

Figure 13. Frequencies of herbicide detection in ground water for the various stages of the MWPS. Data for acetochlor given in table 13 (1994 only).

surface-derived contaminants in ground water might be expected to increase following extensive flooding because of the substantially higher rates of ground-water recharge that occur while the land surface is inundated. The increases in herbicide detection frequencies discussed above for the MWPS during the postplanting sampling in 1991, relative to the preplanting results (Burkart and Kolpin, 1993), may also have been caused in part by enhanced recharge from the spring rains.

Seasonal patterns of pesticide application and ground-water recharge from either precipitation or irrigation are also likely to have been responsible for seasonal fluctuations in pesticide detection frequencies observed during other investigations. Results from other studies indicate that frequencies of pesticide detection in shallow ground water beneath agricultural areas generally increase during late spring and early summer (after major agricultural applications and rainfall have occurred in many areas), diminish during late summer and autumn, and reach their lowest levels during the winter and early spring, after which the cycle repeats. These seasonal fluctuations in pesticide detection frequencies usually become more muted with increasing depth (Barbash and Resek, 1996).

Geographic Relations Between Occurrence and Use of Herbicides

The following sections summarize the principal results from the NAWQA and MWPS investigations, and selected results from the other multistate studies, for each of the seven herbicides of interest. For six of the herbicides (all except acetochlor), the discussion of the results from the USGS studies for each compound is accompanied by the following:

- A frequency distribution plot comparing the detection frequencies among the different multistate studies that examined the herbicide, in relation to the reporting limits employed by each investigation (table 4);
- A nationwide map comparing the geographic distribution of detection frequencies in ground water during the NAWQA LUSs and SUSs with geographic patterns of agricultural use;
- A nationwide map comparing the geographic distribution of upper 90th-percentile concentrations from the NAWQA LUSs and

SUSs with the distribution of agricultural use; and

- A map comparing the concentrations measured in individual wells during the MWPS with the distribution of agricultural use throughout the 12-state MWPS study area.

Data for acetochlor are not shown in these figures for two reasons. First, as discussed below, acetochlor was detected at only two sites—out of 953 sampled for it—during the NAWQA Program. Second, the 1992 sampling for the MWPS did not include analyses for acetochlor because use of the herbicide did not begin until 1994 (table 13). Of the six other parent compounds of interest, data on geographic patterns of agricultural use are shown only for the five PMP herbicides; as noted earlier, no such data are currently available for prometon.

The geographic distributions of agricultural use shown in the occurrence maps are based on the data from Gianessi and Anderson (1995) and are displayed in terms of the pounds of active ingredient (lb a.i.) applied annually per acre of harvested cropland and pasture within each county. As noted in previous presentations of these types of maps (Barbash and Resek, 1996; Larson and others, 1997), distortion can occur when use data are displayed on a countywide basis. In areas where pesticide applications take place in only a relatively small proportion of a given county, for example, the areal extent of application will be exaggerated on the map. This distortion can be particularly acute in areas such as the western United States, where counties tend to be larger than in other regions of the country.

As noted above, for each herbicide, geographic patterns of detection from the NAWQA Program are displayed on separate maps for the frequencies of detection and the 90th-percentile concentrations, superimposed in both cases (for the five PMP herbicides) over the distributions of agricultural use. Each sampling network is classified (by symbol shape) according to the four NAWQA study components of interest, and highlighted in bold outline where the sampled ground water represents a current or future source of drinking-water supply (table 8). Because many of the LUSs exhibit partial and, in some cases, complete geographic overlap with SUSs or other LUSs in some study units (for example, ccptlusag2 and ccptlusor1—see table 8), several of the symbols have been moved to reduce or avoid overlap

on the maps and, thus, are only approximate indicators of the actual study locations.

For each herbicide, detection frequencies and 90th-percentile concentrations in the individual NAWQA sampling networks are displayed in relation to the median value among all of the networks with one or more detections, using one of three colors: (1) not detected (blue); (2) detection frequency greater than zero, or 90th-percentile concentration greater than the detection limit, but either parameter less than the median value among all networks with detections (yellow); and (3) detection frequency or 90th-percentile concentration greater than or equal to the median value among all networks with detections

(red). Apparent gaps between the legend categories for some of the detection-frequency and 90th-percentile concentration maps were a consequence of using the actual values involved (for example, “3.5–19” and “20–100”), rather than simply the median values alone (“less than 20” and “greater than or equal to 20”). To determine percentiles for a particular study, all nondetections were treated as tied values below the lowest concentration measured; 90th-percentile concentrations in this range are denoted as not detected (blue) on the maps. The countywide use data are displayed in relation to the median intensity of agricultural use among all counties in the Nation with reported use of the compound: (1) no estimated

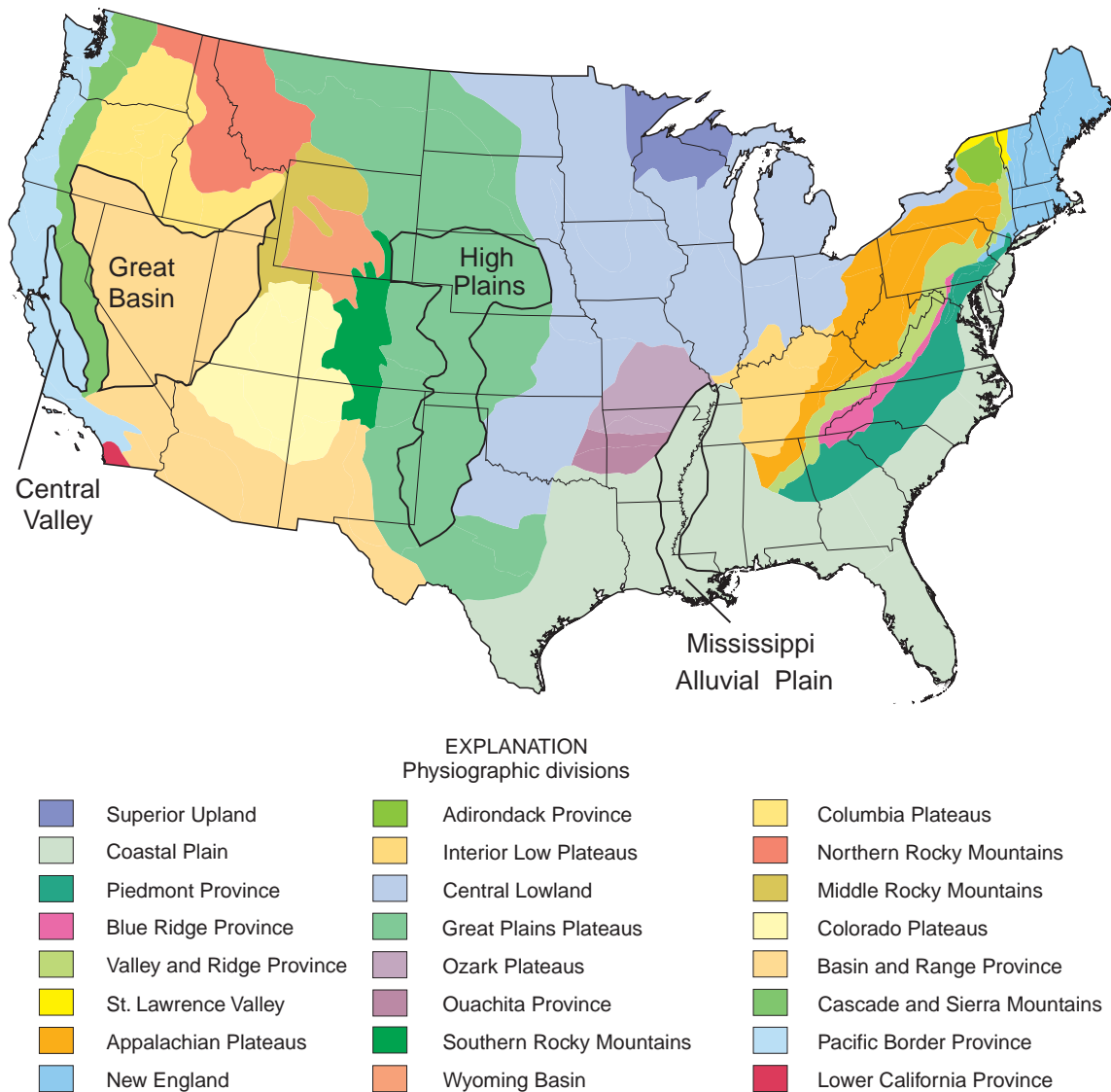


Figure 14. Physical divisions of the United States (modified from Fenneman, 1946). Outlined regions denote areas specifically mentioned in text.

countywide use (white); (2) countywide use greater than zero, but less than the median value among all counties with reported use (tan); and (3) countywide use greater than or equal to the median value (light brown). Figure 14 shows the various physiographic regions of the United States to which the discussions of use and occurrence patterns refer.

To provide the most complete picture of geographic variations in occurrence across the Nation for individual compounds, the frequencies of herbicide detection shown in the national maps summarizing the NAWQA results incorporate all of the detections for each herbicide and, thus, were not adjusted to a uniform reporting limit among all compounds (as was done, for example, for the data displayed in fig. 7 and table 13). Consequently, these maps cannot be employed to compare detection frequencies among different herbicides for a particular area; as noted earlier, such comparisons require that the detection frequencies be adjusted to a common reporting limit.

For six of the herbicides, separate maps show the concentrations measured in individual wells sampled in 12 states of the northern midcontinent in 1992 during the MWPS. (As noted earlier, acetochlor was not yet in use at the time of this sampling and therefore was not examined.) For consistency with the maps showing the NAWQA results, the concentrations measured in each of the MWPS wells are sorted into three categories for the purpose of display: (1) not detected at or above the original reporting limit for each herbicide (blue); (2) concentration greater than or equal to the reporting limit, but less than the median value among all wells with detections of that herbicide (yellow); and (3) concentration greater than or equal to the median value among all wells with detections (red). As with the NAWQA maps, the concentration data for the five PMP herbicides also are superimposed over displays of their countywide agricultural use across the MWPS study area, employing the same use data shown in the national maps for the NAWQA results. For the MWPS maps, however, the use data are displayed in relation to the median value among all of the counties with nonzero use in the 12-state study area, rather than across the entire Nation.

Atrazine

Atrazine was the herbicide detected most frequently for every study component of both NAWQA and the MWPS, with the exception of the

shallow ground water examined by NAWQA in urban areas, where prometon was detected most often (table 13 and fig. 7). These findings are consistent with the use patterns for the two compounds. (The results for prometon will be discussed in the next section.) Of the seven herbicides examined, atrazine was used most extensively in the United States during the period of sampling (table 2 and fig. 1). Atrazine has also been the pesticide detected most frequently in ground water by several other large-scale studies, including the multistate NAWWS (Holden and others, 1992); statewide investigations in Illinois (Goetsch and others, 1992), Iowa (Kross and others, 1990), Kansas (Steichen and others, 1988), Minnesota (Klaseus and others, 1988), Missouri (Sievers and Fulhage, 1992) and Nebraska (Exner and Spalding, 1990); and provincewide studies in Ontario, Canada (Rudolph and others, 1992, 1993).

Figure 15 shows a striking similarity between the results from the NAWQA LUSs in agricultural areas and those from the 1992 MWPS with respect to the frequencies of atrazine detection in shallow ground water, regardless of reporting limit. This is consistent with the focus by both study components on relatively shallow ground water in areas dominated by agricultural activities. Frequencies of atrazine

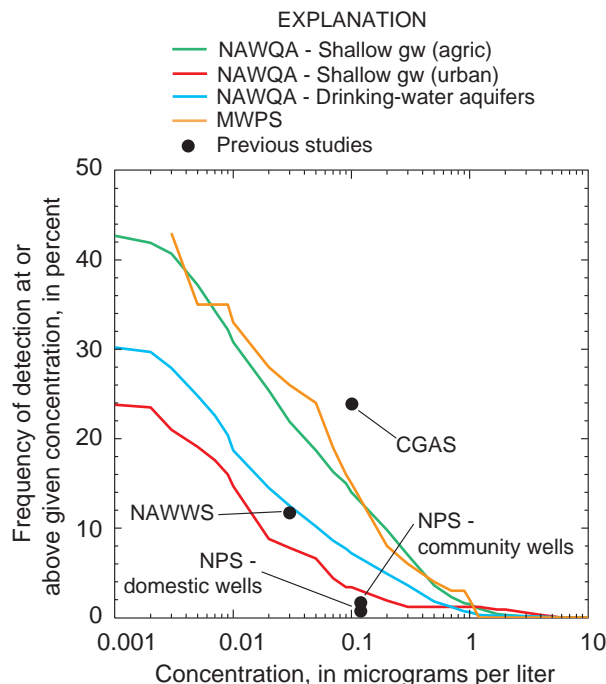


Figure 15. Frequencies of atrazine detection in ground water for the multistate studies in relation to reporting limits. See table 4 for full study names. gw, ground water; agric, agricultural.

detection by NAWQA were considerably lower in urban areas, as might be expected from the primarily agricultural use of the herbicide (table 2). Throughout most of the concentration range examined, detection frequencies in drinking-water aquifers were intermediate between those in the urban and agricultural areas during NAWQA (fig. 15), reflecting the fact that the drinking-water aquifers were sampled in areas with a mixture of the two land-use settings. The NAWWS detected atrazine with a frequency nearly identical to that observed at the same reporting limit by NAWQA in drinking-water aquifers. The NPS, however, detected atrazine—in either rural domestic or community supply wells—with a frequency considerably lower than that observed by any of the other studies, perhaps because the NPS focused on a much broader range of land-use settings and well depths. In contrast, the frequency with which atrazine was detected at or above 0.1 µg/L during the CGAS was much higher than what was observed by the other studies for this reporting limit, probably because the CGAS specifically targeted wells in which atrazine detections would be more likely (table 7). A similar phenomenon was observed for metolachlor, as discussed in greater detail for both herbicides in a later section.

Agricultural use of atrazine (fig. 16A) is most intensive (that is, countywide use is at or above the national median) in the High Plains, Central Lowland, Appalachian and Interior Low Plateaus, New England, and the Coastal Plain, but its widespread use in both agricultural and nonagricultural settings throughout most of the Nation led to its detection in nearly every NAWQA network sampled in most regions. Frequencies of detection and upper 90th-percentile concentrations (fig. 16B) were relatively high in high-use areas, in urban as well as agricultural settings, with the pattern being more pronounced in southern New England and the northeastern areas of the High Plains, Central Lowland, Appalachian Plateau, and Valley and Ridge Province than in most of the sampled areas of the Coastal Plain. In contrast, figure 16 indicates that the atrazine detections in areas with lower use, such as the southern Great Basin, southeastern Basin and Range province, Southern Rocky Mountains, northwestern Central Lowland, and western Coastal Plain, were generally at low concentrations, with upper 90th-percentile concentrations often below detection.

Comparisons between use and occurrence at a finer spatial scale in the northern midcontinent, on the basis of the MWPS data (fig. 17), indicate only moderate correspondence between the intensity of atrazine use and atrazine concentrations measured in ground water. While the highest concentrations were usually encountered in areas of highest use, many other wells sampled in high-use areas had no detections. Infrequent detections, despite high use, were particularly common in Indiana and Illinois during the MWPS for atrazine, as well as for the other four PMP herbicides. Previous studies in Illinois have also noted this pattern (Barbash and Resek, 1996), which may be related to the widespread occurrence of low-permeability geologic materials close to the land surface within the state (McKenna, 1990), or to the resulting pervasive use of subsurface drains. A much closer correspondence between atrazine detections and use, however, was observed in Ohio, where use is comparatively intensive and most of the sampled wells contained detectable, albeit low concentrations. This correspondence in Ohio was also seen for simazine, but not for the other three PMP herbicides.

Deethylatrazine (DEA), a major atrazine degradate, was detected in ground water about as frequently as its parent compound in nearly every study component of the NAWQA, MWPS, CGAS (table 11) and Iowa statewide well investigations (table 12). (Both the frequencies of detection and the concentrations may have been underestimated for DEA during the NAWQA study, however, because the analytical recoveries for DEA were considerably lower than those for atrazine.) Another atrazine degradate, deisopropylatrazine (DIA), was detected less frequently than either atrazine or DEA during both the MWPS and the CGAS. Laboratory and field studies indicate, however, that the principal degradate of atrazine is hydroxyatrazine, produced from the hydrolysis of the parent compound (Armstrong and others, 1967). Although hydroxyatrazine was detected during both the CGAS (table 11) and the statewide sampling of Iowa ground water (table 12), its frequency of detection was substantially lower than those for atrazine or DEA during both studies, perhaps because of the strong affinity hydroxyatrazine exhibits toward clays and other soil surfaces (Armstrong and Chesters, 1968; Schiavon, 1988; Loch, 1991; Demon and others, 1994).

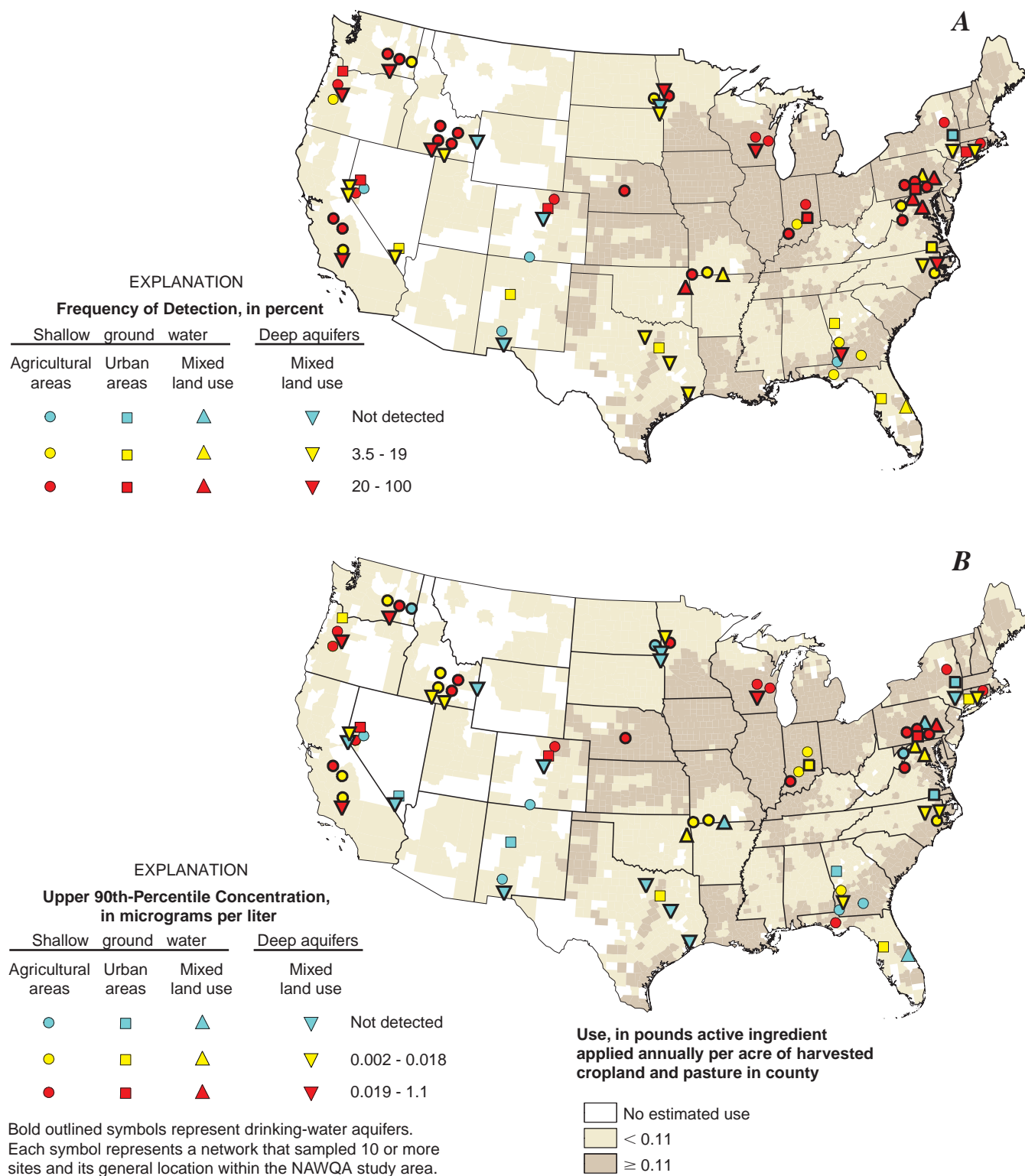


Figure 16. Atrazine occurrence in ground water for the NAWQA study in relation to agricultural use (A) Frequencies of detection. (B) Upper 90th-percentile concentrations. See figures 3 and 4 for areas sampled.

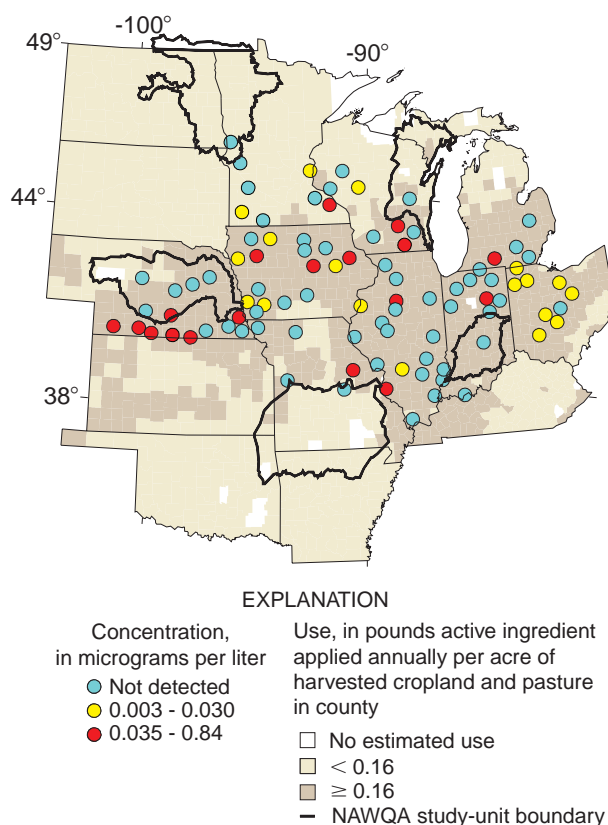


Figure 17. Concentrations of atrazine in near-surface aquifers of the northern midcontinent for the 1992 sampling of the MWPS in relation to agricultural use.

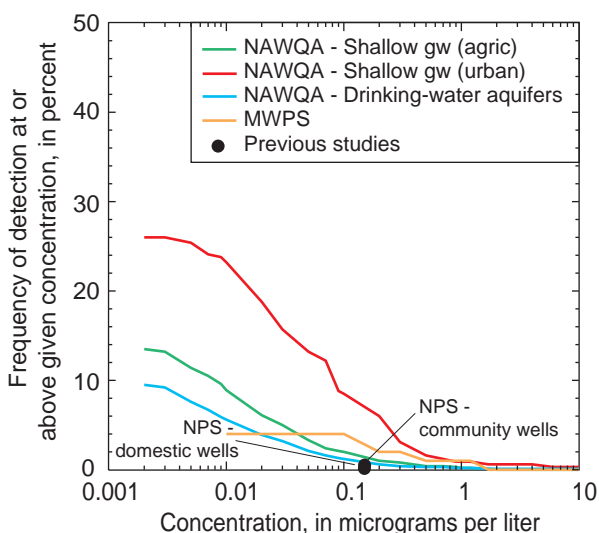


Figure 18. Frequencies of prometon detection in ground water for the multistate studies in relation to reporting limits. See table 4 for full study names. gw, ground water; agric, agricultural.

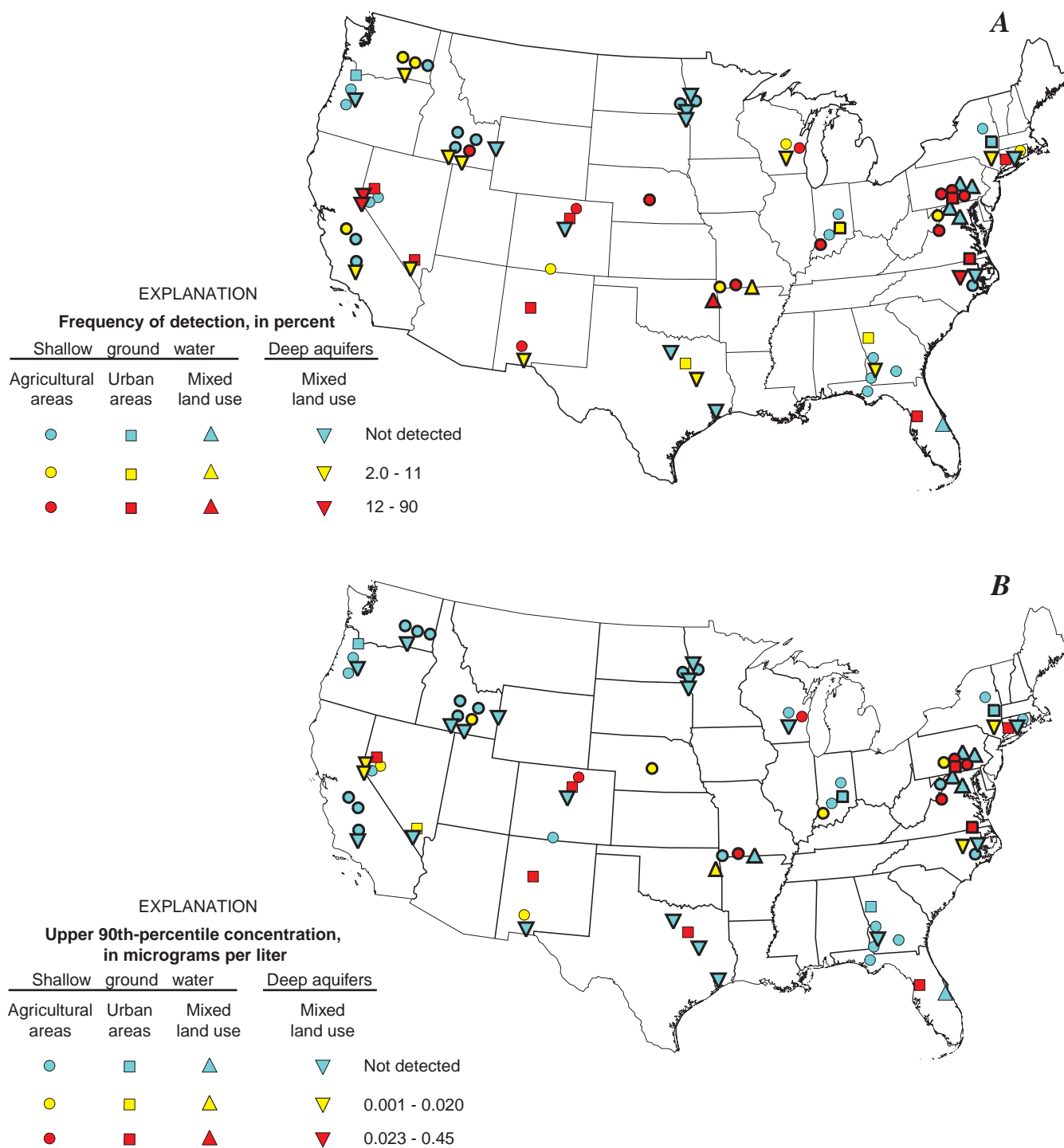
Prometon

Nationwide use data are not currently available for prometon, but the higher frequency of its detection in shallow ground water beneath urban areas relative to agricultural areas (figs. 7 and 18) is consistent with the predominantly nonagricultural use of this nonselective herbicide. Comparisons with the findings of Whitmore and others (1992) indicate that the relative frequencies of detection of prometon and atrazine in the urban areas during the NAWQA study (fig. 7) parallel their relative frequencies of use in residential settings in 1990 (that is, 1,281,000 outdoor applications of prometon, as opposed to 477,000 for atrazine).

Several additional lines of evidence support a close association between prometon occurrence in ground water and urban land use. The frequency of prometon detection during each of the NAWQA LUSs was significantly correlated ($P=0.042$; Spearman rank correlation) with the median percentage of urban land within 1 km of the sampled wells (Kolpin and others, 1998a). During the 1991 sampling for the MWPS, 80 percent of the prometon detections in ground water occurred within 400 m of residential areas or within 3.2 km of golf courses; in comparison, only 36 percent of the other herbicide detections occurred in these areas (Burkart and Kolpin, 1993). Similarly, prometon was detected more frequently in shallow ground water in urban areas than in nonurban (primarily agricultural and forested) areas in central Oklahoma by Christenson and Rea (1993), and in the Albemarle-Pamlico, Lower Susquehanna, and Potomac River Basin study units and surrounding areas by Ator and Ferrari (1997). A correlation between prometon detections and urban (residential) land use was also reported by Land (1996) for surface waters in the Trinity River Basin study unit.

Figure 18 indicates that, unlike any of the other six herbicides examined, prometon was detected much more frequently in urban areas sampled by NAWQA than in areas with either agricultural or mixed land use. As with atrazine (fig. 15), the MWPS results for prometon more closely approximated the NAWQA findings in agricultural areas than those for the urban settings. Consistent with its focus on drinking-water supplies, the NPS detected prometon at about the same frequency as did the NAWQA studies of DWAs (that is, the SUSs).

The distribution of prometon detections in ground water during the NAWQA Program (fig. 19)



Bold outlined symbols represent drinking-water aquifers.
Each symbol represents a network that sampled 10 or more sites and its general location within the NAWQA study area.

Figure 19. Prometon occurrence in ground water for the NAWQA study (A) Frequencies of detection. (B) Upper 90th-percentile concentrations. No data on agricultural use available. See figures 3 and 4 for areas sampled.

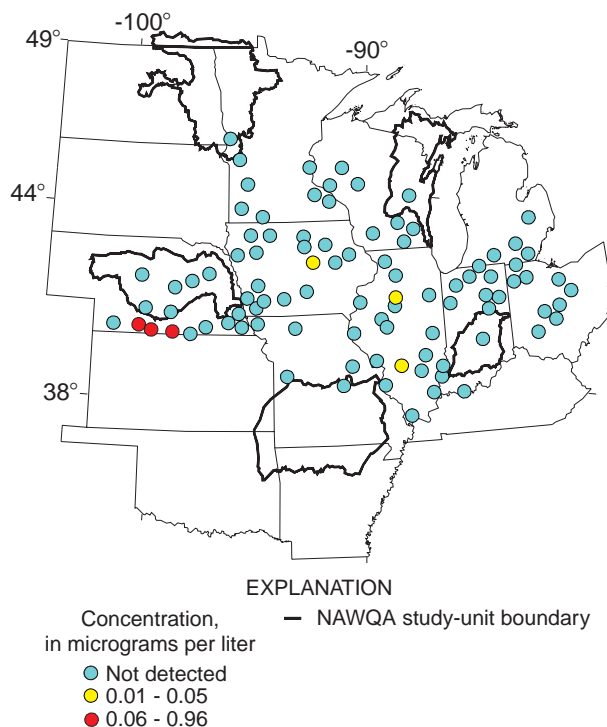


Figure 20. Prometon concentrations measured in near-surface aquifers of the northern midcontinent for the 1992 sampling of the MWPS. No data on agricultural use available.

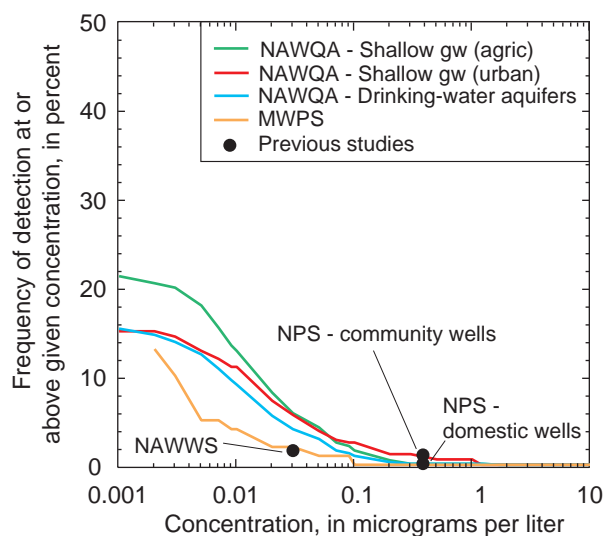


Figure 21. Frequencies of simazine detection in ground water for the multistate studies in relation to reporting limits. See table 4 for full study names. gw, ground water; agric, agricultural.

cannot be compared with spatial patterns of its application because, once again, county-level use data are not available. However, consistent with its primarily nonagricultural use, prometon was detected in shallow ground water in a considerably higher proportion of the studies done in urban settings than in areas with agricultural or mixed land use. While many of the studies done in agricultural or mixed land-use areas had no prometon detections (fig. 19A), the herbicide was detected in every urban area examined by the NAWQA studies except for the urban LUSs undertaken in the Willamette and Hudson River basins. Prometon was not widely detected by the MWPS in 1992 (fig. 20) but, as noted earlier, the wells in which it was detected during the 1991 MWPS sampling were substantially over-represented near residential areas and golf courses (Burkart and Kolpin, 1993).

Simazine

As with figure 7, the NAWQA data shown in figure 21 reflect the similar levels of simazine use in both agricultural and nonagricultural settings (table 2). Indeed, although the herbicide was detected more frequently in agricultural than in urban areas for concentrations below 0.07 µg/L, figure 21 indicates that areas where it was detected above this concentration during the NAWQA studies were more likely to be in urban than in agricultural or mixed land-use settings. The NAWWS detected simazine at a frequency nearly identical to that observed by the MWPS at or above 0.03 µg/L, consistent with the focus of both studies on agricultural areas. The low frequencies of simazine detection at or above 0.4 µg/L by the NPS are close to what would have been expected on the basis of the NAWQA results.

Observations regarding patterns of agricultural use for simazine (fig. 22) must be qualified by what appear to be inconsistencies in the nature of the data from one state to another—a difficulty occasionally evident for the agricultural use data in various parts of the country for each of the PMP herbicides. This limitation notwithstanding, however, agricultural use of simazine is extensive throughout most of the region east of the Mississippi River, with the exception of Wisconsin, Maine, Vermont, Mississippi, Alabama, northern Georgia, and northern Florida. Simazine use is also comparatively high in California, Oregon,

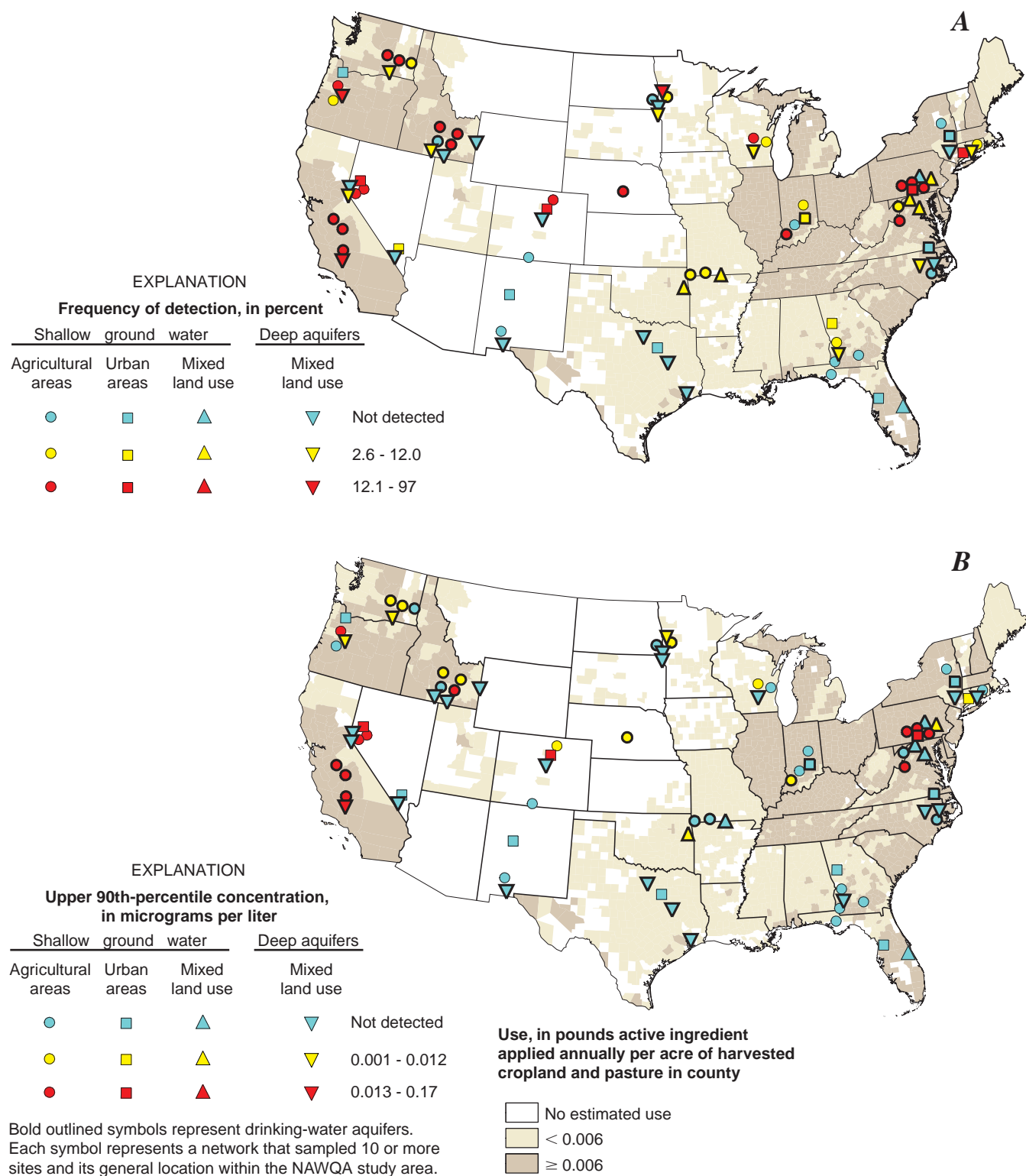


Figure 22. Simazine occurrence in ground water for the NAWQA study in relation to agricultural use (A) Frequencies of detection. (B) Upper 90th-percentile concentrations. See figures 3 and 4 for areas sampled.

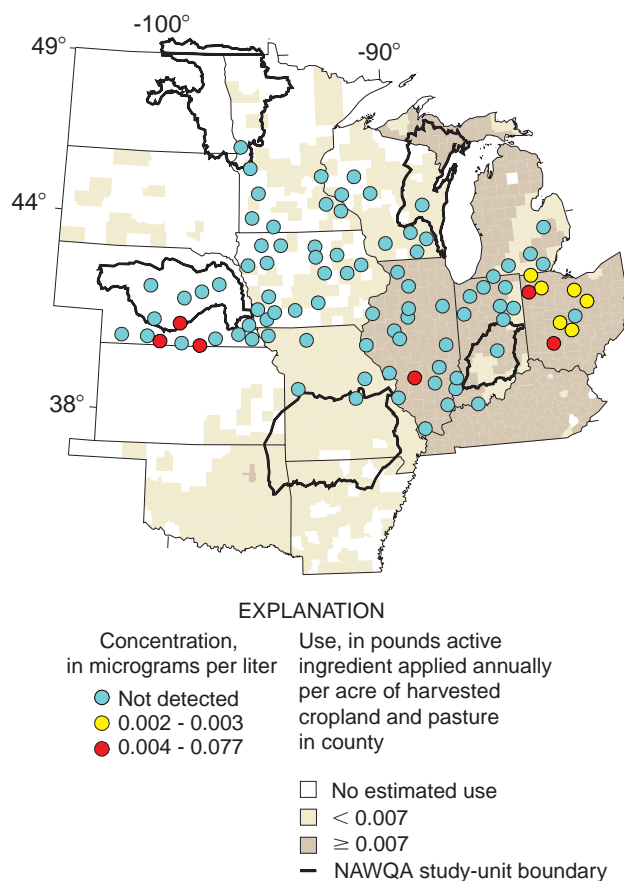


Figure 23. Concentrations of simazine in near-surface aquifers of the northern midcontinent for the 1992 sampling of the MWPS in relation to agricultural use.

Washington, and Idaho, largely as a consequence of its extensive application to orchards, vineyards, and alfalfa.

Although many of the NAWQA sampling networks in high-use areas for simazine had relatively high frequencies of simazine detection, figure 22A indicates that several networks in low-use areas also exhibited high detection frequencies, such as those in the western Great Basin, northern Colorado, central Nebraska and the northwestern Central Lowland. In most of the Southern Rocky Mountains and southeastern Basin and Range Province, both use and detections were sparse, but detections were also infrequent for some of the networks sampled in higher-use areas of the eastern and southeastern Coastal Plain. Simazine concentrations (fig. 22B) were also generally low throughout most of the sampled areas in the Basin and Range Province, Southern Rocky Mountains, Central Lowland, southern New England, and the Coastal Plain. Consistent with the findings reported for

a previous USGS study by Domagalski and Dubrovsky (1991), simazine was frequently detected in the Central Valley of California, an observation attributed by the earlier authors to its extensive use along roadways, as well as in vineyards and other agricultural settings.

As with the nationwide results from NAWQA, pronounced geographic disparities between simazine use and detections in ground water were evident for the MWPS (fig. 23). Although simazine was not detected in the northern central parts of the study area, where its use is minimal, detections were also rare in Illinois and Indiana, where use is high. (As with the NAWQA data, however, comparisons between occurrence and use for the MWPS results are complicated by apparent inconsistencies in the nature of the use data from one state to another.) The infrequent detections of simazine in Illinois, despite considerable use, echo similar findings from the MWPS for the other PMP herbicides, as discussed earlier for atrazine. Also consistent with the atrazine results was the relatively close correspondence between high simazine use and detections in Ohio. Although, as noted earlier, this pattern was not seen in Ohio for the other three PMP herbicides (alachlor, cyanazine, and metolachlor), the data in tables 11 and 12 suggest that the MWPS results for one or more of the principal degradates of these other herbicides may provide a more complete picture of their effects on ground-water quality.

Metolachlor

As was observed for atrazine, the frequencies of metolachlor detection during the MWPS closely matched those encountered in agricultural areas during the NAWQA study throughout most of the concentration range examined (fig. 24). Also consistent with the atrazine results was the similarity between the frequency of metolachlor detection during the NAWWS and that observed in DWAs during NAWQA, once again in agreement with the NAWWS focus on domestic water supplies. As with prometon and simazine, the low frequency of metolachlor detection during the NPS is consistent with the NAWQA data, given the relatively high reporting limit used during the earlier study.

The frequency of metolachlor detection shown in figure 24 for the Metolachlor Monitoring Study, or MMS (Roux and others, 1991a), is much higher than would have been anticipated from any of the other multistate studies that sampled for this herbicide, a pattern also noted earlier for atrazine during the CGAS

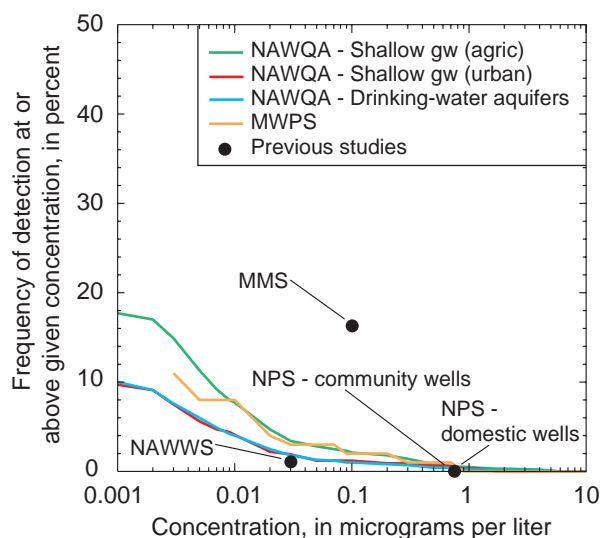


Figure 24. Frequencies of metolachlor detection in ground water for the multistate studies in relation to reporting limits. See table 4 for full study names. gw, ground water; agric, agricultural.

(fig. 15). These findings illustrate the effect of targeted sampling on observed detection frequencies (Barbash and Resek, 1996). In contrast with the stratified random site-selection approaches employed by the other multistate studies examined in figures 15 and 24, the MMS was specifically designed to focus on hydrogeologically vulnerable areas with extensive metolachlor use, whereas the CGAS focused on vulnerable areas with known atrazine contamination (table 7). These approaches led to frequencies of detection of the targeted herbicides that were much higher than those encountered for the same reporting limit by the other multistate studies. Such observations underscore the importance of accounting for variations in study design when comparing the results from different investigations.

As with atrazine, the areas of highest agricultural use of metolachlor in the Nation are in the High Plains, Central Lowland, Appalachian Plateau, Interior Low Plateau, New England, and eastern and southwestern Coastal Plain (fig. 25A). Metolachlor use is also relatively high within the Mississippi Alluvial Plain. In marked contrast with the findings for atrazine and simazine, however, the spatial patterns of metolachlor detection across the Nation during the NAWQA studies align relatively closely with the geographic distribution of its agricultural use (fig. 25), consistent with the highly significant correlation noted earlier between its detection frequency and the intensity of its application in agricultural areas (fig. 11). With only a few exceptions (mostly in the west),

most of the NAWQA networks with high frequencies of metolachlor detection were in areas of high agricultural use. Furthermore, all of the exceptions to this pattern—that is, where the herbicide was detected frequently despite lower use—were in agricultural areas, where metolachlor was most likely to have been used, albeit at rates lower than the national median. High frequencies of metolachlor detection were also encountered in several areas of urban and mixed land use. As discussed earlier, this pattern may have been the result of input from nearby agricultural areas, particularly given that (1) it was only observed in regions of high agricultural use and (2) the majority of areas where metolachlor was not detected at all, regardless of land-use setting, were in areas of low agricultural use.

The relatively close correspondence observed in the NAWQA data between the occurrence and agricultural use of metolachlor is not reflected in the results from the MWPS (fig. 26). Although all of the detections of metolachlor occurred in high-use areas, the herbicide was rarely detected throughout most of the high-use areas sampled. This is in agreement with the patterns observed for atrazine and simazine in Illinois and Indiana, but not in Ohio, where the other two herbicides were detected relatively frequently (figs. 17 and 23). On the basis of the conclusions from the multivariate correlation analysis, this disparity between the metolachlor results and those for atrazine and simazine in Ohio may have been caused by the fact that metolachlor is considerably less persistent than the other two compounds (table 3). This hypothesis is supported by the relative frequencies with which the major degradates of metolachlor and atrazine were detected by Kolpin and others (1998b), relative to their respective parent compounds, in ground water in Iowa (table 12 and fig. 12).

Like the other two acetanilide herbicides discussed in this report (alachlor and acetochlor), metolachlor is readily transformed by soil microorganisms to its respective ethanesulfonic acid (ESA) and oxanilic acid (OA) degradates. These products probably result from the displacement of the chlorine atom on the parent compounds by glutathione, followed by the formation of the ESA and OA degradates by different enzymatic pathways (Field and Thurman, 1996). The statewide sampling in Iowa during the summer of 1996 (table 12), discussed earlier, led to detections of the ESA and OA degradates for all three of the acetanilide herbicides discussed here. For