

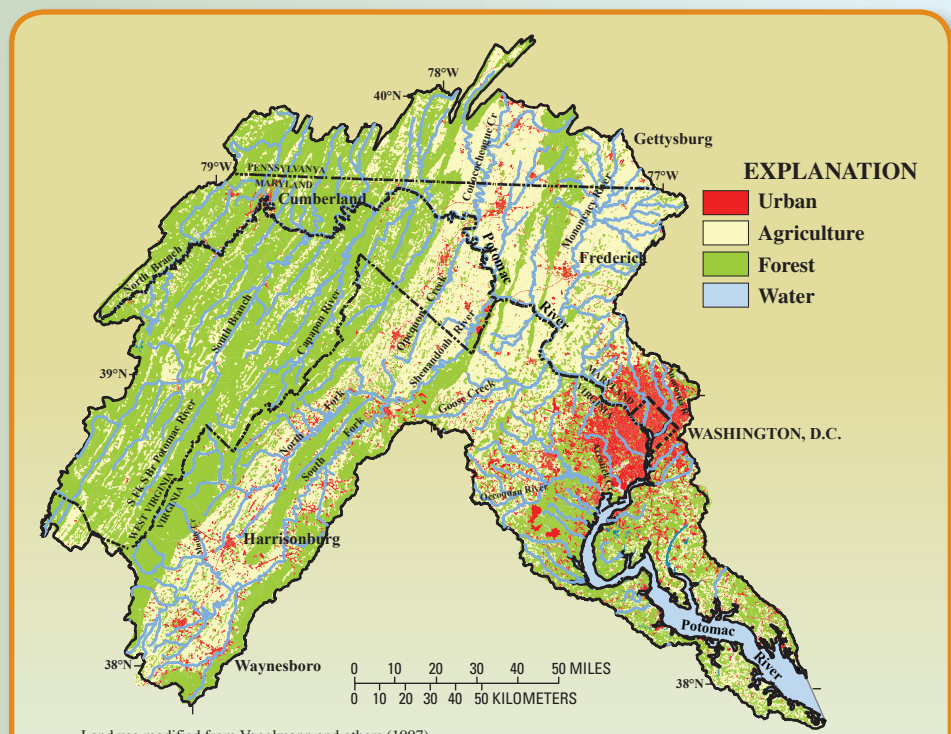
Prepared as part of the National Water-Quality Assessment Program, Source Water-Quality Assessment

# Organic Compounds in Potomac River Water Used for Public Supply near Washington, D.C., 2003–05

**O**rganic compounds studied in this U.S. Geological Survey (USGS) assessment generally are man-made, including, in part, pesticides, solvents, gasoline hydrocarbons, personal-care and domestic-use products, and refrigerants and propellants. A total of 85 of 277 compounds were detected at least once among the 25 samples collected approximately monthly during 2003–05 at the intake of the Washington Aqueduct, one of several community water systems on the Potomac River upstream from Washington, D.C. The diversity of compounds detected indicate a variety of different sources and uses (including wastewater discharge, industrial, agricultural, domestic, and others) and different pathways (including treated wastewater outfalls located upstream, over-land runoff, and ground-water discharge) to drinking-water supplies. Seven compounds were detected year-round in source-water intake samples, including selected herbicide compounds commonly used in the Potomac River Basin and in other agricultural areas across the United States. Two-thirds of the 26 compounds detected most commonly in source water (in at least 20 percent of the samples) also were detected most commonly in finished water (after treatment but prior to distribution). Concentrations for all detected compounds in source and finished water generally were less than 0.1 microgram per liter and always less than human-health benchmarks, which are available for about one-half of the detected compounds. On the basis of this screening-level assessment, adverse effects to human health are expected to be negligible (subject to limitations of available human-health benchmarks).

## Introduction

An investigation by the National Water-Quality Assessment (NAWQA) Program of the USGS characterizes the occurrence of 277 organic compounds in source water (defined as stream water collected at a surface-water intake prior to water treatment) and finished water (defined as water that has passed through treatment processes but prior to distribution) at the Washington Aqueduct, one of several community water systems that uses the Potomac River as its sole source of water supply upstream from Washington, D.C. (fig. 1). Samples were collected approximately monthly from the Potomac River during 2003–05 and included 25 source- and 13 finished-water samples. The samples were analyzed for pesticides and selected pesticide degradates, solvents, gasoline hydrocarbons, disinfection by-products, personal care and domestic-use products, and other compounds. Community water systems are required to monitor finished water for compounds regulated under the Safe Drinking Water Act. Most of the compounds included in this study are not regulated under U.S. Environmental Protection Agency (USEPA) Federal drinking-water standards (U.S. Environmental Protection Agency, 2007a). The Potomac River study is part of an ongoing national NAWQA investigation of community water systems across the United States. More detailed information and references on the sampling



**Figure 1.** About 11,500 square miles of the Potomac River Basin are upstream from major community water systems that serve the Washington, D.C., metropolitan area, including Washington Aqueduct. The area includes a large amount of forest (60 percent of the area), agriculture (about 35 percent), and urban areas, all of which can potentially affect source-water quality. About 500 million gallons per day are taken directly from the Potomac River near Washington, D.C., to serve water needs of about 5 million people. <http://www.potomacriver.org/cms/>.

## What "Detections" May Mean to Human Health

The analytical methods used in this study have low detection levels—typically 100 to 1,000 times lower than State and Federal standards and guidelines for protecting water quality. Detections, therefore, do not necessarily indicate a concern to human health but rather help to identify the environmental presence of a wide variety of chemicals not commonly monitored in water resources and to track changes in their occurrence and concentrations over time. These findings complement ongoing drinking-water monitoring required by Federal, State, and local programs, which focus primarily on post-treatment compliance monitoring of contaminants regulated by USEPA in drinking water. Many of the compounds analyzed by USGS are not included in other source- and finished-water monitoring programs such as the Unregulated Contaminant Monitoring Regulation (U.S. Environmental Protection Agency, 2007a) and the U.S. Department of Agriculture's Pesticide Data Program (U.S. Department of Agriculture, 2008).

design, methodology, specific compounds monitored, and the national study are described by Carter and others (2007). Additional USGS information on water quality in the Potomac River Basin is available in a companion NAWQA study (Ator and others, 1998).

## Occurrence of Organic Compounds in Source Water

About one-third of the 277 compounds were detected in at least one source-water sample. These compounds represent many different sources and uses and include pesticides, gasoline hydrocarbons, personal care products, and solvents. Seven compounds were detected year-round, including selected herbicide compounds commonly used in the Potomac River Basin.

Recent advances in laboratory analytical methods have given scientists the tools to detect a wide variety of contaminants in the environment at low concentrations—typically 100 to 1,000 times lower than

**Table 1.** A total of 35 of 277 organic compounds were detected commonly (in at least 20 percent of the samples) in source water and (or) finished water. Twenty-six compounds were detected commonly in source water, and about two-thirds of these compounds (17) also were detected commonly in finished water. The diversity of compounds indicate a variety of different uses—including industrial, agricultural, and domestic—and different pathways—including treated wastewater outfalls located upstream, overland runoff, and ground-water discharge—of the compounds entering drinking-water supplies.

[Black text indicates compounds detected in both source and finished water; orange text indicates compounds detected in only source water; blue text indicates compounds detected in only finished water; *italics* indicates pesticide degradates; ESA, ethane sulfonic acid; OA, oxanilic acid]

<b>Herbicides and herbicide degradates</b>	<b>Personal care and domestic-use products</b>
Atrazine	HHCB (Hexahydrohexamethylcyclopentabenzopyran)
<i>Deethylatrazine (DEA)</i>	
Metolachlor	<b>Manufacturing additives</b>
<i>Metolachlor ESA</i>	FYROL CEF (Tri(2-chloroethyl) phosphate)
Simazine	FYROL PCF (Tris(dichloroisopropyl) phosphate)
<i>2-Hydroxy atrazine</i>	
<i>Deisopropyl atrazine</i>	<b>Gasoline hydrocarbons and oxygenates</b>
<i>Metolachlor OA</i>	MTBE (methyl <i>tert</i> -butyl ether)
<i>Alachlor ESA</i>	<b>Benzene</b>
2,4-D	<b>Pavement- and combustion-derived compounds</b>
Prometon	Phenanthrene
<b>Diuron</b>	Fluoranthene
<b>3,4-Dichloroaniline</b>	Pyrene
<i>Acetochlor/metolachlor 2nd amide ESA</i>	
<b>Insecticides and insecticide degradates</b>	<b>Solvents</b>
<i>Desulfenyl fipronil</i>	Carbon tetrachloride
<b>Fipronil</b>	Methylene chloride
<b>Diazinon</b>	<b>Organic synthesis compounds</b>
<b>Carbaryl</b>	Anthraquinone
	Carbazole
<b>Plant- or animal-derived biochemicals</b>	<b>Disinfection by-products</b>
<b>Cholesterol</b>	Chloroform
<b>3-beta-Coprostanol</b>	Bromodichloromethane
	Dibromochloromethane

drinking-water standards (see inset). Eighty-five of the 277 compounds were detected in at least one source-water sample. A total of 192 compounds were not detected in any samples (Carter and others, 2007; Kingsbury and others, 2008).

Twenty-six compounds were detected in at least 20 percent of the source-water samples (table 1). Overall, the compounds detected most commonly in water from the Potomac River are among those most commonly detected in ambient stream water in the Potomac River Basin (Ator and others, 1998) and across the Nation (Gilliom and others, 2006).

Seven compounds were detected year-round (in more than 95 percent of the source-water samples). The continuous occurrence may be attributed to ground-

water discharge and (or) treated wastewater discharge from municipalities located upstream (Ator and others, 1998; Kingsbury and others, 2008). Three of the compounds include the herbicides atrazine, metolachlor, and simazine, which commonly are used on row crops and for weed control in urban and residential areas in the Potomac River Basin and across the Nation (Ator and others, 1998; Gilliom and others, 2006). Herbicide degradates (or "break-down products"), including deethylatrazine (DEA), metolachlor ethane sulfonic acid (ESA), and metolachlor oxanilic acid (OA), also were present year-round. The seventh compound detected year-round is the disinfection by-product chloroform, which may be related to treated wastewater outfalls (Kingsbury and others, 2008).



## Comparisons Between Source and Finished Water

*About two-thirds of the compounds detected most commonly in source water also were detected most commonly in finished water, and generally at similar concentrations, typically less than 0.1 microgram per liter.*

Comparisons between source and finished water are not intended to characterize treatment efficacy, but to provide a preliminary indication of the potential importance of compounds found in source water to the quality of finished water prior to distribution (see inset).

Seventeen of the 26 most commonly detected compounds in source water also were detected commonly in finished water for paired samples, and typically at lower or similar low-level concentrations (fig. 2). Two compounds in particular, metolachlor ESA and chloroform, were detected in 100 percent of both source- and finished-water samples, although concentrations of chloroform in source-water samples were low, with most at less than 0.1 microgram per liter.

The remaining 9 of the 26 most commonly detected compounds in source water were not detected as commonly in finished water. These include the insecticides fipronil, diazinon, and carbaryl, and their decreased detection in finished water may be due to degradation or transformation associated with disinfection treatment (Valder and others, 2008). Cholesterol and 3- $\beta$ -coprostanol also were detected

commonly in source water but not as commonly in finished water (fig. 2). Processes affecting the occurrence of these plant or animal-derived biochemicals are not well understood.

A total of nine compounds were detected commonly in finished water but not commonly in source water. These include two disinfection by-products (bromodichloromethane and dibromochloromethane; table 2), as well as carbon tetrachloride and methylene chloride (fig. 2). The presence of disinfection by-products in finished water is well documented, understood, and regulated, and is an expected outcome of drinking-water disinfection. The source of low-level detections of carbon tetrachloride in finished-water samples may be due to its presence as a contaminant in the chlorine used for disinfection (Christman, 1980), or possibly as a disinfection by-product (Krasner and others, 2006). The source of low-level detections of methylene chloride is not known.

## A Closer Look at Agricultural Herbicides and Degradates

*Detections and concentrations of commonly used herbicides and their degradates are relatively similar in source and finished water. Occurrence and concentrations of degradate compounds compared to their respective parent compounds differ compound by compound, depending on chemical properties, use, and hydrologic pathways.*

A more detailed analysis of the most commonly occurring herbicides highlights interesting relations between parent and degradate compounds in source and finished water. The percentage of detections and concentrations of parent and degradate compounds were relatively similar in source and finished water (fig. 2). Herbicide degradation mostly is driven by microbial activity in the soil zone before reaching the water table (Gilliom and others, 2006). Although concentrations of parent compounds generally are highest during spring applications, both the parent and degradate compounds were detected year-round. This is, in part, due to continuous contributions from ground-water discharge to the Potomac River and its tributaries (Ator and others, 1998).

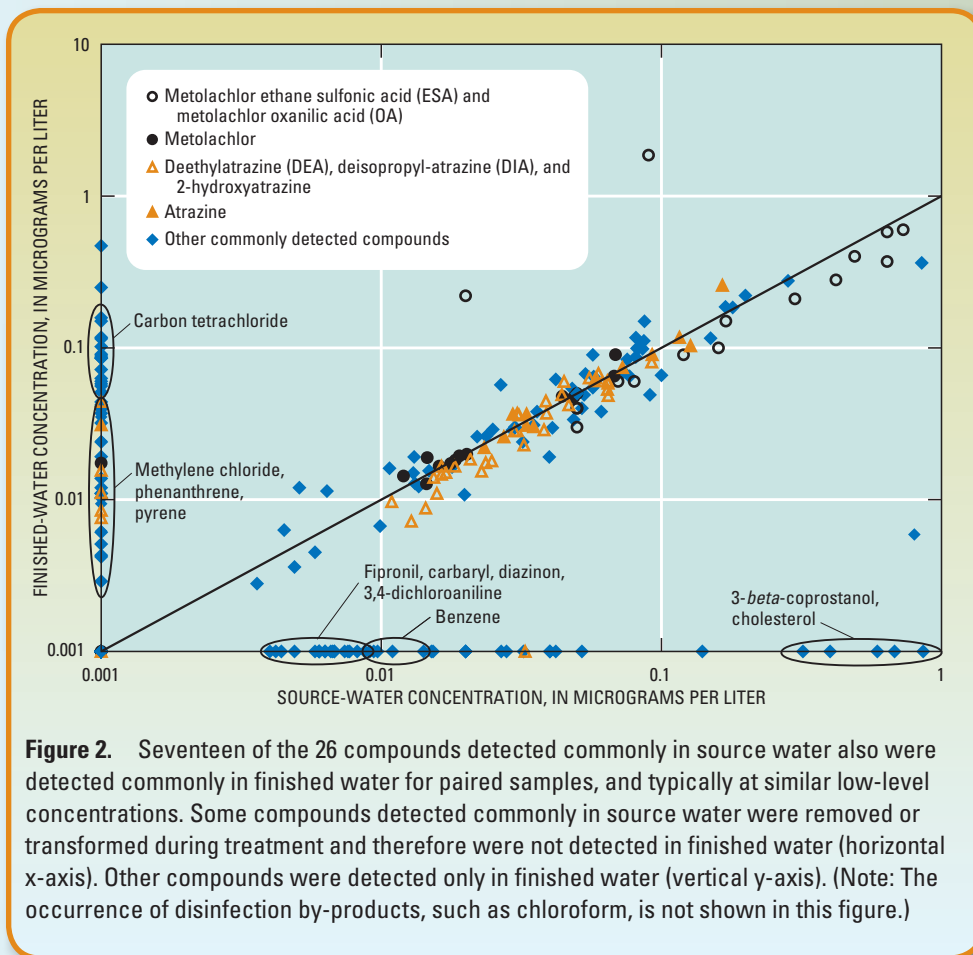
Summed concentrations of degradate compounds typically were similar to or greater than the parent herbicide concentrations, such as for atrazine, although summed concentrations of degradates can be less than parent concentrations due to differences in chemical properties and usage. Specifically, atrazine is chemically more stable, allowing it to persist longer in the hydrologic system than metolachlor, which tends to break down more quickly in the soil zone (Gilliom and others, 2006). As a result, the degradate metolachlor ESA was detected at concentrations 10 times greater than its parent concentrations in most samples. Alachlor presents a different story. Use of the herbicide alachlor has decreased substantially in recent years (Gilliom and others, 2006). As a result, the parent compound was not detected, but its degradate alachlor ESA was detected in about 65 percent of the source-water samples. In fact, alachlor ESA was one of the most commonly detected compounds, probably because it is still present in discharging ground water.

Transformation can result in the conversion of a parent compound to a compound that is commonly less toxic, but some degradates have toxicities that are similar to, or greater than, that of their parent pesticide (Gilliom and others, 2006). Herbicide degradate compounds are not regulated under the Safe Drinking Water Act; however, all large public water systems (including Washington Aqueduct) and 800 medium and small water systems nationwide are required under USEPA's Unregulated Contaminant Monitoring Rule 2 to monitor for three parent acetanilides (acetochlor, alachlor, and metolachlor) and six degradates (acetochlor ESA, acetochlor OA, alachlor ESA, alachlor OA, metolachlor ESA, and metolachlor OA) during a 12-month period between January 2008 and December 2010 (U.S. Environmental Protection Agency, 2007b, c).

## Finished-Water Sampling, Water Treatment, and Significance of Comparisons to Source Water

The Washington Aqueduct uses conventional water treatment: coagulation/flocculation using aluminum sulfate sedimentation, filtration through anthracite and sand, and disinfection with chlorine and chloramine. Powdered activated carbon is used occasionally to treat for taste and odor issues. Finished-water samples were collected at the Washington Aqueduct approximately 48 hours after source-water samples to account for treatment plant retention time of the water (L. Nolan, U.S. Army Corps of Engineers, oral commun., 2003). Some differences between source- and finished-water quality might be attributable to changes in source-water quality that are not represented by the finished-water samples because of sample timing and variations in retention time, and potential analytic variability associated with low concentrations at or near laboratory reporting levels (Kingsbury and others, 2008). It also is possible that some compounds detected in source water were removed or transformed during the treatment process into compounds that were not monitored as part of this study.

The study sampling design and resulting comparisons are not intended to characterize treatment efficacy, but to provide a preliminary indication of the potential importance of compounds found in source water to the quality of finished water prior to distribution. In general, conventional treatment is not specifically designed to remove most of the organic compounds monitored in this study.



**Figure 2.** Seventeen of the 26 compounds detected commonly in source water also were detected commonly in finished water for paired samples, and typically at similar low-level concentrations. Some compounds detected commonly in source water were removed or transformed during treatment and therefore were not detected in finished water (horizontal x-axis). Other compounds were detected only in finished water (vertical y-axis). (Note: The occurrence of disinfection by-products, such as chloroform, is not shown in this figure.)

## Potential Effects on Human Health

*Concentrations for all detected compounds in source and finished water generally were less than 0.1 microgram per liter and always less than human-health benchmarks, which are available for about one-half of the detected compounds. On the basis of this screening-level assessment, adverse effects to human health are expected to be negligible (subject to limitations of available human-health benchmarks, see inset).*

Although the type of conventional water treatment used by this community water system (which is typical of many systems across the Nation) is not specifically designed to remove most of the organic compounds, concentrations generally were less than 0.1 microgram per liter. For perspective, reporting limits for public drinking-water commonly are set through Federal regulations at 0.5 microgram per liter, and water utilities generally are not required to measure below this limit.

Concentrations of 10 compounds that were detected commonly in source and (or) finished water were greater than or equal to

0.1 microgram per liter (table 2). In general, compounds with concentrations greater than 0.1 microgram per liter, such as atrazine, metolachlor degradates, and the gasoline oxygenate methyl *tert*-butyl ether (MTBE), reflect their relatively widespread use in the Potomac River Basin and their physical properties that allow them to persist in the environment (Gilliom and others, 2006; Zogorski and others, 2006). Concentrations did not exceed USEPA drinking-water standards (MCLs) for regulated compounds (table 2) in any sample. Concentrations also were less than USGS Health-Based Screening Levels (HBSLs) established for selected unregulated compounds (see inset).

The USGS screening-level assessment also identified compounds at concentrations less than, but within a factor of 10, of human-health benchmarks. Only four regulated compounds were detected at concentrations less than, but within a factor of 10 of the USEPA MCL, including atrazine and total trihalomethanes (including chloroform, bromodichloromethane, and dibromochloromethane) (table 2). The regulated compound carbon tetrachloride was commonly detected in finished water but concentrations were not within a factor of 10 of the USEPA MCL (table 2). Although these compounds are regularly monitored

## Human-Health Benchmarks Used in This Assessment

A screening-level assessment of the potential significance of detected compounds to human health was based on a comparison of measured concentrations to available human-health benchmarks. Specifically, concentrations of regulated compounds were compared to USEPA Maximum Contaminant Levels (MCLs), and concentrations of unregulated compounds that have USEPA published toxicity information were compared to USGS Health-Based Screening Levels, which were developed in collaboration with USEPA, New Jersey Department of Environmental Protection, and Oregon Health & Science University (HBSLs; Toccalino and others, 2007). About one-half of the detected compounds do not have human-health benchmarks or adequate toxicity information for evaluating results in a human-health context. Human-health benchmarks are developed for individual compounds and not mixtures. The screening-level assessment provides an initial perspective on the potential importance of “man-made” organic compounds in source water; it is not a substitute for a comprehensive risk assessment, which includes many more factors, such as additional avenues of exposure.

in finished water by community water systems, those occurring in 20 percent or more of source-water samples and with concentrations within a factor of 10 of their MCL may warrant their consideration in low-concentration trends monitoring to better understand their transport and fate within the watershed. Human-health benchmarks are not available for the remaining five compounds that were detected most commonly at concentrations greater than 0.1 microgram per liter (table 2).

An important consideration in assessing potential effects for human health is the common occurrence of mixtures of organic compounds in source- and finished-water samples. For example, the median number of compounds in

**Table 2.** Only 10 compounds that were commonly detected in source and (or) finished water had concentrations greater than 0.1 microgram per liter. None of these concentrations exceeded a human-health benchmark; however, benchmarks are only available for 5 of the 10 compounds included in this table.

[µg/L, microgram per liter; MCL, Maximum Contaminant Level; HBSL, Health-Based Screening Level; ESA, ethane sulfonic acid; OA, oxanilic acid; MTBE, methyl *tert*-butyl ether; --, no data; E, estimated; ND, not detected]

Name of compound	Number of samples		Percent occurrence <sup>1</sup>		Reporting level <sup>2</sup> (µg/L)	MCL or HBSL <sup>3</sup> (µg/L)	Maximum concentration (µg/L)	
	Source water	Finished water	Source water	Finished water			Source water	Finished water
<b>Herbicides and herbicide degradates<sup>4</sup></b>								
Atrazine	25	13	28	23	0.007	<b>3</b>	1.750	0.258
<i>Metolachlor ESA</i>	20	10	90	90	.05	--	.770	1.860
<i>Metolachlor OA</i>	20	10	20	20	.05	--	.160	.220
<b>Gasoline hydrocarbons and oxygenates</b>								
MTBE	25	13	48	54	0.17	--	0.850	0.363
<b>Solvents</b>								
Carbon tetrachloride	25	13	0	31	0.06	<b>5</b>	ND	0.158
<b>Disinfection by-products</b>								
Chloroform	25	13	4	100	0.24	<b>80 total THMs<sup>5</sup></b>	0.130	40.55
Bromodichloromethane	25	13	0	100	.048		ND	12.00
Dibromochloromethane	25	13	0	100	.18		ND	1.88
<b>Plant- or animal-derived biochemicals</b>								
Cholesterol	25	13	24	8	2	--	E1.20	E0.47
3- <i>beta</i> -Coprostanol	25	13	20	8	2	--	E1.0	E.25

<sup>1</sup> Percent occurrence of samples with concentrations equal to or greater than 0.1 µg/L; estimated concentrations are used for compounds that have reporting level greater than 0.1 µg/L.

<sup>2</sup> Reporting level shown is higher value of either source or finished water.

<sup>3</sup> MCL values are shown in **bold**.

<sup>4</sup> Herbicide degradates are shown in *italics*.

<sup>5</sup> MCL of 80 is for total THMs (trihalomethanes), including chloroform, bromoform, bromodichloromethane, and dibromochloromethane.

source-water samples at the Potomac River was 17. This is comparable to findings from eight additional community water systems sampled by the USGS (Kingsbury and others, 2008). The potential human-health effects of mixtures of co-occurring organic compounds are largely unknown and have not been extensively studied. The effect of one compound on another's toxicity may be additive, antagonistic, or synergistic. With a few exceptions for pesticides with common modes of action, human-health benchmarks generally are not available for specific mixtures. Continued research is needed because MCLs and other human-health benchmarks generally are based on toxicity data for individual compounds, and the effects of specific mixtures of compounds at low levels are not well understood (Gilliom and others, 2006).

### Potomac River Findings in a National Context and Possible Implications

Overall, the compounds detected most commonly in water from the Potomac River (tables 1 and 2) are among those most commonly detected in ambient stream water and ground water across the Nation (Gilliom

and others, 2006; Zogorski and others, 2006). In addition, the occurrence and concentrations of compounds in source and finished water sampled from the Potomac River were similar to those detected at other community water systems sampled as part of an ongoing national NAWQA investigation of rivers, many of which have upstream wastewater facilities and that drain considerable agricultural and urban land (Kingsbury and others, 2008). Findings in a national context, however, are considered preliminary because some compounds

included in this study have only recently been monitored systematically in source and finished water, including, for example, plant- or animal-derived biochemicals (such as cholesterol and 3-*beta*-coprostanol) and those used for personal care, such as acetyl hexamethyl tetrahydronaphthalene (AHTN) and hexahydrohexamethylcyclopentabenzopyran (HHCB). Continued research is needed to better understand sources, transport mechanisms, trends, fate in the environment, and possible linkages of these compounds to human health.

### Source Water-Quality Assessments by the NAWQA Program Conducted Across the Nation

Beginning in 2002, NAWQA initiated "Source Water-Quality Assessments" (SWQAs) at selected community water systems across the United States (Delzer and Hamilton, 2007). The long-term goal is to complete as many as 30 SWQAs at systems that withdraw water from streams by 2012 using standard protocols and nationally consistent methods (U.S. Geological Survey, 1997–2006).

This fact sheet highlights findings from the Potomac River study, which is one of the first nine community water systems sampled. The fact sheet serves as a companion product to a USGS Data Series Report and a USGS Scientific Investigations Report that present findings for the nine systems across the United States (Carter and others, 2007; Kingsbury and others, 2008). <http://water.usgs.gov/nawqa/swqa>



USGS will continue to collaborate with, and complement the work of other Federal, State, and local organizations, and continue to communicate findings and possible implications and future needs, including, for example:

- ◆ Increased emphasis on watershed management and source-water protection strategies to help minimize the sources and transport of compounds to source water and ultimately to finished water.
- ◆ Continued research to enhance toxicity information for commonly occurring unregulated compounds and mixtures that are commonly detected in source and finished water.
- ◆ Current and future monitoring and assessment to identify compounds not typically monitored in source water but commonly present in finished water, which may ultimately identify or lead to the development of treatment technologies for their removal.

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## USGS promotes public access to water-quality information

This fact sheet, additional data and investigations reports, and other information are available on the World Wide Web at <http://water.usgs.gov/nawqa/swqa>. Included at this Web site are downloadable data on organic compound occurrence, information on sampling designs and methodology, background on data analyses, and frequently asked questions.

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