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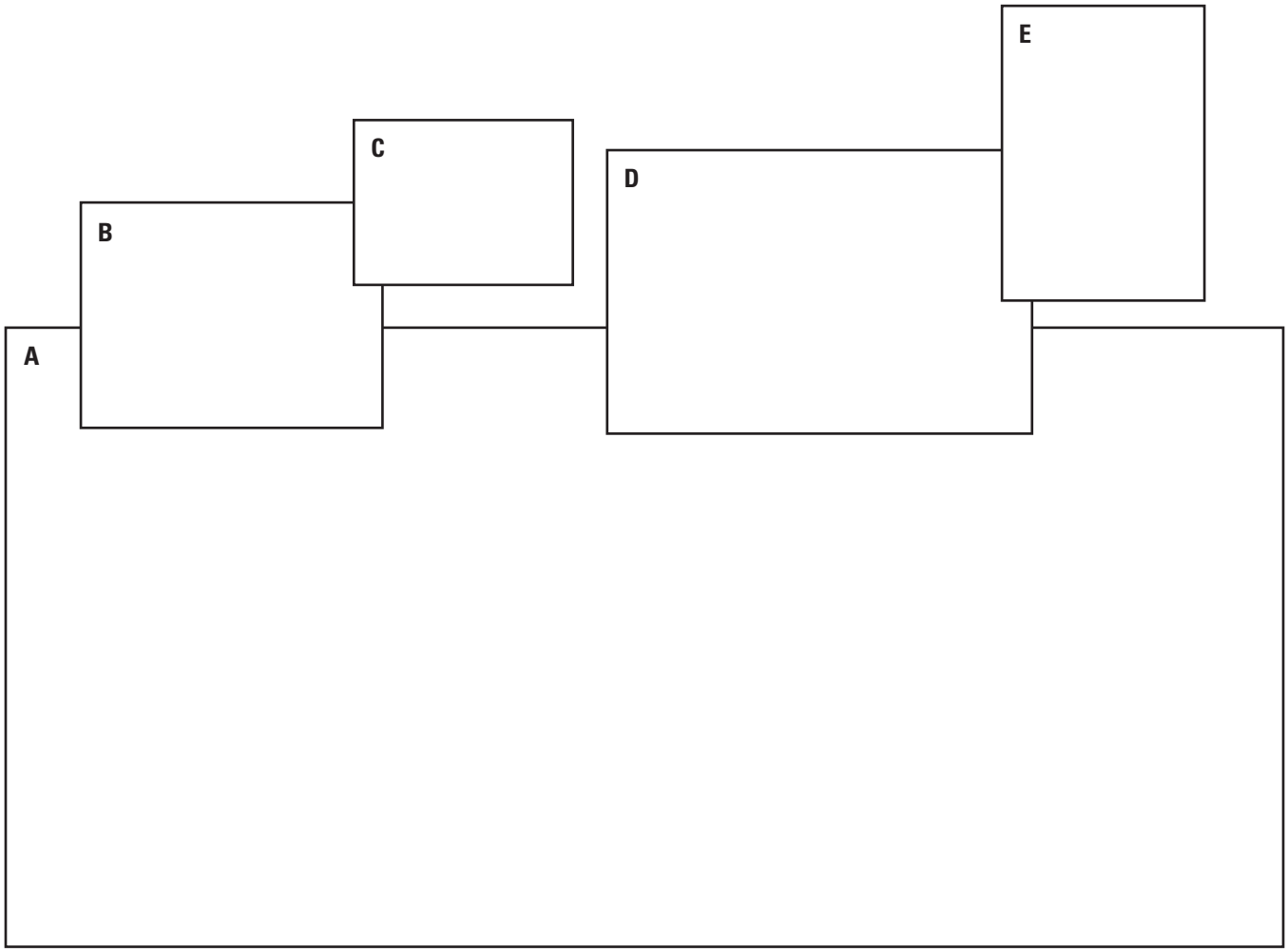
# Occurrence of Volatile Organic Compounds in Selected Urban Streams in the United States, 1995–2003

Scientific Investigations Report 2009–5203

U.S. Department of the Interior
U.S. Geological Survey




**Cover.** A; Aberjona River at Winchester, Mass.
B; Little Neshaminy Creek near Neshaminy, Penn.
C; Great Egg Harbor River near Sicklerville, N.J.
D; Aberjona River at Winchester, Mass.
E; Arcade Creek near Del Paso Heights, Calif.

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By David A. Bender, Gregory C. Delzer, Curtis V. Price, and John S. Zogorski

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**U.S. Department of the Interior**
**U.S. Geological Survey**

**U.S. Department of the Interior**
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# Foreword

The U.S. Geological Survey (USGS) is committed to providing the Nation with credible scientific information that helps to enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (http://www.usgs.gov/). Information on the Nation's water resources is critical to ensuring long-term availability of water that is safe for drinking and recreation and is suitable for industry, irrigation, and fish and wildlife. Population growth and increasing demands for water make the availability of that water, now measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, State, and local information needs and decisions related to water-quality management and policy (http://water.usgs.gov/nawqa). The NAWQA Program is designed to answer: What is the condition of our Nation's streams and groundwater? How are conditions changing over time? How do natural features and human activities affect the quality of streams and groundwater, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. From 1991–2001, the NAWQA Program completed interdisciplinary assessments and established a baseline understanding of water-quality conditions in 51 of the Nation's river basins and aquifers, referred to as Study Units (http://water.usgs.gov/nawqa/studyu.html).

Multiple national and regional assessments are ongoing in the second decade (2001–2012) of the NAWQA Program as 42 of the 51 Study Units are reassessed. These assessments extend the findings in the Study Units by determining status and trends at sites that have been consistently monitored for more than a decade, and filling critical gaps in characterizing the quality of surface water and groundwater. For example, increased emphasis has been placed on assessing the quality of source water and finished water associated with many of the Nation's largest community water systems. During the second decade, NAWQA is addressing five national priority topics that build an understanding of how natural features and human activities affect water quality, and establish links between sources of contaminants, the transport of those contaminants through the hydrologic system, and the potential effects of contaminants on humans and aquatic ecosystems. Included are topics on the fate of agricultural chemicals, effects of urbanization on stream ecosystems, bioaccumulation of mercury in stream ecosystems, effects of nutrient enrichment on aquatic ecosystems, and transport of contaminants to public-supply wells. These topical studies are conducted in those Study Units most affected by these issues; they comprise a set of multi-Study-Unit designs for systematic national assessment. In addition, national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, selected trace elements, and aquatic ecology are continuing.

The USGS aims to disseminate credible, timely, and relevant science information to address practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, regional, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

Matthew C. Larsen
Associate Director for Water

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## Conversion Factors and Datums

| Multiply | By | To obtain |
|---|---|---|
| | Area | |
| square mile ($mi^2$) | 259.0 | hectare (ha) |
| square mile ($mi^2$) | 2.590 | square kilometer ($km^2$) |
| | Volume | |
| ounce, fluid (fl. oz) | 0.02957 | liter (L) |
| pint (pt) | 0.4732 | liter (L) |
| quart (qt) | 0.9464 | liter (L) |
| gallon (gal) | 3.785 | liter (L) |
| | Flow rate | |
| cubic foot per second ($ft^3/s$) | 0.02832 | cubic meter per second ($m^3/s$) |

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8\times°C)+32$$

Horizontal coordinate information is referenced to North American Datum of 1983 (NAD 83)

Concentrations of chemical constituents in water are given in micrograms per liter (µg/L).

## Study Unit Abbreviations, Other Abbreviations, and Symbols

| | |
|---|---|
| ACAD | Acadian-Pontchartrain Drainages |
| ACFB | Apalachicola-Chattahoochee-Flint River Basins |
| ALBE | Albemarle-Pamlico Drainage Basins |
| ALMN | Allegheny-Monongahela River Basins |
| CAZB | Central Arizona Basins |
| CCPT | Central Columbia Plateau |
| CNBR | Central Nebraska Basins |
| CONN | Connecticut, Housatonic, and Thames River Basins |
| COOK | Cook Inlet Basin |
| DELR | Delaware River Basin |
| DLMV | Delmarva Peninsula |
| EIWA | Eastern Iowa Basins |
| GAFL | Georgia-Florida Coastal Plain |
| GRSL | Great Salt Lake Basins |
| HDSN | Hudson River Basin |
| HPGW | High Plains Regional Groundwater Study |
| KANA | Kanawha-New River Basins |
| LERI | Lake Erie-Lake St. Clair Drainages |

| | |
|---|---|
| LINJ | Long Island-New Jersey Coastal Drainages |
| LIRB | Lower Illinois River Basin |
| LSUS | Lower Susquehanna River Basin |
| LTEN | Lower Tennessee River Basin |
| MIAM | Great and Little Miami River Basins |
| MISE | Mississippi Embayment |
| MOBL | Mobile River Basin |
| NECB | New England Coastal Basins |
| NROK | Northern Rockies Intermontane Basins |
| NVBR | Nevada Basin and Range |
| OAHU | Oahu |
| OZRK | Ozark Plateaus |
| PUGT | Puget Sound Basin |
| REDN | Red River of the North Basin |
| RIOG | Rio Grande Valley |
| SACR | Sacramento River Basin |
| SANA | Santa Ana Basin |
| SANJ | San Joaquin-Tulare Basins |
| SANT | Santee River Basin and Coastal Drainages |
| SCTX | South-Central Texas |
| SOCA | Southern California Basins |
| SOFL | Southern Florida Drainages |
| SPLT | South Platte River Basin |
| TRIN | Trinity River Basin |
| UCOL | Upper Colorado River Basin |
| UIRB | Upper Illinois River Basin |
| UMIS | Upper Mississippi River Basin |
| USNK | Upper Snake River Basin |
| UTEN | Upper Tennessee River Basin |
| WHMI | White, Great and Little Miami River Basins |
| WILL | Willamette Basin |
| WMIC | Western Lake Michigan Drainages |
| YELL | Yellowstone River Basin |
| $\alpha$ | significance level for statistical tests |

| | |
|---|---|
| $\chi^2$ | chi-squared statistic |
| µg/L | microgram per liter |
| °C | degrees Celsius |
| < | less than |
| ≤ | less than or equal to |
| > | greater than |
| ≥ | greater than or equal to |
| BTEX | benzene, toluene, ethylbenzene, and xylenes |
| CAA | Clean Air Act |
| CDF | cumulative distribution function |
| CWA | Clean Water Act |
| CWS | community water system |
| CWSS | Community Water Supply Survey |
| DF | degrees of freedom |
| DIPE | diisopropyl ether |
| DWA | Drinking Water Advisory |
| DWB | drinking-water benchmark |
| ETBE | ethyl *tert*-butyl ether |
| GC/MS | gas chromatography/mass spectrometry |
| HBSL | Health-Based Screening Level |
| $LT_{Q,est_i}$ | estimated long-term streamflow for a short-term record site for percentile *i* |
| $LT_{Q,conc_i}$ | streamflow for long-term station for each percentile, *i*, of interest for the concurrent period of record |
| $LT_{Q,record_i}$ | streamflow for each corresponding percentile for the entire period of record for the long-term station for percentile *i* |
| LT–MDL | long-term method detection level |
| MCL | Maximum Contaminant Level |
| MSA | metropolitan statistical area |
| MS4 | municipal separate storm sewer system |
| MTBE | methyl *tert*-butyl ether |
| NAWQA | U.S. Geological Survey National Water-Quality Assessment |
| NOMS | U.S. Environmental Protection Agency National Organics Monitoring Survey |
| NORS | U.S. Environmental Protection Agency National Organics Reconnaissance Survey |
| NPDES | U.S. Environmental Protection Agency National Pollutant Discharge Elimination System |
| NURP | U.S. Environmental Protection Agency National Urban Runoff Program |

| | |
|---|---|
| NWQL | U.S. Geological Survey National Water Quality Laboratory |
| ODS | Organics Detection System |
| ORSANCO | Ohio River Valley Water Sanitation Commission |
| p-value | probability value |
| QA/QC | quality assurance/quality control |
| SDWA | Safe Drinking Water Act |
| $ST_{Q,conc_i}$ | streamflow for short-term record site for each percentile, *i*, of interest for the concurrent period of record |
| TAME | *tert*-amyl methyl ether |
| THM | trihalomethane |
| TTHMs | total trihalomethanes |
| USEPA | U.S. Environmental Protection Agency |
| USGS | U.S. Geological Survey |
| VOC | volatile organic compound |
| $Z$ | Wilcoxon sign-rank and rank-sum test statistics |

# Occurrence of Volatile Organic Compounds in Selected Urban Streams in the United States, 1995–2003

By David A. Bender, Gregory C. Delzer, Curtis V. Price, and John S. Zogorski

## Abstract

As part of the U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program, urban indicator sites were monitored to (1) characterize the stream quality from drainage basins with predominantly residential and commercial land use, and (2) determine which selected natural and anthropogenic factors affect stream quality. A total of 869 water samples were collected from 37 urban streams during 1995–2003 and were analyzed for 87 volatile organic compounds (VOCs). The occurrence of VOCs in urban streams is described in this report for (1) all samples as a single dataset, (2) all samples grouped by streamflow pentiles, and (3) all samples grouped by warmer (April through September) and cooler (October through March) months by the detection frequency and (or) concentration of (a) any VOC, (b) VOC groups, and (c) individual compounds. An assessment level of 0.02 microgram per liter (µg/L) was used to compute the detection frequencies and concentrations of VOCs. Concentrations of VOCs were compared to (1) U.S. Environmental Protection Agency's (USEPA) drinking-water Maximum Contaminant Levels (MCLs) or Drinking Water Advisories, (2) Health-Based Screening Levels (HBSLs) developed by the USGS in collaboration with the USEPA and other agencies, and (3) USEPA and Canadian aquatic-life criteria.

One or more VOCs were detected in 97.1 percent of 869 samples, and one or more VOCs were detected frequently (greater than 80 percent) at all sites. The median total VOC concentration for all samples was 0.57 µg/L, and total VOC concentrations in a single sample ranged from not detected to 698 µg/L. About 85 percent of the samples contained two or more VOCs, and about one-half contained five or more VOCs. The gasoline hydrocarbons were the most frequently occurring VOC group followed by solvents, trihalomethanes (THMs), gasoline oxygenates, organic synthesis compounds, fumigants, and refrigerants. Concentration ranges for most VOC groups were distributed over at least two orders of magnitude. Fifty-seven of the 87 VOCs analyzed were detected in at least one sample at an assessment level of 0.02 µg/L. More than one-half of the 30 VOCs not detected in samples were organic synthesis compounds. Fifteen compounds had detection frequencies greater than or equal to 10 percent. With the exception of toluene and chloroform, the median concentration of each VOC for all samples was less than the assessment level. Furthermore, the median concentrations of detections for the 15 most frequently occurring VOCs ranged from 0.03 to 3.9 µg/L, and typically were less than or equal to 0.10 µg/L.

The 869 samples from the 37 sites were stratified into five streamflow pentiles (less than 20, 20–less than 40, 40–less than 60, 60–less than 80, and greater than or equal to 80 percent of estimated long-term streamflow statistics) for comparison of the occurrence of VOCs. The detection frequency of one or more VOCs by streamflow pentile varied only slightly from 96.7 to 97.7 percent. The median total VOC concentrations in samples for the five streamflow pentiles ranged from 0.39 to 1.0 µg/L. Two or more VOCs were present in more than 80 percent of samples in each of the five pentiles. The gasoline hydrocarbons, solvents, THMs, and gasoline oxygenates occurred frequently (greater than 30 percent) in all streamflow pentiles, in contrast to the organic synthesis compounds, fumigants, and refrigerants that occurred less frequently in urban streams under all streamflow conditions. The median total VOC concentrations for gasoline hydrocarbons, solvents, gasoline oxygenates, and organic synthesis compounds generally increased as streamflow increased. In contrast, the median total VOC concentrations for THMs and fumigants generally decreased as streamflow increased. The median total VOC concentrations for refrigerants showed no pattern as streamflow increased.

Because differences between VOC occurrence and streamflow pentiles were small for most comparisons, the overall patterns of occurrence for VOCs in urban streams were stratified by warmer (April through September) and cooler (October through March) months. One or more VOCs were detected frequently in both warmer (96 percent of 410 samples) and cooler months (98 percent of 459 samples). However, median concentrations of detections were about twice as large in cooler months (0.80 µg/L) than in warmer months (0.41 µg/L). The median number of VOCs reported in samples in warmer and cooler months was 4 and 5, respectively. In general, the detection frequency of most VOC groups was similar or larger in cooler months than in warmer months.

None of the samples had concentrations greater than or equal to an MCL or HBSL. However, six compounds (trichloroethene, perchloroethene, *cis*-1,2-dichloroethene,

dichloromethane, vinyl chloride, and dibromochloropropane) had concentrations less than but within 10 percent of an MCL. Three compounds (acetone, 1,1,2,2-tetrachloroethane, and acrolien) had concentrations less than but within 10 percent of an HBSL. Concentrations of methyl *tert*-butyl ether in 59 samples were less than but within 10 percent of the lower limit of the USEPA Taste and Odor Drinking Water Advisory of 20 µg/L, and concentrations in 5 samples were greater than or equal to this lower limit. Toluene and chloroform had concentrations greater than the aquatic-life criteria. Five additional compounds (trichloroethene, chlorobenzene, naphthalene, acrolien, and 1,2-dichlorobenzene) had concentrations less than but within 10 percent of the aquatic-life criteria.

# Introduction

The U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program was implemented in 1991. The primary goals of the NAWQA Program are to describe the status and trends of the water quality of the Nation's water resources and to identify natural and anthropogenic factors affecting the water quality. The NAWQA Program consists of Study Units that include parts of most of the Nation's major river basins (fig. 1) and aquifer systems. Most of the NAWQA Program's efforts to collect water-quality data are focused in the Study Units. Collectively, the Study Units include a large percentage of the Nation's population and water use.

Gilliom and others (1995) described the overall design of the NAWQA Program in detail. The NAWQA Program's surface-water design includes monitoring the water quality of streams at (1) indicator sites that drain relatively homogenous land-use and physiographic conditions, (2) integrator sites that drain mixed land use (usually larger river systems), and (3) reference sites that are relatively unaffected by human influences. Streams are monitored for streamflow, specific conductance, water temperature, and chemical and biological constituents (Lopes and Price, 1997). Urban and agricultural land uses are the two main land uses being investigated in the NAWQA Program. The primary objectives of monitoring at the urban indicator sites are to (1) characterize the stream quality from drainage basins with predominantly residential and commercial land use, and (2) determine which selected natural and anthropogenic factors affect stream quality. Lopes and Price (1997) provided guidance on the distribution of urban indicator sites, site selection criteria, chemical and biological sampling, and the basic ancillary data needed to identify factors affecting stream quality to foster consistency among the Study Units.

Most studies on urban streams in the last few decades were completed to characterize the quality of runoff including (1) U.S. Environmental Protection Agency's (USEPA's) National Urban Runoff Program (NURP), and (2) the National Pollutant Discharge Elimination System (NPDES) permitting process for cities with populations greater than 100,000 and for some smaller cities within urban areas. The NURP and NPDES studies sampled only stormwater. In contrast, multiple sampling events in the NAWQA Program focused on the ambient quality of selected urban streams that have perennial flow.

The NAWQA Program began collecting samples for analyses of volatile organic compounds (VOCs) at urban indicator (urban stream) sites and selected integrator (large river) sites in 1995 (in Study Units that started in 1994) and continued in studies with Study Units that started in 1997 and 2001. The urban streams were selected to meet certain criteria to assure consistency in chemical data for regional and national comparisons, and to address the goals of the ecology component of the NAWQA Program. Samples collected from a total of 37 urban indicator sites on urban streams were analyzed for 87 VOCs (fig. 1).

VOCs are of concern because of their releases to the environment resulting from large-scale and widespread use in industry, commerce, and everyday products, and because of their human toxicity and persistence in the environment for some compounds. Federal regulation of VOCs to protect public health and welfare began in the 1970s with the passage of the Clean Air Act (CAA), Clean Water Act (CWA), Safe Drinking Water Act (SDWA), and Resource Conservation and Recovery Act (Zogorski and others, 2006).

## Purpose and Scope

The purpose of the report is to describe the occurrence of 87 VOCs in 37 urban streams in 31 Study Units that were sampled in the United States between 1995 and 2003 as part of the NAWQA Program. The occurrence of VOCs is characterized nationally by the detection frequency, concentrations, spatial distribution, streamflow pentiles, seasonal distribution, and the number of compounds in samples. VOC concentrations are compared to drinking-water benchmarks and aquatic-life criteria to describe the significance of VOC occurrence in urban streams to human health and aquatic life.

A total of 869 water samples collected from 37 urban streams were analyzed for VOCs using a low-level, "information rich" analytical method (Connor and others, 1998) at the USGS's National Water Quality Laboratory (NWQL). The occurrence of VOCs is described for (1) all samples as a single dataset, (2) all samples grouped by streamflow pentiles, and (3) all samples grouped by warmer (April through September) and cooler (October through March) months. The first approach provides a general national-scale perspective on the occurrence of VOCs. The second approach examines the similarities or differences in VOC occurrence on the basis of streamflow condition, and the third approach examines the similarities or differences on the basis of warmer and cooler months.

The occurrence of VOCs is characterized by the detection frequency and (or) concentration of (1) any VOC (that is,

**Figure 1.** Location of urban stream sites that were sampled for this study, U.S. Geological Survey National Water-Quality Assessment Program Study Units, and the major river basin in which the site is located.

detection of one or more compounds in a sample), (2) VOC groups (that is, gasoline hydrocarbons, solvents, trihalomethanes (THMs), gasoline oxygenates, organic synthesis compounds, fumigants, and refrigerants), and (3) individual VOCs. VOC concentrations are compared to (1) USEPA's drinking-water Maximum Contaminant Levels (MCLs) or Drinking Water Advisories (DWAs), (2) Health-Based Screening Levels (HBSLs) developed by the USGS in collaboration with the USEPA, the New Jersey Department of Environmental Protection, and the Oregon Health & Science University, and (3) aquatic-life criteria.

## Previous Investigations

Many water-quality studies for rivers and streams, to date, have focused on large drinking-water sources, stormwater quality for permitting purposes (for example, NPDES permits), and other contamination issues within a specific drainage basin. In addition, some studies in urban rivers and streams have been undertaken to identify specific sources of water-quality degradation. Summaries of selected studies with emphasis on findings for surface waters are included in this section.

The USEPA has been active in characterizing VOCs in drinking water supplies since the 1970s with the passage of the SDWA in 1974. Westrick (1990) described and presented some of the results for each of the following surveys: (1) the National Organics Reconnaissance Survey (NORS), (2) the National Organics Monitoring Survey (NOMS), and (3) the Community Water Supply Survey (CWSS).

The NORS sampling was one of the earliest data gathering efforts (January–April 1975) for the SDWA and emphasized THMs and two other VOCs (1,2-dichloroethane and carbon tetrachloride). The NORS sampling, in early 1975, included 80 water supplies, of which 64 were surface-water supplies. Minimum quantifiable concentrations for NORS sampling ranged from 0.2 to 0.4 microgram per liter (µg/L) for 1,2-dichloroethane and from 1 to 2 µg/L for carbon tetrachloride.

The NOMS sampling focused on vulnerable water-supply systems and supplies with selected THM data. The NOMS sampling included 113 water systems, of which 92 were surface-water systems, in three phases. Phase I had fairly high minimum quantitation limits, and the analytical methodology was not well documented; therefore, the results were not discussed by Westrick (1990). Samples from Phase II were analyzed for nine VOCs, with minimum reporting levels ranging from 0.005 to 0.2 µg/L. The most frequently occurring VOCs in surface water sampled during Phase II were trichloroethene (22 of 92 samples), carbon tetrachloride (10 of 89 samples), 1,4-dichlorobenzene (6 of 92 samples), and benzene (5 of 92 samples). Samples from Phase III were analyzed for 10 VOCs, with minimum reporting levels ranging from 0.005 to 0.4 µg/L. In Phase III, the most frequently occurring VOCs in surface water were trichloroethene (17 of 88 samples), carbon tetrachloride (11 of 88 samples), 1,4-dichlorobenzene (27 of 89 samples), and trichlorobenzene (10 of 89 samples).

The CWSS sampling began in 1976 to characterize the drinking water supplied by community water supply systems with respect to contaminants in the National Interim Primary Drinking Water Regulations. A secondary objective of the CWSS sampling was to obtain additional data on THMs and synthetic VOCs in community water systems (CWSs). The CWSS sampling included 436 CWSs, of which 106 were surface-water systems. Samples for the CWSS were analyzed for 14 VOCs with a minimum reporting level for all VOCs of 0.5 µg/L. The most frequently detected VOCs in the 106 surface-water systems were xylenes (7 of 100 samples), toluene (3 of 100 samples), carbon tetrachloride (3 of 106 samples), perchloroethene (3 of 106 samples), and 1,1,1-trichloroethane (3 of 106 samples).

In 1978, the Ohio River Valley Water Sanitation Commission (ORSANCO) implemented the Organics Detection System (ODS) to monitor VOCs and other contaminants from accidents and spills and to identify exceedances of drinking-water regulations (Lundgren and Lopes, 1999). The NAWQA Program conducted a retrospective analysis of data from ORSANCO's ODS for 1987–96 to assess VOCs in the Ohio River and its major tributaries that are used by public water suppliers (Lundgren and Lopes, 1999). Briefly, the NAWQA analysis included 15 ORSANCO monitoring sites and 21 VOCs regulated in drinking water at an assessment level of 0.05 µg/L. The five most frequently detected VOCs were chloroform (26 percent), benzene (11 percent), toluene (6.4 percent), dichloromethane (3.9 percent), and 1,3-dichlorobenzene (3.4 percent). All 21 VOCs were detected in one or more samples. Most of the 21 VOCs had similar or larger detection frequencies in cooler months (October through March) than in warmer months (April through September) with the exceptions of chloroform, dichloromethane, 1,4-dichlorobenzene, chlorobenzene, and 1,1,1-trichloroethane. Fourteen VOCs had downward trends during 1987–96 in monthly mean concentrations and nine VOCs had significant downward trends in percentage detection.

Achten, Kolb, and Püttmann (2002) and Achten, Kolb, Püttmann, and others (2002) provided an overview of methyl *tert*-butyl ether (MTBE) in rivers and wastewater in Germany. The method detection limit for these studies was 0.01 µg/L. MTBE concentrations in the lower parts of the Rhine and Main Rivers ranged from 0.23 to 0.3 µg/L and 0.08 to 0.21 µg/L, respectively. They also measured MTBE in small urban streams with and without large industrial inputs. Concentrations were larger in the urban streams with industrial input (0.15 to 0.30 µg/L) than in urban streams without industrial inputs (0.025 to 0.10 µg/L). MTBE concentrations were slightly greater than the method detection limit in rural streams. MTBE concentrations in rivers also were correlated with increased measured concentrations of MTBE in precipitation. Wastewater samples from two sewage plants showed MTBE concentrations of about 0.10 to 0.30 µg/L. Riverbank

water also was sampled from the Lower Rhine and Lower Main Rivers with average concentrations of about 0.08 µg/L in the Lower Rhine riverbank waters and concentrations ranging from 0.052 to 0.25 µg/L in the Lower Main riverbank waters.

The occurrence of 41 VOCs in surface waters and treated wastewater in Greece was investigated by Nikolaou and others (2002). The method detection limit for compounds in this study ranged from 0.01 to 0.25 µg/L. Samples were collected from 10 rivers, 7 lakes, 3 gulfs, and 4 wastewater treatment plants from October 1998 to September 1999. Sixteen individual VOCs were detected in surface waters: chloroform, trichloroethene, perchloroethene, carbon tetrachloride, hexachlorobutadiene, 1,2,4-trichlorobenzene, 1,1,2-trichloroethane, toluene, 2-chlorotoluene, 4-chlorotoluene, 1,3,5-trimethylbenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,-dichlorobenzene, naphthalene, and 1,2,3-trichlorobenzene.

Yamamoto and others (1997) monitored 30 sites within urban rivers and estuaries of Osaka, Japan, to determine the concentrations and distribution of 55 VOCs. The method detection limits for VOCs in this study ranged from 0.05 to 0.98 µg/L. Forty VOCs were detected, and 30 VOCs were detected in 5 percent or more of the samples. Solvents were the most ubiquitous of the VOCs detected in samples. All the rivers and estuaries sampled contained dichloromethane and chloroform. Four VOC occurrence patterns were noted by Yamamoto and others (1997): (1) the most common VOCs showed maximum concentration fluctuations due to irregular spills and loadings; (2) one VOC (*cis*-1,2-dichloroethene) showed a stable concentration distribution due to fixed loading; (3) some VOCs were specific to an industrial site; and (4) some VOCs had uniform concentration profiles and entered the rivers from multiple sources. Diurnal variations of some VOCs also were noted.

Grady (2003) and Delzer and Ivahnenko (2003) provided results from a national survey of MTBE in drinking-water sources for a random survey and a focused survey, respectively. The random and focused surveys were designed to provide information on the occurrence and distribution of MTBE and 65 other VOCs in untreated groundwater and surface-water sources of drinking water used by CWSs in the United States at a common assessment level of 0.2 µg/L. The random survey included 954 drinking-water sources, of which 171 rivers, streams, aqueducts, or canals were sampled. The focused survey sampled 20 rivers and (or) streams used as a source water by CWSs that were known or suspected to be contaminated by MTBE. The random and focused studies showed that VOCs frequently occur in rivers and streams used as source waters. THMs were the most frequently occurring VOC group in the random survey in river and (or) stream waters followed by MTBE, gasoline hydrocarbons, solvents, organic synthesis compounds, and fumigants.

The USEPA NURP program was designed to provide information to determine whether urban runoff was causing water-quality problems and to provide an information base for policy decisions for urban stormwater runoff and control (U.S. Environmental Protection Agency, 1982, 1983a, 1983b). For the NURP program, 121 urban runoff samples from 28 locations in the United States were analyzed for priority pollutants. The most frequently detected VOCs were dichloromethane (11 percent), chloroform (9 percent), naphthalene (9 percent), trichloroethene (6 percent), 1,1,1-trichloroethane (6 percent), and ethylbenzene (6 percent).

The primary objective of the CWA is to restore and maintain the chemical, physical, and biological integrity of the Nation's waters (U.S. Environmental Protection Agency, 2000a). To achieve the objective and goals of the CWA, a variety of programs to control the discharge of pollutants to receiving waters were established by the USEPA. Section 402 of the CWA established the NPDES permit program to specifically control the discharge of pollutants from point-source dischargers. The NPDES program covers animal feeding operations, combined sewer overflows, industrial and commercial facilities, municipalities and wastewater treatment plants, sanitary sewer overflows, and stormwater. The NPDES stormwater permit program has two phases. Phase I of the stormwater permit program requires NPDES permits from two broad categories of stormwater discharges: (1) municipal separate storm sewer systems (MS4s) serving populations of 100,000 or more and (2) discharges associated with industrial activity. The Phase II regulations address discharges from smaller municipalities with populations of 50,000 or more (U.S. Environmental Protection Agency, 1999a). The rule also allows municipalities covered in Phase I that are automatically designated because they are within a larger urbanized area to obtain a waiver from the otherwise applicable requirements if the discharges from small municipalities are not causing impairment of a receiving water body. Delzer and others (1996) provided a summary of the occurrence of select VOCs in urban stormwater in the United States during 1991–95 for NPDES studies completed by the USGS in 16 cities. The 10 most frequently detected VOCs at an assessment level of 0.2 µg/L were toluene, xylenes, chloroform, trimethylbenzenes, perchloroethene, naphthalene, MTBE, dichloromethane, bromodichloromethane, and ethylbenzene. The median concentrations for individual VOCs were less than 1 µg/L, with the exception of MTBE (1.5 µg/L).

Lopes and Dionne (1998) provided a summary of VOCs in highway runoff and urban stormwater. Briefly, VOCs were present in highway runoff and urban stormwater with larger concentrations from industrial areas and during winter months than in nonindustrial areas and during summer months. This indicates that urban land surfaces may be the primary nonpoint source of most VOCs. Temperature also may be an important factor in the occurrence of VOCs in surface waters with more VOCs present at lower temperatures than at higher temperatures. Lopes and Dionne (1998) also reported that VOCs were present in precipitation and snowmelt.

Many of the NAWQA Study Units that collected VOC samples at urban indicator sites provided summaries: Cook Inlet Basin (COOK; Glass and others, 2004); Delaware River Basin (DELR; Fischer and others, 2004); Great Salt Lake Basins (GRSL; Thiros, 2000; Waddell and others, 2004);

Long Island-New Jersey Coastal Drainages (LINJ; O'Brien and others, 1997; Terracciano and O'Brien, 1997; Reiser and O'Brien, 1998; Ayers and others, 2000); Great and Little Miami River Basins (MIAM; Rowe and others, 2004); New England Coastal Basins (NECB; Campo and others, 2003; Robinson and others, 2004); Northern Rockies Intermontane Basins (NROK; Clark and others, 2004); Oahu (OAHU; Anthony and others, 2004); Santa Ana River Basin (SANA; Belitz and others, 2004); South-Central Texas (SCTX; Ging and others, 1997; Ging, 1999; Bush and others, 2000); Upper Illinois River Basin (UIRB; Fitzpatrick and Colman, 1992; Groschen and others, 2001); and Upper Mississippi River Basin (UMIS; Andrews and others, 1995; Stark and others, 2001).

### Potential Sources of Volatile Organic Compounds in Urban Streams

Urban environments provide many potential sources of VOCs to surface waters. Some VOCs found in urban streams and rivers may be associated with their use in gasoline and other petroleum products, or as industrial solvents, carriers, and solvents in pesticides and paints (U.S. Environmental Protection Agency, 1999b). Other VOCs may be associated with their use as metal degreasers, industrial solvents, dry-cleaning agents, paint and ink formulations, synthetic polymers, and plastic wrap, and are usually associated with groundwater (U.S. Environmental Protection Agency, 1999b, 2000b). Some VOCs also may be formed in chlorinated drinking water by the reaction of free chlorine with organic matter (Ivahnenko and Zogorski, 2006). Some VOCs reported in urban streams have the potential to originate from the atmosphere (Pankow and others, 1997; Lopes and Bender, 1998; Lopes and others, 2000; Bender and others, 2000; Scott J. Kenner, U.S. Geological Survey, oral commun., 2006) and runoff from parking lots (Lopes and others, 2000). Many organic compounds may be scavenged from the atmosphere by precipitation (Kawamura and Kaplan, 1983; Ligocki and others, 1985; Knap and others, 1988; Dewulf and Langenove, 1999; Lopes and others, 2000). Surface waters are vulnerable to many contaminants from one or more sources in the upstream watershed (for example, point-source discharges and stormwater) but also have a potential to reduce the occurrence and concentrations of contaminants through dilution and outgassing to the atmosphere.

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## Study Approach

This section provides an overview of the approach for this study. Site selection, field methods, analytical method, selection of the VOC data for analyses, quality assurance/quality control, assessment level, statistical methods, and the extension of the streamflow record are described.

### Site Selection

As noted previously, urban indicator sites were selected to meet certain criteria and assure consistency in data for regional and national comparisons. The urban indicator sites were selected in residential and commercial land uses and ideally were integrated with other NAWQA study components for a more comprehensive understanding of hydrologic, chemical, and biological processes in urban environments (Lopes and Price, 1997). Ideal settings were drainage areas of 19.3 square miles (50 square kilometers) or larger, with perennial streamflow and well-defined drainage boundaries. Ideally, the sampling reaches were to have riparian and channel conditions representative of the urban setting and have channels suitable for ecological studies. The drainage for the urban indicator sites could contain urban stormwater but not have point sources or large industrial and agricultural land uses because these sources can mask the water-quality signature of the residential/commercial land use (Lopes and Price, 1997). The population density of the drainage basin was to be representative of the residential/commercial areas in the metropolitan statistical area (MSA), and the age of the urban development should be known.

### Field Methods

Water samples and associated field quality-assurance/quality-control (QA/QC) samples were collected following guidelines described in Shelton (1997) and in the USGS National Field Manual (U.S. Geological Survey, variously dated). Briefly, VOC stream samples were collected with the VOC hand sampler at the centroid of the stream or by hand dipping sample vials if the VOC sampler could not be fully submerged in the stream. All VOC samples were preserved with 1:1 hydrochloric acid to a pH of 2, chilled to 4 degrees Celsius (°C), and shipped to the NWQL for analysis. Field quality-control samples included source-solution and field blanks, replicate samples, and field matrix spikes following guidelines described in Shelton (1997) and Mueller and others (1997).

## Analytical Method

The VOC samples from the urban streams were analyzed at the NWQL using the low-level analytical method described in Connor and others (1998). The method analyzes for 87 VOCs (table 1) by purge and trap gas chromatography/mass spectrometry (GC/MS) and tentatively identifies unknowns within the sample. Because *m*- and *p*-xylene co-elute in the method, the reported concentration is counted as one compound in the analyses and results for individual VOCs. The use of GC/MS provides enhanced qualitative compound identification before the determination of the compound's concentration. The reporting by NWQL of low-level concentrations is supported, in part, by the use of laboratory QA/QC samples including, for example, bracketing blanks. The method also uses a long-term method detection level (LT–MDL) that accounts for the long-term variance of multiple instruments, multiple operators, and multiple calibrations for individual compounds over several months in a year (Connor and others, 1998; Childress and others, 1999). The LT–MDL varies for each compound and also can vary with time. The method reports concentrations below the lowest calibration standard as estimated using an "E" remark code (Childress and others, 1999).

## Selection of Volatile Organic Compound Data

The results of the VOC analyses for the urban stream samples were retrieved from the USGS NAWQA data warehouse (*http://water.usgs.gov/nawqa/data*) on March 4, 2004. The selection criteria required that a site be classified as an urban indicator site, have samples collected over a minimum of 6 months, and have a minimum of six samples spread over the sampling period. These selection criteria resulted in 903 samples from 37 urban indicator sites. The 37 sites are listed and described in table 2. Information given for each site includes the major river basin and Study Unit in which the site is located, station name and identification number, drainage area, MTBE-use area, percentage of urban land use in the watershed, sampling period, and estimated streamflow pentiles. MTBE-use areas are classified as low or high, with high MTBE use in areas of the United States where MTBE was present in gasoline at higher levels (greater than or equal to 3 percent by volume in gasoline) during the sampling period (Moran and others, 2004). The Spokane River (site 12424500), with a large drainage area, is included because it was classified as an urban indicator site and because of the rapid urbanization in the lower part of the basin (at and upstream from the urban indicator site).

Some samples for VOC analysis are diluted at the NWQL because of known or suspected large concentrations or sample foaming. When samples are diluted, the reporting levels for the analyses are raised in the same ratio as the sample dilution (for example, a twofold dilution raises the reporting levels by a factor of 2). A review of the dilution ratios for the 903 samples resulted in 869 samples that were not diluted or diluted only twofold (that is, 50–50 dilution; fig. 2). The remaining 34 analyses were removed from further consideration in this report because dilution ratios greater than 2 raise the laboratory reporting levels larger than most reported concentrations for urban streams. Removal of the 34 samples diluted three or more times does not affect the individual VOC occurrence and concentration summaries, with the exception of methyl butyl ketone, which would have had more frequent occurrence and larger concentrations if the 34 samples had been retained in the dataset.

## Quality Assurance/Quality Control

The VOC dataset and field QA/QC samples from the 37 sites were reviewed for systematic contamination before attempting to interpret the environmental data. Characterization of systematic contamination in surface-water samples was based on data from associated source-solution and field-equipment blanks. Systematic contamination is defined as one-directional and typically similar in magnitude. Three guidelines were used to determine systematic contamination: (1) direct evidence of contamination, (2) the contamination is sufficiently understood to allow some interpretation of the environmental data (generally, this requires that the contamination can be shown to be systematic and that the source and magnitude can be identified), and (3) the concentration of the contamination is substantial relative to the environmental concentration.

Source-solution blanks are blanks used to describe the quality of the source of water used for field-equipment blanks and the degree to which the composition of the blank solution could have changed from the time of laboratory certification to the time of use (U.S. Geological Survey, variously dated). Field-equipment blanks are used to determine the concentrations of target analytes that could be present in environmental samples attributable to field procedures for equipment cleaning and sample handling (U.S. Geological Survey, variously dated). Table 3 provides a summary of VOC detections for source-solution and field-equipment blank samples collected as part of the urban stream sampling. Because VOCs were detected in source-solution blanks and the subsequent field-equipment blanks, a study was completed to evaluate carryover contamination of VOCs (Taglioli and others, 2000). The carryover study showed that, even when source-solution water containing VOCs was used to collect field-equipment blanks, VOCs did not carryover to subsequently collected surface-water samples. This was likely due to extensive rinsing with native water prior to sample collection. Concentrations of VOCs detected in field-equipment blanks generally were less than or equal to 0.02 µg/L.

None of the 869 urban stream samples showed systematic contamination and, therefore, no additional samples were removed before analyses and interpretations. The urban stream VOC dataset was not reviewed for random contamination.

**Table 1.** Volatile organic compounds included in the U.S. Geological Survey's National Water-Quality Assessment Program.

[USGS, U.S. Geological Survey; VOC, volatile organic compound; --, not applicable]

| Compound name | Chemical Abstract Service number[1] | USGS parameter code | VOC group | Alternate name or abbreviation |
|---|---|---|---|---|
| Bromomethane | 74–83–9 | 34413 | Fumigant | -- |
| Dibromochloropropane | 96–12–8 | 82625 | Fumigant | DBCP; 1,2-Dibromo-3-chloropropane. |
| 1,4-Dichlorobenzene | 106–46–7 | 34571 | Fumigant | -- |
| 1,2-Dichloropropane | 78–87–5 | 34541 | Fumigant | -- |
| *cis*-1,3-Dichloropropene | 10061–01–5 | 34704 | Fumigant | -- |
| *trans*-1,3-Dichloropropene | 10061–02–6 | 34699 | Fumigant | -- |
| Ethylene dibromide | 106–93–4 | 77651 | Fumigant | EDB; 1,2-Dibromoethane. |
| 1,2,3-Trichloropropane | 96–18–4 | 77443 | Fumigant | -- |
| Benzene | 71–43–2 | 34030 | Gasoline hydrocarbon | -- |
| *n*-Butylbenzene | 104–51–8 | 77342 | Gasoline hydrocarbon | -- |
| *sec*-Butylbenzene | 135–98–8 | 77350 | Gasoline hydrocarbon | -- |
| *tert*-Butylbenzene | 98–06–6 | 77353 | Gasoline hydrocarbon | -- |
| Ethylbenzene | 100–41–4 | 34371 | Gasoline hydrocarbon | -- |
| 2-Ethyltoluene | 611–14–3 | 77220 | Gasoline hydrocarbon | 1-Ethyl-2-methylbenzene. |
| Isopropylbenzene | 98–82–8 | 77223 | Gasoline hydrocarbon | -- |
| 4-Isopropyltoluene | 99–87–6 | 77356 | Gasoline hydrocarbon | -- |
| Naphthalene | 91–20–3 | 34696 | Gasoline hydrocarbon | -- |
| Styrene | 100–42–5 | 77128 | Gasoline hydrocarbon | Ethenylbenzene. |
| Toluene | 108–88–3 | 34010 | Gasoline hydrocarbon | Methylbenzene. |
| 1,2,3-Trimethylbenzene | 526–73–8 | 77221 | Gasoline hydrocarbon | -- |
| 1,2,4-Trimethylbenzene | 95–63–6 | 77222 | Gasoline hydrocarbon | -- |
| 1,3,5-Trimethylbenzene | 108–67–8 | 77226 | Gasoline hydrocarbon | -- |
| 1,2,3,4-Tetramethylbenzene | 488–23–3 | 49999 | Gasoline hydrocarbon | -- |
| 1,2,3,5-Tetramethylbenzene | 527–53–7 | 50000 | Gasoline hydrocarbon | -- |
| *o*-Xylene | 95–47–6 | 77135 | Gasoline hydrocarbon | 1,2-Dimethylbenzene. |
| *m*- and *p*-Xylene | *m:*108–38–3<br>*p:*106–42–3 | 85795 | Gasoline hydrocarbon | 1,3- and 1,4-Dimethylbenzene. |
| *tert*-Amyl methyl ether | 994–05–8 | 50005 | Gasoline oxygenate | TAME. |
| Diisopropyl ether | 108–20–3 | 81577 | Gasoline oxygenate | DIPE. |
| Ethyl *tert*-butyl ether | 637–92–3 | 50004 | Gasoline oxygenate | ETBE. |
| Methyl *tert*-butyl ether | 1634–04–4 | 78032 | Gasoline oxygenate | MTBE; 2-Methoxy-2-methyl propane. |
| Acrolien | 107–02–8 | 34210 | Organic synthesis compound | 2-Propenal. |
| Acrylonitrile | 107–13–1 | 34215 | Organic synthesis compound | 2-Propenenitrile. |
| Bromochloromethane | 74–97–5 | 77297 | Organic synthesis compound | -- |
| Carbon disulfide | 75–15–0 | 77041 | Organic synthesis compound | -- |
| 3-Chloro-1-propene | 107–05–1 | 78109 | Organic synthesis compound | -- |
| *trans*-1,4-Dichloro-2-butene | 110–57–6 | 73547 | Organic synthesis compound | -- |
| 1,1-Dichloroethene | 75–35–4 | 34501 | Organic synthesis compound | -- |
| 1,3-Dichloropropane | 142–28–9 | 77173 | Organic synthesis compound | -- |
| 2,2-Dichloropropane | 594–20–7 | 77170 | Organic synthesis compound | -- |
| 1,1-Dichloropropene | 563–58–6 | 77168 | Organic synthesis compound | -- |
| Ethyl methacrylate | 97–63–2 | 73570 | Organic synthesis compound | -- |
| Hexachlorobutadiene | 87–68–3 | 39702 | Organic synthesis compound | -- |
| Iodomethane | 74–88–4 | 77424 | Organic synthesis compound | Methyl iodide. |
| Methyl acrylate | 96–33–3 | 49991 | Organic synthesis compound | -- |
| Methyl acrylonitrile | 126–98–7 | 81593 | Organic synthesis compound | -- |

**Table 1.** Volatile organic compounds included in the U.S. Geological Survey's National Water-Quality Assessment Program.—Continued

[USGS, U.S. Geological Survey; VOC, volatile organic compound; --, not applicable]

| Compound name | Chemical Abstract Service number[1] | USGS parameter code | VOC group | Alternate name or abbreviation |
|---|---|---|---|---|
| Methyl methacrylate | 80–62–6 | 81597 | Organic synthesis compound | -- |
| 1,2,3-Trichlorobenzene | 87–61–6 | 77613 | Organic synthesis compound | -- |
| Vinyl acetate | 108–05–4 | 77057 | Organic synthesis compound | -- |
| Vinyl bromide | 593–60–2 | 50002 | Organic synthesis compound | Bromoethene. |
| Vinyl chloride | 75–01–4 | 39175 | Organic synthesis compound | Chloroethene. |
| Dichlorodifluoromethane | 75–71–8 | 34668 | Refrigerant | CFC–12. |
| Trichlorofluoromethane | 75–69–4 | 34488 | Refrigerant | CFC–11. |
| Trichlorotrifluoroethane | 76–13–1 | 77652 | Refrigerant | CFC–113; 1,1,2-Trichloro-1,2,2-trifluoroethane. |
| Acetone | 67–64–1 | 81552 | Solvent | 2-Propanone. |
| Bromobenzene | 108–86–1 | 81555 | Solvent | -- |
| Carbon tetrachloride | 56–23–5 | 32102 | Solvent | Tetrachloromethane. |
| Chlorobenzene | 108–90–7 | 34301 | Solvent | -- |
| Chloroethane | 75–00–3 | 34311 | Solvent | -- |
| Chloromethane | 74–87–3 | 34418 | Solvent | Methyl chloride. |
| 2-Chlorotoluene | 95–49–8 | 77275 | Solvent | -- |
| 4-Chlorotoluene | 106–43–4 | 77277 | Solvent | -- |
| 1,2-Dichlorobenzene | 95–50–1 | 34536 | Solvent | -- |
| 1,3-Dichlorobenzene | 541–73–1 | 34566 | Solvent | -- |
| 1,1-Dichloroethane | 75–34–3 | 34496 | Solvent | -- |
| 1,2-Dichloroethane | 107–06–2 | 32103 | Solvent | -- |
| *cis*-1,2-Dichloroethene | 156–59–2 | 77093 | Solvent | -- |
| *trans*-1,2-Dichloroethene | 156–60–5 | 34546 | Solvent | -- |
| Diethyl ether | 60–29–7 | 81576 | Solvent | -- |
| Dibromomethane | 74–95–3 | 30217 | Solvent | Methylene bromide. |
| Hexachloroethane | 67–72–1 | 34396 | Solvent | 1,1,1,2,2,2-Hexachloroethane. |
| Methyl butyl ketone | 591–78–6 | 77103 | Solvent | 2-Hexanone. |
| Dichloromethane | 75–09–2 | 34423 | Solvent | Methylene chloride. |
| Methyl ethyl ketone | 78–93–3 | 81595 | Solvent | 2-Butanone. |
| Methyl isobutyl ketone | 108–10–1 | 78133 | Solvent | 4-Methyl-2-pentanone. |
| Perchloroethene | 127–18–4 | 34475 | Solvent | PCE; Tetrachloroethene. |
| *n*-Propylbenzene | 103–65–1 | 77224 | Solvent | -- |
| 1,1,1,2-Tetrachloroethane | 630–20–6 | 77562 | Solvent | -- |
| 1,1,2,2-Tetrachloroethane | 79–34–5 | 34516 | Solvent | -- |
| Tetrahydrofuran | 109–99–9 | 81607 | Solvent | -- |
| 1,2,4-Trichlorobenzene | 120–82–1 | 34551 | Solvent | -- |
| 1,1,1-Trichloroethane | 71–55–6 | 34506 | Solvent | -- |
| 1,1,2-Trichloroethane | 79–00–5 | 34511 | Solvent | -- |
| Trichloroethene | 79–01–6 | 39180 | Solvent | TCE. |
| Bromoform | 75–25–2 | 32104 | Trihalomethane (THM) | Tribromomethane. |
| Bromodichloromethane | 75–27–4 | 32101 | Trihalomethane (THM) | -- |
| Chloroform | 67–66–3 | 32106 | Trihalomethane (THM) | Trichloromethane. |
| Dibromochloromethane | 124–48–1 | 32105 | Trihalomethane (THM) | -- |

[1]This report contains Chemical Abstract Service numbers (CASRN)®, which is a Registered Trademark of the American Chemical Society. A CASRN is a numeric identifier that can contain up to nine digits, divided by dashes into three parts. For example, 67–66–3 is the CASRN for chloroform. The online database provides a source for the latest registry number information: *http://www.cas.org/*. Chemical Abstracts Services recommends the verification of the CASRNs through CAS Client Services℠.

**Table 2.** List of urban stream sampling sites by major river basin and Study Unit with drainage area, use areas of methyl *tert*-butyl ether (MTBE), percentage urban land use in basin, sampling dates, and streamflow discharge statistics by pentile.

[<, less than; ≤, less than or equal to; ≥, greater than or equal to; --, no data]

| Study Unit abbreviation (see fig. 1) | Station name | Station identification number | Drainage area (square miles) | MTBE-use area | Percentage urban land use in basin | Sample dates (month/day/year) | | Discharge range in each of the streamflow pentiles (cubic feet per second[1]) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Begin | End | ≤20 percent 1 | 20–<40 percent 2 | 40–<60 percent 3 | 60–<80 percent 4 | ≥80 percent 5 |
| New England and Mid-Atlantic Major River Basin[2] | | | | | | | | | | | | |
| NECB | Aberjona River at Winchester, Mass. | 01102500 | 27.4 | High | 79.3 | 05/14/1999 | 03/28/2000 | <7.7 | 7.7–<16 | 16–<27 | 27–≤47 | ≥47 |
| CONN | Norwalk River at Winnipauk, Conn. | 01209710 | 33 | High | 50.2 | 11/30/2001 | 09/24/2002 | <9.6 | 9.6–<23 | 23–<44 | 44–<82 | ≥82 |
| LINJ | Saddle River at Ridgewood, N.J. | 01390500 | 21.6 | High | 90.0 | 05/01/1996 | 01/28/1997 | <9.0 | 9.0–<16 | 16–<24 | 24–<41 | ≥41 |
| LINJ | Bound Brook at Middlesex, N.J. | 01403900 | 48.4 | High | 75.0 | 04/23/1996 | 07/09/2002 | <16 | 16–<29 | 29–<47 | 47–<82 | ≥82 |
| LINJ | Great Egg Harbor River near Sicklerville, N.J. | 01410784 | 15.1 | High | 35.8 | 04/01/1996 | 03/17/1998 | <5.2 | 5.2–<9.4 | 9.4–<14 | 14–<21 | ≥21 |
| DELR | Little Neshaminy Creek at Valley Road near Neshaminy, Pa. | 01464907 | 26.8 | High | 37.3 | 02/11/1999 | 10/12/2000 | <5.9 | 5.9–<12 | 12–<24 | 24–<58 | ≥58 |
| DELR | Cooper River at Haddonfield, N.J. | 01467150 | 17 | High | 69.4 | 12/03/1998 | 10/02/2000 | <11 | 11–<15 | 15–<22 | 22–<32 | ≥32 |
| LSUS | Cedar Run at Eberlys Mill, Pa. | 01571490 | 12.6 | High | 59.0 | 01/10/1994 | 08/09/1995 | <6.7 | 6.7–<9.5 | 9.5–<14 | 14–<20 | ≥20 |
| PODL | Accotink Creek near Annandale, Va. | 01654000 | 23.9 | High | 85.2 | 10/23/2001 | 09/10/2002 | <3.7 | 3.7–<7.8 | 7.8–<13 | 13–<27 | ≥27 |
| South Atlantic-Gulf and Tennessee Major River Basin[2] | | | | | | | | | | | | |
| ALBE | Swift Creek near Apex, N.C. | 02087580 | 21 | Low | 33.2 | 10/12/2001 | 07/14/2003 | <1.0 | 1.0–<3.9 | 3.9–<10 | 10–<21 | ≥21 |
| SANT | Gills Creek at Columbia, S.C. | 02169570 | 59.6 | Low | 48.9 | 02/22/1996 | 03/24/1998 | <21 | 21–<35 | 35–<57 | 57–<99 | ≥99 |
| GAFL | Rocky Creek at State Highway 587 at Citrus Park, Fla. | 02306774 | 17.5 | Low | 40.8 | 01/31/2002 | 07/16/2003 | <0.3 | 0.3–<1.2 | 1.2–<4.2 | 4.2–<14 | ≥14 |
| ACFB | Sope Creek near Marietta, Ga. | 02335870 | 29.2 | Low | 60.7 | 10/11/2001 | 09/06/2002 | <13 | 13–<20 | 20–<28 | 28–<47 | ≥47 |

**Table 2.** List of urban stream sampling sites by major river basin and Study Unit with drainage area, use areas of methyl *tert*-butyl ether (MTBE), percentage urban land use in basin, sampling dates, and streamflow discharge statistics by pentile.—Continued

[<, less than; ≤, less than or equal to; ≥, greater than or equal to; --, no data]

| Study Unit abbreviation (see fig. 1) | Station name | Station identification number | Drainage area (square miles) | MTBE-use area | Percentage urban land use in basin | Sample dates (month/day/year) | | Discharge range in each of the streamflow pentiles (cubic feet per second[1]) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Begin | End | ≤20 percent 1 | 20–<40 percent 2 | 40–<60 percent 3 | 60–<80 percent 4 | ≥80 percent 5 |
| South Atlantic-Gulf and Tennessee Major River Basin[2]—Continued | | | | | | | | | | | | |
| MOBL | Three Mile Branch at North Boulevard at Montgomery, Ala. | 02419977 | 8.79 | Low | 82.5 | 01/12/1999 | 06/07/2001 | <3.6 | 3.6–<5.1 | 5.1–<7.6 | 7.6–<16 | ≥16 |
| MOBL | Cahaba Valley Creek at Cross Creek Road at Pelham, Ala. | 0242354750 | 25.6 | Low | 11.8 | 01/06/1999 | 06/28/2001 | <8.2 | 8.2–<13 | 13–<26 | 26–<50 | ≥50 |
| Great Lakes, Ohio, Upper Mississippi, and Souris-Red-Rainy Major River Basin[2] | | | | | | | | | | | | |
| ALMN | Deer Creek near Dorseyville, Pa. | 03049646 | 27 | Low | 14.5 | 01/27/1997 | 08/26/1998 | <7.6 | 7.6–<16 | 16–<18 | 18–<31 | ≥31 |
| WHMI | Little Buck Creek near Indianapolis, Ind. | 03353637 | 17 | Low | 54.9 | 03/14/2001 | 09/25/2002 | <1.3 | 1.3–<6.9 | 6.9–<12 | 12–<23 | ≥23 |
| WHMI | Holes Creek in Huffman Park at Kettering, Ohio | 393944084120700 | 19 | Low | 65.4 | 03/09/1999 | 09/11/2002 | <2.4 | 2.4–<6.5 | 6.5–<14 | 14–<28 | ≥28 |
| WMIC | Lincoln Creek at 47th Street at Milwaukee, Wis. | 040869415 | 9.56 | Low | 90.8 | 11/14/2001 | 09/10/2002 | <1.2 | 1.2–<2.0 | 2–<3 | 3–<6.6 | ≥6.6 |
| LERI | Clinton River at Sterling Heights, Mich. | 04161820 | 309 | Low | 29.0 | 10/31/1996 | 06/03/1998 | <122 | 122–<180 | 180–<250 | 250–<360 | ≥360 |
| UMIS | Shingle Creek at Queen Avenue in Minneapolis, Minn. | 05288705 | 28.2 | Low | 70.4 | 08/05/1996 | 11/10/1998 | <2.3 | 2.3–<4.5 | 4.5–<9.8 | 9.8–<27 | ≥27 |
| UMIS | Nine Mile Creek near James Circle at Bloomington, Minn. | 05330902 | 44.6 | Low | 79.6 | 01/21/1997 | 12/22/1997 | <0.9 | 0.9–<2.7 | 2.7–<8.8 | 8.8–<28 | ≥28 |
| UIRB | Salt Creek at Western Springs, Ill. | 05531500 | 115 | Low | 81.5 | 03/02/1999 | 03/08/2000 | <66 | 66–<89 | 89–<128 | 128–<223 | ≥223 |

**Table 2.** List of urban stream sampling sites by major river basin and Study Unit with drainage area, use areas of methyl *tert*-butyl ether (MTBE), percentage urban land use in basin, sampling dates, and streamflow discharge statistics by pentile.—Continued

[<, less than; ≤, less than or equal to; ≥, greater than or equal to; --, no data]

| Study Unit abbreviation (see fig. 1) | Station name | Station identification number | Drainage area (square miles) | MTBE-use area | Percentage urban land use in basin | Sample dates (month/day/year) | | Discharge range in each of the streamflow pentiles (cubic feet per second[1]) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Begin | End | ≤20 percent 1 | 20–<40 percent 2 | 40–<60 percent 3 | 60–<80 percent 4 | ≥80 percent 5 |
| Missouri Major River Basin[2] | | | | | | | | | | | | |
| SPLT | Cherry Creek at Denver, Colo. | 06713500 | 409 | Low | 11.5 | 10/10/2001 | 09/05/2002 | <12 | 12–<18 | 18–<25 | 25–<41 | ≥41 |
| Lower Mississippi, Arkanasas-White-Red, and Texas-Gulf Major River Basin[2] | | | | | | | | | | | | |
| MISE | Fletcher Creek at Sycamore View Road at Memphis, Tenn. | 07031692 | 30.5 | Low | 54.3 | 10/01/1996 | 09/24/1997 | <0.8 | 0.8–<2.8 | 2.8–<6.5 | 6.5–<26 | ≥26 |
| ACAD | Dawson Creek at Bluebonnet Boulevard near Baton Rouge, La. | 07379960 | 15.1 | Low | 90.2 | 01/14/1999 | 02/09/2001 | <1.8 | 1.8–<6.4 | 6.4–<19 | 19–<94 | ≥94 |
| TRIN | White Rock Creek at Greenville Avenue, Dallas, Tex. | 08057200 | 66.4 | High | 61.2 | 10/10/2001 | 09/11/2002 | <13 | 13–<25 | 25–<43 | 43–<84 | ≥84 |
| SCTX | Salado Creek at Loop 13 at San Antonio, Tex. | 08178800 | 189 | Low | 41.3 | 01/23/1997 | 01/31/1998 | <9.3 | 9.3–<15 | 15–<22 | 22–<37 | ≥37 |
| Rio Grande, Colorado, and Great Basin Major River Basin[2] | | | | | | | | | | | | |
| NVBR | Las Vegas Wash below Flamingo Wash confluence near Las Vegas, Nev. | 094196783 | 1,352 | Low | 9.9 | 10/11/2001 | 08/20/2002 | <4.7 | 4.7–<6.7 | 6.7–<9.4 | 9.4–<11 | ≥11 |
| GRSL | Little Cottonwood Creek at Jordan River near Salt Lake City, Utah | 10168000 | 46 | Low | 26.8 | 03/23/1999 | 04/20/2000 | <0.9 | 0.9–<3.9 | 3.9–<9.3 | 9.3–<21 | ≥21 |
| California Major River Basin[2] | | | | | | | | | | | | |
| SANA | Warm Creek near San Bernardino, Calif. | 11060400 | 11 | High | 84.6 | 11/16/1998 | 06/13/2002 | <0.6 | 0.6–<2.3 | 2.3–<6.9 | 6.9–<20 | ≥20 |
| SACR | Arcade Creek near Del Paso Heights, Calif. | 11447360 | 31.4 | High | 95.4 | 03/05/1996 | 04/23/1998 | <0.9 | 0.9–<1.8 | 1.8–<2.8 | 2.8–<5.3 | ≥5.3 |

**Table 2.** List of urban stream sampling sites by major river basin and Study Unit with drainage area, use areas of methyl *tert*-butyl ether (MTBE), percentage urban land use in basin, sampling dates, and streamflow discharge statistics by pentile.—Continued

[<, less than; ≤, less than or equal to; ≥, greater than or equal to; --, no data]

| Study Unit abbreviation (see fig. 1) | Station name | Station identification number | Drainage area (square miles) | MTBE-use area | Percentage urban land use in basin | Sample dates (month/day/year) | | Discharge range in each of the streamflow pentiles (cubic feet per second[1]) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Begin | End | ≤20 percent 1 | 20–<40 percent 2 | 40–<60 percent 3 | 60–<80 percent 4 | ≥80 percent 5 |
| | | | | | Pacific Northwest Major River Basin[2] | | | | | | | |
| PUGT | Thornton Creek near Seattle, Wash. | 12128000 | 12.1 | Low | 94.4 | 03/07/1996 | 05/14/1998 | <5.6 | 5.6–<7.8 | 7.8–<10 | 10–<16 | ≥16 |
| NROK | Spokane River at 7 Mile Bridge near Spokane, Wash. | 12424500 | 5,020 | Low | 3.2 | 02/09/1999 | 10/21/1999 | <1,980 | 1,980–<2,660 | 2,660–<5,360 | 5,360–<11,860 | ≥11,860 |
| WILL | Fanno Creek at Durham, Oreg. | 14206950 | 31.5 | Low | 75.7 | 03/01/1993 | 09/24/2002 | <3.0 | 3.0–<10 | 10–<32 | 32–<55 | ≥55 |
| | | | | | Alaska Basins[2] | | | | | | | |
| COOK | Chester Creek at Arctic Boulevard at Anchorage, Alaska | 15275100 | 27.4 | Low | -- | 01/19/1999 | 09/08/1999 | <12 | 12–<16 | 16–<20 | 20–<26 | ≥26 |
| | | | | | Hawaii Basins[2] | | | | | | | |
| OAHU | Manoa Stream at Kanewai Field, Honolulu, Oahu, Hawaii | 16242500 | 5.05 | Low | -- | 07/22/1999 | 06/20/2000 | <4.3 | 4.3–<5.9 | 5.9–<7.9 | 7.9–<14 | ≥14 |

[1]Discharge range in each of the streamflow pentiles based on the most recent 20-year discharge record from the last sampling date (see "Streamflow Record Extension" section).

[2]Seaber and others (1987).

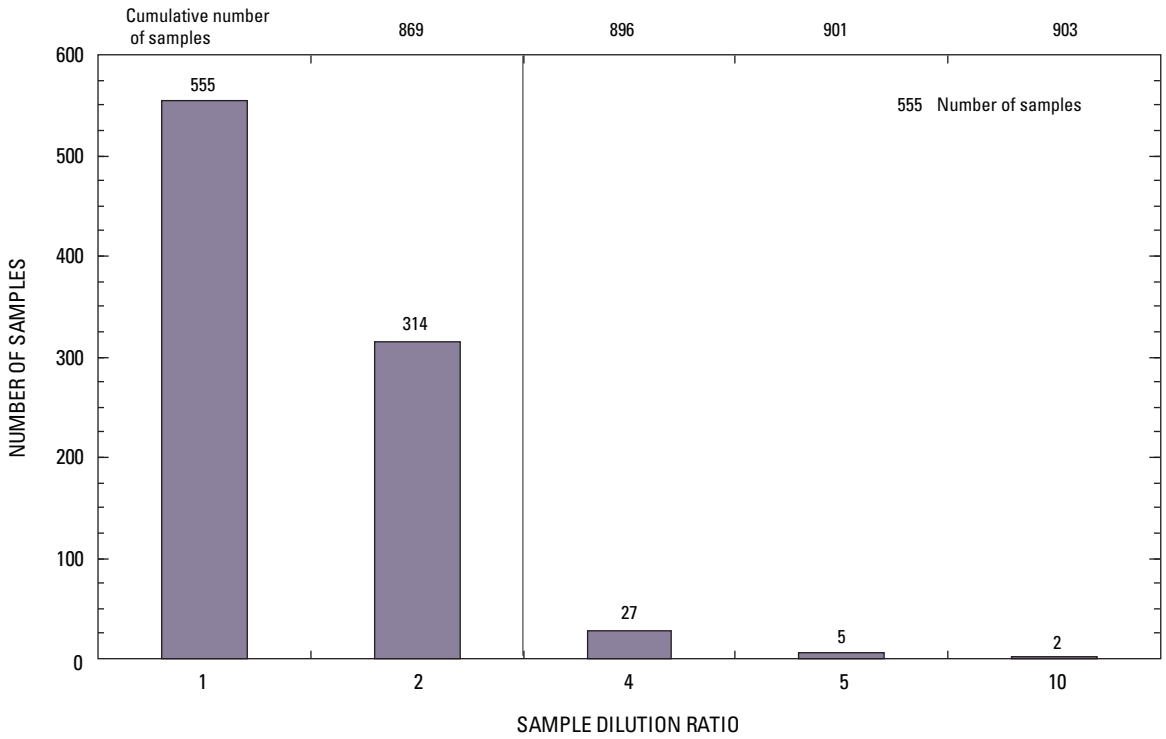


**Figure 2.** Number of samples by dilution ratio of the urban stream samples, 1995–2003.

## Assessment Level

An assessment level of 0.02 µg/L was used to compute the detection frequencies and concentration summaries of VOCs, in part, because of the varying LT–MDLs for each compound included in the low-level VOC method. The use of an assessment level allows a scientifically based, direct comparison between groups of VOCs and between individual VOCs. However, detection frequencies computed at this assessment level are considered to underestimate the true detection in urban streams because of the potential loss of information by the censoring of qualified, reported concentrations less than 0.02 µg/L. The statistical summary for concentrations is based on all the samples with concentrations censored at the assessment level of 0.02 µg/L. Most of the samples had VOC concentrations that were less than the assessment level (that is, less than (<) 0.02 µg/L). Median concentrations of detections in the report are for the subset of samples that had concentrations equal to or greater than the assessment level. Total VOC concentrations were calculated as the sum of all quantified concentrations (at an assessment level of 0.02 µg/L or greater) for all VOCs analyzed in a sample. Moran and others (2006) provide a more detailed discussion of applying an assessment level to water-quality datasets.

## Statistical Methods

Non-parametric statistics were used in the analyses presented in this report because the data were not assumed to be normally distributed. Information on the statistical tests can be found in Helsel and Hirsch (1992) and Ott and Longnecker (2001). All statistical tests used a significance value (α) of 0.05 for all two-sided test statistics. All statistical tests used within this report provide the probability (p-value) for the comparisons of the test. The p-value is a measure of the confidence that what is observed in the sample is true for the population. This significance value was used as the acceptance level for the subsequent test statistics (that is, accept null hypothesis if p-value is less than α). A Wilcoxon rank-sum test was used to compare two independent groups of continuous data. A Wilcoxon sign-rank test was used to compare paired data. The alternative hypothesis states that observations from one group tend to produce larger (or smaller) values compared to the other group (Helsel and Hirsch, 1992). The Wilcoxon rank-sum and sign-rank tests report a standardized normal score (Z value) and the probability (p-value). An example of this is the comparison between total VOC concentrations in warmer and cooler months. If the alternative hypothesis is rejected, then the total concentrations are larger (or smaller)

**Table 3.** Statistical summaries of analytical results for volatile organic compounds in source-solution and field-equipment blank samples from 37 urban stream sites at no assessment level, 1995–2003.

[E, estimated concentration less than the long-term method detection level; --, not applicable]

| Compound | Source-solution blank | | | | | Field-equipment blank | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Number of samples | Number of detections | Statistical summary of reported concentrations (micrograms per liter) | | | Number of samples | Number of detections | Statistical summary of reported concentrations (micrograms per liter) | | |
| | | | Minimum concentration | Median concentration | Maximum concentration | | | Minimum concentration | Median concentration | Maximum concentration |
| Toluene | 32 | 15 | E0.006 | E0.024 | 2.3 | 104 | 39 | E0.007 | E0.023 | 3.6 |
| Chloroform | 32 | 2 | .019 | -- | .040 | 104 | 27 | E.006 | .050 | .50 |
| *m*- and *p*-Xylene | 32 | 8 | E.006 | E.025 | .079 | 103 | 17 | E.007 | .030 | .10 |
| Ethylbenzene | 32 | 4 | E.009 | E.014 | .038 | 104 | 16 | E.003 | E.010 | .040 |
| Acetone | 32 | 5 | E.95 | 2.7 | 3.7 | 103 | 15 | E.60 | 2.4 | 7.2 |
| Styrene | 32 | 6 | E.003 | E.015 | .027 | 104 | 15 | E.003 | E.010 | .14 |
| *o*-Xylene | 32 | 2 | .022 | -- | .047 | 103 | 10 | E.010 | .019 | .038 |
| Dichloromethane | 32 | 1 | -- | -- | .054 | 104 | 9 | E.007 | .40 | 4.7 |
| 1,2-Dichloropropane | 32 | 1 | -- | -- | E.020 | 104 | 8 | E.009 | E.010 | .020 |
| Tetrahydrofuran | 32 | 1 | -- | -- | E.50 | 103 | 8 | E.30 | E.50 | 8.1 |
| Chloromethane | 32 | 0 | -- | -- | -- | 104 | 7 | E.004 | E.010 | E.040 |
| 1,4-Dichlorobenzene | 32 | 2 | E.003 | -- | .030 | 104 | 7 | E.006 | E.010 | .083 |
| Methyl ethyl ketone | 32 | 1 | -- | -- | E.60 | 103 | 7 | E.20 | E.40 | 1.6 |
| Chlorobenzene | 32 | 1 | -- | -- | E.010 | 104 | 6 | E.004 | E.010 | .020 |
| Carbon disulfide | 32 | 0 | -- | -- | -- | 103 | 6 | E.003 | E.010 | .020 |
| 1,2,4-Trimethylbenzene | 32 | 2 | E.013 | -- | .043 | 104 | 6 | E.007 | E.018 | E.024 |
| Benzene | 32 | 1 | -- | -- | .026 | 104 | 5 | E.008 | .016 | .034 |
| Bromodichloromethane | 32 | 0 | -- | -- | -- | 104 | 4 | E.010 | E.010 | E.010 |
| 1,1,1-Trichloroethane | 32 | 0 | -- | -- | -- | 104 | 4 | E.001 | E.015 | .034 |
| 4-Isopropyltoluene | 32 | 0 | -- | -- | -- | 104 | 2 | E.005 | -- | E.008 |
| Methyl *tert*-butyl ether | 32 | 0 | -- | -- | -- | 104 | 2 | E.030 | -- | E.051 |
| Perchloroethene | 32 | 1 | -- | -- | E.004 | 104 | 2 | E.003 | -- | .013 |
| Trichlorofluoromethane | 32 | 1 | -- | -- | 2.5 | 104 | 2 | .13 | -- | .171 |
| Dichlorodifluoromethane | 32 | 0 | -- | -- | -- | 104 | 1 | -- | -- | E.041 |
| Ethyl *tert*-butyl ether | 32 | 0 | -- | -- | -- | 103 | 1 | -- | -- | .044 |
| Isopropylbenzene | 32 | 0 | -- | -- | -- | 104 | 1 | -- | -- | .003 |
| Methyl isobutyl ketone | 32 | 0 | -- | -- | -- | 103 | 1 | -- | -- | E.040 |
| Naphthalene | 32 | 0 | -- | -- | -- | 104 | 1 | -- | -- | E.020 |
| *n*-Propylbenzene | 32 | 1 | -- | -- | E.012 | 104 | 1 | -- | -- | E.003 |
| Trichloroethene | 32 | 1 | -- | -- | E.005 | 104 | 1 | -- | -- | E.008 |
| 1,1,2-Trichloro-1,2,2-fluoroethane | 32 | 0 | -- | -- | -- | 104 | 1 | -- | -- | E.007 |
| Vinyl chloride | 32 | 0 | -- | -- | -- | 104 | 1 | -- | -- | .050 |

in one season than the other. Alternatively, a one-sided null hypothesis was used to determine if warmer months had significantly larger concentrations than cooler months using $\alpha = 0.025$ (one-sided test statistics). Contingency tables were used to measure the association between categorical variables (for example, detection frequency between VOC groups) using the chi-square ($\chi^2$) statistic to test the null hypothesis. The null hypothesis is that the two variables are independent (Helsel and Hirsch, 1992). The Kruskal-Wallis rank-sum test was performed on the number of VOCs present in samples to determine if the number of VOCs present in samples were statistically different. The null hypothesis tests that the groups of data have identical distributions. The Kolmogorov-Smirnov goodness-of-fit test was performed on the total concentrations to determine if they were from independent distributions. The null hypothesis tests that the two variables are from the same continuous distribution. These statistical tests are described in table 4.

**Table 4.** Statistical tests used in the report.

[VOC, volatile organic compound; MTBE, methyl *tert*-butyl ether; NE, not equal, <, less than; >, greater than; Prob, probability or p-value]

| Statistical test | Test statistic | Hypothesis | Examples as used in this report |
|---|---|---|---|
| Contingency tables | Chi-square ($\chi^2$) | Null hypothesis:<br>$H_0$: The variables are independent<br><br>Alternate hypothesis:<br>$H_1$: The variables are not independent | Determine the independence of the number of detections and number of samples between VOC groups, flow pentiles, seasons, low and high MTBE-use areas. |
| Kolmogorov-Smirnov goodness-of-fit test | *ks* | Null hypothesis:<br>$H_0$: The data are from the same continuous distribution<br><br>Alternate hypothesis:<br>$H_1$: The data are not from the same distributions | Determine if the concentrations of VOC groups, flow pentiles, and seasons of the year are from the same distributions. |
| Kruskal Wallis | Chi-square ($\chi^2$) | Null hypothesis:<br>$H_0$: All of the groups of data being compared have identical distributions<br><br>Alternate hypothesis:<br>$H_1$: At least one group differs in its distribution | Determine if the number of VOCs present in samples are statistically different. |
| Wicoxon sign-rank | *Z* | Null hypothesis:<br>$H_0$: Prob[$x > y$] = 0.5<br><br>Alternative hypothesis:<br>$H_1$: Prob[$x > y$] NE 0.5<br>$H_2$: Prob[$x > y$] > 0.5<br>$H_3$: Prob[$x > y$] < 0.5 | Determine if the number of samples in warmer and cooler months are statistically different. |
| Wilcoxon rank-sum | *Z* | Null hypothesis:<br>$H_0$: $x_i$ and $y_i$ are from same distribution<br>$H_0$: Prob[$x_i > y_i$] = 0.5<br><br>Alternate hypothesis:<br>$H_1$: $x_i$ is from a distribution that generally is lower than that of $y_i$<br>$H_1$: Prob[$x_i > y_i$] < 0.5 | Determine if concentrations are statistically different between low and high MTBE-use areas, and seasons. |

## Streamflow Record Extension

The water quality of urban streams can be affected by streamflow. Many of the NAWQA Program's urban streams are small and flashy with short-term (1–2 years) streamflow records that limited the ability to compare the water-quality results on the basis of streamflow on a national or regional scale. A simple and robust methodology was used to estimate long-term streamflow percentiles at sites with short-term streamflow records. Two methodologies were tested for this purpose: (1) Matalas and Jacobs (1964) (also cited in U.S. Interagency Advisory Committee on Water Data, 1982) and (2) a simple flow-ratio method suggested by Kenneth L. Wahl (U.S. Geological Survey, oral commun., 2002), which is an adaptation of the normal-ratio method described by Gupta (2001), hereafter referred to as the flow-ratio method. The flow-ratio method was chosen on the basis of simplicity of use, no transformation of data was required, there was no serial correlation of data, and an assessment that the flow-ratio method provided a reasonable estimate of long-term streamflow characteristics for short-term sites.

An annual cumulative distribution function (CDF) of streamflow for each sampling site was calculated on the basis of about 20 years of streamflow information for each site. If a site had at least 20 years of record, then the annual CDF was calculated for the most recent 20-year record (17 of the sites). If the site had a short-term streamflow record (1–2 years; 20 of the sites), then a nearby, hydrologically similar long-term gaging station (with at least 17 years of streamflow data) was used to estimate streamflow for the sampling site. The long-term streamflow data for the sampling site was then estimated on the basis of the ratios of streamflow between the short-term site and the long-term gaging station by using the following equation (Andrew J. Long, U.S. Geological Survey, written commun., April 2007):

$$LT_{Q,est_i} = \frac{ST_{Q,conc_i}}{LT_{Q,conc_i}} LT_{Q,record_i} , \qquad (1)$$

where $LT_{Q,est_i}$ is the estimated long-term streamflow for the short term site; $ST_{Q,conc_i}$ and $LT_{Q,conc_i}$ are the streamflow rates for each percentile of interest for the concurrent period of record for the short-term site and long-term station, respectively; $LT_{Q,record_i}$ is the streamflow rate for each corresponding percentile for the entire period of record for the long-term station; and $i$ indicates the percentile of interest. For example, $i$ = 10, 20, …, 100 for every tenth percentile.

To provide valid sample statistics with a sufficient number of samples in each streamflow category, the water samples analyzed for VOCs were distributed into five annual streamflow pentiles (less than 20, 20 to less than 40, 40 to less than 60, 60 to less than 80, and greater than or equal to 80 percent of estimated long-term streamflow statistics). Table 2 contains a summary of the five pentiles of streamflow for each sampling site. VOC occurrence interpretations for the five streamflow pentiles are contained in the subsequent section "Patterns of VOC Occurrence by Streamflow Pentile." Figures showing the streamflow and annual percentiles of streamflow for each site are provided in Appendix 1.

The numbers of samples from the 37 sites per month, in warmer and cooler months, and by the five streamflow pentiles are shown in table 5. The statistical difference (Wilcoxon sign-rank two-tailed test statistic ($Z$) = -2.3496, p-value = 0.0188) in the total number of samples is significant between the warmer and cooler months, and more samples were collected in cooler months (Wilcoxon sign-rank single-tailed test statistic ($Z$) = -2.3496, p-value = 0.0094).

# Occurrence of Volatile Organic Compounds in Urban Streams

This section describes the occurrence of VOCs in urban streams on the basis of analyses of 869 samples from 37 urban indicator sites. The occurrence of one or more VOCs, VOC groups, and individual VOCs at all sites is presented. Detection frequencies and a summary of concentrations are presented. Also, for the occurrence of one or more VOCs, a summary of the number of VOCs per sample is presented. Similarly, occurrence by streamflow pentile and by warmer (April through September) and cooler (October through March) months also is presented for one or more VOCs, VOC groups, and individual VOCs. Comparisons of concentrations to the previously noted benchmarks describe the significance of VOCs in urban streams to human health and aquatic life.

## Overall Occurrence Patterns of Volatile Organic Compounds

This section describes the overall patterns of VOC occurrence in urban streams. All samples were included in computations as a group without consideration of streamflow condition during sampling or season of the year. The occurrence of one or more VOCs, VOC groups, and individual VOCs at all sites is presented.

### One or More Volatile Organic Compounds

One or more VOCs were detected in 97.1 percent of 869 samples, and one or more VOCs were detected frequently at all sites. Detection frequencies for one or more VOCs ranged from 85.7 percent for Fletcher Creek at Memphis, Tenn., to 100 percent at 27 of the urban indicator sites.

The median total VOC concentration for all samples was 0.57 µg/L (fig. 3). The total VOC concentrations ranged from not detected to 698 µg/L. About 57 percent of the total VOC concentrations were less than or equal to 1 µg/L, and about 93 percent of concentrations were less than 10 µg/L. The

**Table 5.** Number of samples per month, in cooler and warmer months, and in the five streamflow pentiles from 37 urban streams, 1995–2003.

| Streamflow pentile | | Number of samples | | | | | | | | | | | | Number of samples in cooler months | Number of samples in warmer months | Total number of samples |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cooler months | | | Warmer months | | | | | | Cooler months | | | | | |
| | | J | F | M | A | M | J | J | A | S | O | N | D | | | |
| Low flow | 1 | 6 | 7 | 6 | 4 | 4 | 15 | 19 | 11 | 18 | 11 | 14 | 9 | 53 | 71 | 124 |
| | 2 | 21 | 18 | 11 | 6 | 10 | 18 | 9 | 22 | 10 | 18 | 18 | 16 | 102 | 75 | 177 |
| | 3 | 15 | 20 | 13 | 15 | 19 | 8 | 9 | 8 | 6 | 9 | 17 | 14 | 88 | 65 | 153 |
| | 4 | 14 | 26 | 18 | 14 | 22 | 10 | 3 | 7 | 1 | 6 | 15 | 4 | 83 | 57 | 140 |
| High flow | 5 | 25 | 25 | 32 | 58 | 23 | 12 | 20 | 17 | 12 | 10 | 16 | 25 | 133 | 142 | 275 |
| **Total number of samples** | | **81** | **96** | **80** | **97** | **78** | **63** | **60** | **65** | **47** | **54** | **80** | **68** | **459** | **410** | **869** |

largest total VOC concentrations were dominated by the presence of acetone. The larger total concentrations (>10 µg/L) are spatially distributed across the Nation, except for Alaska and Hawaii, and occurred at about one-half of the sampling sites (17 urban streams). Total VOC concentrations were greater than 10 µg/L in about one-half of the samples from two sites, Bound Brook at Middlesex, N.J., and Shingle Creek at Queen Avenue in Minneapolis, Minn.

The number of VOCs detected per sample ranged from 0 to 27, with about 84.5 percent of the samples containing two or more VOCs (fig. 4). No VOCs were found in 2.9 percent of samples and only one VOC was present in 12.6 percent of samples. Forty-nine percent of the samples had 5 or more VOCs present, and 25 percent of the samples had 8 or more VOCs present. The samples with 27 VOCs (1 sample) and 20 VOCs (2 samples) were collected from Bound Brook at Middlesex, N.J. Samples with less than 18 VOCs included various samples from all the urban stream sites.

## Volatile Organic Compound Groups

The seven VOC groups had statistically different probabilities of occurrence (contingency table $\chi^2$ = 2,531.269, degrees of freedom (DF) = 6, p-value = 0) in urban stream samples. One or more of the gasoline hydrocarbons occurred most frequently and were reported in about 79 percent of all samples (fig. 5). Solvents, THMs, and gasoline oxygenates also were detected frequently and were found in about 71, 55, and 40 percent of samples, respectively. In contrast, the organic synthesis compounds, fumigants, and refrigerant compounds were detected in 14, 5.5, and 4.5 percent of samples, respectively.

The occurrence of gasoline hydrocarbons was dominated by the presence of benzene, toluene, ethylbenzene, and *o*-, *m*-, and *p*-xylene (BTEX compounds), which comprised about 78 percent of the detections of gasoline hydrocarbons (fig. 6). The occurrence of solvents was dominated by perchloroethene, trichloroethene, *cis*-1,2-dichloroethene, and acetone, which collectively comprised about 64 percent of the solvent detections (fig. 7). Also, 22 of the 30 solvent compounds analyzed in samples were detected in at least one sample. The occurrence of THMs was dominated by chloroform, which comprised about 80 percent of the THM detections (fig. 8).

The occurrence of the gasoline oxygenate group was dominated by MTBE, which comprised about 87 percent of the gasoline oxygenate detections, followed by *tert*-amyl methyl ether (TAME), which comprised about 11 percent of the gasoline oxygenate detections (fig. 9). Also, gasoline oxygenates had a much higher detection frequency in high MTBE-use areas than in low MTBE-use areas of the United States with about 70 percent of the detections in the high MTBE-use areas (figs. 10 and 11*A*). MTBE was the most frequently detected gasoline oxygenate in both low and high MTBE-use areas. TAME had a larger percentage of the detections (15 percent) in high MTBE-use areas than in low MTBE-use areas (1 percent; fig. 10), similar to results of the national survey of MTBE in drinking-water sources for the focused survey (Carter and others, 2006). The only detection of ethyl *tert*-butyl ether (ETBE) was in a high MTBE-use area (Cooper River at Haddonfield, N.J). Furthermore, the other gasoline oxygenate, diisopropyl ether (DIPE), had several detections in a low MTBE-use area (Cahaba Valley Creek at Cross Creek Road at Pelham, Ala.). The detection frequencies for gasoline oxygenates were about 18 percent and 86 percent in low and high MTBE-use areas, respectively (fig. 11*A*), and were statistically different (contingency table $\chi^2$ = 366.8698, DF = 1, p-value = 0) between the low and high MTBE-use areas of the United States.

The concentration distributions between VOC groups were all statistically different (Kolmogorov-Smirnov (KS) p-values < 0.05) except between the fumigants and refrigerants (KS p-value = 0.9999). The median total concentrations of samples with detections were as follows: gasoline hydrocarbons, 0.08 µg/L; solvents, 0.87 µg/L; THMs, 0.04 µg/L;

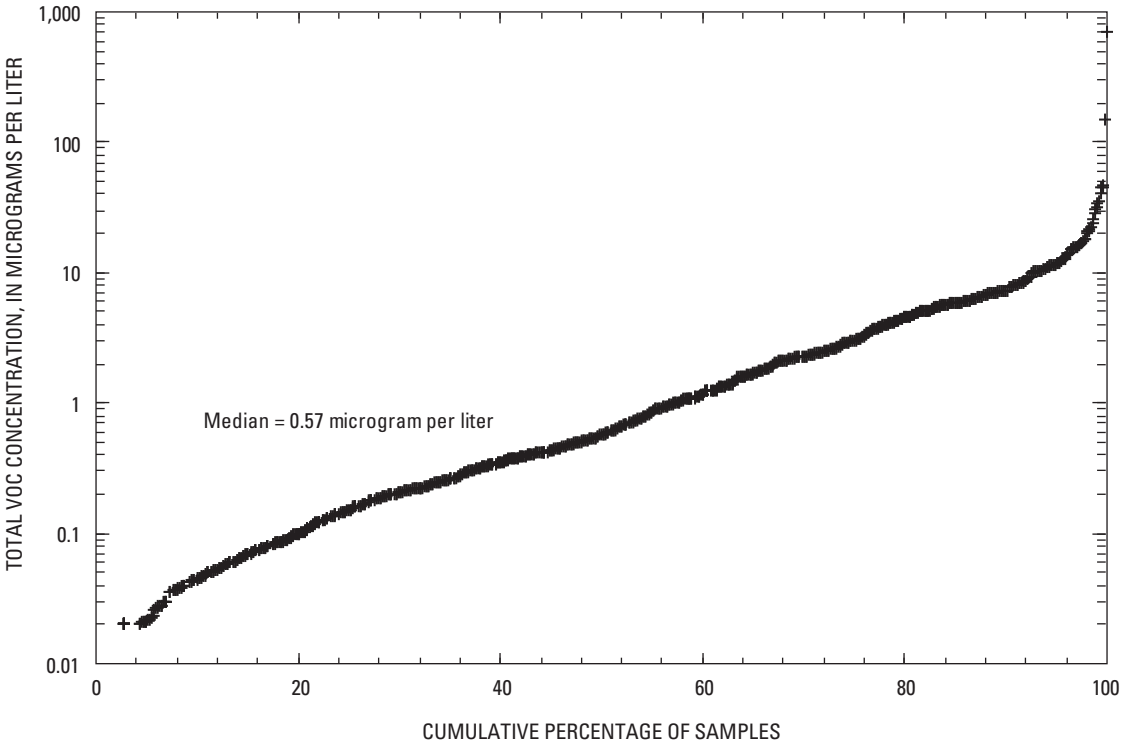


**Figure 3.** Cumulative distribution of total concentrations of volatile organic compounds (VOCs) in 869 samples from 37 urban stream sites at an assessment level of 0.02 microgram per liter, 1995–2003.

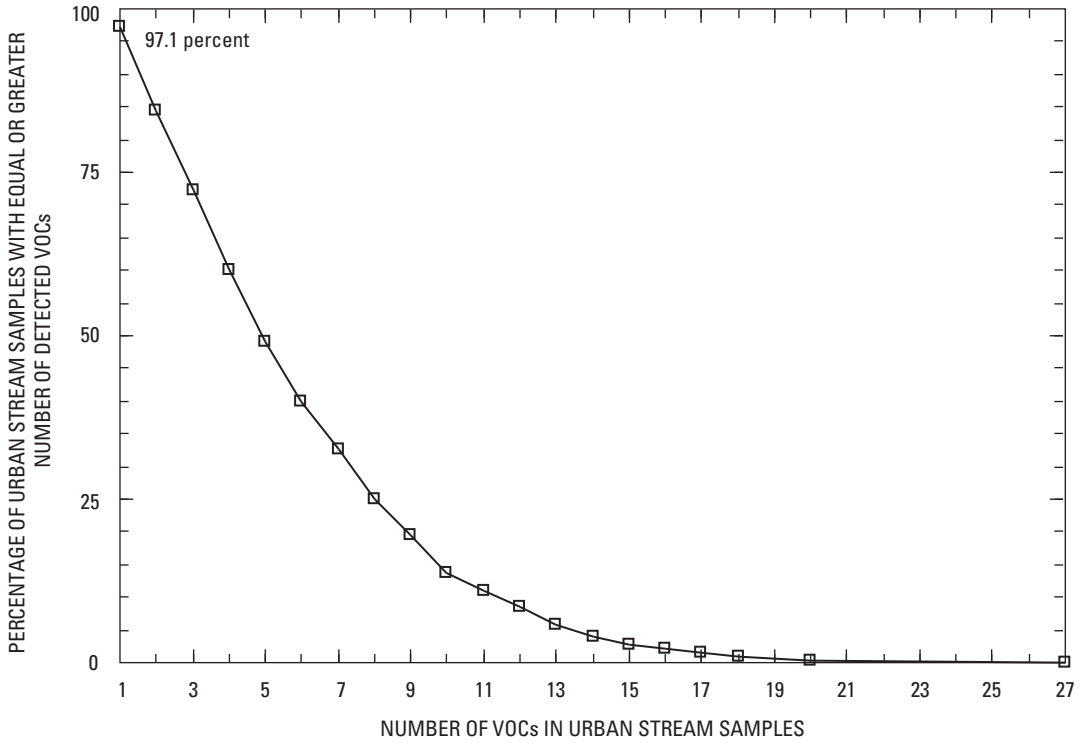


**Figure 4.** Relation between the percentage of 869 urban stream samples and the number of volatile organic compounds (VOCs) detected at an assessment level of 0.02 microgram per liter, 1995–2003.

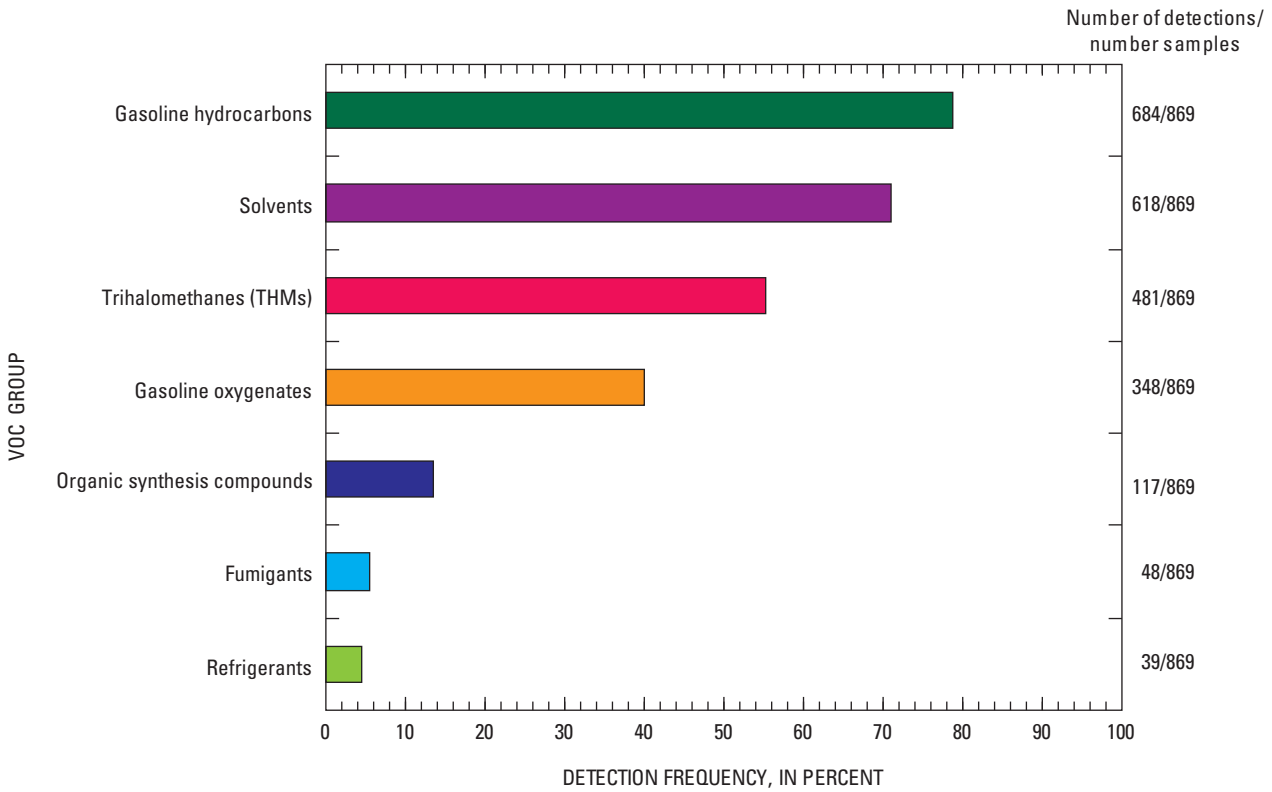


**Figure 5.** Detection frequencies of seven volatile organic compound (VOC) groups in urban stream samples at an assessment level of 0.02 microgram per liter, 1995–2003.

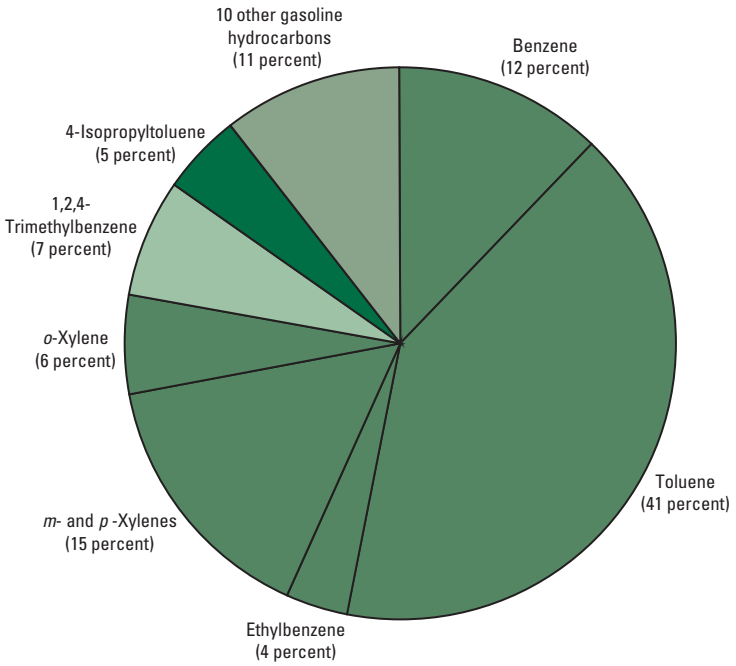


**Figure 6.** Distribution of the total number of detections of gasoline hydrocarbons in urban stream samples at an assessment level of 0.02 microgram per liter, 1995–2003. Of the 18 gasoline hydrocarbons analyzed for in urban stream samples, 17 were detected in at least one sample. Benzene, toluene, ethylbenzene, and the xylenes constitute the BTEX compounds (1,589 detections).

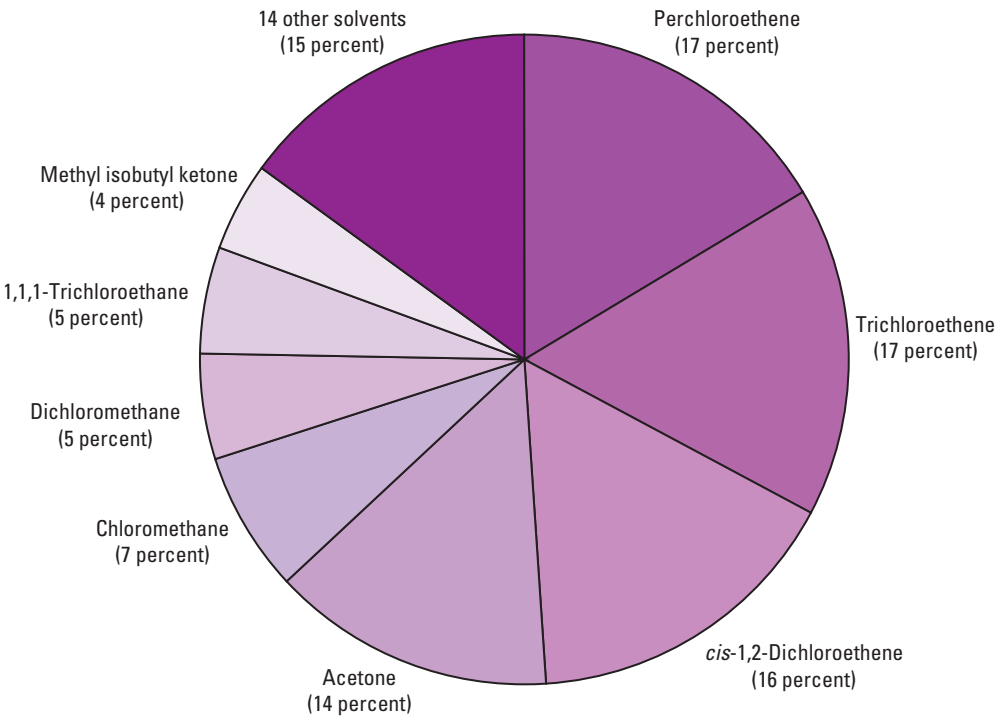


**Figure 7.** Distribution of the total number of detections of solvents in urban stream samples at an assessment level of 0.02 microgram per liter, 1995–2003. Of the 30 solvents analyzed for in urban stream samples, 22 were detected in at least one sample (1,824 detections).

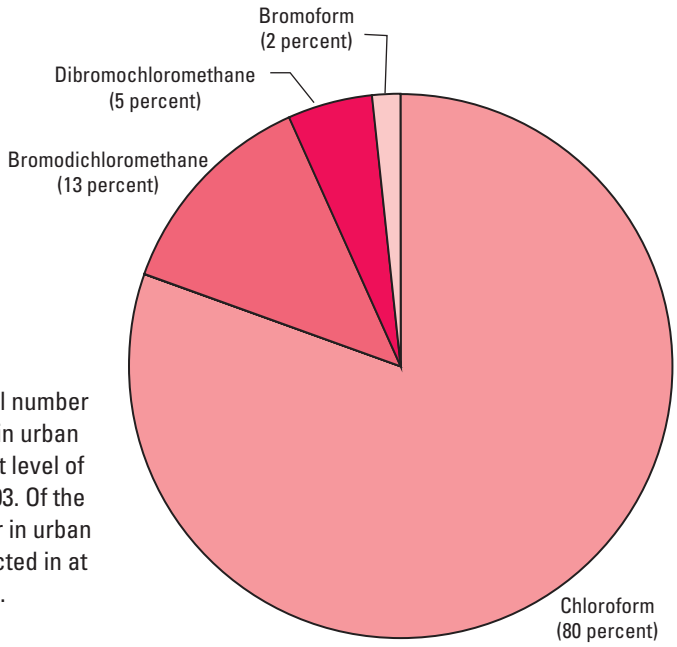


**Figure 8.** Distribution of the total number of detections of trihalomethanes in urban stream samples at an assessment level of 0.02 microgram per liter, 1995–2003. Of the four trihalomethanes analyzed for in urban stream samples, each were detected in at least one sample (596 detections).

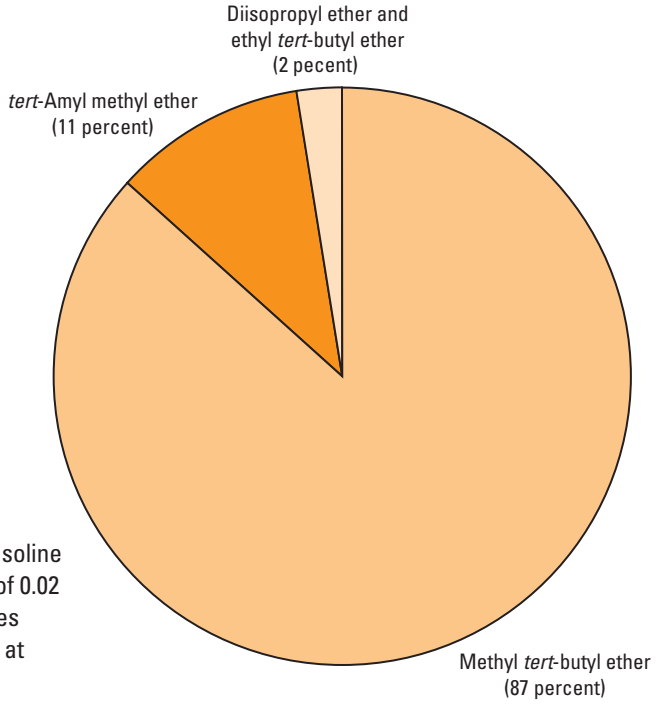


**Figure 9.** Distribution of the total number of detections of gasoline oxygenates in urban stream samples at an assessment level of 0.02 microgram per liter, 1995–2003. Of the four gasoline oxygenates analyzed for in urban stream samples, each were detected in at least one sample (401 detections).

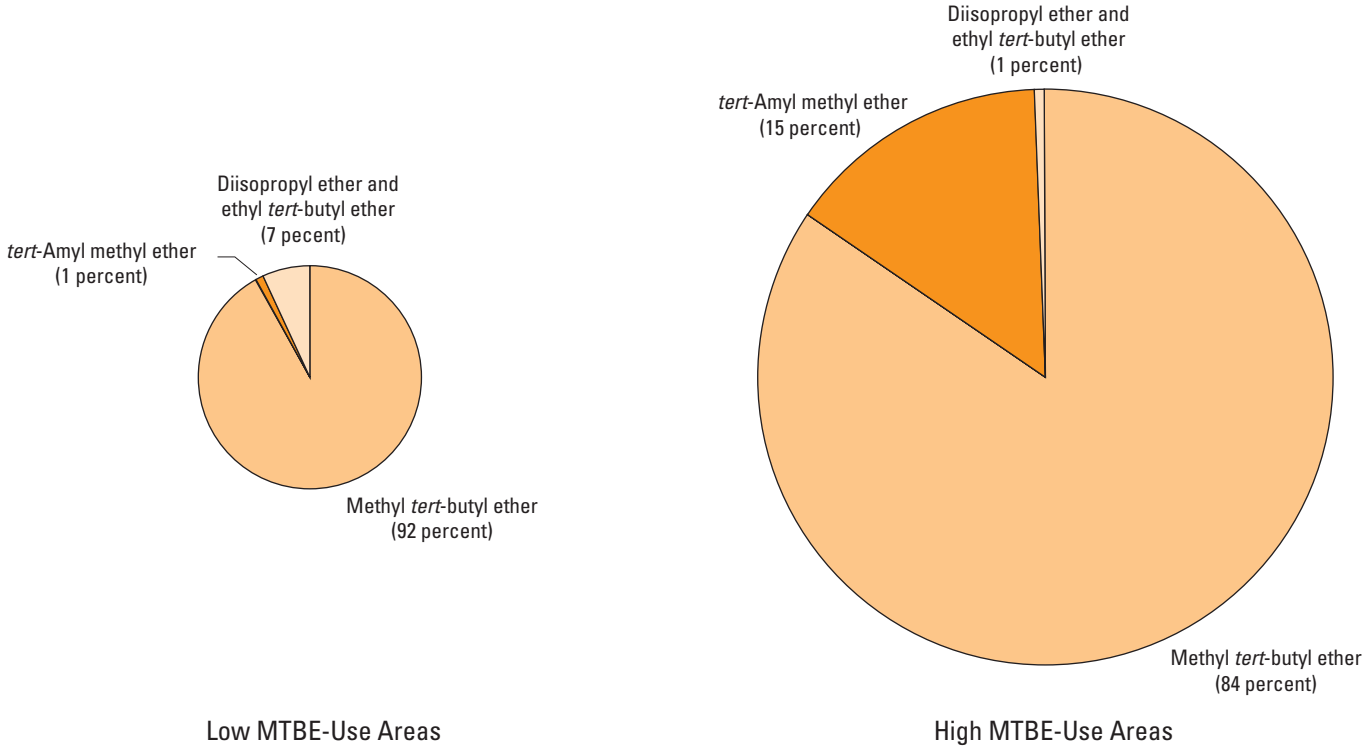


**Figure 10.** Distribution of the total number of detections of gasoline oxygenates in urban stream samples in low and high methyl *tert*-butyl ether (MTBE)-use areas at an assessment level of 0.02 microgram per liter, 1995–2003. The size of the pie represents the proportion of detections in the low (113 detections) and high (289 detections) MTBE-use areas.

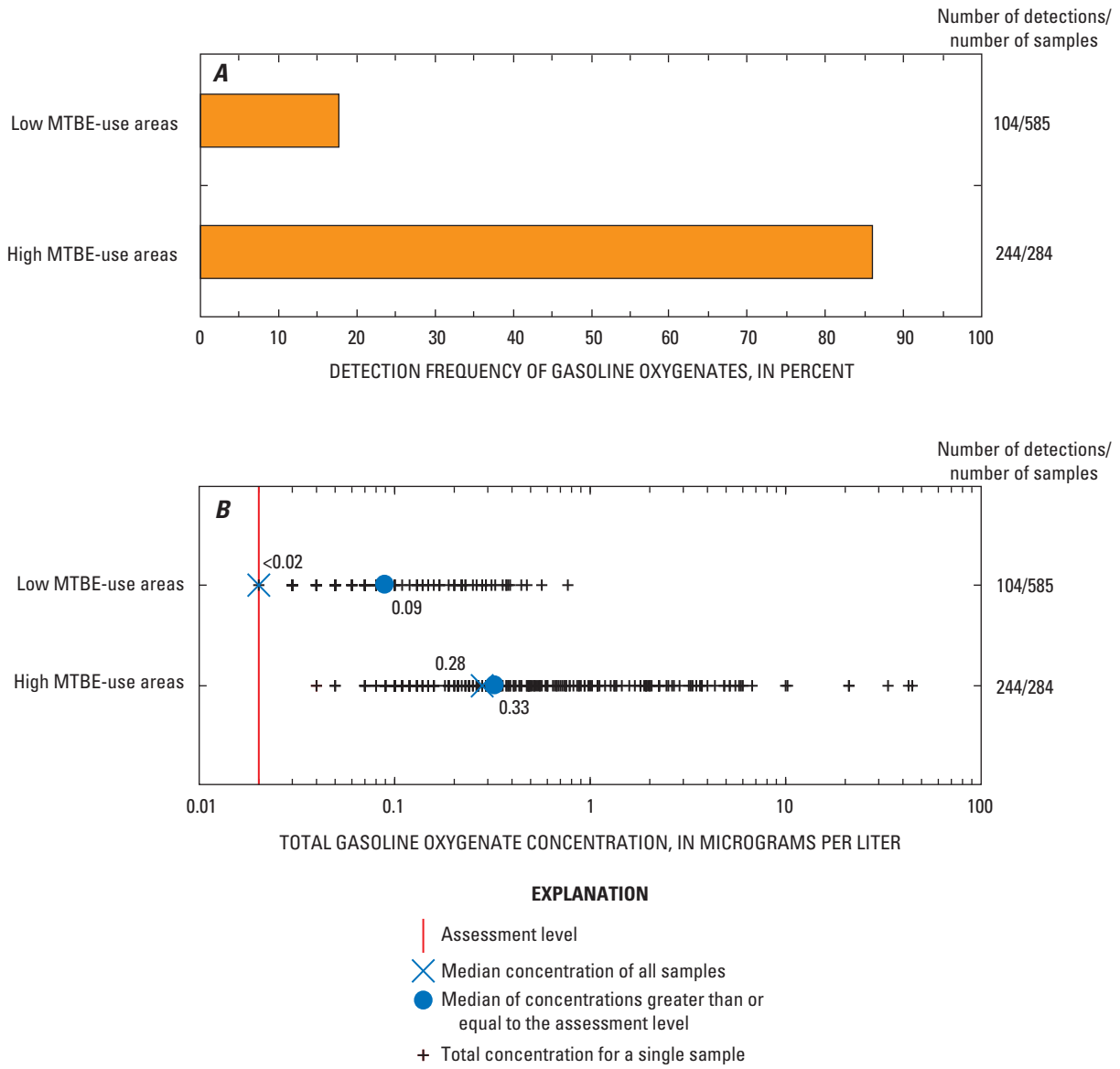


**Figure 11.** Relation between (*A*) detection frequencies, and (*B*) total concentrations for gasoline oxygenates in urban stream samples in low and high methyl *tert*-butyl ether (MTBE)-use areas of the United States at an assessment level of 0.02 microgram per liter, 1995–2003.

gasoline oxygenates, 0.24 µg/L; organic synthesis compounds, 0.03 µg/L; fumigants, 0.03 µg/L; and refrigerants, 0.05 µg/L (fig. 12). Furthermore, the concentration ranges for most groups were distributed over at least two orders of magnitude, with solvent concentrations distributed over more than four orders of magnitude. As noted previously, the large total concentrations of solvents were affected by large concentrations of acetone in some samples.

The total concentrations of the gasoline oxygenates were statistically different between the high and low MTBE-use areas of the United States (fig. 11*B*) with statistically larger total gasoline oxygenate concentrations in high MTBE-use areas (Wilcoxon rank-sum $Z = 9.8648$, one-sided p-value = 0). The median total gasoline oxygenate concentrations were 0.09 µg/L and 0.33 µg/L in low and high MTBE-use areas, respectively. Furthermore, total gasoline oxygenate concentrations had a much larger concentration range in high MTBE-use areas.

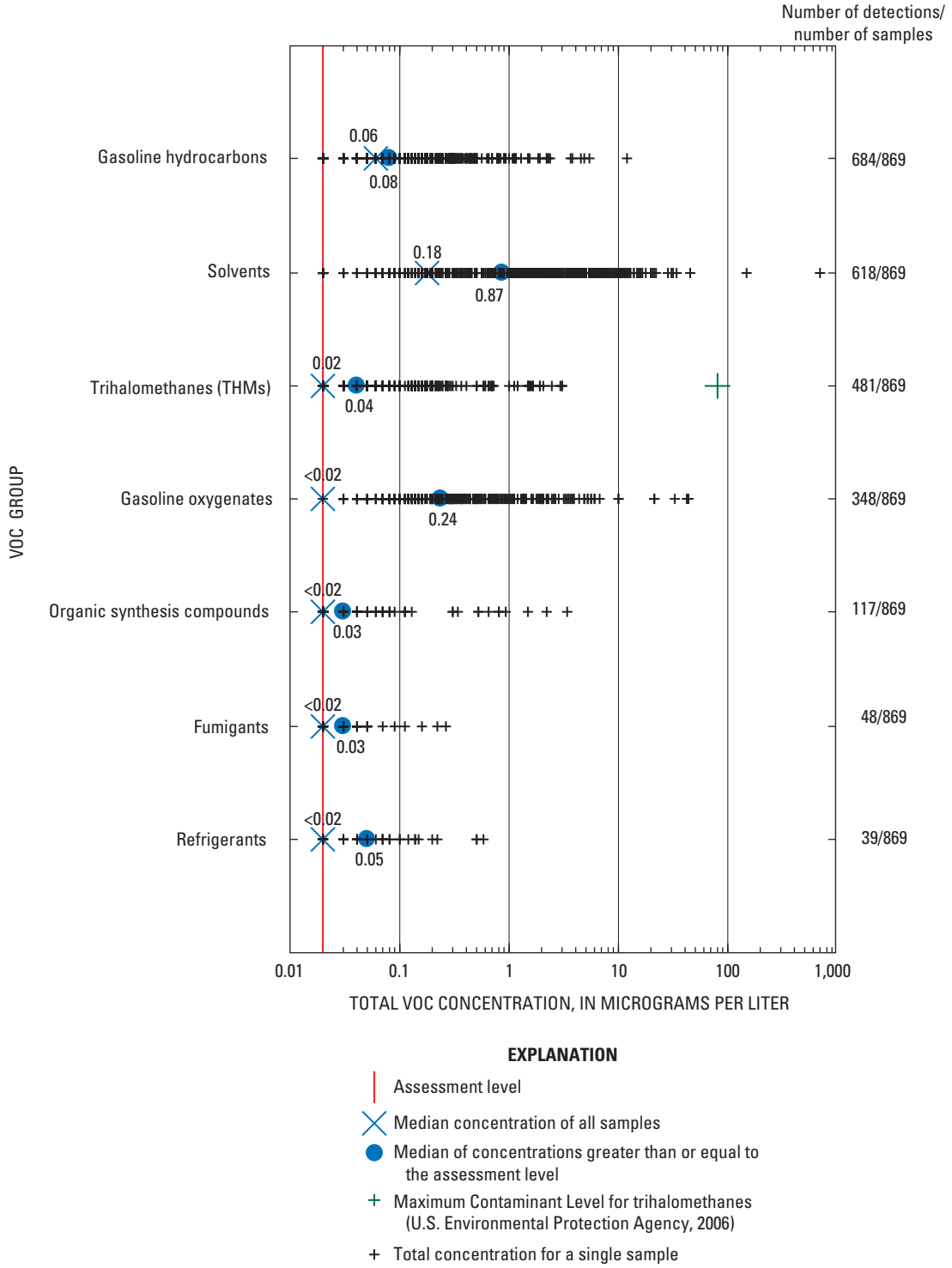


**Figure 12.** Total volatile organic compound (VOC) concentrations in urban stream samples by the seven VOC groups at an assessment level of 0.02 microgram per liter, 1995–2003.

## Individual Volatile Organic Compounds

Of the 87 VOCs analyzed for in water samples, 57 compounds were detected at least once in urban streams at concentrations greater than or equal to the assessment level of 0.02 µg/L (table 6). In contrast, 30 VOCs (16 organic synthesis compounds, 8 solvents, 5 fumigants, and 1 gasoline hydrocarbon) were not detected at concentrations greater than or equal to this assessment level at any of the sites.

Fifteen of the 57 detected VOCs had detection frequencies greater than or equal to 10 percent, and toluene and chloroform had detection frequencies greater than 50 percent. The 15 most frequently detected compounds (table 6; fig. 13) included 5 gasoline hydrocarbons, 1 trihalomethane, 1 gasoline oxygenate, and 8 solvents. No refrigerants, fumigants, or organic synthesis compounds were detected in 10 percent or more of the samples.

The concentrations of the 15 most frequently detected VOCs are shown in figure 14. Collectively, the concentrations for these VOCs ranged over almost five orders of magnitude. Concentrations ranged over at least 2 orders of magnitude for most of the 15 VOCs.

Considering all samples, including those with nondetections (censored values), median concentrations of toluene (0.04 µg/L) and chloroform (0.02 µg/L), the two most frequently detected compounds, were equal to or greater than the assessment level of 0.02 µg/L. The remaining compounds had median concentrations less than the assessment level of 0.02 µg/L when all samples were considered (table 6); these censored median concentrations are shown as 0.02 µg/L on figure 14). Medians of concentrations greater than or equal to the assessment level (referred to as median concentrations of the detections) for the 15 most frequently detected VOCs ranged from 0.03 µg/L for four compounds to 3.9 µg/L for acetone. Most median concentrations of detections were less than or equal to 0.10 µg/L, with the exceptions of those for MTBE (0.24 µg/L), acetone (3.9 µg/L), and methyl isobutyl ketone (0.2 µg/L).

The detection frequencies (contingency table $\chi^2 = 366.8698$, DF = 1, p-value = 0) and total concentrations of MTBE were statistically different between the low and high MTBE-use areas of the United States (Wilcoxon rank-sum $Z = 21.1983$, one-sided p-value = 0), with more frequent detections and larger MTBE concentrations in high MTBE-use areas than in low MTBE-use areas (fig. 15). MTBE was detected in 18 percent of samples from low MTBE-use areas and in 86 percent of samples from high MTBE-use areas. The median MTBE concentrations were 0.09 µg/L and 0.33 µg/L in low and high MTBE-use areas, respectively. Also, the MTBE concentrations in high MTBE-use areas had a larger range of concentrations than in low MTBE-use areas.

# Occurrence Patterns of Volatile Organic Compounds by Streamflow Pentile

Many studies have shown that water quality in streams varies with streamflow condition (for example, low flow compared to high flow; Whitfield and Schreier, 1981; Sanders and others, 1983). This section describes the overall patterns of occurrence for VOCs in urban streams stratified into the five streamflow pentiles. The 869 samples from the 37 sites were stratified into five streamflow pentiles (less than 20, 20 to less than 40, 40 to less than 60, 60 to less than 80, and greater than or equal to 80 percent of estimated long-term streamflow statistics) for comparison of the occurrence of VOCs. All of the samples for 37 sites were considered as a group. Occurrence for one or more VOCs, VOC groups, and individual VOCs at all sites is presented.

## One or More Volatile Organic Compounds

The detection frequency of one or more VOCs by streamflow pentile is summarized in table 7 and figure 16. The detection frequencies of one or more VOCs were not significantly different (contingency table $\chi^2 = 0.5722$, DF = 4, p-value = 0.9661) and did not vary markedly among the pentiles of streamflow (fig. 16). Detection frequencies ranged from 96.7 percent in the fifth pentile (highest flows) to 97.7 percent in the second pentile (fig. 16).

The median total VOC concentrations in samples for each of the streamflow pentiles were 0.39, 1.0, 0.49, 0.45, and 0.81 µg/L for the first, second, third, fourth, and fifth pentiles, respectively (table 7). The total VOC concentrations were statistically different (Kruskal-Wallis $\chi^2 = 17.6145$, DF = 4, p-value = 0.0015) between the streamflow pentiles. The distribution of the concentrations in each streamflow pentile is shown in figure 17. The second streamflow pentile (20 to less than 40 percent of streamflow) had the largest total VOC concentrations for about 48 percent of the samples, and the fifth pentile (highest streamflow) had the largest total VOC concentrations for about 52 percent of the samples. The largest total VOC concentration (698 µg/L) was from the second streamflow pentile.

The numbers of VOCs detected in samples were statistically different among the streamflow pentiles (Kruskal-Wallis $\chi^2 = 12.4974$, DF = 4, p-value = 0.014). The total number of VOC detections and median number of VOCs reported per sample were highest in the fifth pentile (1,657 VOC detections and 6 VOCs per sample; table 7). The lowest total number of VOC detections and median number of VOCs were in the first pentile (554 VOC detections and 3 VOCs per sample). The first and fourth pentiles had a maximum of 16 VOCs present

**Table 6.** Summary of the detection frequencies and concentrations of volatile organic compounds at an assessment level of 0.02 microgram per liter, 1995–2003, listed in order of decreasing detection frequency.

[VOC, volatile organic compound; <, less than; ND, not detected; E, estimated]

| Compound name | VOC group | Number of sites | Number of samples | Number of samples with detections | Detection frequency (percent) | Statistical summary for concentrations including non-detections (micrograms per liter) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Minimum | 25th percentile | Median | 75th percentile | Maximum |
| Toluene | Gasoline hydrocarbon | 37 | 867 | 648 | 75 | <0.04 | <0.04 | 0.04 | 0.09 | 11 |
| Chloroform | Trihalomethane (THM) | 37 | 869 | 480 | 55 | <.02 | <.02 | .02 | .04 | 1.9 |
| Methyl *tert*-butyl ether | Gasoline oxygenate | 37 | 869 | 348 | 40 | <.11 | <.11 | <.11 | .15 | 44 |
| Trichloroethene | Solvent | 37 | 869 | 299 | 34 | <.04 | <.04 | <.04 | .05 | 1.5 |
| Perchloroethene | Solvent | 37 | 869 | 297 | 34 | <.03 | <.03 | <.03 | .04 | 1.1 |
| *cis*-1,2-Dichloroethene | Solvent | 37 | 869 | 294 | 34 | <.02 | <.02 | <.02 | .04 | 7.6 |
| Acetone | Solvent | 36 | 856 | 261 | 30 | <4.9 | <4.9 | <4.9 | 1.7 | 698 |
| *m*- and *p*-Xylene | Gasoline hydrocarbon | 36 | 856 | 239 | 28 | <.06 | <.06 | <.06 | E.02 | .69 |
| Benzene | Gasoline hydrocarbon | 37 | 869 | 194 | 22 | <.02 | <.02 | <.02 | <.02 | .21 |
| Chloromethane | Solvent | 37 | 868 | 128 | 15 | <.17 | <.17 | <.17 | <.17 | .30 |
| 1,2,4-Trimethylbenzene | Gasoline hydrocarbon | 37 | 869 | 108 | 12 | <.06 | <.06 | <.06 | <.06 | .99 |
| *o*-Xylene | Gasoline hydrocarbon | 36 | 856 | 97 | 11 | <.04 | <.04 | <.04 | <.04 | .36 |
| Dichloromethane | Solvent | 37 | 869 | 95 | 11 | <.06 | <.06 | <.06 | <.06 | 1.4 |
| 1,1,1-Trichloroethane | Solvent | 37 | 869 | 94 | 11 | <.03 | <.03 | <.03 | <.03 | 1.3 |
| Methyl isobutyl ketone | Solvent | 36 | 856 | 82 | 10 | <.37 | <.37 | <.37 | <.37 | 1.5 |
| Carbon disulfide | Organic synthesis compound | 36 | 856 | 81 | 9.5 | <.04 | <.04 | <.04 | <.04 | .20 |
| Methyl ethyl ketone | Solvent | 36 | 855 | 78 | 9.1 | <1.6 | <1.6 | <1.6 | <1.6 | 5.7 |
| Bromodichloromethane | Trihalomethane (THM) | 37 | 869 | 77 | 8.9 | <.03 | <.03 | <.03 | <.03 | .88 |
| 4-Isopropyltoluene | Gasoline hydrocarbon | 37 | 869 | 74 | 8.5 | <.07 | <.07 | <.07 | <.07 | 2.1 |
| 1,1-Dichloroethane | Solvent | 37 | 869 | 66 | 7.6 | <.03 | <.03 | <.03 | <.03 | .16 |
| Ethylbenzene | Gasoline hydrocarbon | 37 | 869 | 60 | 6.9 | <.03 | <.03 | <.03 | <.03 | .13 |
| Chlorobenzene | Solvent | 37 | 869 | 46 | 5.3 | <.03 | <.03 | <.03 | <.03 | .37 |
| 1,4-Dichlorobenzene | Fumigant | 37 | 868 | 45 | 5.2 | <.03 | <.03 | <.03 | <.03 | .26 |
| *tert*-Amyl methyl ether | Gasoline oxygenate | 36 | 856 | 44 | 5.1 | <.08 | <.08 | <.08 | <.08 | .17 |
| Naphthalene | Gasoline hydrocarbon | 37 | 869 | 38 | 4.4 | <.25 | <.25 | <.25 | <.25 | .30 |
| 1,1-Dichloroethene | Organic synthesis compound | 37 | 869 | 31 | 3.6 | <.02 | <.02 | <.02 | <.02 | .06 |

**Table 6.** Summary of the detection frequencies and concentrations of volatile organic compounds at an assessment level of 0.02 microgram per liter, 1995–2003, listed in order of decreasing detection frequency.—Continued

[VOC, volatile organic compound; <, less than; ND, not detected; E, estimated]

| Compound name | VOC group | Number of sites | Number of samples | Number of samples with detections | Detection frequency (percent) | Statistical summary for concentrations including non-detections (micrograms per liter) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Minimum | 25th percentile | Median | 75th percentile | Maximum |
| Dibromochloromethane | Trihalomethane (THM) | 37 | 868 | 29 | 3.3 | <0.1 | <0.1 | <0.1 | <0.1 | 0.50 |
| 1,2,3-Trimethylbenzene | Gasoline hydrocarbon | 36 | 856 | 28 | 3.3 | <.06 | <.06 | <.06 | <.06 | .22 |
| Styrene | Gasoline hydrocarbon | 37 | 869 | 27 | 3.1 | <.04 | <.04 | <.04 | <.04 | .10 |
| Trichlorotrifluoroethane | Refrigerant | 37 | 869 | 27 | 3.1 | <.03 | <.03 | <.03 | <.03 | .15 |
| 1,3,5-Trimethylbenzene | Gasoline hydrocarbon | 37 | 869 | 24 | 2.8 | <.04 | <.04 | <.04 | <.04 | .25 |
| 2-Ethyltoluene | Gasoline hydrocarbon | 36 | 856 | 22 | 2.6 | <.06 | <.06 | <.06 | <.06 | .18 |
| Tetrahydrofuran | Solvent | 36 | 856 | 22 | 2.6 | <1.2 | <1.2 | <1.2 | <1.2 | 3.3 |
| 1,2,3,5-Tetramethylbenzene | Gasoline hydrocarbon | 36 | 856 | 14 | 1.6 | <.14 | <.14 | <.14 | <.14 | .14 |
| Chloroethane | Solvent | 37 | 869 | 14 | 1.6 | <.12 | <.12 | <.12 | <.12 | .10 |
| Dichlorodifluoromethane | Refrigerant | 37 | 869 | 11 | 1.3 | <.1 | <.1 | <.1 | <.1 | .58 |
| Tetrachloromethane | Solvent | 37 | 869 | 11 | 1.3 | <.06 | <.06 | <.06 | <.06 | .04 |
| Diisopropyl ether | Gasoline oxygenate | 35 | 763 | 9 | 1.2 | <.1 | <.1 | <.1 | <.1 | .05 |
| Bromoform | Trihalomethane (THM) | 37 | 869 | 10 | 1.2 | <.06 | <.06 | <.06 | <.06 | .54 |
| *n*-Propylbenzene | Solvent | 37 | 869 | 10 | 1.2 | <.04 | <.04 | <.04 | <.04 | .08 |
| Diethyl ether | Solvent | 36 | 856 | 9 | 1.1 | <.08 | <.08 | <.08 | <.08 | .43 |
| 1,2,3,4-Tetramethylbenzene | Gasoline hydrocarbon | 36 | 856 | 9 | 1.1 | <.14 | <.14 | <.14 | <.14 | .35 |
| Vinyl chloride | Organic synthesis compound | 37 | 869 | 9 | 1.0 | <.06 | <.06 | <.06 | <.06 | .94 |
| Acrolien | Organic synthesis compound | 13 | 308 | 3 | .97 | <1.5 | <1.5 | <1.5 | <1.5 | 3.4 |
| *trans*-1,2-Dichloroethene | Solvent | 37 | 869 | 6 | .69 | <.03 | <.03 | <.03 | <.03 | 3.5 |
| *n*-Butylbenzene | Gasoline hydrocarbon | 37 | 869 | 5 | .58 | <.12 | <.12 | <.12 | <.12 | E.04 |
| 2-Chlorotoluene | Solvent | 37 | 869 | 4 | .46 | <.03 | <.03 | <.03 | <.03 | .07 |
| 1,2-Dichloropropane | Fumigant | 37 | 869 | 2 | .23 | <.03 | <.03 | <.03 | <.03 | .03 |
| 1,1,2,2-Tetrachloroethane | Solvent | 37 | 869 | 2 | .23 | <.09 | <.09 | <.09 | <.09 | .08 |
| Trichlorofluoromethane | Refrigerant | 37 | 869 | 2 | .23 | <.03 | <.03 | <.03 | <.03 | .08 |
| Ethyl *tert*-butyl ether | Gasoline oxygenate | 36 | 856 | 1 | .12 | <.05 | <.05 | <.05 | <.05 | .02 |

**Table 6.** Summary of the detection frequencies and concentrations of volatile organic compounds at an assessment level of 0.02 microgram per liter, 1995–2003, listed in order of decreasing detection frequency.—Continued

[VOC, volatile organic compound; <, less than; ND, not detected; E, estimated]

| Compound name | VOC group | Number of sites | Number of samples | Number of samples with detections | Detection frequency (percent) | Statistical summary for concentrations including non-detections (micrograms per liter) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Minimum | 25th percentile | Median | 75th percentile | Maximum |
| *sec*-Butylbenzene | Gasoline hydrocarbon | 37 | 869 | 1 | 0.12 | <0.03 | <0.03 | <0.03 | <0.03 | 0.02 |
| Dibromochloropropane | Fumigant | 37 | 869 | 1 | .12 | <.21 | <.21 | <.21 | <.21 | .09 |
| 1,2-Dichlorobenzene | Solvent | 37 | 869 | 1 | .12 | <.05 | <.05 | <.05 | <.05 | .18 |
| 1,3-Dichlorobenzene | Solvent | 37 | 869 | 1 | .12 | <.03 | <.03 | <.03 | <.03 | .02 |
| 1,2-Dichloroethane | Solvent | 37 | 869 | 1 | .12 | <.13 | <.13 | <.13 | <.13 | E.03 |
| Isopropylbenzene | Gasoline hydrocarbon | 37 | 869 | 1 | .12 | <.03 | <.03 | <.03 | <.03 | .03 |
| Acrylonitrile | Organic synthesis compound | 36 | 858 | 0 | ND | <1.2 | <1.2 | <1.2 | <1.2 | <1.2 |
| Bromobenzene | Solvent | 37 | 869 | 0 | ND | <.03 | <.03 | <.03 | <.03 | <.03 |
| Bromochloromethane | Organic synthesis compound | 37 | 869 | 0 | ND | <.04 | <.04 | <.04 | <.04 | <.04 |
| Bromomethane | Fumigant | 37 | 869 | 0 | ND | <.15 | <.15 | <.15 | <.15 | <.15 |
| *tert*-Butylbenzene | Gasoline hydrocarbon | 37 | 869 | 0 | ND | <.05 | <.05 | <.05 | <.05 | <.05 |
| 3-Chloro-1-propene | Organic synthesis compound | 36 | 856 | 0 | ND | <.07 | <.07 | <.07 | <.07 | <.07 |
| 4-Chlorotoluene | Solvent | 37 | 869 | 0 | ND | <.05 | <.05 | <.05 | <.05 | <.05 |
| Dibromomethane | Solvent | 37 | 869 | 0 | ND | <.05 | <.05 | <.05 | <.05 | <.05 |
| *trans*-1,4-Dichloro-2-butene | Organic synthesis compound | 36 | 856 | 0 | ND | <.7 | <.7 | <.7 | <.7 | <.7 |
| 1,3-Dichloropropane | Organic synthesis compound | 37 | 869 | 0 | ND | <.06 | <.06 | <.06 | <.06 | <.06 |
| 2,2-Dichloropropane | Organic synthesis compound | 37 | 869 | 0 | ND | <.05 | <.05 | <.05 | <.05 | <.05 |
| 1,1-Dichloropropene | Organic synthesis compound | 37 | 869 | 0 | ND | <.03 | <.03 | <.03 | <.03 | <.03 |
| *cis*-1,3-Dichloropropene | Fumigant | 37 | 869 | 0 | ND | <.05 | <.05 | <.05 | <.05 | <.05 |
| *trans*-1,3-Dichloropropene | Fumigant | 37 | 869 | 0 | ND | <.09 | <.09 | <.09 | <.09 | <.09 |
| Ethylene dibromide | Fumigant | 37 | 869 | 0 | ND | <.04 | <.04 | <.04 | <.04 | <.04 |
| Ethyl methacrylate | Organic synthesis compound | 36 | 856 | 0 | ND | <.18 | <.18 | <.18 | <.18 | <.18 |

**Table 6.** Summary of the detection frequencies and concentrations of volatile organic compounds at an assessment level of 0.02 microgram per liter, 1995–2003, listed in order of decreasing detection frequency.—Continued

[VOC, volatile organic compound; <, less than; ND, not detected; E, estimated]

| Compound name | VOC group | Number of sites | Number of samples | Number of samples with detections | Detection frequency (percent) | Statistical summary for concentrations including non-detections (micrograms per liter) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Minimum | 25th percentile | Median | 75th percentile | Maximum |
| Hexachlorobutadiene | Organic synthesis compound | 37 | 869 | 0 | ND | <0.14 | <0.14 | <0.14 | <0.14 | <0.14 |
| Hexachloroethane | Solvent | 36 | 857 | 0 | ND | <.14 | <.14 | <.14 | <.14 | <.14 |
| Iodomethane | Organic synthesis compound | 36 | 856 | 0 | ND | <.08 | <.08 | <.08 | <.08 | <.08 |
| Methyl acrylate | Organic synthesis compound | 36 | 856 | 0 | ND | <.6 | <.6 | <.6 | <.6 | <.6 |
| Methyl acrylonitrile | Organic synthesis compound | 36 | 856 | 0 | ND | <.6 | <.6 | <.6 | <.6 | <.6 |
| Methyl butyl ketone | Solvent | 36 | 856 | 0 | ND | <.7 | <.7 | <.7 | <.7 | <.7 |
| Methyl methacrylate | Organic synthesis compound | 36 | 856 | 0 | ND | <.35 | <.35 | <.35 | <.35 | <.35 |
| 1,1,1,2-Tetrachloroethane | Solvent | 37 | 869 | 0 | ND | <.03 | <.03 | <.03 | <.03 | <.03 |
| 1,2,3-Trichlorobenzene | Organic synthesis compound | 37 | 869 | 0 | ND | <.27 | <.27 | <.27 | <.27 | <.27 |
| 1,2,4-Trichlorobenzene | Solvent | 37 | 869 | 0 | ND | <.07 | <.07 | <.07 | <.07 | <.07 |
| 1,1,2-Trichloroethane | Solvent | 37 | 869 | 0 | ND | <.06 | <.06 | <.06 | <.06 | <.06 |
| 1,2,3-Trichloropropane | Fumigant | 37 | 869 | 0 | ND | <.07 | <.07 | <.07 | <.07 | <.07 |
| Vinyl acetate | Organic synthesis compound | 12 | 201 | 0 | ND | <5. | <5. | <5. | <5. | <5. |
| Vinyl bromide | Organic synthesis compound | 36 | 856 | 0 | ND | <.1 | <.1 | <.1 | <.1 | <.1 |

in samples, the second and third pentiles had a maximum of 18 VOCs present, and the fifth pentile had a maximum of 27 VOCs present.

Two or more VOCs were detected in more than 80 percent of samples in each of the five pentiles. The fifth pentile had the highest detection frequency (86.6 percent) of two or more VOCs, followed by the second, first, and fourth streamflow pentiles. The third streamflow pentile (40 to less than 60 percent of streamflow) had the smallest detection frequency (82 percent) of two or more VOCs (fig. 18).

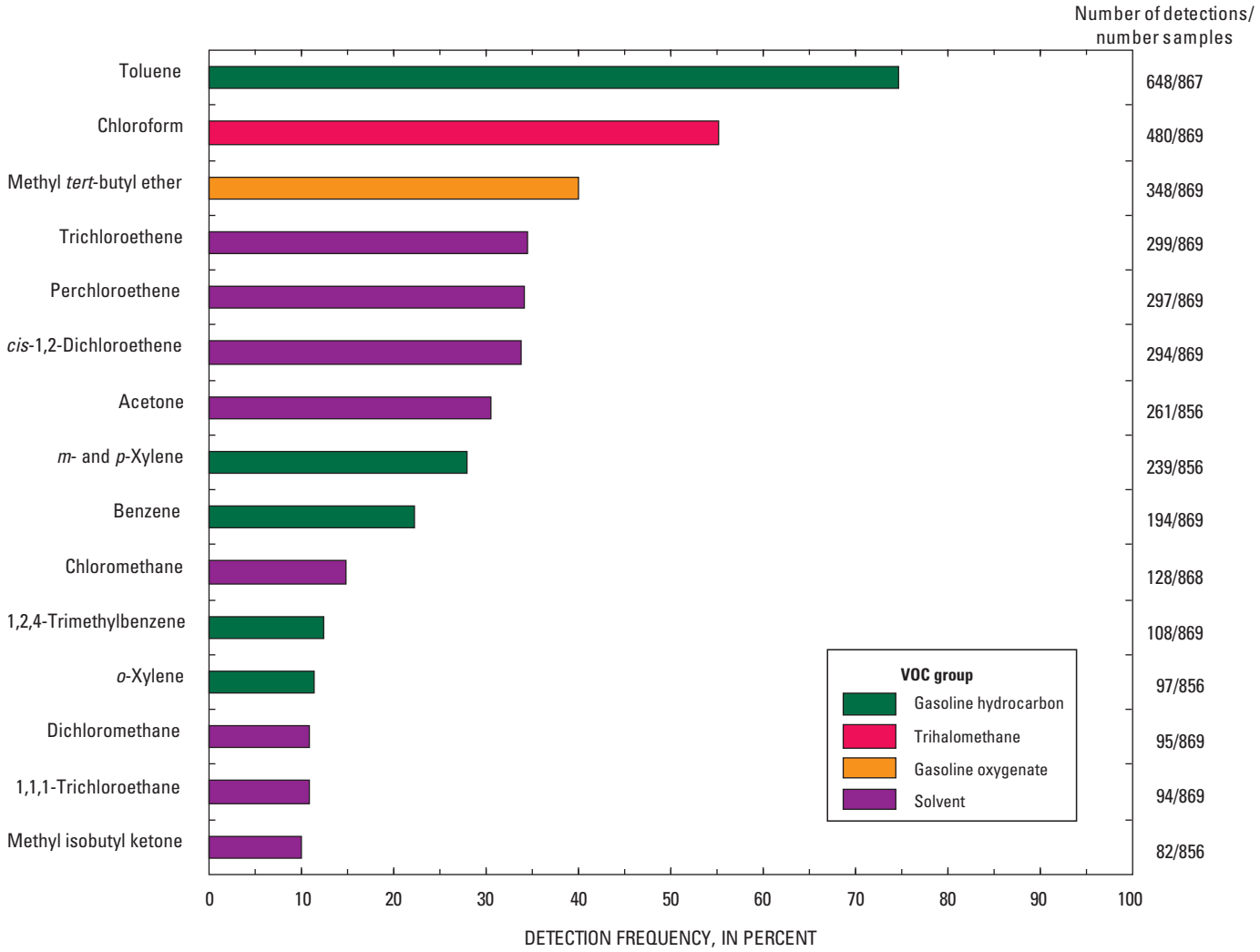


**Figure 13.** Detection frequencies of the 15 most frequently detected volatile organic compounds (VOCs) in urban stream samples at an assessment level of 0.02 microgram per liter, 1995–2003.

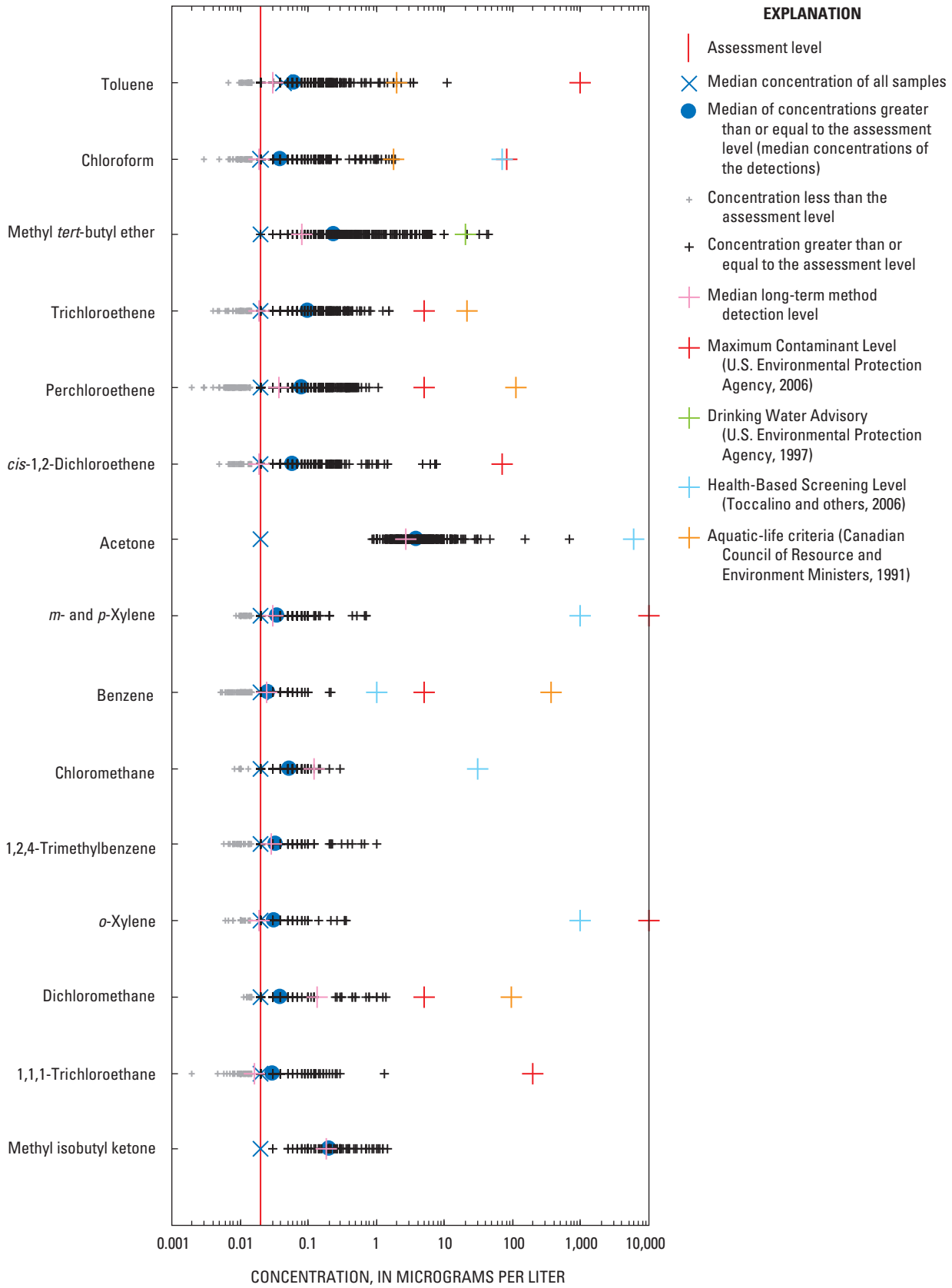


**Figure 14.** Concentrations of the 15 most frequently detected volatile organic compounds in urban stream samples, 1995–2003.

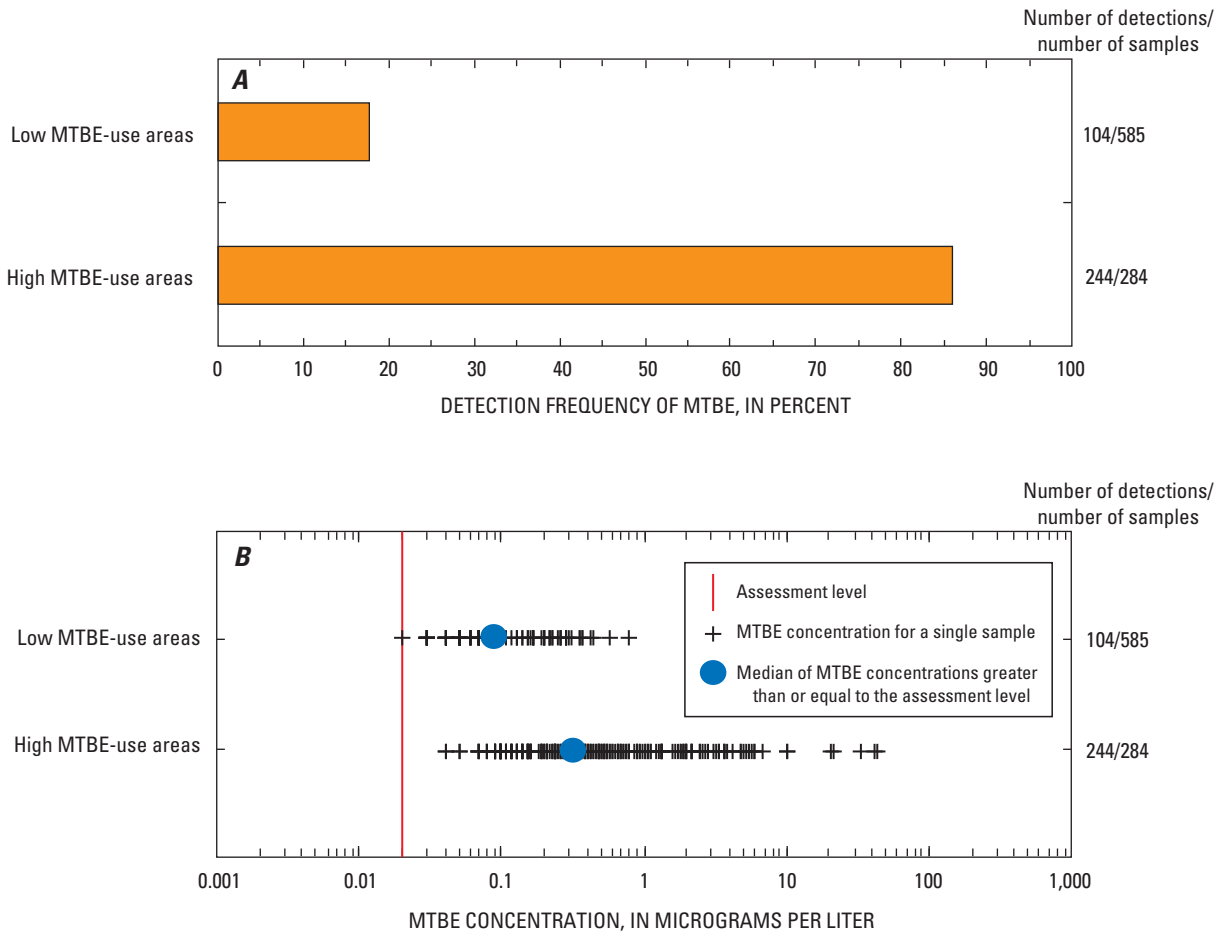


**Figure 15.** Relation between (*A*) detection frequencies, and (*B*) concentrations of methyl *tert*-butyl ether (MTBE) in urban stream samples in low and high MTBE-use areas of the United States at an assessment level of 0.02 microgram per liter, 1995–2003.

**Table 7.** Detection frequencies of one or more volatile organic compounds (VOCs) at all sites, total number of VOC detections, median number of VOCs detected, maximum number of VOCs detected, and median total concentration in urban stream samples by streamflow pentile at an assessment level of 0.02 microgram per liter, 1995–2003.

| Streamflow pentile | | Number of samples | Number of samples with detected VOCs | Detection frequency (percent) | Total number of VOCs detected in all samples | Median number of VOCs detected in samples | Maximum number of VOCs detected in samples | Median total concentration (micrograms per liter) |
|---|---|---|---|---|---|---|---|---|
| Low flow | 1 | 124 | 121 | 97.6 | 554 | 3 | 16 | 0.39 |
| | 2 | 177 | 173 | 97.7 | 921 | 4 | 18 | 1.0 |
| | 3 | 153 | 148 | 96.7 | 750 | 4 | 18 | .49 |
| | 4 | 140 | 136 | 97.1 | 738 | 4 | 16 | .45 |
| High flow | 5 | 275 | 266 | 96.7 | 1,657 | 6 | 27 | .81 |

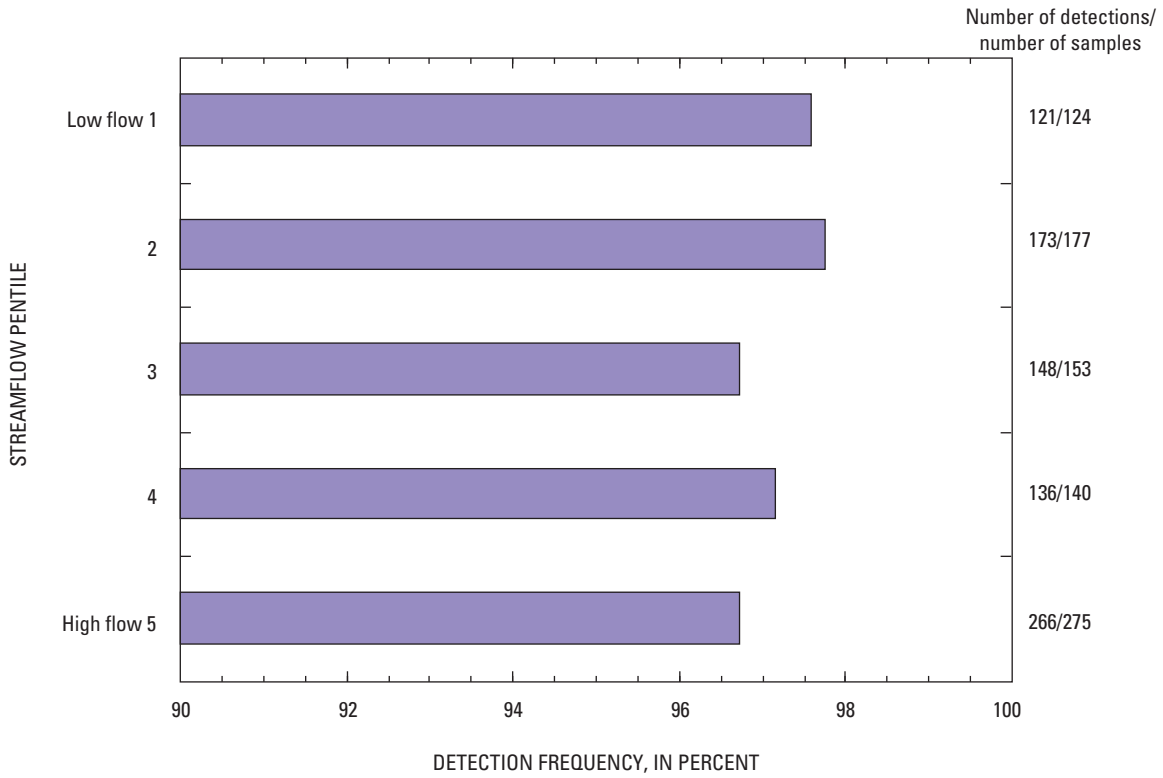


**Figure 16.** Detection frequencies of one or more volatile organic compounds by streamflow pentile in urban stream samples at an assessment level of 0.02 microgram per liter, 1995–2003.

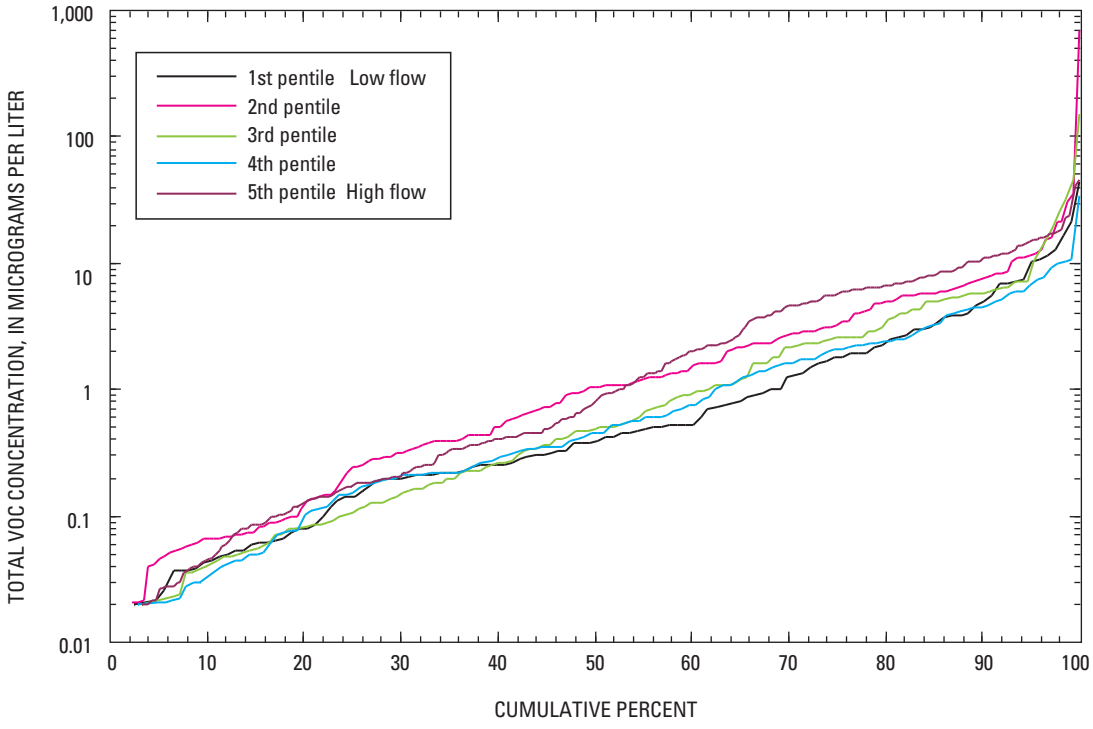


**Figure 17.** Cumulative distribution of total concentrations of volatile organic compound (VOC) concentrations in 869 samples from 37 urban stream sites by streamflow pentile at an assessment level of 0.02 microgram per liter, 1995–2003.

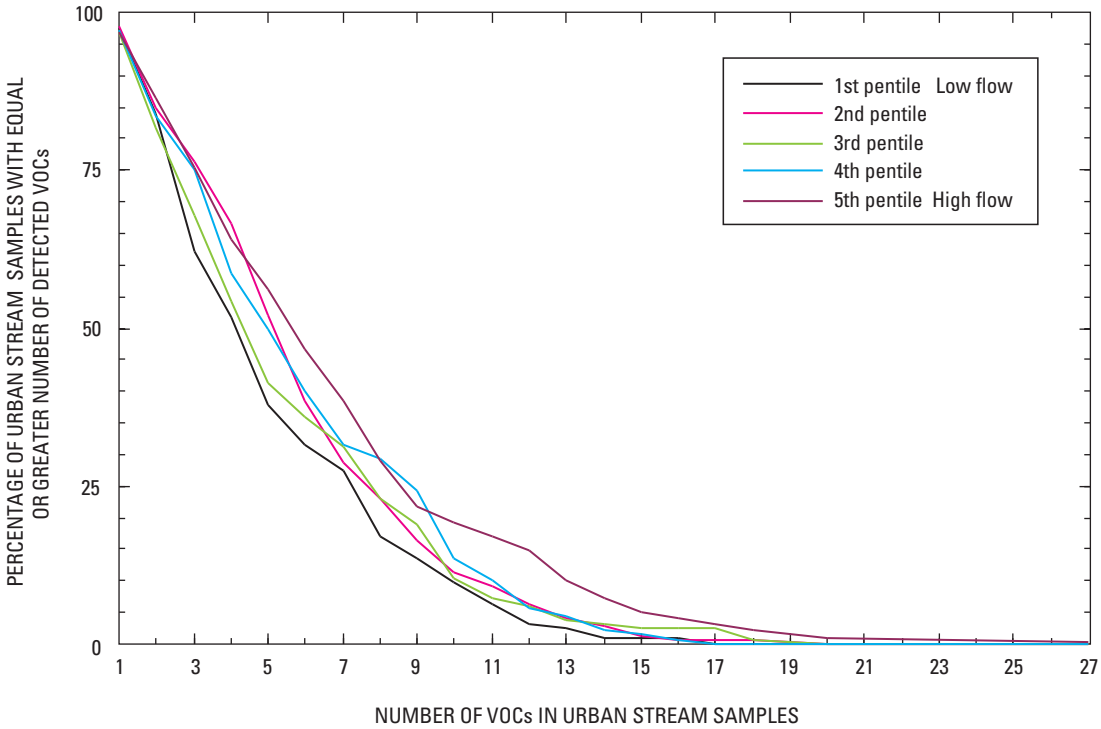


**Figure 18.** Relation between the percentage of urban stream samples and the number of volatile organic compounds (VOCs) detected by streamflow pentile at an assessment level of 0.02 microgram per liter, 1995–2003.

## Volatile Organic Compound Groups

Gasoline hydrocarbons, solvents, THMs, and gasoline oxygenates occurred frequently in all streamflow pentiles, in contrast to the organic synthesis compounds, fumigants, and refrigerants that occurred less frequently in urban streams under all streamflow conditions (fig. 19). The detection frequencies of the VOC groups by streamflow pentiles were from statistically different distributions (contingency table $\chi^2 = 31.5659$, DF = 28, p-value = 0.2925). Furthermore, gasoline hydrocarbons were the most frequently detected VOC group in the first, second, third, and fifth streamflow pentiles, whereas solvents were the most frequently detected VOC group in the fourth streamflow pentile.

Within each individual VOC group, gasoline hydrocarbons occurred most frequently in the first and fifth streamflow pentiles and were from statistically different distributions in all pentiles (contingency table $\chi^2 = 2.0672$, DF = 4, p-value = 0.7234). The solvents occurred most frequently in the fifth streamflow pentile and were from statistically different distributions in all pentiles (contingency table $\chi^2 = 1.321$, DF = 4, p-value = 0.8578). THMs occurred most frequently in the fourth pentile and were from statistically different distributions in all pentiles (contingency table $\chi^2 = 2.2276$, DF = 4, p-value = 0.694). Gasoline oxygenates occurred most frequently in the second pentile and were from statistically different distributions in all pentiles (contingency table $\chi^2 = 7.5864$, DF = 4, p-value = 0.108). Organic synthesis compounds occurred most frequently in the fifth pentile and were from statistically different distributions in all pentiles (contingency table $\chi^2 = 6.9012$, DF = 4, p-value = 0.1412). Fumigants were from statistically different distributions in all pentiles (contingency table $\chi^2 = 3.2795$, DF = 4, p-value = 0.5122), and refrigerants were from statistically different distributions in all pentiles (contingency table $\chi^2 = 0.8781$, DF = 4, p-value = 0.9277).

Three general patterns of occurrence were evident within the VOC groups: (1) a general decrease in the detection frequency of gasoline hydrocarbons, THMs, and gasoline oxygenates was observed as the streamflow increases; (2) a general increase in the detection frequency of solvents and organic synthesis compounds was observed as the streamflow increases; and (3) no general pattern was observed for the fumigants and refrigerants. The detection frequency of the gasoline hydrocarbons, in general, decreased as flow increased until the fourth pentile, then increased from 68 to 83 percent from the fourth to fifth pentile. The detection frequency of the solvents increased as the streamflow increased from the first to the fifth pentile with a large increase (61 to 71 percent) between the first and second pentiles, then a small increase (71 to 74 percent) between the third and fourth pentiles. The detection frequency of the THMs generally decreased as the

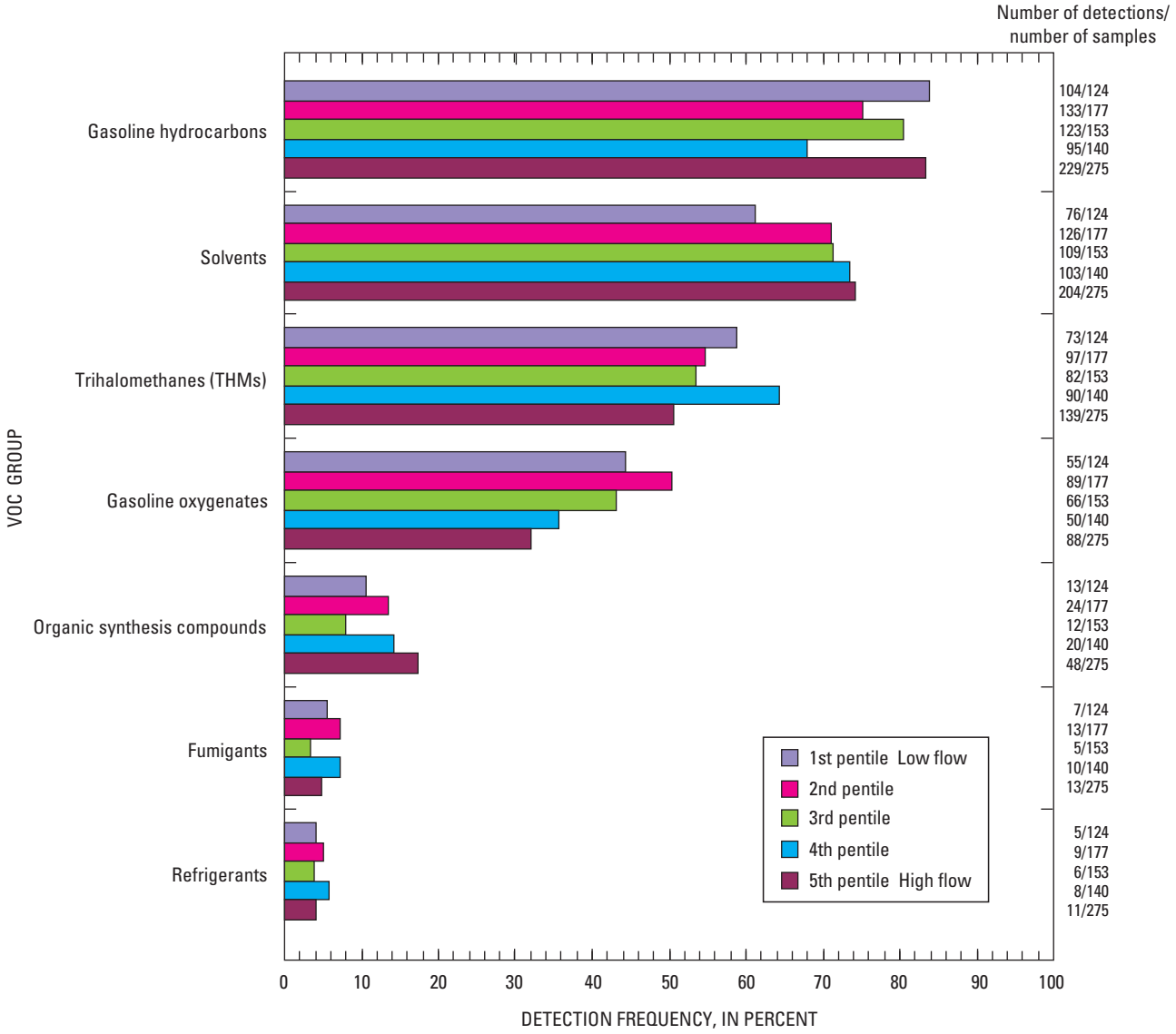


**Figure 19.** Detection frequencies of seven volatile organic compound (VOC) groups in urban stream samples by streamflow pentile at an assessment level of 0.02 microgram per liter, 1995–2003.

streamflow increased with the exception of the fourth pentile, which had the highest detection frequency of 64 percent. The detection frequency of the gasoline oxygenates also, in general, decreased as the streamflow increased with the exception of the second pentile, which had the largest detection frequency of 50 percent. The detection frequency of the organic synthesis compounds generally increased as the streamflow increased. The detection frequencies of the fumigants and refrigerants did not differ markedly as the streamflow increased.

Median total concentrations of detections for gasoline hydrocarbons, solvents, gasoline oxygenates, and organic synthesis compounds generally increased as streamflow increased. In contrast, median total concentrations of detections for THMs and fumigants generally decreased as streamflow increased. The median total concentrations of detections for refrigerants showed no pattern as streamflow increased (fig. 20).

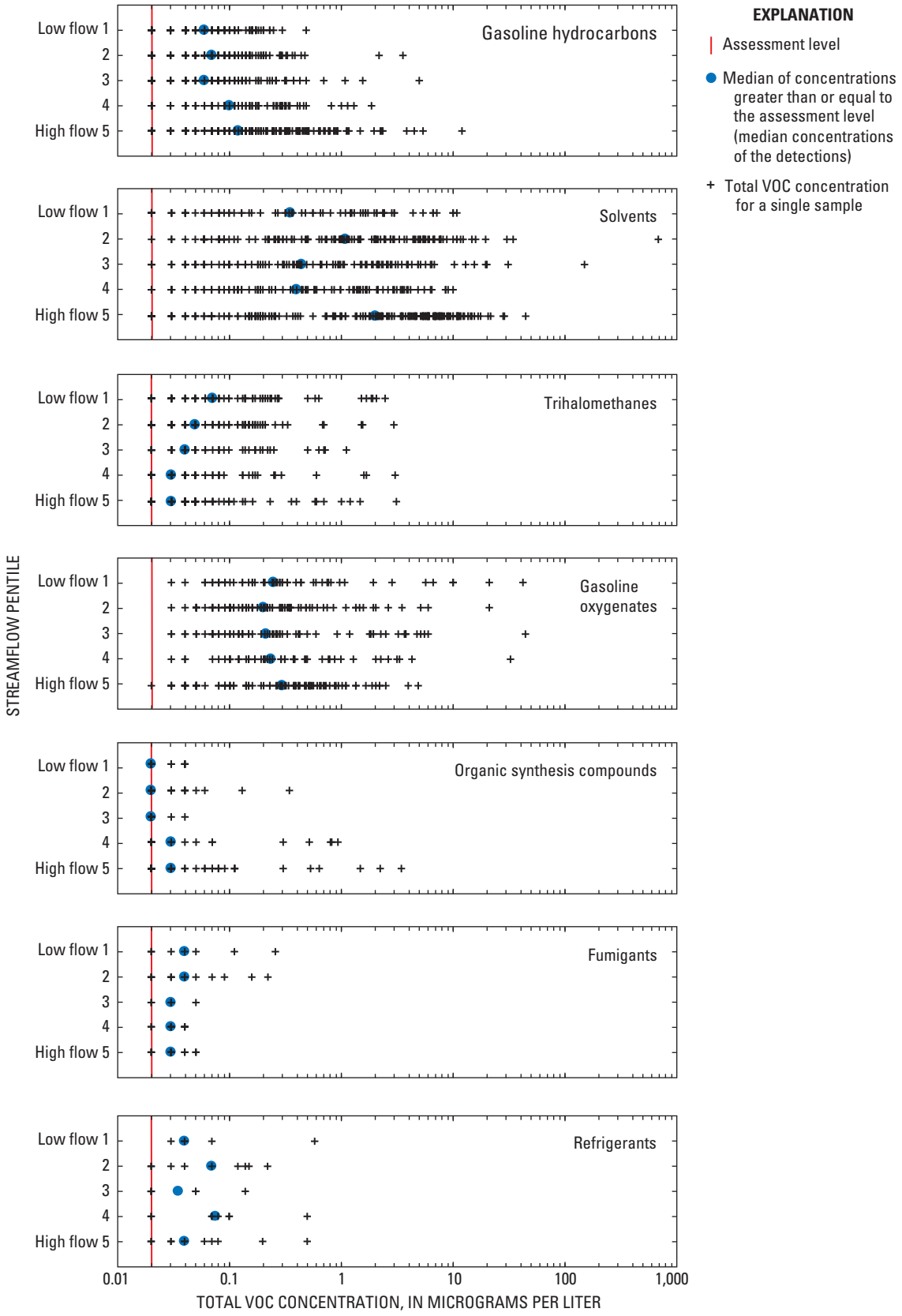


**Figure 20.** Total volatile organic compound (VOC) concentrations of the seven VOC groups in urban stream samples by streamflow pentile at an assessment level of 0.02 microgram per liter, 1995–2003.

## Individual Volatile Organic Compounds

The detection frequencies of the 15 most frequently detected VOCs grouped by streamflow pentile are shown in figure 21. Two general occurrence patterns are evident for many of the 15 compounds: (1) the detection frequency of some compounds generally decreases as streamflow increases and (2) the detection frequency generally increases as streamflow increases. The first pattern may be from VOCs primarily entering the stream from groundwater inflows or small point-source discharges that are diluted with increased streamflow. VOCs that have this general pattern include toluene, chloroform, MTBE, perchloroethene, and dichloromethane. The second pattern, compounds with increasing detection frequency as streamflow increases, also may have similar sources to the first pattern at smaller streamflow and have additional sources, such as stormwater runoff, contributing to the increased presence during larger streamflow conditions. VOCs that have this second pattern include trichloroethene, *cis*-1,2-dichloroethene, acetone, *m*- and *p*-xylene, benzene, chloromethane, 1,2,4-trimethylbenzene, *o*-xylene, and methyl isobutyl ketone.

The detection frequency of toluene generally decreased from the first to fourth pentile with a large increase from the fourth to fifth pentile. The detection frequency of chloroform generally decreased from the first to third pentile with a large increase from the third to fourth pentile, then a decrease from the fourth to fifth pentile, which is consistent with relatively stable sources (for example, contaminated groundwater entering the stream). The detection frequency of MTBE generally decreased from the first to fifth pentile with an increase from the first to second pentile. The detection frequencies of trichloroethene and *cis*-1,2-dichloroethene have similar patterns with an increase from the first to the second pentile, a small decrease to the third pentile, a small increase to the fourth pentile, and a decrease to the fifth pentile. The detection frequencies of *m*- and *p*-xylene, benzene, chloromethane, 1,2,4-trimethylbenzene, *o*-xylene, and methyl isobutyl ketone increased as the streamflow increased, which is consistent with sources associated with increased rainfall runoff (for example, parking lot and street wash-off).

The concentrations of the 15 most frequently detected VOCs grouped by streamflow pentiles are shown in figure 22. The median concentrations of detections also are shown for each streamflow pentile on the figure. In general, three concentration patterns were evident for the 15 most frequently detected VOCs: (1) increasing median concentrations of detections as streamflow increased, (2) decreasing median concentrations of detections as streamflow increased, and (3) no marked difference in median concentrations of detections as streamflow increased. Median concentrations of detections for seven of the compounds (toluene, MTBE, acetone, benzene, chloromethane, *o*-xylene, dichloromethane, and methyl isobutyl ketone) generally increased as streamflow increased from the first pentile to the fifth pentile. Median concentrations of detections for chloroform, perchloroethene, and *cis*-1,2,-dichloroethene generally decreased as streamflow increased from the first pentile to the fifth pentile. Median concentrations of detections for trichloroethene, *m*- and *p*-xylene, 1,2,4-trimethylbenzene, and 1,1,1-trichloroethane had no marked change as streamflow increased from the first pentile to the fifth pentile. Of the 15 most frequently detected compounds, acetone had the largest increase in median concentrations of detections as streamflow increased, and the largest increase occurred between the fourth and fifth pentiles. The increase in acetone concentrations as streamflow increases may be attributed to atmospheric washout and runoff from impervious areas (Lopes and others, 2000).

The detection frequency of MTBE was at least three times larger in high MTBE-use areas than in low MTBE-use areas of the United States in all streamflow pentiles (fig. 23*A*). The detection frequency of MTBE generally decreased as streamflow increased in low MTBE-use areas and slightly increased as streamflow increased in high MTBE-use areas of the United States. In each streamflow pentile, concentrations of MTBE were statistically larger (Wilcoxon rank-sum $Z > 6.8512$, one-sided p-value $<0.025$) in high MTBE-use areas than in low MTBE-use areas. In high MTBE-use areas, concentrations generally increased as streamflow increased, with the largest median concentration of detections (0.49 µg/L) in the fifth pentile (fig. 23*B*). In contrast, concentrations in low MTBE-use areas generally decreased as streamflow increased, with the smallest median concentration of detections (0.05 µg/L) in the fifth pentile.

# Occurrence Patterns of Volatile Organic Compounds by Season

The water quality of urban streams may vary with both season of the year and streamflow (base flow compared to stormflow). In addition to the VOC occurrence and concentration patterns observed by streamflow pentile, seasonal variability is expected for VOCs on the basis of prior studies (Lopes and Bender, 1998; Reiser and O'Brien, 1998; Lundgren and Lopes, 1999). This section describes the overall patterns of occurrence for VOCs in urban streams stratified by warmer (April through September) and cooler (October through March) months. The 869 samples from the 37 urban stream sites were stratified by warmer and cooler months. Occurrence of one or more VOCs, VOC groups, and individual VOCs at all sites is presented.

## One or More Volatile Organic Compounds

The detection frequency of one or more VOCs and the median number of VOCs detected in samples by warmer and cooler months and streamflow pentile are summarized in table 8. One or more VOCs were frequently detected in both warmer (96 percent of 410 samples) and cooler months (98 percent of 459 samples). The detection frequencies were from statistically different distributions (contingency table

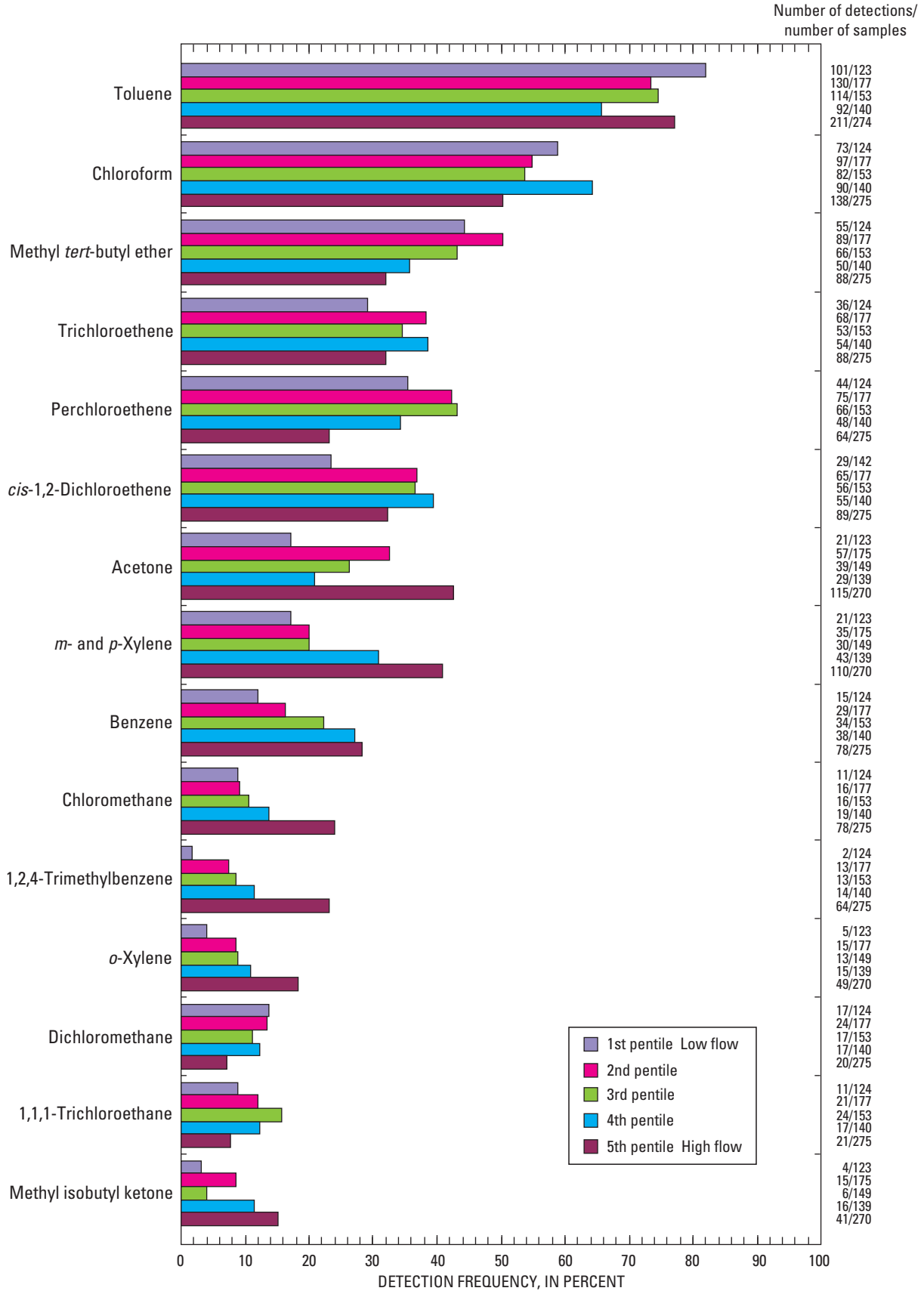


**Figure 21.** Detection frequencies of the 15 most frequently detected volatile organic compounds in urban stream samples by streamflow pentile at an assessment level of 0.02 microgram per liter, 1995–2003.

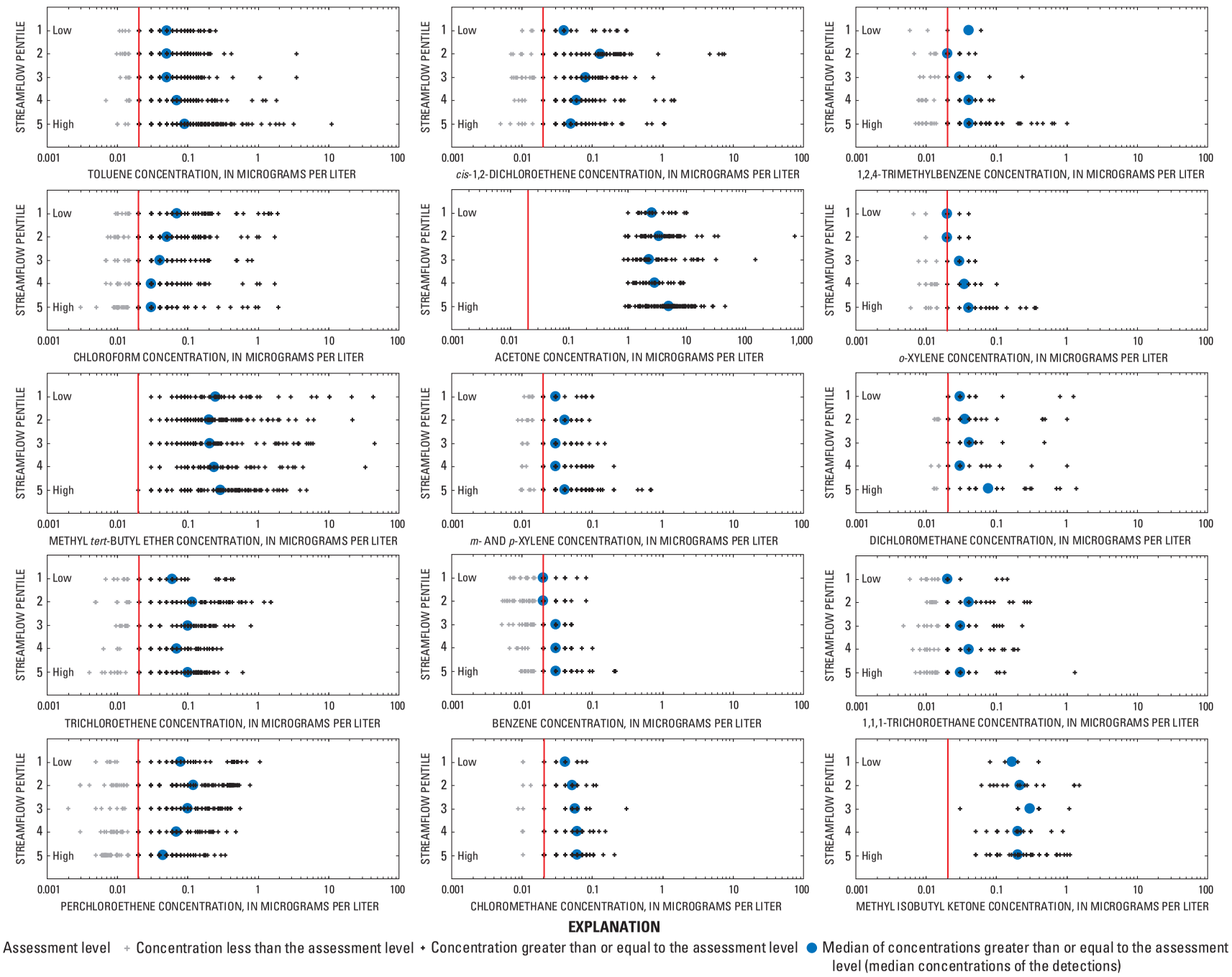


**Figure 22.** Concentrations of the 15 most frequently detected volatile organic compounds in urban stream samples by streamflow pentile, 1995–2003.

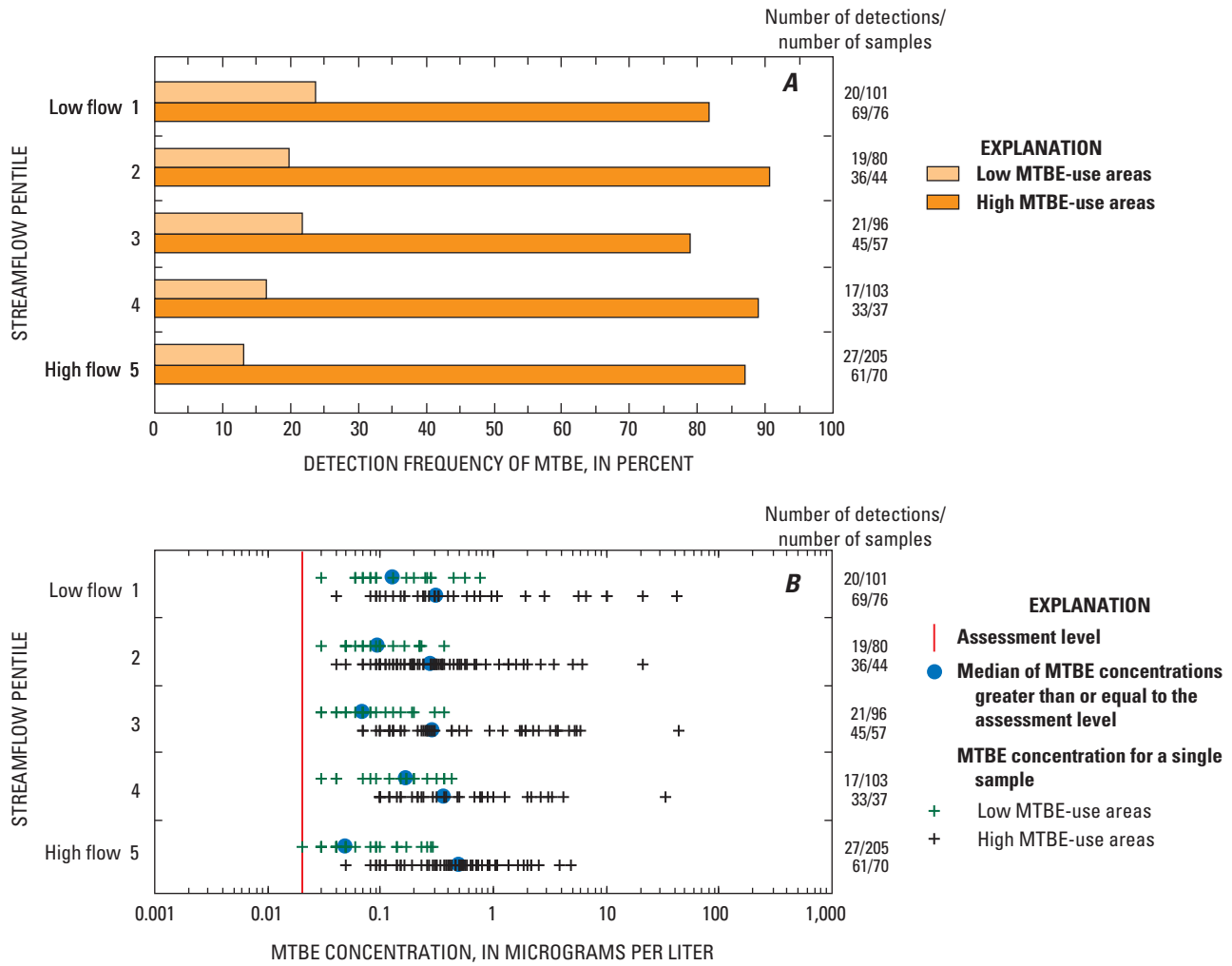


**Figure 23.** Relation between (*A*) detection frequencies, and (*B*) concentrations of methyl *tert*-butyl ether (MTBE) in urban stream samples in low and high MTBE-use areas of the United States by streamflow pentile at an assessment level of 0.02 microgram per liter, 1995–2003.

$\chi^2$ = 0.0119, DF = 1, p-value = 0.9132) between warmer and cooler months, and generally the detection frequencies were larger in cooler months.

The concentration distributions by warmer and cooler months are shown in figure 24. The median total VOC concentration (table 8) was significantly larger (Wilcoxon rank-sum $Z$ = -2.4774, one-sided p-value = 0.0066) in cooler months than in warmer months, with the median concentration of detections for cooler months (0.80 µg/L) about twice as large as the median concentration of detections for warmer months (0.41 µg/L).

The relation between the frequency and the number of VOCs detected in urban stream samples by warmer and cooler months at an assessment level of 0.02 microgram per liter is shown in figure 25. The median number of VOCs and the total number of VOCs detected in samples were statistically larger in cooler months than in warmer months (table 8; Wilcoxon rank-sum $Z$ = -4.7285, p-value = 0).

## Volatile Organic Compound Groups

In general, the detection frequency of most VOC groups was similar or larger in cooler months (October through March) than in warmer months with the exception of the THMs (fig. 26). The detection frequencies of the seven VOC groups, when analyzed individually between warmer and cooler months, were each from statistically different distributions (contingency table $\chi^2 < 3.8414$ (critical value), DF = 1, p-value > 0.05) (for example, the detection frequencies for gasoline hydrocarbons for warmer and cooler months were from statistically different distributions). Similarly, the detection frequencies of the seven VOC groups, combined into

**Table 8.** Detection frequency of one or more volatile organic compounds (VOCs) at all sites, total number of VOCs detected, median number of VOCs detected, the maximum number of VOCs detected, and median total concentration in urban stream samples in warmer and cooler months by streamflow pentile at an assessment level of 0.02 microgram per liter, 1995–2003.

| Streamflow pentile | Number of samples | Number of samples with detections | Detection frequency (percent) | Total number of VOCs detected in all samples | Median number of VOCs detected per sample | Median concentration (micrograms per liter) |
|---|---|---|---|---|---|---|
| **Warmer months (April through September)** | | | | | | |
| Low flow 1 | 71 | 69 | 97.2 | 304 | 3 | 0.30 |
| 2 | 75 | 74 | 98.7 | 337 | 4 | .73 |
| 3 | 65 | 62 | 95.4 | 235 | 3 | .31 |
| 4 | 57 | 53 | 93.0 | 237 | 3 | .26 |
| High flow 5 | 142 | 137 | 96.5 | 744 | 5 | .45 |
| **Totals** | **410** | **395** | **96.3** | **1,857** | **4** | **.41** |
| **Cooler months (October through March)** | | | | | | |
| Low flow 1 | 53 | 52 | 98.1 | 250 | 4 | 0.48 |
| 2 | 102 | 99 | 97.1 | 584 | 5 | 1.1 |
| 3 | 88 | 86 | 97.7 | 515 | 4 | .70 |
| 4 | 83 | 83 | 100 | 501 | 5 | .61 |
| High flow 5 | 133 | 129 | 97.0 | 913 | 6 | 1.1 |
| **Totals** | **459** | **449** | **97.8** | **2,763** | **5** | **.80** |

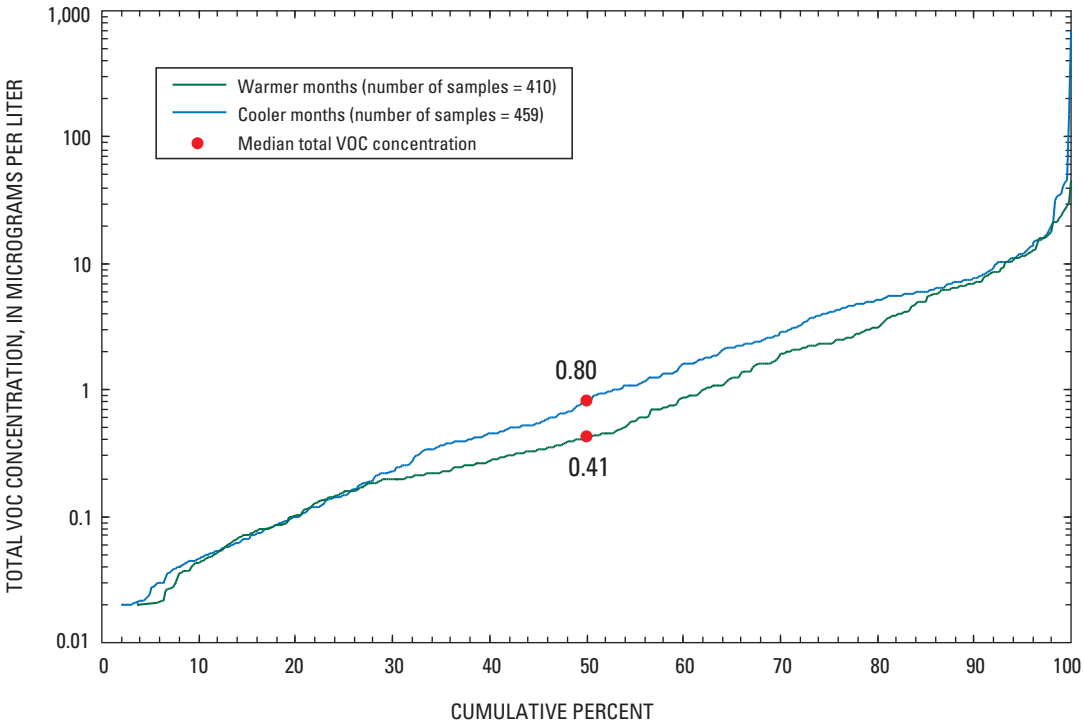


**Figure 24.** Cumulative distribution of total volatile organic compound (VOC) concentrations in 869 samples from 37 urban stream sites by warmer (April through September) and cooler (October through March) months at an assessment level of 0.02 microgram per liter, 1995–2003.

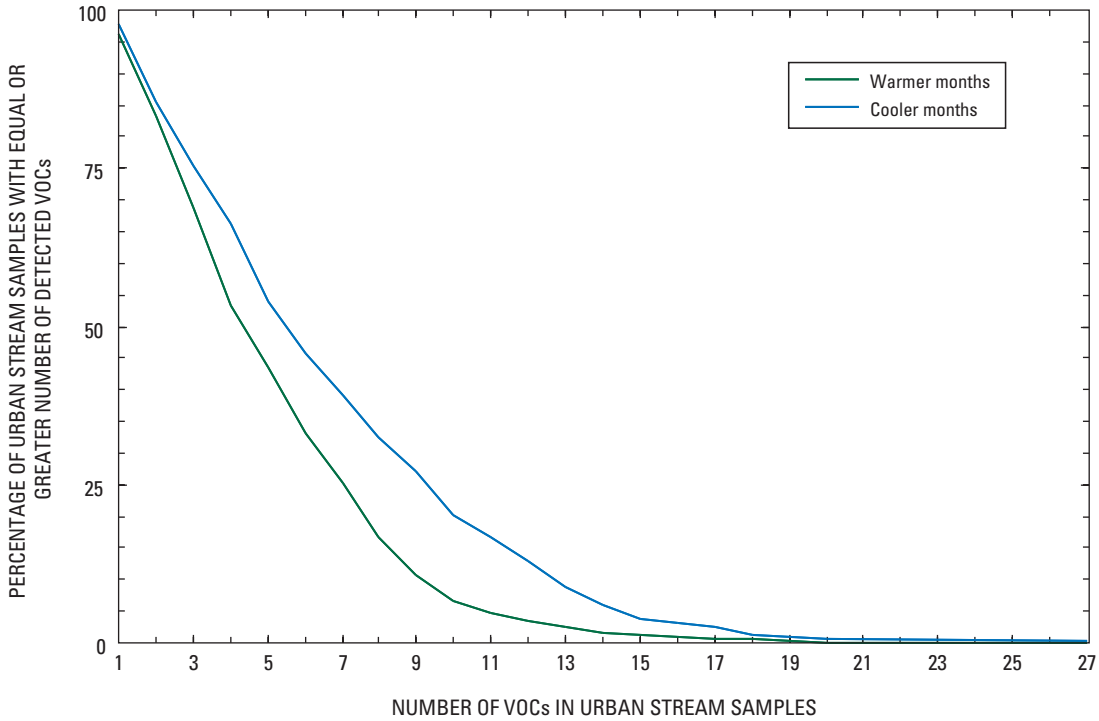


**Figure 25.** Relation between the percentage of urban stream samples and the number of volatile organic compounds (VOCs) detected by warmer (April through September) and cooler (October through March) months at an assessment level of 0.02 microgram per liter, 1995–2003.

a single analysis between warmer and cooler months, also were from statistically different distributions (contingency table $\chi^2 = 9.9964$, DF = 7, p-value = 0.1888). The gasoline hydrocarbons were the most frequently detected VOC group in both warmer and cooler months followed by solvents, THMs, gasoline oxygenates, organic synthesis compounds, fumigants, and refrigerants, which is the same order as the overall VOC group detection frequencies.

Three general patterns were evident for median concentrations of detections of the VOC groups: (1) larger median concentrations in the cooler months, (2) larger median concentrations in the warmer months, and (3) no difference in the median concentrations between the seasons (fig. 27). The first pattern includes the gasoline hydrocarbons, solvents, and gasoline oxygenates, with median concentrations of the detections for the gasoline hydrocarbons and gasoline oxygenates significantly larger in cooler months than in warmer months (Wilcoxon rank-sum $Z > 2.8000$, one-sided p-value <0.025). The second pattern includes the organic synthesis compounds and refrigerants, with the median concentration of the detections for organic synthesis compounds significantly larger in warmer months than in cooler months (Wilcoxon rank-sum $Z = 3.1364$, one-sided p-value = 0.0009). The third pattern includes the THMs and fumigants, with no significant difference in the median concentrations of the detections between the two seasons (Wilcoxon rank-sum $Z > 0.3126$, one-sided p-value > 0.025). The first pattern may be, in part, because the partitioning of VOCs between air and water is based on the Henry's Gas Law, which favors VOCs staying in water as the temperature decreases meaning less volatilization during cooler months (Rathbun, 2000). The second pattern may be from VOCs primarily entering the stream from groundwater inflows or from small point-source discharges entering the stream during warmer months and possibly, from larger use in warmer months. The third pattern may indicate a consistent, year-round source for the compounds in these VOC groups.

## Individual Volatile Organic Compounds

Two general patterns of occurrence for the 15 most frequently detected VOCs in warmer and cooler months were evident: (1) VOCs occur more frequently in cooler months, and (2) VOCs occur slightly more frequently in warmer months (fig. 28). The VOCs occurring more frequently in cooler months than in warmer months include 11 of the 15 most frequently detected VOCs (toluene, MTBE, perchloroethene, acetone, *m*- and *p*-xylene, benzene, 1,2,4-trimethylbenzene, *o*-xylene, dichloromethane, 1,1,1-trichloroethane, and methyl isobutyl ketone). The VOCs occurring slightly more frequently in warmer months than in cooler months include 4 of the 15 most frequently detected VOCs (chloroform, trichloroethene, *cis*-1,2-dichloroethene, and chloromethane). Furthermore, more individual VOCs

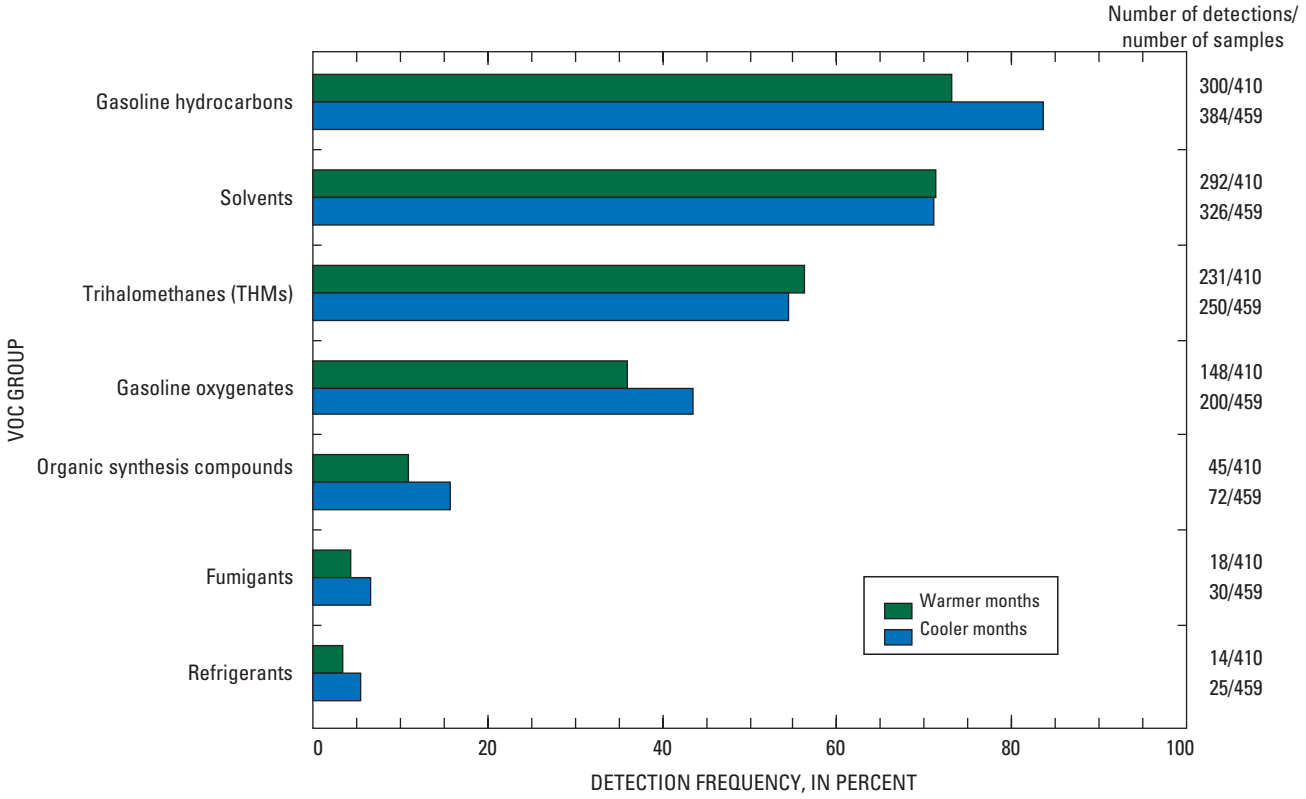


**Figure 26.** Detection frequencies of volatile organic compound (VOC) groups in urban stream samples in warmer (April through September) and cooler (October through March) months at an assessment level of 0.02 microgram per liter, 1995–2003.

were detected in samples from cooler months (55 VOCs) than from warmer months (47 VOCs).

As noted previously, the first pattern may be, in part, because the partitioning of VOCs between air and water is more favorable to VOCs staying in water as the temperature decreases (Rathbun, 2000). The second pattern may be from VOCs primarily entering the stream from groundwater inflows or from small point-source discharges entering the stream during warmer months, and possibly from larger use during warmer months.

The concentrations of the 15 most frequently detected VOCs grouped by warmer and cooler months are shown in figure 29. A summary of the detection frequency and concentration distribution at an assessment level of 0.02 µg/L for all 87 VOCs analyzed is provided in Appendix 2.

Three general patterns were evident in the median concentrations of detections for warmer and cooler months: (1) median concentrations were not different in warmer or cooler months, (2) median concentrations were larger in warmer months, and (3) median concentrations were larger in cooler months. Of the 15 most frequently detected VOCs, toluene, chloroform, perchloroethene, benzene, *o*-xylene, and methyl isobutyl ketone had no difference in median concentrations of detections between warmer and cooler months. Six of the 15 most frequently detected VOCs—trichloroethene, acetone, *m*- and *p*-xylene, 1,2,4-trimethylbenzene, dichloromethane, and 1,1,1-trichoroethane—had slightly larger median concentrations of detections in warmer months. Three of the 15 most frequently detected VOCs—MTBE, *cis*-1,2-dichloroethene, and chloromethane—had larger median concentrations of detections in the cooler months. The concentrations for most of the compounds varied over at least two orders of magnitude, with the largest concentrations in the cooler months for most of the VOCs.

The median concentrations of detections for the 15 most frequently detected VOCs ranged from 0.03 to 4 µg/L in warmer months and from 0.03 to 3.8 µg/L in cooler months. The largest median concentrations of detections were associated with acetone, and the next largest median concentrations of detections were associated with methyl isobutyl ketone. Both acetone and methyl isobutyl ketone are oxygenated solvents and are highly soluble in water.

MTBE was detected more frequently in cooler months in both high MTBE-use areas and low MTBE-use areas of the United States (fig. 30). In addition, MTBE had statistically larger concentrations (Wilcoxon rank-sum $Z = -3.5156$, p-value = 0.0002) in cooler months compared to warmer months. The statistically largest concentrations of MTBE were in cooler months in high MTBE-use areas (Wilcoxon rank-sum $Z > 6.0000$, p-value < 0.025; fig. 30). The median

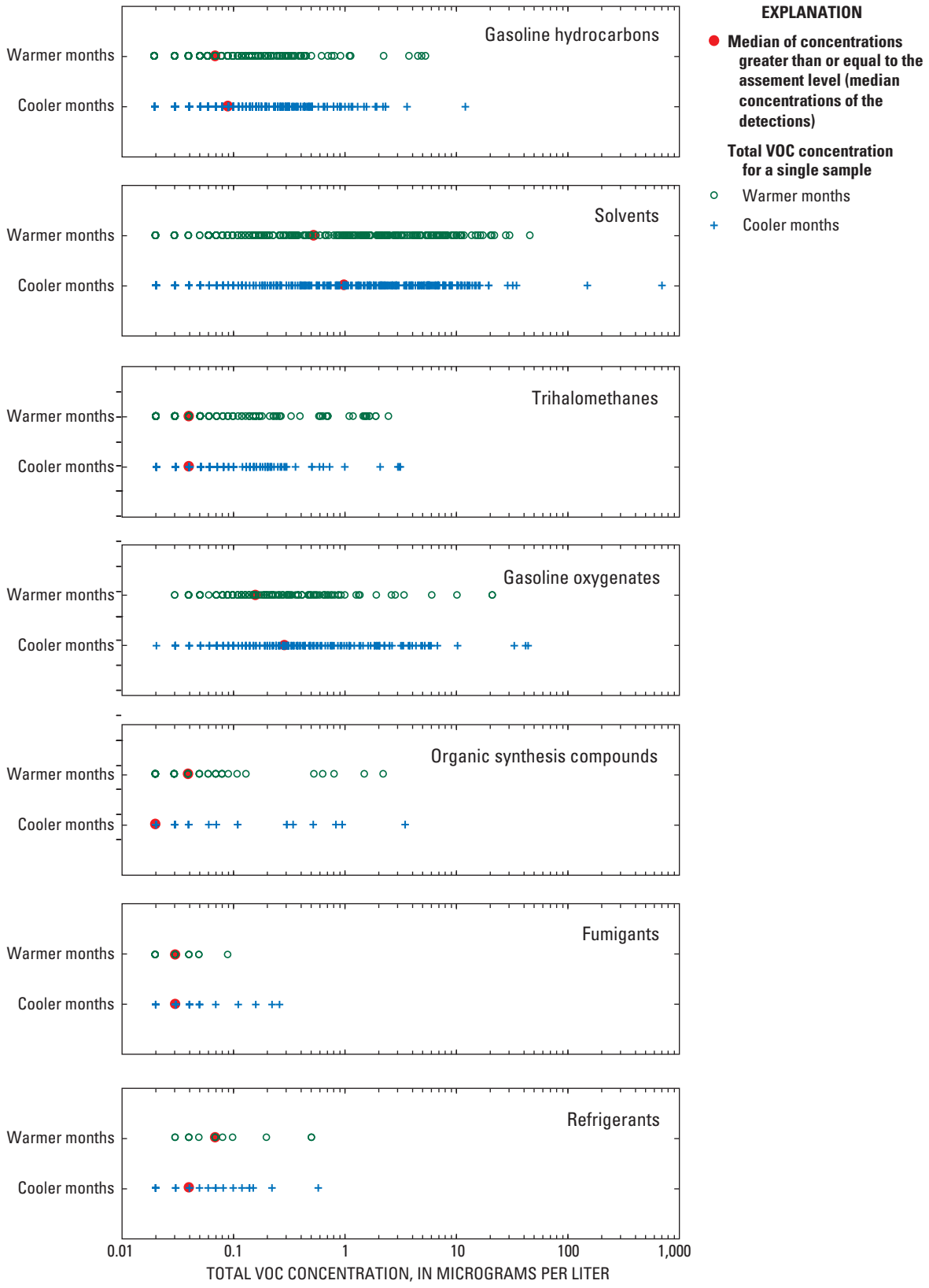


**Figure 27.** Total volatile organic compound (VOC) concentrations in urban stream samples of the seven VOC groups in warmer (April through September) and cooler (October through March) months at an assessment level of 0.02 microgram per liter, 1995–2003.

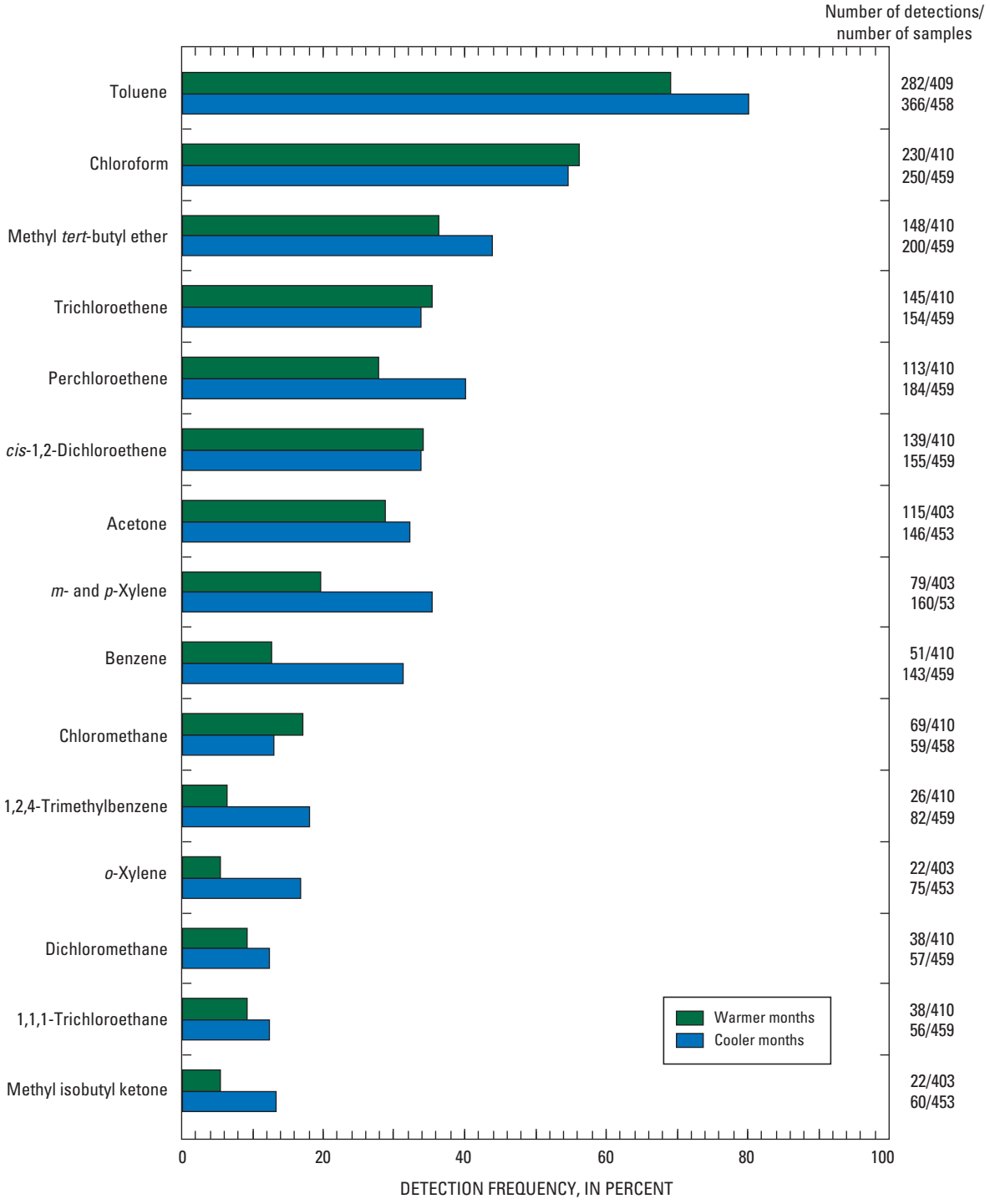


**Figure 28.** Detection frequencies of the 15 most frequently detected volatile organic compounds in urban stream samples by warmer (April through September) and cooler (October through March) months at an assessment level of 0.02 microgram per liter, 1995–2003.

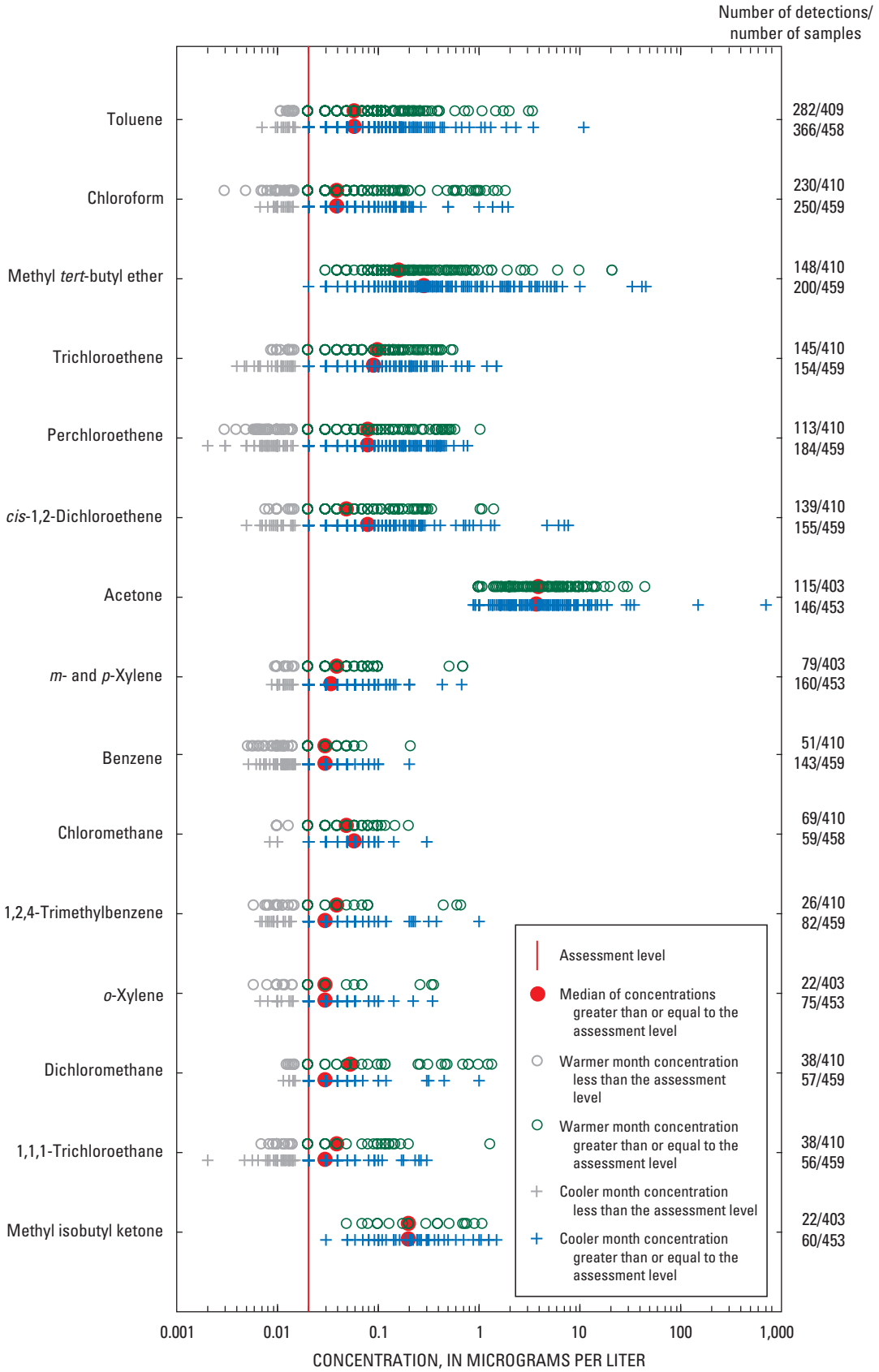


**Figure 29.** Concentrations of the 15 most frequently detected volatile organic compounds in urban stream samples by warmer (April through September) and cooler (October through March) months at an assessment level of 0.02 microgram per liter, 1995–2003.

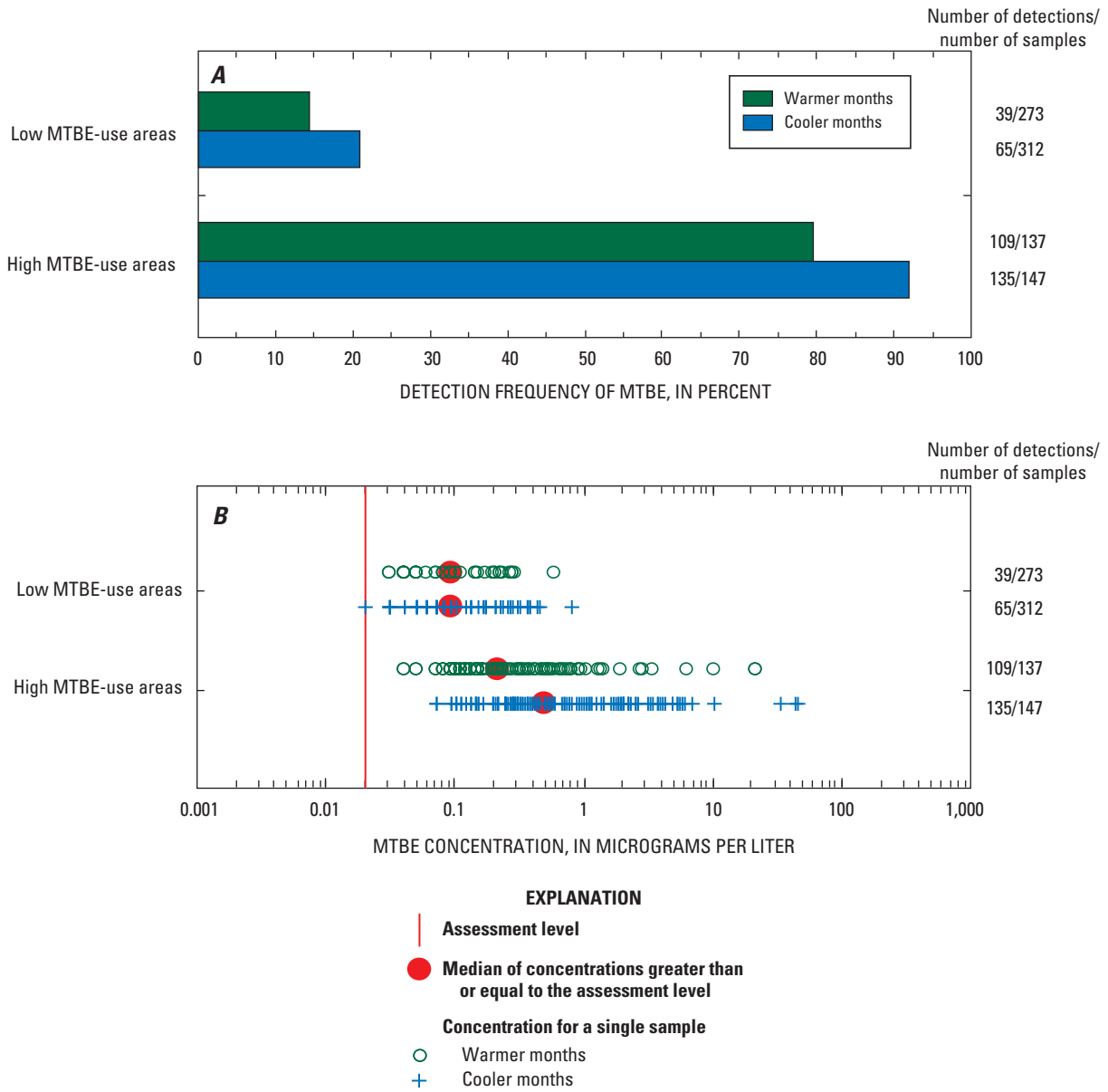


**Figure 30.** Relation between (*A*) detection frequencies, and (*B*) concentrations of methyl *tert*-butyl ether (MTBE) in urban stream samples in low and high MTBE-use areas of the United States by warmer (April through September) and cooler (October through March) months at an assessment level of 0.02 microgram per liter, 1995–2003.

concentrations of detections were 0.09 µg/L in warmer and cooler months in low MTBE-use areas, and 0.21 and 0.48 µg/L in warmer and cooler months, respectively, in high MTBE-use areas. The concentrations of MTBE ranged from 0.03 to 0.57 µg/L in warmer months and from 0.02 to 0.77 µg/L in cooler months in low MTBE-use areas. In contrast, the concentrations of MTBE ranged from 0.04 to 21 µg/L in warmer months and from 0.07 to 44 µg/L in cooler months in high MTBE-use areas.

## Comparison of Volatile Organic Compound Concentrations to Benchmarks

In this section, VOC concentrations are compared to drinking-water and aquatic-life benchmarks to describe the significance of VOCs in urban streams to human health and aquatic life. The drinking-water benchmarks used for comparisons are USEPA's drinking water MCLs (U.S. Environmental Protection Agency, 2006) and HBSLs developed by the USGS in collaboration with the USEPA, the New Jersey Department of Environmental Protection, and the Oregon Health & Science University (Toccalino and others, 2006). The aquatic-life criteria used for comparisons are Canadian Aquatic Guidelines (Canadian Council of Resource and Environment Ministers, 1991) and USEPA fresh-water chronic aquatic-life criteria (U.S. Environmental Protection Agency, 1991). The Canadian Aquatic Guidelines were used because the United States aquatic guidelines currently (2009) are not available from USEPA for many of the VOCs. An aquatic guideline from USEPA was used if available. Ratios of the concentrations to the benchmarks were calculated by dividing the VOC concentration by the drinking-water benchmark or aquatic-life criteria. A concentration to benchmark ratio greater than one indicates that the concentration was greater than the benchmark. Concentration to benchmark ratios greater than 0.1 and less than 1 indicate that the concentration was within 10 percent of the drinking-water benchmark and (or) aquatic-life criteria. The compounds with concentration to benchmark ratios greater than 0.1 may warrant inclusion in low-concentration monitoring programs, like the NAWQA Program, to provide an indication of VOC concentrations approaching levels of potential concern for the beneficial use(s) of the stream.

No samples had concentrations greater than an MCL or HBSL (table 9). However, six compounds (trichloroethene, perchloroethene, *cis*-1,2-dichloroethene, dichloromethane, vinyl chloride, dibromochloropropane) had concentrations less than but within 10 percent of an MCL. Trichloroethene (37 samples), perchloroethene (54 samples), and dichloromethane (16 samples) accounted for the majority of the concentrations within 10 percent of an MCL. Acetone (1 sample), acrolien (3 samples), and 1,1,2,2-tetrachloroethane (2 samples), had concentrations less than but within 10 percent of an HBSL. Concentrations of MTBE in 59 samples were less than but within 10 percent of the lower limit of the USEPA Drinking Water Advisory (20 µg/L; U.S. Environmental Protection Agency, 1997), and concentrations in 5 samples were greater than or equal to this lower limit (table 9). These 10 compounds may warrant inclusion in future low-concentration monitoring programs that focus on drinking-water sources.

Toluene (6 samples) and chloroform (2 samples) had stream concentrations greater than the aquatic-life criteria (table 9). Five additional compounds (trichloroethene, chlorobenzene, naphthalene, acrolien, and 1,2-dichlorobenzene) had concentrations less than but within 10 percent of aquatic-life criteria. Toluene and chloroform accounted for the majority of concentrations within 10 percent or greater than the aquatic-life criteria (table 9). These seven compounds may warrant inclusion in future low-concentration monitoring programs that focus on the protection of aquatic life.

## Summary

The U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program was implemented in 1991. The primary goals of the NAWQA Program are to describe the status and trends of the water quality in the Nation's water resources and identify natural and anthropogenic factors affecting the water quality. The NAWQA Program's surface-water design includes, in part, monitoring the water-quality of streams draining relatively homogenous land uses and physiographic conditions. The objectives of monitoring at the urban indicator sites are to (1) characterize the stream quality from drainage basins with predominantly residential and commercial land use and (2) determine which natural and anthropogenic factors affect stream quality.

The NAWQA Program began collecting samples in 1995 for analyses of volatile organic compounds (VOCs) in urban streams. The urban streams that were sampled have perennial streamflow, no major point-sources, and drain predominantly residential and commercial land uses. The occurrence of 87 VOCs in 869 water samples collected between 1995 and 2003 from 37 urban streams is summarized in this report. The occurrence of VOCs in urban streams is described for (1) all samples as a single dataset, (2) all samples grouped by streamflow pentiles, and (3) all samples grouped by warmer (April through September) and cooler (October through March) months by the detection frequency and (or) concentration of (a) any VOC, (b) VOC groups, and (c) individual compounds. Concentrations of VOCs were compared to (1) U.S. Environmental Protection Agency's (USEPA) drinking-water Maximum Contaminant Levels (MCLs) or Drinking Water Advisories, (2) Health-Based Screening Levels (HBSLs) developed by the USGS in collaboration with USEPA and other agencies, and (3) USEPA and Canadian aquatic-life criteria.

An assessment level of 0.02 microgram per liter (µg/L) was used to compute the detection frequencies and concentration statistics. The detection frequencies are considered minimum estimates because of the potential loss of information when using an assessment level. The use of an assessment level allowed for direct comparisons of occurrence information between VOC groups and individual VOCs.

**Table 9.** Summary by volatile organic compound of the number of samples with stream concentration-to-benchmark ratios greater than or equal to 0.1 and greater than or equal to 1 for drinking-water benchmarks or aquatic-life criteria listed in order of decreasing overall detection frequency, 1995–2003.

[DWB, drinking-water benchmark; µg/L, micrograms per liter; ≥, greater than or equal to; AQCR, aquatic-life criteria; MCL, Maximum Contaminant Level; CAN, Interim Canadian Aquatic Guideline; DWA, Drinking Water Advisory; HBSL, Health-Based Screening Level; FCH, U.S. Environmental Protection Agency fresh-water chronic aquatic-life criteria; --, no criteria or not applicable]

| Compound name | DWB type | DWB (µg/L) | Number of samples with concentration/DWB ratio | | AQCR source | AQCR (µg/L) | Number of samples with concentration/AQCR ratio | |
|---|---|---|---|---|---|---|---|---|
| | | | ≥0.1 | >1 | | | ≥0.1 | ≥1 |
| Volatile organic compounds detected at an assessment level of 0.02 µg/L | | | | | | | | |
| Toluene | MCL | [1]1,000 | 0 | 0 | CAN | [2]2 | 205 | 6 |
| Chloroform | MCL | [1,3]80 | 0 | 0 | CAN | [2]1.8 | 105 | 2 |
| Methyl *tert*-butyl ether | DWA | [4]20 | 59 | 5 | -- | -- | -- | -- |
| Trichloroethene | MCL | [1]5 | 37 | 0 | CAN | [2]21 | 3 | 0 |
| Perchloroethene | MCL | [1]5 | 54 | 0 | CAN | [2]111 | 0 | 0 |
| *cis*-1,2-Dichloroethene | MCL | [1]70 | 4 | 0 | -- | -- | -- | -- |
| Acetone | HBSL | [5]700 | 1 | 0 | -- | -- | -- | -- |
| *m*-and *p*-Xylene | MCL | [1,6]10,000 | 0 | 0 | -- | -- | -- | -- |
| Benzene | MCL | [1]5 | 0 | 0 | CAN | [2]370 | 0 | 0 |
| Chloromethane | HBSL | [5]30 | 0 | 0 | -- | -- | -- | -- |
| *o*-Xylene | MCL | [1,6]10,000 | 0 | 0 | -- | -- | -- | -- |
| Dichloromethane | MCL | [1]5 | 16 | 0 | CAN | [2]98.1 | 0 | 0 |
| 1,1,1-Trichloroethane | MCL | [1]200 | 0 | 0 | -- | -- | -- | -- |
| Carbon disulfide | HBSL | [5]700 | 0 | 0 | -- | -- | -- | -- |
| Methyl ethyl ketone | HBSL | [5]4,000 | 0 | 0 | -- | -- | -- | -- |
| Bromodichloromethane | MCL | [1,3]80 | 0 | 0 | -- | -- | -- | -- |
| Ethylbenzene | MCL | [1]700 | 0 | 0 | CAN | [2]90 | 0 | 0 |
| Chlorobenzene | MCL | [1]100 | 0 | 0 | CAN | [2]1.3 | 38 | 0 |
| 1,4-Dichlorobenzene | MCL | [1]75 | 0 | 0 | CAN | [2]26 | 0 | 0 |
| Naphthalene | HBSL | [5]100 | 0 | 0 | CAN | [2]1.1 | 18 | 0 |
| 1,1-Dichloroethene | MCL | [1]7 | 0 | 0 | -- | -- | -- | -- |
| Dibromochloromethane | MCL | [1,3]80 | 0 | 0 | -- | -- | -- | -- |
| Styrene | MCL | [1]100 | 0 | 0 | -- | -- | -- | -- |
| Trichlorotrifluoroethane | HBSL | [5]200,000 | 0 | 0 | -- | -- | -- | -- |
| Dichlorodifluoromethane | HBSL | [5]1,000 | 0 | 0 | -- | -- | -- | -- |
| Tetrachloromethane | MCL | [1]5 | 0 | 0 | CAN | [2]13.3 | 0 | 0 |
| Bromoform | MCL | [1,3]80 | 0 | 0 | -- | -- | -- | -- |
| Diethyl ether | HBSL | [5]1,000 | 0 | 0 | -- | -- | -- | -- |
| Vinyl chloride | MCL | [1]2 | 9 | 0 | -- | -- | -- | -- |
| Acrolien | HBSL | [5]4 | 3 | 0 | FCH | [7]21 | 3 | 0 |
| *trans*-1,2-Dichloroethene | MCL | [1]100 | 0 | 0 | -- | -- | -- | -- |
| 2-Chlorotoluene | HBSL | [5]100 | 0 | 0 | -- | -- | -- | -- |
| Trichlorofluoromethane | HBSL | [5]2,000 | 0 | 0 | -- | -- | -- | -- |
| 1,2-Dichloropropane | MCL | [1]5 | 0 | 0 | -- | -- | -- | -- |
| 1,1,2,2-Tetrachloroethane | HBSL | [5].3 | 2 | 0 | -- | -- | -- | -- |
| Dibromochloropropane | MCL | [1].2 | 1 | 0 | -- | -- | -- | -- |
| 1,2-Dichlorobenzene | MCL | [1]600 | 0 | 0 | CAN | [2].7 | 1 | 0 |

**Table 9.** Summary by volatile organic compound of the number of samples with stream concentration-to-benchmark ratios greater than or equal to 0.1 and greater than or equal to 1 for drinking-water benchmarks or aquatic-life criteria listed in order of decreasing overall detection frequency, 1995–2003.—Continued

[DWB, drinking-water benchmark; µg/L, micrograms per liter; ≥, greater than or equal to; AQCR, aquatic-life criteria; MCL, Maximum Contaminant Level; CAN, Interim Canadian Aquatic Guideline; DWA, Drinking Water Advisory; HBSL, Health-Based Screening Level; FCH, U.S. Environmental Protection Agency fresh-water chronic aquatic-life criteria; --, no criteria or not applicable]

| Compound name | DWB type | DWB (µg/L) | Number of samples with concentration/DWB ratio | | AQCR source | AQCR (µg/L) | Number of samples with concentration/AQCR ratio | |
|---|---|---|---|---|---|---|---|---|
| | | | ≥0.1 | >1 | | | ≥0.1 | ≥1 |
| Volatile organic compounds detected at an assessment level of 0.02 µg/L—Continued | | | | | | | | |
| 1,3-Dichlorobenzene | HBSL | [5]600 | 0 | 0 | CAN | [2]150 | 0 | 0 |
| 1,2-Dichloroethane | MCL | [1]5 | 0 | 0 | CAN | [2]100 | 0 | 0 |
| Isopropylbenzene | HBSL | [5]700 | 0 | 0 | -- | -- | -- | -- |
| Volatile organic compounds not detected at an assessment level of 0.02 µg/L | | | | | | | | |
| Acrylonitrile | HBSL | [5]0.06–6 | 0 | 0 | -- | -- | -- | -- |
| Bromochloromethane | HBSL | [5]90 | 0 | 0 | -- | -- | -- | -- |
| Bromomethane | HBSL | [5]100 | 0 | 0 | -- | -- | -- | -- |
| 4-Chlorotoluene | HBSL | [5]100 | 0 | 0 | -- | -- | -- | -- |
| 1,2-Dibromoethane | MCL | [1]0.05 | 0 | 0 | -- | -- | -- | -- |
| *cis*-1,3-Dichloropropene | HBSL | [5,8]0.3–30 | 0 | 0 | -- | -- | -- | -- |
| *trans*-1,3-Dichloropropene | HBSL | [5,8]0.3–30 | 0 | 0 | -- | -- | -- | -- |
| Hexachlorobutadiene | HBSL | [5]0.9–90 | 0 | 0 | CAN | [2]1.3 | 0 | 0 |
| Hexachloroethane | HBSL | [5].7 | 0 | 0 | -- | -- | -- | -- |
| Methyl acrylonitrile | HBSL | [5].7 | 0 | 0 | -- | -- | -- | -- |
| Methyl methacrylate | HBSL | [5]10,000 | 0 | 0 | -- | -- | -- | -- |
| 1,1,1,2-Tetrachloroethane | HBSL | [5]90 | 0 | 0 | -- | -- | -- | -- |
| 1,2,3-Trichlorobenzene | -- | -- | -- | -- | CAN | [2]8 | 0 | 0 |
| 1,2,4-Trichlorobenzene | MCL | [1]70 | 0 | 0 | CAN | [2]24 | 0 | 0 |
| 1,1,2-Trichloroethane | MCL | [1]5 | 0 | 0 | -- | -- | -- | -- |
| 1,2,3-Trichloropropane | HBSL | [5]40 | 0 | 0 | -- | -- | -- | -- |
| **Totals** | **--** | **--** | **186** | **5** | **--** | **--** | **373** | **8** |

[1]U.S. Environmental Protection Agency (2006).

[2]Canadian Council of Resource and Environment Ministers (1991).

[3]The MCL is for total trihalomethanes (TTHMs).

[4]The value listed is the lower limit of the U.S. Environmental Protection Agency Drinking Water Advisory: Consumer acceptability advice and health effects analysis on methyl *tert*-butyl ether (MTBE; U.S. Environmental Protection Agency, 1997).

[5]Toccalino and others (2006).

[6]MCL is for total xylenes.

[7]U.S. Environmental Protection Agency (1991).

[8]HBSL range is for total 1,3-dichloropropene; the *cis*- and *trans*- isomers do not have individual HBSLs.

## Overall Occurrence Patterns of Volatile Organic Compounds

One or more VOCs occurred frequently (97 percent of 869 samples) in urban streams with a detection frequency ranging from 86 to 100 percent at the 37 urban stream sites. Twenty-seven of the sites had a detection frequency of 100 percent for one or more VOCs. Total VOC concentrations ranged from not detected to 698 µg/L, with a median total VOC concentration of 0.57 µg/L. About 57 percent of the total VOC concentrations were less than or equal to 1 µg/L. The number of VOCs detected per sample ranged from 0 to 27 VOCs, with a median of 4 VOCs per sample. About 85 percent of the samples contained 2 or more VOCs, and about 25 percent of the samples contained 8 or more VOCs.

The seven VOC groups (gasoline hydrocarbons, solvents, trihalomethanes, gasoline oxygenates, organic synthesis compounds, fumigants, and refrigerants) had statistically different detection frequencies in urban stream samples. The gasoline hydrocarbons, solvents, trihalomethanes, and gasoline oxygenates were detected frequently (in more than 40 percent of the samples); in contrast, the organic synthesis compounds, fumigants, and refrigerants were detected less frequently. An individual VOC or several compounds usually accounted for most of the detections within a VOC group. The gasoline hydrocarbons were dominated by benzene, toluene, ethylbenzene, and *o*-, *m*- and *p*-xylene (collectively known as BTEX compounds). The solvents were dominated by trichloroethene, perchloroethene, *cis*-1,2-dichloroethene, and acetone. Trihalomethanes were dominated by chloroform, and gasoline oxygenates were dominated by methyl *tert*-butyl ether (MTBE). The gasoline oxygenates also had a larger detection frequency and concentrations in high MTBE-use areas of the United States. The larger solvent concentrations were influenced by the large concentrations of acetone in some samples. Median total concentrations of the VOC groups ranged from 0.87 µg/L for the solvents to 0.03 µg/L for the organic synthesis compounds and fumigants.

Fifty-seven of the 87 VOCs analyzed for this study were detected in at least one sample from the 37 urban streams sampled at an assessment level of 0.02 µg/L. Concentrations of 30 VOCs were less than the assessment level including 16 organic synthesis compounds, 8 solvents, 5 fumigants, and 1 gasoline hydrocarbon. Fifteen VOCs had detection frequencies greater than or equal to 10 percent at an assessment level of 0.02 µg/L. These 15 most frequently detected VOCs in urban streams included 6 gasoline related compounds (5 gasoline hydrocarbons—toluene, *m*- and *p*-xylene, benzene, 1,2,4-trimethylbenzene, *o*-xylene—and the gasoline oxygenate, MTBE); 1 trihalomethane (chloroform); and 8 solvents (trichloroethene, perchloroethene, *cis*-1,2-dichloroethene, acetone, chloromethane, dichloromethane, 1,1,1-trichloroethane, and methyl isobutyl ketone). The median concentrations of detections of the 15 most frequently detected VOCs ranged from 0.03 to 3.9 µg/L and typically were less than or equal to 0.10 µg/L, with the exceptions of those for MTBE (0.24 µg/L) and acetone (3.9 µg/L).

## Occurrence Patterns of Volatile Organic Compounds by Streamflow Pentile

Many studies indicate that water quality in streams can vary with streamflow. Because many of the urban streams sampled are small and had short streamflow records, a simple and robust ratio method was used to estimate longer-term streamflow pentiles for each urban stream. The 869 samples were grouped into five streamflow pentiles (less than 20, 20 to less than 40, 40 to less than 60, 60 to less than 80, and greater than or equal to 80 percent of estimated annual long-term streamflow), providing a means to group and compare the water-quality results from the 37 sites on the basis of streamflow conditions.

The detection frequencies of one or more VOCs did not vary markedly between the streamflow pentiles and ranged from 96.7 to 97.7 percent. The median total VOC concentrations ranged from 0.39 to 1.0 µg/L for the pentiles. The median number of VOCs reported per sample was highest in the fifth pentile (largest streamflows), and the lowest was in the first and third pentiles. The fifth pentile also had the most VOCs present (27) in one sample. Two or more VOCs were present in more than 80 percent of samples in each of the pentiles.

Gasoline hydrocarbons, solvents, trihalomethanes, and gasoline oxygenates occurred frequently in all streamflow pentiles. In contrast, organic synthesis compounds, fumigants, and refrigerants occurred less frequently in all pentiles. Overall, the gasoline hydrocarbons occurred more frequently in the first and fifth pentiles, and the solvents occurred most frequently in the fifth pentile. The detection frequency of gasoline hydrocarbons generally decreased as the streamflow increased from the first to fourth pentile then increased from the fourth to fifth pentile. The detection frequency of the solvents and organic synthesis compounds increased as the streamflow increased from the first to the fifth pentile. In contrast, the detection frequency of the trihalomethanes and gasoline oxygenates generally decreased as the streamflow increased. The detection frequency of the fumigants and refrigerants did not differ markedly as streamflow increased.

Median concentrations of detections for gasoline hydrocarbons, solvents, gasoline oxygenates, and organic synthesis compounds generally increased as streamflow increased. Median concentrations of detections for trihalomethanes and fumigants generally decreased as streamflow increased. Median concentrations of detections for refrigerants showed no pattern as streamflow increased.

Two occurrence patterns were evident for most of the 15 most frequently detected VOCs: (1) the detection frequency generally decreases as streamflow increases, and (2) the detection frequency generally increases as the streamflow increases. The first pattern may be from VOCs primarily entering the

stream from groundwater inflows or from small point-source discharges that are diluted with increased streamflow, whereas some VOCs also may have additional sources, such as stormwater runoff, contributing to the increased presence during larger streamflow conditions in the second pattern.

Toluene, chloroform, MTBE, perchloroethene, and dichloromethane generally had decreasing detection frequencies as the streamflow increased. In contrast, gasoline hydrocarbons—*m*- and *p*-xylene, benzene, 1,2,4-trimethylbenzene, and *o*-xylene—and the solvents—trichloroethene, *cis*-1,2-dichloroethene, chloromethane and methyl isobutyl ketone—had increasing detection frequencies as the streamflow increased.

Seven of the 15 most frequently detected VOCs (toluene, MTBE, acetone, chloromethane, *o*-xylene, dichloromethane, and methyl isobutyl ketone) had increasing median concentrations of detections as streamflow increased. In contrast, three VOCs (chloroform, perchloroethene, and *cis*-1,2-dichloroethene) showed a decrease in the median concentrations of detections as streamflow increased. The five other most frequently detected compounds had no significant change in the median concentrations of detections as streamflow increased.

## Occurrence Patterns of Volatile Organic Compounds by Season

Water quality of urban streams may vary with season of the year as well as with streamflow. The patterns of VOC occurrence described in this report were not markedly different between streamflow pentiles for one or more VOCs, VOC groups, and individual VOCs. Because a marked difference between the streamflow pentiles was not evident, the 869 samples from the 37 urban streams were stratified by warmer (April through September) and cooler (October through March) months to compare the effects of seasonality on water quality at these urban sites.

One or more VOCs were frequently detected in both warmer and cooler months and the detection frequencies for warmer and cooler months were not statistically different. However, median total VOC concentrations were significantly larger in cooler months than in warmer months, with the median total VOC concentration at least twice as large in cooler months. Furthermore, the median number and total VOCs detected in samples were statistically larger in cooler months than in warmer months.

The detection frequencies of gasoline hydrocarbons, gasoline oxygenates, organic synthesis compounds, fumigants, and refrigerants generally were similar or larger in cooler months than in warmer months. However, the differences in the detection frequencies between warmer and cooler months within each VOC group were not significant. Gasoline hydrocarbons were the most frequently detected VOC group in both warmer and cooler months.

Three general patterns were evident for the median concentrations of detections for the VOC groups: (1) larger median concentrations in the cooler months, (2) larger median concentrations in the warmer months, and (3) no difference in the median concentrations between the seasons. The first pattern included the gasoline hydrocarbons, solvents, and gasoline oxygenates, with median concentrations of detections for the solvents and gasoline oxygenates significantly larger in cooler months than in warmer months. The second pattern included the organic synthesis compounds and refrigerants, with median concentrations of detections for organic synthesis compounds significantly larger in warmer months than in cooler months. The third pattern included the trihalomethanes and fumigants, with no significant difference in the median concentrations of detections between the two seasons. The first pattern may be, in part, because the partitioning between air and water based on the Henry's Gas Law is more favorable to VOCs staying in water as the temperature decreases meaning less volatilization during cooler months. The second pattern may be from VOCs primarily entering the stream from groundwater inflows or from small point-source discharges entering the stream during warmer months and, possibly, larger use in warmer months. The third pattern may indicate a consistent source for the compounds in these VOC groups.

Eleven (toluene, MTBE, perchloroethene, acetone, *m*- and *p*-xylene, benzene, 1,2,4-trimethylbenzene, *o*-xylene, dichloromethane, 1,1,1-trichloroethane, and methyl isobutyl ketone) of the 15 most frequently detected VOCs occurred more frequently in cooler months than in warmer months. Four (chloroform, trichloroethene, *cis*-1,2-dichloroethene, and chloromethane) of the 15 most frequently detected VOCs occurred slightly more frequently in warmer months than in cooler months. More individual VOCs were detected in samples from cooler months (55 VOCs) than from warmer months (47 VOCs).

Of the 15 most frequently detected VOCs, 6 VOCs (toluene, chloroform, perchloroethene, benzene, *o*-xylene, and methyl isobutyl ketone) had median concentrations of detections that were not different in warmer or cooler months, 6 VOCs (trichloroethene, acetone, *m*- and *p*-xylene, 1,2,4-trimethylbenzene, dichloromethane, and 1,1,1-trichloroethane) had median concentrations of detections that were slightly larger in warmer months, and 3 VOCs (MTBE, *cis*-1,2-dicholoethene, and chloromethane) had median concentrations of detections that were larger in cooler months. The concentrations for most of the compounds varied over at least two orders of magnitude, with the largest concentrations typically in the cooler months for most of the VOCs.

None of the samples had concentrations greater than a U.S. Environmental Protection Agency Maximum Contaminant Level. However, six compounds (trichloroethene, perchloroethene, *cis*-1,2-dichloroethene, dichloromethane, vinyl chloride, dibromochloropropane) had concentrations within 10 percent of a Maximum Contaminant Level. Concentrations of MTBE in five samples were greater than or equal to the lower limit of the USEPA Drinking Water Advisory. Toluene and chloroform had concentrations greater than or equal to aquatic-life criteria. Five additional compounds had concentrations less than but within 10 percent of the aquatic-life criteria.

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# Glossary

**Assessment level** A concentration selected by a scientist and applied to water-quality data that have variable laboratory reporting levels either for a specific compound or between individual compounds. The assessment level is applied to data received from the laboratory and is applied subsequent to the laboratory reporting level. Concentrations reported by the laboratory but less than the assessment level are considered as "non-detections" in the calculation of occurrence statistics. The primary purpose of the assessment level is for accurate comparison of detection frequencies and median concentrations between individual VOCs, groups of VOCs, and to previous studies.

**Concentration** The amount or mass of a substance present in a given volume or mass of sample. Concentrations in this report are expressed in micrograms per liter.

**Fumigant** A compound or mixture of compounds that produces a gas, vapor, fumes, or smoke intended to destroy, repel, or control organisms such as insects, bacteria, or rodents. Bromomethane is an example of a fumigant used for large-scale strawberry farming.

**Gasoline hydrocarbon** A straight, branched, and (or) cyclic structured organic compound containing only carbon and hydrogen atoms that is a common ingredient in gasoline and other petroleum product formulations. Benzene, toluene, ethylbenzene, and xylenes, commonly referred to as BTEX, are a subset of the gasoline hydrocarbons.

**Gasoline oxygenate** A compound that contains oxygen and added to gasoline in order to meet the requirements of the 1990 Clean Air Act Amendments. As used in this report, gasoline oxygenates include the four ethers—MTBE, TAME, DIPE, and ETBE.

**Health-Based Screening Level (HBSL)** An estimate of concentration (for a noncarcinogen) or concentration range (for a carcinogen) in water that (1) may be of potential human-health concern, (2) can be used as a threshold value against which measured concentrations of contaminants in water samples can be compared, and (3) is consistent with USEPA Office of Water methodologies.

**Low-level (analytical) method** An enhanced gas chromatography/mass spectrometry (GC/MS) method for the analysis of VOCs in ambient water samples, USGS method 0–4127–96, which was implemented by the USGS in 1996.

**Major river basin (MRB)** As used in this report, the major surface-water regions of the United States corresponding to the major hydrologic units within each basin.

**Maximum Contaminant Level (MCL)** As used in this report, a USEPA drinking-water standard that is legally enforceable, and that sets the maximum permissible level of a contaminant in water that is delivered to any user of a public water system.

**Median concentration of detections** As used in this report, the median concentration for the subset of samples that had concentrations equal to or greater than the assessment level of 0.02 microgram per liter.

**Organic synthesis compound** A compound that is used in the formation of other organic compounds. Vinyl chloride is an example of an organic synthesis compound used in the production of polyvinyl chloride plastics.

**Pentile** One of five segments of a distribution that has been divided into fifths, each being 20 percent of the range. As used in this report the cumulative distribution of streamflow was divided into fifths, each being 20 percent of the streamflow at a site (for example, less than 20, 20 to less than 40, 40 to less than 60, 60 to less than 80, and greater than or equal to 80 percent).

**Refrigerant** A compound used for producing refrigeration, either as a working substance in a refrigerator or by direct absorption of heat. The chlorofluorocarbons (CFCs) are classified as refrigerants for the purposes of this report.

**Solvent** A compound that is used to dissolve other substances. Two of the more common solvents are trichloroethene (TCE) and perchloroethene (PCE).

**Study Unit** A major hydrologic system of the United States in which NAWQA studies are focused, geographically defined by surface-water or groundwater features and usually encompassing more than 3,861 $mi^2$ (10,000 $km^2$) of land area. The NAWQA studies during the first decade of assessments included 51 of these systems, collectively covering a large part of the Nation, encompassing the majority of population and water use, and including diverse hydrologic settings that differ widely in the natural and human factors that affect water quality.

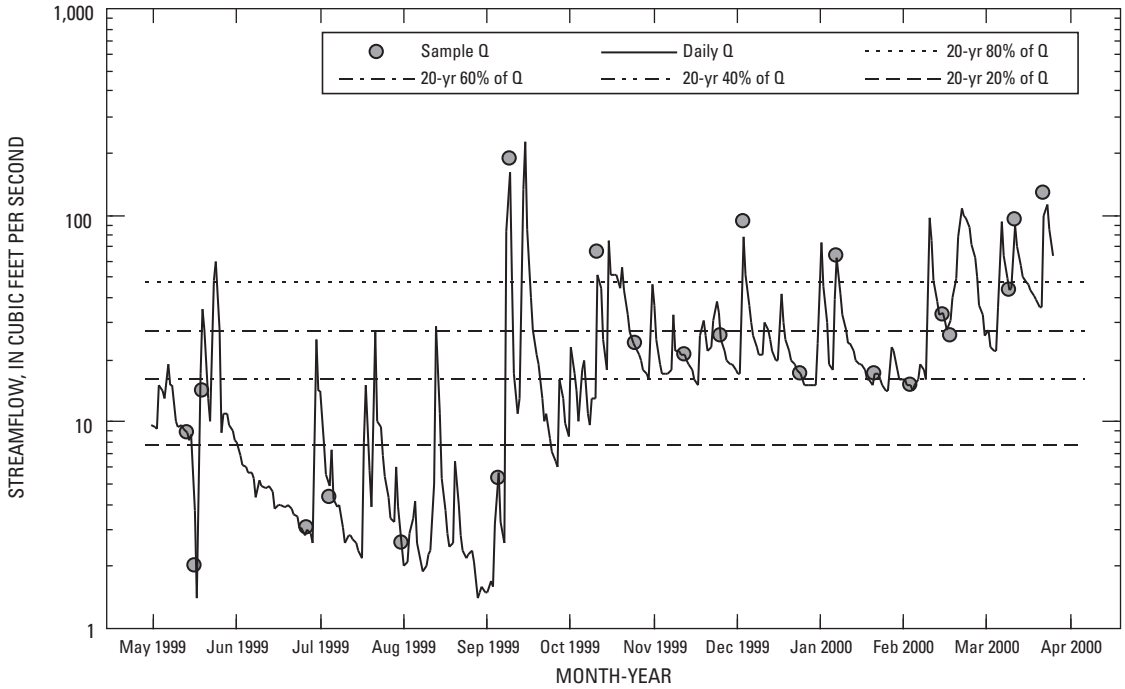
**Total VOC concentration** The sum of all quantified concentrations for all VOCs analyzed in a sample.

**Trihalomethane** As used in this report, a compound belonging to a group of VOCs that includes bromodichloromethane, bromoform, chloroform, and dibromochloromethane. These compounds are known by-products of water chlorination.

**Volatile organic compound (VOC)** An organic chemical that has a high vapor pressure relative to its water solubility. VOCs include components of gasoline, fuel oils, and lubricants, as well as organic solvents, fumigants, some inert ingredients in pesticides, refrigerants, some compounds used in organic synthesis, and some by-products of water chlorination.

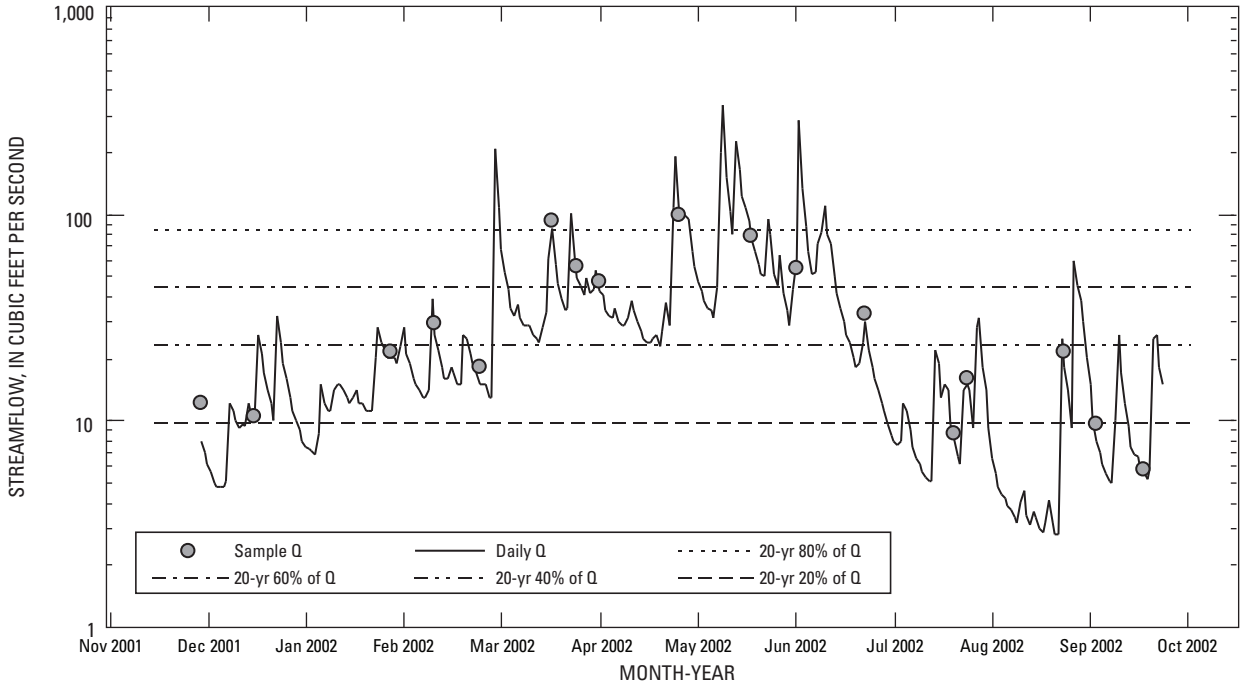
# Appendix 1

# Appendix 1. Figures showing streamflow and statistics for all sites (linked to Streamflow Record Extension section)



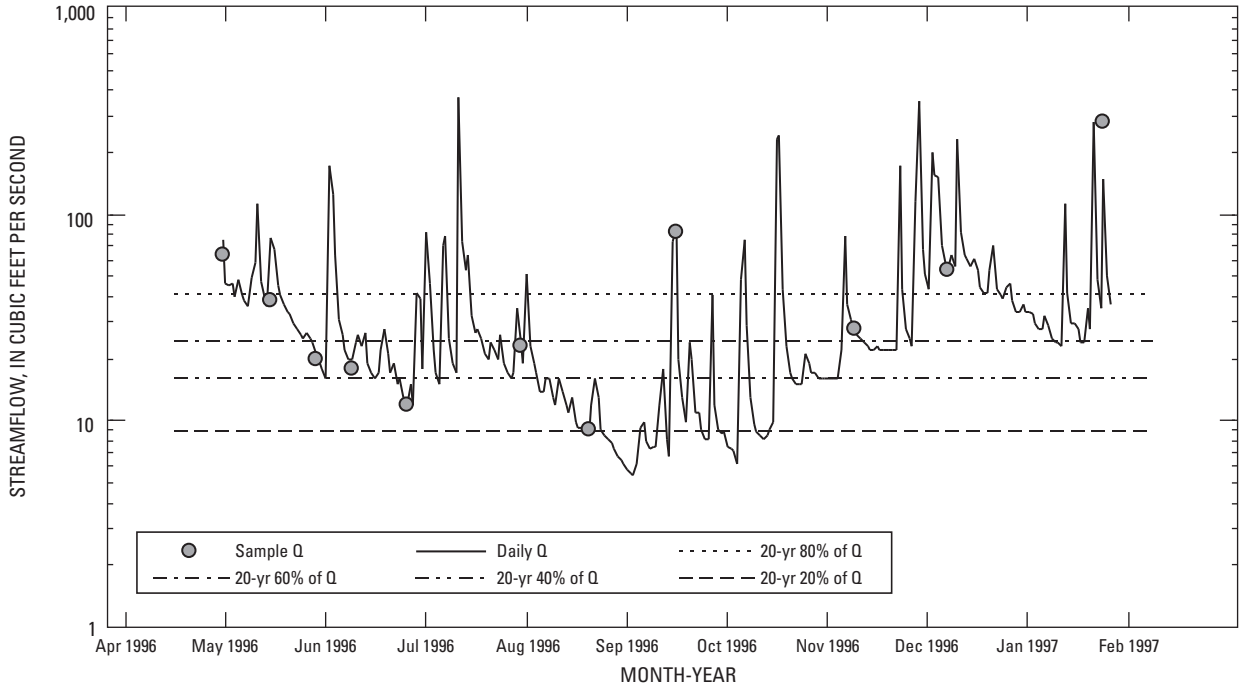

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.1.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 01102500, Aberjona River at Winchester, Mass., from May 1999 to March 2000.



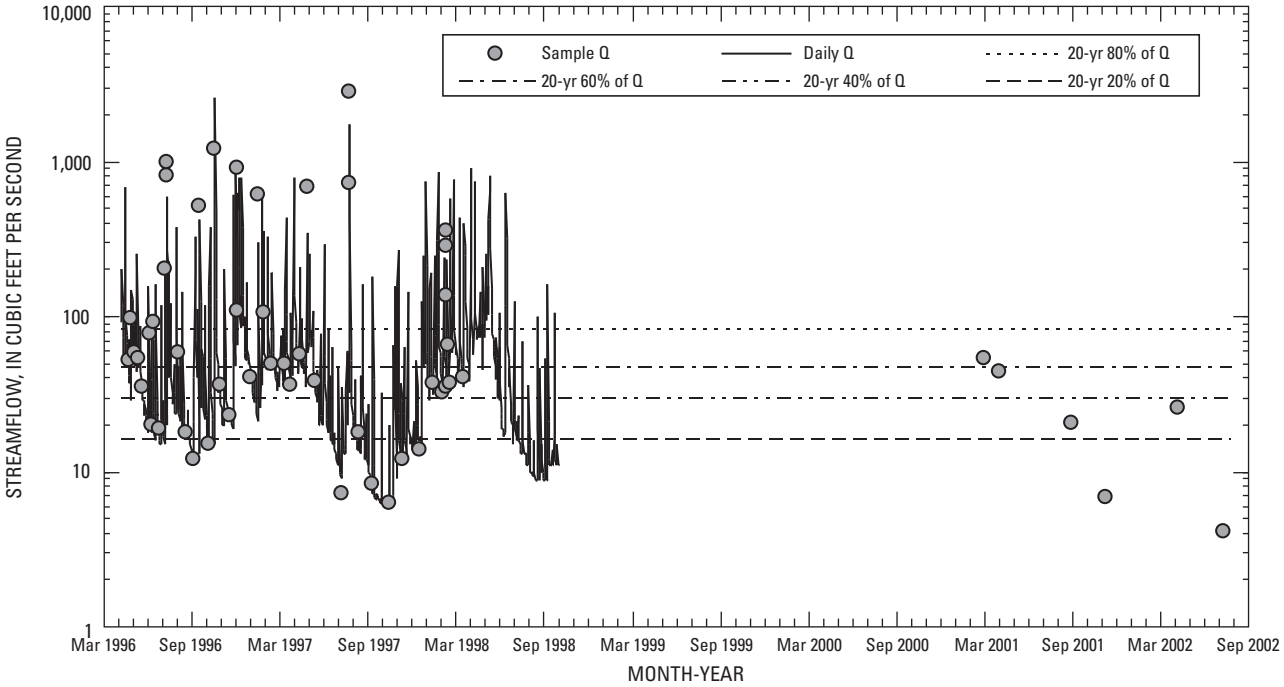

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.2.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 01209710, Norwalk River at Winnipauk, Conn., from November 2001 to September 2002.



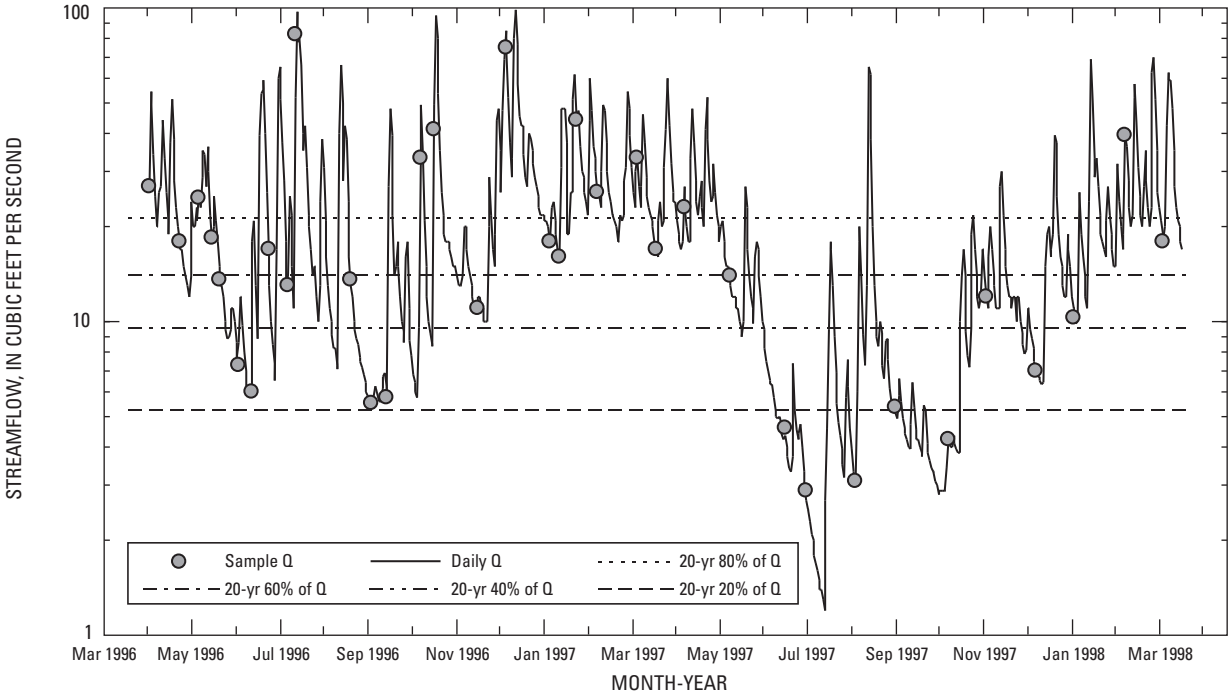

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.3.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 01390500, Saddle River at Ridgewood, N.J., from May 1996 to January 1997.



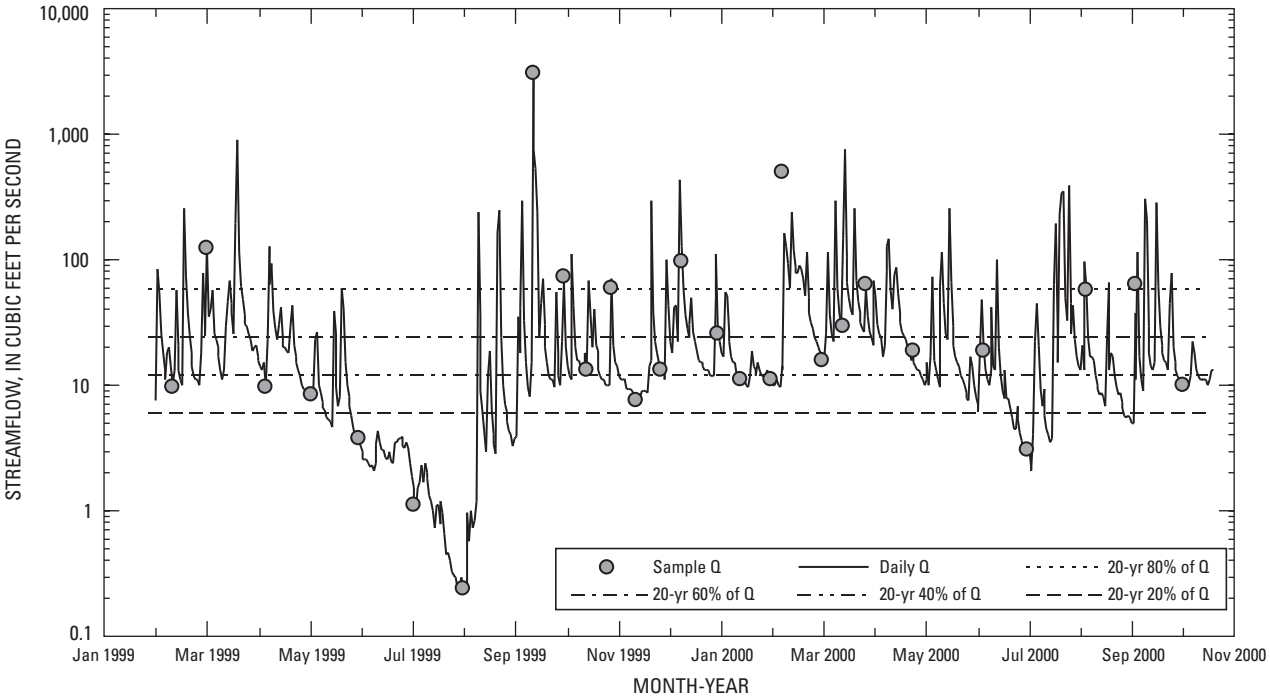

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.4.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 01403900, Bound Brook at Middlesex, N.J., from April 1996 to July 2002.



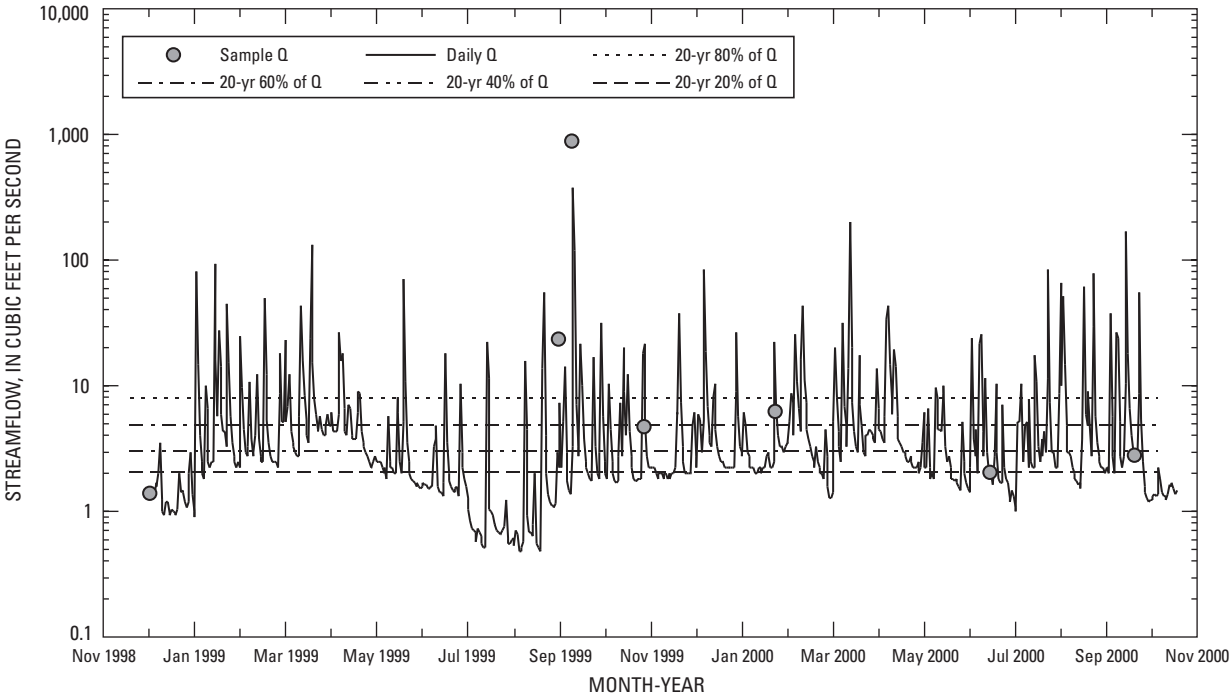

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.5.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 01410784, Great Egg Harbor River near Sicklerville, N.J., from April 1996 to March 1998.



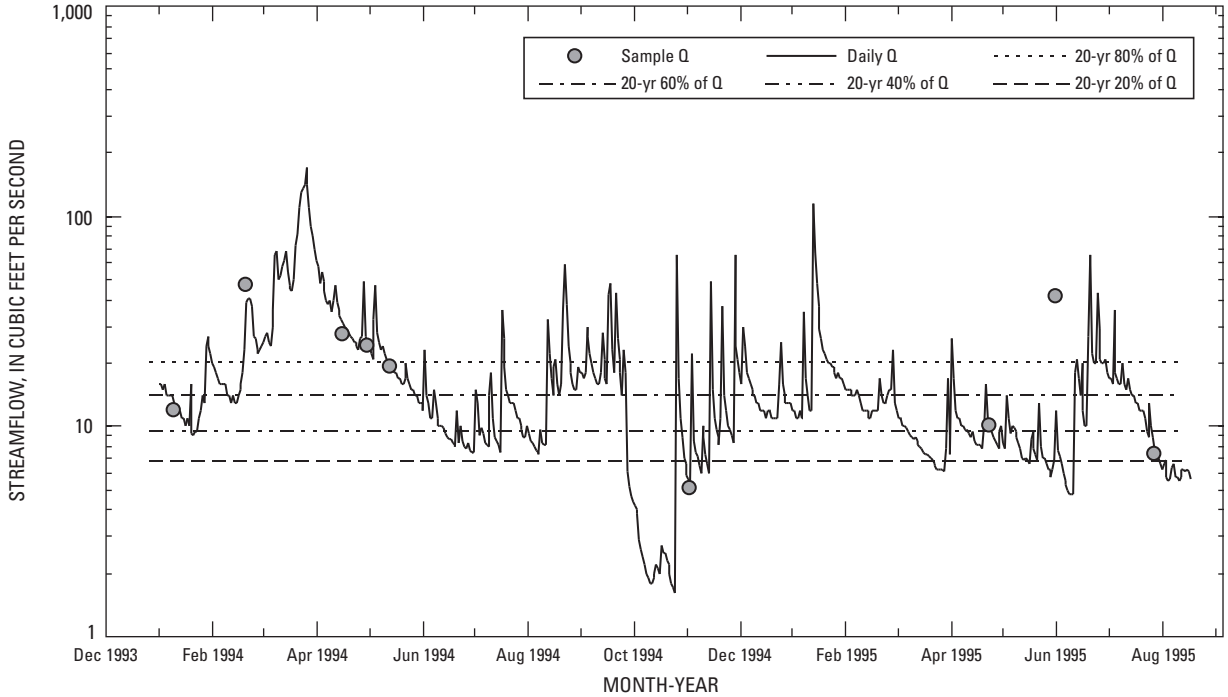

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.6.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 01464907, Little Neshaminy Creek at Valley Road near Neshaminy, Pa., from February 1999 to October 2000.



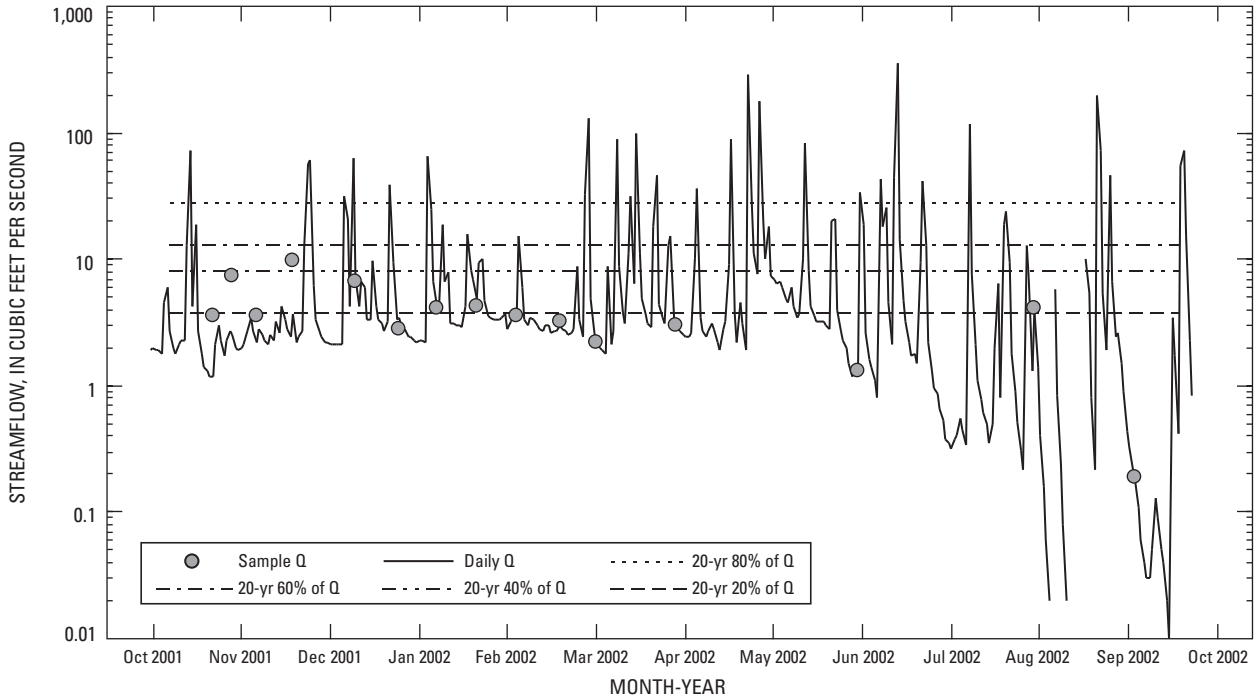

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.7.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 01467150, Cooper River at Haddonfield, N.J., from December 1998 to October 2000.



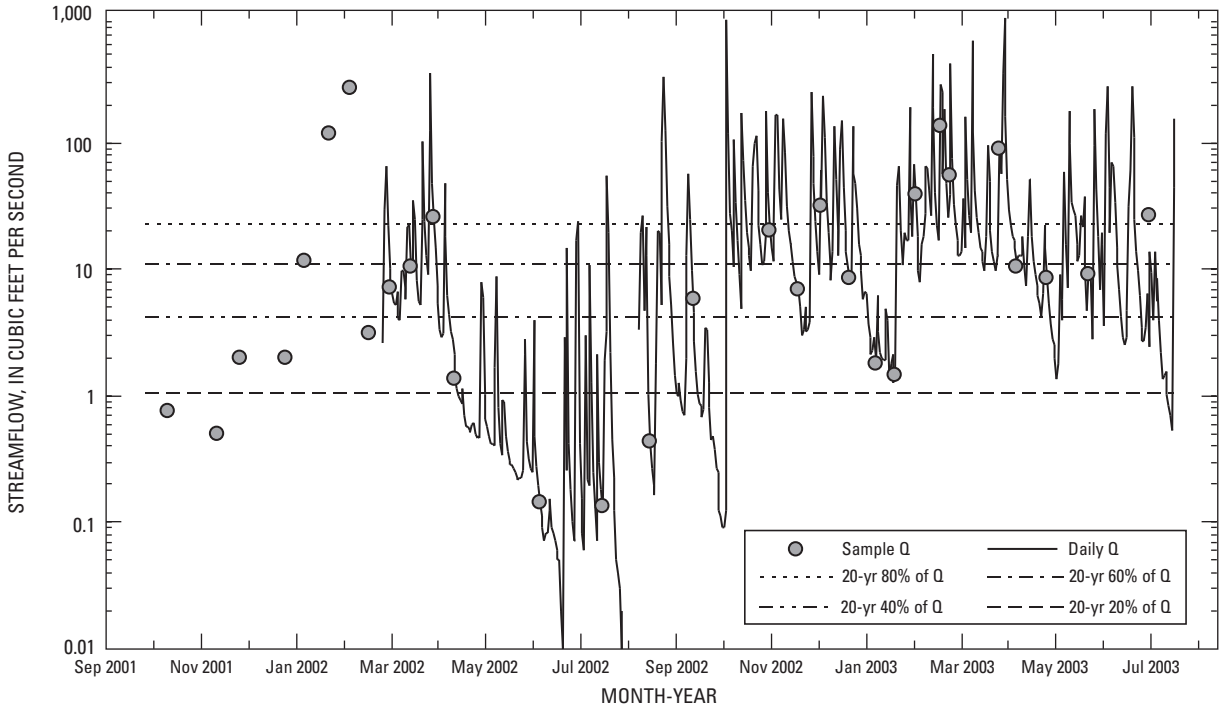

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.8.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 01571490, Cedar Run at Eberlys Mill, Pa., from January 1994 to August 1995.



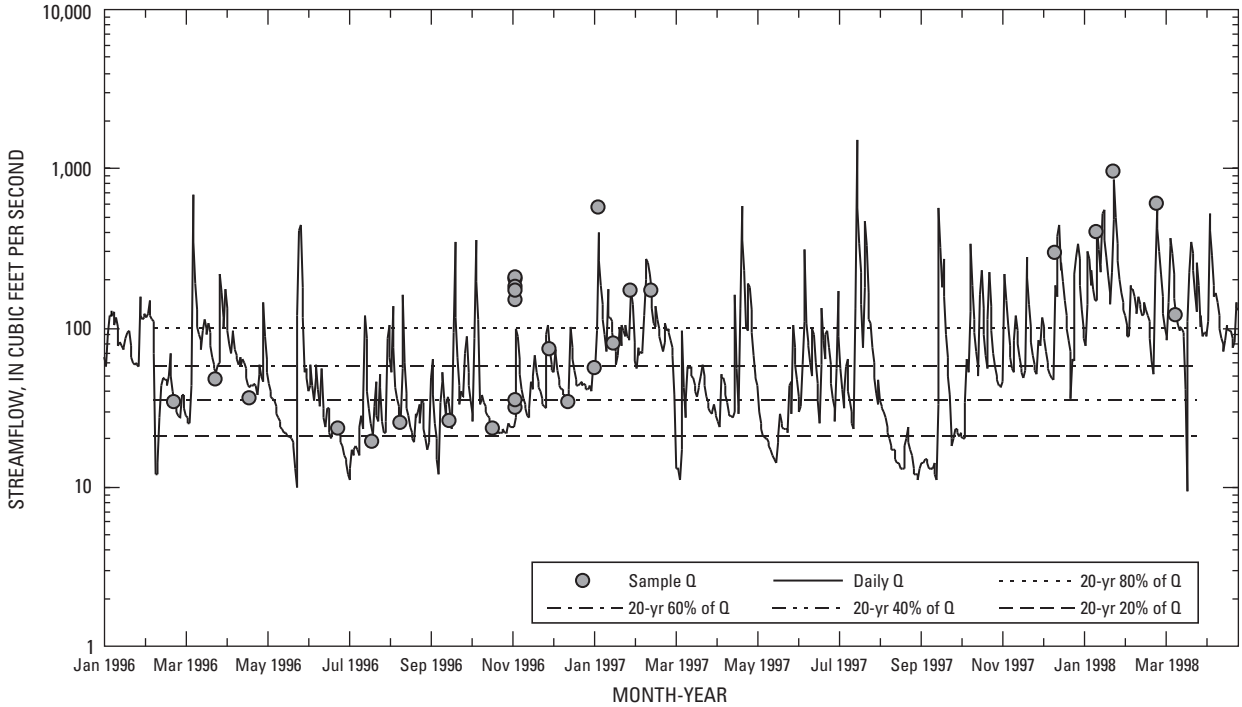

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.9.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 01654000, Accotink Creek near Annandale, Va., from October 2001 to September 2002.



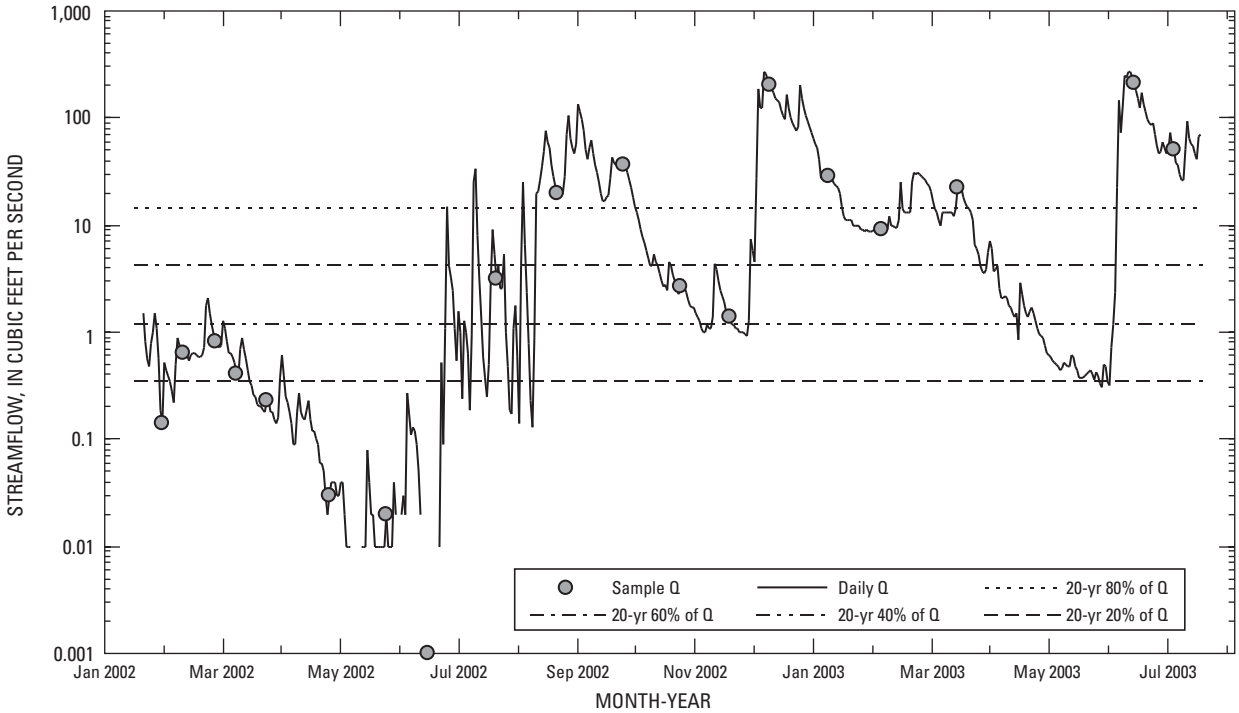

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.10.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 02087580, Swift Creek near Apex, N.C., from October 2001 to July 2003.



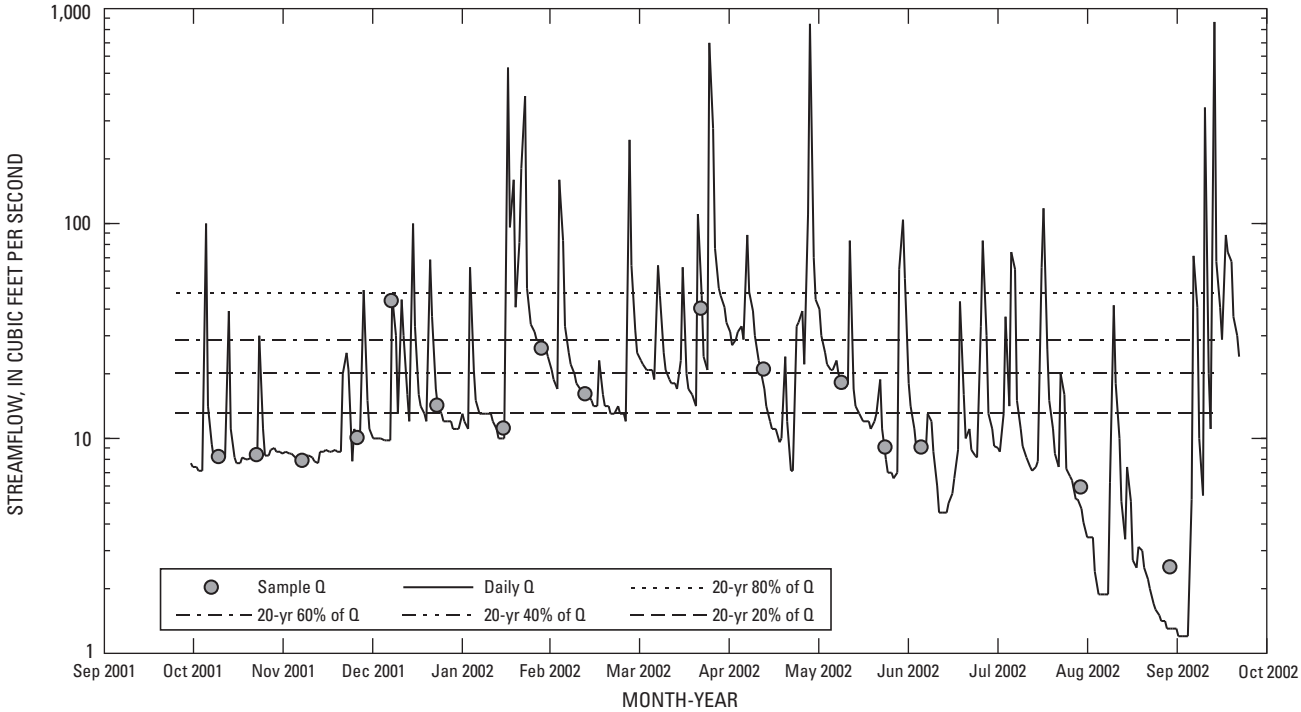

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.11.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 02169570, Gills Creek at Columbia, S.C., from February 1996 to March 1998.



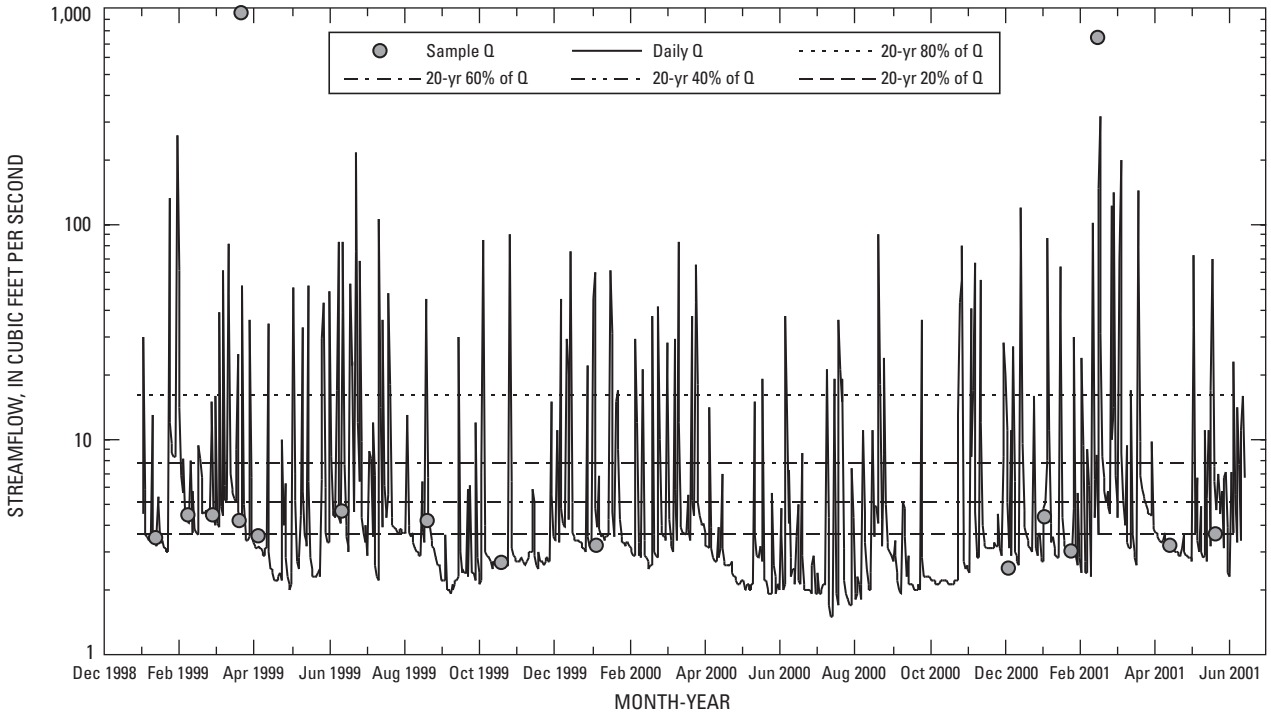

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.12.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 02306774, Rocky Creek at State Highway 587 at Citrus Park, Fla., from January 2002 to July 2003.



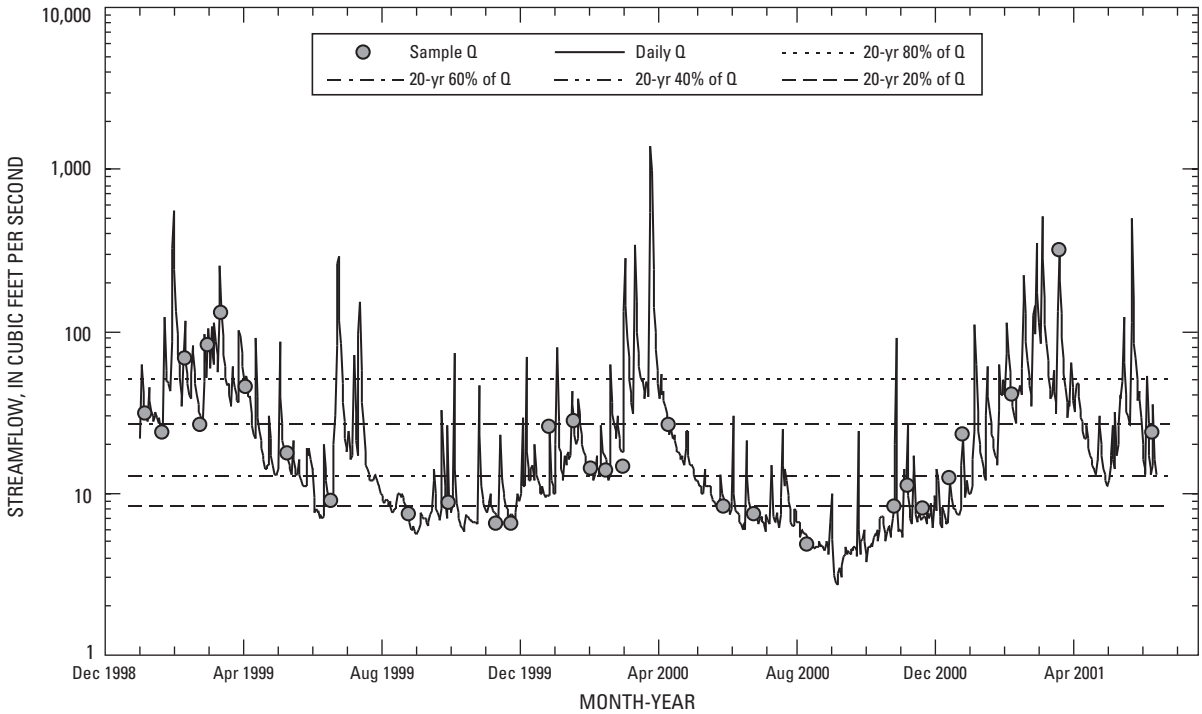

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.13.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 02335870, Sope Creek near Marietta, Ga., from October 2001 to September 2002.



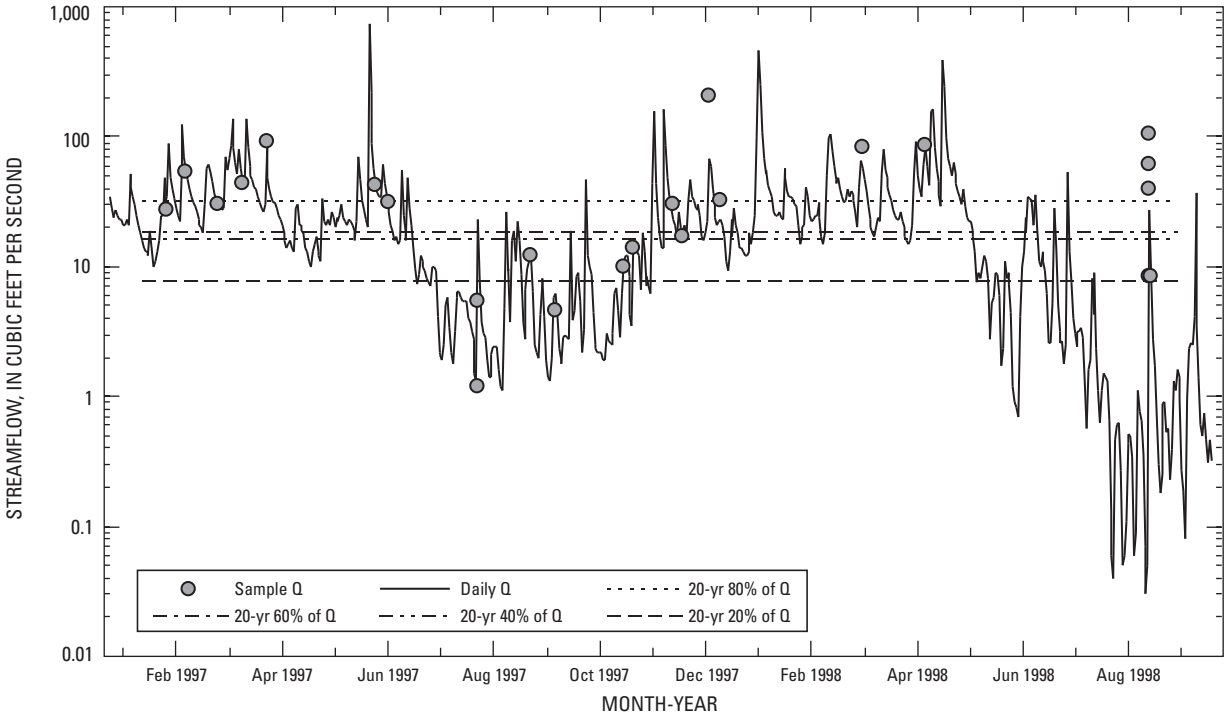

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.14.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 02419977, Three Mile Branch at North Boulevard at Montgomery, Ala., from January 1999 to June 2001.



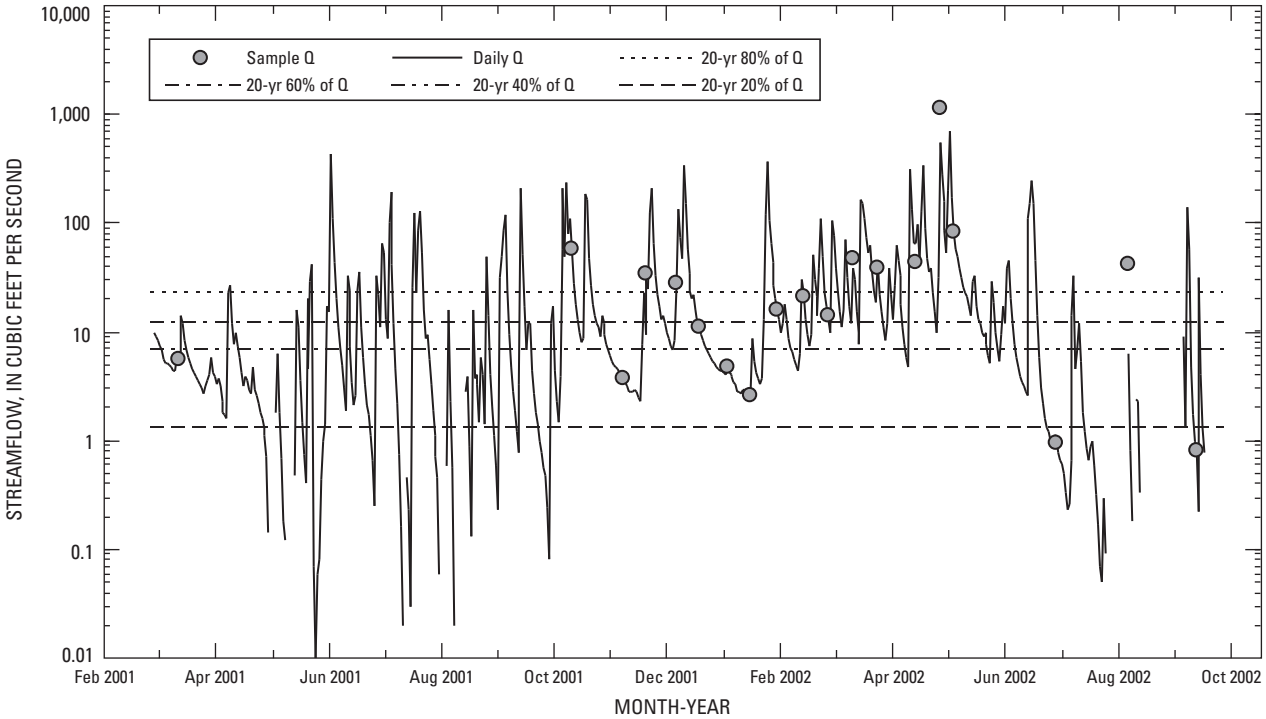

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.15.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 0242354750, Cahaba Valley Creek at Cross Creek Road at Pelham, Ala., from January 1999 to June 2001.



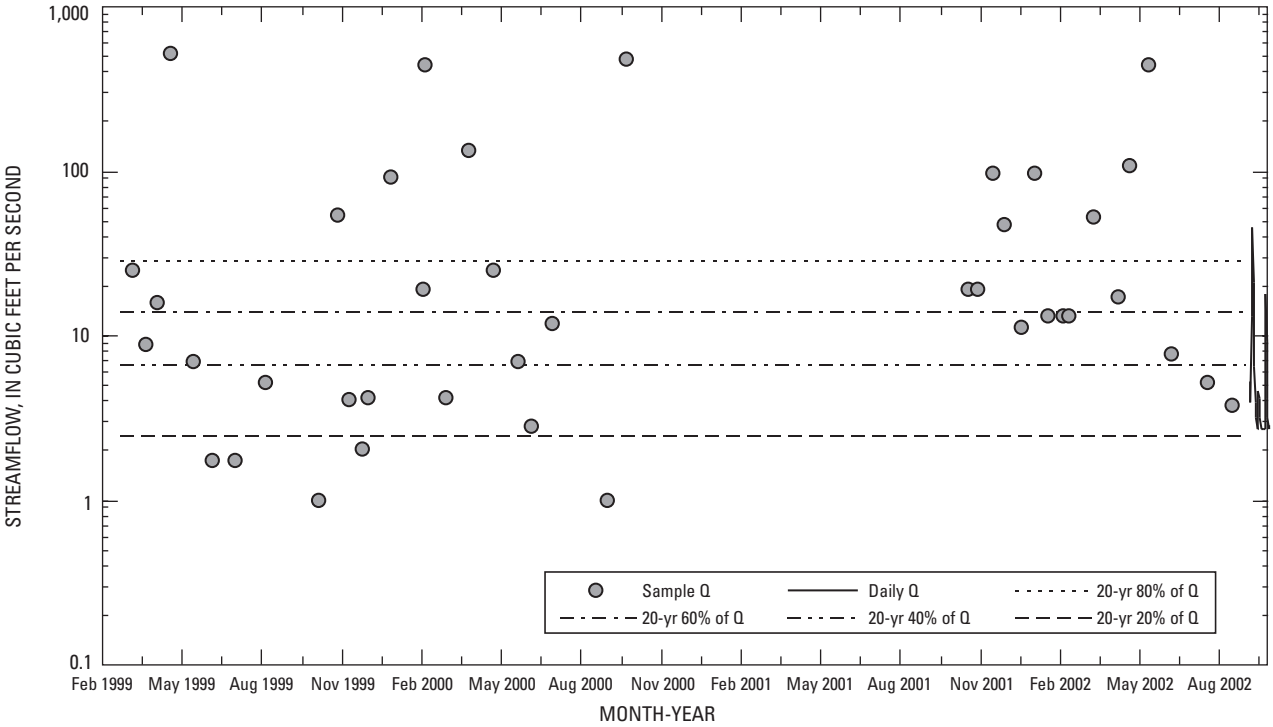

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.16.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 03049646, Deer Creek near Dorseyville, Pa., from January 1997 to August 1998.



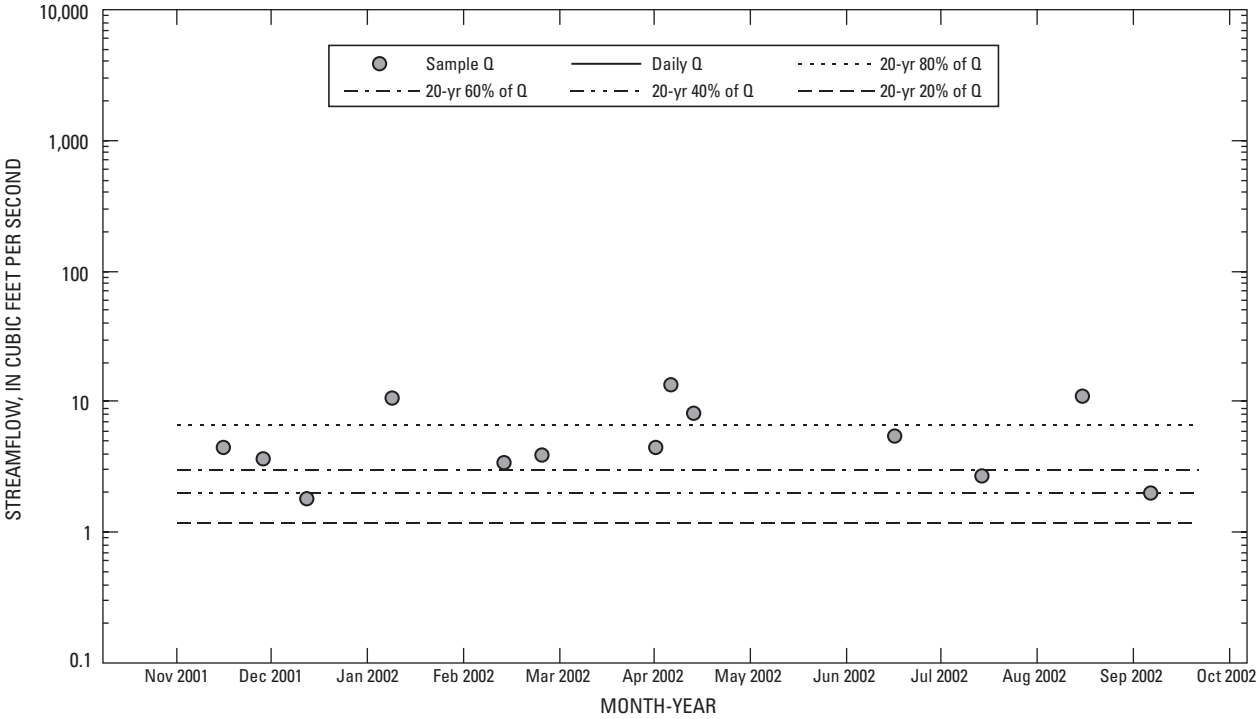

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.17.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 03353637, Little Buck Creek near Indianapolis, Ind., from March 2001 to September 2002.



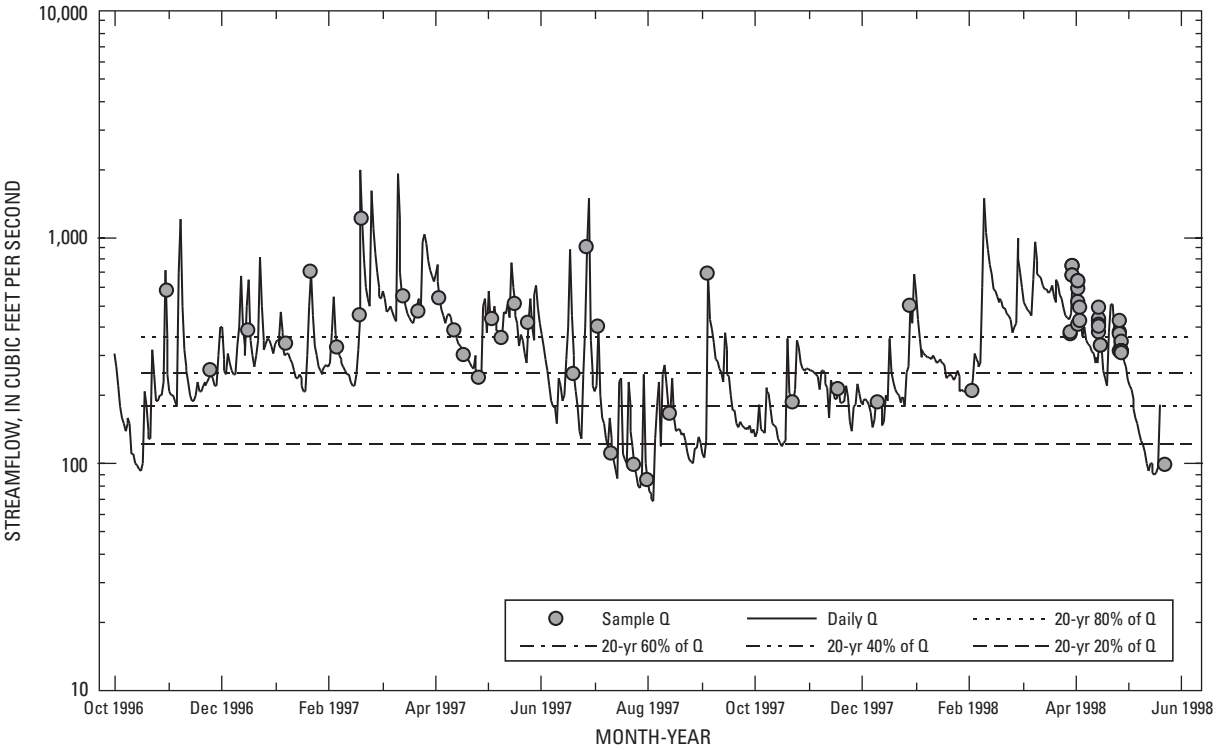

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.18.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 393944084120700, Holes Creek in Huffman Park at Kettering, Ohio, from March 1999 to September 2002.



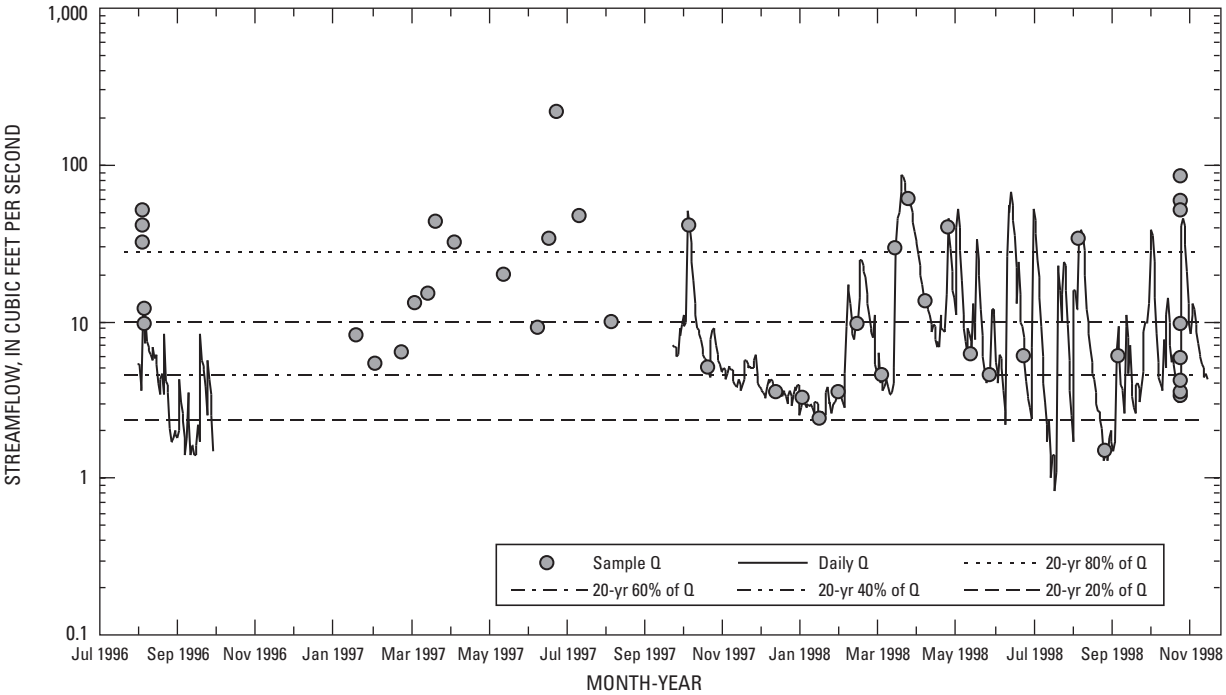

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.19.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 040869415, Lincoln Creek at 47th Street at Milwaukee, Wis., from November 2001 to September 2002.



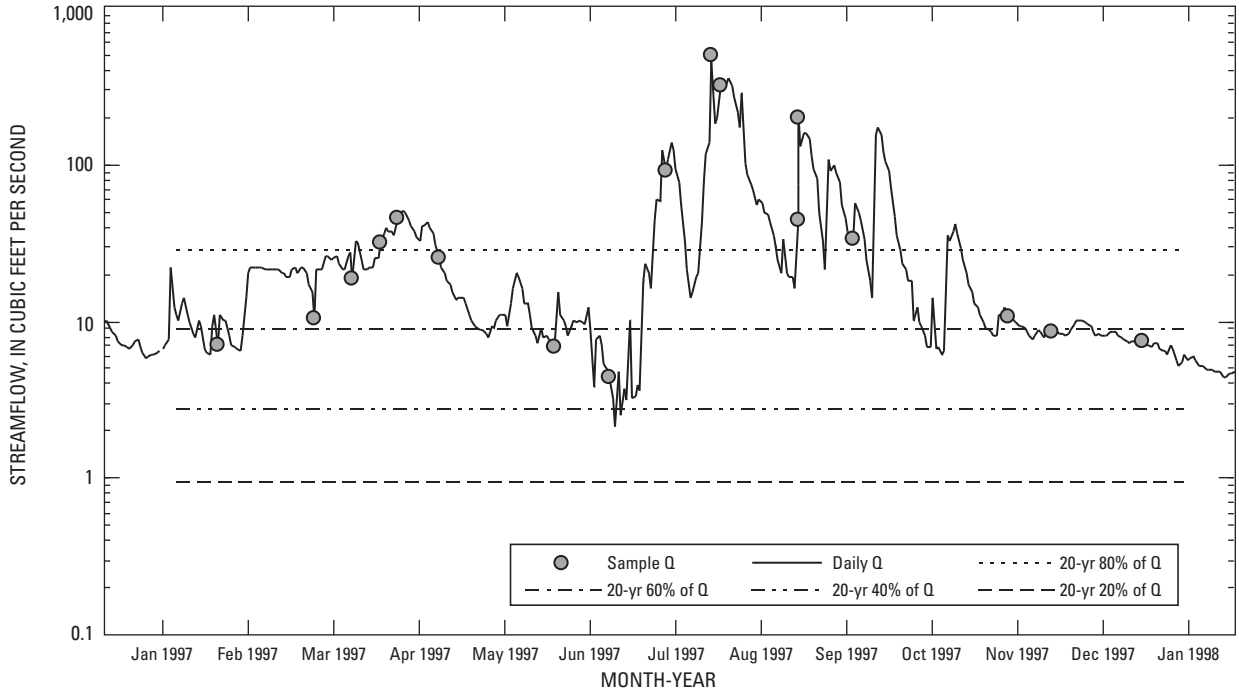

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.20.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 04161820, Clinton River at Sterling Heights, Mich., from October 1996 to June 1998.



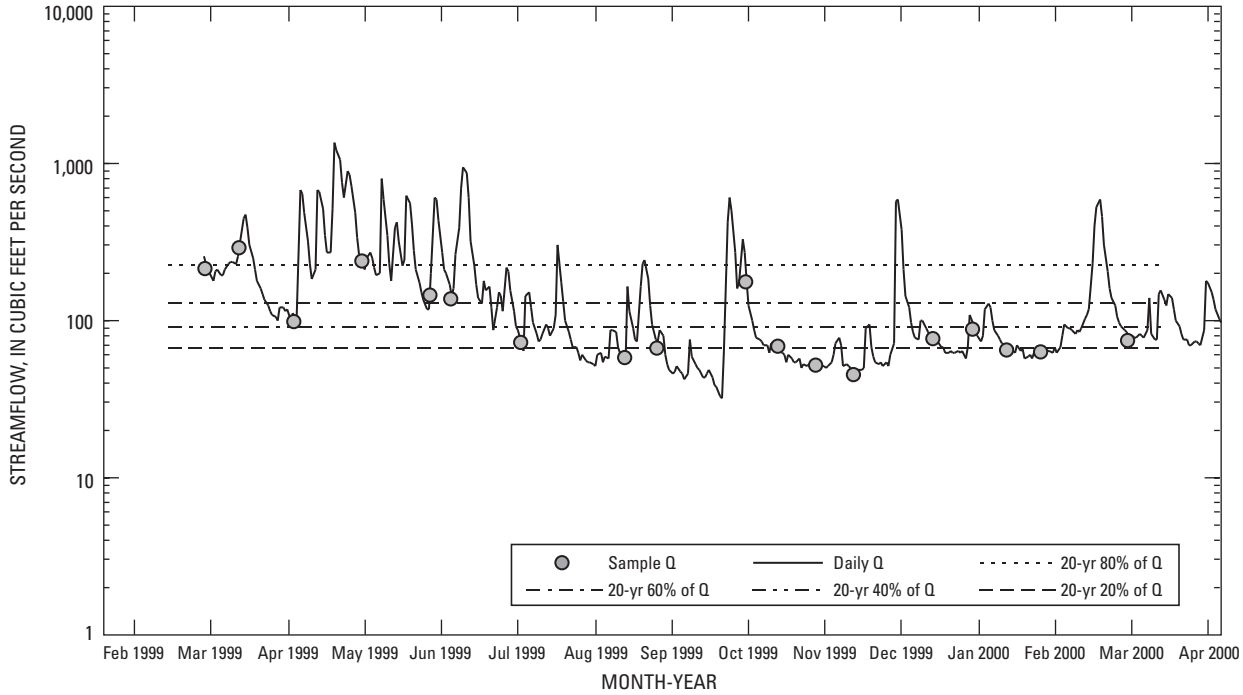

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.21.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 05288705, Shingle Creek at Queen Avenue in Minneapolis, Minn., from August 1996 to November 1998.



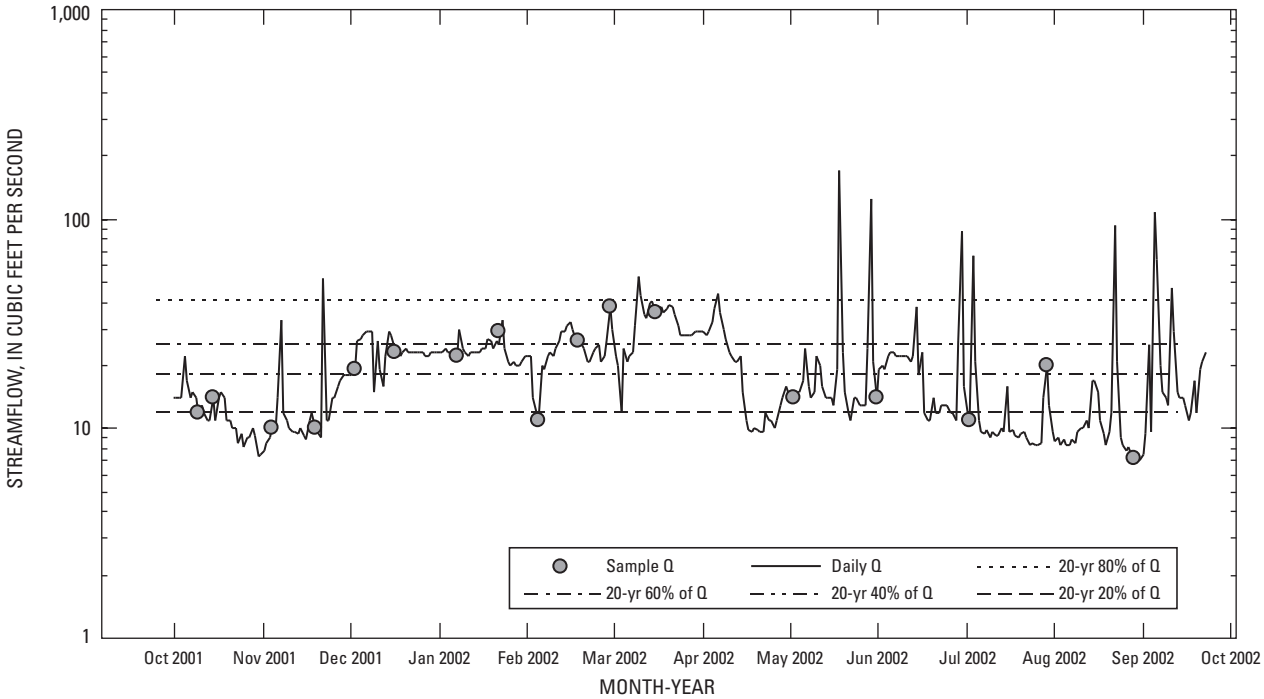

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.22.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 05330902, Nine Mile Creek near James Circle at Bloomington, Minn., from January 1997 to December 1997.



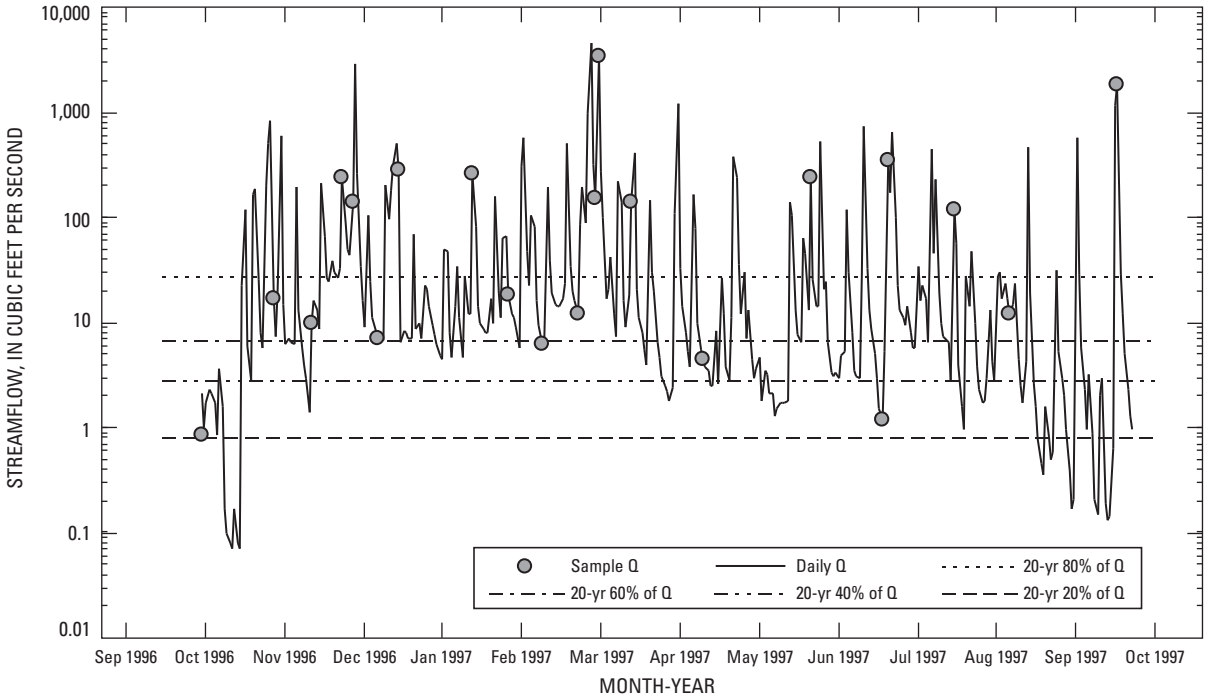

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.23.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 05531500, Salt Creek at Western Springs, Ill., from March 1999 to March 2000.



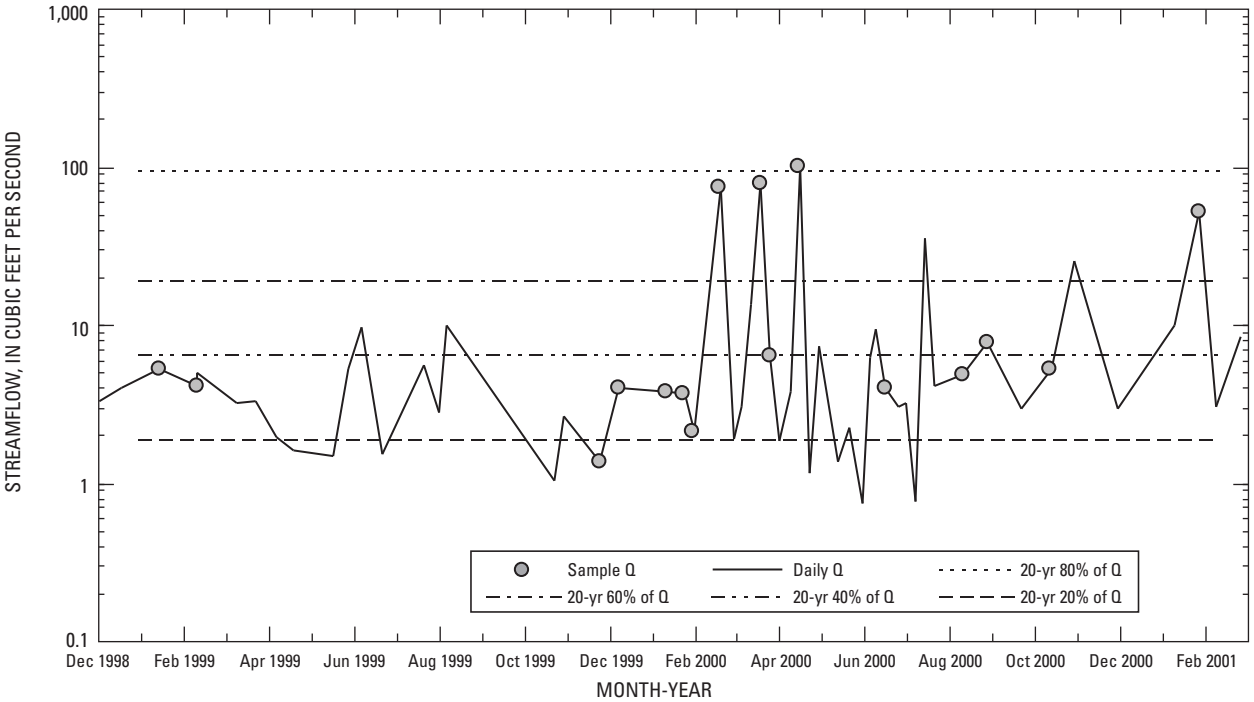

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.24.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 06713500, Cherry Creek at Denver, Colo., from October 2001 to September 2002.



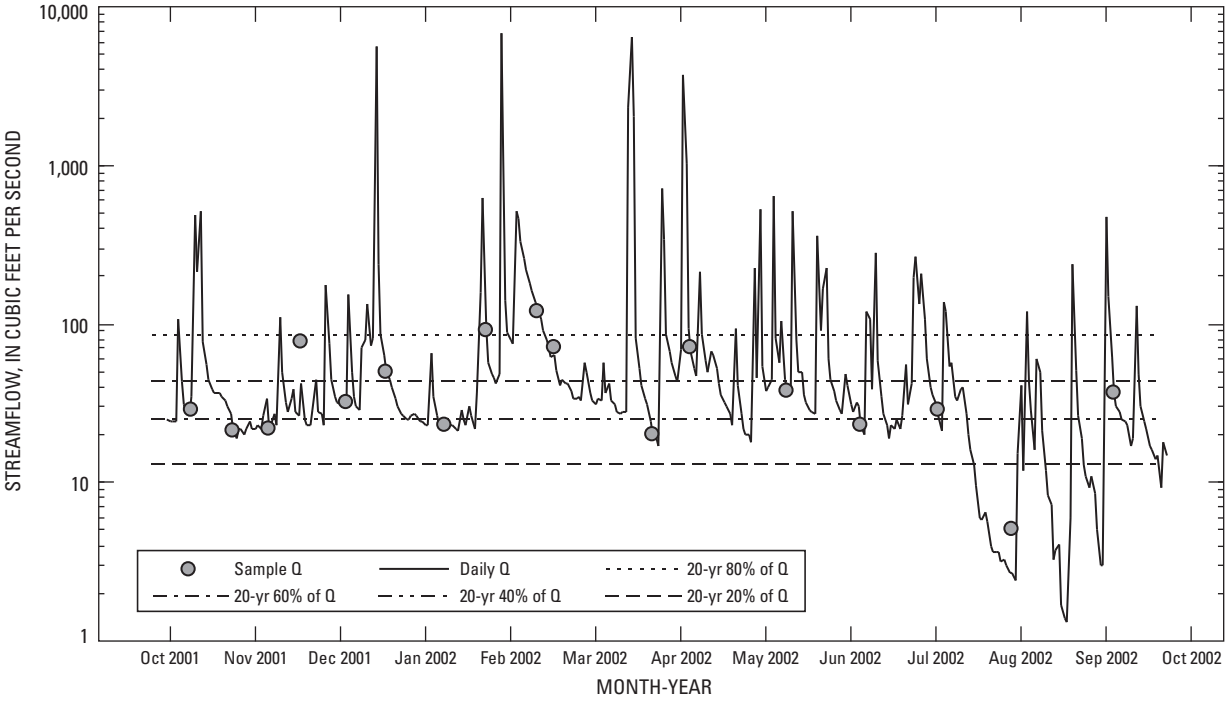

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.25.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 07031692, Fletcher Creek at Sycamore View Road at Memphis, Tenn., from October 1996 to September 1997.



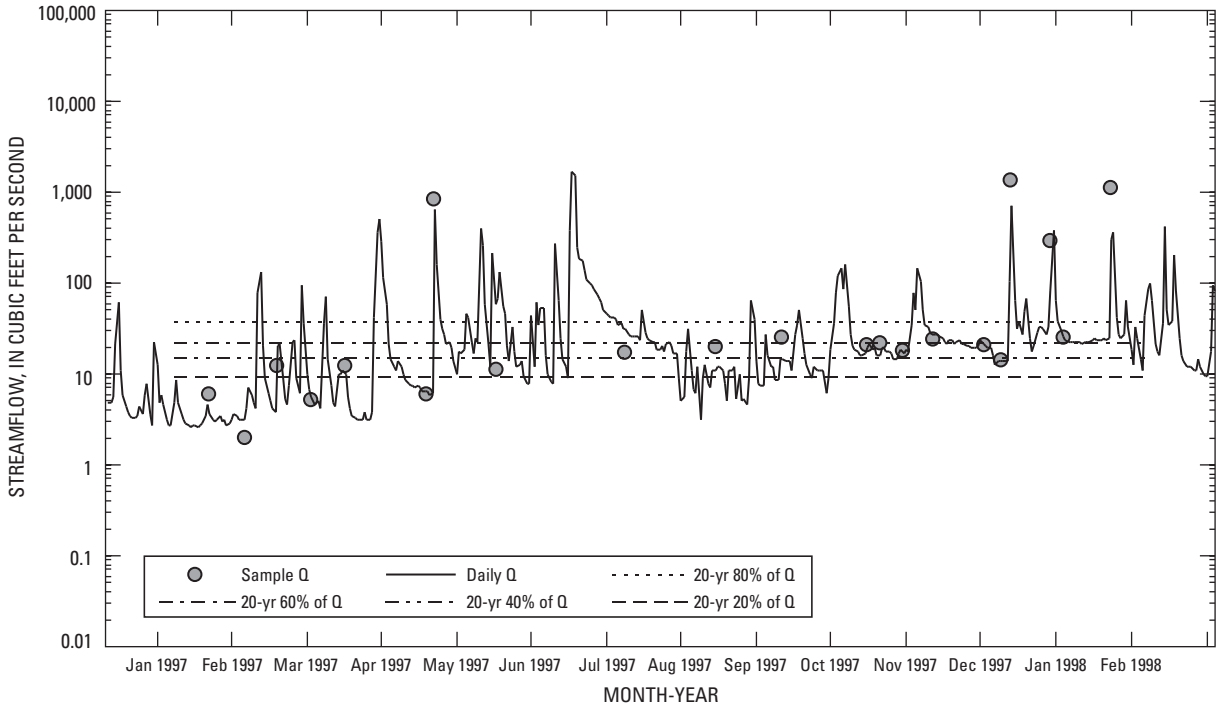

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.26.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 07379960, Dawson Creek at Bluebonnet Boulevard near Baton Rouge, La., from January 1999 to February 2001.



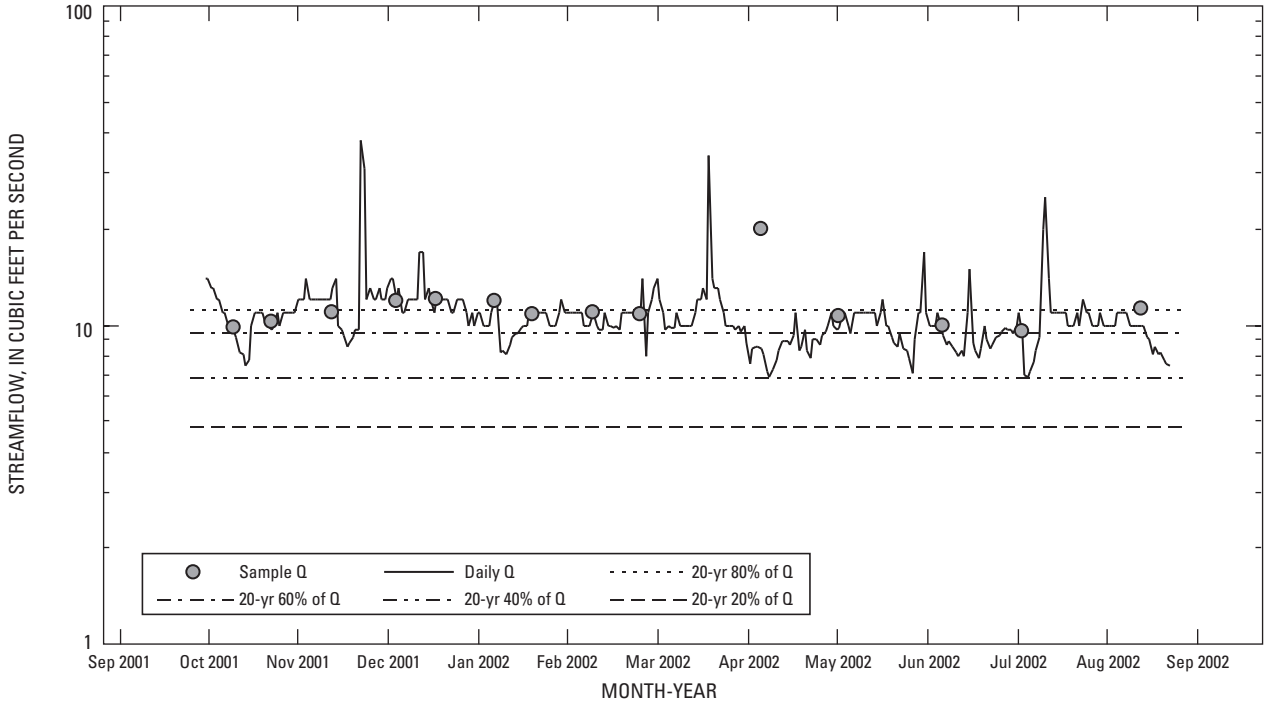

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.27.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 08057200, White Rock Creek at Greenville Avenue, Dallas, Tex., from October 2001 to September 2002.



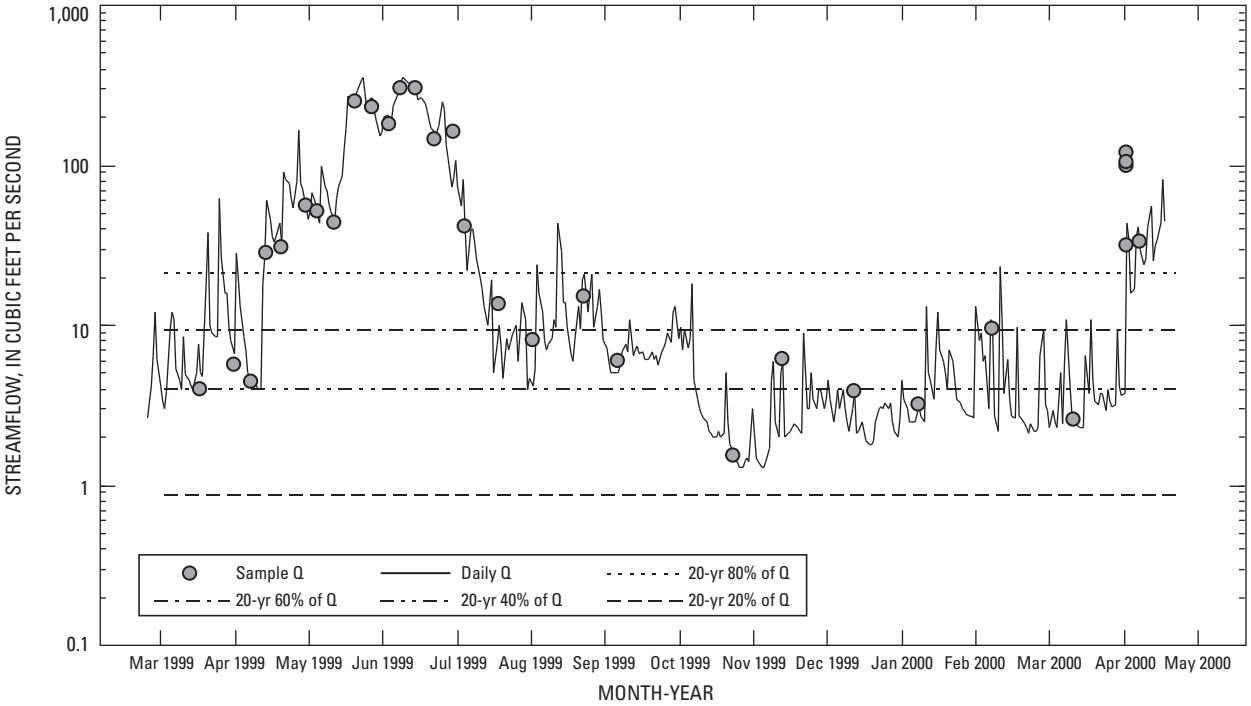

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.28.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 08178800, Salado Creek at Loop 13 at San Antonio, Tex., from January 1997 to January 1998.



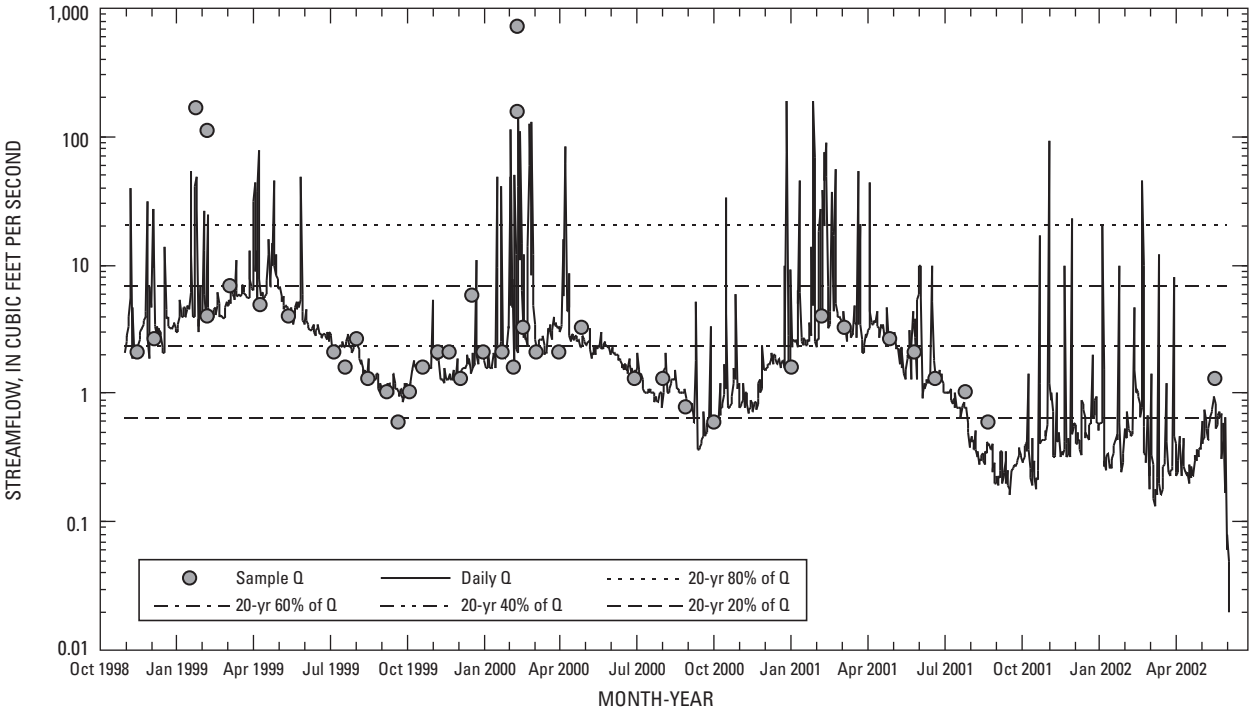

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.29.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 094196783, Las Vegas Wash below Flamingo Wash confluence near Las Vegas, Nev., from October 2001 to August 2002.



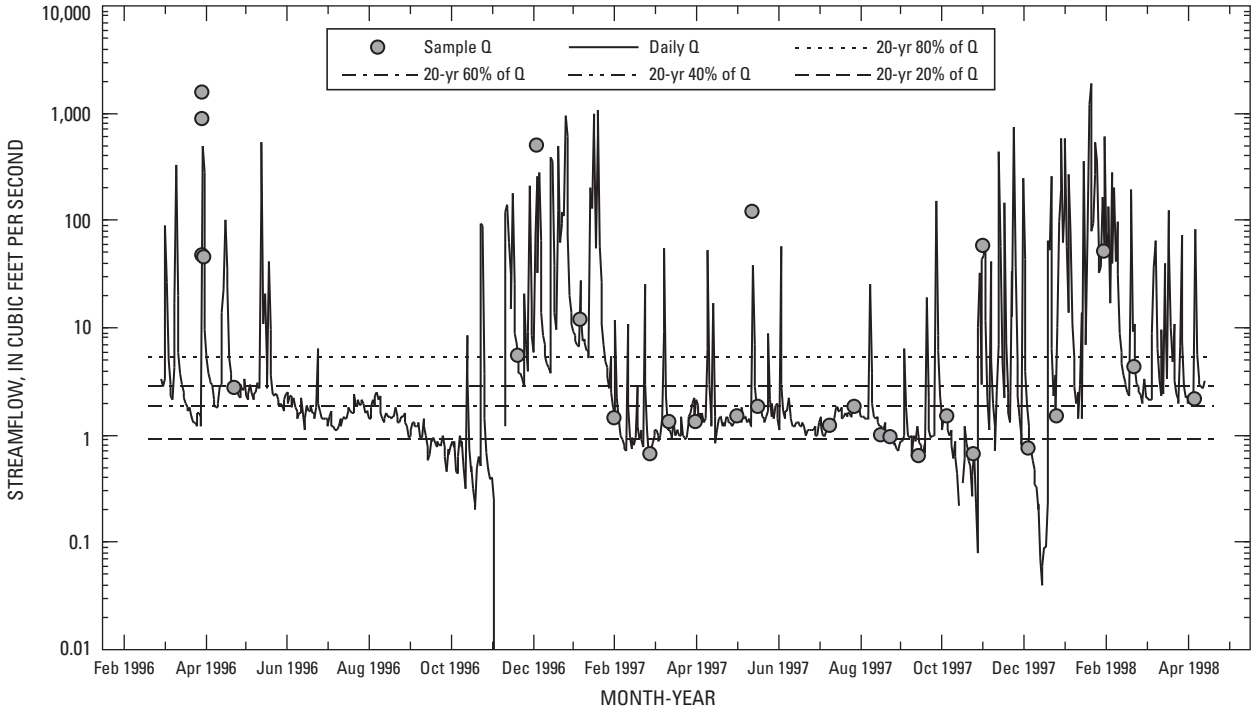

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.30.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 10168000, Little Cottonwood Creek at Jordan River near Salt Lake City, Utah, from March 1999 to April 2000.



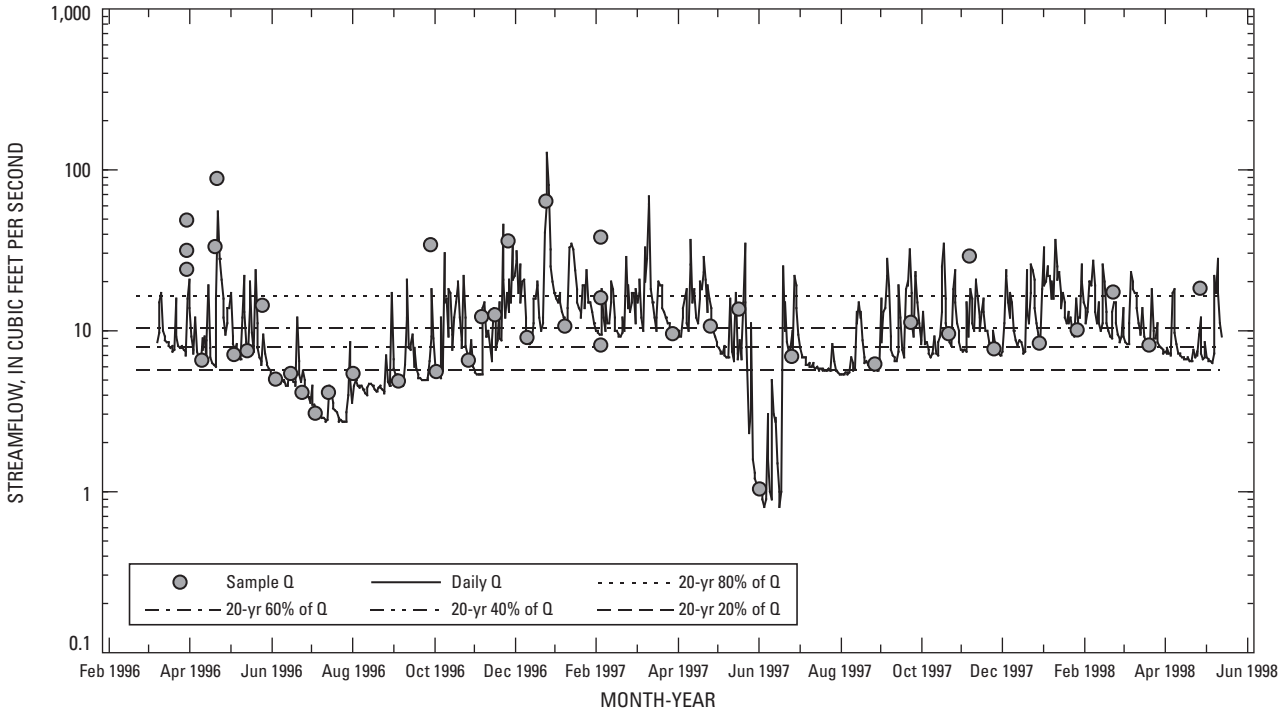

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.31.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 11060400, Warm Creek near San Bernardino, Calif., from November 1998 to June 2002.



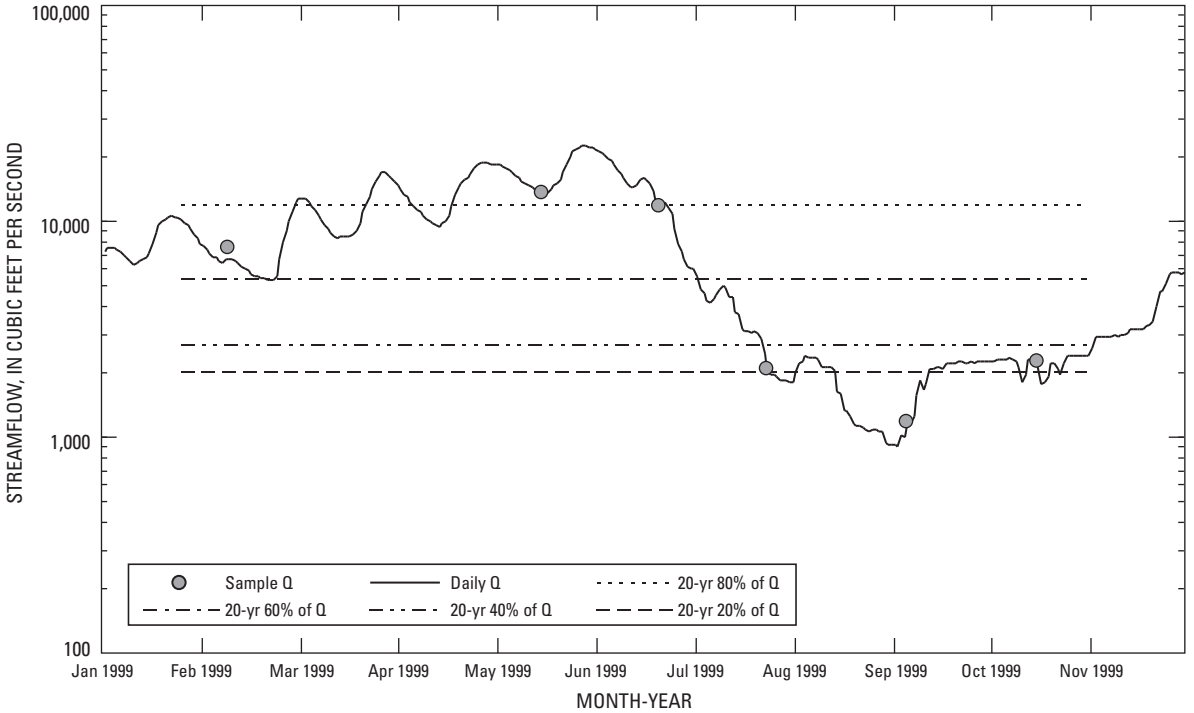

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.32.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 11447360, Arcade Creek near Del Paso Heights, Calif., from March 1996 to April 1998.



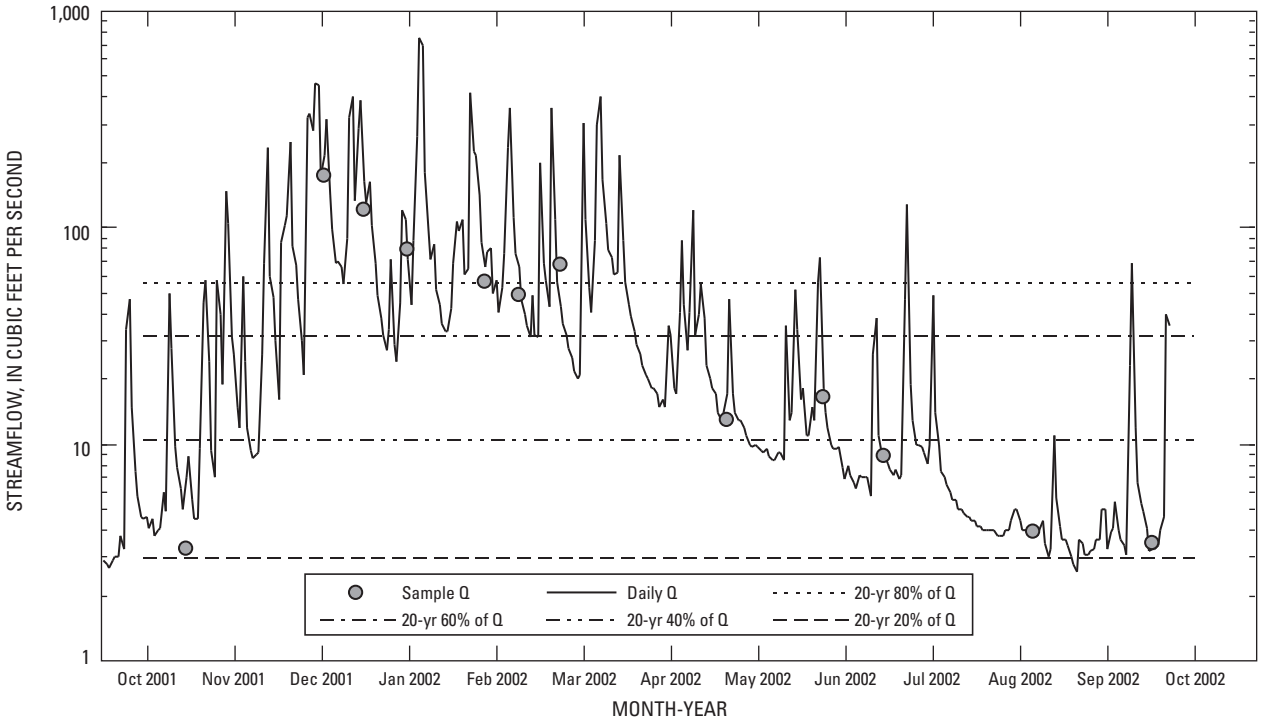

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.33.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 12128000, Thornton Creek near Seattle, Wash., from March 1996 to May 1998.



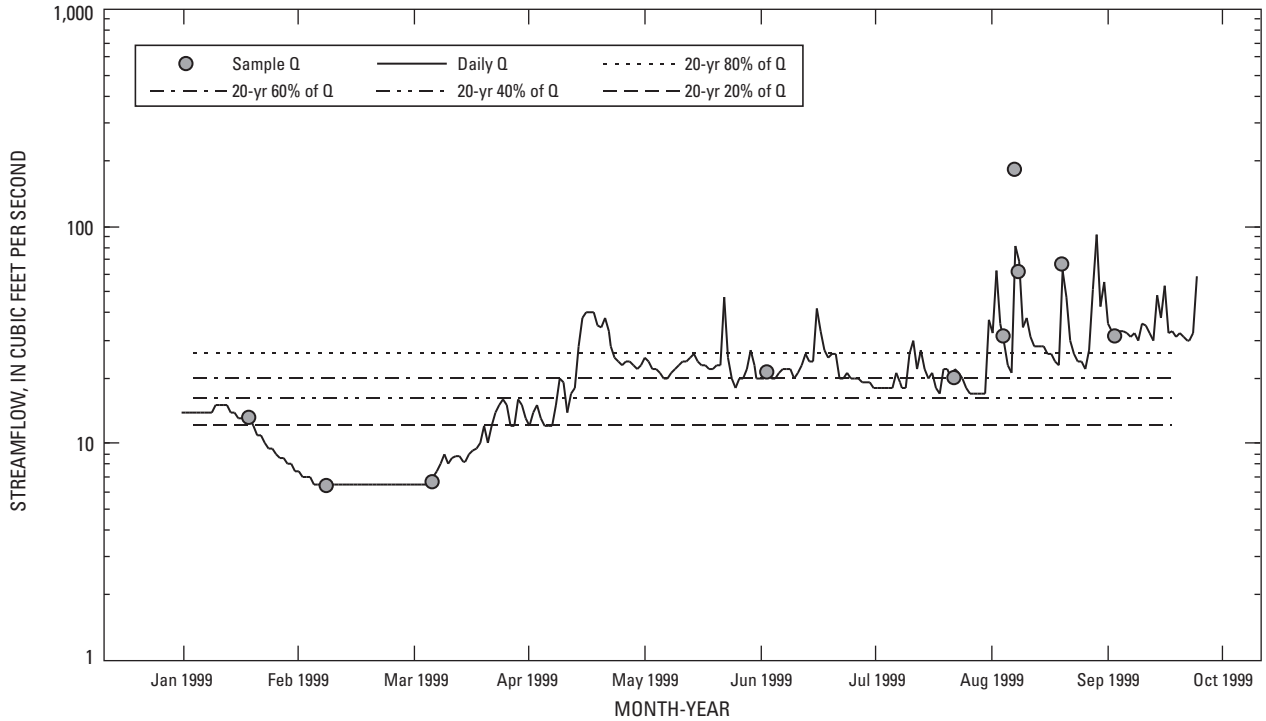

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.34.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 12424500, Spokane River at 7 Mile Bridge near Spokane, Wash., from February 1999 to October 1999.



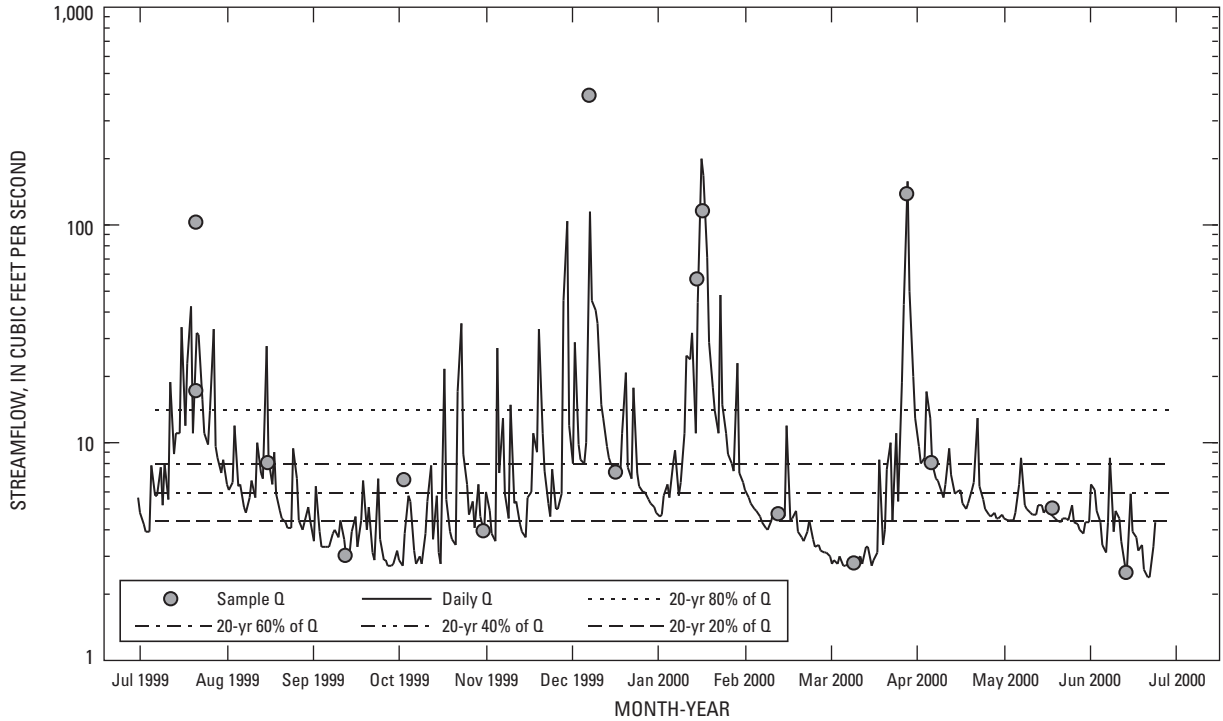

[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.35.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 14206950, Fanno Creek at Durham, Oreg., from October 2001 to September 2002.




[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.36.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 15275100, Chester Creek at Arctic Boulevard at Anchorage, Alaska, from January 1999 to September 1999.




[Sample Q, streamflow during sampling; Daily Q, mean daily streamflow; 20-yr 80% of Q, 80th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 60% of Q, 60th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 40% of Q, 40th percentile of streamflow based on 20-years of mean daily streamflow; 20-yr 20% of Q, 20th percentile of streamflow based on 20-years of mean daily streamflow]

**Figure A1.37.** Daily streamflow and 20-year pentiles of flow, in cubic feet per second, at station 16242500, Manoa Stream at Kanewai Field, Honolulu, Oahu, Hawaii, from July 1999 to June 2000.

# Appendix 2

**Appendix 2.** Summary of the detection frequency and concentrations by warmer (April through September) and cooler (October through March) months for individual volatile organic compounds at an assessment level of 0.02 microgram per liter, 1995–2003.

[VOC, volatile organic compound; USGS, U.S. Geological Survey; F, fumigant; GH, gasoline hydrocarbon; GO, gasoline oxygenate; O, organic synthesis compound; R, refrigerant; S, solvent; T, trihalomethane; <, less than; E, estimated concentration below the long-term method detection level; --, not applicable]

| Compound name | VOC group | USGS parameter code | Warmer months (April through September) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Number of samples | Number of samples with detected VOCs | Detection frequency (percent) | Statistical summary for concentrations (micrograms per liter) | | | | |
| | | | | | | Minimum | 25th percentile | Median | 75th percentile | Maximum |
| Toluene | GH | 34010 | 409 | 282 | 69 | <0.04 | <0.04 | 0.04 | 0.09 | 3.5 |
| Chloroform | T | 32106 | 410 | 230 | 56 | <.02 | <.02 | .02 | .04 | 1.9 |
| Methyl *tert*-butyl ether | GO | 78032 | 410 | 148 | 36 | <.11 | <.11 | <.11 | .10 | 21 |
| Trichloroethene | S | 39180 | 410 | 145 | 35 | <.04 | <.04 | <.04 | .05 | .57 |
| Perchloroethene | S | 34475 | 410 | 113 | 28 | <.03 | <.03 | <.03 | .02 | 1.1 |
| *cis*-1,2-Dichloroethene | S | 77093 | 410 | 139 | 34 | <.02 | <.02 | <.02 | .04 | 1.5 |
| Acetone | S | 81552 | 403 | 115 | 29 | <4.9 | <4.9 | <4.9 | E1.5 | 45 |
| *m*- and *p*-Xylene | GH | 85795 | 403 | 79 | 20 | <.06 | <.06 | <.06 | <.06 | .69 |
| Benzene | GH | 34030 | 410 | 51 | 12 | <.02 | <.02 | <.02 | <.02 | .21 |
| Chloromethane | S | 34418 | 410 | 69 | 17 | <.17 | <.17 | <.17 | <.17 | .20 |
| 1,2,4-Trimethylbenzene | GH | 77222 | 410 | 26 | 6.3 | <.06 | <.06 | <.06 | <.06 | .66 |
| *o*-Xylene | GH | 77135 | 403 | 22 | 5.5 | <.04 | <.04 | <.04 | <.04 | .36 |
| Dichloromethane | S | 34423 | 410 | 38 | 9.3 | <.06 | <.06 | <.06 | <.06 | 1.4 |
| 1,1,1-Trichloroethane | S | 34506 | 410 | 38 | 9.3 | <.03 | <.03 | <.03 | <.03 | 1.3 |
| Methyl isobutyl ketone | S | 78133 | 403 | 22 | 5.5 | <.37 | <.37 | <.37 | <.37 | 1.1 |
| Carbon disulfide | O | 77041 | 403 | 37 | 9.2 | <.04 | <.04 | <.04 | <.04 | .2 |
| Methyl ethyl ketone | S | 81595 | 403 | 27 | 6.7 | <1.6 | <1.6 | <1.6 | <1.6 | 5.7 |
| Bromodichloromethane | T | 32101 | 410 | 34 | 8.3 | <.03 | <.03 | <.03 | <.03 | .48 |
| 4-Isopropyltoluene | GH | 77356 | 410 | 31 | 7.6 | <.07 | <.07 | <.07 | <.07 | 1.4 |
| 1,1-Dichloroethane | S | 34496 | 410 | 29 | 7.1 | <.03 | <.03 | <.03 | <.03 | .11 |
| Ethylbenzene | GH | 34371 | 410 | 13 | 3.2 | <.03 | <.03 | <.03 | <.03 | .13 |
| Chlorobenzene | S | 34301 | 410 | 21 | 5.1 | <.03 | <.03 | <.03 | <.03 | .33 |
| 1,4-Dichlorobenzene | F | 34571 | 410 | 17 | 4.2 | <.03 | <.03 | <.03 | <.03 | .05 |
| *tert*-Amyl methyl ether | GO | 50005 | 403 | 8 | 2.0 | <.08 | <.08 | <.08 | <.08 | .09 |
| Naphthalene | GH | 34696 | 410 | 2 | .49 | <.25 | <.25 | <.25 | <.25 | E.06 |
| 1,1-Dichloroethene | O | 34501 | 410 | 8 | 2.0 | <.02 | <.02 | <.02 | <.02 | .05 |
| Dibromochloromethane | T | 32105 | 410 | 15 | 3.7 | <.1 | <.1 | <.1 | <.1 | .36 |

| Cooler months (October through March) | | | | | | | |
|---|---|---|---|---|---|---|---|
| Number of samples | Number of samples with detected VOCs | Detection frequency (percent) | Statistical summary for concentrations (micrograms per liter) | | | | |
| | | | Minimum | 25th percentile | Median | 75th percentile | Maximum |
| 458 | 366 | 80 | <0.04 | 0.02 | 0.05 | 0.10 | 11 |
| 459 | 250 | 54 | <.02 | <.02 | .02 | .04 | 1.9 |
| 459 | 200 | 44 | <.11 | <.11 | <.11 | .25 | 44 |
| 459 | 154 | 34 | <.04 | <.04 | <.04 | .04 | 1.5 |
| 459 | 184 | 40 | <.03 | <.03 | <.03 | .06 | .78 |
| 459 | 155 | 34 | <.02 | <.02 | <.02 | .04 | 7.6 |
| 453 | 146 | 32 | <4.9 | <4.9 | <4.9 | E1.9 | 698 |
| 453 | 160 | 35 | <.06 | <.06 | <.06 | .03 | .67 |
| 459 | 143 | 31 | <.02 | <.02 | <.02 | .02 | .20 |
| 458 | 59 | 13 | <.17 | <.17 | <.17 | <.17 | .30 |
| 459 | 82 | 18 | <.06 | <.06 | <.06 | <.06 | .99 |
| 453 | 75 | 17 | <.04 | <.04 | <.04 | <.04 | .35 |
| 459 | 57 | 12 | <.06 | <.06 | <.06 | <.06 | .99 |
| 459 | 56 | 12 | <.03 | <.03 | <.03 | <.03 | .30 |
| 453 | 60 | 13 | <.37 | <.37 | <.37 | <.37 | 1.5 |
| 453 | 44 | 9.7 | <.04 | <.04 | <.04 | <.04 | .11 |
| 452 | 51 | 11 | <1.6 | <1.6 | <1.6 | <1.6 | 4.3 |
| 459 | 43 | 9.4 | <.03 | <.03 | <.03 | <.03 | .88 |
| 459 | 43 | 9.4 | <.07 | <.07 | <.07 | <.07 | 2.1 |
| 459 | 37 | 8.1 | <.03 | <.03 | <.03 | <.03 | .16 |
| 459 | 47 | 10 | <.03 | <.03 | <.03 | <.03 | .09 |
| 459 | 25 | 5.5 | <.03 | <.03 | <.03 | <.03 | .37 |
| 458 | 28 | 6.1 | <.03 | <.03 | <.03 | <.03 | .26 |
| 453 | 36 | 8.0 | <.08 | <.08 | <.08 | <.08 | .17 |
| 459 | 36 | 7.8 | <.25 | <.25 | <.25 | <.25 | .30 |
| 459 | 23 | 5.0 | <.02 | <.02 | <.02 | <.02 | .06 |
| 458 | 14 | 3.1 | <.1 | <.1 | <.1 | <.1 | .50 |

**Appendix 2.** Summary of the detection frequency and concentrations by warmer (April through September) and cooler (October through March) months for individual volatile organic compounds at an assessment level of 0.02 microgram per liter, 1995–2003.—Continued

[VOC, volatile organic compound; USGS, U.S. Geological Survey; F, fumigant; GH, gasoline hydrocarbon; GO, gasoline oxygenate; O, organic synthesis compound; R, refrigerant; S, solvent; T, trihalomethane; <, less than; E, estimated concentration below the long-term method detection level; --, not applicable]

| Compound name | VOC group | USGS parameter code | Warmer months (April through September) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Number of samples | Number of samples with detected VOCs | Detection frequency (percent) | Statistical summary for concentrations (micrograms per liter) | | | | |
| | | | | | | Minimum | 25th percentile | Median | 75th percentile | Maximum |
| 1,2,3-Trimethylbenzene | GH | 77221 | 403 | 7 | 1.7 | <0.06 | <0.06 | <0.06 | <0.06 | 0.17 |
| Styrene | GH | 77128 | 410 | 12 | 2.9 | <.04 | <.04 | <.04 | <.04 | .04 |
| Trichlorotrifluoroethane | R | 77652 | 410 | 10 | 2.4 | <.03 | <.03 | <.03 | <.03 | .10 |
| 1,3,5-Trimethylbenzene | GH | 77226 | 410 | 7 | 1.7 | <.04 | <.04 | <.04 | <.04 | .17 |
| 2-Ethyltoluene | GH | 77220 | 403 | 5 | 1.2 | <.06 | <.06 | <.06 | <.06 | .10 |
| Tetrahydrofuran | S | 81607 | 403 | 12 | 3.0 | <1.2 | <1.2 | <1.2 | <1.2 | 3.3 |
| 1,2,3,5-Tetramethylbenzene | GH | 50000 | 403 | 4 | .99 | <.14 | <.14 | <.14 | <.14 | .14 |
| Chloroethane | S | 34311 | 410 | 7 | 1.7 | <.12 | <.12 | <.12 | <.12 | .10 |
| Dichlorodifluoromethane | R | 34668 | 410 | 4 | .98 | <.1 | <.1 | <.1 | <.1 | .50 |
| Tetrachloromethane | S | 32102 | 410 | 3 | .73 | <.06 | <.06 | <.06 | <.06 | .04 |
| Diisopropyl ether | GO | 81577 | 351 | 2 | .57 | <.1 | <.1 | <1 | <.1 | E.02 |
| Bromoform | T | 32104 | 410 | 4 | .98 | <.06 | <.06 | <.06 | <.06 | .54 |
| *n*-Propylbenzene | S | 77224 | 410 | 3 | .73 | <.04 | <.04 | <.04 | <.04 | .05 |
| Diethyl ether | S | 81576 | 403 | 8 | 2.0 | <.08 | <.08 | <.08 | <.08 | .43 |
| 1,2,3,4-Tetramethylbenzene | GH | 49999 | 403 | 0 | -- | <.14 | <.14 | <.14 | <.14 | <.14 |
| Vinyl chloride | O | 39175 | 410 | 3 | .73 | <.06 | <.06 | <.06 | <.06 | .80 |
| Acrolein | O | 34210 | 154 | 2 | 1.3 | <1.5 | <1.5 | <1.5 | <1.5 | 2.1 |
| *trans*-1,2-Dichloroethene | S | 34546 | 410 | 1 | .24 | <.03 | <.03 | <.03 | <.03 | .03 |
| *n*-Butylbenzene | GH | 77342 | 410 | 0 | -- | <.12 | <.12 | <.12 | <.12 | <.12 |
| 2-Chlorotoluene | S | 77275 | 410 | 2 | .49 | <.03 | <.03 | <.03 | <.03 | .05 |
| 1,2-Dichloropropane | F | 34541 | 410 | 0 | -- | <.03 | <.03 | <.03 | <.03 | <.03 |
| 1,1,2,2-Tetrachloroethane | S | 34516 | 410 | 0 | -- | <.09 | <.09 | <.09 | <.09 | <.09 |
| Trichlorofluoromethane | R | 34488 | 410 | 0 | -- | <.03 | <.03 | <.03 | <.03 | <.03 |
| Ethyl *tert*-butyl ether | GO | 50004 | 403 | 0 | -- | <.05 | <.05 | <.05 | <.05 | <.05 |
| *sec*-Butylbenzene | GH | 77350 | 410 | 0 | -- | <.03 | <.03 | <.03 | <.03 | <.03 |

| Cooler months (October through March) | | | | | | | |
|---|---|---|---|---|---|---|---|
| Number of samples | Number of samples with detected VOCs | Detection frequency (percent) | Statistical summary for concentrations (micrograms per liter) | | | | |
| | | | Minimum | 25th percentile | Median | 75th percentile | Maximum |
| 453 | 21 | 4.6 | <0.06 | <0.06 | <0.06 | <0.06 | 0.22 |
| 459 | 15 | 3.3 | <.04 | <.04 | <.04 | <.04 | .10 |
| 459 | 17 | 3.7 | <.03 | <.03 | <.03 | <.03 | .15 |
| 459 | 17 | 3.7 | <.04 | <.04 | <.04 | <.04 | .25 |
| 453 | 17 | 3.8 | <.06 | <.06 | <.06 | <.06 | .18 |
| 453 | 10 | 2.2 | <1.2 | <1.2 | <1.2 | <1.2 | 1.5 |
| 453 | 10 | 2.2 | <.14 | <.14 | <.14 | <.14 | .10 |
| 459 | 7 | 1.5 | <.12 | <.12 | <.12 | <.12 | .09 |
| 459 | 7 | 1.5 | <.1 | <.1 | <.1 | <.1 | .58 |
| 459 | 8 | 1.7 | <.06 | <.06 | <.06 | <.06 | .04 |
| 412 | 7 | 1.7 | <.1 | <.1 | <.1 | <.1 | .05 |
| 459 | 6 | 1.3 | <.06 | <.06 | <.06 | <.06 | .13 |
| 459 | 7 | 1.5 | <.04 | <.04 | <.04 | <.04 | .08 |
| 453 | 1 | .22 | <.08 | <.08 | <.08 | <.08 | .07 |
| 453 | 9 | 2.0 | <.14 | <.14 | <.14 | <.14 | .35 |
| 459 | 6 | 1.3 | <.06 | <.06 | <.06 | <.06 | .94 |
| 154 | 1 | .65 | <1.5 | <1.5 | <1.5 | <1.5 | 3.4 |
| 459 | 5 | 1.1 | <.03 | <.03 | <.03 | <.03 | 3.52 |
| 459 | 5 | 1.1 | <.12 | <.12 | <.12 | <.12 | E.04 |
| 459 | 2 | .44 | <.03 | <.03 | <.03 | <.03 | .07 |
| 459 | 2 | .44 | <.03 | <.03 | <.03 | <.03 | .03 |
| 459 | 2 | .44 | <.09 | <.09 | <.09 | <.09 | .08 |
| 459 | 2 | .44 | <.03 | <.03 | <.03 | <.03 | .08 |
| 453 | 1 | .22 | <.05 | <.05 | <.05 | <.05 | E.02 |
| 459 | 1 | .22 | <.03 | <.03 | <.03 | <.03 | .02 |

**Appendix 2.** Summary of the detection frequency and concentrations by warmer (April through September) and cooler (October through March) months for individual volatile organic compounds at an assessment level of 0.02 microgram per liter, 1995–2003.—Continued

[VOC, volatile organic compound; USGS, U.S. Geological Survey; F, fumigant; GH, gasoline hydrocarbon; GO, gasoline oxygenate; O, organic synthesis compound; R, refrigerant; S, solvent; T, trihalomethane; <, less than; E, estimated concentration below the long-term method detection level; --, not applicable]

| Compound name | VOC group | USGS parameter code | Warmer months (April through September) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Number of samples | Number of samples with detected VOCs | Detection frequency (percent) | Statistical summary for concentrations (micrograms per liter) | | | | |
| | | | | | | Minimum | 25th percentile | Median | 75th percentile | Maximum |
| Dibromochloropropane | F | 82625 | 410 | 1 | 0.24 | <0.21 | <0.21 | <0.21 | <0.21 | E0.09 |
| 1,2-Dichlorobenzene | S | 34536 | 410 | 0 | -- | <.05 | <.05 | <.05 | <.05 | <.05 |
| 1,3-Dichlorobenzene | S | 34566 | 410 | 0 | -- | <.03 | <.03 | <.03 | <.03 | <.03 |
| 1,2-Dichloroethane | S | 32103 | 410 | 1 | .24 | <.13 | <.13 | <.13 | <.13 | E.03 |
| Isopropylbenzene | GH | 77223 | 410 | 0 | -- | <.03 | <.03 | <.03 | <.03 | <.03 |
| Acrylonitrile | O | 34215 | 404 | 0 | -- | <1.2 | <1.2 | <1.2 | <1.2 | <1.2 |
| Bromobenzene | S | 81555 | 410 | 0 | -- | <.03 | <.03 | <.03 | <.03 | <.03 |
| Bromochloromethane | O | 77297 | 410 | 0 | -- | <.04 | <.04 | <.04 | <.04 | <.04 |
| Bromomethane | F | 34413 | 410 | 0 | -- | <.15 | <.15 | <.15 | <.15 | <.15 |
| *tert*-Butylbenzene | GH | 77353 | 410 | 0 | -- | <.05 | <.05 | <.05 | <.05 | <.05 |
| 3-Chloro-1-propene | O | 78109 | 403 | 0 | -- | <.07 | <.07 | <.07 | <.07 | <.07 |
| 4-Chlorotoluene | S | 77277 | 410 | 0 | -- | <.05 | <.05 | <.05 | <.05 | <.05 |
| Dibromomethane | S | 30217 | 410 | 0 | -- | <.05 | <.05 | <.05 | <.05 | <.05 |
| *trans*-1,4-Dichloro-2-butene | O | 73547 | 403 | 0 | -- | <.7 | <.7 | <.7 | <.7 | <.7 |
| 1,3-Dichloropropane | O | 77173 | 410 | 0 | -- | <.06 | <.06 | <.06 | <.06 | <.06 |
| 2,2-Dichloropropane | O | 77170 | 410 | 0 | -- | <.05 | <.05 | <.05 | <.05 | <.05 |
| 1,1-Dichloropropene | O | 77168 | 410 | 0 | -- | <.03 | <.03 | <.03 | <.03 | <.03 |
| *cis*-1,3-Dichloropropene | F | 34704 | 410 | 0 | -- | <.05 | <.05 | <.05 | <.05 | <.05 |
| *trans*-1,3-Dichloropropene | F | 34699 | 410 | 0 | -- | <.09 | <.09 | <.09 | <.09 | <.09 |
| Ethylene dibromide | F | 77651 | 410 | 0 | -- | <.04 | <.04 | <.04 | <.04 | <.04 |
| Ethyl methacrylate | O | 73570 | 403 | 0 | -- | <.18 | <.18 | <.18 | <.18 | <.18 |
| Hexachlorobutadiene | O | 39702 | 410 | 0 | -- | <.14 | <.14 | <.14 | <.14 | <.14 |
| Hexachloroethane | S | 34396 | 404 | 0 | -- | <.14 | <.14 | <.14 | <.14 | <.14 |
| Iodomethane | O | 77424 | 403 | 0 | -- | <.08 | <.08 | <.08 | <.08 | <.08 |
| Methyl acrylate | O | 49991 | 403 | 0 | -- | <.6 | <.6 | <.6 | <.6 | <.6 |

| Cooler months (October through March) | | | | | | | |
|---|---|---|---|---|---|---|---|
| Number of samples | Number of samples with detected VOCs | Detection frequency (percent) | Statistical summary for concentrations (micrograms per liter) | | | | |
| | | | Minimum | 25th percentile | Median | 75th percentile | Maximum |
| 459 | 0 | -- | <0.21 | <0.21 | <0.21 | <0.21 | <0.21 |
| 459 | 1 | 0.22 | <.05 | <.05 | <.05 | <.05 | .18 |
| 459 | 1 | .22 | <.03 | <.03 | <.03 | <.03 | .02 |
| 459 | 0 | -- | <.13 | <.13 | <.13 | <.13 | <.13 |
| 459 | 1 | .22 | <.03 | <.03 | <.03 | <.03 | .03 |
| 454 | 0 | -- | <1.2 | <1.2 | <1.2 | <1.2 | <1.2 |
| 459 | 0 | -- | <.03 | <.03 | <.03 | <.03 | <.03 |
| 459 | 0 | -- | <.04 | <.04 | <.04 | <.04 | <.04 |
| 459 | 0 | -- | <.15 | <.15 | <.15 | <.15 | <.15 |
| 459 | 0 | -- | <.05 | <.05 | <.05 | <.05 | <.05 |
| 453 | 0 | -- | <.07 | <.07 | <.07 | <.07 | <.07 |
| 459 | 0 | -- | <.05 | <.05 | <.05 | <.05 | <.05 |
| 459 | 0 | -- | <.05 | <.05 | <.05 | <.05 | <.05 |
| 453 | 0 | -- | <.7 | <.7 | <.7 | <.7 | <.7 |
| 459 | 0 | -- | <.06 | <.06 | <.06 | <.06 | <.06 |
| 459 | 0 | -- | <.05 | <.05 | <.05 | <.05 | <.05 |
| 459 | 0 | -- | <.03 | <.03 | <.03 | <.03 | <.03 |
| 459 | 0 | -- | <.05 | <.05 | <.05 | <.05 | <.05 |
| 459 | 0 | -- | <.09 | <.09 | <.09 | <.09 | <.09 |
| 459 | 0 | -- | <.04 | <.04 | <.04 | <.04 | <.04 |
| 453 | 0 | -- | <.18 | <.18 | <.18 | <.18 | <.18 |
| 459 | 0 | -- | <.14 | <.14 | <.14 | <.14 | <.14 |
| 453 | 0 | -- | <.14 | <.14 | <.14 | <.14 | <.14 |
| 453 | 0 | -- | <.08 | <.08 | <.08 | <.08 | <.08 |
| 453 | 0 | -- | <.6 | <.6 | <.6 | <.6 | <.6 |

**Appendix 2.** Summary of the detection frequency and concentrations by warmer (April through September) and cooler (October through March) months for individual volatile organic compounds at an assessment level of 0.02 microgram per liter, 1995–2003.—Continued

[VOC, volatile organic compound; USGS, U.S. Geological Survey; F, fumigant; GH, gasoline hydrocarbon; GO, gasoline oxygenate; O, organic synthesis compound; R, refrigerant; S, solvent; T, trihalomethane; <, less than; E, estimated concentration below the long-term method detection level; --, not applicable]

| Compound name | VOC group | USGS parameter code | Warmer months (April through September) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Number of samples | Number of samples with detected VOCs | Detection frequency (percent) | Statistical summary for concentrations (micrograms per liter) | | | | |
| | | | | | | Minimum | 25th percentile | Median | 75th percentile | Maximum |
| Methyl acrylonitrile | O | 81593 | 403 | 0 | -- | <0.6 | <0.6 | <0.6 | <0.6 | <0.6 |
| Methyl butyl ketone | S | 77103 | 403 | 0 | -- | <.7 | <.7 | <.7 | <.7 | <.7 |
| Methyl methacrylate | O | 81597 | 403 | 0 | -- | <.35 | <.35 | <.35 | <.35 | <.35 |
| 1,1,1,2-Tetrachloroethane | S | 77562 | 410 | 0 | -- | <.03 | <.03 | <.03 | <.03 | <.03 |
| 1,2,3-Trichlorobenzene | O | 77613 | 410 | 0 | -- | <.27 | <.27 | <.27 | <.27 | <.27 |
| 1,2,4-Trichlorobenzene | S | 34551 | 410 | 0 | -- | <.07 | <.07 | <.07 | <.07 | <.07 |
| 1,1,2-Trichloroethane | S | 34511 | 410 | 0 | -- | <.06 | <.06 | <.06 | <.06 | <.06 |
| 1,2,3-Trichloropropane | F | 77443 | 410 | 0 | -- | <.07 | <.07 | <.07 | <.07 | <.07 |
| Vinyl acetate | O | 77057 | 95 | 0 | -- | <5 | <5 | <5 | <5 | <5 |
| Vinyl bromide | O | 50002 | 403 | 0 | -- | <.1 | <.1 | <.1 | <.1 | <.1 |

| Cooler months (October through March) | | | | | | | |
|---|---|---|---|---|---|---|---|
| Number of samples | Number of samples with detected VOCs | Detection frequency (percent) | Statistical summary for concentrations (micrograms per liter) | | | | |
| | | | Minimum | 25th percentile | Median | 75th percentile | Maximum |
| 453 | 0 | -- | <0.6 | <0.6 | <0.6 | <0.6 | <0.6 |
| 453 | 0 | -- | <.7 | <.7 | <.7 | <.7 | <.7 |
| 453 | 0 | -- | <.35 | <.35 | <.35 | <.35 | <.35 |
| 459 | 0 | -- | <.03 | <.03 | <.03 | <.03 | <.03 |
| 459 | 0 | -- | <.27 | <.27 | <.27 | <.27 | <.27 |
| 459 | 0 | -- | <.07 | <.07 | <.07 | <.07 | <.07 |
| 459 | 0 | -- | <.06 | <.06 | <.06 | <.06 | <.06 |
| 459 | 0 | -- | <.07 | <.07 | <.07 | <.07 | <.07 |
| 106 | 0 | -- | <5 | <5 | <5 | <5 | <5 |
| 453 | 0 | -- | <.1 | <.1 | <.1 | <.1 | <.1 |

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