

In cooperation with the Ohio Water Development Authority; National Park Service; Cities of Aurora, Bedford, Bedford Heights, Solon, and Twinsburg; Portage and Summit Counties; and in collaboration with the Ohio Environmental Protection Agency

Occurrence of Organic Wastewater Compounds in the Tinkers Creek Watershed and Two Other Tributaries to the Cuyahoga River, Northeast Ohio



Scientific Investigations Report 2008–5173

Cover image: View of Tinkers Creek near Dunham Road, Cuyahoga County, Ohio (photograph by John S. Tertuliani, U.S. Geological Survey).

Occurrence of Organic Wastewater Compounds in the Tinkers Creek Watershed and Two Other Tributaries to the Cuyahoga River, Northeast Ohio

By J.S. Tertuliani, D.A. Alvarez, E.T. Furlong, M.T. Meyer, S.D. Zaugg,
and G.F. Koltun

In cooperation with the Ohio Water Development Authority; National Park Service;
Cities of Aurora, Bedford, Bedford Heights, Solon, and Twinsburg; Portage and
Summit Counties; and in collaboration with the Ohio Environmental Protection Agency

Scientific Investigations Report 2008–5173

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

U.S. Department of the Interior
DIRK KEMPTHORNE, Secretary

U.S. Geological Survey
Mark D. Myers, Director

U.S. Geological Survey, Reston, Virginia: 2008

For product and ordering information:

World Wide Web: <http://www.usgs.gov/pubprod>

Telephone: 1-888-ASK-USGS

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment:

World Wide Web: <http://www.usgs.gov>

Telephone: 1-888-ASK-USGS

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this report is in the public domain, permission must be secured from the individual copyright owners to reproduce any copyrighted materials contained within this report.

Suggested citation:

Tertuliani, J.S., Alvarez, D.A., Furlong, E.T., Meyer, M.T, Zaugg, S.D., and Koltun, G.F., 2008, Occurrence of organic wastewater compounds in the Tinkers Creek watershed and two other tributaries to the Cuyahoga River, Northeast Ohio: U.S. Geological Survey Scientific Investigations Report 2008–5173, 60 p.

Contents

Abstract.....	1
Introduction.....	2
Purpose and Scope	2
Study Area.....	5
Methods.....	5
Passive Sampling Technology	5
Polar Organic Chemical Integrative Samplers (POCIS)	7
Semipermeable Membrane Devices (SPMDs).....	8
Sampling-Site Selection and Sampler Deployment.....	8
Streambed-Sediment Sampling	10
Laboratory Analyses.....	11
Reporting of Data	11
Quality Control	12
Trip Blanks.....	12
Field Replicates	13
Reagent and Matrix Spikes.....	13
Method Blanks and Surrogate and Internal Standards	14
Results	14
Compounds in Water.....	15
Antibiotic Compounds.....	15
Pharmaceutical Compounds.....	16
Wastewater Compounds	16
Hydrophobic Compounds	16
Compounds in Streambed Sediments	18
Pharmaceutical Compounds.....	18
Wastewater Compounds	19
Summary and Conclusions.....	20
References Cited.....	21
Appendix A. Detailed Analytical Methods and Passive Sampling Theory.....	24
POCIS and SPMD Media Preparation and Extraction	24
Chemical Analysis of POCIS and SPMD Extracts	24
Chemical Analysis of Streambed Sediments	25
Passive Sampling Theory	26
Estimation of Ambient Water Concentrations.....	26
References Cited.....	27
Appendix B. Organic Wastewater Compound Analytes and Reporting Levels, by Sample Media and Analytical Method.....	28
References Cited.....	36
Appendix C. Quality-Control Data	37
Appendix D. Organic Wastewater Compounds in Polar Organic Chemical Integrative Sampler (POCIS) Extracts	43
Appendix E. Organic Wastewater Compounds in Semipermeable Membrane Device (SPMD) Extracts	51
Appendix F. Organic Wastewater Compounds in Streambed Sediments	54

Figures

1–3. Maps Showing—	
1. Locations of sampling sites within the Tinkers Creek watershed	3
2. Locations of reference sampling sites relative to the Tinkers Creek watershed	4
3. Land cover in the Tinkers Creek watershed.....	6
4. Photographs of passive-sampler canister in stream and with polar organic integrative sampler (POCIS) disks removed.....	7
5. Component view of a POCIS disk.....	7
6. Photograph of lipid-filled polyethylene membrane tube from a semipermeable membrane device (SPMD)	8
7. Schematic of sampling-site locations near the Bedford Heights wastewater-treatment-plant outfall	10
8. Graph showing numbers of detections of antibiotic, pharmaceutical, wastewater, and hydrophobic compounds in water (as determined by analysis of POCIS and SPMD media) upstream and downstream from wastewater treatment plants in the Tinkers Creek watershed.....	15
9. Graph showing numbers of detections of pharmaceutical and wastewater compounds in streambed sediments upstream and downstream from wastewater-treatment plants in the Tinkers Creek watershed	19

Tables

1. Land-cover percentages in the Tinkers Creek watershed based on 1992 National Land Cover Dataset	5
2. Wastewater-treatment-plant (WWTP) information and passive-sampler locations	9
3. Matrix of quality-control measures used as a function of media and analytical method	12
4. Numbers of detections of chemical compounds in water (as determined by analysis of POCIS and SPMD media) and streambed sediments in the Tinkers Creek watershed and two other tributaries to the Cuyahoga River, 2006	14
5. Organic wastewater compounds detected most frequently (>50 percent detections in one or more groupings) in water (as determined by analysis of POCIS and SPMD media) in the Tinkers Creek watershed and two other tributaries to the Cuyahoga River, 2006.....	17
6. Organic wastewater compounds detected most frequently (>50 percent detections in one or more groupings) in streambed sediments in the Tinkers Creek watershed and two other tributaries to the Cuyahoga River, 2006.....	18
B1. Antibiotic method for POCIS extracts, including compound names, uses, classes, and Chemical Abstract Service registry numbers for antibiotic compounds	28
B2. Pharmaceutical method for POCIS extracts, including compound names, uses, classes, and Chemical Abstract Service registry numbers for pharmaceutical compounds	29
B3. Wastewater method for POCIS extracts, including compound names, suspected endocrine disruptor, CAS number, and possible compound uses.....	30
B4. Hydrophobic method for SPMD extracts, including compound names, types, and Chemical Abstract Service registry numbers for hydrophobic compounds	32

B5.	Pharmaceutical method for streambed-sediment samples, including compound names, uses, classes, and Chemical Abstract Service registry numbers for pharmaceutical compounds	33
B6.	Wastewater method for streambed-sediment samples, including compound names, endocrine-disrupting potential, and possible compound uses.....	34
C1.	Summary of results for analysis of Polar Organic Chemical Integrative Sampler (POCIS) extracts by the antibiotic, pharmaceutical, and wastewater methods in trip blanks collected in Tinkers Creek and its tributaries and two other tributaries of the Cuyahoga River in 2006.....	37
C2.	Summary of results for analysis of Semipermeable Membrane Device (SPMD) extracts by the hydrophobic method in trip blanks collected in Tinkers Creek and its tributaries and two other tributaries of the Cuyahoga River in 2006	37
C3.	Results for analysis of Polar Organic Chemical Integrative Sampler (POCIS) extracts by the antibiotic, pharmaceutical, and wastewater methods for replicate POCIS deployed in Tinkers Creek in 2006.....	38
C4.	Results for analysis of Semipermeable Membrane Device (SPMD) extracts by the hydrophobic method for replicate SPMDs deployed in Tinkers Creek in 2006	39
C5.	Summary of results for analysis of streambed-sediment replicates by the pharmaceutical and wastewater methods for samples collected in Tinkers Creek in 2006	40
C6.	Summary of reagent-water spike-recovery data for wastewater compounds	41
C7.	Summary of spike-recovery data for pharmaceutical compounds in streambed-sediment samples collected in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006	42
D1.	Results of analysis of POCIS extracts by the antibiotic method for POCIS deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006	43
D2.	Summary of results for analysis of POCIS extracts by the antibiotic method for POCIS deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.....	44
D3.	Results for analysis of POCIS extracts by the pharmaceutical method for POCIS deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.....	45
D4.	Summary of results for analysis of POCIS extracts by the pharmaceutical method for POCIS deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.....	46
D5.	Results for analysis of POCIS extracts by the wastewater method for POCIS deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.....	47
D6.	Summary of results for analysis of POCIS extracts by the wastewater method for POCIS deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.....	49
E1.	Results for analysis of SPMD extracts by the hydrophobic method for SPMDs deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.....	51
E2.	Summary of results for analysis of SPMD extracts by the hydrophobic method for SPMDs deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.....	53

Tables—Continued

F1. Results for analysis of streambed-sediment samples by the pharmaceutical method for samples collected in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006	54
F2. Summary of results for analysis of streambed-sediment samples by the pharmaceutical method for samples collected in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.....	55
F3. Results for analysis of streambed-sediment samples by the wastewater method for samples collected in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.....	56
F4. Summary of results for analysis of streambed-sediment samples by the wastewater method for samples collected in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.....	59

Conversion Factors and Abbreviations

Multiply	By	To obtain
Length		
millimeter (mm)	0.03937	inch (in.)
centimeter (cm)	0.3937	inch (in.)
mile (mi)	1.609	kilometer (km)
Area		
square centimeter (cm ²)	0.155 0	square inch (in ²)
square mile (mi ²)	2.590	square kilometer (km ²)
Volume		
liter (L)	0.2642	gallon (gal)
Flow rate		
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m ³ /s)
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
Pressure		
pascal (Pa)	0.0001450	pound-force per square inch (lbf/in ²)

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

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$$

Concentrations of compounds in polar organic chemical integrative sampler (POCIS) extracts are given in nanograms (ng) per POCIS. Concentrations of compounds in semipermeable membrane device (SPMD) extracts are given in nanograms per liter (ng/L). Estimated concentrations of compounds in water are given in milligrams per liter (mg/L). Concentrations of compounds in sediment are given in micrograms per kilogram (µg/kg). There are 1,000 micrograms in a gram and 1,000 nanograms in a microgram.

Amounts and concentrations of analytical reagents are given in milliliters (mL), microliters (µL), and nanograms (ng) and as micrograms per liter (µg/L), nanograms per microliter (ng/µL), and millimolar (mM).

Occurrence of Organic Wastewater Compounds in the Tinkers Creek Watershed and Two Other Tributaries to the Cuyahoga River, Northeast Ohio

By J.S. Tertuliani, D.A. Alvarez, E.T. Furlong, M.T. Meyer, S.D. Zaugg, and G.F. Koltun

Abstract

The U.S. Geological Survey—in cooperation with the Ohio Water Development Authority; National Park Service; Cities of Aurora, Bedford, Bedford Heights, Solon, and Twinsburg; and Portage and Summit Counties—and in collaboration with the Ohio Environmental Protection Agency, did a study to determine the occurrence and distribution of organic wastewater compounds (OWCs) in the Tinkers Creek watershed in northeastern Ohio. In the context of this report, OWCs refer to a wide range of compounds such as antibiotics, prescription and nonprescription pharmaceuticals, personal-care products, household and industrial compounds (for example, antimicrobials, fragrances, surfactants, fire retardants, and so forth) and a variety of other chemicals.

Canisters containing polar organic integrative sampler (POCIS) and semipermeable membrane device (SPMD) media were deployed instream for a 28-day period in May and June 2006 at locations upstream and downstream from seven wastewater-treatment-plant (WWTP) outfalls in the Tinkers Creek watershed, at a site on Tinkers Creek downstream from all WWTP discharges, and at one reference site each in two nearby watersheds (Yellow Creek and Furnace Run) that drain to the Cuyahoga River. Streambed-sediment samples also were collected at each site when the canisters were retrieved.

POCIS and SPMDs are referred to as “passive samplers” because they sample compounds that they are exposed to without use of mechanical or moving parts. OWCs detected in POCIS and SPMD extracts are referred to in this report as “detections in water” because both POCIS and SPMDs provided time-weighted measures of concentration in the stream over the exposure period. Streambed sediments also reflect exposure to OWCs in the stream over a long period of time and provide another OWC exposure pathway for aquatic organisms.

Four separate laboratory methods were used to analyze for 32 antibiotic, 20 pharmaceutical, 57 to 66 wastewater, and 33 hydrophobic compounds. POCIS and streambed-sediment extracts were analyzed by both the pharmaceutical and wastewater methods. POCIS extracts also were analyzed

by the antibiotic method, and SPMD extracts were analyzed by the hydrophobic-compound method. Analytes associated with a given laboratory method are referred to in aggregate by the method name (for example, antibiotic-method analytes are referred to as “antibiotic compounds”) even though some analytes associated with the method may not be strictly classified as such. In addition, some compounds were included in the analyte list for more than one laboratory method. For a given sample matrix, individual compounds detected by more than one analytical method are included independently in counts for each method.

A total of 12 antibiotic, 20 pharmaceutical, 41 wastewater, and 22 hydrophobic compounds were detected in water at one or more sites. Eight pharmaceutical and 37 wastewater compounds were detected in streambed sediments. The numbers of detections at reference sites tended to be in the low range of detection counts observed in the Tinkers Creek watershed for a given analytical method. Also, the total numbers of compounds detected in water and sediment at the reference sites were less than the total numbers of compounds detected at sites in the Tinkers Creek watershed.

With the exception of hydrophobic compounds, it was common at most sites to have more compounds detected in samples collected downstream from WWTP outfalls than in corresponding samples collected upstream from the outfalls. This was particularly true for antibiotic, pharmaceutical, and wastewater compounds in water. In contrast, it was common to have more hydrophobic compounds detected in samples collected upstream from WWTP outfalls than downstream.

Caffeine, fluoranthene, N,N-diethyl-meta-toluamide (DEET), phenanthrene, and pyrene were detected in water at all sites in the Tinkers Creek watershed, irrespective of whether the site was upstream or downstream from a WWTP. Some, but not all of these compounds, also were detected in water at the reference sites; however, concentrations generally were at the low end of the range of concentrations observed in the Tinkers Creek watershed.

Carbamazepine, sulfamethoxazole, trimethoprim, and hexahydrohexamethylcyclopentabenzopyran (HHCB) were detected in water at 100 percent of the sites downstream from WWTP outfalls, yet their frequency of detection at sites

2 Occurrence of Organic Wastewater Compounds in the Tinkers Creek Watershed, Northeast Ohio

upstream from outfalls was statistically smaller (occurring in about 29 percent or less of the samples). None of these compounds were detected in water at the Yellow Creek reference site, and only two of the compounds (carbamazepine and sulfamethoxazole) were detected at the Furnace Run site. HHCb, a synthetic musk used in some personal care products, has been shown to demonstrate antiestrogenic activity and is thought to disrupt endocrine function in fish.

Fifteen wastewater compounds (2,6-dimethylnaphthalene, 2-methylnaphthalene, 3-methyl-1H-indole, anthraquinone, acetophenone, benzo[*a*]pyrene, β -sitosterol, bis(2-ethylhexyl) phthalate, carbazole, cholesterol, fluoranthene, indole, naphthalene, *p*-cresol, and pyrene) were detected in streambed sediments at all sites in the Tinkers Creek watershed, irrespective of whether the site was upstream or downstream from a WWTP. Three of the fifteen compounds (benzo[*a*]pyrene, bis(2-ethylhexyl) phthalate, and *p*-cresol) are known or suspected endocrine disruptors.

Many of the pharmaceutical compounds detected in sediment also were detected in water. One notable exception was miconazole, which was detected in more than a quarter of the streambed-sediment samples yet never detected in water. In contrast, some pharmaceutical compounds (such as trimethoprim and carbamazepine) that were detected in water at all sites downstream from WWTP outfalls were either not detected or detected at a much lower frequency in streambed sediments.

Introduction

Treated wastewater commonly contains organic wastewater compounds (OWCs) such as antibiotics, prescription and nonprescription pharmaceuticals, personal-care products, household and industrial compounds (for example, antimicrobials, fragrances, surfactants, fire retardants, and so forth) and a variety of other chemicals (Spongberg and Witter, 2008). Some of the same OWCs present in treated wastewater are also delivered to streams and lakes through other environmental pathways. Many OWCs are characterized as “contaminants of emerging concern” because they currently are not included in routine monitoring programs but may be candidates for future regulation once more becomes known about their toxicity and health effects (Glassmeyer, 2007).

OWCs frequently are present in streams receiving discharge from wastewater-treatment plants (WWTPs) (Ashton and others, 2004; Glassmeyer and others, 2005; Herberer, 2002; Kolpin and others, 2002) and some OWCs are sufficiently persistent that they, or their degradates, are being found in ground water, lakes, and reservoirs in the United States (Barnes and others, 2008; Focazio and others, 2008; Herberer and others, 2001; Kolpin and others, 2002, 2004). In fact, Kolpin and others (2002) reported detections of at least one OWC in 80 percent of 139 streams sampled in 30 U.S. states. Urban streams and ground water may be particularly vulnerable to OWC contamination because of the myriad of

potential sources of OWCs in such highly engineered systems (Sprague and Battaglin, 2004). For example, Rowe and others (2004) reported that low concentrations of at least one OWC were present in 76 percent of the shallow urban water wells sampled in the Great and Little Miami River Basins in Ohio. In addition, that study concluded that the number of OWCs detected increased with increasing amounts of urban land use (Rowe and others, 2004).

Because OWCs are continually released into the environment (frequently in complex mixtures), there is considerable concern about the effect of chronic exposure on aquatic biota (Sumpter and Johnson, 2005). Several common OWCs are known or suspected to disrupt or influence endocrine function in fish, which can cause reproductive problems and other anomalies (Sumpter and Johnson, 2005). Some OWCs have been shown to survive conventional water-treatment processes and persist in drinking-water supplies (Stackelberg and others, 2004, 2007), yet the prevalence and potential human-health effects of consuming low concentrations of mixtures of OWCs is largely unknown. Other human-health concerns include the presence of antibiotics in water supplies and the potential for the development of antibiotic resistant strains of bacteria (Kummerer, 2004; Lee and others, 2004; Sando and others, 2006).

The U.S. Geological Survey—in cooperation with the Ohio Water Development Authority; National Park Service; Cities of Aurora, Bedford, Bedford Heights, Solon, and Twinsburg; and Portage and Summit Counties—and in collaboration with the Ohio Environmental Protection Agency, investigated the occurrence and distribution of OWCs in the Tinkers Creek watershed and two other tributaries to the Cuyahoga River. The Tinkers Creek watershed was chosen for study in response to biological surveys by the Ohio Environmental Protection Agency (Ohio EPA). Those surveys indicated that although the available habitat in Tinkers Creek and its tributaries was generally adequate, the fish population was impaired (based on a comparison of habitat and biological indices to ecoregional expectations); yet, conventional water-quality data did not fully explain the impairment (Ohio Environmental Protection Agency, 2003). Because effluent from WWTPs constitutes a continuous and sometimes large proportion of the flow in Tinkers Creek and its tributaries (sometimes greater than or equal to 80 percent), there was concern that OWCs in wastewater may have contributed to the impairment of the fish population. However, no data were available on the occurrence or distribution of OWCs in the Tinkers Creek watershed that could support or refute that concern. To address that concern, this study focuses primarily on identifying the presence of OWCs in streams near WWTP outfalls.

Purpose and Scope

The purpose of this report is to describe the methods and results of the USGS study on the occurrence and distribution of OWCs in the Tinkers Creek watershed and at reference sites on two other tributaries to the Cuyahoga River (figs. 1 and 2).

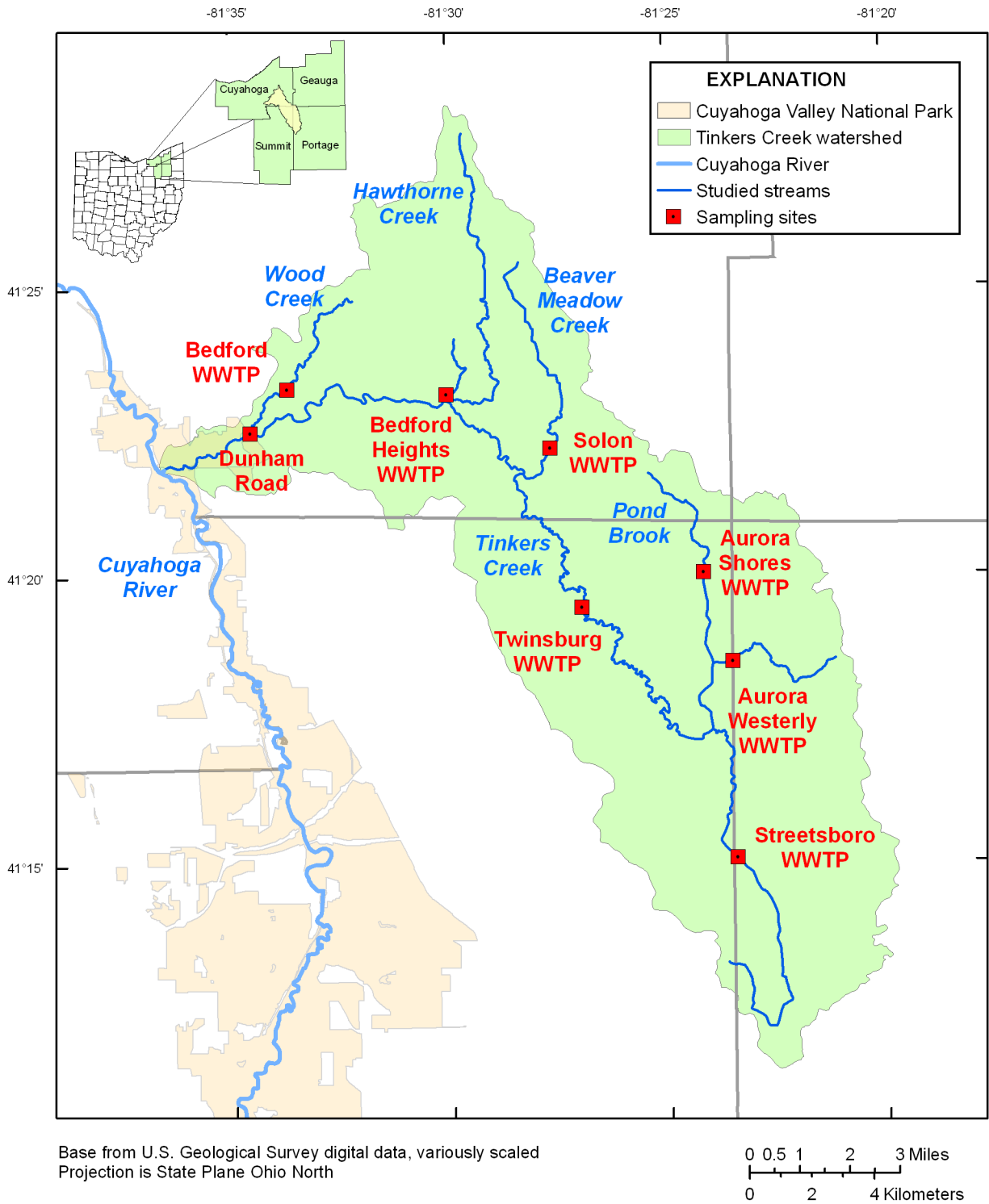


Figure 1. Locations of sampling sites within the Tinkers Creek watershed.

4 Occurrence of Organic Wastewater Compounds in the Tinkers Creek Watershed, Northeast Ohio

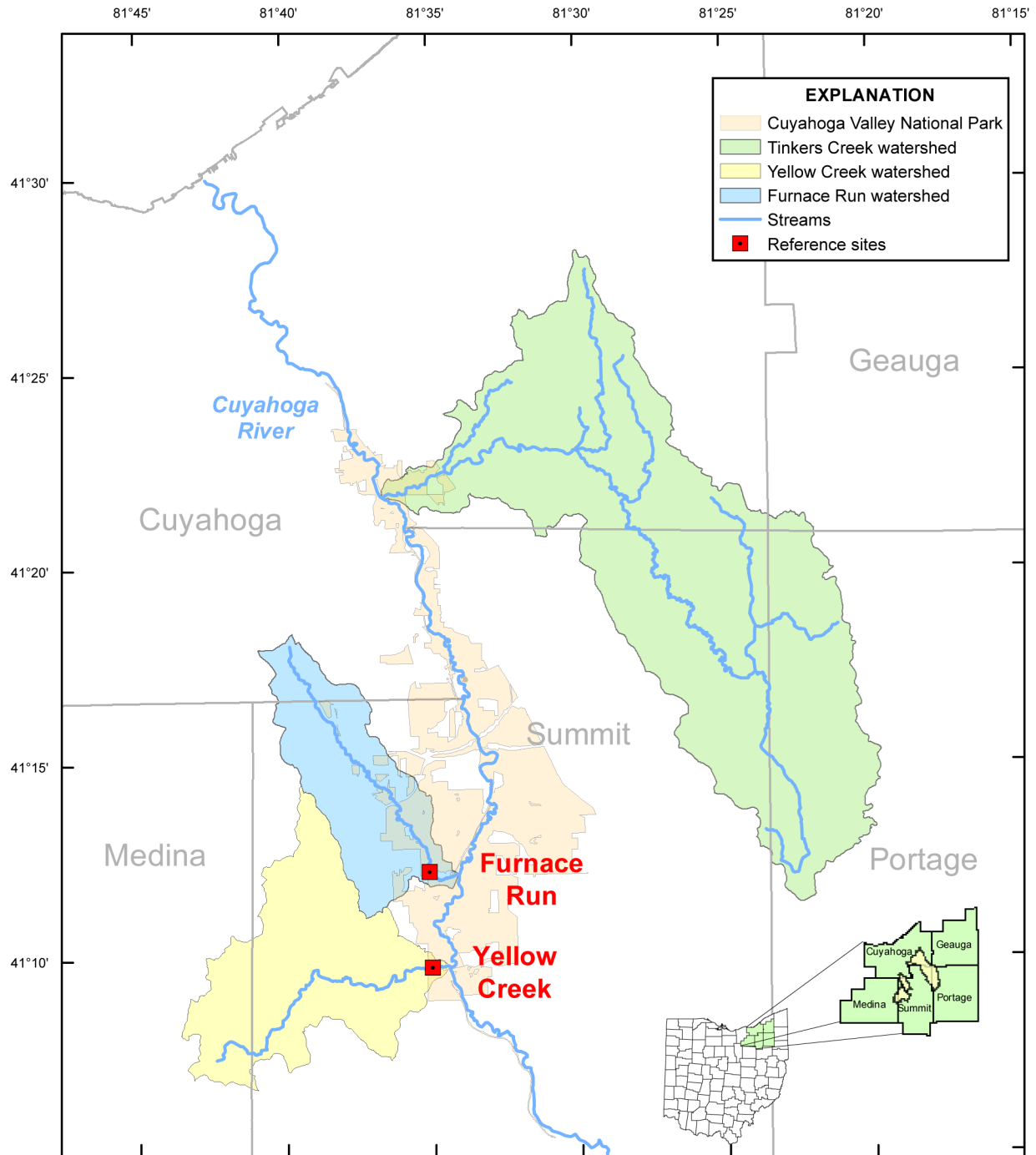


Figure 2. Locations of reference sampling sites relative to the Tinkers Creek watershed.

The water results are based on a 28-day May–June 2006 exposure period, during which a total of 20 canisters (7 on the mainstem of Tinkers Creek, 11 on tributaries to Tinkers Creek, and 2 on nearby tributaries to the Cuyahoga River) were deployed that contained both polar organic chemical integrative sampler (POCIS; Alvarez and others, 2004) and semipermeable membrane device (SPMD; Huckins and others, 2002) passive-sampler media. Streambed-sediment samples also were collected at each site when the canisters were retrieved. Passive-sampler media and streambed sediments were subsequently analyzed for a 32 antibiotic, 20 pharmaceutical, 57 to 66 wastewater, and 33 hydrophobic compounds. Considerable text is devoted to discussion of POCIS and SPMD technologies, both of which are relatively new technologies for surface-water- and ground-water-quality assessments, particularly relating to OWCs. Also, appendixes are provided that contain detailed information on analytical methods, passive-sampler theory, and quality assurance and laboratory results.

Study Area

Tinkers Creek originates in northwest Portage County and flows west to northwest through Summit County and then into Cuyahoga County, where it eventually discharges to the Cuyahoga River near Independence, Ohio (figs. 1–2). Tinkers Creek is the largest tributary to the Cuyahoga River, with a drainage area of 96 mi². Long-term (1963–2006) mean annual streamflow for the USGS streamgage on Tinkers Creek at Bedford (04207200), located 5.5 mi upstream from the mouth, is 137 ft³/s.

The study focused on the Tinkers Creek watershed in which seven WWTPs are located (fig. 1). Several tributaries enter Tinkers Creek within this area. Pond Brook, the largest tributary to Tinkers Creek, receives discharge from the Aurora Shores WWTP and indirectly (by way of an unnamed tributary) from the Aurora Westerly WWTP. Other tributaries include Beaver Meadow Run, which receives discharge from the Solon WWTP; Hawthorne Creek, which indirectly receives discharge from the Bedford Heights WWTP (the WWTP discharges to an unnamed tributary to Hawthorne Creek near its confluence with Hawthorne Creek); and Wood Creek, which receives discharge from the Bedford WWTP.

Land cover in the watershed varies along the length of Tinkers Creek (table 1 and fig. 3). About 47 percent of the land in the watershed is classified as wetland or forest, 21 percent as agricultural, and about 27 percent as residential or commercial/industrial/transportation (table 1). Land use in the northern half of the watershed tends to be more urban and developed than in the southern half (fig. 3). The seven WWTPs in the study are in or near one of the larger cities in the Tinkers Creek watershed. The population ranges from approximately 11,375 people in Bedford Heights to approximately 21,800 people in Solon (U.S. Census Bureau, 2000).

Like Tinkers Creek, the streams where reference sites were established are tributary to the Cuyahoga River (fig. 2). Both

Table 1. Land-cover percentages in the Tinkers Creek watershed based on 1992 National Land Cover Dataset¹.

[Percentages add up to less than 100 percent because of independent rounding]

Land cover	Percentage of watershed
Open water	1.9
Low-intensity residential	16.1
High-intensity residential	1.8
Commercial/Industrial/Transportation	9.3
Transitional	0.5
Deciduous forest	40.3
Evergreen forest	1.0
Mixed forest	0.5
Grasslands/Herbaceous	0.1
Pasture/Hay	14.0
Row crops	6.9
Urban/Recreational grasses	1.4
Wetlands	5.2

¹U.S. Geological Survey (2000).

Furnace Run and Yellow Creek discharge to the Cuyahoga River within the boundary of the Cuyahoga Valley National Park. Furnace Run, which drains about 20.4 mi², flows through park lands in the lower third of the watershed. In contrast, almost all of Yellow Creek's 31.0-mi² drainage area is outside of the park. The percentages of the Furnace Run and Yellow Creek watersheds classified as residential or commercial/industrial/transportation land covers, 6.8 and 12.4 percent, respectively, are less than half that of the Tinkers Creek watershed. The predominant land cover in both watersheds is forest, followed by agricultural classes.

Methods

The occurrence of OWCs was assessed by analyzing sequestration media from passive sampling devices and by analyzing streambed sediments. The following sections describe (1) the passive sampling technologies, (2) site-selection and sampler-deployment criteria, (3) methods used to collect streambed sediments, (4) laboratory analytical techniques, and (5) quality-control procedures.

Passive Sampling Technology

Passive samplers are nonmechanical devices consisting of an encased medium that can accumulate compounds of interest over time (Alvarez and others, 2004, 2008; Chambers and others, 2006; Huckins and others, 2002). The advantages of the passive-sampler approach include the ability to integrate exposure over a range of hydrologic conditions and the ability to concentrate ultratrace to trace levels of chemicals, which

6 Occurrence of Organic Wastewater Compounds in the Tinkers Creek Watershed, Northeast Ohio

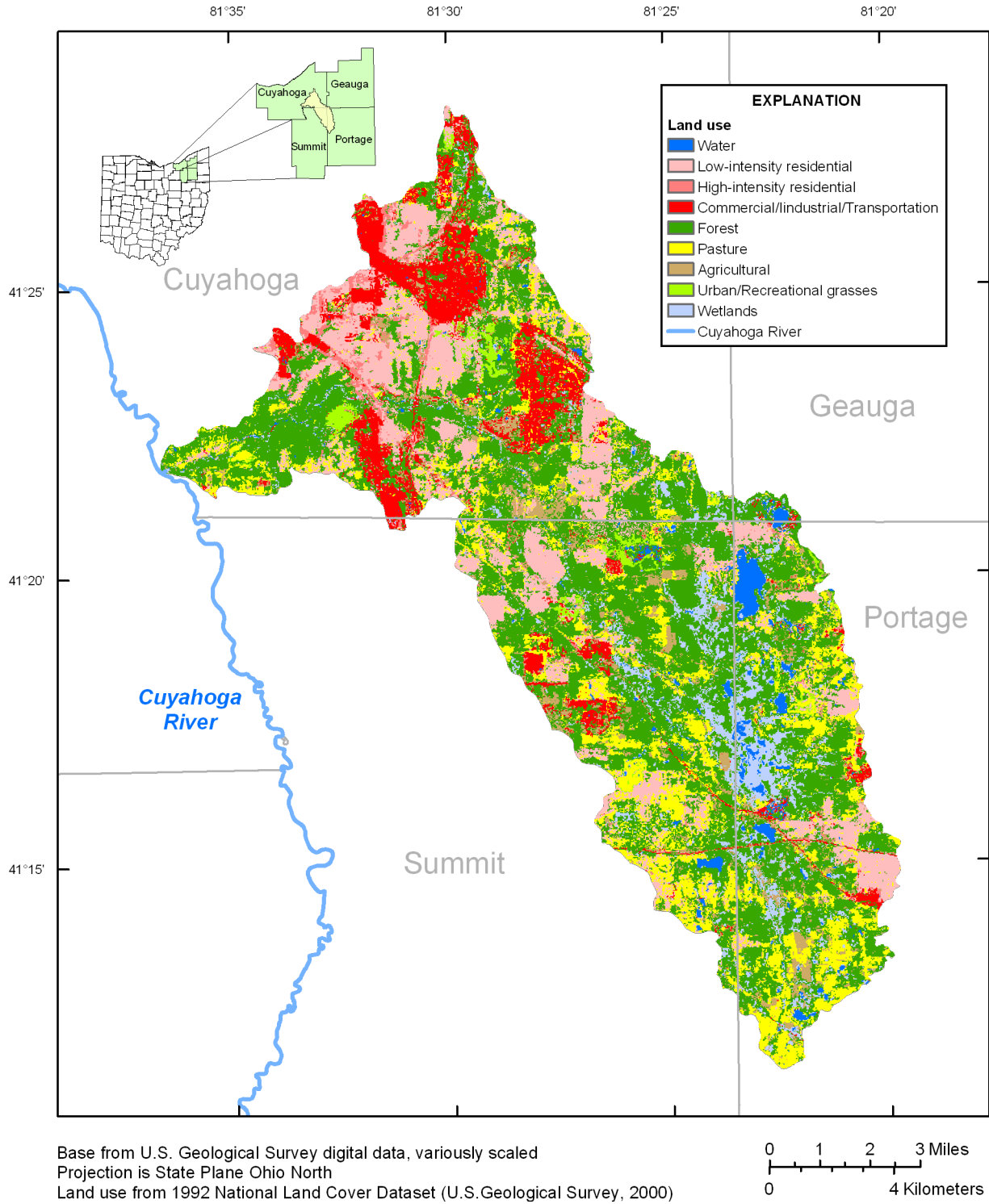


Figure 3. Land cover in the Tinkers Creek watershed.

can result in a detectable amount of a compound that might otherwise be present in streamwater grab samples at concentrations below detection (Chambers and others, 2006; Alvarez and others, 2004). Integrating and accumulating exposure over time also increases the likelihood of detecting chemicals that are present in the stream only sporadically.

Passive-sampler media were packaged together in a protective plastic canister for deployment in the streams (fig. 4). The canisters have slotted openings at both ends to facilitate the flow of water over the media.

Polar Organic Chemical Integrative Samplers (POCIS)

The Polar Organic Chemical Integrative Sampler (POCIS) is designed to sample water-soluble (polar or

hydrophilic) organic chemicals from aqueous environments. The POCIS is a passive integrative sampler that yields time-weighted concentrations of chemicals over deployment periods ranging from weeks to months. The POCIS samples chemicals in the dissolved phase, mimicking the respiratory exposure of aquatic organisms (Alvarez and others, 2004).

Each POCIS disk consists of a solid-phase sorbent or mixture of sorbents sandwiched between two sheets of a microporous polyethersulfone membrane (fig. 5). The type of sorbent used depends on the specific chemicals or chemical classes of interest. The membranes allow water and dissolved chemicals to pass through to the sorbent material (where the chemicals are sequestered) while excluding particulate matter such as suspended detritus and sediment. The membranes are resistant to biofouling, which can reduce the amount of chemical sampled. The samplers deployed in this study contained six POCIS disks.

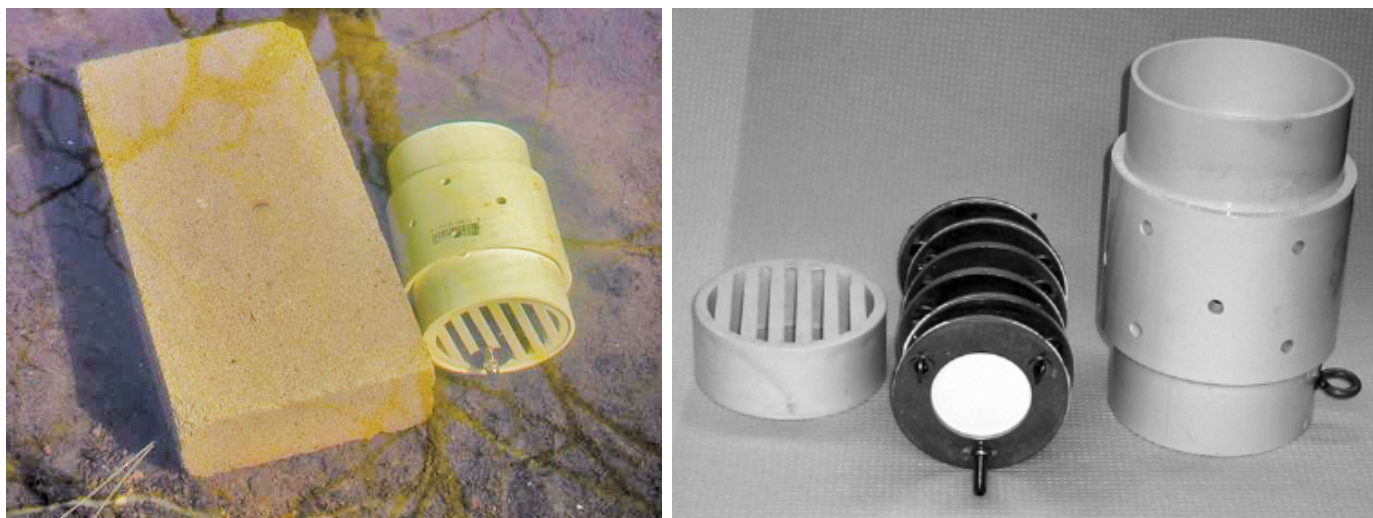


Figure 4. Photographs of passive-sampler canister in stream and with polar organic integrative sampler (POCIS) disks removed.

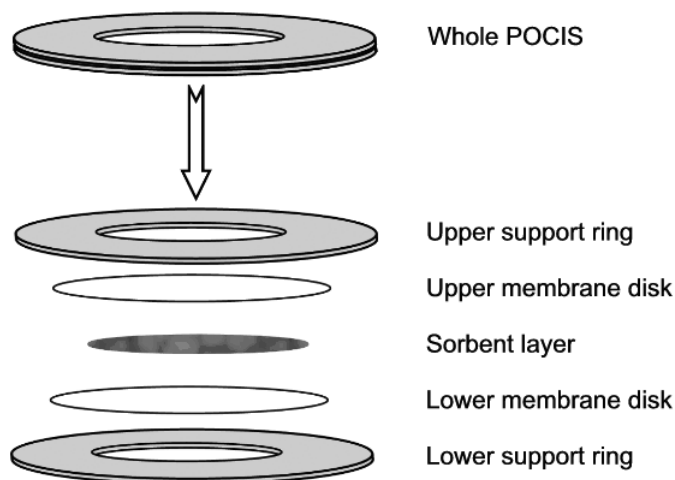


Figure 5. Component view of a POCIS disk.

Two configurations of the POCIS, differing in the type of sorbents incorporated, were used in this study. The “pesticide” POCIS is the original design optimized for the sampling of many pesticides, biogenic and synthetic hormones, wastewater-related compounds, and other water-soluble organic chemicals. The “pharmaceutical” POCIS was designed to permit the recovery of certain classes of chemicals that contain multiple functional groups (as do many pharmaceuticals). The use of both configurations during the Tinkers Creek study permitted a broad range of OWCs to be sampled. Some overlap exists in the types of chemicals sampled by each configuration (Alvarez and others, 2004, 2007; Jones-Lepp and others, 2004; Petty and others, 2004), so 11 compounds have more than 1 result reported.

Semipermeable Membrane Devices (SPMDs)

Semipermeable membrane devices (SPMDs) were used in conjunction with the POCIS. The SPMD is designed to sample lipid or fat-soluble (nonpolar or hydrophobic) semivolatile organic chemicals from water and air (Huckins and others, 2002, 2006). The SPMD is an integrative sampler similar in function to the POCIS device. The SPMD consists of a small volume of a neutral, high-molecular-weight lipid, such as synthetic triolein (as used for this study), which is contained in a thin-walled, low-density polyethylene membrane tube (fig. 6). The semipermeable membrane allows the nonpolar chemicals to pass through to the lipid, where the chemicals are concentrated. Larger molecules and particulate matter are excluded.

SPMDs were used to gather information on selected chemicals that are more hydrophobic than those sampled for by POCIS (Alvarez and others, 2004, 2007; Jones-Lepp and others, 2004; Petty and others, 2000). Chemicals sampled by SPMDs include hydrophobic, bioavailable organic chemicals such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides, dioxins and

furans, selected organophosphate and pyrethroid pesticides, and other nonpolar organic chemicals.

Sampling rates (the liters of water extracted per day) can vary with changes in water flow, turbulence, and temperature and as a function of the amount of biofilm on the surface areas of the membrane tube. A performance reference compound (PRC) approach was used to account for site-specific environmental factors that can affect sampling rates (Huckins and others, 2002). A PRC compound was added to the SPMD during its construction. The amount of PRCs lost to the surrounding water during deployment was used to adjust SPMD-derived sampling rates.

Sampling-Site Selection and Sampler Deployment

Sampling sites were established upstream and downstream from seven WWTP outfalls in the Tinkers Creek watershed (table 2). In one case (at the Bedford Heights WWTP), a third site was established to sample a second upstream location. Sampling sites also were established on Tinkers Creek at Dunham Road (about 2.4 mi upstream from the mouth of Tinkers Creek and downstream from all WWTP inputs (fig. 1)) and near the mouths of Furnace Run and Yellow Creek within the boundary of the Cuyahoga Valley National Park (fig. 2). The Furnace Run and Yellow Creek sites were considered reference sites because they were near Tinkers Creek and were in similar environmental settings, plus the Ohio EPA had determined that both streams had Index of Biological Integrity (IBI) scores (a measure of fish species diversity and species populations) indicating full attainment of their aquatic life uses (Ohio Environmental Protection Agency, 2003).

Several criteria were considered when selecting where to deploy the samplers at a given site. Adequate water depth was a priority to ensure the sampler remained submerged for the entire period of deployment. Exposure to the atmosphere was minimized (before, during, and after deployment) because



Figure 6. Photograph of lipid-filled polyethylene membrane tube from a semipermeable membrane device (SPMD).

Table 2. Wastewater-treatment-plant (WWTP) information and passive-sampler locations.

[Mgal/d, million gallons per day; °, degrees; ′, minutes; ″, seconds; n/a, not applicable]

Location/WWTP	County	Permitted discharge (Mgal/d)	Population served (in 2004)	Upstream sampler location	Downstream sampler location	Deployment period (all dates in 2006)
Streetsboro	Portage	4	18,066	41°14′56″ 81°23′17″	41°14′60″ 81°23′20″	5/10–6/7
Aurora Westerly	Portage	1.4	4,897	41°18′45″ 81°23′03″	41°18′32″ 81°23′30″	5/9–6/6
Aurora Shores	Summit	0.5	2,347	41°20′03″ 81°24′06″	41°19′59″ 81°24′10″	5/9–6/6
Twinsburg	Summit	4.95	19,353	41°19′23″ 81°26′57″	41°19′23″ 81°26′54″	5/10–6/7
Solon	Cuyahoga	5.8	22,000	41°22′17″ 81°27′33″	41°22′05″ 81°27′40″	5/9–6/6
Bedford	Cuyahoga	3.2	15,000	41°23′15″ 81°33′42″	41°23′12″ 81°33′49″	5/9–6/6
Bedford Heights	Cuyahoga	7.5	14,256	41°23′09″ 81°29′57″ ^a 41°23′06″ 81°29′55″ ^b	41°23′05″ 81°29′59″	5/8–6/5
Tinkers Creek at Dunham Road	Cuyahoga	n/a	n/a	41°22′30″ 81°34′33″	n/a	5/8–6/5
Furnace Run ^c	Cuyahoga	n/a	n/a	41°12′14″ 81°35′08″	n/a	5/10–6/7
Yellow Creek ^c	Cuyahoga	n/a	n/a	41°09′47″ 81°35′03″	n/a	5/10–6/7

^aLocation upstream from outfall on unnamed tributary to Hawthorne Creek.^bLocation on Hawthorne Creek upstream from confluence with unnamed tributary.^cReference site.

atmospheric exposure presents a risk of contamination from airborne chemicals that can confound the identification and quantification of waterborne chemicals. Samplers were placed where water would flow over them; however, deployment in the fastest or deepest section of the channel was not always possible. Protection of samplers from floating debris and vandalism and options for securing the samplers played a major role in determining sampler placement.

Reconnaissance of each sampling site was completed in April 2006, during a period of low to moderate flow. Of particular interest were the mixing zones below the seven WWTP outfalls. The downstream location for a sampling site was established where the WWTP effluent was estimated to be well mixed with the receiving water. Another concern was proximity to the nearest tributary. If any tributaries entered close to the WWTP outfall, the sampler preferably was positioned between the WWTP outfall and the nearest tributary. Three samplers were used to bracket the Bedford Heights WWTP because its outfall on an unnamed tributary to Hawthorne Creek is so close to the mouth that the effluent could not mix completely with the receiving stream before it

enters Hawthorne Creek (fig. 7). Consequently, one sampler was placed in the unnamed tributary above the WWTP outfall, the second in Hawthorne Creek above the confluence with the unnamed tributary, and the third in Hawthorne Creek below the confluence with the unnamed tributary (where it appeared that the two streams were fully mixed).

Streamflow in Tinkers Creek during the passive-sampler deployment period can be characterized as being greater than normal. Daily mean streamflows determined for the USGS streamgage on Tinkers Creek at Bedford, Ohio (station 04207200), for May 8, 2006, through June 7, 2006, were compared to mean daily streamflows determined for those same calendar days based on gage data collected from 1962 to 2007. That comparison indicates that the 2006 daily mean streamflows exceeded their corresponding long-term mean daily streamflows on 19 of the 31 calendar days and that the average streamflow for that period in 2006 (283 ft³/s) was over twice the historical average (127 ft³/s) for the same calendar days.

Passive samplers were deployed for a 28-day period beginning in May 2006 and ending in June 2006. Specific beginning and ending dates of deployments at each loca-

EXPLANATION

- Wastewater outfall
- ▽ Sampling location

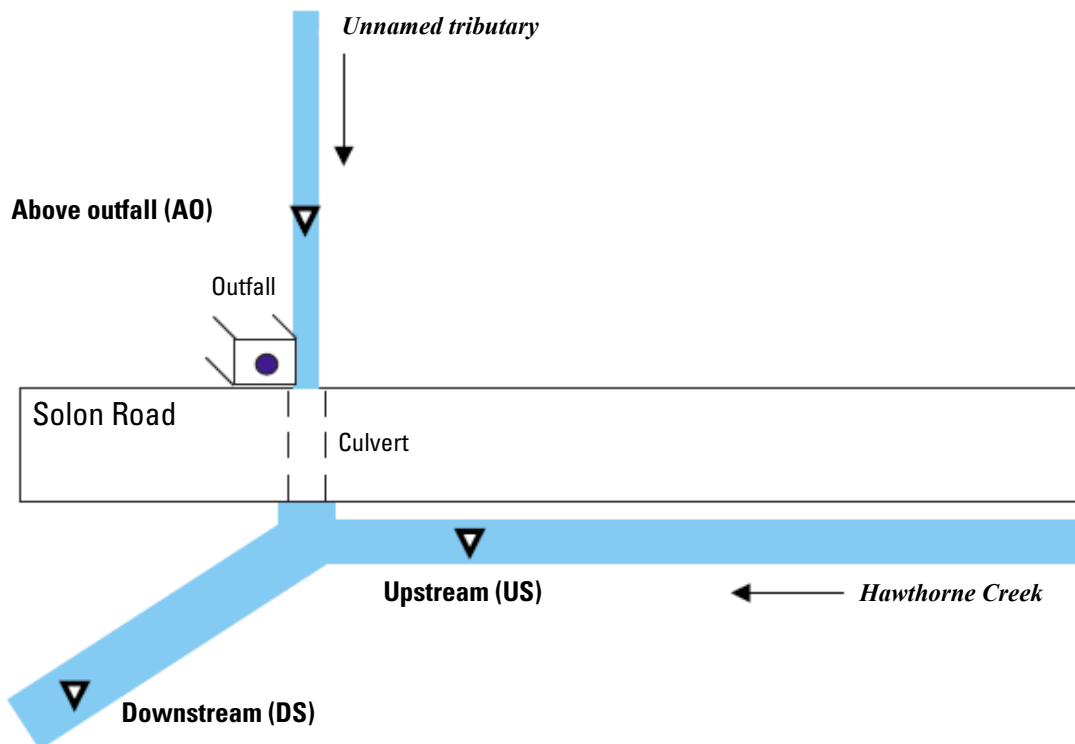


Figure 7. Schematic of sampling-site locations near the Bedford Heights wastewater-treatment-plant outfall.

tion are listed in table 2. Field personnel were instructed to avoid use of compounds that were in the list of analytes being measured (both in passive samplers and streambed sediments), and basic good field practices were followed (U.S. Geological Survey, 2006). So, for example, field personnel did not wear insect repellent containing DEET when handling or processing samples. Passive samplers were stored in airtight containers on ice for transport to and from the study area and to the laboratory.

Streambed-Sediment Sampling

Streambed-sediment samples were collected at each sampling location before the passive samplers were retrieved. Streambed-sediment samples were collected slightly downstream from the passive samplers, and sediments and samplers were collected in a downstream-to-upstream order so as to prevent contamination from upstream disturbances. The top 1 to 2 cm of streambed sediment was sampled from 5 to 10 deposi-

tional zones, and the samples were composited with samples from other depositional zones sampled at the same site. The number of samples collected from each zone was roughly proportional to the relative size of each zone (for example, the larger the area of the depositional zone, the larger the number of samples collected). The purpose of compositing subsamples from different depositional zones was to reduce local scale variability and gather samples that were most representative of the average contaminant concentration at the site.

Streambed-sediment samples were collected and processed in the field according to the organic-contaminant methods described by Shelton and Capel (1994). Streambed-sediment samples from each depositional zone were collected with stainless steel spoons, then composited in a basin before being poured through a 2-mm stainless steel sieve. Approximately 100 g of material was collected at a sampling site for each of the analytical schedules used. Streambed-sediment samples were placed in baked amber glass jars and placed on ice for transport from the study area and to the laboratory.

Laboratory Analyses

The following is a brief overview of the methods used to analyze the passive-sampler media and streambed-sediment samples. A detailed description of the methods is given in Appendix A, and lists of the analytes by medium and analytical method are given in Appendix B.

A solvent (or mixture of solvents) was used to extract analytes from the POCIS media at the USGS Columbia Environmental Research Center (CERC) in Columbia, Mo. The extracts were concentrated, filtered, and sealed in ampoules for shipment to the analytical laboratories. Each POCIS sample analyzed in the laboratory was a composite of extracts from two POCIS disks, which served to increase the total mass of sampled compounds and thereby effectively lowered the analytical detection limits.

POCIS sample extracts were analyzed for 66 wastewater compounds at the USGS National Water Quality Laboratory (NWQL) in Denver, Colo., by means of full-scan positive-ion gas chromatography (GC)-mass spectrometry (MS), operating in electron impact mode (Zaugg and others, 2007). POCIS sample extracts were analyzed for pharmaceuticals at the NWQL by means of positive-mode electrospray ionization (ESI) high-performance liquid chromatography (LC)-mass spectrometry (Cahill and others, 2004). To confirm the identity of pharmaceuticals, selected POCIS extracts also were analyzed by means of liquid chromatography tandem mass spectrometry (LC/MS/MS), operated in multiple-reaction monitoring mode.

Antibiotic and degradation products were separated from the POCIS extracts by means of a liquid chromatography (LC) gradient elution. Individual antibiotic compounds were analyzed by means of selected ion monitoring liquid chromatography/tandem mass spectrometry at the USGS Organic Geochemistry Research Laboratory (OGRL) in Lawrence, Kans. The antibiotic analysis includes some analytes that are not antibiotics (such as ibuprofen and carbamazepine); however, the 32 compound analyte list will be referred to generically hereafter as “antibiotic compounds.”

Analytes and performance reference compounds (PRCs) were extracted from SPMDs by means of two-stage dialysis with a solvent. The extracts were concentrated, and size exclusion chromatography (SEC) was used to separate the compounds into fractions based on their size. Fractions from the SEC were further processed by means of gravity-column chromatography to remove potential interferences and to enrich the PRCs and analytes. Analysis of SPMD extracts for PRCs and 33 hydrophobic compounds was done at the CERC by means of GC/MS, using positive ion electron-impact ionization in the selected-ion mode (Alvarez and others, 2008; Petty and others, 2000) (table B4).

Pressurized solvent extractions were used to extract analytes from streambed-sediment samples. After extraction, pharmaceutical analyses (20 compounds) were done at the NWQL by means of high-performance LC/MS, using positive

electrospray ionization operated in the selected-ion monitoring mode (Kinney and others, 2006). Wastewater compounds of interest were isolated from potential matrix interferences by means of solid-phase extraction (SPE). The SPE cartridges were dried with nitrogen gas, and the sorbed compounds were eluted with a solvent mixture. The eluate was analyzed for 57 wastewater compounds at the NWQL by means of capillary-column GC/MS (Burkhardt and others, 2006).

Eleven OWCs in passive-sampler extracts were analyzed by more than one analytical method. For those compounds, concentrations are reported independently for each method because sensitivities—and consequently, method detection levels—differ by method. Four compounds (azithromycin, carbamazepine, sulfamethoxazole, and trimethoprim) in POCIS extracts were analyzed by means of the antibiotic and pharmaceutical methods. Two compounds (caffeine and cotinine) were analyzed in POCIS extracts by means of the pharmaceutical and wastewater methods. Five other compounds (2-methylnaphthalene, anthracene, benzo[*a*]pyrene, naphthalene, and pyrene) were analyzed in POCIS extracts by means of the wastewater method and also in SPMD extracts.

Reporting of Data

POCIS and SPMD media were processed to determine concentrations of target analytes. The resulting raw concentration data are reported in units of nanograms (ng) per unit of media (for example, nanograms per POCIS disk or per SPMD). If uptake kinetics (sampling rates) of the sampling media can be determined, time-weighted water concentrations can be estimated. Unfortunately, a variety of site-specific environmental factors (for example, temperature and water velocity over the media) can affect sampling rates. Sampling rates can be estimated for SPMDs through the use and analysis of performance reference compounds (PRCs) embedded in the media. (See Appendix A for more details.) Because loss and sampling rates are equal (isotropic), the rate of PRC loss during field deployment can be used to adjust laboratory-determined sampling rates to account for site-specific factors. Consequently, time-weighted water concentrations are estimated and reported in units of micrograms per liter for SPMD analytes. However, the POCIS media are so strongly sorptive that the PRC approach does not work. Consequently, concentrations of analytes determined from POCIS must be reported in units of nanograms per POCIS disk, and these concentrations cannot be adjusted for variable sampling rates. Because the concentrations of analytes from POCIS cannot be adjusted for sampling rate, care must be taken in their interpretation. For that reason, this report focuses primarily on the detection/nondetection of analytes in POCIS and assumes (possibly incorrectly) that sampling rates were approximately equal at all locations.

Each laboratory determined laboratory reporting levels (LRLs) for the analytes included in their respective analytical schedules. LRLs are the smallest measured concentration that

the laboratory could measure reliably for a given analytical method. Method detection limits (MDLs) are also determined for some analytical methods. MDLs are defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero for the given sample matrix. LRLs and MDLs (where applicable) are reported in Appendix B.

In some cases, values are reported for compounds at concentrations below the LRL. That was done because information-rich analytical methods (such as GC/MS and LC/MS) provide qualifying information that enhances analyte identification (Childress and others, 1999). Concentrations reported below the LRL and above the MDL (identified in data tables by an “e” in front of the concentration) met the same criteria for qualitative identification as concentrations above the reporting level; however, there is greater uncertainty associated with the calculated concentration. An “e” code may also be used for other reasons, such as when results are extrapolated above the calibration curve or when analyte performance does not meet acceptable method-specific criteria. For more information on reporting procedures, see Childress and others (1999). All values qualified with an “e” code in this report were counted as detections.

Occasionally, compounds are detected below the average MDL (identified in tables by an “m,” indicating that the compound is present but is not quantified). This can happen because the low-level sensitivity can vary between analytical instrument setups and may at times be more sensitive than indicated by the average MDL. When compounds were not detected, concentrations were censored at (reported as less than) the reporting level.

A detection was censored (identified in tables by a “dc”) for a given compound if the concentration in the environmental sample was less than 3 times the concentration in the corresponding trip blank. If the concentration of the compound in the environmental sample was between 3 and 5 times the corresponding concentration in the trip blank, it was footnoted to indicate that the compound was also detected in the corresponding trip blank.

The methods used to process and analyze POCIS media are still in development and have not been fully validated. Consequently, we emphasize that all POCIS results should be treated as estimates.

Quality Control

Various quality-control (QC) measures were employed in this study to help assess sampling and analytical variability and bias and to aid accurate quantification of target analytes. As is evident from table 3, the types of QC measures used varied as a function of sampling media and analytical method. The QC measures are discussed in the sections that follow, with detailed information given on trip blanks and replicate analyses.

Trip Blanks

The POCIS and SPMD devices have the potential to accumulate airborne contaminants when exposed to the atmosphere. Consequently, at each of the 18 sampling locations, trip blanks were used. Trip blanks consisted of deployment canisters containing POCIS and SPMD media that were identical in construction to those placed in the water. The trip blanks were exposed to the atmosphere at each sampling location during the same time and for the same duration that field-deployed canisters were exposed to the atmosphere (as they were being deployed into or retrieved from the stream). The trip blanks were stored in airtight containers on ice for transport to and from the study area. Between deployment and retrieval of the field-deployed canisters, trip blanks were stored in their airtight containers at less than 0°C.

No antibiotics were detected in POCIS trip blanks; however, 4 of 20 pharmaceutical compounds and 10 of 66 wastewater compounds were detected (appendix table C1). For most compounds, detections occurred at from one to three locations. Three compounds, diethylhexyl phthalate (a plasticizer), fluoxetine (an antidepressant), and diphenhydramine (an antihistamine) were found in four or more trip blanks.

Table 3. Matrix of quality-control measures used as a function of media and analytical method.

[X indicates that a quality-control measure was used; POCIS, polar organic chemical integrative sampler; SPMD, semipermeable membrane device]

Media	Analytical method	Trip blank	Replicate	Method blank	Reagent spike	Matrix spike	Surrogate standards	Internal standards
POCIS	Antibiotic	X	X				X	X
POCIS	Pharmaceutical	X	X					
POCIS	Wastewater	X	X	X	X			X
SPMD	Hydrophobic	X	X	X				X
Sediment	Pharmaceutical		X	X	X	X	X	
Sediment	Wastewater		X	X	X		X	X

Of the 33 hydrophobic compounds analyzed for, 14 were detected in SPMD trip blanks (appendix table C2). Of the 14 compounds, 9 were detected in more than half of the samples, and 3 of those 9 (phenanthrene, 1-methylnaphthalene, and 2-methylnaphthalene; all fuel-related compounds) were detected in 100 percent of the samples.

Field Replicates

Field replicates were collected at two locations (Streetsboro and Twinsburg, both downstream from WWTP outfalls) to assess variability of the environmental data. POCIS replicates (appendix table C3) and SPMD replicates (appendix table C4) consisted of a second passive-sampler canister (containing POCIS and SPMD media) deployed on the same tether side by side with the primary sampler (the designation of one sampler as primary and the other as a replicate was done at random). A streambed-sediment replicate (appendix table C5) consisted of a second sample collected at the same time as the environmental sample. Locations downstream from the Streetsboro and Twinsburg WWTPs were chosen for replicate sampling because each WWTP discharges directly into Tinkers Creek, and the likelihood of detecting OWCs was expected to be greatest at sites downstream from WWTP outfalls.

Of the 236 environmental replicate pairs of POCIS analytes (118 analytes total from three methods \times 2 sets of replicates = 236), the detection or nondetection of the analyte was confirmed in about 94 percent of the pairs. Only in 15 pairs were there detections in only one of the paired samples (appendix table C3). Similarly, for SPMDs and streambed sediments, an analyte's detection or nondetection was confirmed in replicate samples about 97 and 94 percent of the time, respectively. In most cases, the concentration of the detection was either estimated or near the LRL when an analyte was detected in only one of the replicate pairs.

The variability of the results for field replicate samples was assessed by calculating the absolute relative percent difference (RPD) in concentration for the two environmental samples forming the replicate pair. The RPD is calculated as follows:

$$\text{RPD} = 100 \times |(R_1 - R_2) / (0.5(R_1 + R_2))|$$

where

- R_1 is the concentration of analyte in the first sample of the replicate pair, and
 R_2 is the concentration of analyte in second sample of the replicate pair.

RPDs for POCIS replicates ranged from 4.2 to 120 percent (appendix table C3). Some RPDs were high, and in several instances a compound was detected in one sample in the replicate but not the other (RPDs were not calculated when

a compound was detected in only one sample of the replicate pair). This can be expected when comparing chemical concentrations at or near detection levels (Sando and others, 2006). One factor that could result in differing concentrations between replicate samples is the slightly different environmental exposures (such as due to each sampler's position in the stream). RPDs for SPMD replicates ranged from 4.3 to 27 percent (appendix table C4). The largest RPD (27 percent) was for phenanthrene, a compound found in 100 percent of the trip blanks.

RPDs for streambed-sediment replicates ranged from 0 to 120 percent. For a given compound, RPDs determined for different replicate pairs could be very different. For example, the RPD for β -stigmastanol (a plant sterol) was 9.5 percent in one replicate pair and 120 percent in the other replicate pair. This difference in variability may reflect the ability to obtain representative streambed-sediment replicates, as well as reflecting analytical variability.

Reagent and Matrix Spikes

Reagent spikes consist of analyte-free reagents that were "spiked" by adding known concentrations of the target analytes. In contrast, matrix spikes consist of environmental samples that are spiked with known concentrations of target analytes. Reagent and matrix spike samples were used to assess analytical bias due to variable analyte recovery and to check the performance of an analytical method at the time that environmental samples were analyzed, respectively.

The recoveries of the reagent-water spikes for wastewater compounds ranged from 20 percent (for tetrachloroethylene) to 107 percent (metaxyl) (appendix table C6). The median reagent-water-spike recovery was 89.5 percent, and about 84 percent of the recoveries equaled or exceeded 60 percent.

The recoveries of pharmaceuticals in reagent spikes for sediments ranged from 11 percent (for azithromycin) to 150 percent (for sulfamethoxazole), with a median recovery of 68.5 percent (appendix table C7). Recoveries of less than 50 percent occurred in both sediment reagent spike samples for azithromycin and fluoxetine. One of the two sediment reagent-spike samples showed greater than 100 percent recovery for half of the analytes, whereas the other sediment reagent-spike sample indicated recoveries in the range of 61 to 72 percent for those same analytes.

The recoveries of pharmaceuticals in matrix spikes for two streambed-sediment samples were quite variable (appendix table C7). Recoveries of miconazole and ranitidine were consistently low (<10 percent), and percent recoveries for some other compounds such as 1,7-dimethylxanthine, cimetidine, and dehydronifedipine varied by more than 50 percentage points. The poor recoveries for some analytes and high variability for others suggests that matrix effects can be significant.

Method Blanks and Surrogate and Internal Standards

Method blank samples consisted of analyte-free POCIS and SPMD media or reagent-grade sand that were processed and analyzed in the laboratory along with the environmental samples.

Surrogate standards are analytically noninterfering compounds that are similar to the target analytes in both physical and chemical properties but are not expected to be present in the environment. Surrogates are added to environmental and quality-control samples immediately prior to analysis and used to monitor the recovery efficiency of the analytical method for the unique environmental-sample matrix.

Internal standards are similar in concept and application to surrogate standards except that their primary purpose is to improve quantification by facilitating corrections for loss of analyte.

Quantitative information about method blank and surrogate and internal standard results is not presented in this report; however, those data were examined and used to ensure the reporting of valid and accurate data.

Results

The numbers of OWCs detected by sample matrix and analytical method are presented in table 4. Numbers of detections downstream from WWTPs are bolded in table 4 if they are larger than corresponding upstream numbers. A one-sided Fisher's exact test (Sokal and Rohlf, 1981) was done to determine whether the number of detections at the downstream location was significantly greater (at a 5-percent level) than at the corresponding upstream location. Those counts that were significantly greater at the downstream locations are italicized as well as bolded.

For a given sample matrix (that is, water or sediment), individual compounds that were detected by more than one analytical method are included separately in counts for each method. Percentages of detections of the most frequently detected compounds in the POCIS and SPMD extracts and in bed-sediments samples are presented in tables 5 and 6, and numbers of detections by WWTP and analytical method are shown in figures 8 and 9, respectively. The minimum, median, maximum, and frequency of detection for the individual compounds are presented by sample matrix and analytical method in Appendixes D through F.

Table 4. Numbers of detections of chemical compounds in water (as determined by analysis of POCIS and SPMD media) and streambed sediments in the Tinkers Creek watershed and two other tributaries to the Cuyahoga River, 2006.

[Number of analytes for the method shown in parentheses; WWTP, wastewater-treatment plant; US, upstream from WWTP outfall; DS, downstream from WWTP outfall; bold values indicate number of DS detections that were greater than their respective US detections; italicized values indicate number of DS detections that were statistically greater (at a 5-percent level) than their respective US detections]

Sample area	Numbers of detections, by indicated media and analytical method																	
	Water								Streambed sediment									
	Antibiotic method (32)		Pharmaceutical method (20)		Wastewater method (66)		Hydrophobic method (33)		Pharmaceutical method (20)		Wastewater method (57)							
US	DS	US	DS	US	DS	US	DS	US	DS	US	DS							
Streetsboro	0	7	1	5	9	22	6	4	0	3	23	25						
Aurora Westerly	0	7	1	6	9	16	5	3	2	4	24	26						
Aurora Shores	0	4	1	4	8	8	4	3	2	2	21	26						
Twinsburg	4	5	5	5	13	11	10	10	0	1	24	23						
Solon	0	10	1	12	17	20	15	12	1	1	20	31						
Bedford	2	7	2	5	23	29	20	17	1	1	29	29						
Bedford Heights	0 ^a	0 ^b	6	2 ^a	1 ^b	5	9 ^a	12 ^b	22	16 ^a	17 ^b	18	2 ^a	1 ^b	4	20 ^a	20 ^b	23
Tinkers Creek at Dunham Road	6		10		21		13		2		28							
Furnace Run	3		1		5		3		1		20							
Yellow Creek	0		2		1		5		2		18							

^aThe number of detections at the unnamed tributary site located upstream from the WWTP outfall.

^bThe number of detections at the Hawthorne Creek site located upstream from the unnamed tributary.

Compounds in Water

The following sections contain information about the time-weighted concentrations of OWCs in the water column as determined by analyzing extracts from POCIS or SPMD passive-sampler media.

Antibiotic Compounds

Twelve compounds were detected in one or more POCIS extracts by means of the antibiotic method (appendix table D2). Sulfamethoxazole and trimethoprim (two antibiotics that are commonly combined to treat a variety of infections) and carbamazepine (an anticonvulsant and suspected endocrine disruptor¹) were each detected in more than 50 percent of the

¹ Endocrine disruptors are natural or synthetic compounds that can mimic or block the action of an organism's natural hormones.

samples (table 5). Antibiotic compounds were not detected at most sites upstream from WWTPs addressed in this study but were detected at all sites downstream from WWTP outfalls (table 4 and fig. 8) and at the Furnace Run reference site (which has a wastewater source about 5 mi upstream from the sampling site).

Antibiotic compounds were detected at sites upstream from the Twinsburg and Bedford WWTP outfalls (table 4 and fig. 8). Potential sources of those compounds at Twinsburg include the Aurora Westerly, Aurora Shores, and Streetsboro WWTPs, all of which discharge to Tinkers Creek or its tributaries upstream from Twinsburg. Three out of four antibiotic compounds detected upstream from Twinsburg also were detected downstream from all three upstream WWTPs, and the fourth (erythromycin-H₂O (anhydroerythromycin), an antibiotic degradate) was detected downstream from two of the three upstream WWTPs. In both cases where antibiotics were detected upstream from WWTPs, the number of detections at the corresponding downstream locations was greater.

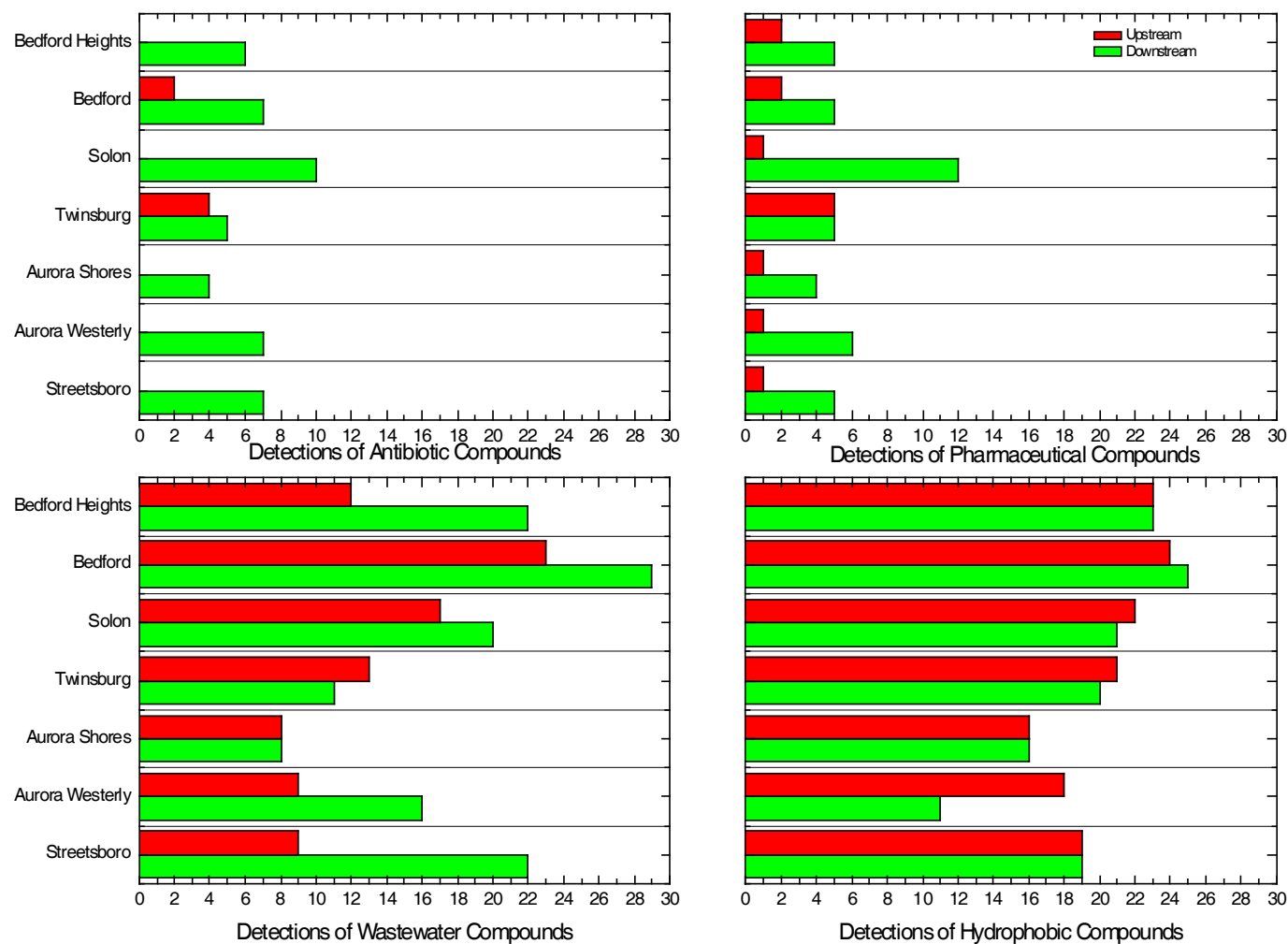


Figure 8. Numbers of detections of antibiotic, pharmaceutical, wastewater, and hydrophobic compounds in water (as determined by analysis of POCIS and SPMD media) upstream and downstream from wastewater-treatment plants in the Tinkers Creek watershed.

Six antibiotic compounds were detected at the Dunham Road site (table 4), the most downstream sampling site on Tinkers Creek. By comparison, the median number of antibiotics detected downstream from the WWTPs was seven. No antibiotic compounds were detected at the Yellow Creek reference site; however, three compounds were detected at the Furnace Run site (which has a wastewater source about 5 mi upstream from the sampling site). Two of the antibiotic compounds (carbamazepine and sulfamethoxazole) detected at Furnace Run had been found downstream from all WWTP outfalls in the Tinkers Creek watershed. The third antibiotic compound, ormetoprim (commonly used in combination with sulfadimethoxine to treat skin and soft-tissue infections in animals), was not detected at any other site.

Pharmaceutical Compounds

Fifteen compounds were detected in one or more POCIS extracts by means of the pharmaceutical method (appendix table D3). Caffeine (a stimulant), trimethoprim, and carbamazepine were detected in 50 percent or more of the samples (table 5). Frequent detections of trimethoprim and carbamazepine had also occurred in samples analyzed by the antibiotic method; however, sulfamethoxazole, which had been detected in more than 50 percent of the samples analyzed by means of the antibiotic method (table 5), was detected only once by means of the pharmaceutical method. The difference in frequency of detection between the two analytical methods is due in part to the higher reporting level for sulfamethoxazole by the pharmaceutical method (5 ng/POCIS) as compared to the antibiotic method (1 ng/POCIS).

The spatial pattern of pharmaceutical compound detections was similar to that of the antibiotic compounds (fig. 8) with exception that at least one pharmaceutical compound (caffeine) was detected upstream from each WWTP. Caffeine was detected in all but one sample (appendix table D4). The number of pharmaceutical-compound detections at sites downstream from WWTP outfalls was greater than at upstream sites except at Twinsburg, where the same number of detections occurred in both upstream and downstream samples (fig. 8).

Caffeine was detected at both reference sites, although at lower concentrations than found in the Tinkers Creek watershed (appendix table D3). Fluoxetine (an antidepressant) also was detected at the Yellow Creek reference site. In general, the number of detections of pharmaceutical compounds at reference sites was similar in magnitude to the number of detections observed at sites upstream from the WWTP outfalls.

Wastewater Compounds

Forty-one compounds were detected in one or more POCIS extracts by means of the wastewater method (appendix table D6). Eleven of the compounds were detected in more than 50 percent of the samples (table 5). Caffeine was the most frequently detected compound, with detections in all but one sample (table 5). Other compounds detected in more than 50

percent of the samples include atrazine and metolachlor (herbicides), diethyl phthalate (plasticizer), N,N-diethyl-meta-toluamide (DEET) (topical insect repellent), anthraquinone (used to produce dyes and occurs naturally in some plants), *p*-cresol (disinfectant and wood preservative), ethanol,2-butoxy-phosphate (fungicide), hexahydrohexamethylcyclopentabenzopyran (HHCB) (synthetic musk), and tris(2-chloroethyl)phosphate and tris(dichloroisopropyl)phosphate (flame retardants). HHCB, a synthetic musk used in some personal care products, has been shown to have antiestrogenic activity (Schreurs and others, 2005) and is thought to disrupt endocrine function in fish. Atrazine and diethyl phthalate are also known or suspected endocrine disruptors (appendix table B6).

Wastewater compounds generally were detected with greater frequency downstream from WWTP outfalls than upstream (table 4 and fig. 8). Twinsburg was the only location where more compounds were detected upstream from the outfall than downstream. Appreciably fewer detections of wastewater compounds occurred at the reference sites than at sites in the Tinkers Creek watershed (table 4).

Hydrophobic Compounds

Twenty-two hydrophobic compounds were detected in one or more SPMD extracts (appendix table E1). Ten of the compounds were detected in over 50 percent of the samples (table 5). Fluoranthene and pyrene (combustion by-products and coal tar derivatives) were the most frequently detected hydrophobic compounds, occurring in 100 percent of the samples (appendix table E2). Other compounds detected in more than 50 percent of the samples include phenanthrene, chrysene, 2-methylphenanthrene, benzo[*b*]fluoranthene, benzo[*a*]anthracene, benzo[*b*]naphtha[2,1-*d*]thiophene, benzo[*e*]pyrene, and benzo[*k*]fluoranthene.

Compounds detected more frequently downstream than upstream from WWTPs are bolded in table 5. A one-sided Fisher's exact test (Sokal and Rohlf, 1981) was done to determine whether the frequency of detection at the downstream location was significantly greater (at a 5-percent level) than at the corresponding upstream location. Those detection frequencies that are significantly greater at the downstream locations are italicized as well as bolded.

Unlike the antibiotic, pharmaceutical, and wastewater compounds, hydrophobic compounds generally were detected in about the same or greater numbers at sites upstream of WWTP outfalls than at corresponding downstream sites (table 4 and fig. 8). Many hydrophobic compounds strongly sorb to particulate matter such as soils and sludge, which are removed during the wastewater-treatment process. Consequently, the reason for fewer detections of hydrophobic compounds downstream of WWTP outfalls (relative to upstream) may be due to dilution of stream water by the WWTP effluents.

Hydrophobic compounds were detected at the reference sites; however, the frequencies of detection tended to be in the lower range of frequencies observed for sites in the Tinkers Creek watershed (table 4).

Table 5. Organic wastewater compounds detected most frequently (>50 percent detections in one or more groupings) in water (as determined by analysis of POCIS and SPMD media) in the Tinkers Creek watershed and two other tributaries to the Cuyahoga River, 2006.

[US, upstream from wastewater-treatment plant (WWTP); DS, downstream from wastewater-treatment plant; AS, all sites (including reference sites); bold values indicate DS detection frequencies that were greater than their respective US frequencies; italicized values indicate DS detection frequencies that were statistically greater (at a 5-percent level) than their respective US frequencies]

Compound	Percentage of detections, by indicated media and analytical method											
	POCIS									SPMD		
	Antibiotic method			Pharmaceutical method			Wastewater method			Hydrophobic method		
	US	DS	AS	US	DS	AS	US	DS	AS	US	DS	AS
Azithromycin	0	86	39									
Carbamazepine (by antibiotic method)	14	100	56									
Erythromycin-H ₂ O	14	86	44									
Sulfamethoxazole	29	100	61									
Trimethoprim	29	100	56									
Lincomycin	0	57	28									
Ofloxacin	0	57	22									
Caffeine (by pharmaceutical method)				100	86	94						
Carbamazepine (by pharmaceutical method)				14	100	50						
Diphenhydramine				0	86	39						
Thiabendazole				14	71	39						
Trimethoprim				29	100	56						
N,N-diethyltoluamide (DEET)							100	100	83			
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)							14	86	44			
Atrazine							100	86	89			
Anthraquinone							71	71	67			
Caffeine (by wastewater method)							100	100	94			
Diethyl phthalate							86	86	83			
Ethanol,2-butoxy-,phosphate							57	71	56			
Hexahydrohexamethyl-cyclopentabenzopyran (HHCB)							29	100	56			
Metolachlor							100	43	72			
4-Nonylphenol monoethoxylate (NP1EO; sum of all isomers)							29	57	39			
4-Octylphenol monoethoxylate (OP1EO; sum of all isomers)							14	57	33			
<i>p</i> -Cresol							86	71	67			
<i>p</i> -Nonylphenol, total							29	57	39			
3-methyl-1(H)-indole							14	57	28			
Tris(2-chloroethyl) phosphate							43	86	56			
Tris(dichlorisopropyl) phosphate							43	86	56			
2-methylphenanthrene										57	57	61
Benz[<i>a</i>]anthracene										57	57	56
Benzo[<i>b</i>]fluoranthene										71	57	61
Benzo[<i>b</i>]naphtho[2,1- <i>d</i>]thiophene										57	57	56
Benzo[<i>e</i>]pyrene										57	57	56
Benzo[<i>k</i>]fluoranthene										57	57	56
Chrysene										100	71	89
Fluoranthene										100	100	100
Phenanthrene										100	100	94
Pyrene										100	100	100

Compounds in Streambed Sediments

The following sections discuss analytical results for streambed-sediment samples. Streambed-sediment chemistry can reflect long-term exposure to stream water but also can reflect other contaminant sources, such as airborne deposition or sediments washed off urban or agricultural landscapes.

Pharmaceutical Compounds

Eight pharmaceutical compounds were detected in one or more streambed-sediment samples (appendix table F1). One compound (diphenhydramine, an antihistamine) was detected in 50 percent of the samples (table 6). A comparison of phar-

maceutical compounds detected in sediment to those detected in POCIS extracts indicates that many of the compounds detected in sediment also were present in water. One notable exception is miconazole (an antifungal compound), which was detected in 28 percent of the streambed-sediment samples but was not detected in water. Miconazole's poor solubility in water explains why it partitions preferentially onto particulate phases. In general, concentrations of pharmaceutical compounds in sediment, when detected, were higher in samples collected downstream from WWTP outfalls than in samples collected upstream from the outfalls (table 6 and fig. 9).

Some pharmaceutical compounds (such as trimethoprim and carbamazepine) that were detected in water at all sites downstream from WWTP outfalls were either not detected or

Table 6. Organic wastewater compounds detected most frequently (>50 percent detections in one or more groupings) in streambed sediments in the Tinkers Creek watershed and two other tributaries to the Cuyahoga River, 2006.

[US, upstream from wastewater-treatment plant (WWTP); DS, downstream from wastewater-treatment plant; AS, all sites (including reference sites); –, not analyzed for with the method; bold values indicate DS detection frequencies that were greater than their respective US frequencies; italicized values indicate DS detection frequencies that were statistically greater (at a 5-percent level) than their respective US frequencies]

Compound	Percentage of detections in streambed sediments, by analytical method					
	Wastewater method			Pharmaceutical method		
	US	DS	AS	US	DS	AS
Diphenhydramine				43	71	50
1-Methylnaphthalene	86	86	67			
2,6-Dimethylnaphthalene	100	100	56			
2-Methylnaphthalene	100	100	94			
3-β-Coprostanol	86	100	83			
3-Methyl-1H-indole	100	100	100			
4-Nonylphenol	14	57	28			
Anthraquinone	100	100	100			
Acetophenone	100	100	90			
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	29	86	50			
Anthracene	100	86	94			
Benzo[<i>a</i>]pyrene	100	100	100			
β-Sitosterol	100	100	100			
β-Stigmastanol	86	100	83			
Bis(2-ethylhexyl) phthalate	100	100	94			
Carbazole	100	100	94			
Cholesterol	100	100	100			
4-Nnonylphenol diethoxylate (NPEO2; sum of all isomers)	43	71	44			
Fluoranthene	100	100	100			
Hexahydrohexamethyl cyclopentabenzopyran (HHCB)	29	86	50			
Indole	100	100	100			
4-Nonylphenol monoethoxylate (NPEO1; sum of all isomers)	29	71	39			
Naphthalene	100	100	94			
<i>p</i> -Cresol	100	100	89			
Phenanthrene	100	86	94			
Phenol	100	86	83			
Pyrene	100	100	100			

detected at a much lower frequency in streambed sediments (appendix tables D3 and F1). Results such as these reinforce the need to sample both sediments and water when assessing the occurrence and distribution of OWCs.

Pharmaceutical compounds were detected in sediments at the reference sites (table 4). Sulfamethoxazole was detected at both reference sites, and erythromycin (an antibiotic) also was detected at very low concentration at the Yellow Creek reference site (appendix table F1).

Wastewater Compounds

Thirty-seven wastewater compounds were detected in one or more streambed-sediment samples (appendix table F3). Twenty-two compounds were detected in more than 50 percent of the samples, and 12 of those compounds (2,6-dimethylnaphthalene, 2-methylnaphthalene, 3-methyl-1H-indole, anthraquinone, benzo[*a*]pyrene, β -sitosterol, carbazole, cholesterol, fluoranthene, indole, naphthalene, and pyrene) were detected at all sites (table 6). Fourteen of the wastewater compounds detected (three of which were detected in more than 50 percent of the samples) are known or suspected endocrine disruptors (appendix table B6).

Fifteen wastewater compounds (2,6-dimethylnaphthalene, 2-methylnaphthalene, 3-methyl-1H-indole, anthraquinone, acetophenone, benzo[*a*]pyrene, β -sitosterol, bis(2-ethylhexyl) phthalate, carbazole, cholesterol, fluoranthene, indole, naphthalene, *p*-cresol, and pyrene) were detected in sediments at all sites in the Tinkers Creek watershed, irrespective of whether the site was upstream or downstream from a WWTP (table 6). Sources of those compounds likely are diffuse within the watershed. Three of the seventeen compounds (benzo[*a*]pyrene, bis(2-ethylhexyl) phthalate, and *p*-cresol) are known or suspected endocrine disruptors.

In all cases except one (at Solon), the number of detections of wastewater compounds in streambed sediments was equal or greater (although generally not statistically greater) in samples collected downstream from WWTP outfalls as compared to corresponding upstream samples (table 4 and fig. 9). Three compounds (hexahydrohexamethyl-cyclopentabenzopyran (HHCB), acetyl-hexamethyl-tetrahydro-naphthalene (AHTN), and triclosan) were detected in sediments downstream from WWTP outfalls at least 3 times more frequently than at upstream sites.

Concentrations of wastewater compounds in sediments downstream from the Aurora Westerly, Aurora Shores, and Solon WWTP outfalls tended to be higher than their corresponding upstream concentrations (appendix table F3). In contrast, concentrations of wastewater compounds in sediments downstream from the Streetsboro and Twinsburg WWTP outfalls tended to be somewhat lower than their corresponding upstream concentrations. Higher concentrations of wastewater compounds in sediments upstream from Twinsburg are not completely unexpected given the number of upstream wastewater sources; however, the reason for the higher concentrations upstream from Streetsboro is not known.

In spite of their low water solubilities, some wastewater compounds, such as atrazine and DEET, were not detected in streambed sediments in spite of being detected in water at most sites downstream from WWTP outfalls (appendix tables D3 and F4). Some other wastewater compounds, such as AHTN and HHCB, were detected in both water and sediment, with detections in both matrices occurring appreciably more frequently downstream from WWTPs as compared to upstream. Once again, these results reinforce the need to sample both sediments and water when assessing the occurrence and distribution of OWCs.

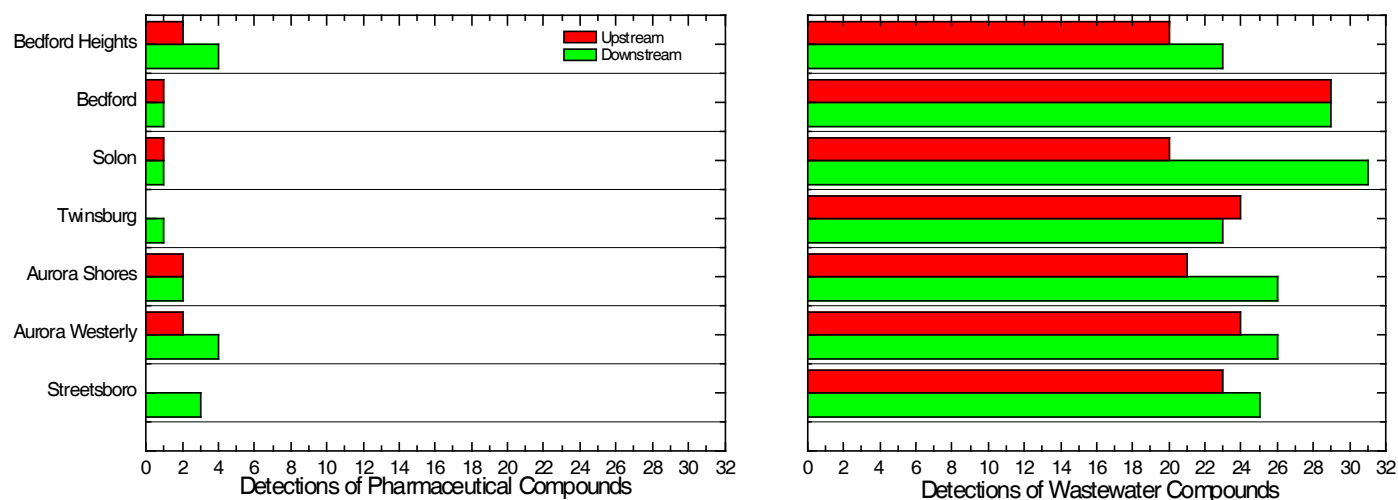


Figure 9. Numbers of detections of pharmaceutical and wastewater compounds in streambed sediments upstream and downstream from wastewater-treatment plants in the Tinkers Creek watershed.

Wastewater compounds were detected in sediments at the reference sites (table 4), generally with detection frequencies slightly lower than observed for sites upstream from WWTPs in the Tinkers Creek watershed.

Summary and Conclusions

This report presents the results of a study to determine the occurrence and distribution of a wide variety of organic wastewater compounds (OWCs) in the Tinkers Creek watershed and in reference sites on two other tributaries to the Cuyahoga River. The study was done by U.S. Geological Survey in cooperation with the Ohio Water Development Authority; National Park Service; Cities of Aurora, Bedford, Bedford Heights, Solon, and Twinsburg; Counties of Portage and Summit; and in collaboration with the Ohio Environmental Protection Agency. Samples were collected at sites in the Tinkers Creek watershed upstream and downstream from seven wastewater-treatment plants (WWTPs) serving the communities of Aurora, Bedford, Bedford Heights, Solon, Streetsboro, and Twinsburg, Ohio, at one site downstream from all upstream WWTP inputs, and at reference sites outside of the Tinkers Creek watershed near the mouths of Furnace Run and Yellow Creek.

Water-column results were based on a 28-day May–June 2006 exposure period, during which a total of 20 canisters containing passive sampler media were deployed instream. The canisters contained both polar organic chemical integrative sampler (POCIS) and semipermeable membrane device (SPMD) media. The POCIS and SPMD media are designed to sample OWCs in water in a manner that yields a time-weighted concentration for the exposure period. Streambed-sediment samples also were collected at each site when the passive-sampler canisters were retrieved.

POCIS media extracts were analyzed by means of three separate laboratory methods predominately targeting antibiotic, pharmaceutical, or wastewater compounds. SPMD media extracts were analyzed by means of a laboratory method that targeted hydrophobic compounds. Streambed sediments also were analyzed by means of separate laboratory methods targeting pharmaceutical or wastewater compounds. Results are reported by analytical method and sample matrix (water or sediment).

Analytes associated with a given laboratory method are referred to in aggregate by the method name. For example, analytes associated with the antibiotic method are referred to as “antibiotic compounds.” This is true even though some of the analytes quantified with the method (for example, ibuprofen and carbamazepine) are not antibiotics. In addition, 11 compounds were in the analyte list of more than 1 method. Individual compounds that were detected by more than one analytical method are included independently in counts for each analytical method.

On the basis of an examination of data from all sites, a total of 12 antibiotic, 20 pharmaceutical, 41 wastewater, and 22 hydrophobic compounds were detected in water, and

8 pharmaceutical and 37 wastewater compounds were detected in streambed sediments. The numbers of detections at reference sites tended to be in the low range of detection counts observed in the Tinkers Creek watershed for a given analytical method. Also, the total numbers of compounds detected in water and sediment at the reference sites (3 antibiotic, 2 pharmaceutical, 5 wastewater, and 4 hydrophobic compounds in water and 2 pharmaceutical and 22 wastewater compounds in sediment) were less than the total numbers of compounds detected at sites in the Tinkers Creek watershed.

With the exception of hydrophobic compounds, it was common at most sites to have more compounds detected in samples collected downstream from WWTP outfalls than in corresponding samples collected upstream from the outfalls. This was particularly true for antibiotic, pharmaceutical, and wastewater compounds in water. In contrast, it was common to have more hydrophobic compounds detected in samples collected upstream from WWTP outfalls than downstream, possibly because of dilution of stream water by WWTP effluents having lower concentrations of hydrophobic compounds. The numbers of detections of compounds upstream and downstream from the Twinsburg WWTP generally were about equal. This was attributed to the fact that several WWTPs discharge to Tinkers Creek or its tributaries upstream from Twinsburg, yielding potential sources for the compounds detected at the upstream location.

Caffeine, fluoranthene, N,N-diethyl-meta-toluamide (DEET), phenanthrene, and pyrene were detected in water at all sites in the Tinkers Creek watershed, irrespective of whether the site was upstream or downstream from a WWTP. This finding suggests that these compounds were diffuse in the Tinkers Creek watershed. Some, but not all of these compounds, were also detected in water at the reference sites, but at concentrations that generally were at the low end of the range of concentrations observed in the Tinkers Creek watershed.

Carbamazepine, sulfamethoxazole, trimethoprim, and hexahydrohexamethylcyclopentabenzopyran (HHCB) were detected in water at 100 percent of the sites downstream from WWTP outfalls, yet their frequency of detection at sites upstream from outfalls was appreciably smaller (occurring in about 29 percent or less of the samples). This pattern suggests a strong association between the presence of these compounds and wastewater discharges. None of these compounds were detected in water at the Yellow Creek reference site, and only two of the compounds (carbamazepine and sulfamethoxazole) were detected at the Furnace Run reference site.

Fifteen wastewater compounds (2,6-dimethylnaphthalene, 2-methylnaphthalene, 3-methyl-1H-indole, anthraquinone, acetophenone, benzo[*a*]pyrene, β -sitosterol, bis(2-ethylhexyl) phthalate, carbazole, cholesterol, fluoranthene, indole, naphthalene, *p*-cresol, and pyrene) were detected in sediments at all sites in the Tinkers Creek watershed, irrespective of whether the site was upstream or downstream from a WWTP. Sources of those compounds likely are diffuse within the watershed.

Many of the pharmaceutical compounds detected in sediment also were present in water. One notable exception was miconazole (an antifungal compound), which was detected in more than a quarter of the streambed-sediment samples yet never detected in water. In contrast, some pharmaceutical compounds (such as trimethoprim and carbamazepine) that were detected in water at all sites downstream from WWTP outfalls were either not detected or detected at a much lower frequency in streambed sediments. Results such as these reinforce the need to sample both sediments and water when assessing the occurrence and distribution of OWCs.

References Cited

- Alvarez, D.A., Petty, J.D., Huckins, J.N., Jones-Lepp, T.L., Getting, D.T., Goddard, J.P., and Manahan, S.E., 2004, Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments: *Environmental Toxicology and Chemistry*, v. 23, no. 3, p. 1640–1648.
- Alvarez, D.A.; Huckins, J.N.; Petty, J.D.; Jones-Lepp, Tammy; Stuer-Lauridsen, Frank; Getting, D.T.; Goddard, J.P.; and Gravell, Anthony, 2007, Tool for monitoring hydrophilic contaminants in water—Polar organic chemical integrative sampler (POCIS), *in* Greenwood, R., Mills, G., and Vrana, B., eds., *Passive sampling techniques in environmental monitoring*, v. 48 of *Wilson & Wilson's Comprehensive analytical chemistry*: Amsterdam, Elsevier, chap. 8, p. 171–197.
- Alvarez, D.A., Cranor, W.L., Perkins, S.D., Clark, R.C., and Smith, S.B., 2008, Chemical and toxicologic assessment of organic contaminants in surface water using passive samplers: *Journal of Environmental Quality*, v. 37, no. 3, p. 1024–1033.
- Ashton, D., Hilton, M., and Thomas, K.V., 2004, Investigating the environmental transport of human pharmaceuticals to streams in the United Kingdom: *Science of the Total Environment*, v. 333, nos. 1–3, p. 167–184.
- Barnes, K.K., Kolpin, D.W., Furlong, E.T., Zaugg, S.D., Meyer, M.T., and Barber, L.B., 2008, A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States – I) Ground water: *Science of the Total Environment* (in press).
- Burkhardt, M.R., Zaugg, S.D., Smith, S.G., and ReVello, R.C., 2006, Determination of wastewater compounds in sediment and soil by pressurized solvent extraction, solid-phase extraction, and capillary-column gas chromatography/mass spectrometry: *U.S. Geological Survey Techniques and Methods*, book 5, sec. B, chap. 2, 33 p.
- Cahill J.D., Furlong, E.T., Burkhardt, M.R., Kolpin, D.W., and Anderson L.G., 2004, Determination of pharmaceutical compounds in surface- and ground-water samples by solid-phase extraction and high-performance liquid chromatography—Electrospray ionization mass spectrometry: *Journal of Chromatography A*, v. 1041, p. 171–180.
- Chambers, D.B., and Leiker, T. J., 2006, A reconnaissance for emerging contaminants in the South Branch Potomac River, Cacapon River, and Williams River Basins, West Virginia, April–October 2004: *U.S. Geological Survey Open-File Report 2006–1393*, 23 p., accessed October 5, 2007, at <http://pubs.usgs.gov/of/2006/1393>
- Childress, C.J.O., Foreman, W.T., Connor, B.F., and Maloney, T.J., 1999, New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U.S. Geological Survey National Water Quality Laboratory: *U.S. Geological Survey Open-File Report 99–193*, 19 p.
- Focazio, M.J., Kolpin, D.W., Barnes, K.K., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Barber, L.B., and Thurman, E.M., 2008, A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States – II) Untreated drinking water sources: *Science of the Total Environment* (in press).
- Glassmeyer, S.T., 2007, The cycle of emerging contaminants: *Water Resources Impact*, v. 9, no. 3, p. 5–7.
- Glassmeyer, S.T., Furlong, E.T., Kolpin, D.W., Cahill, J.D., Zaugg, S.D., Werner, S.L., Meyer, M.T., and Kryak, D.D., 2005, Transport of chemical and microbial compounds from known wastewater discharges—Potential for use as indicators of human fecal contamination: *Environmental Science & Technology*, v. 39, p. 5157–5169.
- Herberer, T.H., 2002, Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment—A review of recent research data: *Toxicology Letters*, v. 131, p. 5–17.
- Herberer, Thomas; Verstraeten, I.M.; Meyer, M.T.; Mechlin-ski, Andy; and Reddersen, Kirsten, 2001, Occurrence and fate of pharmaceuticals during bank filtration—Preliminary results from investigations in Germany and the United States: *Water Resources Update*, v. 120, p. 4–17.
- Huckins, J., Petty, J., Prest, H., Clark, R., Alvarez, D., Orazio, C., Lebo, J., Cranor, W., and Johnson, B., 2002, A guide for the use of semipermeable membrane devices (SPMDs) as samplers of waterborne hydrophobic organic contaminants: Washington, D.C., American Petroleum Institute, API Publication 4690.
- Huckins, J.N., Petty, J.D., and Booij, Kees, 2006, *Monitors of organic chemicals in the environment—Semipermeable membrane devices*: New York, Springer, 223 p.

- Jones-Lepp, T.L., Alvarez, D.A., Petty, J.D., and Huckins, J.N., 2004, Polar organic chemical integrative sampling and liquid chromatography–electrospray/ion-trap mass spectrometry for assessing selected prescription and illicit drugs in treated sewage effluents: *Archives of Environmental Contamination and Toxicology*, v. 47, no. 4, p. 427–439.
- Kinney, C.A., Furlong, E.T., Werner, S.L., and Cahill, J.D., 2006, Presence and distribution of wastewater-derived pharmaceuticals in soil irrigated with reclaimed water: *Environmental Toxicology and Chemistry*, v. 25, no. 2, p. 317–326.
- Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., and Buxton, H.T., 2002, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000—A national reconnaissance: *Environmental Science & Technology*, v. 36, no. 6, p. 1202–1211.
- Kolpin, D.W.; Skopec, Mary; Meyer, M.T.; Furlong, E.T.; and Zaugg, S.D., 2004, Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions: *Science of the Total Environment*, v. 328, nos. 1–3, p. 119–130.
- Kümmerer, K., 2004, Resistance in the environment: *Journal of Antimicrobial Chemotherapy*, v. 54, no. 2, p. 311–320.
- Lee, K.E., Barber, L.B., Furlong, E.T., Cahill, J.D., Kolpin, D.W., Meyer, M.T., and Zaugg, S.D., 2004, Presence and distribution of organic wastewater compounds in wastewater, surface, ground, and drinking waters, Minnesota, 2000–02: U.S. Geological Survey Scientific Investigations Report 2004–5138, 47 p.
- Ohio Environmental Protection Agency, 2003, Total Maximum Daily Loads for the Lower Cuyahoga River—Final report, accessed July 14, 2008, at http://www.epa.state.oh.us/dsw/tmdl/Cuyahoga_lower_final_report.pdf
- Petty, J.D., Orazio, C.E., Huckins, J.N., Gale, R.W., Lebo, J.A., Meadows, J.C., Echols, K.R., and Cranor, W.L., 2000, Considerations involved with the use of semipermeable membrane devices for monitoring environmental contaminants: *Journal of Chromatography A*, v. 879, no. 1, p. 83–95.
- Petty, J.D., Huckins, J.N., Alvarez, D.A., Brumbaugh, W.G., Cranor, W.L., Gale, R.W., Rastall, A.C., Jones-Lepp, T.L., Leiker, T.J., Rostad, C.E., and Furlong, E.T., 2004, A holistic passive integrative sampling approach for assessing the presence and potential impacts of waterborne environmental contaminants: *Chemosphere*, v. 54, no. 6, p. 695–705.
- Rowe, G.L., Jr., Reutter, D.C., Runkle, D.L., Hambrook, J.A., Janosy, S.D., and Hwang, L.H., 2004, Water quality in the Great and Little Miami River basins: U.S. Geological Survey Circular 1229, 40 p.
- Sando, S.K., Furlong, E.T., Gray, J.L., and Meyer, M.T., 2006, Occurrence of organic wastewater compounds in drinking water, wastewater effluent, and the Big Sioux River in or near Sioux Falls, South Dakota, 2001–2004: U.S. Geological Survey Scientific Investigations Report 2006–5118, 168 p.
- Schreurs, R.H.M.M.; Sonneveld, E.; van der Saag, P.T.; van der Burg, B.; and Seinen, W., 2005, Examination of the in vitro (anti)estrogenic, (anti)androgenic and (anti)dioxin-like activities of tetralin, indane and isochroman derivatives using receptor-specific bioassays; *Toxicology Letters*, v. 156, no. 2, p. 264–275.
- Shelton, L.R., and Capel, P.D., 1994, Guidelines for collecting and processing samples of streambed sediment for analysis of trace elements and organic contaminants for the National Water-Quality Assessment program: U.S. Geological Survey Open-File Report 94–458, 20 p.
- Sokal, R.R., and Rohlf, F.J., 1981, *Biometry—The principles and practice of statistics in biological research* (2d ed.): New York, W.H. Freeman and Co., p. 738–743.
- Spongberg, A.L., and Witter, J.D., 2008, Pharmaceutical compounds in the wastewater process stream in northwest Ohio: *Science of the Total Environment*, v. 397, p. 148–157.
- Sprague, L.A., and Battaglin, W.A., 2004, Wastewater chemicals in Colorado's streams and ground water: U.S. Geological Survey Fact Sheet 2004–3127, 4 p.
- Stackelberg, P.E., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Henderson, A.K., and Reisman, D.B., 2004, Persistence of pharmaceutical compounds in and other wastewater contaminants in a conventional drinking-water treatment plant: *Science of the Total Environment*, v. 329, nos. 1–3, p. 99–113.
- Stackelberg, P.E.; Gibs, Jacob; Furlong, E.T.; Meyer, M.T.; Zaugg, S.D.; and Lippincott, R.L., 2007, Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds: *Science of the Total Environment*, v. 377, nos. 2–3, p. 255–272.
- Sumpter, J.P., and Johnson, A.C., 2005, Lessons from endocrine disruption and their application to other issues concerning trace organics in the aquatic environment: *Environmental Science & Technology*, v. 39, no. 12, p. 4321–4332.
- U.S. Census Bureau, 2000, Census 2000 summary file 1: Generated using American FactFinder, accessed March 10, 2008, at <http://factfinder.census.gov>
- U.S. Geological Survey, 2000, National Land Cover Dataset: U.S. Geological Survey Fact Sheet 108–00, accessed November 27, 2007, at <http://erg.usgs.gov/isb/pubs/factsheets/fs10800.html>

- U.S. Geological Survey, 2006, Collection of water samples (ver. 2.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, accessed July 9, 2008, <http://pubs.water.usgs.gov/twri9A4/>
- Zaugg, S.D., Smith, S.G., Schroeder, M.P., Barber, L.B., and Burkhardt, M.R., 2007, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of wastewater compounds by polystyrene-divinylbenzene solid-phase extraction and capillary-column gas chromatography/mass spectrometry (ver. 1.1): U.S. Geological Survey Water-Resources Investigations Report 01-4186, 37 p.

Appendix A. Detailed Analytical Methods and Passive Sampling Theory

Traditional methods for determining organic wastewater compounds in natural-water samples generally are optimized for one or two classes of compounds and use liquid-liquid extraction with an organic solvent followed by analysis with gas chromatography (GC) and nitrogen-phosphorus, electron-capture, or mass spectrometry (MS) detection. Analytical methods that use solid-phase extraction (SPE) as an alternative to liquid-liquid extraction were adopted for this study.

POCIS and SPMD Media Preparation and Extraction

A detailed description of the preparation of the POCIS is given by Alvarez and others (2004, 2005, 2007). POCIS of both the pesticide and pharmaceutical configurations were used in this study. The pesticide POCIS disk contained media composed of a triphasic admixture of (80:20 w:w) Isolute ENV+ and S-X3 dispersed Ambersorb 1500, and the pharmaceutical POCIS disk contained Oasis HLB media. Each POCIS disk had an effective sampling surface area of 41 cm². The membrane surface area to total sorbent mass ratio of POCIS used in this study was approximately 180 cm²/g. This ratio conforms to the definition of a standard POCIS as defined by Alvarez and others (2004). Three pesticide and three pharmaceutical POCIS were placed inside each deployment canister.

Procedures for the recovery of the sequestered chemical residues from environmental and quality control POCIS are described in detail by Alvarez and others (2004). Briefly, the POCIS were disassembled, and the sorbent was transferred into glass gravity-flow chromatography columns. Chemical residues were recovered from the sorbent by organic solvent elution. Methanol was used to recover analytes from the pharmaceutical POCIS, and a combination of 1:1:8 (v:v:v) methanol:toluene:dichloromethane was used to recover chemicals from the pesticide POCIS. The extracts were reduced in volume by rotary evaporation and under a gentle stream of nitrogen, filtered through glass-fiber filter, solvent exchanged as necessary, and sealed in amber ampoules under nitrogen for shipment to the collaborating analytical laboratories. Each sample was a composite of extracts from two individual POCIS disks to increase the total mass of sequestered residues and thereby lower analytical detection limits.

SPMDs were prepared as described by Huckins and others (2006) and Petty and others (2000 and 2004). Briefly, the SPMD were constructed by adding 59 μ L of triolein to a 10-cm piece of low-density polyethylene (LDPE) tubing (5 cm between the lipid containment seals). A mixture of perdeuterated PAHs (500 ng each of acenaphthylene-*d*₁₀, acenaphthene-*d*₁₀, fluorene-*d*₁₀, phenanthrene-*d*₁₀, pyrene-*d*₁₀

and dibenz[*a,h*]anthracene-*d*₁₄) were also added to the SPMDs to serve as performance reference compounds (PRCs). PRCs are used to correct sampling rate data for the site-specific factors such as flow, temperature, and biofouling, which can affect the uptake kinetics of passive samplers. A single SPMD was added to each deployment sampler.

Recovery of the PRCs and other chemicals of interest (that is, PAHs sampled from the study sites) was achieved using a two-stage dialysis of the SPMD with hexane. Following dialysis, the extracts were concentrated and the chemicals of interest isolated using a size exclusion chromatographic (SEC) system. Then, the fractions from the SEC system were applied to a gravity-flow chromatographic column containing acidic, basic, and neutral silica gel to remove additional potential interferences and to enrich the PAHs and PRCs prior to analysis.

Chemical Analysis of POCIS and SPMD Extracts

POCIS extracts were analyzed for compounds in the macrolide, sulfonamide, quinoline, and tetracycline classes of antibiotics as well as for chlroamphenicol, lincomycin, ormetoprim, and trimethoprim and the pharmaceuticals carbamazepine and ibuprofen. Clinafloxacin, demeclocycline, erythromycin-¹³C₂, erythromycin-H₂O-¹³C₂, simatone, and sulfamethoxazole-¹³C₆ were used as internal standards and oleandomycin, meclocyline, nalidixic acid, and sulfamethazine-¹³C₆ as surrogate standards. Samples were analyzed using the method of standard addition.

Internal standard and surrogate standard solutions were combined and diluted to 0.1 ng/ μ L solutions with 50 mM phosphoric acid (H₃PO₄) pH 7 to a final volume of 2 mL in a 2-mL glass chromatography vial. The 1 ng/ μ L standard mix for standard addition also was diluted to 0.1 ng/ μ L with 50 mM H₃PO₄ pH 7 to a final volume of 2 mL in a 2-mL glass chromatography vial. A blank solution of methanol and reagent water (50/50) was added to a 2-mL glass chromatography vial. The internal and surrogate standard solution, standard mix solution, and blank solution were added to the liquid-chromatography (LC) auto sampler along with the methanol POCIS extracts and reagent water blank.

Each POCIS extract was analyzed two times. The LC auto sampler first pulled and mixed 20 μ L of sample, 20 μ L of internal and surrogate standard, and 20 μ L of blank solution and injected it into the LC auto sampler for analysis. The LC then pulled 20 μ L of sample, 20 μ L of internal and surrogate standard, and 20 μ L of standard mix and injected it into the LC for analysis. The second sample analysis was the equivalent of spiking the sample at 100 μ g/L. Standard solutions of 1 to 1,000 μ g/L were injected and analyzed by standard addition to

assess the linearity of the concentration range for the standard addition and to estimate the analyte detection levels.

The antibiotics were separated using a LC gradient with the 0.3 percent formic acid mobile phase A and acetonitrile/methanol (80/20) mobile phase B. A 3.0 × 150 mm Luna C18(2) (Phenomenex) LC column with 3- μ m packing was used to separate the antibiotics. The LC column was rinsed for 5 minutes with 100 percent mobile phase B at the end of the gradient and then equilibrated at initial conditions for 5 minutes before the next sample analysis.

Individual antibiotic compounds were analyzed using selected ion monitoring liquid chromatography/tandem mass spectrometry and were identified using retention times and the ratios of the quantifying ion to one or two confirming ions. Detected antibiotic compounds were quantitated using the ratio of the area of the base-peak ion of the analyte to the area of the base-peak ion of the internal standard. The antibiotic compounds may also have been quantitated by the method of standard addition using the following equation:

$$C = (R_{us} / (R_{sp} - R_{us})) C_{sp} \quad (1)$$

where

C	is the concentration of the analyte in the unspiked sample,
R_{us}	is the ratio of area of the quantitation-ion of the analyte to the area of the quantitation-ion of the internal standard in the unspiked sample,
R_{sp}	is the ratio of area of the quantitation-ion of the analyte to the area of the quantitation-ion of the internal standard in the spiked sample, and
C_{sp}	is the concentration of the analytes in the spiked sample due to the spike.

The method of standard addition corrects for matrix effects and can result in more accurate quantitation of individual analytes.

The analytical method for the determination of wastewater compounds in POCIS extracts targets 66 compounds typically found in domestic and industrial wastewater. The wastewater method is an efficient means of detecting important toxic and estrogenic compounds that otherwise might not be reported because they are unregulated or not included in other USGS or U.S. Environmental Protection Agency methods (Zaugg and others, 2007). Analysis of the alkylphenol ethoxylate nonionic surfactant compounds is particularly important because they are persistent indicators of wastewater. Other method compounds are representative of fragrances, food additives, antioxidants, flame retardants, plasticizers, industrial solvents, disinfectants, fecal sterols, PAHs, and high-use domestic pesticides.

The POCIS extracts analyzed for organic wastewater compounds at the USGS National Water Quality Laboratory arrived in sealed ampoules containing methylene chloride,

approximately 0.5 mL in volume. Each ampoule was opened, and 20 μ L of a five-compound internal standard mixture [(1,4-dichlorobenzene-*d*4 (IS1), naphthalene-*d*8 (IS2), acenaphthene-*d*10 (IS3), phenanthrene-*d*10 (IS4), chrysene-*d*12 (IS5)] was added to the vial before transferring the entire contents using a disposable Pasteur pipette to a labeled 2-mL GC/MS vial. To ensure complete transfer of sample extracts, an additional 400 μ L of methylene chloride was used to rinse the open ampoules and the rinsate was transferred to the GC/MS vial using the same pipette. The sample extracts (in 900–1,000 μ L of methylene chloride) were analyzed by full scan positive-ion GC/MS in the electron impact mode (Model 5975 quadrupole mass spectrometer; Hewlett-Packard/Agilent, Palo Alto, Calif.), along with a set of multiple-level analytical standard solutions; this was the same as the normal analytical schedule 1433 method (Zaugg and others, 2007).

Each POCIS extract analyzed for pharmaceuticals was analyzed first with positive mode electrospray ionization interface on a liquid chromatography/mass spectrometer (LC/MS) system (Model LC/MSD quadrupole mass spectrometer; Hewlett-Packard/Agilent, Palo Alto, Calif.), along with a set of multiple-level analytical standard solutions. A binary water: acetonitrile gradient was used on a reversed phase LC column. The instrument procedure used followed the analytical methodology initially described in Cahill and others (2004) but included additional pharmaceutical compounds. Selected POCIS extracts also were analyzed using a LC/MS/MS system, operated in the multiple-reaction monitoring mode, to confirm the identity of pharmaceuticals. For the reasons described later in this appendix, pharmaceutical concentrations are reported as nanograms per POCIS.

Analysis of the SPMD extracts for hydrophobic compounds (PAHs and PRCs) was done using an Agilent 6890 GC (Agilent Technologies, Inc., Wilmington, Del.) coupled to a 5973N mass selective detector (MSD; Agilent Technologies, Inc., Palo Alto, Calif.). An HP-5MS (30 m x 0.25 mm i.d. x 0.25- μ m film thickness) capillary column (Agilent Technologies, Inc., Wilmington, Del.) was used with the temperature program of injection at 50°C, held for 2 min, ramped at 25°C/min to 130°C, held for 1 minute, then ramped at 6°C/min to 310°C and held at 310°C for 5 minutes. Detector zone temperatures were set at 310°C for the MSD transfer line, 150°C at the quadrupole, and 230°C at the source. Quantitation of the analytes was accomplished using a six-point curve with internal calibration. Concentrations of calibration standards bracketed the range of 20 to 4,000 μ g/L for each of the analytes with the 2-methylnaphthalene-*d*₁₀ and benzo[*e*]pyrene-*d*₁₂ maintained at 0.25 μ g/mL as the instrumental internal standard.

Chemical Analysis of Streambed Sediments

Streambed-sediment samples were processed with standard approved and custom laboratory methods (Burkhardt and others, 2006). Streambed-sediment samples were analyzed for pharmaceuticals and other wastewater compounds at NWQL.

The list of targeted pharmaceutical compounds in bed-sediment is presented in table B1, and the wastewater compounds are in table B3.

Pharmaceuticals in sediment were determined by the method described in Kinney and others (2006a, b) for the analysis of soils and biosolids. Briefly, an aliquot of wet sediment, equivalent to 10 g of dry solids, is extracted by using pressurized solvent extraction, which minimizes degradation of these polar, labile compounds. Five sequential extractions were carried out using 70 percent acetonitrile/30 percent water at a temperature of 130°C and a pressure of 10.34×10^7 Pa (15,000 lbf/in²). Typically, the final volume of extract was about 20 mL. A 1-mL extract subsample was filtered using a 0.20-mm syringe filter into a high-performance liquid chromatography (HPLC) vial, and then the acetonitrile was evaporated under nitrogen. The concentrated aqueous extract volume (approximately 0.3 mL) was increased to 1 mL with 0.050 mL of a 1.59×10^{-4} mM nicotinamide-2,4,5,6-*d*₄ solution, added as an internal standard, and approximately 0.65 mL of a 10 mM aqueous ammonium formate buffer. The sediment extracts were analyzed in a similar manner to the POCIS extracts, using the method of Cahill and others (2004), but including additional pharmaceuticals. As noted in Kinney and others (2006a), mean recoveries of individual pharmaceuticals in three soil types ranged between 39 and 94 percent. Recoveries of pharmaceuticals from streambed sediment from Tinkers Creek were expected to be similar.

Streambed-sediment samples analyzed for wastewater compounds were extracted using a pressurized solvent extraction system with water/isopropyl alcohol as the extraction solvent (Burkhardt and others, 2006). Following extraction, the compounds of interest were isolated from potentially interfering matrix components using disposable solid-phase extraction (SPE) cartridges containing chemically modified polystyrene-divinylbenzene resin. The cartridges were dried with nitrogen gas, then sorbed compounds were eluted with methylene chloride (80 percent)-diethyl ether (20 percent) through a Florisil/sodium sulfate SPE cartridge and then analyzed by capillary-column gas chromatography/mass spectrometry (GC/MS). Initial method reporting levels for single-component compounds ranged from 50 to 500 µg/kg.

Passive Sampling Theory

Estimation of Ambient Water Concentrations

SPMD and POCIS uptake kinetic data (sampling rates) are required to accurately estimate aquatic concentrations of environmental contaminants. Using models previously developed (Alvarez and others, 2004, 2007; Huckins and others, 2006), data from the analysis of the PRC concentrations and from calibration studies (when available), the bioavailable (that is, via respiration from the dissolved phase) concentrations of analytes in POCIS and SPMDs deployed in the study sites can be estimated for selected chemicals.

Method detection limits (MDL) and laboratory reporting level (LRL) for SPMD results were estimated from low-level standards as determined by the signal-to-noise ratio of the response from the instrumental analysis of the sample blanks. LRLs were determined as the mean of the response of a coincident peak present in the analysis of the blanks plus 3 standard deviations of the response of the coincident peak present during instrumental analysis (Keith, 1991). The LRLs were determined as the greater of the mean plus 10 standard deviations or the concentration of the low-level calibration standard (Keith, 1991). In cases where no coincident peak was present, the LRL was set at the low-level calibration standard, and the MDL was estimated to be 20 percent of the LRL.

The effects of exposure conditions on SPMD and POCIS uptake and dissipation rates are largely a function of (1) facial velocity-turbulence at the membrane surface, which in turn is affected by the design of the deployment canister, (2) exposure medium temperature, and (3) membrane biofouling. PRCs are analytically noninterfering organic compounds having a moderate to high fugacity from SPMDs that are added to the lipid prior to membrane enclosure and field deployment (Huckins and others, 2006). By comparing the rate of PRC loss during field exposures to that of laboratory studies, an exposure adjustment factor (EAF) can be derived and used to adjust laboratory sampling rates to more accurately reflect actual in situ sampling rates. PRCs will undergo increased loss as the logarithm of their octanol-water partition coefficient (that is, $\log K_{ow}$) value decreases. The loss rate is isotropic, meaning the uptake rate is equal to the loss rate, and is dependent on the same environmental factors influencing chemical uptake. Because of the strong sorptive properties of the adsorbents used in the POCIS, attempts to incorporate PRCs into the POCIS have failed (Alvarez and others, 2007).

Uptake of hydrophobic chemicals into SPMDs follows linear, curvilinear, and equilibrium phases of sampling. Integrative (or linear) sampling is the predominant phase for compounds with $\log K_{ow}$ values ≥ 5.0 and exposure periods of up to 1 month. During the linear uptake phase, the ambient chemical concentration (C_w) is determined by

$$C_w = N / (R_s t) \quad (2)$$

where

- N is the amount of the chemical sampled by an SPMD (typically in nanograms),
- R_s is the SPMD sampling rate (liters per day), and
- t is the exposure time (days).

Estimation of a chemical's site-specific R_s in an SPMD and its ambient C_w requires the derivation of the EAF as described by Huckins and others (2006). A key feature of the EAF is that it is relatively constant for all chemicals that have the same rate-limiting barrier to uptake, which allows PRC data

to be applied to a range of chemicals. Thus, the in situ or site specific sampling rate, R_{si} , of an analyte is the EAF times its laboratory calibration R_s .

Uptake of hydrophilic organic chemicals by the POCIS is controlled by many of the same rate-limiting barriers, allowing the use of the same models to determine ambient water concentrations. Previous data indicate that many chemicals of interest remain in the linear phase of sampling for at least 56 days (Alvarez and others, 2004, 2007); therefore, the use of a linear uptake model (eq. 2) for the calculation of ambient water concentrations would be justified in cases where the R_s for a chemical was known. Such R_s data for the chemicals targeted in this study are largely unknown; therefore, the POCIS data presented in this report are expressed as nanograms of chemical sequestered per POCIS disk. In spite of the inability to estimate concentrations in the water surrounding each sampler, the data produced are useful for the positive identification of target analytes and for comparison of the relative amounts of chemicals sampled at each site.

References Cited

- Alvarez, D.A., Petty, J.D., Huckins, J.N., Jones-Lepp, T.L., Getting, D.T., Goddard, J.P., and Manahan, S.E., 2004, Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments: *Environmental Toxicology and Chemistry*, v. 23, no. 3, p. 1640–1648.
- Alvarez, D.A., Stackelberg, P.E., Petty, J.D., Huckins, J.N., Furlong, E.T., Zaugg, S.D., and Meyer, M.T., 2005, Comparison of a novel passive sampler to standard water-column sampling for organic contaminants associated with wastewater effluents entering a New Jersey stream: *Chemosphere*, v. 61, no. 5, p. 610–622.
- Alvarez, D.A.; Huckins, J.N.; Petty, J.D.; Jones-Lepp, Tammy; Stuer-Lauridsen, Frank; Getting, D.T.; Goddard, J.P.; and Gravell, Anthony, 2007, Tool for monitoring hydrophilic contaminants in water—Polar organic chemical integrative sampler (POCIS), in Greenwood, R., Mills, G., and Vrana, B., eds., *Passive sampling techniques in environmental monitoring*, v. 48 of *Wilson & Wilson's Comprehensive analytical chemistry*: Amsterdam, Elsevier, chap. 8, p. 171–197.
- Burkhardt, M.R., Zaugg, S.D., Smith, S.G., and ReVello, R.C., 2006, Determination of wastewater compounds in sediment and soil by pressurized solvent extraction, solid-phase extraction, and capillary-column gas chromatography/mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, sec. B, chap. 2, 33 p.
- Cahill J.D., Furlong, E.T., Burkhardt, M.R., Kolpin, D.W., and Anderson L.G., 2004, Determination of pharmaceutical compounds in surface- and ground-water samples by solid-phase extraction and high-performance liquid chromatography—Electrospray ionization mass spectrometry: *Journal of Chromatography A*, v. 1041, nos. 1–2, p. 171–180.
- Huckins, J.N., Petty, J.D., and Booij, Kees, 2006, *Monitors of organic chemicals in the environment—Semipermeable membrane devices*: New York, Springer, 223 p.
- Keith, L.H., 1991, *Environmental sampling and analysis—A practical guide*: Boca Raton, Fla., CRC Press, p. 101–113.
- Kinney, C.A., Furlong, E.T., Werner, S.L., and Cahill, J.D., 2006a, Presence and distribution of wastewater-derived pharmaceuticals in soil irrigated with reclaimed water: *Environmental Toxicology and Chemistry*, v. 25, no. 2, p. 317–326.
- Kinney, C.A., Furlong, E.T., Zaugg, S.D., Burkhardt, M.R., Werner, S.L., Cahill, J.D., and Jorgensen, G.R., 2006b, Survey of organic wastewater contaminants in biosolids destined for land application: *Environmental Science & Technology*, v. 40, no. 23, p. 7207–7215.
- Petty, J.D., Orazio, C.E., Huckins, J.N., Gale, R.W., Lebo, J.A., Meadows, J.C., Echols, K.R., and Cranor, W.L., 2000, Considerations involved with the use of semipermeable membrane devices for monitoring environmental contaminants: *Journal of Chromatography A*, v. 879, no. 1, p. 83–95.
- Petty, J.D., Huckins, J.N., Alvarez, D.A., Brumbaugh, W.G., Cranor, W.L., Gale, R.W., Rastall, A.C., Jones-Lepp, T.L., Leiker, T.J., Rostad, C.E., and Furlong, E.T., 2004, A holistic passive integrative sampling approach for assessing the presence and potential impacts of waterborne environmental contaminants: *Chemosphere*, v. 54, p. 695–705.
- Zaugg, S.D., Smith, S.G., Schroeder, M.P., Barber, L.B., and Burkhardt, M.R., 2007, *Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of wastewater compounds by polystyrene-divinylbenzene solid-phase extraction and capillary-column gas chromatography/mass spectrometry (ver. 1.1)*: U.S. Geological Survey Water-Resources Investigations Report 01–4186, 37 p.

Appendix B. Organic Wastewater Compound Analytes and Reporting Levels, by Sample Media and Analytical Method

Appendix B contains CAS Registry Numbers®, which is a Registered Trademark of the American Chemical Society. CAS recommends the verification of the CASRNs through CAS Client ServicesSM.

Table B1. Antibiotic method for POCIS extracts, including compound names, uses, classes, and Chemical Abstract Service registry numbers for antibiotic compounds.

[ng/POCIS, nanograms per extract for one polar organic chemical integrative sampler disk; CAS, Chemical Abstract Service]

Compound name	Laboratory reporting level (ng/POCIS)	Use	CAS number
Azithromycin	1.0	Antibiotic (human and veterinary; macrolide class)	83905-01-5
Carbamazepine	1.0	Anticonvulsant, antineuralgic (prescription)	298-46-4
Chloramphenicol	10.0	Antibiotic (veterinary)	56-75-7
Chlortetracycline	5.0	Antibiotic (veterinary; tetracycline class)	57-62-5
Ciprofloxacin	1.0	Antibiotic (human and veterinary; quinolone class)	85721-33-1
Doxycycline	5.0	Antibiotic (human and veterinary; tetracycline class)	564-25-0
Enrofloxacin	1.0	Antibiotic (veterinary; quinolone class)	93106-60-6
Epi-chlortetracycline	5.0	Chlortetracycline degradate	57-62-5
Epi-iso-chlortetracycline	5.0	Chlortetracycline degradate	57-62-5
Epi-oxytetracycline	5.0	Oxytetracycline degradate	79-57-2
Epi-tetracycline	5.0	Tetracycline degradate	60-54-8
Erythromycin-H ₂ O (Anhydroerythromycin)	1.0	Erythromycin degradate	114-07-8
Ibuprofen	10.0	Anti-inflammatory (nonprescription)	15687-27-1
Iso-chlortetracycline	5.0	Chlortetracycline degradate	57-62-5
Lincomycin	1.0	Antibiotic (veterinary; macrolide class)	154-21-2
Lomefloxacin	1.0	Antibiotic (veterinary; quinolone class)	98079-51-7
Norfloxacin	1.0	Antibiotic (human and veterinary; quinolone class)	70458-96-7
Ofloxacin	1.0	Antibiotic (human and veterinary; quinolone class)	83380-47-6
Ormetoprim	1.0	Antibiotic (veterinary; sulfonamide class)	6981-18-6
Oxytetracycline	5.0	Antibiotic (veterinary; tetracycline class)	79-57-2
Roxithromycin	1.0	Antibiotic (human and veterinary; macrolide class)	80214-83-1
Sarafloxacin	1.0	Antibiotic (veterinary; quinolone class)	98105-99-8
Sulfachlorpyridazine	1.0	Antibiotic (veterinary; sulfonamide class)	80-32-0
Sulfadiazine	1.0	Antibiotic (veterinary; sulfonamide class)	68-35-9
Sulfadimethoxine	1.0	Antibiotic (veterinary; sulfonamide class)	122-11-2
Sulfamethoxazole	1.0	Antibiotic (human and veterinary; sulfonamide class)	723-46-6
Sulfamethazine	1.0	Antibiotic (veterinary; sulfonamide class)	57-68-1
Sulflathiazole	1.0	Antibiotic (veterinary; sulfonamide class)	72-14-0
Tetracycline	5.0	Antibiotic (human and veterinary; tetracycline class)	60-54-8
Trimethoprim	1.0	Antibiotic (human and veterinary; sulfonamide class)	738-70-5
Tylosin	1.0	Antibiotic (veterinary; macrolide class)	1401-69-0
Virginiamycin	1.0	Antibiotic (veterinary; macrolide class)	21411-53-0

Table B2. Pharmaceutical method for POCIS extracts, including compound names, uses, classes, and Chemical Abstract Service registry numbers for pharmaceutical compounds.

[ng/POCIS, nanograms per extract for one polar organic chemical integrative sampler disk; CAS, Chemical Abstract Service]

Compound name	Laboratory reporting level (ng/POCIS)	Use	CAS number
1,7-Dimethylxanthine	5.0	Precursor is a stimulant	611-59-6
Acetaminophen	5.0	Analgesic	103-90-2
Albuterol	5.0	Bronchodilator	18559-94-9
Azithromycin	5.0	Antibiotic	83905-01-5
Caffeine	5.0	Stimulant	58-08-2
Carbamazepine	5.0	Antiepileptic	298-46-4
Cimetidine	5.0	Inhibits production of stomach acid	51481-61-9
Codeine	5.0	Opiate agonist	76-57-3
Cotinine	5.0	Naturally occurring alkaloid stimulant	486-56-6
Dehydronifedipine	5.0	Precursor is an antiangial	67035-22-7
Diltiazem	5.0	Antihypertensive	42399-41-7
Diphenhydramine	5.0	Antipruritic	58-73-1
Erythromycin	5.0	Antibiotic	114-07-8
Fluoxetine	5.0	Antidepressant	54910-89-3
Miconazole	5.0	Antifungal	22916-47-8
Ranitidine	5.0	Antacid	66357-35-5
Sulfamethoxazole	5.0	Antibiotic	723-46-6
Thiabendazole	5.0	Anthelmintic, fungicide	148-79-8
Trimethoprim	5.0	Antibiotic	738-70-5
Warfarin	5.0	Anticoagulant, rodenticide	81-81-2

30 Occurrence of Organic Wastewater Compounds in the Tinkers Creek Watershed, Northeast Ohio

Table B3. Wastewater method for POCIS extracts, including compound names, suspected endocrine disruptor, CAS number, and possible compound uses (modified from Zaugg and others, 2007).

[EDC, known or suspected endocrine disruptor; Y, yes; -, no or status is not known; CAS, Chemical Abstract Service; F, fungicide; H, herbicide; I, insecticide; GUP, general-use pesticide; FR, flame retardant; WW, wastewater; Mfr, manufacturing; %, percent; >, greater than; CP, combustion product; UV, ultraviolet; ng/POCIS, nanograms per extract for one polar organic chemical integrative sampler disk]

Compound name	EDC	CAS number	Possible compound uses or sources ⁴	Laboratory reporting level (ng/POCIS)
1,4-Dichlorobenzene ^{1,5}	Y	106-46-7	Moth repellent, fumigant, deodorant	200
1-Methylnaphthalene	-	90-12-0	2-5% of gasoline, diesel fuel, or crude oil	200
2-butoxyetanol phosphate	-	39454-62-1	Solvent	200
2,6-Dimethylnaphthalene ⁵	-	581-42-0	Present in diesel/kerosene (trace in gasoline)	200
2-Methylnaphthalene	-	91-57-6	2-5% of gasoline, diesel fuel, or crude oil	200
3-β-Coprostanol	-	360-68-9	Carnivore fecal indicator	200
3-Methyl-1(H)-indole (Skatole)	-	83-34-1	Fragrance, stench in feces and coal tar	200
3- <i>tert</i> -Butyl-4-hydroxy anisole (BHA) ¹	Y	25013-16-5	Antioxidant, general preservative	200
4-Cumylphenol	Y	599-64-4	Nonionic detergent metabolite	200
4- <i>n</i> -Octylphenol	Y	1806-26-4	Nonionic detergent metabolite	200
4- <i>tert</i> -Octylphenol	Y	140-66-9	Nonionic detergent metabolite	200
5-Methyl-1H-benzotriazole ⁷	-	136-85-6	Antioxidant in antifreeze and deicers	200
Acetophenone	-	98-86-2	Fragrance in detergent and tobacco, flavor in beverages	200
Acetyl hexamethyl tetrahydronaphthalene (AHTN)	Y	21145-77-7	Musk fragrance, persistent and widespread, in ground water, concern for bioaccumulation & toxicity	200
Anthracene ⁵	-	120-12-7	Wood preservative, component of tar, diesel, or crude oil, CP	200
Anthraquinone ⁵	-	84-65-1	Dye mfr and textiles, seed treatment, bird repellent	200
Atrazine ^{5,6}	Y	1912-24-9	Selective triazine herbicide	200
Benzo[<i>a</i>]pyrene ⁵	Y	50-32-8	Regulated PAH, used in cancer research, CP	200
Benzophenone	Y	119-61-9	Fixative for perfumes and soaps	200
β-Sitosterol	-	83-46-5	Plant sterol	200
β-Stigmastanol	-	19466-47-8	Plant sterol	200
Bisphenol A	Y	80-05-7	Mfr polycarbonate resins, antioxidant, FR	200
Bromacil ⁵	-	314-40-9	H (GUP), >80% noncrop usage on grass/brush	200
Bromoform ^{1, 5,7}	-	75-25-2	WW ozonation byproduct, military/explosives	200
Caffeine ^{5,7}	-	58-08-2	Beverages, diuretic, very mobile/biodegradable	200
Camphor	-	76-22-2	Flavor, odorant, ointments	200
Carbaryl ^{2, 5,7}	Y	63-25-2	I, crop and garden uses, low persistence	200
Carbazole	-	86-74-8	I, Mfr dyes, explosives, and lubricants	200
Chlorpyrifos ⁵	Y	2921-88-2	I, domestic pest and termite control (domestic use restricted as of 2001)	200
Cholesterol	-	57-88-5	Often a fecal indicator, also a plant sterol	200
Cotinine ⁷	-	486-56-6	Naturally occurring alkaloid stimulant	200
Cumene (Isopropylbenzene) ¹	-	98-82-8	Mfr phenol/acetone, fuels and paint thinner	200
Diazinon ⁵	Y	333-41-5	I, > 40% nonagricultural usage, ants, flies	200
Diethylhexyl phthalate (DEHP) ^{5,6}	Y	117-81-7	Plasticizer for polymers and resins, pesticide inert	200
Diethyl phthalate (DEP) ^{5,6}	Y	84-66-2	Plasticizer for polymers and resins	200
d-Limonene ¹	-	5989-27-5	F, antimicrobial, antiviral, fragrance in aerosols	200
Ethyl citrate	-	77-93-0	Flavoring	
Fluoranthene ⁵	-	206-44-0	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), CP	200
Hexahydrohexamethylcyclopentabenzopyran (HHCB)	Y	1222-05-5	Musk fragrance, persistent and widespread, in ground water, concern for bioaccumulation and toxicity	200
Indole	-	120-72-9	Pesticide inert ingredient, fragrance in coffee	200
Isoborneol	-	124-76-5	Fragrance in perfumery, in disinfectants	200
Isophorone ⁵	-	78-59-1	Solvent for lacquer, plastic, oil, silicon, resin	200

Table B3. Wastewater method for POCIS extracts, including compound names, suspected endocrine disruptor, CAS number, and possible compound uses (modified from Zaugg and others, 2007).—Continued

Compound name	EDC	CAS number	Possible compound uses or sources ⁴	Laboratory reporting level (ng/POCIS)
Isoquinoline ⁵	-	119-65-3	Flavors and fragrances	200
Menthol	-	89-78-1	Cigarettes, cough drops, liniment, mouthwash	200
Metalaxyl ⁵	-	57837-19-1	H, F (GUP), mildew, blight, pathogens, golf/turf	200
Methyl salicylate	-	119-36-8	Liniment, food, beverage, UV-absorbing lotion	200
Metolachlor ⁵	-	51218-45-2	H (GUP), indicator of agricultural drainage	200
N,N-diethyl-meta-toluamide (DEET)	-	134-62-3	I, urban uses, mosquito repellent	200
Naphthalene ⁵	-	91-20-3	Fumigant, moth repellent, major component (about 10%) of gasoline	200
4-Nonylphenol diethoxylate (NP2EO; sum of all isomers) ³	Y	26027-38-3	Nonionic detergent metabolite	200
4-Nonylphenol monoethoxylate (NP1EO; sum of all isomers) ^{3,6}	Y	N/A	Nonionic detergent metabolite	200
4-Octylphenol diethoxylate (OP2EO; sum of all isomers) ³	Y	26636-32-8	Nonionic detergent metabolite	200
4-Octylphenol monoethoxylate (OP1EO; sum of all isomers) ³	Y	26636-32-8	Nonionic detergent metabolite	200
<i>p</i> -Cresol ⁵	-	106-44-5	Wood preservative	200
<i>p</i> -Nonylphenol (total) ³	Y	84852-15-3	Nonionic detergent metabolite	200
Phenanthrene ⁵	-	85-01-8	Mfr explosives, component of tar, diesel fuel, or crude oil, CP	200
Phenol ⁵	-	108-95-2	Disinfectant, mfr several products, leachate	200
Polybrominated diphenyl ether	Y	5436-43-1	Textiles and electronics, flame retardant	200
Prometon ⁵	-	1610-18-0	H (noncrop only), applied prior to blacktop	200
Pyrene ⁵	-	129-00-0	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), CP	200
Tetrachloroethylene ^{1,5,7}	-	127-18-4	Solvent, degreaser, veterinary anthelmintic	200
Tris(2-chloroethyl) phosphate	-	115-96-8	Plasticizer, flame retardant	200
Tri(1,3-dichloro-2-propyl) phosphate	-	13674-87-8	Flame retardant	200
Tributyl phosphate	-	126-73-8	Antifoaming agent, flame retardant	200
Triclosan	Y	3380-34-5	Disinfectant, antimicrobial (concern for acquired microbial resistance)	200
Triethyl citrate (ethyl citrate)	-	77-93-0	Cosmetics, pharmaceuticals	200
Triphenyl phosphate	-	115-86-6	Plasticizer, resin, wax, finish, roofing paper, FR	200
Tri(2-butoxyethyl) phosphate	-	78-51-3	Flame retardant	200

¹Concentration is always estimated because recovery is less than 60 percent or variability is greater than 25 percent RSD.

²Concentration is always estimated because of unstable instrument response.

³Concentration is always estimated because the reference standard is from a technical mixture.

⁴Web links to compound uses, URL: <http://www.nwql.cr.usgs.gov/USGS/Reno/lc8033.html>; ChemFinder Webserver: <http://chemfinder.camsoft.com/>; NTP National toxicology program health & safety data: http://ntp-server.niehs.nih.gov/Main_Pages/Chem-HS.html; NIST Chemistry WebBook: <http://webbook.nist.gov/>; Spectrum Laboratories, Inc.: <http://www.speclab.com/compound/chemabc.htm>; RxList: <http://www.rxlist.com/>; EXTension TOXicology NETwork (EXTOXNET): <http://ace.ace.orst.edu/info/extoxnet/>

⁵Compound determined by at least one other method at the National Water Quality Laboratory.

⁶Compound only available with lab code 8033 or 8050—not approved for schedule 1433.

⁷Compound not available with sediment analysis (lab code 8050).

Table B4. Hydrophobic method for SPMD extracts, including compound names, types, and Chemical Abstract Service registry numbers for hydrophobic compounds.

[ng/L, nanograms per liter; CAS, Chemical Abstract Service; PAH, polycyclic aromatic hydrocarbon. Water concentrations are estimated on the basis of recovery of performance reference compounds]

Compound name	Compound type	CAS number	Estimated method detection level (ng/L)	Laboratory reporting level (ng/L)
1,2-Dimethylnaphthalene	PAH	573-98-8	0.5	2.4
1-Ethylnaphthalene	PAH	1127-76-0	0.4	2.2
1-Methylfluorene	PAH	1730-37-6	0.3	1.5
1-Methylnaphthalene	PAH	90-12-0	0.6	4.8
2,3,5-Trimethylnaphthalene	PAH	2245-38-7	0.3	1.5
2-Methylfluoranthene	PAH	33543-31-6	0.0	1.4
2-Methylnaphthalene	PAH	91-57-6	1.3	4.8
2-Methylphenanthrene	PAH	2531-84-2	0.1	1.5
3,6-Dimethylphenanthrene	PAH	1576-67-6	0.0	1.4
4-Methylbiphenyl	Flavoring agent	644-08-6	2.8	6.9
9-Methylantracene	PAH	779-02-2	0.0	1.4
Acenaphthene	PAH	83-32-9	0.4	2.7
Acenaphthylene	PAH	208-96-8	0.7	3.3
Anthracene	PAH	120-12-7	0.3	1.9
Benzo[<i>a</i>]anthracene	PAH	56-55-3	0.0	1.5
Benzo[<i>a</i>]pyrene	PAH	50-32-8	0.0	1.7
Benzo[<i>b</i>]fluoranthene	PAH	205-99-2	0.0	1.4
Benzo[<i>b</i>]naphtho[2,1- <i>d</i>]thiophene	PAH	239-35-0	0.0	1.4
Benzo[<i>b</i>]thiophene	PAH	95-15-8	9.3	46.7
Benzo[<i>e</i>]pyrene	PAH	192-97-2	0.1	1.8
Benzo[<i>g,h,i</i>]perylene	PAH	191-24-2	0.0	2.3
Benzo[<i>k</i>]fluoranthene	PAH	207-08-9	0.0	1.6
Biphenyl	PAH	92-52-4	0.9	4.4
Chrysene	PAH	218-01-9	0.1	1.4
Dibenz[<i>a,h</i>]anthracene	PAH	53-70-3	0.0	1.9
Dibenzothiophene	PAH	132-65-0	0.1	2.2
Fluoranthene	PAH	206-44-0	1.0	2.6
Fluorene	PAH	86-73-7	0.2	2.2
Indeno[1,2,3- <i>c,d</i>]pyrene	PAH	193-39-5	0.4	2.1
Naphthalene	PAH	91-20-3	2.5	12.3
Perylene	PAH	198-55-0	0.3	1.5
Phenanthrene	PAH	85-01-8	1.7	4.1
Pyrene	PAH	129-00-0	0.5	1.4

Table B5. Pharmaceutical method for streambed-sediment samples, including compound names, uses, classes, and Chemical Abstract Service registry numbers for pharmaceutical compounds.

[MDL, method detection limit; LRL, laboratory reporting levels determined by using matrix-free ashed sand; CAS, Chemical Abstract Service; µg/kg, micrograms per kilogram]

Compound name	Use	CAS number	Estimated MDL ² (µg/kg)	Interim LRL ³ (µg/kg)
1,7-Dimethylxanthine	Precursor is a stimulant	611-59-6	2.03	4.06
Acetaminophen ¹	Analgesic	103-90-2	0.76	1.52
Albuterol ¹	Bronchodilator	18559-94-9	1.09	2.18
Azithromycin	Antibiotic	83905-01-5		
Caffeine	Stimulant	58-08-2	1.32	2.65
Carbamazepine	Antiepileptic	298-46-4	1.65	3.3
Cimetidine ¹	Inhibits production of stomach acid	51481-61-9	0.88	1.76
Codeine	Opiate agonist	76-57-3	1.32	2.64
Cotinine	Naturally occurring alkaloid stimulant	486-56-6	1.3	2.61
Dehydronifedipine	Precursor is an antiangial	67035-22-7	1.69	3.38
Diltiazem ¹	Antihypertensive	42399-41-7	1.48	2.96
Diphenhydramine	Antipruritic	58-73-1	1.35	2.71
Erythromycin	Antibiotic	114-07-8	1.66	3.32
Fluoxetine ¹	Antidepressant	54910-89-3	2.17	4.35
Miconazole ¹	Antifungal	22916-47-8	0.97	1.94
Ranitidine ¹	Antacid	66357-35-5	1.11	2.22
Sulfamethoxazole	Antibiotic	723-46-6	1.58	3.16
Thiabendazole	Anthelmintic, fungicide	148-79-8	1.04	2.08
Trimethoprim	Antibiotic	738-70-5	1.47	2.95
Warfarin	Anticoagulant, rodenticide	81-81-2	1.26	2.53

¹Concentrations of these compounds should be routinely reported as estimates. Qualitative identification of compound meets all identification criteria, but recovery falls between 35 and 59 percent.

²Estimated MDLs determined according to the procedure of U.S. Environmental Protection Agency (2005).

³Interim LRLs are determined according to the procedure of Childress and others (1999).

34 Occurrence of Organic Wastewater Compounds in the Tinkers Creek Watershed, Northeast Ohio

Table B6. Wastewater method for streambed-sediment samples, including compound names, endocrine-disrupting potential, and possible compound uses (modified from Burkhardt and others, 2006).

[EDC, known or suspected endocrine disruptor; Y, yes; -, no or status is not known; CAS, Chemical Abstracts Service; F, fungicide; H, herbicide; I, insecticide; FR, flame retardant; GUP, general-use pesticide; WW, wastewater; Manuf, manufacturing; >, greater than; CP, combustion product; PAH, polycyclic aromatic hydrocarbon; UV, ultraviolet; NA, not applicable; µg/kg, micrograms per kilogram]

Compound name	EDC ¹	CAS number	Possible compound uses or sources ²	Long-term method detection level (µg/kg)	Laboratory reporting level (µg/kg)
1,4-Dichlorobenzene	Y	106-46-7	Moth repellent, fumigant, deodorant	27.6	50
1-Methylnaphthalene	-	90-12-0	2-5 percent of gasoline, diesel fuel, or crude oil	27.8	50
2,2',4,4'-tetrabromodiphenyl ether	Y	5436-43-1	Flame retardant	19.1	50
2,6-Dimethylnaphthalene	-	581-42-0	Present in diesel/kerosene (trace in gasoline)	24.8	50
2-Methylnaphthalene	-	91-57-6	2-5 percent of gasoline, diesel fuel, or crude oil	27.8	50
3-β-Coprostanol	-	360-68-9	Carnivore fecal indicator	360	500
3-Methyl-1(H)-indole (Skatole)	-	83-34-1	Fragrance, stench in feces and coal tar	30.9	50
3- <i>tert</i> -Butyl-4-hydroxy anisole (BHA)	Y	25013-16-5	Antioxidant, general preservative	101	150
4-Cumylphenol	Y	599-64-4	Nonionic detergent metabolite	33.7	50
4- <i>n</i> -Octylphenol	Y	1806-26-4	Surfactant	36.8	50
4-Nonylphenol	Y	104-40-5	Surfactant	498	750
4- <i>tert</i> -Octylphenol	Y	140-66-9	Nonionic detergent metabolite	22.9	50
Acetophenone	-	98-86-2	Fragrance in detergent and tobacco, flavor in beverages	100	150
Acetyl hexamethyl tetrahydronaphthalene (AHTN)	-	21145-77-7	Musk fragrance (widespread use), persistent in ground water; endocrine disruptor	12.5	50
Anthracene ³	-	120-12-7	Wood preservative, component of tar, diesel, or crude oil, CP	19.8	50
Atrazine	Y	1912-24-9	Selective triazine herbicide	58.9	100
Benzo[<i>a</i>]pyrene ³	Y	50-32-8	Regulated PAH, used in cancer research, CP	24.6	50
Benzophenone	Y	119-61-9	Fixative for perfumes and soaps	31.8	50
β-Sitosterol	-	83-46-5	Plant sterol	363	500
β-Stigmastanol	-	19466-47-8	Plant sterol	367	500
bis(2-Ethylhexyl) phthalate	Y	117-81-7	Plasticizer for polymers and resins, pesticides	138	250
Bisphenol A	Y	80-05-7	Manuf polycarbonate resins, antioxidant, FR	31.2	50
Bromacil ³	-	314-40-9	H (GUP), >80 percent noncrop usage on grass/brush	254	500
Camphor	-	76-22-2	Flavor, odorant, ointments	27	50
Carbazole	-	86-74-8	I, Manuf dyes, explosives, and lubricants	22.4	50
Chlorpyrifos ³	Y	2921-88-2	I, domestic pest and termite control (domestic use restricted as of 2001)	33.6	50
Cholesterol	-	57-88-5	Often a fecal indicator	168	250
Diazinon ³	Y	333-41-5	I, > 40 percent nonagricultural usage, ants, flies	48.6	50
Diethyl phthalate	Y	84-66-2	Plasticizer for polymers and resins	46.7	100
d-Limonene	-	5989-27-5	F, antimicrobial, antiviral, fragrance in aerosols	23.7	50
Fluoranthene ³	-	206-44-0	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), CP	23.2	50
Hexahydrohexamethylcyclopentabenzopyran (HHCB)	-	1222-05-5	Musk fragrance (widespread use) persistent in ground water; endocrine disruptor	16.5	50
Indole	-	120-72-9	Pesticide inert ingredient, fragrance in coffee	53.5	100

Table B6. Wastewater method for bed-sediment samples, including compound names, endocrine-disrupting potential, and possible compound uses (modified from Burkhardt and others, 2006).—Continued

Compound name	EDC ¹	CAS number	Possible compound uses or sources ²	Long-term method detection level (µg/kg)	Laboratory reporting level (µg/kg)
Isoborneol	-	124-76-5	Fragrance in perfumery, in disinfectants	39.3	50
Isophorone ³	-	78-59-1	Solvent for lacquer, plastic, oil, silicon, resin	43.4	50
Isopropylbenzene (cumene)	-	98-82-8	Manuf phenol/acetone, fuels and paint thinner	86.6	100
Isoquinoline ³	-	119-65-3	Flavors and fragrances	83.1	100
Menthol	-	89-78-1	Cigarettes, cough drops, liniment, mouthwash	42	50
Metolachlor ³	-	51218-45-2	H (GUP), indicator of agricultural drainage	37.2	50
N,N-diethyl-meta-toluamide (DEET)	-	134-62-3	I, urban uses, mosquito repellent	56.2	100
Naphthalene ³	-	91-20-3	Fumigant, moth repellent, major component (about 10 percent) of gasoline	23.5	50
4-Nonylphenol diethoxylate (NP2EO; sum of all isomers)	Y	26027-38-3	Nonionic detergent metabolite	161	250
4-Nonylphenol monoethoxylate (NP1EO; sum of all isomers)	-	NA	Nonionic detergent metabolite; endocrine disruptor	20.7	50
4-Octylphenol diethoxylate (OP2EO; sum of all isomers)	Y	26636-32-8	Nonionic detergent metabolite	38.3	50
4-Octylphenol monoethoxylate (OP1EO; sum of all isomers)	Y	26636-32-8	Nonionic detergent metabolite	44.2	50
<i>p</i> -Cresol	Y	106-44-5	Wood preservative	20.6	50
Anthraquinone	-	84-65-1	Dye mfr and textiles, seed treatment, bird repellent	24.3	50
Phenanthrene ³	-	85-01-8	Manuf explosives, component of tar, diesel fuel, or crude oil, CP	39.3	50
Phenol ³	-	108-95-2	Disinfectant, manuf several products, leachate	43.4	50
Prometon ³	-	1610-18-0	H (noncrop only), applied prior to blacktop	86.6	100
Pyrene ³	-	129-00-0	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), CP	83.1	100
Tris(2-butoxyethyl) phosphate	-	78-51-3	Flame retardant	98.5	150
Tris(2-chloroethyl) phosphate	Y	115-96-8	Plasticizer, flame retardant	70.3	100
Tri(1,3-dichloro-2-propyl) phosphate	Y	13674-87-8	Flame retardant	73	100
Tributylphosphate	-	126-73-8	Antifoaming agent, flame retardant	39.3	50
Triclosan	Y	3380-34-5	Disinfectant, antimicrobial (concern for acquired microbial resistance)	49.6	50
Triphenyl phosphate	-	115-86-6	Plasticizer, resin, wax, finish, roofing paper, FR	46	50

¹World Wildlife Fund Canada (1999).²ChemFinder Webservice (2001); National Toxicology Program (2001); National Institute of Standards and Technology (2001); Spectrum Laboratories, Inc. (2001); HealthCentral.com (2001); EXTension TOXicology NETwork (2001).³Compound determined by at least one other method at the National Water Quality Laboratory.

References Cited

- Burkhardt, M.R., Zaugg, S.D., Smith, S.G., and ReVello, R.C., 2006, Determination of wastewater compounds in sediment and soil by pressurized solvent extraction, solid-phase extraction, and capillary-column gas chromatography/mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, sec. B, chap. 2, 33 p.
- Childress, C.J.O., Foreman, W.T., Connor, B.F., and Maloney, T.J., 1999, New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U.S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Open-File Report 99-193, 19 p.
- U.S. Environmental Protection Agency, 2005, Guidelines establishing test procedures for the analysis of pollutants (App. B, Part 136, Definition and procedures for the determination of the method detection limit): U.S. Code of Federal Regulations, Title 40, revised as of July 1, 2005, p. 319-322.
- Zaugg, S.D., Smith, S.G., Schroeder, M.P., Barber, L.B., and Burkhardt, M.R., 2007, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of wastewater compounds by polystyrene-divinylbenzene solid-phase extraction and capillary-column gas chromatography/mass spectrometry (ver. 1.1): U.S. Geological Survey Water-Resources Investigations Report 01-4186, 37 p.

Appendix C. Quality-Control Data

Table C1. Summary of results for analysis of Polar Organic Chemical Integrative Sampler (POCIS) extracts by the antibiotic, pharmaceutical, and wastewater methods in trip blanks collected in Tinkers Creek and its tributaries and two other tributaries of the Cuyahoga River in 2006.

[All results are considered estimates because a method validation has not been completed for POCIS extracts. Table lists only those compounds that were detected. There were no detections of antibiotic compounds in trip blanks. Concentrations are reported per extract from one POCIS disk. e, estimated concentration]

Compound	Number of detections	Frequency of detection (percent)	Number of environmental samples censored	Concentrations of detections, in nanograms per POCIS		
				Minimum	Maximum	Median
Pharmaceutical method						
Fluoxetine	7	39	0	e0.24	e0.51	e0.34
Diphenhydramine	4	22	1	e0.34	e2.8	e0.58
1,7-dimethylxanthine	1	6	0	e4.2	e4.2	e4.2
Caffeine	1	6	0	e0.32	e0.32	e0.32
Wastewater method						
Diethylhexyl phthalate	11	61	11	e48	43,000	e63
Cholesterol	4	22	2	e810	e1,300	e1,100
Diethyl phthalate	3	17	3	e100	3,800	e280
Phenol	3	17	1	410	2,300	770
Bisphenol A	2	11	0	e54	e70	e62
4-Nonylphenol diethoxylate (NP2EO; sum of all isomers)	2	11	0	e3,100 ¹	e3,200	e3,100
3- β -Coprostanol	1	6	0	e640	e640	e640
β -Sitosterol	1	6	0	e730	e730	e730
β -Stigmastanol	1	6	0	e960	e960	e960
4-Octylphenol diethoxylate (OP2EO; sum of all isomers)	1	6	0	e150	e150	e150

¹Rounded to two significant digits.

Table C2. Summary of results for analysis of Semipermeable Membrane Device (SPMD) extracts by the hydrophobic method in trip blanks collected in Tinkers Creek and its tributaries and two other tributaries of the Cuyahoga River in 2006.

[Water concentration results are estimated on the basis of recovery of performance reference compounds. Table lists only those compounds that were detected.]

Compound	Number of detections	Frequency of detection (percent)	Concentrations of detections, in nanograms per liter		
			Minimum	Maximum	Median
1-Methylnaphthalene	18	100	0.26	0.82	0.5
2-Methylnaphthalene	18	100	0.48	1.7	0.84
Phenanthrene	18	100	1.1	8.1	2.6
4-Methylbiphenyl	17	94	0.94	10	8.9
Pyrene	17	94	0.67	36	1.5
Fluoranthene	15	83	0.83	7.8	2.4
Chrysene	13	72	0.1	0.55	0.18
Benz[<i>a</i>]anthracene	10	56	0.02	0.11	0.04
Fluorene	10	56	0.2	0.79	0.28
Benzo[<i>e</i>]pyrene	8	44	0.09	0.17	0.12
Acenaphthene	6	33	0.52	0.91	0.62
2-Methylphenanthrene	4	22	0.28	0.52	0.34
Anthracene	1	6	2.7	2.7	2.7
Perylene	1	6	3.2	3.2	3.2

Table C3. Results for analysis of Polar Organic Chemical Integrative Sampler (POCIS) extracts by the antibiotic, pharmaceutical, and wastewater methods for replicate POCIS deployed in Tinkers Creek in 2006.

[All results are considered estimates because a method validation has not been completed for POCIS extracts. Results are reported as nanograms per POCIS disk. R₁, sample 1 of replicate pair; R₂, sample 2 of replicate pair; RPD, absolute relative percent difference; e, estimated concentration; –, not detected (less than laboratory reporting level); nc, RPD not calculated because compound was not detected in one or both samples of the replicate pair]

Compound	Replicate A			Replicate B		
	R ₁	R ₂	RPD	R ₁	R ₂	RPD
Antibiotic method						
Azithromycin	12	21	51	2.5	e0.5	130
Carbamazepine	46	56	22	57	130	79
Erythromycin-H ₂ O	10	12	17	12	13	12
Ibuprofen	30	–	nc	–	–	nc
Ofloxacin	1	e0.5	67	–	1	nc
Sulfamethoxazole	3	2	40	3.5	3.5	0
Trimethoprim	9.5	10	5.1	16	19	14
Pharmaceutical method						
Caffeine	12	6.3	66	6.4	e4.2	41
Carbamazepine	5.8	e4.6	23	e4.3	e3.4	25
Diphenhydramine	e2.5	e3.2	25	e1.3	2.9	74
Erythromycin	7.7	–	nc	–	–	nc
Thiabendazole	–	e1.2	nc	e0.87	e0.78	11
Trimethoprim	e2.2	e2.5	11	e3.7	e2.7	30
Wastewater method						
1,4-Dichlorobenzene	e31	–	nc	–	–	nc
Acetyl hexamethyl tetrahydronaphthalene (AHTN)	e120	e120	0	e85	e88	3.1
Anthraquinone	–	–	nc	210	nc	4.9
Atrazine	e130	e150	10	210	250	19
Benzophenone	e120	e130	4.7	–	–	nc
β-Sitosterol	e2,100	–	nc	–	–	nc
Caffeine	e110	e140	23	e160	220	29
Cotinine	e30	e30	0	–	e30	nc
Diethyl phthalate	340	510	40	–	–	nc
Ethanol,2-butoxy-,phosphate	420	400	5.7	390	480	21
Hexahydrohexamethylcyclopentabenzopyran (HHCB)	520	610	15	320	410	24
Indole	590	190	100	–	–	nc
Metolachlor	e39	e46	18	e53	e68	25
N,N-Diethyltoluamide (DEET)	e180	240	30	270	370	31
4-Nonylphenol monoethoxylate (NP1EO; sum of all isomers)	670	–	nc	–	–	nc
4-Nonylphenol diethoxylate (NP2EO; sum of all isomers)	e3,000	–	nc	–	–	nc
4-Octylphenol diethoxylate (OP2EO; sum of all isomers)	e130	–	nc	–	–	nc
<i>p</i> -Cresol	3,600	1,200	100	260	–	nc
<i>p</i> -Nonylphenol (total)	e970	–	nc	–	–	nc
Phenol	380	–	nc	–	–	nc
Prometon	–	–	nc	–	e180	nc
3-Methyl-1(H)-indole (Skatole)	e26	–	nc	–	–	nc
Tris(2-chloroethyl) phosphate	e170	e190	13	210	250	18
Tri(1,3-dichloro-2-propyl) phosphate	e190	220	14	220	220	0

Table C4. Results for analysis of Semipermeable Membrane Device (SPMD) extracts by the hydrophobic method for replicate SPMDs deployed in Tinkers Creek in 2006.

[Results are reported as nanograms per liter. -, not detected (less than laboratory reporting level); R₁, sample 1 of replicate pair; R₂, sample 2 of replicate pair; RPD, absolute relative percent difference; nc, RPD not calculated because compound was not detected in one or both samples of the replicate pair. Water concentration results are estimated on the basis of recovery of performance reference compounds]

Compound	Replicate A			Replicate B		
	R ₁	R ₂	RPD	R ₁	R ₂	RPD
1-Methylfluorene	-	-	nc	-	1.9	nc
2-Methylphenanthrene	-	-	nc	2.5	2.2	13
Benz[<i>a</i>]anthracene	-	-	nc	1.9	-	nc
Benzo[<i>b</i>]fluoranthene	-	-	nc	3.6	3.0	18
Benzo[<i>b</i>]naphtho[2,1- <i>d</i>]thiophene	-	-	nc	2.0	1.9	5.1
Benzo[<i>e</i>]pyrene	-	-	nc	3.6	3.2	12
Benzo[<i>k</i>]fluoranthene	-	-	nc	2.3	2.4	4.3
Chrysene	5.2	4.7	10	14	12	15
Fluoranthene	20	22	9.5	53	47	12
Phenanthrene	8.4	11	27	15	16	6.5
Pyrene	13	15	14	34	30	12

40 Occurrence of Organic Wastewater Compounds in the Tinkers Creek Watershed, Northeast Ohio

Table C5. Summary of results for analysis of streambed-sediment replicates by the pharmaceutical and wastewater methods for samples collected in Tinkers Creek in 2006.

[µg/kg, micrograms per kilogram; m, compound detected, but value is highly variable by this method; R₁, sample one of replicate pair; R₂, sample 2 of replicate pair; RPD, absolute relative percent difference ; –, not detected (less than laboratory reporting level); e, estimated concentration; m, compound presence verified through qualitative criteria, but concentration could not be quantified; nc, RPD not calculated because compound was not detected in one or both samples of the replicate pair]

Compound	Replicate A			Replicate B		
	R ₁	R ₂	RPD	R ₁	R ₂	RPD
Pharmaceutical method						
Dehydronifedipine	12	–	nc	–	26	nc
Diltiazem	–	–	nc	–	5.3	nc
Diphenhydramine	12	14	11	13	26	69
Miconazole	6.1	5.5	9.9	–	3.5	nc
Wastewater method						
1-Methylnaphthalene	e10	e11	8.6	m	e5.0	nc
2,6-Dimethylnaphthalene	e40	e30	29	m	–	nc
2-Methylnaphthalene	e20	e16	22	e10	e7.4	29
3-β-Coprostanol	e90	e90	0	e60	e57	4.5
3-Methyl-1H-indole	100	62	47	m	e7.8	nc
Anthraquinone	71	e46	42	55	e42	27
Acetophenone	e20	9.4	72	m	e6.8	nc
Acetyl hexamethyl tetrahydronaphthalene (AHTN)	e20	e11	55	e10	e8.9	12
Anthracene	e30	e19	45	60	57	5.8
Benzo[a]pyrene	80	51	45	170	120	33
β-Sitosterol	e1,400	e1,500	6.2	e640	e450	34
β-Stigmastanol	e380	e420	9.5	e30	e120	120
bis(2-Ethylhexyl) phthalate	e50	e36	33	e50	e38	27
Carbazole	e40	e30	28	50	e29	53
Cholesterol	e870	e910	4.2	e600	e390	42
4-Nonylphenol diethoxylate (NP2EO; sum of all isomers)	e250	–	nc	–	–	nc
Fluoranthene	310	240	26	600	490	20
Hexahydrohexamethylcyclopentabenzopyran (HHCB)	70	e38	59	e20	e16	25
Indole	780	430	58	100	94	6.2
4-Nonylphenol monoethoxylate (NP1EO; sum of all isomers)	e190	–	nc	–	–	nc
Naphthalene	e20	e22	10	e10	e7.6	27
<i>p</i> -Cresol	e120	e46	89	e10	e19	62
Phenanthrene	110	89	21	290	230	22
Phenol	e150	–	nc	–	e24	nc
Pyrene	240	180	30	440	350	22
Tris(2-butoxyethyl) phosphate	–	–	nc	e30	e30	0

Table C6. Summary of reagent-water spike-recovery data for wastewater compounds.

[All results are averages of nine measurements made during the time that POCIS samples were being processed]

Compound	Recovery (percent)
1,4-Dichlorobenzene	51
1-Methylnaphthalene	64
2,6-Dimethylnaphthalene	50
2-Methylnaphthalene	57
3- β -Coprostanol	71
3- <i>tert</i> -Butyl-4-hydroxy anisole (BHA)	52
4-Cumylphenol	90
4- <i>n</i> -Octylphenol	70
4- <i>tert</i> -Octylphenol	89
5-methyl-1H-benzotriazole	67
Acetophenone	104
Anthracene	81
Anthraquinone	93
Benzo[<i>a</i>]pyrene	77
Benzophenone	98
β -Sitosterol	66
β -Stigmastanol	67
Bisphenol A	39
Bromacil	95
Bromoform	61
Caffeine	97
Camphor	95
Carbaryl	60
Carbazole	93
Chlorpyrifos	91
Cholesterol	76
Cotinine	53
Cumene	36
Diazinon	101
d-Limonene	25
Ethanol,2-butoxy-,phosphate	100
Ethylcitrate	96
Fluoranthene	91
Hexahydrohexamethylcyclopentabenzopyran (HHCB)	85
Indole	86
Isoborneol	96
Isophorone	99
Isoquinoline	91
Menthol	98
Metalaxyl	107
Methylsalicylate	95
Metolachlor	102
N,N-diethyl-meta-toluamide (DEET)	102
Naphthalene	72

Table C6. Summary of reagent-water spike-recovery data for wastewater compounds.—Continued

[All results are averages of nine measurements made during the time that POCIS samples were being processed]

Compound	Recovery (percent)
4-Nonylphenol monoethoxylate (NP1EO; sum of all isomers)	80
4-Nonylphenol diethoxylate (NP2EO; sum of all isomers)	80
4-Octylphenol monoethoxylate (OP1EO; sum of all isomers)	88
4-Octylphenol diethoxylate (OP2EO; sum of all isomers)	103
<i>p</i> -Cresol	91
<i>p</i> -Nonylphenol (total)	78
Phenanthrene	87
Phenol	96
Prometon	98
Pyrene	92
3-Methyl-1(H)-indole (Skatole)	91
Tetrachloroethylene	20
Acetyl hexamethyl tetrahydronaphthalene (AHTN)	87
Tris(2-chloroethyl) phosphate	99
Tri(1,3-dichloro-2-propyl) phosphate	100
Tributylphosphate	99
Triclosan	89
Triphenyl phosphate	96

42 Occurrence of Organic Wastewater Compounds in the Tinkers Creek Watershed, Northeast Ohio

Table C7. Summary of spike-recovery data for pharmaceutical compounds in streambed-sediment samples collected in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.

[ng/g (µg/kg), nanograms per gram (micrograms per kilogram); –, not detected; na, not analyzed; <rl, less than reporting level established by the U.S. Geological Survey National Water Quality Laboratory (NWQL)]

Compound	Set 1 blank ng/g (µg/kg)	Set 1 reagent spike recovery (percent)	Set 2 blank ng/g (µg/kg)	Set 2 reagent spike recovery (percent)	Lab-selected matrix spike-1 recovery (percent)	Lab-selected matrix spike-2 recovery (percent)
1,7-Dimethylxanthine	–	130	–	65	89	<rl
Acetaminophen	–	94	–	120	68	69
Albuterol	–	45	–	60	Interference	27
Azithromycin	–	17	–	11	na	<rl
Caffeine	–	93	–	62	100	84
Carbamazepine	–	110	–	75	71	69
Cimetidine	–	41	–	55	8.6	66
Codeine	–	120	–	64	4.6	50
Cotinine	–	120	–	72	65	52
Dehydronifedipine	–	130	–	68	56	110
Diltiazem	–	87	–	66	61	51
Diphenhydramine	–	110	–	69	58	68
Erythromycin	–	68	–	130	na	38
Fluoxetine	–	45	–	44	24	3.8
Miconazole	8.7	94	8.7	21	9.6	<rl
Ranitidine	–	78	–	48	<rl	2.9
Sulfamethoxazole	–	150	–	68	57	33
Thiabendazole	–	130	–	61	83	66
Trimethoprim	2.8	120	2.8	68	44	55
Warfarin	–	130	–	67	72	82

Table D2. Summary of results for analysis of POCIS extracts by the antibiotic method for POCIS deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.

[All results are considered estimates because a method validation has not been completed for POCIS extracts. –, not detected; e, estimated concentration below the reporting level]

Compound	Number of detections	Frequency of detection (percent)	Concentrations of detections, in nanograms per POCIS		
			Minimum	Maximum	Median
Sulfamethoxazole	11	61	e0.5	67	e4
Carbamazepine	10	56	1.7	420	65
Trimethoprim	10	56	e0.5	86	e13
Erythromycin-H ₂ O	8	44	5.5	42	20
Azithromycin	7	39	e0.5	260	e12
Lincomycin	5	28	1	16	2
Ofloxacin	4	22	1	33	12
Ibuprofen	2	11	30	89	60
Ormetoprim	1	6	e0.92	e0.92	e0.92
Roxithromycin	1	6	1	1	1
Sulfadiazine	1	6	12	12	12
Sulfamethazine	1	6	1.5	1.5	1.5
Chloramphenicol	0	0	–	–	–
Chlortetracycline	0	0	–	–	–
Ciproflaxacin	0	0	–	–	–
Doxycycline	0	0	–	–	–
Enrofloxacin	0	0	–	–	–
Epi-chlortetracycline	0	0	–	–	–
Epi-iso-chlortetracycline	0	0	–	–	–
Epi-oxytetracycline	0	0	–	–	–
Epi-tetracycline	0	0	–	–	–
Iso-chlortetracycline	0	0	–	–	–
Lomefloxacin	0	0	–	–	–
Norfloxacin	0	0	–	–	–
Oxytetracycline	0	0	–	–	–
Sarafloxacin	0	0	–	–	–
Sulfachlorpyridazine	0	0	–	–	–
Sulfadimethoxine	0	0	–	–	–
Sulfathiazole	0	0	–	–	–
Tetracycline	0	0	–	–	–
Tylosin	0	0	–	–	–
Virginiamycin	0	0	–	–	–

Table D4. Summary of results for analysis of POCIS extracts by the pharmaceutical method for POCIS deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.

[All results are considered estimates because a method validation has not been completed for POCIS extracts. –, not detected; e, estimated concentration below the reporting level]

Compound	Number of detections	Frequency of detection (percent)	Concentrations of detections, in nanograms per POCIS		
			Minimum	Maximum	Median
Caffeine	17	94	e0.30	45	e11
Trimethoprim	10	56	e0.16	120	e4.0
Carbamazepine	9	50	e2.0	28	e7.5
Diphenhydramine ¹	7	39	e1.3	27	e2.5
Thiabendazole	7	39	e0.87	12	e1.8
Erythromycin	4	22	7.7	64	18
Codeine	3	17	4.2	34	12
Albuterol	2	11	1.9	13	7.5
Cimetidine	2	11	1.7	14	7.9
Diltiazem	2	11	6.9	21	14
Fluoxetine ¹	2	11	e0.003	e0.16	e0.08
Azithromycin	1	6	19	19	19
Cotinine	1	6	e3.9	e3.9	e3.9
Ranitidine	1	6	6.8	6.8	6.8
Sulfamethoxazole	1	6	e0.67	e0.67	e0.67
1,7-Dimethylxanthine	0	0	–	–	–
Acetaminophen	0	0	–	–	–
Dehydronifedipine	0	0	–	–	–
Miconazole	0	0	–	–	–
Warfarin	0	0	–	–	–

¹Data censored for one station.

Table D5. Results for analysis of POCIS extracts by the wastewater method for POCIS deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.—Continued

[All results are considered estimates because a method validation has not been completed for POCIS extracts; Street, Streetsboro; Aur W, Aurora Westerly; Aur Sh, Aurora Shores; Twins, Twinsburg; Sol, Solon; Bed, Bedford; Bed Hgts, Bedford Heights; DR, Tinkers Creek at Dunham Road; FR, Furnace Run; YC, Yellow Creek; US, upstream; DS, downstream; AO, above outfall; e, estimated concentration less than reporting limit or due to laboratory quality-control factors; dc, data censored for quality assurance purposes; lt, less than reporting level of 200 ng/POCIS. Data in bold print were either not detected or detected at a lower concentration in the upstream sample]

Compound	Concentrations at sampling locations, in nanograms per POCIS																	
	Street		Aur W		Aur Sh		Twins		Sol		Bed		Bed Hgts			DR	FR	YC
	US	DS	US	DS	US	DS	US	DS	US	DS	US	DS	AO	US	DS			
Isophorone	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt
Isoquinoline	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt
Menthol	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt
Metalaxyl	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt
Methylsalicylate	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt
Metolachlor	e55	e39	e28	lt	e39	e54	e27	e53	91	lt	51	lt	e34	e43	lt	e120	e24	lt
N,N-Diethyl-meta-toluamide (DEET)	e140	e180	e140	250	e130	e140	e170	270	e140	500	e170	544	lt	e140	210	800	lt	lt
Naphthalene	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt
4-Nonylphenol diethoxylate (NP2EO; sum of all isomers)	lt	e670	lt	lt	lt	lt	lt	lt	e810	e2,100	e1,700	e1,200	lt	lt	lt	e2,200	lt	lt
4-Nonylphenol monoethoxylate (NP1EO; sum of all isomers)	lt	3,000	lt	lt	lt	lt	lt	lt	3,900	4,100	4,600	5,500	lt	lt	3,400	6,900	lt	lt
4-Octylphenol diethoxylate (OP2EO; sum of all isomers)	lt	e130	lt	lt	lt	lt	lt	lt	lt	e350	e310	e220	lt	lt	e200	e580	lt	lt
4-Octylphenol monoethoxylate (OP1EO; sum of all isomers)	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	e770	lt	lt	lt	e370	lt	lt
<i>p</i> -Cresol	2,900	3,600	3,200	lt	810	700	lt	260	1,000	lt	350	1,200	lt	e190	1,800	2,200	lt	lt
<i>p</i> -Nonylphenol (total)	lt	e970	lt	lt	lt	lt	lt	lt	e1,100	e1,200	e1,500	e4,900	lt	lt	e1,100	e1,400	lt	lt
Phenanthrene	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	e170	lt	lt	lt	lt	lt	lt
Phenol	lt	380	dc	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	240	lt	lt	lt
Polybrominated diphenyl ether	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt
Prometon	lt	lt	lt	230	e180	200	lt	lt	lt	lt	260	250	160	lt	lt	310	lt	lt
Pyrene	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	e160	350	lt	lt	lt	lt	lt	lt
Tetrachlorethylene	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt	lt
Tris(2-chloroethyl) phosphate	lt	e170	lt	670	lt	lt	lt	210	e180	e180	e160	300	lt	e140	200	400	lt	lt
Tris(dichloroisopropyl) phosphate	lt	e190	lt	650	lt	lt	e160	220	e150	e180	e160	260	lt	lt	220	360	lt	lt
Tributyl phosphate	lt	lt	lt	lt	lt	lt	lt	lt	lt	e100	lt	lt	lt	lt	400	lt	lt	lt
Triclosan	lt	lt	lt	lt	lt	lt	lt	lt	lt	e140	lt	600	lt	lt	lt	220	lt	lt
Triphenyl phosphate	lt	lt	lt	lt	lt	lt	lt	lt	lt	e160	e110	260	lt	lt	lt	lt	lt	lt

Table D6. Summary of results for analysis of POCIS extracts by the wastewater method for POCIS deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.

[All results are considered estimates because a method validation has not been completed for POCIS extracts. e, estimated concentration less than reporting limit or due to laboratory quality-control factors; –, not detected]

Compound	Number of detections	Frequency of detection (percent)	Concentrations of detections, in nanograms per POCIS		
			Minimum	Maximum	Median
Caffeine	17	94	e18	640	e98
Atrazine	16	89	e100	330	e160
Diethyl phthalate ¹	15	83	e72	690	220
N,N-diethyl-meta-toluamide (DEET)	15	83	e130	800	e170
Metolachlor	13	72	e24	e120	e43
Anthraquinone	12	67	e160	520	220
<i>p</i> -Cresol	12	67	e190	3,600	1,100
Ethanol,2-butoxy-phosphate	10	56	390	27,000	660
Hexahydrohexamethylcyclopentabenzopyran (HHCB)	10	56	e24	3,800	550
Tris(2-chloroethyl) phosphate	10	56	e140	670	e190
Tris(dichloroisopropyl) phosphate	10	56	e150	650	e210
Acetyl hexamethyl tetrahydronaphthalene (AHTN)	8	44	e40	560	390
Bisphenol A	7	39	e140	460	260
<i>p</i> -Nonylphenol (total)	7	39	e970	e4,900	e1,200
4-Nonylphenol monoethoxylate (NP1EO; sum of all isomers)	7	39	3,000	6,900	4,100
Prometon	7	39	e160	310	230
Diethylhexyl phthalate ²	6	33	e150	350	230
4-Nonylphenol diethoxylate (NP2EO; sum of all isomers)	6	33	e670	e2,200	e1,500
4-Octylphenol monoethoxylate (OP1EO; sum of all isomers)	6	33	e130	e580	e260
5-Methyl-1H-benzotriazole	5	28	e22	700	e40
Benzophenone	5	28	e120	e180	e140
Cholesterol	5	28	e1,200	e2,600	e1,400
3-Methyl-1(H)-indole (Skatole)	5	28	e26	e98	e31
β -Sitosterol	4	22	e1,700	e4,600	e2,000
Indole	4	22	e38	590	e190
1,4-Dichlorobenzene	3	17	e31	e59	e32
Cotinine	3	17	e20	e56	e30
Ethylcitrate	3	17	e23	e90	e25
Triclosan	3	17	e140	600	e220
Triphenyl phosphate	3	17	e110	260	e160
Bromacil	2	11	590	2,600	1,600
Fluoranthene	2	11	250	450	350
4-Octylphenol monoethoxylate (OP1EO; sum of all isomers)	2	11	e370	e770	e570
Phenol	2	11	240	380	310
Pyrene	2	11	e160	350	e250
Tributyl phosphate	2	11	e100	400	e250
3- β -Coprostanol	1	6	e1,300	e1,300	e1,300
4-Cumylphenol	1	6	e130	e130	e130

Table D6. Summary of results for analysis of POCIS extracts by the wastewater method for POCIS deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.—Continued

[All results are considered estimates because a method validation has not been completed for POCIS extracts. e, estimated concentration less than reporting limit or due to laboratory quality-control factors; —, not detected]

Compound	Number of detections	Frequency of detection (percent)	Concentrations of detections, in nanograms per POCIS		
			Minimum	Maximum	Median
Benzo[<i>a</i>]pyrene	1	6	e160	e160	e160
Diazinon	1	6	e90	e90	e90
Phenanthrene	1	6	e170	e170	e170
1-Methylnaphthalene	0	0	—	—	—
2,6-Dimethylnaphthalene	0	0	—	—	—
2-Methylnaphthalene	0	0	—	—	—
3- <i>tert</i> -Butyl-4-hydroxy anisole (BHA)	0	0	—	—	—
4- <i>n</i> -Octylphenol	0	0	—	—	—
4- <i>tert</i> -Octylphenol	0	0	—	—	—
Acetophenone	0	0	—	—	—
Anthracene	0	0	—	—	—
β-Stigmastanol	0	0	—	—	—
Bromoform	0	0	—	—	—
Camphor	0	0	—	—	—
Carbaryl	0	0	—	—	—
Carbazole	0	0	—	—	—
Chlorpyrifos	0	0	—	—	—
Cumene	0	0	—	—	—
d-Limonene	0	0	—	—	—
Isoborneol	0	0	—	—	—
Isophorone	0	0	—	—	—
Isoquinoline	0	0	—	—	—
Menthol	0	0	—	—	—
Metalaxyl	0	0	—	—	—
Methylsalicylate	0	0	—	—	—
Naphthalene	0	0	—	—	—
Polybrominated diphenyl ether	0	0	—	—	—
Tetrachlorethylene	0	0	—	—	—

¹Data censored for 3 environmental samples.²Data censored for 11 environmental samples.

Appendix E. Organic Wastewater Compounds in Semipermeable Membrane Device (SPMD) Extracts

Table E1. Results for analysis of SPMD extracts by the hydrophobic method for SPMDs deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.

[Street, Streetsboro; Aur W, Aurora Westerly; Aur Sh, Aurora Shores; Twins, Twinsburg; Sol, Solon; Bed, Bedford; Bed Hgts, Bedford Heights; DR, Tinkers Creek at Dunham Road; FR, Furnace Run; YC, Yellow Creek; US, upstream; DS, downstream; AO, above outfall; <, less than. Data in bold print were either not detected or detected at a lower concentration in the upstream sample. Water concentration results are estimated on the basis of recovery of performance reference compounds]

Compound	Concentrations at sampling location, in nanograms per liter																		
	Street		Aur W		Aur Sh		Twins		Sol		Bed		Bed Hgts		DR	FR	YC		
	US	DS	US	DS	US	DS	US	DS	US	DS	US	DS	AO	US	DS				
1,2-Dimethylnaphthalene	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
1-Ethyl-naphthalene	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
1-Methylfluorene	<0.3	<1.5	<1.5	<0.3	<1.5	<1.5	<1.5	<1.5	0.99	<0.3	3.9	8.2	1.3	8.2	3.5	1.7	<1.5	<1.5	<1.5
1-Methylnaphthalene	<0.6	<0.6	<4.8	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6	<4.8	<4.8	<4.8	<0.6	<4.8	<0.6	<0.6	<0.6	<0.6	<0.6
2,3,5-Trimethylnaphthalene	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	2.3	<1.5	<1.5	<1.5	<1.5	<0.3	<0.3	<0.3	<0.3
2-Methylfluoranthene	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4	1.9	1.2	1.5	1.7	1.7	8.8	2.7	1.4	<0.02	<1.4	<1.4
2-Methylnaphthalene	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<4.8	<4.8	<1.3	<4.8	<1.3	<1.3	<1.3	<1.3	<1.3
2-Methylphenanthrene	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	1.8	2.5	2.1	2.2	4.8	5.0	3.4	28	5.7	3.1	<1.5	<1.5	1.8
3,6-Dimethylphenanthrene	<1.4	<1.4	<0.03	<1.4	<0.03	<1.4	<1.4	<1.4	<1.4	<1.4	1.6	0.93	0.93	6.9	1.6	<1.4	<1.4	<1.4	<1.4
4-Methylbiphenyl	<2.8	<2.8	<2.8	<2.8	<2.8	<2.8	<2.8	<2.8	<2.8	<2.8	<2.8	<2.8	<2.8	<2.8	<2.8	<2.8	<2.8	<2.8	<2.8
9-Methylanthracene	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Acenaphthene	<2.7	<2.7	6.0	<2.7	<2.7	<2.7	<2.7	<2.7	<0.4	<2.7	2.7	2.7	<2.7	<2.7	<2.7	<2.7	<0.4	<0.4	<2.7
Acenaphthylene	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7
Anthracene	<1.9	<1.9	<1.9	<0.3	<0.3	<0.3	<1.9	<1.9	<1.9	<1.9	1.5	1.4	1.4	6.3	3.6	<1.9	<0.3	<0.3	<1.9L
Benzo[<i>a</i>]anthracene	<1.5	<1.5	<1.5	<0.02	<1.5	<1.5	1.9	1.9	4.0	2.7	5.8	2.9	4.5	27	9.1	3.2	<1.5	<1.5	<1.5
Benzo[<i>a</i>]pyrene	<1.7	<1.7	<0.01	<1.7	<1.7	<1.7	<1.7	<1.7	1.9	1.4	4.1	1.0	2.3	7.4	4.8	1.5	<1.7	<1.7	<1.7
Benzo[<i>b</i>]fluoranthene	1.4	<1.4	<1.4	<0.02	<1.4	<1.4	2.9	3.6	8.8	4.9	1.3	4.1	5.8	25	11	5.1	<1.4	<1.4	<1.4
Benzo[<i>b</i>]naphtho[2,1- <i>d</i>]thiophene	<1.4	<1.4	<1.4	<0.02	<1.4	<1.4	1.8	2.0	3.8	2.6	5.0	2.4	2.4	12	4.1	2.6	<1.4	<1.4	<1.4
Benzo[<i>b</i>]thiophene	<9.3	<9.3	<9.3	<9.3	<9.3	<9.3	<9.3	<9.3	<9.3	<9.3	<9.3	<9.3	<9.3	<9.3	<9.3	<9.3	<9.3	<9.3	<9.3
Benzo[<i>e</i>]pyrene	<1.8	<1.8	<1.8	<1.8	<1.8	<1.8	2.9	3.6	6.8	4.6	11	4.0	5.0	22	8.7	5.5	<1.8	<1.8	<1.8

Table E1. Results for analysis of SPMD extracts by the hydrophobic method for SPMDs deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.—Continued

Compound	Concentrations at sampling location, in nanograms per liter																		FR	YC				
	Street			Aur W			Aur Sh			Twins			Sol			Bed					Bed Hgts			DR
	US	DS	DS	US	DS	DS	US	DS	DS	US	DS	DS	US	DS	DS	US	DS	DS			US	DS		
Benzo[<i>g,h,i</i>]perylene	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<2.3	<2.3	1.8	<2.3	2.8	1.1	<2.3	<2.3	<2.3	2.4	<2.3	<2.3	<2.3	<0.04	<0.04	
Benzo[<i>k</i>]fluoranthene	<1.6	<1.6	<0.02	<1.6	<1.6	<1.6	<1.6	<1.6	3.0	2.3	4.9	3.7	8.8	3.2	5.4	27	6.1	6.1	27	6.1	3.0	<0.02	<1.6	
Biphenyl	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	<0.9	
Chrysene	3.8	5.2	8.4	<1.4	<1.4	<1.4	<1.4	<1.4	12	14	26	17	36	15	18	87	27	27	87	27	19	0.90	3.1	
Dibenz[<i>a,h</i>]anthracene	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<1.9	<0.03	<0.03	<1.9	<0.03	<0.03	<1.9	<1.9	<0.03	<0.03	<0.03	<0.03	<0.03	
Dibenzothiophene	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	2.3	<2.2	<2.2	5.7	2.3	2.3	<2.2	<2.2	<2.2	<2.2	<2.2	
Fluoranthene	16	20	49	3.8	<2.2	<2.2	7.4	30	41	53	71	60	120	56	66	340	85	85	66	340	85	4.3	21	
Fluorene	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	2.4	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<2.2	<0.2	<2.2	
Indeno[1,2,3- <i>c,d</i>]pyrene	<2.1	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<2.1	<2.1	1.7	<2.1	2.8	<2.1	1.7	7.9	2.7	2.7	1.7	7.9	2.7	<0.4	<0.4	
Naphthalene	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<12.3	<12.3	<12.3	<12.3	<12.3	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	
Perylene	1.7	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<0.3	<0.3	
Phenanthrene	7.4	8.4	30	3.1	4.4	15	4.4	15	13	15	11	13	35	18	17	100	29	29	17	100	29	<4.1	13	
Pyrene	12	13	27	2.2	5.3	21	5.3	21	27	34	46	36	73	39	44	230	59	59	44	230	59	3.5	13	

Table E2. Summary of results for analysis of SPMD extracts by the hydrophobic method for SPMDs deployed in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.

[-, not detected. Water concentration results are estimated on the basis of recovery of performance reference compounds]

Compound	Number of detections	Frequency of detection (percent)	Concentrations of detections, in nanograms per liter		
			Minimum	Maximum	Median
Fluoranthene	18	100	3.8	340	51
Pyrene	18	100	2.2	230	30
Phenanthrene	17	94	3.1	100	15
Chrysene	16	89	0.9	87	14
2-Methylphenanthrene	11	61	1.8	28	3.1
Benzo[<i>b</i>]fluoranthene	11	61	1.4	25	5.1
Benz[<i>a</i>]anthracene	10	56	1.9	27	3.6
Benzo[<i>b</i>]naphtho[2,1- <i>d</i>]-thiophene	10	56	1.8	12	2.6
Benzo[<i>e</i>]pyrene	10	56	2.9	22	5.2
Benzo[<i>k</i>]fluoranthene	10	56	2.3	27	4.3
2-Methylfluoranthene	8	44	1.2	8.8	1.8
Benzo[<i>a</i>]pyrene	8	44	1.0	7.4	2.1
1-Methylfluorene	6	33	1.0	8.2	2.6
3,6-Dimethylphenanthrene	5	28	0.9	6.9	1.6
Anthracene	5	28	1.4	6.3	2.1
Indeno[1,2,3- <i>c,d</i>]pyrene	5	28	1.7	7.9	2.7
Benzo[<i>g,h,i</i>]perylene	4	22	1.1	2.8	2.1
Dibenzothiophene	3	17	2.3	5.7	2.3
2,3,5-Trimethylnaphthalene	2	11	2.1	2.3	2.2
Acenaphthene	2	11	2.7	6.	4.4
Fluorene	1	6	2.4	2.4	2.4
Perylene	1	6	1.7	1.7	1.7
1,2-Dimethylnaphthalene	0	0	–	–	–
1-Ethylnaphthalene	0	0	–	–	–
1-Methylnaphthalene	0	0	–	–	–
2-Methylnaphthalene	0	0	–	–	–
4-Methylbiphenyl	0	0	–	–	–
9-Methylanthracene	0	0	–	–	–
Acenaphthylene	0	0	–	–	–
Benzo[<i>b</i>]thiophene	0	0	–	–	–
Biphenyl	0	0	–	–	–
Dibenz[<i>a,h</i>]anthracene	0	0	–	–	–
Naphthalene	0	0	–	–	–

Table F2. Summary of results for analysis of streambed-sediment samples by the pharmaceutical method for samples collected in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.

[e, estimated concentration less than the reporting limit; –, not detected]

Compound	Number of detections	Frequency of detection (percent)	Concentrations of detections, in micrograms per kilogram		
			Minimum	Maximum	Median
Diphenhydramine	9	50	e0.34	75	e12
Caffeine	5	28	1.5	12	7.7
Miconazole	5	28	6.1	11	7.7
Sulfamethoxazole	4	22	1.8	3.3	2.0
Diltiazem	2	11	e0.79	25	e13
Erythromycin	2	11	e0.50	8.2	e4.4
Trimethoprim	2	11	e0.29	7.4	e3.8
Dehydronifedipine	1	6	12	12	12
1,7-Dimethylxanthine	0	0	–	–	–
Acetaminophen	0	0	–	–	–
Albuterol	0	0	–	–	–
Azithromycin	0	0	–	–	–
Carbamazepine	0	0	–	–	–
Cimetidine	0	0	–	–	–
Codeine	0	0	–	–	–
Cotinine	0	0	–	–	–
Fluoxetine	0	0	–	–	–
Ranitidine	0	0	–	–	–
Thiabendazole	0	0	–	–	–
Warfarin	0	0	–	–	–

Table F3. Results for analysis of streambed-sediment samples by the wastewater method for samples collected in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.

[Street, Streetsboro; Aur W, Aurora Westerly; Aur Sh, Aurora Shores; Twins, Twinsburg; Sol, Solon; Bed, Bedford; Bed Hgts, Bedford Heights; DR, Tinkers Creek at Dunham Road; FR, Furnace Run; YC, Yellow Creek; US, upstream; DS, downstream; AO, above outfall; na, not available; e, estimated concentration; m, compound presence verified through qualitative criteria, but concentration could not be quantified. Data in bold print were not detected or detected at a lower concentration in the upstream sample.]

Compound	Concentrations at sampling locations, in micrograms per kilogram																		
	Street		Aur W		Aur Sh		Twins		Sol		Bed		Bed Hgts		DR	FR	YC		
	US	DS	US	DS	US	DS	US	DS	US	DS	US	DS	AO	US	DS				
1,4-Dichlorobenzene	<55	<40	<45	m	<35	<60	<30	<30	e16	m	<25	<30	<25	<30	<30	<25	<30	<25	
1-Methylnaphthalene	e10	e10	m	e20	<40	<60	m	e30	e40	e20	e20	e10	e20	e10	e10	e30	e10	m	
2,6-Dimethylnaphthalene	e50	e40	e30	e60	e20	60	e20	e10	e10	e10	m	m	m	m	m	m	m	m	m
2-Methylnaphthalene	e20	e20	e10	e30	m	e10	e10	e40	e50	e30	e20	e20	e20	e30	e20	e40	e20	e10	e10
3-β-Coprostanol	e120	e90	e80	e300	e60	e150	e80	<300	e220	e60	e150	e30	e20	<300	e30	e40	<300	e50	e50
3-Methyl-1H-indole	150	100	e40	80	e20	70	e20	m	e10	m	m	e10	e10	m	e10	m	m	m	m
3- <i>tert</i> -Butyl-4-hydroxy-anisole	<160	<120	<140	<200	<100	<180	<90	<90	<80	<80	<80	<90	<80	<90	<90	<80	<90	<80	<80
4-Cumylphenol	<60	<40	<40	<60	<40	<60	<30	<30	<20	<20	<20	<30	<20	<30	<30	<20	<30	<20	<20
4- <i>n</i> -Octylphenol	<60	<40	<40	<60	<40	<60	<30	<30	<20	<20	<20	<30	<20	<30	<30	<20	<30	<20	<20
4-Nonylphenol	<820	<600	<680	e320	<520	e210	<450	<450	e190	e180	e190	<450	<380	<450	<450	<380	<450	<380	<380
4- <i>tert</i> -Octylphenol	<60	<40	<40	<60	<40	<60	<30	<30	<20	<20	<20	<30	e20	<30	e20	e10	<30	<20	<20
Anthraquinone	110	71	57	e48	e38	67	98	55	130	190	130	190	68	54	88	87	e20	e22	e22
Acetophenone	e20	e20	e20	e20	m	e20	e10	m	e90	e30	e50	e40	<80	e40	e40	e60	e50	<80	<80
Acetyl hexamethyl tetra-hydronaphthalene (AHTN)	<60	e20	<40	80	<40	e40	m	e10	e50	e20	e20	<30	<20	<30	<30	m	<30	<20	<20
Anthracene	60	e30	e20	<60	e10	e10	e50	60	e50	110	60	110	50	e20	50	e40	e10	e30	e30
Atrazine	<110	<80	<90	<130	<70	<120	<60	<60	<50	<50	<50	<60	<50	<60	<60	<50	<60	<50	<50
2,2',4,4'-tetrabromodiphenyl ether	<55	<40	<45	<65	<35	<60	<30	<30	<25	<25	<25	<30	<25	<30	<30	<25	<30	<25	<25
Benzo[<i>a</i>]pyrene	150	80	80	e30	e50	80	160	170	230	390	260	200	200	60	220	130	e30	50	50
Benzophenone	<60	<40	<40	<60	<40	<60	<30	<30	<20	<20	<20	<30	<20	<30	<30	<20	<30	<20	<20
β-Sitosterol	e2,500	e1,400	e2,100	e2,300	e1,100	e2,100	e890	e640	e600	e3000	e210	e310	e370	e480	e310	e250	e490	e790	e790
β-Stigmastanol	e590	e380	e290	e1,100	e280	e640	e190	e30	e100	e60	e50	e60	e60	<300	e60	<250	e70	e140	e140
bis(2-Ethylhexyl) phthalate	e80	e50	e60	e60	e40	e110	e50	e50	e120	e90	e120	e50	e60	<300	e50	<250	e70	e140	e140
Bisphenol A	na	na	na	na	na	na	e60	na	e20	na	na	na	na	na	e50	na	na	na	na
Bromacil	<550	<400	<450	<650	<350	<600	<300	<300	<250	<250	<250	<300	<250	<300	<300	<250	<300	<250	<250
Camphor	<60	<40	<40	<60	<40	<60	<30	<30	<20	<20	<20	<30	<20	<30	<30	<20	<30	<20	<20
Carbazole	60	e40	e30	e30	e20	e30	60	50	70	110	60	60	60	e20	e50	50	m	e20	e20
Chlorpyrifos	<60	<40	<40	<60	<40	<60	<30	<30	<20	<20	<20	<30	<20	<30	<30	<20	<30	<20	<20

Table F3. Results for analysis of streambed-sediment samples by the wastewater method for samples collected in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.—Continued

[Street, Streetsboro; Aur W, Aurora Westerly; Aur Sh, Aurora Shores; Twins, Twinsburg; Sol, Solon; Bed, Bedford; Bed Hgts, Bedford Heights; DR, Tinkers Creek at Dunham Road; FR, Furnace Run; YC, Yellow Creek; US, upstream; DS, downstream; AO, above outfall; na, not available; e, estimated concentration; m, compound presence verified through qualitative criteria, but concentration could not be quantified. Data in bold print were not detected or detected at a lower concentration in the upstream sample]

Compound	Concentrations at sampling locations, in micrograms per kilogram																	
	Street		Aur W		Aur Sh		Twins		Sol		Bed		Bed Hgts		DR	FR	YC	
	US	DS	US	DS	US	DS	US	DS	US	DS	US	DS	AO	US	DS			
Cholesterol	e1,400	e870	e2,800	e2,400	e520	e1,300	e690	e600	e320	e1,000	e400	e410	e340	e480	e310	e260	e410	e810
N,N-diethyl-meta-toluamide (DEET)	<110	<80	<90	<130	<70	<120	<60	<60	<60	<50	<50	<50	<50	<60	<60	<50	<60	<50
Diazinon	<60	<40	<40	<60	<40	<60	<30	<30	<30	<20	<20	<20	<20	<30	<30	<20	<30	<20
4-Nonylphenol diethoxylate (NP2EO; sum of all isomers)	e330	e250	<900	e450	e200	e900	<600	<600	<600	e390	e320	e910	<500	<600	<600	<500	<600	<500
4-Octylphenol diethoxylate (OP2EO; sum of all isomers)	<60	<40	<40	<60	<40	<60	<30	<30	<30	e20	<20	e20	e10	<30	e20	e10	<30	<20
Diethyl phthalate	e10	<80	e30	<130	<70	<120	<60	<60	<60	<50	<50	<50	<50	<60	<60	m	e10	<50
d-Limonene	<60	<40	m	<60	<40	e10	<30	<30	<30	<20	<20	<20	<20	<30	<30	<20	<30	<20
4-Octylphenol monoethoxylate (OPIEO; sum of all isomers)	<280	<200	<220	<320	<180	<300	<150	<150	<150	<120	<120	<120	<120	<150	<150	e20	<150	<120
Fluoranthene	670	310	270	80	180	280	680	600	990	820	1,400	1,400	580	280	680	490	80	210
Hexahydrohexamethylcyclopentabenzopyran (HHCB)	<60	70	<40	230	<40	220	e20	e20	<30	390	m	50	<20	<30	<30	e30	<30	<20
Indole	1,100	780	380	760	300	670	250	100	e30	e50	e40	e40	e30	e40	e50	e40	e60	e50
Isoborneol	<60	<40	<40	<60	<40	<60	<30	<30	<30	<20	<20	<20	<20	<30	<30	<20	<30	<20
Isophorone	<60	<40	<40	<60	<40	<60	<30	<30	<30	<20	<20	<20	<20	<30	<30	<20	<30	<20
Isopropylbenzene (cumene)	<110	<80	<90	<130	<70	<120	<60	<60	<60	<50	<50	<50	<50	<60	<60	m	<60	<50
Isoquinoline	<110	<80	<90	<130	<70	<120	<60	<60	<60	<50	<50	<50	<50	<60	<60	<50	<60	<50
Menthol	<60	<40	<40	<60	<40	<60	<30	<30	<30	<20	<20	<20	<20	<30	<30	<20	<30	<20
Metolachlor	<60	<40	<40	<60	<40	<60	<30	<30	<30	<20	<20	<20	<20	<30	<30	<20	<30	<20
4-Nonylphenol monoethoxylate (NP1EO; sum of all isomers)	<550	e190	e150	e500	<350	e370	<300	<300	<300	e260	e200	e290	<250	<300	<300	<250	<300	<250
Naphthalene	e30	e20	e10	e30	m	e20	e20	e10	e30	e40	e20	e20	e20	e20	e20	e30	e10	e10
p-Cresol	e140	e120	e60	e260	e30	e100	e50	e10	e30	e50	e40	e30	<120	e30	e30	e30	e30	<120
Phenanthrene	210	110	110	<60	80	120	300	290	560	310	720	340	290	140	290	250	60	120
Phenol	e80	e150	e70	e100	e80	e200	e60	<30	e40	220	e20	e30	<20	e30	e70	e50	e70	<20

Table F3. Results for analysis of streambed-sediment samples by the wastewater method for samples collected in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.—Continued

[Street, Streetsboro; Aur W, Aurora Westerly; Aur Sh, Aurora Shores; Twins, Twinsburg; Sol, Solon; Bed, Bedford; Bed Hgts, Bedford Heights; DR, Tinkers Creek at Dunham Road; FR, Furnace Run; YC, Yellow Creek; US, upstream; DS, downstream; AO, above outfall; na, not available; e, estimated concentration; m, compound presence verified through qualitative criteria, but concentration could not be quantified. Data in bold print were not detected or detected at a lower concentration in the upstream sample]

Compound	Concentrations at sampling locations, in micrograms per kilogram																	
	Street		Aur W		Aur Sh		Twins		Sol		Bed		Bed Hgts		DR	FR	YC	
	US	DS	US	DS	US	DS	US	DS	US	DS	US	DS	US	DS				
Prometon	<60	<40	<40	<60	<40	<60	<30	<30	<30	<20	<20	<20	<20	<30	<20	<30	<20	
Pyrene	510	240	200	70	140	210	490	440	720	590	1,100	450	210	520	370	60	150	
Tributyl phosphate	<60	<40	<40	<60	<40	<60	<30	<30	<30	<20	<20	<20	<30	<30	<20	<30	<20	
Triclosan	<55	<40	<45	e56	<35	<60	<30	<30	<30	e36	e30	<25	<30	<30	<25	<30	<25	
Triphenyl phosphate	<60	<40	<40	<60	<40	<60	<30	<30	<30	<20	m	<20	<30	<30	<20	<30	<20	
Tris(2-butoxyethyl) phosphate	<160	<120	<140	<200	<100	<180	<30	e30	e30	e50	e70	<80	e30	<90	e20	<90	<80	
Tris(2-chloroethyl) phosphate	<110	<80	<90	<130	<70	<120	<90	<60	<60	<50	<50	<50	<60	<60	<50	<60	<50	
Tris(dichloroisopropyl) phosphate	<110	<80	<90	<130	<70	<120	<90	<60	<60	<50	<50	<50	<60	<60	<50	<60	<50	

Table F4. Summary of results for analysis of streambed-sediment samples by the wastewater method for samples collected in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.

[e, estimated concentration; –, not detected; nqd, no quantified detections]

Compound	Number of detections	Frequency of detection (percent)	Concentrations of detections, in micrograms per kilogram		
			Minimum	Maximum	Median
2,6-Dimethylnaphthalene ¹	18	100	e10	60	e25
2-Methylnaphthalene ¹	18	100	e10	e50	e20
3-Methyl-1H-indole ¹	18	100	e10	150	e30
Anthraquinone	18	100	e20	240	e70
Benzo[<i>a</i>]pyrene	18	100	e30	390	e140
β -Sitosterol	18	100	e210	e2,500	e620
Carbazole ¹	18	100	e20	130	e50
Cholesterol	18	100	e260	e2,800	e560
Fluoranthene	18	100	80	1,400	540
Indole	18	100	e30	1,100	e55
Naphthalene ¹	18	100	e10	e40	e20
Pyrene	18	100	60	1,100	400
Anthracene	17	94	e10	110	e50
bis(2-Ethylhexyl) phthalate	17	94	e30	e120	e60
Phenanthrene	17	94	60	720	250
1-Methylnaphthalene ¹	16	89	e10	e40	e20
Acetophenone ¹	16	89	e10	e90	e35
<i>p</i> -Cresol	16	89	e10	e260	e35
3- β -Coprostanol	15	83	e20	e300	e80
β -Stigmastanol	15	83	e30	e1,100	e140
Phenol	15	83	e20	220	e70
Acetyl hexamethyl tetrahydronaphthalene (AHTN) ¹	10	56	e10	80	e30
Hexahydrohexamethylcyclopentabenzopyran (HHCB) ¹	9	50	e20	390	e60
4-Nonylphenol diethoxylate (NP2EO; sum of all isomers)	8	44	e200	e910	e360
4-Nonylphenol monoethoxylate (NP1EO; sum of all isomers)	7	39	e150	e500	e260
Tris(2-butoxyethyl) phosphate	7	39	e20	e70	e30
4-Nonylphenol	5	28	e180	e320	e190
4-Octylphenol diethoxylate (OP2EO; sum of all isomers)	5	28	e10	e20	e20
Diethyl phthalate ¹	4	22	e10	e30	e10
1,4-Dichlorobenzene ¹	3	17	e16	e16	e16
4- <i>tert</i> -Octylphenol	3	17	e10	e20	e20
Triclosan	3	17	e30	e56	e36
Bisphenol A	2	11	e20	e60	e40
d-Limonene ¹	2	11	e10	e10	e10
4-Octylphenol monoethoxylate (OP1EO; sum of all isomers)	1	6	e20	e20	e20
3- <i>tert</i> -Butyl-4-hydroxy anisole ¹	1	6	nqd	nqd	nqd
Isopropylbenzene ¹	1	6	nqd	nqd	nqd
Triphenyl phosphate	0	0	–	–	–
4-Cumylphenol	0	0	–	–	–

Table F4. Summary of results for analysis of streambed-sediment samples by the wastewater method for samples collected in Tinkers Creek and its tributaries and two other tributaries to the Cuyahoga River in 2006.—Continued

[e, estimated concentration; –, not detected; nqd, no quantified detections]

Compound	Number of detections	Frequency of detection (percent)	Concentrations of detections, in micrograms per kilogram		
			Minimum	Maximum	Median
4- <i>n</i> -Octylphenol	0	0	–	–	–
Atrazine	0	0	–	–	–
2,2',4,4'-Tetrabromodiphenyl ether	0	0	–	–	–
Benzophenone	0	0	–	–	–
Bromacil	0	0	–	–	–
Camphor	0	0	–	–	–
Chlorpyrifos	0	0	–	–	–
N,N-Diethyl-meta-toluamide (DEET)	0	0	–	–	–
Diazinon	0	0	–	–	–
Isoborneol	0	0	–	–	–
Isophorone	0	0	–	–	–
Isoquinoline	0	0	–	–	–
Menthol	0	0	–	–	–
Metolachlor	0	0	–	–	–
Prometon	0	0	–	–	–
Tributylphosphate	0	0	–	–	–
Tris(2-chloroethyl) phosphate	0	0	–	–	–
Tris(dichloroisopropyl) phosphate	0	0	–	–	–

¹ Compound was detected in one or more samples but not quantified. Statistics of concentrations reported for this compound are based only on quantified concentrations.

ISBN 978-1-4113-2278-3



9 781411 322783