

UNITED STATES GEOLOGICAL SURVEY



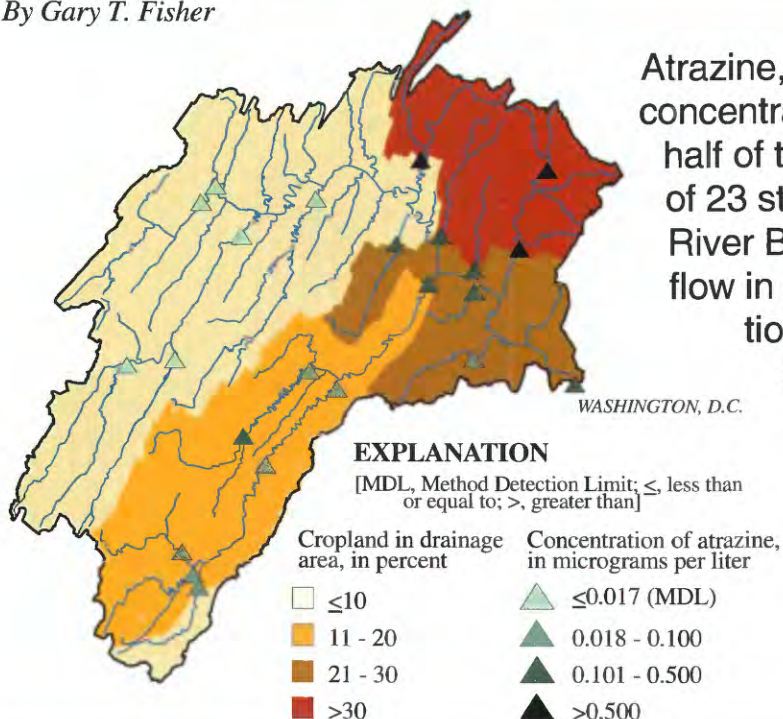
SELECTED HERBICIDES IN MAJOR STREAMS IN THE POTOMAC RIVER BASIN UPSTREAM FROM WASHINGTON, D.C.



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Potomac River Basin

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Atrazine, simazine, metolachlor, and prometon concentrations were detected in more than one-half of the water samples collected from each of 23 streams throughout the upper Potomac River Basin during a period of normal streamflow in early June 1994. Atrazine concentrations were highest in areas with intensive cropland; a sample from Conococheague Creek contained a maximum atrazine concentration of 0.73 micrograms per liter. None of the herbicide concentrations exceeded criteria for the protection of human health or aquatic life.

Relation of atrazine concentrations to cropland. Concentrations of atrazine in 23 sampled streams increased with the percentage of cropland drained.

INTRODUCTION

Contamination of water resources by pesticides is a major concern for protecting human health and aquatic life. Herbicides account for most pesticide use in the United States and include many compounds that are readily dissolved in and transported by water. Herbicides in streamflow are an important issue for people who are concerned about the quality of the freshwater resources of the Potomac River Basin and the Chesapeake Bay. An understanding of the problems associated with this issue is needed for cost-effective

water-quality-management programs to protect human health, aquatic life, and economic resources, and for restoration of the Bay. Herbicides are widely used in agricultural and urban areas for weed control on cropland, pasture, orchards, and lawns; along roads, power lines, and right-of-ways; and around buildings and other structures. The U.S. Geological Survey (USGS) has evaluated the occurrence of herbicides in surface water in the Potomac River Basin, which is one of 60 study units in USGS's National Water-Quality Assessment (NAWQA) program. Streamwater samples were collected during June 5-

16, 1994, at 23 sites throughout the study area and analyzed for concentrations of selected herbicides.

Major agricultural herbicides used in the study area include atrazine and cyanazine for corn, simazine for corn and alfalfa, and alachlor and metolachlor for soybeans and corn. Simazine is also used in apple orchards, which are common in the Shenandoah and Hagerstown Valleys and in the headwaters part of the Monocacy River subbasin. Prometon is an important herbicide used in noncrop and industrial areas for total vegetation control. Atrazine is a "toxic of con-

cern" for the Chesapeake Bay, and alachlor and metolachlor are being considered for that designation (U.S. Environmental Protection Agency, Chesapeake Bay Program, Annapolis, Md.).

The limited amount of data from previous sampling near the mouth of the Shenandoah River suggests that highest concentrations of herbicides occur in streams in the study area during May through June following the application of herbicides to farm fields and residential lawns. Unfortunately, data on herbicides from previous studies are sparse. A one-time sampling effort was designed to evaluate the geographic distribution of herbicides in streams during the late spring period of expected high herbicide concentrations. Highest concentrations can be expected in streamflow resulting from large storms that immediately follow herbicide applications. Distribution of rainfall amounts over a wide area is rarely uniform, so comparisons between results of storm sampling would be difficult. Therefore, sampling was done only when no significant rainfall occurred during the sampling period or for at least 10 days prior to sampling, so that the effects of storms on surface runoff could be minimized.

DESCRIPTION OF STUDY AREA

The Potomac River Basin encompasses 14,670 mi² (square miles) in Virginia, Maryland, West Virginia, Pennsylvania, and the District of Columbia. The study area was limited to the 11,670 mi² of the basin draining to the Potomac River upstream from Washington, D.C., and includes most of the area in the Potomac River Basin that is thought to contribute herbi-

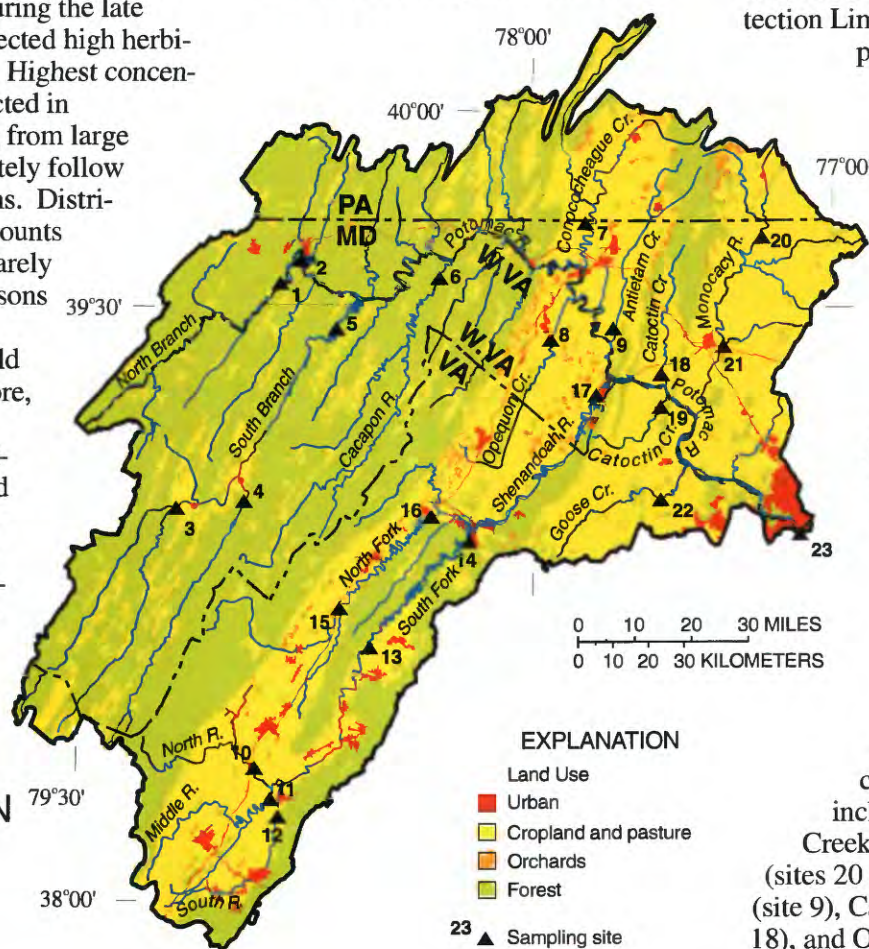
cides to the Chesapeake Bay. A Temperate climate and moderate rainfall generally produce year-round flow in streams throughout the area. During 1951-90, streams in the study area supplied an average of 15 percent of freshwater inflow to the Chesapeake Bay, making the Potomac River the second largest tributary to the Bay. The study area has a complex environmental setting that is affected by various combinations of natural processes and human activities. It contains parts of six physiographic provinces that are underlain by a wide variety of rock types. Physiography and rock type, along with associated soil types and drainage patterns, have had a significant effect on patterns of human

development since Colonial times. Land use in 1990 was about one-half forested, one-third agricultural, and less than one-tenth urban. Most of the forests are in the western half of the study area, most of the agriculture is in the central valleys and eastward, and the largest urban areas are in the vicinity of Washington, D.C. About two-thirds of the 4.67 million people who lived in the Potomac River Basin in 1990 resided in the Washington area.

SELECTED HERBICIDES IN MAJOR STREAMS

Concentrations of four herbicides exceeded laboratory Method Detection Limits (MDL's) in water samples from more than one-half of the streams; maximum concentrations were 0.730 µg/L for atrazine, 0.220 µg/L for simazine, 0.700 µg/L for metolachlor, and 0.063 µg/L for prometon. MDL's were 0.017 µg/L for atrazine, 0.008 µg/L for simazine, 0.009 µg/L for metolachlor, and 0.008 µg/L for prometon. The highest concentrations of atrazine, simazine, metolachlor, and prometon were generally found in streams draining most intensively cropped parts of the basin, including Conococheague Creek (site 7), Monocacy River (sites 20 and 21), Antietam Creek (site 9), Catoclin Creek (Md.) (site 18), and Opequon Creek (site 8). High concentrations of simazine and metolachlor were also found in the Shenandoah River subbasin (sites 15 and 17).

Three other herbicides were also found at concentrations exceeding the MDL. Concentrations of cyanazine exceeded the MDL of 0.013 µg/L in six stream-water samples; a maxi-



Location of sites where streamwater samples were collected. The study area encompasses a region of diverse land uses, including forested, agricultural, and urban areas.

Streams from which water samples were collected, selected basin characteristics, streamflow, and concentrations of selected herbicides.

[mi², square miles; ft³/s, cubic feet per second; µg/L, micrograms per liter. Concentrations were determined using a Method Detection Limit with 99 percent confidence that the analyte concentration is greater than zero.]

Site no.	USGS station number and name	Drainage area (mi ²)	Land use (percent)			Streamflow (ft ³ /s)	Concentration (µg/L)			
			Forest	Agriculture	Urban		Atrazine	Simazine	Metolachlor	Prometon
1	01600000 N. Br. Potomac R. at Pinto, Md.	596	83	12	2	435	<0.017	<0.008	<0.009	<0.008
2	01603000 N. Br. Potomac R. near Cumberland, Md.	875	82	13	3	590	<0.017	<0.008	<0.009	<0.008
3	01606500 S. Br. Potomac R. near Petersburg, W.Va.	642	79	21	<0.1	226	<0.017	.029	<0.009	<0.008
4	01608000 S. Fk. S. Br. Potomac R. near Moorefield, W.Va.	283	85	14	<1	52	<0.017	<0.008	<0.009	<0.008
5	01608500 S. Br. Potomac R. near Springfield, W.Va.	1,480	78	22	<1	435	<0.017	.024	<0.009	<0.008
6	01611500 Cacapon R. near Great Cacapon, W.Va.	677	82	18	<1	219	<0.017	.090	<0.009	<0.008
7	01614500 Conococheague Cr. at Fairview, Md.	494	36	60	4	342	.730	.095	.600	.043
8	01616500 Opequon Cr. near Martinsburg, W.Va.	272	24	70	6	165	.190	.041	.078	.035
9	01619500 Antietam Cr. near Sharpsburg, Md.	281	24	69	7	302	.300	.083	.088	.063
10	01622000 North R. at Burkettown, Va.	379	59	34	7	154	.094	.039	.028	.018
11	01625000 Middle R. near Grottoes, Va.	375	31	60	8	163	.049	.016	.015	.026
12	01627500 South R. at Harrison, Va.	212	59	30	11	104	.028	.010	<0.009	.016
13	01629500 S. Fk. Shenandoah R. near Luray, Va.	1,377	50	42	8	640	.069	.027	.023	.017
14	01631000 S. Fk. Shenandoah R. at Front Royal, Va.	1,642	51	40	8	776	.078	.037	.033	.014
15	01633000 N. Fk. Shenandoah R. at Mt. Jackson, Va.	506	55	40	5	170	.140	.220	.290	.018
16	01634000 N. Fk. Shenandoah R. near Strasburg, Va.	768	54	40	6	297	.065	.064	.086	.018
17	01636500 Shenandoah R. at Millville, W.Va.	3,040	51	41	7	1,350	.150	.110	.300	.019
18	01638050 Catoctin Cr. at Olive, Md.	112	26	71	2	38	.230	.150	.060	.013
19	01638480 Catoctin Cr. at Taylorstown, Va.	89.6	18	81	1	24	.120	.071	.150	<0.008
20	01639000 Monocacy R. at Bridgeport, Md.	173	20	78	2	31	.570	.130	.700	.017
21	01643020 Monocacy R. near Frederick, Md.	817	23	73	3	312	.510	.140	<0.009	.025
22	01644000 Goose Cr. near Leesburg, Va.	322	29	66	4	93	.054	.015	.029	<0.008
23	01646580 Potomac R. at Washington, D.C.	11,670	55	40	4	3,860	.170	.081	.085	.022

maximum concentration of 0.069 µg/L was found in the Monocacy River at Bridgeport (site 20). Alachlor was found at a concentration of 0.018 µg/L in the Monocacy River near Frederick (site 21), but its concentration did not exceed the MDL of 0.009 µg/L at any other site. Concentrations of terbacil, which is used for weed control in alfalfa and in orchards, exceeded the MDL of 0.030 µg/L in water samples from three streams in the North and South Branches of the Potomac River, and were 0.200, 0.120, and 0.120 µg/L at sites 1, 2, and 4, respectively.

An approach to defining potential environmental problems associated with the herbicide concentrations found is to compare the concentrations with criteria for the protection of human health or aquatic life. Available criteria for comparison include the U.S. Environmental Protection Agency's maximum contaminant levels and health advisories for drinking water (1992) and Environment Canada's guidelines for the protection

of aquatic life (1988). Criteria for atrazine, simazine, metolachlor, cyanazine, and alachlor are listed below. None of the herbicide concentrations found in stream-water samples exceeded the established criteria.

Criteria for the protection of human health and aquatic life.			
[µg/L, micrograms per liter; —, none available]			
Herbicide	Maximum contaminant level (µg/L)	Health advisory level (µg/L)	Canadian aquatic-life guidelines (µg/L)
Atrazine	3	—	2
Simazine	4	4	10
Metolachlor	—	100	8
Alachlor	2	—	—
Cyanazine	—	1	2

The results of analysis for herbicides were compared with those from a previous study to show that the recent sampling was representative of longer-term conditions. In the Potomac River at Washington (site 23), which is the most downstream site at which stream-water samples were collected and where the composite water quality of the entire study area can be monitored, concentrations of five of six selected herbicides were found to

exceed the MDL's. Concentrations of atrazine, simazine, metolachlor, prometon, cyanazine, and alachlor in the streamwater sample taken on June 9, 1994, were compared to those in a streamwater sample collected under similar conditions on May 29, 1992, for the Fall Line Toxics Program (U.S. Environmental Protection Agency, Chesapeake Bay Program, Annapolis, Md.). Actual streamflow on the day of sampling was about 82 percent greater in 1992 than it was in 1994. However, mean streamflows in May 1992 and May 1994 were within 17 percent of the 1959-94 mean streamflow for May, indicating similar antecedent-flow conditions. The magnitudes of herbicide concentrations in the streamwater samples collected in 1992 and 1994 were similar. Concentrations in 1992 were 0.207 µg/L for atrazine, 0.123 µg/L for simazine, 0.085 µg/L for metolachlor, 0.011 µg/L for prometon, and 0.090 µg/L for cyanazine. The concentration of alachlor, which did not exceed the MDL in 1994, was 0.009 µg/L in 1992.

Several factors must be considered when interpreting the concentration of a herbicide in a stream. Foremost, the herbicide must be used somewhere in the area drained by the stream. More than one type of land use may contribute herbicides to a stream. For example, simazine and metolachlor are used on cropland and in orchards. Because all of the herbicides considered in this report are water soluble, residues on soil, vegetation, or other surfaces can be easily carried by surface runoff into streams. These residues can also be leached to the water table and be carried by ground-water flow into streams. The proximity of herbicide use to streams also is an important factor. Herbicides used near a stream have a greater potential for delivery to the stream than those used farther away. The time it takes for a herbicide to move down a stream or along a path of ground-water flow (travel time) may also affect concentration. In-stream processes upstream from a sampling point may reduce concentrations with increasing travel time and distance through time-dependent processes, such as chemical degradation; assimilation processes, such as adsorption to sediments or biological uptake; or dilution by intermediate inflows. Similar processes may occur in ground water that discharges to streams. Finally, the physical and chemical characteristics of individual herbicides can affect the transport and fate of a herbicide from its point of use through its transport to a stream-sampling site.

With the limited data available from this study, any interpretations made concerning the sources or mechanisms responsible for the herbicide concentrations found must be considered preliminary. Additional factors that can affect the availability and movement of herbicides include crop type, application rate, cultivation and conservation practices, weather, and stream-channel characteristics. These factors can be highly variable from place to place and over time and must be considered in a complete evaluation. For example, an isolated thunderstorm occurred in the headwaters of Conococheague and Antietam

Creeks about 1 day prior to sampling those two streams. Rainfall of 0.72 inches was reported at Chambersburg, Pa., and produced relatively small stream-discharge peaks about one-half day prior to sampling. Although these weather conditions are not believed to have affected the interpretations that follow, they probably had some impact on the magnitude of herbicide concentrations in the two streams.

The occurrence of atrazine, simazine and metolachlor in streams is attributed to use of the herbicides on cropland. In general, the concentrations of these herbicides in streams are proportional to the percentage of cropland in the streams' drainage areas. However, high concentrations of simazine were also found in streams that drain areas with comparatively low percentages of cropland in the Capon River (site 6) and parts of the Shenandoah River subbasin (sites 15 and 17). Use of simazine in orchards, which are relatively plentiful in these areas, was a possible source of the herbicide. High concentrations of metolachlor were also found at sites 15 and 17. These high concentrations cannot be explained with the limited data available, but they may be related to the proximity of cropland to the sampling sites; at site 15, the stream was bordered by a large corn field for a distance of about 1 mile upstream from the sampling location. Prometon was found at relatively low concentrations at most sites. Because it is not an agricultural herbicide, its presence and concentration at any site are probably related to the intensity of nonagricultural human activities in the drainage area.

In-stream processes appear to be important in the stream reach between sites 15 and 16 on the North Fork Shenandoah River. At upstream site 15, simazine and metolachlor concentrations were among the highest found. However, at site 16, concentrations of atrazine, simazine, and metolachlor had decreased to about one-third of their upstream concentrations. Although the sites are only 23 miles apart, there is considerable meandering of the stream channel be-

tween the sites and the actual river distance is 50 miles. In this long distance, there is sufficient time for in-stream processes to reduce concentrations through degradation or assimilation of the herbicides.

NEEDS FOR ADDITIONAL STUDY

Additional study is needed to verify apparent relations between cropland and orchards and herbicide concentrations in streams. Additional sampling in Conococheague, Antietam, Opequon, and Catoctin (Md.) Creeks, the Monocacy River, and at the mouth of the Shenandoah River would indicate their relative contributions to total herbicide transport in the study area. Further study also is needed to determine the processes in ground water and streams that are most important for transporting herbicides to and through the stream system. In particular, study of simazine and metolachlor in the North Fork Shenandoah River subbasin would improve understanding of in-stream processes. Additional sampling would also help to explain the relatively high concentrations of metolachlor at site 15, which could not be directly attributed to use of this herbicide on cropland upstream from the site.

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