, but not be detected, so the percentage of samples with BQ > 1 may be underestimated.

Reporting Levels and Detection Frequencies

A reporting level is the "less than" concentration reported when a pesticide is not detected (for example: <0.005 µg/L). Procedures used by NWQL to set reporting levels, the types of reporting levels, and considerations for data analysis are discussed elsewhere (Childress et al. 1999). Consistent with the approach used by Gilliom et al. (2006, Appendix 8B) for computing pesticide occurrence, all reporting levels for pesticide nondetections were changed to the maximum value of the long-term method detection limit (LT-MDL) determined by the NWQL (National Water Quality Laboratory 2012). Nondetections of pesticides attributable to analytical difficulties, such as matrix interference, were removed from the dataset. Detection frequencies were calculated using all detections (detections at any concentration) for all 83 pesticide compounds; none of the detections were censored.

Changes in Pesticide Concentrations

Decadal-scale changes in pesticide concentrations between Decade 1 and Decade 2 were evaluated for 35 compounds using nonparametric statistical analyses for (1) individual well networks and (2) all wells in networks nationally aggregated by land use, after accounting for changes in laboratory recovery (as explained below). Statistical analyses focused on changes in concentration, rather than changes in overall detection frequencies, because this allowed for the retention of information contained within paired samples for each well. Paired decadal samples enabled determination of the direction, magnitude, and statistical significance of changes in concentration.

Results of the statistical evaluation are referred to as "changes" rather than "trends" because there are insufficient data (two samples per well) to determine sustained trends or to predict the direction of future changes (Lindsey and Rupert 2012). The limitation of assessing decadal-scale changes using two temporal data points per well is mitigated, however, by the statistical power derived from numerous spatially distributed sample pairs and the ability to assess changes in concentrations for many constituents over varied hydrogeologic environments and land-use settings. To evaluate alternatives to decadal-scale sampling, biennial and quarterly sampling of a subset of wells during Decade 2 was used to assess changes in concentration (Rosen and Lapham 2008). Lindsey and Rupert (2012) found the analysis of a biennial dataset for chloride, dissolved solids, and nitrate in groundwater yielded similar results to an analysis of a decadal-scale dataset. Rosen et al. (2008) concluded that quarterly sampling for 1 year did not provide enough information to justify its expense.

Recovery Adjustment

Prior to conducting statistical analyses for identifying decadal-scale changes in pesticide concentrations, the dataset was adjusted to account for changes in laboratory recovery, as assessed through laboratory spikes (Martin and Eberle 2011); see Appendix S1. Laboratory recovery adjustments were performed for only 35 of the 83 pesticide compounds because adjustments were limited to those pesticides that were (1) analyzed using GC/MS and (2) analyzed in most (typically >96%) of the samples (Table S2). As a result, decadal-scale changes in concentrations were assessed for 35 pesticide compounds.

Statistical Methods

For each individual well network, and for all wells in networks nationally aggregated by land use, the Wilcoxon-Pratt signed-rank test was used to determine whether pesticide concentrations in well networks sampled in Decade 1 were significantly different than concentrations in the same well networks sampled in Decade 2. A 90% confidence level ($p < 0.1$) was used to identify well networks with significant differences in concentrations, consistent with previous studies (Bexfield 2008; Lindsey and Rupert 2012). The Wilcoxon signed-rank test is commonly used to evaluate statistical changes in paired datasets (Helsel and Hirsch 2002), but a modification of the test that accounts for tied values was used because tied paired were common in the pesticide dataset, such as when both samples were nondetections. This modification was described by Pratt (1959), and is referred to herein as the Wilcoxon-Pratt signed-rank test.

The Wilcoxon-Pratt signed-rank test was applied to each of the 58 well networks and to three nationally aggregated land-use categories for the five most frequently detected pesticide compounds: atrazine, deethylatrazine, metolachlor, prometon, and simazine. For the remaining 30 pesticide compounds, the test was only applied to those networks for which there were three or more detections because at least three detections were required in order for there to be any possibility of a significant change in concentration between decades. The "wilcox-sign_test (zero.method = c ("Pratt"))" command in the "coin" library of the R statistical package was used (Hothorn et al. 2008). Results of the Wilcoxon-Pratt signed-rank test generally were not affected by how detections near reporting levels were assessed (Appendix S1).

For individual well networks and for wells aggregated by land use that had a significant change in concentration ($p < 0.1$), the direction of the change among the paired data was determined from graphical analysis using one-to-one plots and counts of the number of sample pairs with positive or negative changes in concentration. The magnitude of change in concentration in a network was estimated by computing the median value of change for non-tied pairs. First, the concentration in Decade

1 was subtracted from the concentration in Decade 2 for each sample, then the median of the differences (Decade 2 – Decade 1) was computed. If a pesticide compound was not detected during one of the decades, the reporting level was used as the concentration.

Fisher's exact test was used to determine whether the proportion of samples with concentrations approaching human-health benchmarks (BQ > 0.1) differed significantly between Decade 1 and Decade 2 (Helsel and Hirsch 2002). A two-by-two matrix was populated with the number of samples that have BQ > 0.1 and that do not have BQ > 0.1 in Decade 1 and Decade 2. Fisher's exact test (or, for networks aggregated by land use, the chi-square test with Yates's continuity correction) was implemented in the Spotfire S+® software package (TIBCO Software Inc., Boston, Massachusetts, version 8.1, 2008).

Pesticide Occurrence

The first objective of this study was to assess the occurrence of 83 pesticide compounds in untreated groundwater from wells sampled over two decades. The overall occurrence findings from this study confirm and reinforce the findings reported in a NAWQA assessment of groundwater sampled during 1992–2001 (Gilliom et al. 2006). As a result, the key comparative findings about pesticide occurrence in Decade 1 and Decade 2 are summarized here, and the reader is referred to Gilliom et al. (2006) for more detailed explanations about the occurrence of the most frequently detected pesticides with respect to pesticide use, land use, geographic distributions, and physical and chemical properties of the pesticides.

Detection Frequency

Pesticides were frequently detected in groundwater samples, and detection frequencies were similar between the first and second decades. Overall, one or more pesticide compounds were detected in 51% of the samples collected during Decade 1 and 54% of the samples collected during Decade 2. The highest frequencies of detection were in shallow groundwater beneath agricultural land-use areas, where more than two-thirds of the samples had detections of one or more pesticide compounds. Pesticides were detected in about half of the samples collected from shallow groundwater beneath urban land-use areas, and from more than one-third of samples from deeper groundwater in major aquifers (Figure 2). These findings are consistent with previous studies, which show that shallow groundwater, because of its proximity to the land surface, is more vulnerable to contamination from pesticide applications and other human activities than deep groundwater (Gilliom et al. 2006; Haarstad and Ludvigsen 2007; Toccalino et al. 2010; Close and Skinner 2012).

Altogether, 68 pesticide compounds were detected in one or more groundwater samples (Table S2). The five most frequently detected pesticide compounds were triazine herbicides—atrazine, deethylatrazine (a degradate of atrazine), simazine, and prometon—and an acetanilide herbicide—metolachlor. Twenty additional

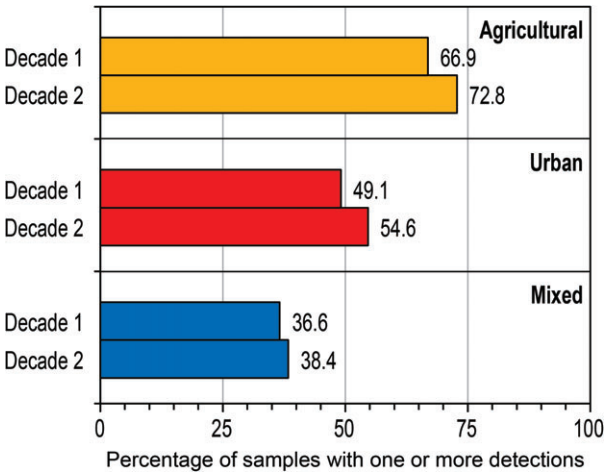

Figure 2. Detection frequencies of pesticide compounds—by land use—for groundwater samples collected from 1271 wells during Decade 1 (1993–2001) and Decade 2 (2002–2011).

pesticide compounds with a variety of agricultural and nonagricultural uses each were detected in more than 2% of wells in agricultural, urban, or mixed land-use settings in Decade 1 or Decade 2 (Figure 3). The occurrence of some herbicides and insecticides generally corresponded to land use and pesticide use (Figures 3 and 4). For example, herbicides and insecticides used primarily in agriculture—such as metolachlor, bentazon, carbofuran, and aldicarb—were detected more frequently in agricultural land-use areas than in urban or mixed land-use areas. Herbicides with substantial agricultural and nonagricultural use—such as atrazine and simazine—were the most frequently detected pesticides across all land-use settings.

Findings from this study are consistent with previous studies that have shown that pesticide degradates can be detected more frequently, or at higher concentrations, than their parent pesticides (Gilliom et al. 2006; Hopple et al. 2009; Loos et al. 2010), depending on their rate of formation and relative persistence. For example, deethylatrazine—a degradate of atrazine and other triazine herbicides—and aldicarb sulfone and aldicarb sulfoxide—degradates of the insecticide aldicarb—were detected more frequently than their parent pesticides in Decade 2 in some land-use settings, and were detected more frequently in Decade 2 than in Decade 1 (Figure 3).

Human-Health Benchmark Exceedances

Pesticide concentrations seldom exceeded human-health benchmarks in groundwater. Altogether, 1.4% of Decade 1 samples and 2.2% of Decade 2 samples had concentrations of one or more pesticides greater than a benchmark. In Decade 1, dinoseb, *alpha*-HCH, and norflurazon each were detected once at a concentration greater than their respective benchmarks. Dieldrin, however, accounted for most benchmark exceedances in Decade 1 and all benchmark exceedances in Decade 2 (Table 1). Groundwater networks with one or more wells

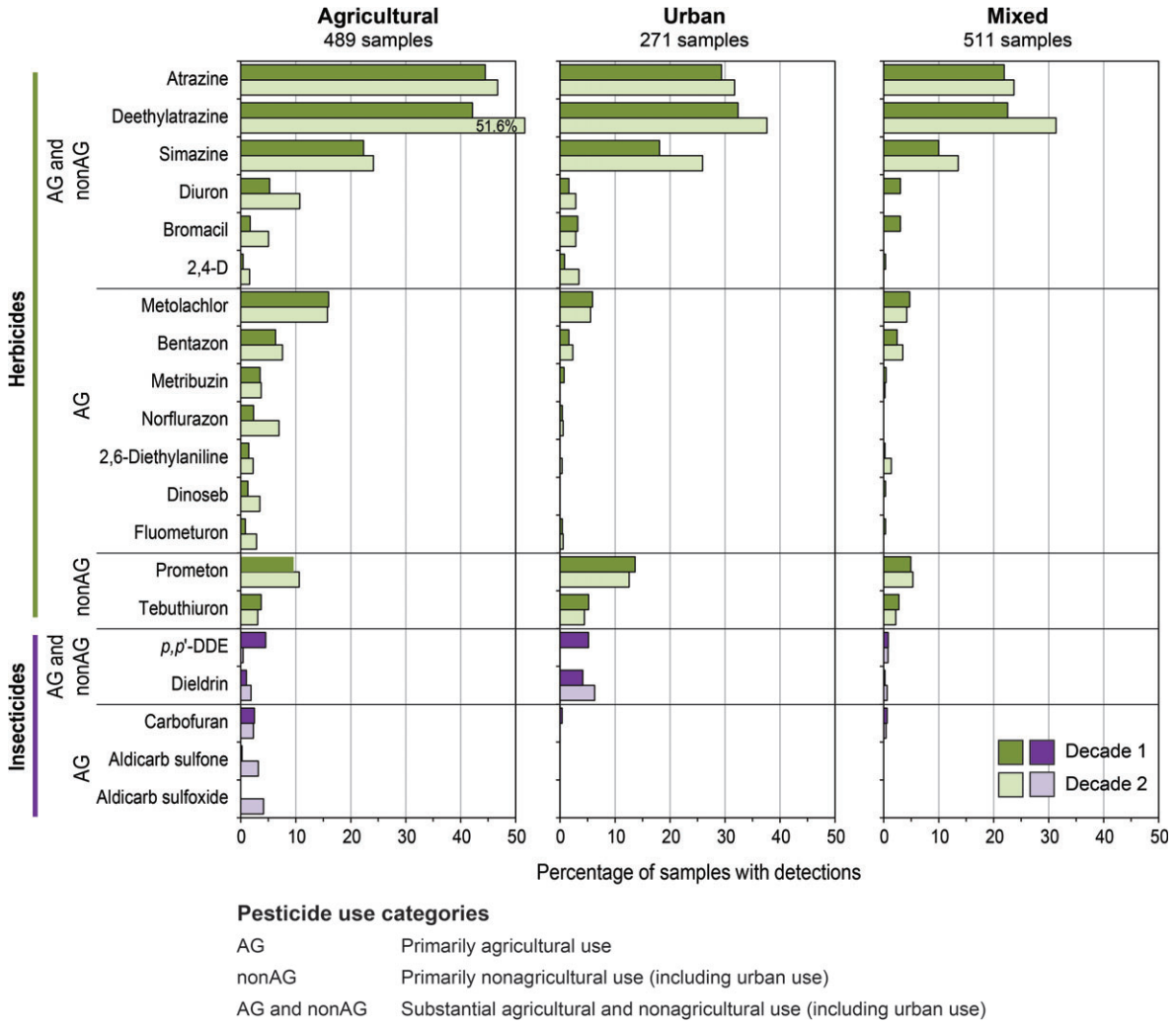

Figure 3. Detection frequencies—by land use—for 20 pesticide compounds each detected in more than 2% of groundwater samples collected during Decade 1 (1993–2001) or Decade 2 (2002–2011). Each bar represents the total for all detections; no common assessment level was applied.

Table 1

Summary of the Occurrence of Pesticide Compounds Detected at Concentrations Greater Than Human-Health Benchmarks—by Land Use and Well Type—for 1271 Wells Sampled During Decade 1 (1993–2001) and Decade 2 (2002–2011)

	Public-Supply Wells		Domestic Wells		Observation Wells	
Land Use	Number of Wells Sampled	Number of Wells with BQ > 1[1]	Number of Wells Sampled	Number of Wells with BQ > 1[1]	Number of Wells Sampled	Number of Wells with BQ > 1[1]
Decade 1						
Agricultural	1	0	168	4 (3 dieldrin, 1 dinoseb, 1 *alpha*-HCH)[2]	320	3 (2 dieldrin, 1 norflurazon)
Urban	0	0	0	0	271	10
Mixed (major aquifers)	125	0	326	1	60	0
Decade 2						
Agricultural	1	0	168	2	320	6
Urban	0	0	0	0	271	17
Mixed (major aquifers)	125	1	326	2	60	0

[1] All benchmark exceedances were accounted for by dieldrin unless noted otherwise.
[2] One sample had benchmark exceedances for both dieldrin and *alpha*-HCH.

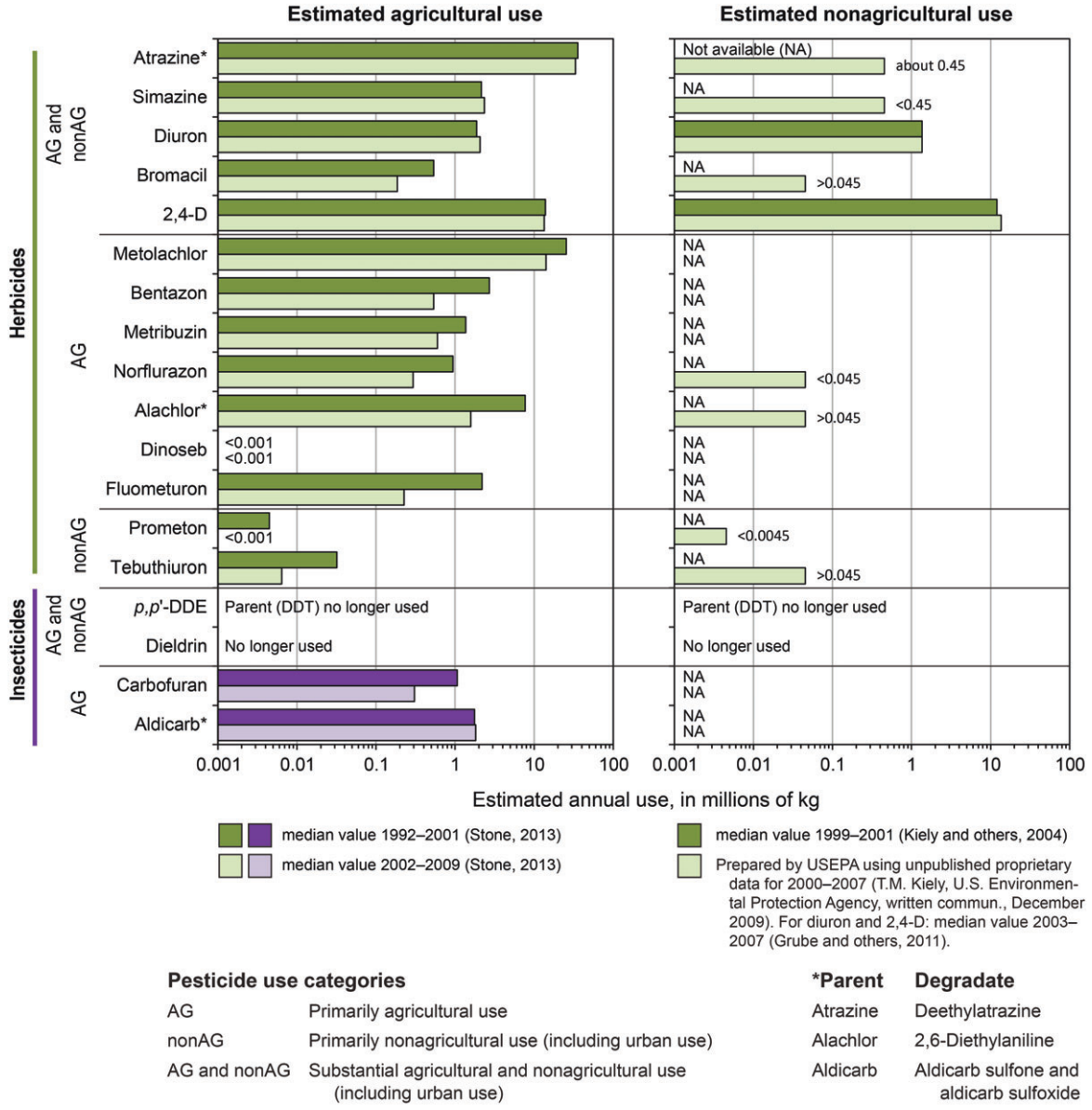

Figure 4. Estimated annual agricultural and nonagricultural use for 20 pesticide compounds detected in more than 2% of groundwater samples collected during Decade 1 or Decade 2.

with benchmark exceedances were widely distributed across the United States with no clear geographic patterns (Appendix S1).

Dieldrin, a highly persistent organochlorine insecticide compound, originates from historical applications of dieldrin and aldrin, which degrades to dieldrin in the environment. Historically, dieldrin was used to control insects on some crops, and to control locusts, mosquitoes, and termites. The USEPA banned all uses of dieldrin in 1987 (Agency for Toxic Substances and Disease Registry 2002). As a result, detections of dieldrin reflect pesticide use practices that are no longer allowed, and illustrate that source-water protection strategies that rely on changes in human activities and practices at the land surface to achieve water-quality objectives can take many decades to affect the quality of some groundwater resources (McMahon et al. 2008).

Across both decades, 78% of samples (36 of 46) with BQ > 1 were collected from observation wells that are not sources of drinking water; moreover, 27 of these 36 samples were from urban land-use areas. Less than 1% of samples from domestic wells or public-supply wells had one or more pesticide compounds with BQ > 1 (Table 1). Altogether, benchmarks were exceeded in 5% of samples from urban land-use areas, <2% of samples from agricultural areas, and <1% of samples from mixed land-use areas, consistent with findings from Gilliom et al. (2006). The greater prevalence of benchmark exceedances in groundwater from urban areas compared to other land uses may have resulted from urban applications of dieldrin for termite control, which were permitted until 1987, whereas USEPA banned all other uses more than a decade earlier (Agency for Toxic Substances and Disease Registry 2002).

Table 2

Summary of Decadal-Scale Changes Between Decade 1 (1993–2001) and Decade 2 (2002–2011) for Individual Well Networks and for All Wells in Networks Nationally Aggregated by Land Use for Atrazine, Deethylatrazine, Simazine, Metolachlor, and Prometon

	Individual Well Networks			All Wells in Networks Nationally Aggregated by Land Use		
Type of Well Network	Number of Networks	Number of Networks with $p < 0.1$ (Range of Median Change, µg/L)		Number of Wells (Sample Pairs)	Direction and Median Value of Change for Non-Tied Pairs, µg/L	p-Value
		With Increase	With Decrease			
Atrazine						
Agricultural land use	24	3 (0.003 to 0.005)	6 (−0.087 to −0.001)	485	(−) 0.002	0.002
Urban land use	12	1 (0.016)	0	269	(+) 0.0006	0.47
Major aquifer	22	2 (0.004 to 0.006)	1 (−0.002)	511	(+) 0.001	0.19
Deethylatrazine						
Agricultural land use	24	5 (0.007 to 0.028)	6 (−0.061 to −0.003)	486	(+) 0.003	0.82
Urban land use	12	4 (0.009 to 0.011)	0	269	(+) 0.009	< 0.001
Major aquifer	22	8 (0.003 to 0.012)	0	511	(+) 0.007	< 0.001
Simazine						
Agricultural land use	24	1 (0.008)	0	488	(+) 0.002	0.20
Urban land use	12	3 (0.003 to 0.005)	2 (−0.009 to −0.004)	270	(+) 0.002	0.11
Major aquifer	22	3 (0.002 to 0.009)	0	511	(+) 0.003	< 0.001
Metolachlor						
Agricultural land use	24	0	2 (−0.014 to −0.006)	489	(−) 0.003	0.07
Urban land use	12	0	0	271	(−) 0.0007	0.72
Major aquifer	22	0	0	506	(−) 0.0008	0.87
Prometon						
Agricultural land use	24	1 (0.004)	2 (−0.041 to −0.009)	489	(−) 0.004	0.096
Urban land use	12	0	1 (−0.045)	271	(−) 0.005	0.04
Major aquifer	22	0	3 (−0.06 to −0.002)	511	(−) 0.002	0.12

$p < 0.1$, indicates statistically significant change in concentration at greater than a 90% confidence level based on Wilcoxon-Pratt signed-rank test results; statistically significant changes in aggregated concentrations are indicated by green (decrease) or pink (increase) highlights.

Decadal-Scale Changes in Pesticide Concentrations

The second objective of this study was to evaluate decadal-scale changes in concentrations for 35 pesticide compounds between the first and second decades of the NAWQA Program. Wilcoxon-Pratt signed-rank test results for (1) individual well networks and (2) all wells in networks nationally aggregated by land use are summarized in Table 2 for the five most frequently detected pesticide compounds.

For all 24 agricultural land-use networks combined (nationally aggregated), there were statistically significant ($p < 0.1$) changes in concentration between decades for atrazine, metolachlor, and prometon, with concentrations decreasing from Decade 1 to Decade 2 (Table 2). For the 12 urban land-use networks combined, changes in concentration were statistically significant for deethylatrazine and prometon; concentrations of deethylatrazine increased and concentrations of prometon decreased from Decade 1 to Decade 2. For the 22 major aquifer networks combined, deethylatrazine and simazine had significant concentration changes, with concentrations increasing for both compounds (Table 2).

Altogether, 36 of the 58 individual well networks showed statistically significant changes in concentration for one or more pesticides between Decade 1 and Decade 2 (Table S3). About half of these 36 networks had increases in pesticide concentrations and half had decreases. The five most frequently detected pesticides accounted for most of the significant concentration changes for individual networks (Table S3), but 11 additional pesticide compounds each had a significant change in concentration in one well network. These compounds were azinphos-methyl, carbofuran, chlorpyrifos, 2,6-diethylaniline, dacthal, diazinon, dieldrin, S-ethyl dipropylthiocarbamate (EPTC), metribuzin, molinate, and thiobencarb.

For the five most frequently detected pesticide compounds, results for decadal-scale changes for individual well networks (Table 2 and Figure 5) were consistent with the above results for wells aggregated nationally for each type of network. For example, atrazine concentrations decreased in all agricultural land-use networks combined, and most individual agricultural well networks with significant changes had decreasing atrazine concentrations (six had decreases, three had increases). Similarly, deethylatrazine concentrations increased in all urban and major aquifer networks combined, and all significant changes in individual urban and major aquifer networks were increases (Table 2 and Figure 5). Simazine, metolachlor, and prometon had similar comparative consistencies between the nationally combined analyses and the individual network results. The magnitudes of

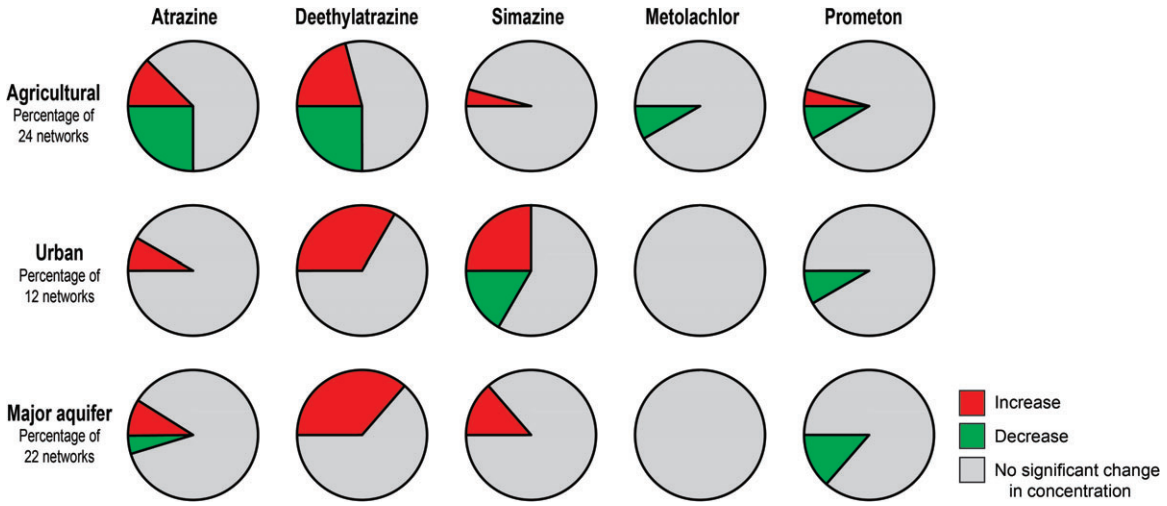

Figure 5. Percentage of individual well networks with significant changes in concentrations of atrazine, deethylatrazine, simazine, metolachlor, and prometon—by type of well network—between Decade 1 (1993–2001) and Decade 2 (2002–2011).

concentration changes for individual well networks were small, but included substantially lower and higher values than the changes derived from aggregated data for some compounds. Median decadal-scale concentration changes for individual networks ranged from about −0.09 to 0.03 µg/L (Table 2).

Because deethylatrazine is a degradation product of atrazine, the individual well networks that showed statistically significant changes in both atrazine and deethylatrazine concentrations were examined more closely (Table S3). With the exception of one network (eiwaluscr1 from the Eastern Iowa Basins), when atrazine concentrations either increased or decreased from Decade 1 to Decade 2, deethylatrazine concentrations showed the same direction of change (Table S4). This result is consistent with Tesoriero et al. (2007) and Stackelberg et al. (2012), who found that the mole fraction of atrazine and deethylatrazine present as deethylatrazine did not vary as a function of groundwater age.

The geographic distribution of the direction of change for the five most frequently detected pesticide compounds among the 58 individual well networks revealed that there was no clear geographic pattern for any of the five compounds (Figure 6). For example, six of the seven individual networks with decreases in atrazine concentrations were agricultural land-use networks (Table 2), but these six networks were widely distributed across the country. Similarly, the eight major aquifer networks with increasing concentrations of deethylatrazine were widely distributed across the United States, although half were in western states ranging from Washington to Arizona (Figure 6).

Changes in Pesticide Use

National agricultural use data for 1992–2009 (Stone 2013) were used to evaluate basic relations between pesticide use and concentration changes for atrazine, deethylatrazine, metolachlor, and simazine in agricultural networks (Figure 7). Deethylatrazine is a degradation product of atrazine and other triazine herbicides with agricultural uses. Prometon is not used on crops and there are no consistent data for nonagricultural uses for any of the pesticides (Figure 4). Figure 7 shows constant to slightly reduced use of atrazine during 1992–2009, generally constant use of simazine, and a major reduction in metolachlor use.

Decadal-scale changes in atrazine concentrations in agricultural land-use networks generally were consistent with national agricultural use data for atrazine; decreasing atrazine concentrations were more prevalent (six networks) than increasing concentrations (three networks). Although most individual agricultural networks (15 of them) showed no significant change in atrazine concentration, data for all wells aggregated across agricultural networks showed a significant, but slight, decrease in concentration (Table 2). Findings for deethylatrazine were more mixed, with roughly equal numbers of agricultural networks having decreasing (six networks) and increasing (five networks) concentrations, and no significant change across aggregated agricultural networks. Decadal-scale simazine concentration changes also were consistent with its relatively constant use during 1992–2009; only one agricultural land-use network had a significant change (decrease), and there was no significant change across aggregated agricultural networks (Table 2). Lastly, the historical use of metolachlor had a much different pattern than atrazine and simazine; metolachlor use decreased by about half between Decades 1 and 2 (Figure 7). Although metolachlor concentrations also decreased in all agricultural networks combined, only two individual agricultural networks showed decreases (Table 2).

Although the relations between agricultural use and changes in concentrations for atrazine, simazine, and metolachlor in agricultural well networks generally were consistent, they were not compelling and leave much unexplained. Previous studies also have found weak correlations between pesticide use and changes in pesticide concentrations in groundwater (Bexfield 2008;

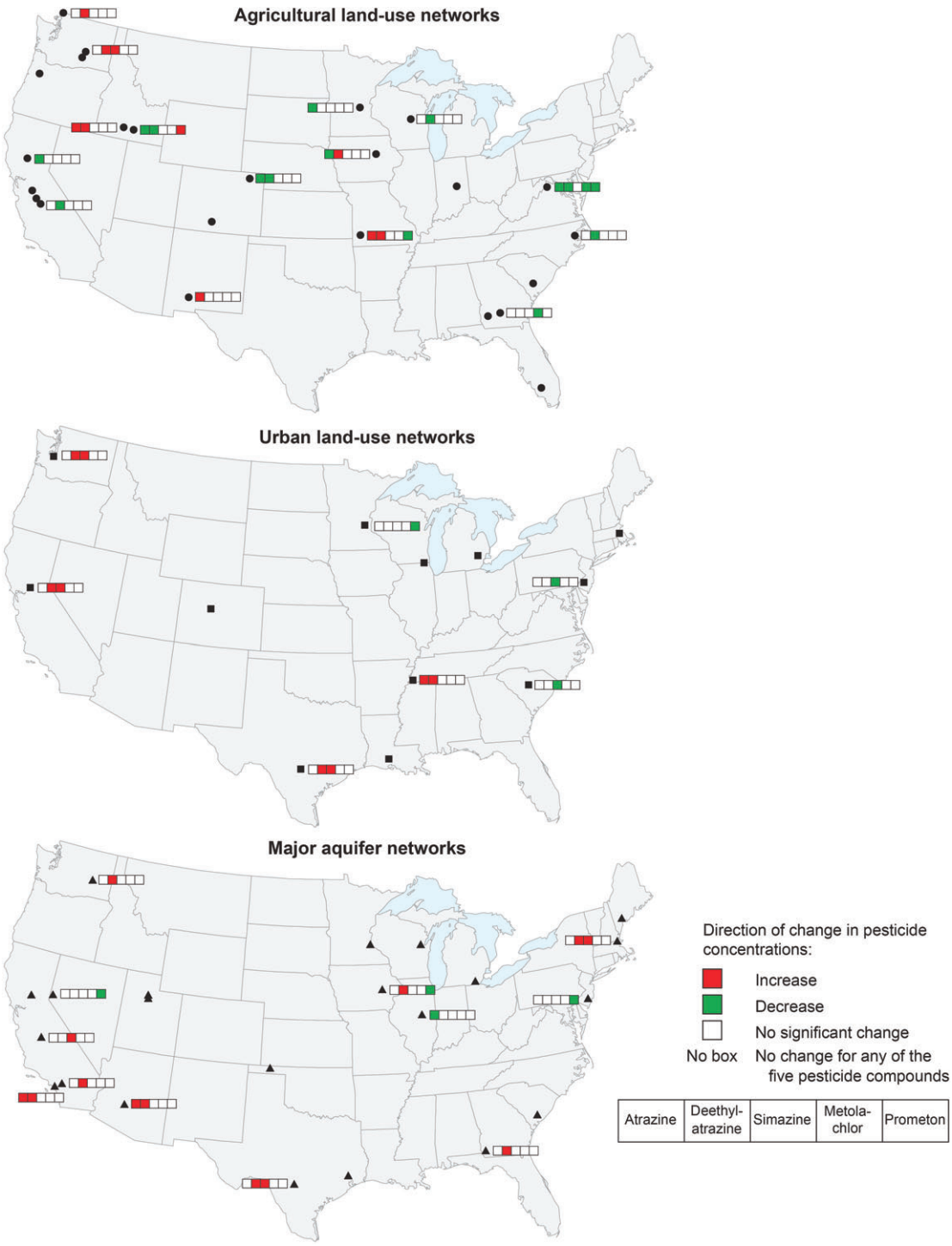

Figure 6. Map showing significant decadal-scale changes in concentrations of atrazine, deethylatrazine, simazine, metolachlor, and prometon—by type of well network—in 58 well networks sampled during 1993–2011.

Stackelberg et al. 2012). For example, Stackelberg et al. (2012) found that current atrazine use was a poor predictor of atrazine in groundwater, perhaps because it does not represent the use of atrazine at the time of recharge of the sampled groundwater, and because the likelihood that atrazine and deethylatrazine will reach the water table is affected by other factors operating within the unsaturated zone, such as soil characteristics, artificial drainage, and water movement.

It was not expected that data on estimated pesticide use, by itself, would strongly correlate with changes in pesticide concentrations with time. Pesticide concentrations in groundwater may respond slowly to changes in pesticide use or land-management practices, often lagging by years or decades, depending on the nature and complexity of the flow system and the rate of groundwater flow (Fogg and LaBolle 2006; McMahon et al. 2008). Bexfield (2008) suggested that factors such as limited

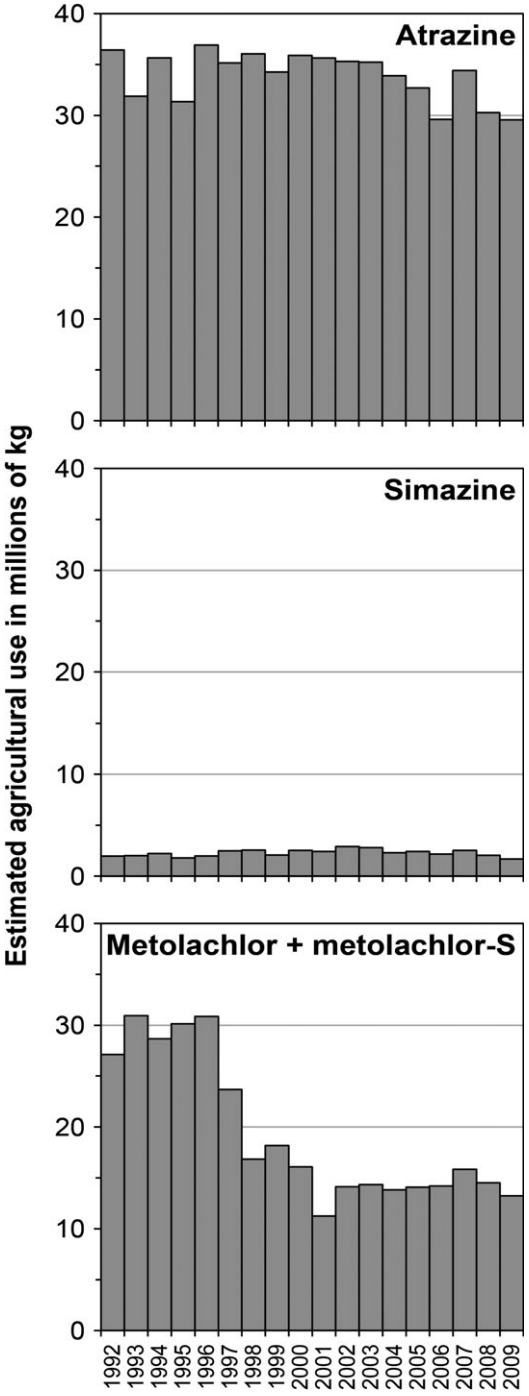

Figure 7. Estimated agricultural use of atrazine, simazine, and metolachlor, 1992–2009 (data are from Stone 2013).

persistence of some pesticides, unfavorable conditions for the transport of pesticides to groundwater in some areas where they are most used, and local use patterns that differ from overall patterns at the national scale, could contribute to the lack of correlation between pesticide use and changes in pesticide concentrations with time.

Potential Human-Health Relevance of Concentration Changes

Relatively few samples had pesticide concentrations greater than, or approaching, human-health benchmarks (Tables 1 and S5). Results of the Fisher's exact test show that the number of samples with concentrations approaching benchmarks ($BQ > 0.1$) was not significantly different between Decade 1 and Decade 2 for most (56 of the 58) of the well networks. Only two agricultural land-use networks—the Potomac River Basin (potolusag1a) and the South Platte River Basin (spltluscr1)—as well as all agricultural land-use networks combined, showed statistically significant decreases ($p < 0.1$) in the number of samples with $BQ > 0.1$ between decades. For both individual networks, the significant decrease resulted from fewer detections of atrazine, prometon, and (or) dacthal with $BQ > 0.1$ in Decade 2 than in Decade 1 (Table S5).

For individual well networks with significant changes in concentrations, the absolute values of decadal-scale concentration changes were 35-fold (for atrazine) to about 230,000-fold (for prometon) less than human-health benchmarks. With the exception of atrazine in the South Platte River Basin, the magnitude of change was at least 100-fold less than benchmarks for atrazine, simazine, metolachlor, and prometon in all networks with $p < 0.1$ (a benchmark is not currently available for deethylatrazine). Because the median value of change for each well network was calculated using non-tied sample pairs (zero-difference pairs were excluded), the median may overestimate the amount of change in pesticide concentrations.

Continued monitoring over the next decades is important for determining the potential human-health relevance of future concentration changes. The small magnitude of concentration changes between Decade 1 and Decade 2 may suggest that these changes have little potential human-health relevance at the national scale. However, much of the groundwater that we drink is substantially older than the pesticides introduced into the environment, and the legacy of various contaminant sources may last for many decades (Fogg and LaBolle 2006). Increasing benchmark exceedances for dieldrin (Table 1), despite being banned for more than 25 years, and increasing and frequent detections of pesticide degradates (Figure 3), some without available human-health benchmarks, highlight the need for continued monitoring, particularly in well networks with increasing concentrations.

Conclusions

Results from two decades of monitoring and assessment (1993–2011) confirm and reinforce previously reported findings on the occurrence of pesticides in groundwater of the United States. Pesticides were frequently detected (53% of all samples), but concentrations seldom exceeded human-health benchmarks (1.8% of all samples). The frequent detections (>36%) of pesticides in samples from major aquifers used for drinking-water supplies, however, indicates the vulnerability of these aquifers to contamination from human activities at the land surface and emphasizes the importance of wellhead protection

programs and other strategies designed to reduce groundwater contamination from man-made sources.

This study provides the most comprehensive evaluation to date of decadal-scale changes in pesticide concentrations in groundwater of the United States. The five most frequently detected pesticide compounds—atrazine, deethylatrazine, simazine, metolachlor, and prometon—each had statistically significant ($p < 0.1$) changes in concentrations between the first and second decades of sampling in one or more categories of well networks nationally aggregated by land use. In agricultural land-use networks, concentrations of atrazine, metolachlor, and prometon decreased between the first and second decades. In urban networks, deethylatrazine concentrations increased and prometon concentrations decreased. In major aquifer networks (mixed land use), deethylatrazine and simazine concentrations increased.

For the five most frequently detected pesticide compounds, the directions of concentration changes for individual well networks generally were consistent with changes determined from nationally aggregated data. Altogether, 36 of the 58 well networks had statistically significant changes in one or more pesticide concentrations between decades, with the majority of these changes attributed to the five most frequently detected pesticide compounds. The magnitudes of median decadal-scale concentration changes in individual networks were small—ranging from about −0.09 to 0.03 µg/L—and were typically more than two orders of magnitude below human-health benchmarks. There was no clear pattern for the geographic distribution of the direction of concentration changes. Historical agricultural use of atrazine, simazine, and metolachlor generally was consistent with changes in the concentrations of these pesticides in agricultural well networks, but these relations were not compelling and leave much unexplained.

Continued long-term decadal-scale monitoring in key land-use settings and aquifers throughout the nation is important for determining the potential human-health relevance of future concentration changes and for tracking long-term responses to changes in pesticide use and land-management practices. Additionally, addressing several information gaps would improve our understanding of changes in pesticide concentration with time (Gilliom et al. 2006; Bexfield 2008; Rosen and Lapham 2008; Rupert 2008):

- Pesticide use: Continued improvements in spatial and temporal quantitative data on pesticide use—particularly nonagricultural use—would improve the assessment and management of pesticides in groundwater.
- Pesticide degradates: Measurement of a broader suite of pesticide degradates is needed to better characterize pesticide fate and the effects of changing pesticide use on groundwater quality.
- Groundwater age information: The availability of estimates of groundwater age derived from age-dating tracers would help characterize the movement of groundwater in aquifers and place the observed concentration changes in the context of historical use and land-use practices.
- Temporal variability in concentrations: A better understanding of short-term variability of pesticide concentrations in groundwater would help elucidate both the drivers of change, and the potential effects of short-term variability, on observed decadal-scale changes.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Appendix S1. Supplemental methods, geographic distribution of benchmark exceedances, and effect of reporting levels on concentration changes.

Table S1. Characteristics of 58 Well Networks Sampled for Pesticide Compounds by the USGS National Water-Quality Assessment Program, 1993–2011

Table S2. List of 83 Pesticide Compounds Analyzed in Groundwater Samples Collected During Decade 1 (1993–2001) and Decade 2 (2002–2011), Including Reporting Levels, Human-Health Benchmarks, and Number of Detections

Table S3. Results of the Wilcoxon-Pratt Signed-Rank Test Showing Decadal-Scale Changes in Concentrations of Atrazine, Deethylatrazine, Simazine, Metolachlor, Prometon, and 35 Pesticides Combined in 58 Well Networks Sampled During Decade 1 (1993–2001) and Decade 2 (2002–2011)

Table S4. The Direction of Change Among Paired Data and the Median Value of Change for Non-Tied Pairs (Decade 2 – Decade 1 Concentrations) for Well Networks with Significant ($p < 0.1$) Changes in Pesticide Concentrations Using the Wilcoxon-Pratt Signed-Rank Test

Table S5. Results of Fisher's Exact Test Showing Changes in the Proportion of Samples with Concentrations Approaching Human-Health Benchmarks ($BQ > 0.1$) Between Decade 1 (1993–2001) and Decade 2 (2002–2011)

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