

Summary of Pesticide Data from Streams and Wells in the Potomac River Basin, 1993-96

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Abstract

Eighty-five water-soluble pesticides and pesticide degradation products were analyzed in 384 surface-water and ground-water samples collected from the Potomac River Basin during March 1993 through September 1996. Thirty-nine of these compounds were detected in surface-water samples and 16 were detected in ground-water samples. At least one pesticide was detected in 86 percent of the streams sampled and 45 percent of the wells sampled. Pesticides were detected more frequently and at higher concentrations in surface water than in ground water. The following four herbicides and one degradation product were the most frequently detected pesticides in both surface water and ground water: atrazine and metolachlor, which are used primarily on corn and soybean crops; prometon, which is used primarily in nonagricultural (urban and suburban) areas; simazine, which is used in both agricultural and nonagricultural areas; and desethylatrazine, which is one of the degradation products of atrazine. Insecticides were detected more frequently in surface water than in ground water. Diazinon, chlorpyrifos, and gamma-HCH (lindane) were found in more than 10 percent of surface-water samples, but in none of the ground-water samples.

Introduction

Contamination of streams and ground water by pesticides is a major concern to human and aquatic health. Pesticides (for example, herbicides and insecticides) are chemicals used to control unwanted organisms such as weeds and insects. Pesticides in surface water and ground water, even at very low concentrations, can render the water unfit for human consumption and make it toxic to aquatic organisms. Pesticides in surface water and ground water in the Potomac River Basin were analyzed by the U.S. Geological Survey (USGS) as part of the National Water Quality Assessment (NAWQA) program. This report presents the results of pesticide sampling that was done for the Potomac NAWQA study.

An estimated 4.94 million pounds of pesticides are used annually for agricultural purposes in the Potomac River Basin (Gianessi and Puffer, 1990; 1992a-b). Nonagricultural applications of pesticides are difficult to quantify, but the U.S. Environmental Protection Agency estimated that nationwide, agricultural applications accounted for 75 percent of the total pesticide usage in

1993 (Asplin, 1994). Atrazine and metolachlor are the most widely applied agricultural pesticides in the Potomac River Basin, with estimated annual applications of 697,000 pounds and 539,000 pounds, respectively (Gianessi and Puffer, 1990; 1992a-b), and are the two pesticides most frequently detected in this study (fig. 1). Of the 20 most widely applied agricultural pesticides in

the Potomac River Basin, 13 were detected in either ground water or surface water and 1 was not detected; the samples were not analyzed for the other 6 pesticides (fig. 1). A complete list of pesticides and degradation products for which the samples were analyzed is shown in table 1. Of the 85 compounds for which samples were analyzed, 43 were detected in at least one sample.



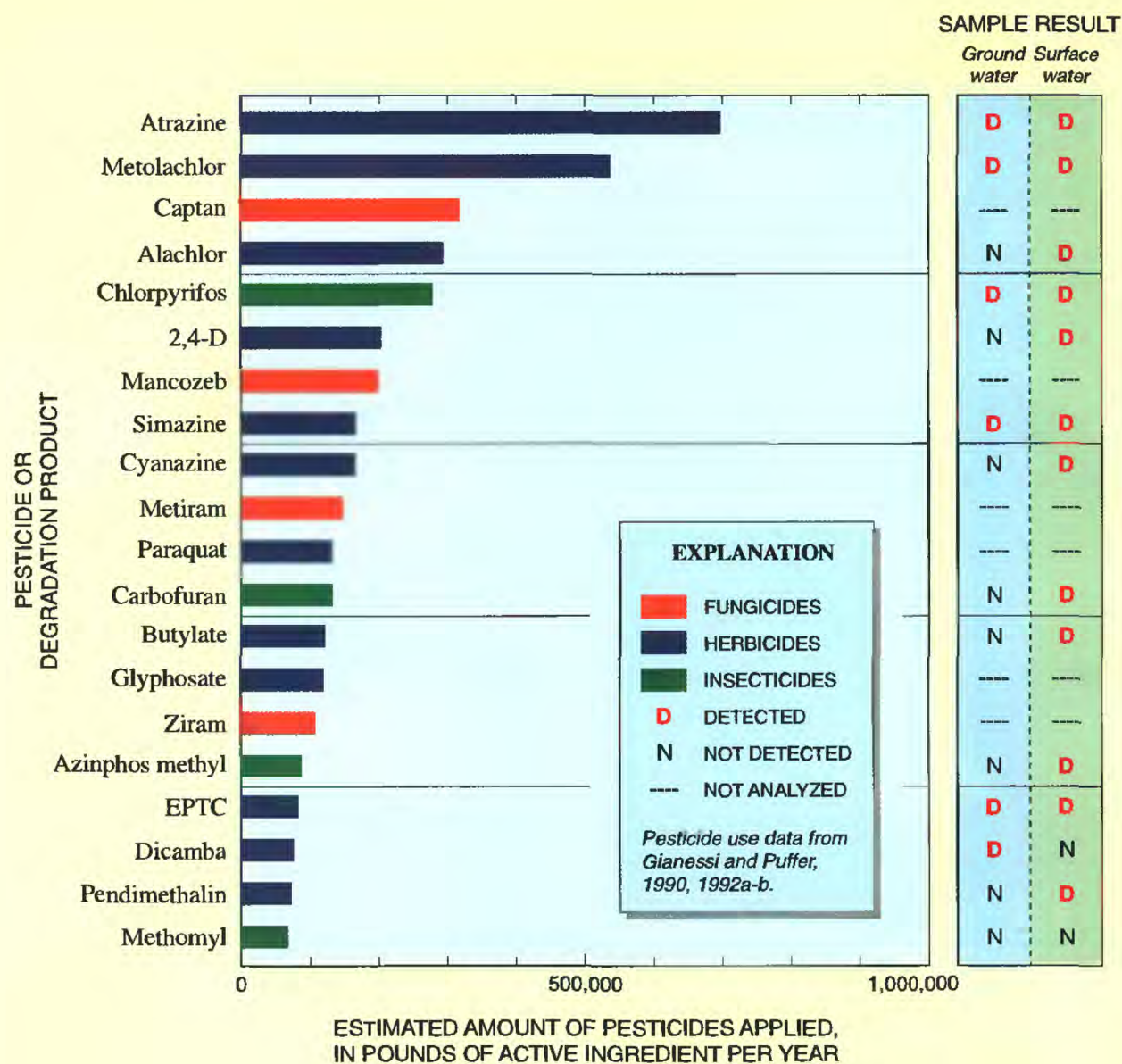


Figure 1. Major agricultural pesticides used in the Potomac River Basin and sampling results.

Surface Water

Three sampling approaches — multiple-sample monitoring, subunit synoptic surveys, and a survey of major tributaries — were used by the USGS to assess the quality of surface water in the Potomac River Basin (Gerhart and Brakebill, 1996). For the multiple-sample monitoring, 11 sites were sampled repeatedly and were designated as either “fixed indicator” or “fixed integrator” sites. Indicator sites drain small to intermediate size watersheds (less than 400 square miles) having relatively homogeneous environmental settings. Integrator sites drain relatively large areas (greater than 400 square miles) and represent the combined effects of all natural and human water-quality factors in the watersheds they drain (Gerhart and Brakebill, 1996). The water at these fixed sites was monitored throughout the study for nutrients, major inorganic elements, and suspended sediment (Shelton, 1994). Four of these sites were intensively monitored for pesticide concentrations (table 2). The frequency of sample collection at the Muddy Creek monitoring site is shown in figure 3; samples were collected at similar frequencies at the Accotink Creek and the Monocacy River at Bridgeport, Md. fixed sites. The Shenandoah River at Millville, W. Va., was sampled less frequently than Muddy Creek, Accotink Creek, and the Monocacy River. Samples were collected even less frequently at the other fixed sites (table 2). In addition, four fixed

Sampling Design

The Potomac River Basin drains 14,670 square miles in parts of four states — Maryland, Pennsylvania, Virginia, and West Virginia — and the District of Columbia. Major land uses in the basin include forest (50 percent), agriculture (35 percent), and urban (10 percent) (Hitt, 1994; fig. 2). For the purposes of NAWQA water-quality investigations, the Potomac River Basin was subdivided into eight subunits based on physiographic and geologic characteristics (Blomquist and others, 1996). Seven physiographic provinces and sub-provinces are included in the Potomac River Basin — the Appalachian Plateau, Valley and Ridge, Great Valley, Blue Ridge, Piedmont, Triassic Lowlands, and Coastal Plain. Differences in the geology of the Great Valley subprovince were considered important enough to further subdivide that subprovince into carbonate and noncarbonate subunits. Four of the subunits — Valley and Ridge, Great Valley Carbonate, Piedmont, and Triassic Lowlands — were selected for

sampling emphasis. A more detailed discussion of the Potomac NAWQA sampling design may be found in Gerhart and Brakebill (1996). A detailed discussion of the national NAWQA sampling design guidelines may be found in Gilliom and others (1995).

Table 1. Pesticides measured in water samples from the Potomac River Basin
(Italicized compounds are degradation products of pesticides; **Bold-faced** compounds were detected.)

Acetochlor	2,4-DB	gamma-HCH	Phorate
Acifluorfen	DCPA	<i>3-Hydroxycarbofuran</i>	Picloram
Alachlor	<i>p,p'-DDE</i>	Linuron	Prometon
Aldicarb	<i>Desethylatrazine</i>	Malathion	Pronamide
<i>Aldicarb sulfone</i>	Diazinon	MCPA	Propachlor
<i>Aldicarb sulfoxide</i>	Dicamba	MCPB	Propanil
Atrazine	Dichlorobenil	Methiocarb	Propargite
Azinphos-methyl	Dichlorprop	Methomyl	Propham
Benfluralin	Dieldrin	Methyl parathion	Propoxur
Bentazon	<i>2,6-Diethylalanine</i>	Metolachlor	Silvex
Bromacil	Dinoseb	Metribuzin	Simazine
Bromoxynil	Disulfoton	Molinate	2,4,5-T
Butylate	Diuron	<i>1-Naphthol</i>	Tebuthiuron
Carbaryl	DNOC	Napropamide	Terbacil
Carbofuran	EPTC	Neburon	Terbufos
Chloramben	Esfenvalerate	Norflurazon	Thiobencarb
Chlorothalonil	Ethalfuralin	Oryzalin	Triallate
Chlorpyrifos	Ethoprop	Oxamyl	Triclopyr
Clopyralid	Fenuron	Parathion	Trifluralin
Cyanazine	Fluometuron	Pebulate	
2,4-D	Fonofos	Pendimethalin	
<i>Dacthal (mono acid)</i>	alpha-HCH	<i>cis-Permethrin</i>	

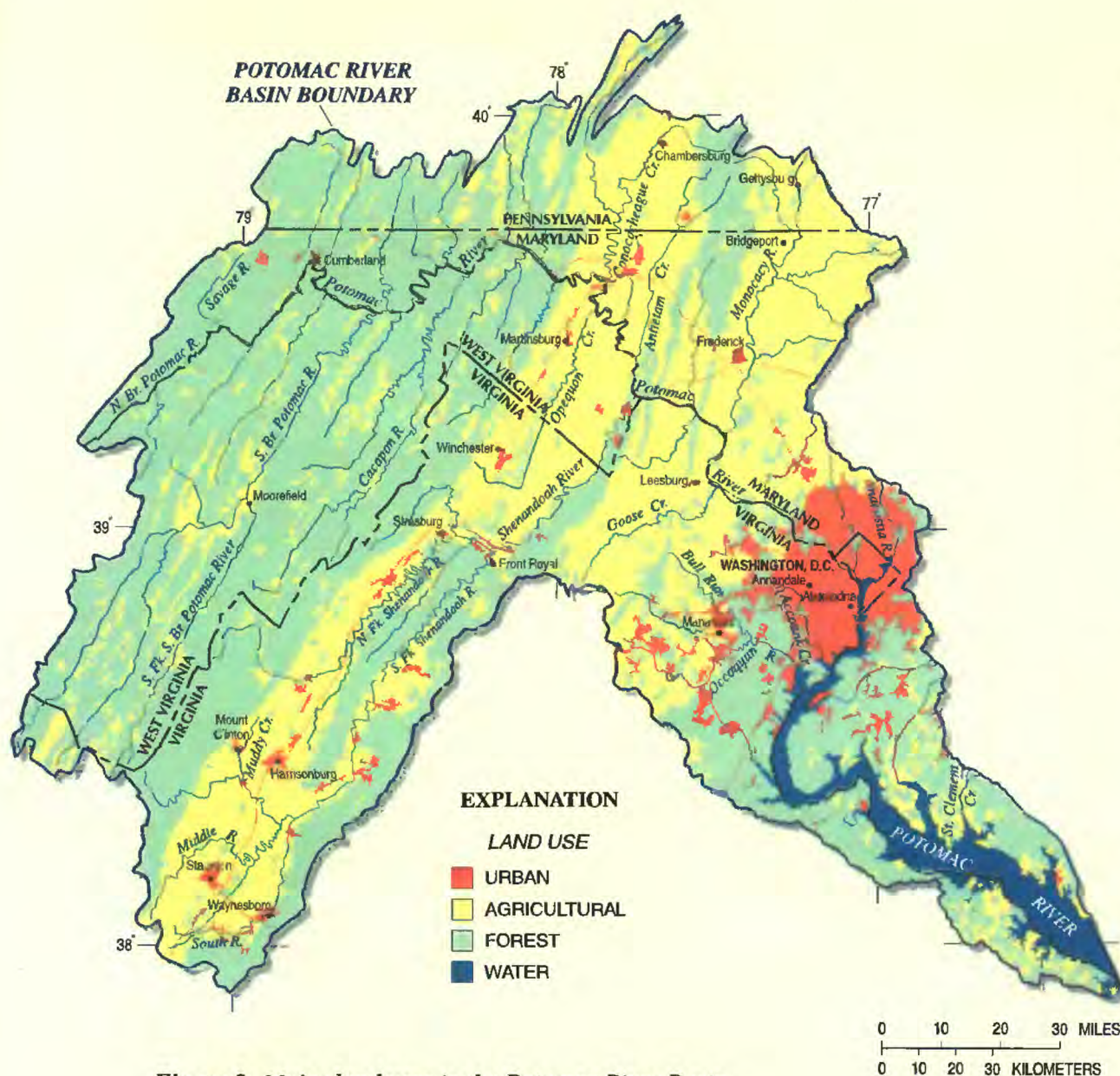


Figure 2. Major land uses in the Potomac River Basin.

sites were sampled in June 1996 during high-flow conditions resulting from extremely heavy, local rainfall in the Conococheague Creek and Monocacy River watersheds.

The four subunits (Valley and Ridge, Great Valley Carbonate, Piedmont, and Triassic Lowlands) selected for sampling emphasis encompass most of the Potomac River Basin. Synoptic sampling (single samples collected over a relatively short period of time) of small streams (those draining

generally less than 10 square miles) during low-flow conditions in late August or September was conducted in each of these subunits. Synoptic samples were collected over a period of 3 years from the following subunits: Great Valley Carbonate subunit (27 samples), September 1993; Piedmont (25 samples) and Triassic Lowlands (12 samples) subunits, August 1994; Valley and Ridge subunit (25 samples), August 1995.

In addition to the subunit surveys, 23 major tributary sites were sampled

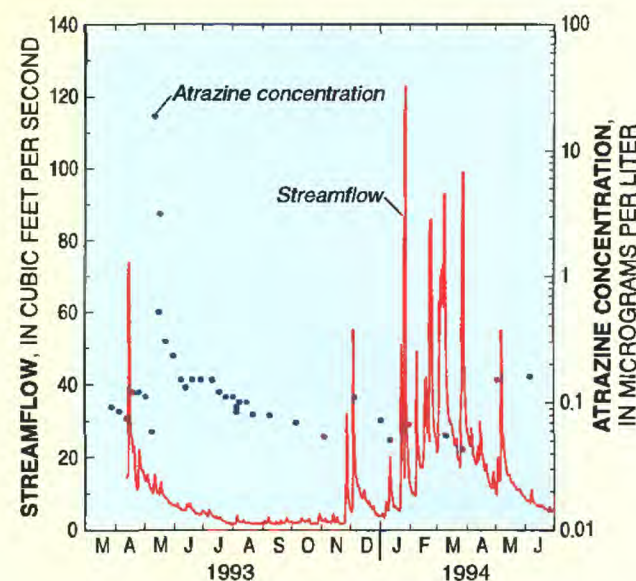


Figure 3. Example of streamflow and atrazine concentration data for the Muddy Creek monitoring site at Mount Clinton, Va., March 1993 through June 1994.

synoptically during June 1994 under stable-flow conditions (Fisher, 1995). Sampling under stable-flow conditions made spatial comparisons possible.

Ground water

Ground-water investigations in the Potomac NAWQA study focused on synoptic sampling in two of the subunits — the Piedmont and Triassic Lowlands — as well as synoptic sampling of agricultural land-use areas within the Great Valley Carbonate and Valley and Ridge subunits. Synoptic samples were collected over a period of 3 years (Great Valley Carbonate subunit, June through September 1993; Piedmont and Triassic Lowlands subunits, June through August 1994; Valley and Ridge subunit, June through July 1995). Wells were randomly selected for sampling within the target area of each subunit

Table 2. Summary of fixed surface-water monitoring sites in the Potomac River Basin

STATION NAME	DRAINAGE AREA (mi ²)	NUMBER OF SAMPLES	PERIOD OF SAMPLING	WATERSHED DESCRIPTION
North Branch Potomac River at Cumberland, Md.	875	1	6/94	Integrator site for the Appalachian Plateau subunit
South Fork South Branch Potomac River near Moorefield, W. Va.	283	4	6/94-8/95	Indicator site for the forested areas of the Valley and Ridge subunit
South Branch Potomac River at Springfield, W. Va.	1,471	4	6/94-9/96	Integrator site for the Valley and Ridge subunit
Conococheague Creek at Fairview, Md.	494	6	6/94-6/96	Integrator site for the northern Great Valley
Muddy Creek at Mount Clinton, Va.	14.2	39	3/93-5/95	Indicator site for the agricultural areas of the Great Valley Carbonate subunit
Shenandoah River at Millville, W. Va.	3,040	23	3/93-9/96	Integrator site for the southern Great Valley
Catoctin Creek at Taylorstown, Va.	89.6	2	6/94-7/94	Indicator site for the agricultural areas of the Piedmont subunit
Monocacy River at Bridgeport, Md.	173	42	6/92-6/96	Indicator site for the agricultural areas of the Triassic Lowlands subunit
Monocacy River near Frederick, Md.	817	5	6/94-6/96	Integrator site for the Piedmont and Triassic Lowlands subunits
Potomac River at Washington, D.C.	11,560	10	6/94-9/96	Integrator site for the Potomac River
Accotink Creek near Annandale, Va.	23.5	42	6/94-8/95	Indicator site for the urbanized areas of the Piedmont subunit

Table 3. Summary of pesticides detected in surface water and ground water in the Potomac River Basin

[MDL: Method Detection Limit; MRL: Minimum Reporting Limit; (E): concentration estimated; µg/L: micrograms per liter; <: less than]

CHEMICAL NAME	MDL or MRL (µg/L)	SURFACE WATER					GROUND WATER			
		NUMBER OF SAMPLES COLLECTED	NUMBER OF SITES WHERE PESTICIDE DETECTED	PERCENT OF SAMPLES HAVING DETECTABLE CONCENTRATION	90th PERCENTILE CONCENTRATION (µg/L)	MAXIMUM REPORTED CONCENTRATION (µg/L)	NUMBER OF SITES SAMPLED	NUMBER OF SITES WHERE PESTICIDE DETECTED	90th PERCENTILE CONCENTRATION (µg/L)	MAXIMUM REPORTED CONCENTRATION (µg/L)
Samples analyzed by gas chromatography with detection by mass spectrometry (Zaugg and others, 1995) (112 surface-water sites sampled for this analysis method)										
Alachlor	0.002	279	14	24.4 ^a	0.029	3.100	105	1 ^a	<0.002	0.005
Atrazine	.001	279	92	88.2 ^a	.730	25.0 (E)	105	36	.250	1.20
Azinphos-methyl	.001	275	4	3.6 ^a	<.001	.130 (E)	104	0	<.001	<.001
Benfluralin	.002	277	1	0.7	<.002	.030	104	0	<.002	<.002
Butylate	.002	277	2	0.7	<.002	.018	104	0	<.002	<.002
Carbaryl	.003	279	23	28.3 ^a	.064	2.00 (E)	105	0	<.003	<.003
Carbofuran	.003	279	7	5.7 ^a	<.003	.460 (E)	105	0	<.003	<.003
Chlorpyrifos	.004	277 ^b	12	17.0 ^a	.008	.041	104	0	<.004	<.004
Cyanazine	.004	279 ^b	17	23.3 ^a	.078	3.00	105	0	<.004	<.004
DCPA	.002	277 ^c	9	12.6 ^a	.002	.045	104 ^c	1 ^a	<.002	.001 (E)
p,p'-DDE	.006	277 ^c	6	2.2 ^a	<.006	.023	104 ^c	10 ^a	<.006	.001 (E)
Desethylatrazine	.002	279 ^b	80	79.6 ^a	.150	.690 (E)	105 ^b	38 ^a	.140	1.40 (E)
Diazinon	.002	277	21	30.0 ^a	.071	1.40	104	0	<.002	<.002
Dieldrin	.001	277	2	0.7	<.001	.018	104	0	<.001	<.001
2,6-Diethylalanine	.003	277 ^b	1	0.4 ^a	<.003	.014 (E)	104	0	<.003	<.003
EPTC	.002	277	5	3.6 ^a	<.002	.012	104	3 ^a	<.002	.013
Ethoprop	.003	279	1	0.4	<.003	.027	105	0	<.003	<.003
Fonofos	.003	277	3	2.2 ^a	<.003	.084	104	0	<.003	<.003
gamma-HCH	.004	277	2	1.1	<.004	.025	104	0	<.004	<.004
Linuron	.002	277	5	10.5	.009	1.40	104	0	<.002	<.002
Malathion	.005	277	5	5.1 ^a	<.005	.410	104	0	<.005	<.005
Methyl parathion	.006	277	4	3.6 ^a	<.006	.080	104	0	<.006	<.006
Metolachlor	.002	279 ^b	83	84.9 ^a	.990	23.0 (E)	105	20 ^a	.009	.460
Metribuzin	.004	277	9	11.6 ^a	.008	.160	104	2 ^a	<.004	.012
Napropamide	.003	279	2	0.7	<.003	.024	105	0	<.003	<.003
Pebulate	.004	277	0	0.0	<.004	<.004	104	1 ^a	<.004	.004 (E)
Pendimethalin	.004	277	5	13.4 ^a	.022	.320	104	0	<.004	<.004
Prometon	.018	279 ^c	68	71.7 ^a	.077	1.70 (E)	105 ^c	16 ^a	.018	.900 (E)
Propachlor	.007	279 ^b	1	1.4 ^a	<.007	.046	105	0	<.007	<.007
Simazine	.005	279 ^b	83	84.9 ^a	.510	4.40	105	23 ^a	.065	.210
Tebuthiuron	.010	279 ^c	22	21.5 ^a	.010	.220	105	2 ^a	<.010	.086
Terbacil	.007	274 ^b	7	6.9 ^a	<.007	.130 (E)	104 ^c	1 ^a	<.007	.260 (E)
Trifluralin	.002	277	9	4.7	<.002	.027	104	0	<.002	<.002
Samples analyzed by high-performance liquid chromatography with detection by ultraviolet spectroscopy (Werner and others, 1996) (8 surface-water sites sampled for this analysis method)										
Chlorothalonil	.035	126	1	0.8 ^a	<.035	.100	82	0	<.035	<.035
2,4-D	.035	127	4	19.7 ^a	.340	2.80	82	0	<.035	<.035
Dicamba	.035	127	0	0.0	<.035	<.100	82	1	<.035	.070
Dichlobenil	.020	128	0	0.0	<.020	<.100	82	1 ^a	<.020	.100 (E)
Dichlorprop	.032	127	1	0.8	<.032	.150	82	0	<.032	<.032
Diuron	.020	128 ^b	2	14.8 ^a	.090	.690 (E)	82	0	<.020	<.040
MCPA	.050	127	1	1.6	<.050	1.30	82	0	<.050	<.050
Oryzalin	.019	128	1	6.3 ^a	<.019	1.90	82	0	<.090	<.038
Propoxur	.035	118	0	0.0	<.035	<.035	77	1	<.035	.060
Triclopyr	.050	127	2	3.9 ^a	<.050	.830	82	0	<.050	<.050

^a Some detections of estimated values were reported for this pesticide.

^b Less than 50 percent of detectable concentrations were estimated below the MDL or MRL.

^c 50 percent or more of detectable concentrations were estimated below the MDL or MRL.

All samples were analyzed by the U.S. Geological Survey National Water Quality Laboratory (NWQL).

(either a specific land use within the subunit or the entire subunit) to create a spatially unbiased network within that area, and were sampled using trace-level protocols (Koterba and others, 1995). Three additional wells within the forested areas of the Valley and Ridge were sampled to provide information on the background water-quality conditions in that subunit.

Sample Analysis

The laboratory analyses for the pesticide data presented in this report were performed by the USGS National Water Quality Laboratory (NWQL), in Denver, Colo. All surface-water and ground-water samples were analyzed by the NWQL for selected pesticides and their degradation products by gas chromatog-

raphy with detection by mass spectrometry (Zaugg and others, 1995). Surface-water samples from 8 fixed sites and ground-water samples from the Great Valley Carbonate, Triassic Lowlands, Piedmont, and five wells from the Valley and Ridge subunits also were analyzed for additional pesticides by high-performance liquid chromatography with detection by ultraviolet spectroscopy

(Werner and others, 1996). The different analytes detected by these methods and the results of those analyses are shown in table 3. Some detectable concentrations of pesticides are qualified as “estimated”. Estimated concentrations occur when the actual concentration is greater than or less than the calibrated range for the laboratory analysis method. All concentrations of carbaryl, carbofuran, desethylatrazine, dichlobenil, and methyl azinphos are reported as estimated due to comparably small or variable recovery in the analysis (Zaugg and others, 1995; Werner and others, 1996).

Pesticides in Surface Water

Selected pesticides and degradation products (table 1) were analyzed in 279 water samples collected from 112 stream sites in the Potomac River Basin. Sampling locations and the number of compounds detected at each site are shown in figure 4. The number of pesticides detected in surface-water samples ranged from 0 to 27; sixteen sites had no pesticides detected. Pesticides were detected most frequently in the Great Valley Carbonate, Triassic Lowlands, and Piedmont subunits — areas with a high percentage of agricultural land use. Conversely, pesticides were detected less frequently in the Valley and Ridge subunit, an area that is heavily forested. Thirty-nine compounds were detected in surface-water samples, with detection frequencies ranging from 0.4 to 88.2

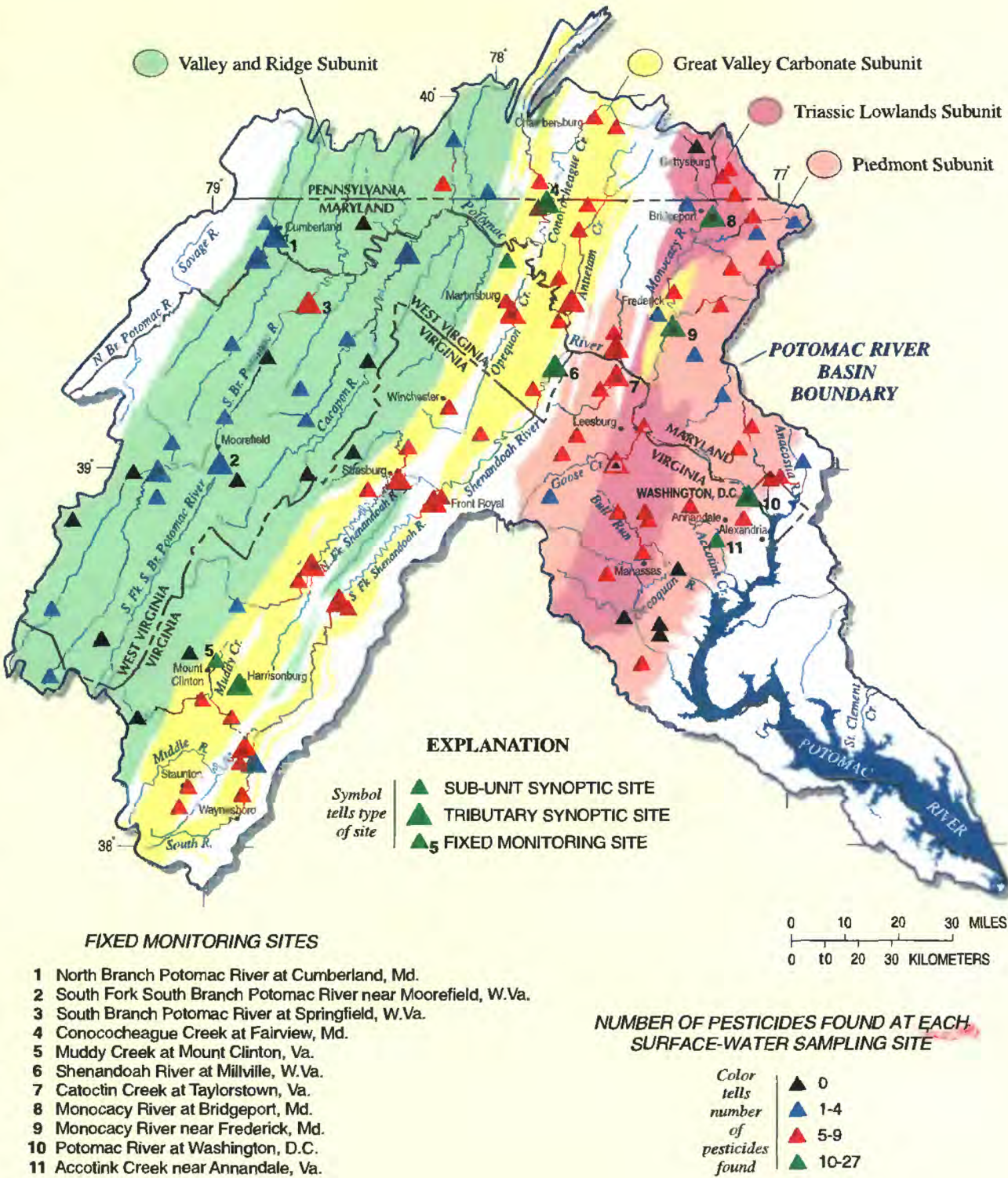


Figure 4. Location of study subunits and surface-water sampling sites, and the number of pesticides detected at each site.

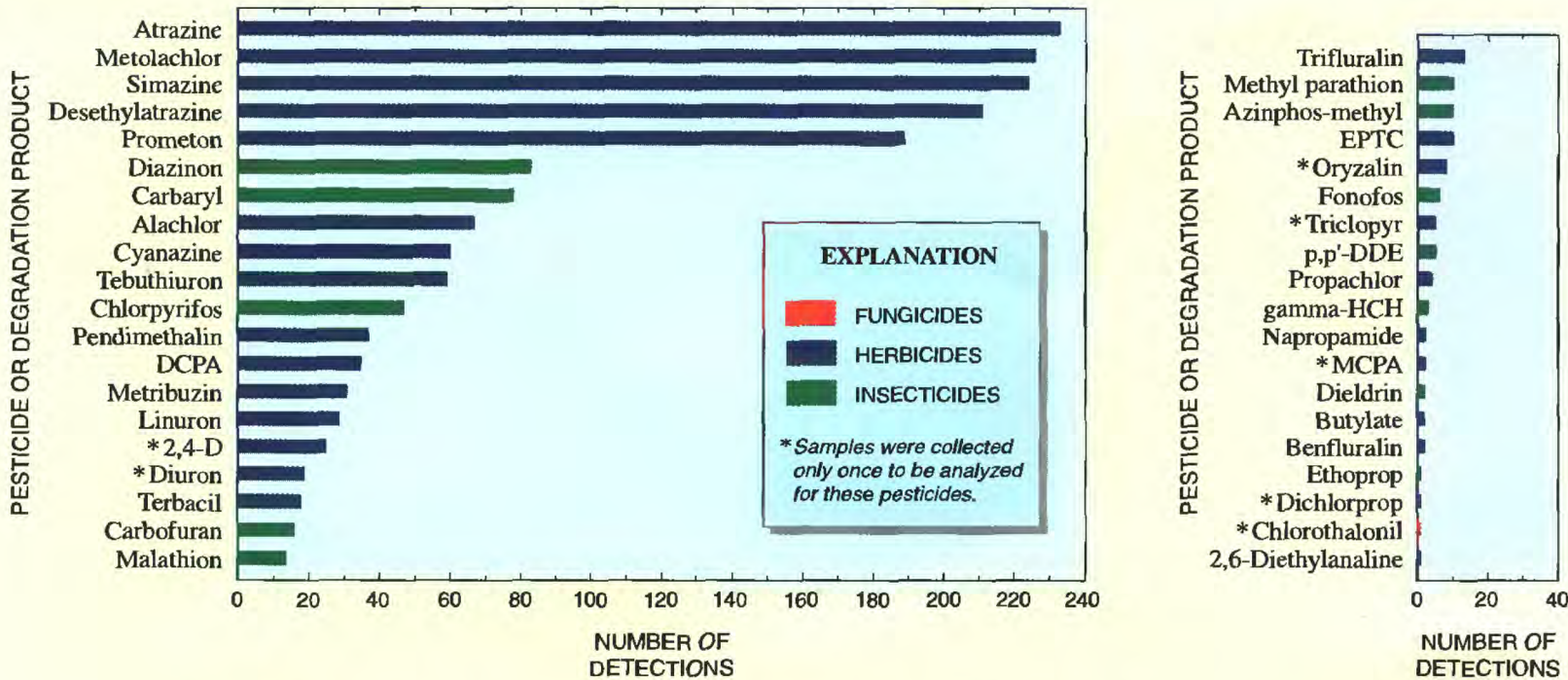


Figure 5. Pesticides and degradation products detected in surface water in the Potomac River Basin, March 1993 through September 1996.

Table 4. Federal drinking-water standards for pesticides analyzed in the NAWQA program in the Potomac River Basin

[MCL: Maximum Contaminant Level; MCL's set by U.S. Environmental Protection Agency (1994)]

PESTICIDE	MCL, IN MICROGRAMS PER LITER	NUMBER OF DETECTIONS IN SURFACE-WATER SAMPLES ABOVE MCL ^a	NUMBER OF SURFACE-WATER SITES WHERE DETECTED ABOVE MCL
Alachlor	2	1	1 ^b
Aldicarb	3	0	0
Aldicarb sulfone	2	0	0
Aldicarb sulfoxide	4	0	0
Atrazine	3	16	5 ^c
Carbofuran	40	0	0
2,4-D	70	0	0
Dinoseb	7	0	0
gamma-HCH	0.2	0	0
Oxamyl	200	0	0
Picloram	500	0	0
Simazine	4	2	2 ^d

^aNo pesticides were detected above MCL's in any ground-water sample.

^bMonocacy River at Bridgeport, Md.

^cConococheague Creek at Fairview, Md.; Muddy Creek at Mount Clinton, Va.; Monocacy River at Bridgeport, Md.; Monocacy River at Frederick, Md.; and Potomac River at Washington, D.C.

^dMuddy Creek at Mount Clinton, Va. and Accotink Creek near Annandale, Va.



percent of all samples (table 3). The compounds detected most frequently (fig. 5) and at the greatest number of sites were atrazine (92 sites), metolachlor (83 sites), simazine (83 sites), desethylatrazine (80 sites), and prometon (68 sites) (table 3). These five pesticides were detected more frequently and at higher concentrations in surface water than in ground water. All other pesticides were detected less frequently and at fewer than 25 percent of the surface-water sites.

More pesticides were detected at fixed monitoring sites, where samples were collected most frequently, than at sites sampled only once (synoptically). For example, 10 or more pesticides were detected at 7 of the 11 fixed sites (figure 4). The greatest number of pesticides (27) were detected at the Monocacy River at Bridgeport, Md., and Accotink Creek near Annandale, Va. More pesticides were detected and often at higher concentrations during periods of surface-water runoff after

storms. The highest pesticide concentrations also occurred during the spring/summer application period. Typical results from one of the frequently sampled surface-water monitoring sites, Muddy Creek at Mount Clinton, Va., are shown in figure 3. The highest concentration of atrazine in Muddy Creek was 14.9 micrograms per liter ($\mu\text{g/L}$) in May 1993, during a storm that followed a seasonal application of pesticides. Median concentrations of atrazine, desethylatrazine, and metolachlor analyzed in all surface-water samples were 0.057 $\mu\text{g/L}$, 0.028 $\mu\text{g/L}$, and 0.024 $\mu\text{g/L}$, respectively. The median concentrations of all other pesticides were at the detection limit (table 3).

Federal drinking-water standards have been established for 11 of the 85 compounds analyzed in the NAWQA study (U.S. Environmental Protection Agency, 1994; table 4). Concentrations of three of those compounds — alachlor, atrazine, and simazine — were higher than the maximum contaminant levels (MCL's) in 17 samples collected. MCL's are strictly applicable only to treated drinking water and are used here only as a point of reference. These elevated levels were detected at six sites and persisted for short periods of time during periods of surface-water runoff conditions following spring storms.



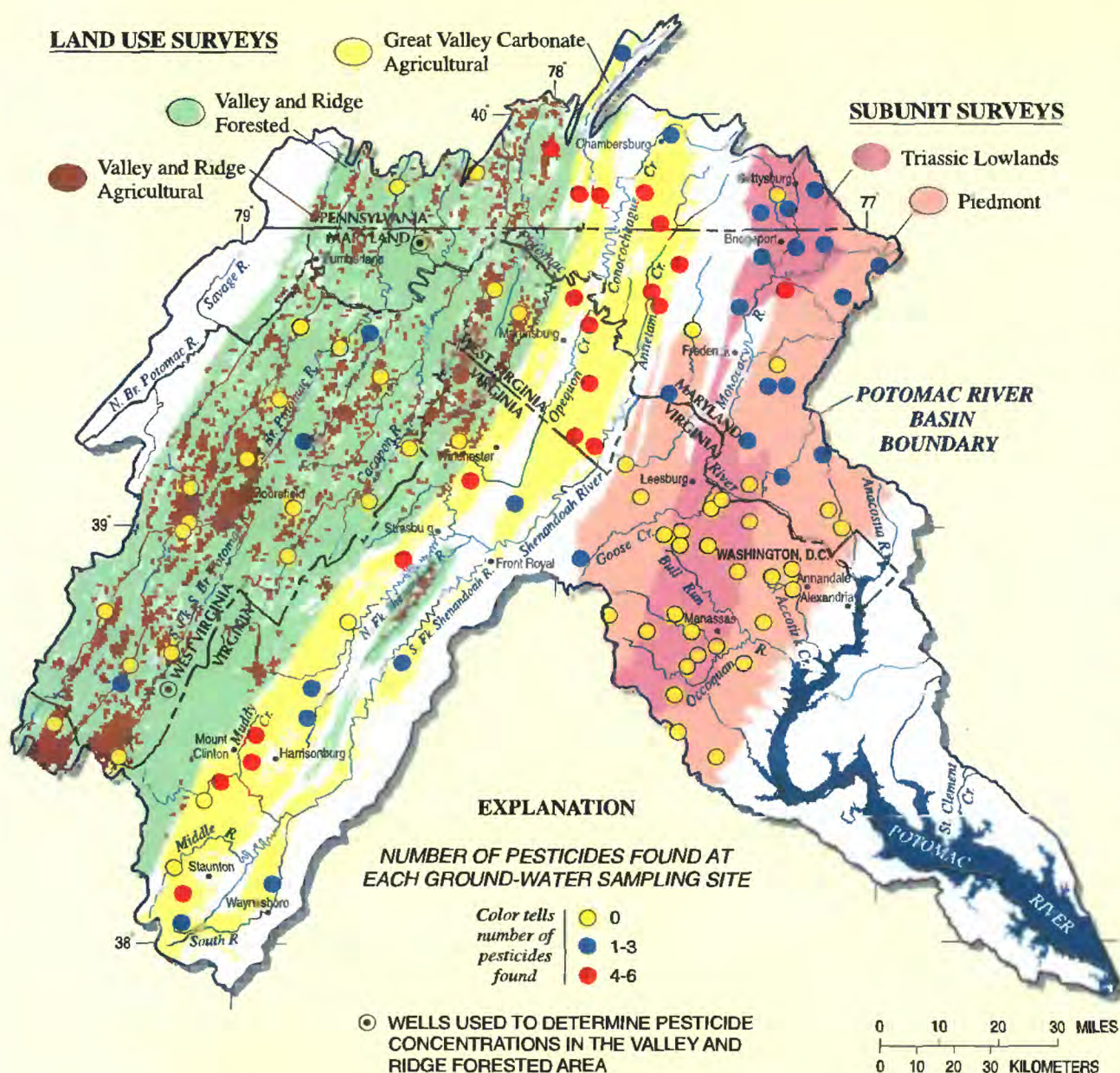


Figure 6. Location of land use and subunit surveys, ground-water sampling sites, and the number of pesticides detected at each site.

Pesticides in Ground Water

Water samples were collected from 105 wells in the Potomac River Basin and analyzed for selected pesticides and degradation products (table 1). Sampling locations and the number of compounds

detected at each site are shown in figure 6. Sixty wells had no detectable concentrations of pesticides or degradation products. The greatest number of pesticides detected in any ground-water samples was six. Figure 6 also shows that

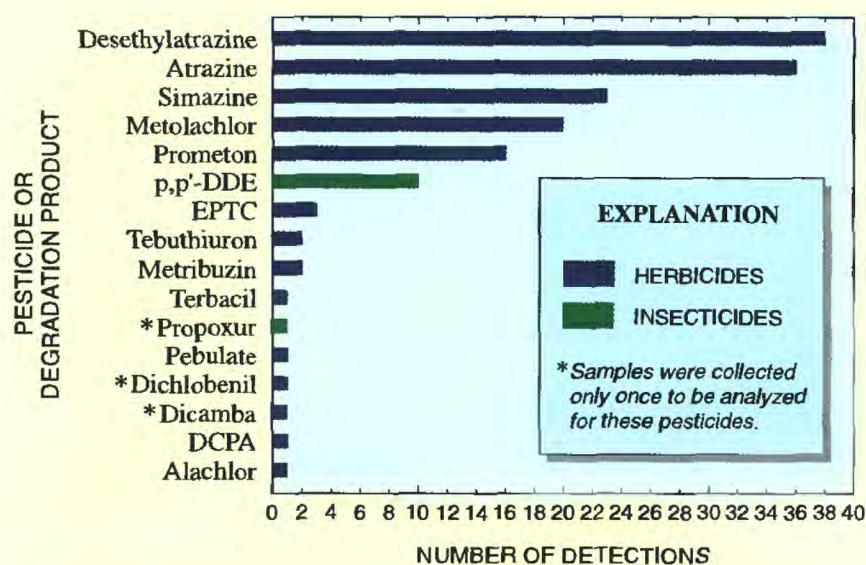


Figure 7. Pesticides and degradation products detected in ground water in the Potomac River Basin, June 1993 through July 1995.

pesticides were detected most frequently in the Great Valley Carbonate subunit.

Sixteen different compounds were detected in the ground-water samples, with the number of detections ranging from 1 to 38 (table 3). Desethylatrazine, atrazine, simazine, metolachlor, and prometon were the compounds detected most frequently, with 38, 36, 23, 20, and 16 detections, respectively (fig. 7). Except for the compound p,p'-DDE, which had 10 detections, all other compounds detected were found in three or fewer samples. The USGS found that detections of these chemicals occurred at concentrations that are substantially below current drinking-water MCL's (U.S. Environmental Protection Agency, 1994). Again, only 11 of the compounds analyzed have established MCL values. However, multiple pesticides were frequently detected in the same well and the health effects of combinations of pesticides in drinking water are not well understood.





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