

Prepared in cooperation with the City of Atlanta

Occurrence of Organic Wastewater-Indicator Compounds in Urban Streams of the Atlanta Area, Georgia, 2003–2006













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Streamside health hazard warning sign along an Atlanta-area stream. Photo by Daniel J. Hippe, USGS.

Base flow in Intrenchment Creek (INT-1). Photo by Jacob H. LaFontaine, USGS.

Stormflow in Nancy Creek (NAN-3) and unnamed tributary. Photo by Jacob H. LaFontaine, USGS. Streamside signs warning of sewage contamination in an Atlanta-area stream. Photo by Andrew C. Hickey, USGS.

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By Stephen J. Lawrence and Jacob H. LaFontaine

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

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Conversion Factors

Multiply	Ву	To obtain
	Length	
centimeter (cm)	0.3937	inch
millimeter (mm)	0.03937	inch
micrometer (µm)	0.03937	inch
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Area	
square meter (m ²)	10.76	square foot (ft ²)
hectare (ha)	0.003861	square mile (mi ²)
square kilometer (km ²)	0.3861	square mile (mi ²)
	Volume	
milliliter (mL)	0.0338140	ounce, U.S. fluid (oz)
liter (L)	0.2642	gallon (gal)
cubic meter (m ³)	264.2	gallon (gal)
cubic meter (m ³)	0.0002642	million gallons (Mgal)
	Flow rate	
meter per second (m/s)	3.281	foot per second (ft/s)
cubic meter per second (m ³ /s)	35.31	cubic foot per second (ft ³ /s)
centimeter per hour (cm/hr)	0.3937	inch per hour (inch/hour)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
milligram (mg)	35.274	ounce, avoirdupois (oz)
microgram (µg)	35,274	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
microgram per gram (µg/g)	1	part per billion (ppb)
milligram per gram (mg/g)	1	part per million (ppm)
nanogram per gram (ng/g)	1	part per trillion (ppt)

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

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

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

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

Altitude, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μ S/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L). Densities of fecal coliform bacteria are reported in colonies per 100 milliliters (col/100 mL). Densities of *Escherichia coli (E. coli)* bacteria are reported in most probable number per 100 milliliters (MPN/100 mL).

Acronyms Used in this Report

14DCB	1,4-dichlorobenzene
AHTN	7-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene
BHA	3- <i>tert</i> -butyl-4-hydroxyanisole
BOD_{5}	5-day biochemical oxygen demand
BQS	USGS Branch of Quality Systems
CFR	Code of Federal Regulations
COA	City of Atlanta
CS0	combined sewer overflow
CSS	combined sewer system
DEET	<i>N,N</i> -diethyl- <i>meta</i> -toluamide
14DCB	1,4-dichlorobenzene
DNA	deoxyribonucleic acid
DO	dissolved oxygen
E. coli	Escherichia coli
EWI	equal-width interval
GAEPD	Georgia Environmental Protection Division
GAWSC	Georgia Water Science Center
ннсв	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran
HHCB INT	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran Intrenchment Creek
HHCB INT LRB	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran Intrenchment Creek laboratory reagent blank
HHCB INT LRB LRL	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran Intrenchment Creek laboratory reagent blank laboratory reporting level
HHCB INT LRB LRL LRS	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran Intrenchment Creek laboratory reagent blank laboratory reporting level laboratory reference sample
HHCB INT LRB LRL LRS LT-MDL	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran Intrenchment Creek laboratory reagent blank laboratory reporting level laboratory reference sample long-term method detection level
HHCB INT LRB LRL LRS LT-MDL MDL	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran Intrenchment Creek laboratory reagent blank laboratory reporting level laboratory reference sample long-term method detection level method detection limit
HHCB INT LRB LRL LRS LT-MDL MDL NAN	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran Intrenchment Creek Iaboratory reagent blank Iaboratory reporting level Iaboratory reference sample Iong-term method detection level method detection limit Nancy Creek
HHCB INT LRB LRL LRS LT-MDL MDL NAN NDMC	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran Intrenchment Creek laboratory reagent blank laboratory reporting level laboratory reference sample long-term method detection level method detection limit Nancy Creek non-ionic detergent metabolite compound
HHCB INT LRB LRL LRS LT-MDL MDL NAN NDMC NPEO2	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran Intrenchment Creek Iaboratory reagent blank Iaboratory reporting level Iaboratory reference sample Iong-term method detection level method detection limit Nancy Creek non-ionic detergent metabolite compound 4-Nonylphenol diethoxylate
HHCB INT LRB LRL LRS LT-MDL MDL NAN NDMC NPE02 NWQL	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran Intrenchment Creek Iaboratory reagent blank Iaboratory reporting level Iaboratory reference sample Iong-term method detection level method detection limit Nancy Creek non-ionic detergent metabolite compound 4-Nonylphenol diethoxylate National Water Quality Laboratory
HHCB INT LRB LRL LRS LT-MDL MDL NAN NDMC NPE02 NWQL NURP	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran Intrenchment Creek Iaboratory reagent blank Iaboratory reporting level Iaboratory reference sample Iong-term method detection level method detection limit Nancy Creek non-ionic detergent metabolite compound 4-Nonylphenol diethoxylate National Water Quality Laboratory National Urban Runoff Program
HHCB INT LRB LRL LRS LT-MDL MDL NAN NDMC NPE02 NWQL NURP NWIS	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran Intrenchment Creek Iaboratory reagent blank Iaboratory reporting level Iaboratory reference sample Iong-term method detection level method detection limit Nancy Creek non-ionic detergent metabolite compound 4-Nonylphenol diethoxylate National Water Quality Laboratory National Urban Runoff Program
HHCB INT LRB LRL LRS LT-MDL MDL NAN NDMC NPE02 NWQL NURP NWIS OPE01	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran Intrenchment Creek Iaboratory reagent blank Iaboratory reporting level Iaboratory reference sample Iong-term method detection level method detection limit Nancy Creek non-ionic detergent metabolite compound 4-Nonylphenol diethoxylate National Water Quality Laboratory National Urban Runoff Program National Water Information System 4-Octylphenol monoethoxylate
HHCB INT LRB LRL LRS LT-MDL MDL NAN NDMC NPE02 NVVQL NURP NWIS OPE01 OPE02	 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran Intrenchment Creek Iaboratory reagent blank Iaboratory reporting level Iaboratory reference sample Iong-term method detection level method detection limit Nancy Creek non-ionic detergent metabolite compound 4-Nonylphenol diethoxylate National Water Quality Laboratory National Water Information System 4-Octylphenol diethoxylate 4-Octylphenol diethoxylate
HHCB INT LRB LRL LRS LT-MDL MDL NAN NDMC NPE02 NWQL NURP NWIS OPE01 OPE02 OWIC	 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran Intrenchment Creek laboratory reagent blank laboratory reporting level laboratory reference sample long-term method detection level method detection limit Nancy Creek non-ionic detergent metabolite compound 4-Nonylphenol diethoxylate National Water Quality Laboratory National Water Information System 4-Octylphenol diethoxylate A-Octylphenol diethoxylate organic wastewater-indicator compound

PCA	factor analysis by principal components
PC1	first component
PC2	second component
PC3	third component
PC4	fourth component
PC5	fifth component
PCE	Tetrachloroethene
PCP	Pentachlorophenol
PEA	Peachtree Creek
PMRL	Panola Mountain Research Laboratory
PRO	Proctor Creek
QC	quality control
SAN	Sandy Creek
SC	specific conductance
SOU	South River
SPE	solid-phase extraction
SRL	study reporting limit
SS0	sanitary-sewer overflow
SSS	sanitary-sewer system
TBEP	tris(2-butoxyethyl) phosphate
ТВР	tributyl phosphate
TCEP	tris(2-chloroethyl) phosphate
TDCPP	tris(dichloroisopropyl) phosphate
ТРР	triphenyl phosphate
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UTO	Utoy Creek
WWTP	wastewater treatment plant

Occurrence of Organic Wastewater-Indicator Compounds in Urban Streams of the Atlanta Area, Georgia, 2003–2006

By Stephen J. Lawrence and Jacob H. LaFontaine

Abstract

Between March 2003 and January 2006, 863 water samples were collected from streams in seven urban watersheds with varying land uses within or near the City of Atlanta, Georgia. Sixty-four sampling sites representing three site types were established in those watersheds. The first type consisted of sites within three watersheds not affected by combined sewer overflows; these were designated as the control basins. The second and third site types were established in four watersheds and were designated as sites upstream or downstream from combined sewer outfalls.

Stream samples collected during the study were analyzed for major ions, nutrients, trace metals, and 60 organic compounds commonly found in wastewater (organic wastewaterindicator compounds, OWICs). Inorganic constituents were analyzed to discern possible relations between OWICs and urban runoff, sewage effluent, or combined sewer overflows (CSOs). The OWICs were grouped into nine compound classes based either on an already accepted class of compounds (such as pesticide) or the manner in which the compounds are used (such as automotive uses). The compounds benzo(a)pyrene, 4-cumylphenol, 3-*tert*-butyl-4-hydroxyanisole (BHA), isophorone, isoquinoline, metolachlor, metalaxyl, and 4-octylphenol were not detected in any sample collected during the study.

As many as 33 OWICs were detected above study reporting levels in water samples collected from streams in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds (basins with CSOs), a number markedly higher than the number detected in water samples from the control basins (watersheds without CSOs). Several compounds known to disrupt the endocrine systems of aquatic biota were among the compounds detected.

The median numbers of OWICs detected in base-flow samples from the control basins ranged from 3 to 4 and 7 to 9 in stormflow samples, while the median in base-flow samples from the four CSO-affected watersheds ranged from 4 to 16 and 11 to 19 in stormflow samples. The detection frequencies and concentrations of OWICs in water samples varied depending on flow conditions during sample collection; however, regardless of flow condition, the total OWICs concentrations were strongly related to the numbers of OWICs detected in these samples. In addition, the median number of detectable OWICs and total OWIC concentrations increased linearly with increasing impervious area and stream flashiness (flashiness indicates the rapidity with which streamflow responds to high rainfall amounts).

Four compounds—tris(2-butoxyethyl) phosphate (TBEP), tris(2-chloroethyl) phosphate (TCEP), bromacil, and cholesterol were detected at concentrations greater than study reporting levels in at least 45 percent of all samples collected during the study. On a broad scale, the seasonal distributions of OWICs detected in samples collected during the study period were consistent with use patterns or urban activity, but were markedly different and more variable within individual watersheds.

Seven of the nine OWIC classes were detected with greater frequency in base-flow samples from sites downstream from CSOs than from those upstream from CSOs or from control-basin sites; these OWICs also were detected in a greater percentage of base-flow samples from upstream than control-basin sites. Polycyclic aromatic hydrocarbon (PAH) and automotive-use compounds were detected with similar frequency in base-flow samples from all sites. The pesticides and industrial-use compounds were detected with similar frequency in base-flow samples from sites upstream and downstream from CSOs. The compounds 7-acetyl-1,1,3,4,4,6hexamethyl tetrahydronaphthalene (AHTN), 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta-g-2-benzopyran (HHCB), and triclosan were detected with greater frequency in base-flow than in stormflow samples from all sites. The detection frequencies of these three compounds were particularly high in base-flow samples from downstream sites, especially those from the Intrenchment Creek watershed.

In stormflow samples, only the industrial-use compounds were detected with similar frequency among samples from control basins, and upstream and downstream sites. Caffeine, camphor, and menthol were detected in a greater percentage of stormflow than base-flow samples from all sites. The disinfectant byproduct bromoform was detected with the highest frequency in base-flow samples from the upstream sites, particularly those from the South River watershed.

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Typically, compounds in the pesticide class were detected with similar frequency in base-flow and stormflow samples from upstream and downstream sites, although bromacil and carbaryl were the exceptions. Bromacil was detected with greatest frequency in base-flow samples from all sites, but was detected in a larger percentage of base-flow samples from upstream and downstream sites, especially upstream and downstream sites in the Proctor Creek and South River watersheds. Carbaryl, however, was detected in a greater percentage of stormflow samples from all sites. Although collectively the industrial-use compounds were detected in more stormflow than base-flow samples, tetrachloroethene (PCE) was detected in more base-flow than stormflow samples at all sites. More specifically, PCE was detected with the highest frequency in samples from the upstream sites, particularly those from the Proctor Creek watershed.

The similarity in the pattern and distribution of OWICs in samples at sites upstream and downstream from known CSO outfalls indicates that CSOs were not the dominant source of OWICs during the study period. Other sources may include non-sewage discharges—both permitted, permitted but out of compliance, and non-permitted, contaminated groundwater from leaking sewer lines or septic systems, sanitary-sewer overflows, or dry-weather runoff from outdoor water use. These OWICs may be better suited for identifying sewagecontaminated groundwater than sewage-contaminated surface water because groundwater is not typically affected by the OWICs that are more common in urban runoff.

Introduction

Urbanization greatly alters the landscape and can adversely affect the quality and quantity of water in local rivers and streams, and in downstream receiving waters (U.S. Environmental Protection Agency, 1983; Ellis and others, 1997; Ellis and Revitt, 2008). Adverse effects commonly include: (1) rainfall on impervious surfaces (such as roads, roofs, and sidewalks) that increase the volume of surfacewater runoff reaching rivers and streams and causing increases in the magnitude of peak flows and flood frequency, increased channel erosion, increased sediment transport, and reduced groundwater recharge; (2) increased chemical loads to local and downstream receiving waters from undefined sources during runoff from residential, commercial, or industrial areas, leaking sewer systems, and sewer overflows; (3) erosion of soil directly or indirectly (atmospheric deposition) contaminated by industrial sources, power-generating facilities, or landfills; and (4) geomorphologic changes in stream channels that reduce the quantity and quality of aquatic habitats (Driver and Troutman, 1989; Ellis and others, 1997; Ellis and Revitt, 2008; Rose and Peters, 2001).

The Metropolitan Atlanta area is one of the fastestgrowing urban areas in the United States. Between 1970 and 2000, the population increased by 125 percent; at the same time, urbanization increased about 210 percent (Peters and Kandell, 1999; Atlanta Regional Commission, 2005; Horowitz and Hughes, 2006). During that same 30-year period, however, the population within the Atlanta city limits decreased by 16.1 percent, probably because of population shifts away from urban areas. Conversely, the population of Atlanta increased by 8.8 percent between 2000 and 2006 and is projected to increase during the next several years (Atlanta Regional Commission, 2005). As of 2006, the population density of Atlanta was 3,161 persons per square mile (mi²; U.S. Census Bureau, 2006). The capacity of Atlanta's storm, sanitary, and combined sewer systems has not expanded with the population growth and may not meet future demands of a projected 43-percent increase in population between 2000 and 2030 (Atlanta Regional Commission, 2005).

According to the City of Atlanta (COA), about 2,200 miles (mi) of sanitary sewer pipe lie beneath Atlanta and parts of Fulton County, GA (Clean Water Atlanta, 2003). About 15 percent, or 330 mi, of the current Atlanta sewer system collects stormwater and sanitary waste in the same pipe and conveys that wastewater for treatment at wastewater treatment plants (WWTPs). This combined sewer system (CSS) serves the sewer needs of a 19-mi² area of Atlanta, primarily the older downtown area (Clean Water Atlanta, 2003). During dry weather or small storms, the WWTPs can assimilate and adequately treat the combined wastewater before discharging it into local streams. During storms that send large amounts of urban runoff into the storm-sewer system, the CSS in Atlanta is overwhelmed and treatment facilities are unable to adequately treat the combined sewer inflows. As a result, this overflow is released—after screening and disinfection—to various streams within the COA. According to the COA, more than 300 combined sewer overflows (CSOs), on average, occur per year from Atlanta's seven existing CSS facilities (Clean Water Atlanta, 2003). Because of either urban runoff or CSOs, all streams within the Atlanta city limits exceed Georgia water-quality standards for either fecal coliform bacteria density or trace metal concentrations. The Georgia Environmental Protection Division (GAEPD) 305b report lists these streams as impaired for body-contact recreation, such as swimming or rafting, and for fishing (Georgia Environmental Protection Division, 2006).

During 1998, the COA signed a consent decree compelling the city to reduce the incidence of CSOs and other discharges to permitted limits (U.S. District Court, 1998). Compliance with the consent decree was expected by the end of 2007 for CSOs and is expected by 2014 for sanitary-sewer overflows (SSOs). Compliance with the decree required improvements to the sanitary-sewer infrastructure that included the construction of two large tunnels (about a 360-million-gallon combined capacity) where the CSO flows are stored and then conveyed to two new treatment facilities. In addition, the size of the existing CSS will be reduced from 15 percent of the total sewer capacity to about 10 percent. Furthermore, the COA is required to monitor all SSOs and CSOs on downstream water quality (Clean Water Atlanta, 2003).

During 2001, the COA asked the U.S. Geological Survey (USGS), in conjunction with CH2M Hill, Inc., to design a

water-quality and water-quantity monitoring network that would fulfill, in part, the requirements of the consent decree, provide an evaluation of the planned infrastructural improvements, and monitor the ongoing state of the COA's water quality. Waterquality sampling for this study began in March 2003.

Purpose and Scope

This report presents the results of a study intended to (1) determine if 60 anthropogenic organic wastewaterindicator compounds (OWICs) common in wastewater effluents worldwide also exist in streams within the City of Atlanta, GA; (2) develop a baseline dataset of OWICs in streams within Atlanta before major improvements to the sanitary and combined sewer systems begin in the city; and (3) identify hydrologic and seasonal conditions, and urban and sewer infrastructures that may relate to the sources and variation of OWICs in Atlanta streams. The report also presents descriptions, summaries, and statistical analyses of the presence, detection frequencies, concentrations, and variation of OWICs individually and collectively within compound classes for the seven study watersheds by flow regime and season.

Study Area Description

The City of Atlanta is the hub of the 10-county Atlanta metropolitan area (fig. 1). The city occupies 132 mi² encompassing seven watersheds within Cobb, De Kalb, and Fulton Counties, GA (U.S. Census Bureau, 2006). Drainage areas upstream from the sampling sites range from 0.13 to 90 mi² (table 1). Land use within these urban watersheds is primarily residential, ranging from 43 to 73 percent of the area upstream from the sampling sites (table 2). Commercial, industrial/ commercial, and industrial are major land uses in the study watersheds. Estimated impervious area ranges from less than 17 to 52 percent of the area upstream from the sampling sites.

Physiography, Geology, and Climate

Atlanta is located within the Piedmont Physiographic Province in north-central Georgia (Clark and Zisa, 1976). The city straddles a ridge south of the Chattahoochee River that divides the Chattahoochee River watershed from the headwaters of the Flint and Ocmulgee Rivers. The COA has an average altitude of 1,050 feet (ft) above the North American Vertical Datum of 1988 (NAVD 88). The area is hilly and underlain by regolith composed of semi-consolidated and unconsolidated weathered bedrock (saprolite) of varying thickness. Bedrock typically is igneous rock (crystalline rock) of Precambrian to Paleozoic age and extensively folded and faulted metamorphic rock (primarily biotite gneiss and schist; Clarke and Peck, 1991). Fault zones are numerous in the Piedmont and one fault-the Brevard Zone of Cataclasistrends northeast to southwest through the Metropolitan Atlanta area (Chapman and Peck, 1997). Groundwater occupies fractures in the crystalline rock and in the overlying regolith.

According to the Köppen classification, Atlanta has a humid, subtropical climate characterized by hot, humid summers and cool to mild winters (McKnight and Hess, 2000). The 77-year average-annual maximum temperature is 71.7 degrees Fahrenheit (°F) and the average-annual minimum temperature is 52.2 °F (Southeast Regional Climate Center, 2007). January is typically the coldest month, with a 77-year monthly average maximum of 52.3 °F and minimum of 34.2 °F. Conversely, July is typically the warmest month with a 77-year average-monthly maximum temperature of 88.7 °F and minimum temperature of 70.1 °F (Southeast Regional Climate Center, 2007). During the winter, warm fronts can bring mild temperatures ranging from 60 to 70 °F. Likewise, arctic air masses can lower temperatures to below 21 °F. The 77-year average-annual snowfall is 2.1 inches with most falling in January (Southeast Regional Climate Center, 2007). The average monthly distribution of rainfall is similar among all months, indicating that a strong seasonal trend is not present in these data. From spring through fall, convective storms (thunderstorms) are the primary rainmakers, while frontal storms provide most of the rain that falls during winter. The 77-year average-annual rainfall is 48.6 inches (Southeast Regional Climate Center, 2007).

Surface-Water Hydrology

Small-scale stream drainage and groundwater flow patterns in any given area or region are determined by a combination of geology and climate. Geology commonly governs the shape of the watershed, the type of surface-water drainage pattern (dendritic, rectangular, trellis, and so forth), aquifer properties, and groundwater contributions to surface water (channel incisement). Climate governs the drainage density (Chorley, 1969), the long-term average annual streamflow, and the influence of groundwater discharge to streams.

In the COA study area, stream drainage patterns are typically rectangular or trellis-shaped within elliptical watersheds that trend generally northwest to southeast on the western side and northeast to southwest on the eastern side of the Chattahoochee River (fig. 1). These patterns are determined by local and regional fault zones, bedrock outcrops, and granitic plutons or extrusions (Chapman and Peck, 1997). Streamflow within the study area is generated by storm runoff, wastewatereffluent discharges, groundwater discharge, and dry-weather runoff. Dry-weather runoff typically is municipal water flowing into streams from outdoor water use such as landscape watering, car washing, washing of roads, driveways, or parking lots, and leaking municipal water lines during periods without rain. During the 1954 drought, base flow in Peachtree Creek at Atlanta (PEA-2, USGS station number 02336300), Proctor Creek at Bolton Road, Atlanta (USGS 02336530), and North and South Utoy Creeks (USGS 02336680, USGS 02336710, respectively) was 2.3, 0.95, 0.30, and 0.70 cubic feet per second (ft³/s), respectively. These discharges indicate that even during extreme drought, groundwater levels were high enough to supply water to streams within the study area.

4 Occurrence of Organic Wastewater-Indicator Compounds in Urban Streams of the Atlanta Area, Georgia, 2003–2006



Figure 1. Water-quality sampling sites on streams within seven basins near Atlanta, GA, March 2003 to January 2006.

Table 1. Descriptions of water-quality monitoring sites on streams near Atlanta, GA, March 2003 to January 2006.

[USGS, U.S. Geological Survey; mi², square miles; CSO, combined sewer overflow; monitoring sites, long-term sample collection sites during base-flow and stormflow periods beginning in August 2003; synoptic sites, sites at which samples were collected within two brief time periods (March–June 2003 and July 2003); NB, not in watershed; DS, downstream of CSO; US, upstream of CSO; —, not measured]

Site identifier	USGS site	USGS site name	Latitude	Longitude	Drainage area	Proximity to CSO
(fig. 1)	identifier		(degrees minu	utes seconds)	(mi²)	outfall
		Nancy Creek watershed (NAN)—monit	oring sites			
NAN-1	02336410	Nancy Creek at West Wesley Road, at Atlanta ^a	33° 50' 18"	84° 26' 22"	38	NB
NAN-2	02336380	Nancy Creek at Randall Mill Road, at Atlanta	33° 51' 35"	84° 25' 28"	35	NB
NAN-3	02336360	Nancy Creek at Rickenbacker Drive, at Atlanta ^a	33° 52' 09"	84° 22' 44"	27	NB
		Nancy Creek watershed (NAN)—syno	ptic sites			
1	02336355	Nancy Creek tributary at Wieuca Road, at Atlanta	33° 52' 12"	84° 22' 20"	2.9	NB
2	02336370	Nancy Creek tributary at Lake Forest Drive, at Atlanta	33° 52' 27"	84° 23' 15"	.24	NB
3	02336378	Nancy Creek tributary at Tuxedo Road, at Atlanta	33° 51' 19"	84° 23' 44"	1.2	NB
4	02336405	Nancy Creek tributary at Wood Valley Road, at Atlanta	33° 50' 53"	84° 24' 52"	.13	NB
		Sandy Creek watershed (SAN)—monite	oring sites			
SAN-1	02336644	Sandy Creek at Bolton Road, near Atlantab	33° 46' 46"	84° 29' 58"	3.4	NB
		Sandy Creek watershed (SAN)—syno	ptic sites			
1	02336642	Sandy Creek at Hedgewood Lane, at Atlanta	33° 45' 28"	84° 28' 30"	.15	NB
2	02336643	Sandy Creek tributary at Collier Road, at Atlanta	33° 46' 08"	84° 30' 07"	.17	NB
3	02336647	Sandy Creek at Sandy Creek Road, near Atlanta	33° 47' 00"	84° 30' 47"	4.9	NB
		Utoy Creek watershed (UTO)—monito	ring sites			
UTO-1	02336728	Utoy Creek at Great Southwest Pkwy near Atlanta ^a	33° 44' 36"	84° 34' 06"	34	NB
UTO-2	02336706	South Utoy Creek at Childress Drive, near Ben Hill	33° 42' 54"	84° 29' 26"	9.3	NB
UTO-3	02336658	North Utoy Creek at Peyton Road, near Atlanta ^a	33° 44' 20"	84° 28' 45"	6.4	NB
		Utoy Creek watershed (UTO)—synop	tic sites			
1	02336654	North Fork Utoy Creek at Beecher Road at Atlanta	33° 44' 01"	84° 27' 20"	3.7	NB
2	02336664	North Utoy Creek (Lynhurst Drive) near Atlanta	33° 44' 44"	84° 29' 23"	7.5	NB
3	02336675	North Utoy Creek at Benjamin Mays Drive, near Atlanta	33° 44' 21"	84° 30' 21"	8.6	NB
4	02336702	South Utoy Creek (Campbellton Road) near East Point	33° 42' 08"	84° 28' 12"	6.3	NB
5	023367025	South Utoy Creek tributary at Laurelwood Drive, near Atlanta	33° 42' 37"	84° 28' 02"	.68	NB
6	02336703	South Utoy Creek (Dodson Drive) near East Point	33° 42' 28"	84° 28' 28"	7.4	NB
7	02336704	South Utoy Creek (Harbin Road) near Ben Hill	33° 43' 02"	84° 29' 02"	8.7	NB
8	02336712	Utoy Creek tributary at Melvin Drive, near Atlanta	33° 42' 29"	84° 30' 47"	.91	NB
9	02336716	Utoy Creek tributary at Danforth Road, near Atlanta	33° 43' 34"	84° 31' 54"	1.8	NB
		Intrenchment Creek watershed (INT)—mo	nitoring sites			
INT-1	02203700	Intrenchment Creek near Atlanta ^a	33° 41' 20"	84° 19' 50"	11	DS
		Intrenchment Creek watershed (INT)—sy	noptic sites			
1	02203682	Intrenchment Creek tributary at Gracewood Avenue, at Atlanta	33° 43' 59"	84° 20' 46"	.22	US
2	02203686	Intrenchment Creek at Custer Avenue, at Atlanta	33° 42' 58"	84° 20' 41"	8.3	DS
3	02203693	Intrenchment Creek at Key Road, at Atlanta	33° 42' 04"	84° 19' 56"	10	DS

6 Occurrence of Organic Wastewater-Indicator Compounds in Urban Streams of the Atlanta Area, Georgia, 2003–2006

Table 1. Descriptions of water-quality monitoring sites on streams near Atlanta, GA, March 2003 to January 2006.—Continued

[USGS, U.S. Geological Survey; mi², square miles; CSO, combined sewer overflow; monitoring sites, long-term sample collection sites during base-flow and stormflow periods beginning in August 2003; synoptic sites, sites at which samples were collected within two brief time periods (March–June 2003 and July 2003); NB, not in watershed; DS, downstream of CSO; US, upstream of CSO; —, not measured]

Site identifier	USGS site	USGS site name	Latitude	Longitude	Drainage area	Proximity to CSO
(fig. 1)	identifier		(degrees min	ıtes seconds)	(mi²)	outfall
		Peachtree Creek watershed (PEA)—mon	itoring sites			
PEA-1	02336311	Peachtree Creek at Bohler Road, at Atlanta	33° 49' 20"	84° 25' 45"	90	DS
PEA-2	02336300	Peachtree Creek at Atlanta ^a	33° 49' 10"	84° 24' 28"	87	DS
PEA-3	02336267	Peachtree Creek at Piedmont Road, near Atlanta	33° 49' 02"	84° 22' 01"	70	DS
PEA-4	02336120	North Fork Peachtree Creek, Buford Hwy, near Atlanta ^a	33° 49' 53"	84° 20' 34"	35	NB
PEA-5	02336240	South Fork Peachtree Creek, Johnson Road, near Atlanta ^a	33° 48' 10"	84° 20' 27"	29	NB
LUL-1	02336228	Lullwater Creek at Lullwater Parkway, at Atlanta	33° 46' 46"	84° 19' 59"	_	NB
WOO-1	02336313	Woodall Creek at Defoors Ferry Road, at Atlanta	33° 49' 18"	84° 26' 20"	2.6	NB
		Peachtree Creek watershed (PEA)—syn	optic sites			
1	02336123	North Fork Peachtree Creek tributary (Shady Valley), near Atlanta	33° 49' 44"	84° 21' 03"	2.4	NB
2	02336255	South Fork Peachtree Creek tributary at Wellbourne Drive, at Atlanta	33° 48' 26"	84° 21' 36"	.15	NB
3	02336275	Peachtree Creek tributary at Georgia Highway 236, at Atlanta	33° 49' 16"	84° 22' 28"	.94	NB
4	023362773	Clear Creek at Piedmont Avenue, at Atlanta	33° 47' 46"	84° 22' 12"	1.4	DS
5	02336295	Tanyard Branch at Collier Road, at Atlanta	33° 48' 37"	84° 24' 10"	4.0	DS
6	02336298	Peachtree Creek tributary at Brookdale Drive, at Atlanta	33° 49' 37"	84° 24' 11"	1.3	NB
7	02336309	Peachtree Creek tributary at Rockingham Drive, at Atlanta	33° 49' 57"	84° 24' 55"	.59	NB
		Proctor Creek watershed (PRO)—monit	oring sites			
PRO-1	02336526	Proctor Creek at Jackson Parkway, at Atlanta ^a	33° 47' 39"	84° 28' 28"	13	DS
PRO-2	02336517	Proctor Creek at Hortense Way, at Atlanta ^b	33° 46' 32"	84° 26' 27"	7.2	DS
PRO-3	023365218	Proctor Creek tributary at Spring Road, at Atlanta	33° 47' 34"	84° 28' 08"	3.1	NB
		Proctor Creek watershed (PRO)—syno	ptic sites			
1	02336504	Proctor Creek (Simpson Street) at Atlanta, Georgia	33° 45' 48"	84° 25' 42"	2.4	DS
2	02336516	Proctor Creek tributary 6 at Simpson Street, at Atlanta	33° 45' 50"	84° 26' 47"	.21	NB
3	023365165	Proctor Creek tributary 5 at Simpson Street, at Atlanta	33° 45' 49"	84° 26' 19"	.56	NB
4	023365212	Proctor Creek tributary at Baker Road, at Atlanta	33° 46' 13"	84° 27' 27"	1.5	NB
5	023365214	Proctor Creek tributary at North Grand Avenue, at Atlanta	33° 46' 54"	84° 27' 41"	2.3	NB
6	02336528	Proctor Creek tributary 7 at Watts Road, at Atlanta	33° 47' 28"	84° 29' 05"	.13	NB

Table 1. Descriptions of water-quality monitoring sites on streams near Atlanta, GA, March 2003 to January 2006.—Continued

[USGS, U.S. Geological Survey; mi², square miles; CSO, combined sewer overflow; monitoring sites, long-term sample collection sites during base-flow and stormflow periods beginning in August 2003; synoptic sites, sites at which samples were collected within two brief time periods (March–June 2003 and July 2003); NB, not in watershed; DS, downstream of CSO; US, upstream of CSO; —, not measured]

Site	USGS	IISGS site name	Latitude	Longitude	Drainage	Proximity
(fig. 1)	identifier	USUS Site name	(degrees mini	utes seconds)	(mi ²)	outfall
		South River watershed (SOU)—monito	ring sites			
SOU-1	02203655	South River at Forest Park Road, at Atlanta ^a	33° 40' 44"	84° 21' 29"	23	DS
SOU-2	02203620	South River at Macon Drive, near Hapeville	33° 41' 37"	84° 23' 27"	4.8	NB
SOU-3	02203603	South River at Springdale Road, at Atlanta	33° 41' 02"	84° 24' 55"	2.3	NB
		South River watershed (SOU)—synop	otic sites			
1	02203622	South River Tributary at Joyland Street, at Atlanta	33° 42' 51"	84° 23' 51"	1.2	DS
2	02203623	Tributary to South River Tributary at Pryor Road, at Atlanta	33° 42' 14"	84° 23' 56"	.24	NB
3	02203628	South River Tributary at Cleveland Ave, at Atlanta	33° 40' 54"	84° 22' 14"	3.0	NB
4	02203650	Poole Creek (Jonesboro Road) near Hapeville	33° 39' 22"	84° 22' 09"	4.2	NB
5	02203652	Poole Creek Tributary at Conley Road, near Hapeville	33° 39' 00"	84° 21' 37"	.35	NB
6	02203653	Tributary to Poole Creek Tributary at Forest Park Road, near Hapeville	33° 39' 10"	84° 21' 26"	.66	NB
7	02203654	Poole Creek at Hutchens Road, at Atlanta	33° 40' 05"	84° 21' 53"	6.4	NB
8	02203657	South River Tributary at Constitution Road, at Atlanta	33° 41' 35"	84° 21' 44"	1.5	NB
9	02203658	Tributary to South River Tributary, Constitution Road at Atlanta	33° 41' 35"	84° 21' 22"	.27	NB
10	02203800	South River at Bouldercrest Road at Atlanta	33° 40' 46"	84° 18' 30"	42	DS
11	02203812	Sugar Creek tributary at Georgia Highway 154, at Atlanta	33° 44' 50"	84° 18' 58"	1.1	NB

^aReal-time continuous surface-water and water-quality measurements, automatic sampler.

^bReal-time continuous surface-water measurements.

Table 2. Land-use categories and percentage of watershed area occupied by each land use upstream of long-term monitoring sites in the seven study watersheds near Atlanta, GA, 2001.

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Cito	þ			2	l and-iico	ratennriae (narrant of	watere	ad area)		_		
identi- fication (fig. 1)	USGS site identifier	USGS site name	Residential	Industrial	Industrial/ commercial	Commercial	Other urban	Golf	Agriculture	Wetlands including reservoirs	Woodland and parks	Developed area (percent)	Impervious area (percent)ª
			2	lancy Cree	k Watershe	d—monitorir	ng sites						
NAN-1	02336410	Nancy Creek at West Wesley Road, at Atlanta	65	2.2	1.1	14	4.6	1.4	0.5	0.3	4.8	71	24
NAN-2	02336380	Nancy Creek at Randall Mill Road, at Atlanta	65	2.4	1.1	15	3.7	1.5	S.	4.	3.6	73	I
NAN-3	02336360	Nancy Creek at Rickenbacker Drive, at Atlanta	61	3.1	1.5	17	4.4	2.0	0	Ś	5.7	77	27
				andy Cree	k Watershe	d—monitorir	ng sites						
SAN-1	02336644	Sandy Creek at Bolton Road, near Atlanta	64	0	0	6.6	5.4	0	0	0	11	72	19
				Utoy Creek	Watershed		g sites						
UTO-3	02336658	North Utoy Creek at Peyton Road, near Atlanta	61		3.5	5.3	6.	0	0	0	12	71	19
UTO-2	02336706	South Utoy Creek at Childress Drive, near Ben Hill	62	0	3.3	6.3	3.0	1.6	0	0	13	71	
UTO-1	02336728	Utoy Creek at Great Southwest Pkwy near Atlanta	55	.2	4.8	4.5	2.0	4	0	9.	22	61	17
			Intre	nchment C	reek Water	shed—monit	oring sites						
INT-1	02203700	Intrenchment Creek near Atlanta	46	2.1	6.2	15	15	0	0	2	11	83	35
			Pe	achtree Cre	ek Watersł	ned-monito	ring sites						
PEA-1	02336311	Peachtree Creek at Bohler Road, at Atlanta	61		6.6	14	4.3	Ś	-:	ω	5.2	80	
PEA-2	02336300	Peachtree Creek at Atlanta	61	9.	6.8	15	4.4	S.	.1	ε	4.8	81	31
PEA-3	02336267	Peachtree Creek at Piedmont Road, near Atlanta	73	0	0	8.6	5.2	7.2	0	0	2.8	62	I
PEA-4	02336120	North Fork Peachtree Creek, Buford Hwy, near Atlanta	64	4.	6.9	13	3.2	4	.1	i	5.7	80	30
PEA-5	02336240	South Fork Peachtree Creek, Johnson Road, near Atlanta	64	∞.́	7.2	15	3.2	0	0	ί	2.6	77	24
LUL-1	02336228	Lullwater Creek at Lullwater Parkway, at Atlanta	62	0	6.8	11	3.6	6	<i></i>	Ċ.	8.3	79	I
W00-1	02336313	Woodall Creek at DeFoors Ferry Road											52

Table 2. Land-use categories and percentage of watershed area occupied by each land use upstream of long-term monitoring sites in the seven study watersheds near Atlanta, GA, 2001.—Continued

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Developed Impervious	nd area area (percent) ^a		83 34	93 45			76 31	86 —	92 —
	nds Woodla ing and oirs parks		6.6	5.5	13		16	6.6	5.1
(Wetlar ure includi reservo		0	0	0		Γ.	0	0
rshed area	Agricult		0	0	0			0	0
it of wate	Golf	Proctor Creek Watershed—monitoring sites	0	0	0		1.2	0	0
s (percen	al Other urban		9.3	13	4.2	ring sites	4.7	3.5	5.7
e categorie	, Commerci		9.3	14	6.6	edmonito	12	17	12
Land-us	Industrial, commercia		7.5	12	0	er Watershe	12	9.4	11
	Industrial		Ċİ	0	0	South Rive	1.7	6.7	13
	Residential	-	49	53	66		43	48	48
	USGS site name		Proctor Creek at Jackson Parkway, at Atlanta	Proctor Creek at Hortense Way, at Atlanta	Proctor Creek tributary at Spring Road, at Atlanta		South River at Forest Park Road, at Atlanta	South River at Macon Drive, near Hapeville.	South River at Springdale Road, at Atlanta
USGS	site identifier		02336526	02336517	023365218		02203655	02203620	02203603
Site	fication (fig. 1)		PRO-1	PRO-2	PRO-3		SOU-1	SOU-2	SOU-3

^a Source of percent impervious area: U.S. Geological Survey Land Cover Analysis Tool (LCAT), U.S. Geological Survey, 2009.

Sampling Sites

Sixty-four sampling sites representing three site types were established in the seven study watersheds. The first site type included 23 sites within the Nancy Creek (NAN), Sandy Creek (SAN), and Utoy Creek (UTO) watersheds. Because CSO outfalls were not located in these watersheds, they were designated as control basins. Any OWICs present in these streams probably represent "urban background." The second and third site types were located in the Intrenchment Creek (INT), Peachtree Creek (PEA), Proctor Creek (PRO), and South River (SOU) watersheds; some stream reaches in these watersheds receive CSOs. The second site type includes 27 sites located either upstream from CSO outfalls or in tributary basins not receiving CSOs. Only one site, however, was upstream from a CSO outfall in the INT watershed. The third type includes 14 sites located downstream from CSO outfalls and are commonly affected by CSOs during moderate to large storms. Although anecdotal information indicates that sanitary-sewer overflows occurred intermittently in all seven watersheds as a result of blockages or breaks in sewer lines, specific occurrences were not documented.

Previous Studies of OWICSs in the Environment

Since the early 1900s, the most common wastewater indicator was the 5-day biochemical oxygen demand (BOD₅). Other indicators such as total suspended solids concentration, concentration of methylene-blue active substances, and total or fecal coliform bacteria density were added later (U.S. Environmental Protection Agency, 1983). As wastewater treatment facilities moved to tertiary and advanced tertiary treatment in the late 1970s, those early measurements became increasingly unreliable as indicators of wastewater effluent. Studies for the U.S. Environmental Protection Agency's (USEPA) National Urban Runoff Program (NURP) showed that BOD₅, total suspended solids, and coliform bacteria density were exceptionally high in stormwater runoff, commonly masking the effects of wastewater effluent discharges to urban streams (U.S. Environmental Protection Agency, 1983).

Many streams, rivers, and lakes across the United States are impaired because of fecal coliform bacteria densities that exceed water-quality standards. Although many studies conclude that the source of high fecal coliform bacteria is related to human or confined-animal waste, few studies have been able to show a definitive relation, especially in urban areas. Within the past 10 years, several new methods have been developed and used by researchers to discover the source or sources of fecal coliform bacteria contamination in surface water and the relations among human, confined-animal, pet, or wildlife waste products. Some of these methods are variations of genetic fingerprinting using DNA profiles (ribotyping) of *Escherichia coli* (*E. coli*) bacteria isolated from known sources (such as human, dog, or cat) as references (Hartel and others, 1999; Carson and others, 2001). Because recent studies indicate these ribotyping efforts are not consistently reliable for identifying sources of fecal contamination (Stoeckel and others, 2004), researchers are using advances in analytical instrumentation and chemical methodologies to identify organic compounds common in wastewater effluent in order to isolate sources of human sewage contamination in ambient water (Buerge and others, 2003, 2006; Kolpin and others, 2004; Hinkle and others, 2005). These studies showed that prescription and over-thecounter pharmaceuticals, personal-care and personal-use products, detergent metabolites, and sterol compounds had the most promise for identifying sources of human sewage contamination.

Advances in the analytical chemistry of organic compounds and in laboratory instrumentation in the late 1980s and early 1990s resulted in more cost-effective methods and lower detection limits for the analysis of many organic compounds. Several studies used these advances and analyzed wastewater effluent, air, and natural water bodies for a variety of organic compounds found in food, beverages, or personal-care products used by humans (Simonich and others, 2000; Moll and others, 2001; Karthikeyan and Meyer, 2006).

General Descriptions of OWIC Classes

The sources of compounds listed in table 3 are numerous and diverse ranging from natural sources such as plant and wildlife communities to entirely anthropogenic sources such as fragrances and detergent metabolites. Treated and untreated wastewater effluent, atmospheric deposition, and urban runoff are the major pathways connecting natural and anthropogenic sources of fecal coliform bacteria and organic compounds to rivers, streams, and lakes.

Personal-Use Compounds

Personal-use compounds include fragrances added to lotions, soaps, and perfumes, compounds added to personalcare products such as camphor and methyl salicylate, and compounds in beverages such as caffeine or in tobacco such as cotinine, a nicotine metabolite. In a report to the U.S. Food and Drug Administration in 1994, the major tobacco companies listed at least 599 compounds that were added to tobacco during cigarette manufacturing. Several of these compounds grouped in the personal-use class of this report: acetophenone, benzophenone, caffeine, menthol, and methyl salicylate (Tobacco.org, 1994, 599 ingredients added to cigarettes, accessed March 12, 2007, at *http://www.tobacco. org/Resources/599ingredients.html*).

In a report by Frick and Zaugg (2003), caffeine and triclosan were detected in 69 and 100 percent of samples from WWTPs effluent in the northern part of Metropolitan Atlanta. In a study by Simonich and others (2000), the fragrances 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl cyclopenta- γ -2-benzopyran (HHCB) and 7-acetyl-1,1,3,4,4,6- hexamethyl

Table 3. Organic wastewater-indicator compounds analyzed in water samples from streams near Atlanta, GA, March 2003 to January 2006.

[CAS, Chemical Abstract Service; NWQL, USGS National Water Quality Laboratory; $\mu g/L$, microgram per liter; bold compounds are not included in the study because of excessive false positives in laboratory blanks or in blind blank samples, or they were not detected in any sample; italicized compounds are potential endocrine disruptors; —, not determined; β , beta; VOC, volatile organic compound]

Compound	CAS numberª	Parameter code ^b	NWQL reporting level (µg/L)	Study reporting level° (µg/L)	Possible uses or sources ^d			
Personal-use compounds								
3-Methyl-1(H)-indole (skatol)	83-34-1	62058	0.50	—	Fragrance, stench of feces and coal tar, tobacco			
3-tert-Butyl-4-hydroxyanisole (BHA)	25013-16-5	62059	5.0	2.5	Antioxidant and preservative; common food additive			
7-acetyl-1,1,3,4,4,6-hexamethyl tetra- hydronaphthalene (AHTN), tonalide	21145-77-7	62065	.50	.05	Musk fragrance, widespread and persistent in the environment			
Acetophenone ^e	98-86-2	62064	.50	.25	Detergent and tobacco fragrance, beverage flavor			
Benzophenone	119-61-9	62067	.50	.10	Fixative for perfumes and soaps, sunscreen, tobacco			
Caffeine ^e	58-08-2	50305	.50	.18	Stimulant added to beverages and tobacco			
Camphor	76-22-2	62070	.50	.05	Flavorant and fragrance in personal- care ointments			
Cotinine	486-56-6	62005	1.0	.10	Primary nicotine metabolite			
1,3,4,6,7,8-hexahydro-4,6,6,7,8, 8-hexamethyl cyclopenta-γ-2- benzopyran (HHCB, galaxolide) ^e	1222-05-5	62075	.50	.08	Musk fragrance			
Indole	120-72-9	62076	.50	.01	Fragrance in personal-care and house- hold products, pheromone in insect bait traps			
Isoborneol	124-76-5	62077	.50	.10	Fragrance in perfumes and disinfectants			
Isoquinoline	119-65-3	62079	.50	.25	Flavorant and fragrance			
Menthol	89-78-1	62080	.50	.10	Fragrance in tobacco, mouthwash, cough drops, and other personal-care products			
Methyl salicylate	119-36-8	62081	.50	.05	Ingredient in personal-care liniments, sun screens (UV-absorbant)			
N,N-diethyl-meta-toluamide (DEET) ^e	134-62-3	62082	.50	.34	Personal-use insect repellant			
Triclosan	3380-34-5	62090	1.0	.05	Disinfectant, antimicrobial soap additive			
Triethyl citrate (ethyl citrate)	77-93-0	62091	.50	.05	Cosmetics and pharmaceuticals, tobacco			
		Disinfectior	n compounds					
Tribromomethane (Bromoform)	75-25-2	34288	.50	.01	Water treatment disinfection byproduct and VOC			
Phenol	108-95-2	34466	.20	—	Disinfectant			
		Pesticide	compounds					
1,4-Dichlorobenzene (14DCB) ^e	106-46-7	34572	.50	.05	Deodorizer, moth repellant, fumigant			
Bromacil	314-40-9	04029	.50	.10	General-use herbicide			
Carbaryl	63-25-2	82680	1.0	.01	Crop and garden insecticide			
Chlorpyrifos	2921-88-2	38933	.50	.01	Insecticide for pest and termite control, restricted in 2001			
Diazinon	333-41-5	39572	.50	.01	Lawn and garden insecticide, restricted beginning in 2006			

12 Occurrence of Organic Wastewater-Indicator Compounds in Urban Streams of the Atlanta Area, Georgia, 2003–2006

 Table 3.
 Organic wastewater-indicator compounds analyzed in water samples from streams near Atlanta, GA, March 2003 to January 2006.—Continued

[CAS, Chemical Abstract Service; NWQL, USGS National Water Quality Laboratory; $\mu g/L$, microgram per liter; bold compounds are not included in the study because of excessive false positives in laboratory blanks or in blind blank samples, or they were not detected in any sample; italicized compounds are potential endocrine disruptors; —, not determined; β , beta; VOC, volatile organic compound]

Compound	CAS numberª	Parameter code ^b	NWQL reporting level (µg/L)	Study reporting level° (µg/L)	Possible uses or sources ^d			
Pesticide compounds—Continued								
Dichlorvos ^f	62-73-7	30218			Insecticide used in pet collars; naled or trichlofon degradate			
Metalaxyl	57837-19-1	50359	.50	.50	General-use fungicide for mildew, turf grass, blight			
Metolachlor	51218-45-2	39415	.50	.50	General-use herbicide			
Prometon	1610-18-0	04037	.50	.01	General-use herbicide for brush and weed removal from ditches and rights-of-way			
		Sterol co	mpounds					
Cholesterol ^g	57-88-5	62072	2.0	.25	Plant sterol; animal fecal sterol			
3-β-coprostanol ^g	360-68-9	62057	2.0	.25	Fecal sterol in carnivores			
β-Sitosterol ^g	83-46-5	62068	2.0	.25	Primarily a vegetation-derived sterol, but also found in animal feces			
β-Stigmastanol ^g	19466-47-8	62086	2.0	.25	Primarily a vegetation-derived sterol, but also found in animal feces			
		Industrial-us	e compounds					
Anthraquinone	84-65-1	62066	.50	.30	Dyes used in manufacturing of textiles, seed treatment, bird repellant			
Bisphenol-A	80-05-7	62069	1.0	.30	Plasticizer from the production of poly- carbonate resins, added to some flame retardant formulations			
Carbazole	86-74-8	62071	.50	.03	Production of dyes and pharmaceuticals			
Isophorone	78-59-1	34409	.50	.50	Solvent for lacquer, plastic, resin, silicon, oil			
<i>d</i> -Limonene	5989-27-5	62073	.50	.01	Fungicide, antiviral, citrus fragrance, ad- ditive in household cleaning products			
Tetrachloroethene (PCE)	127-18-4	34476	.50	.05	Solvent used for degreasing purposes in dry cleaning operations, and in a variety of manufacturing operations and VOC.			
Triphenyl phosphate (TPP)	115-86-6	62092	.50	.10	Plasticizer in resin, wax, roofing paper, flame retardant formulations			
	Polyc	yclic aromatic l	hydrocarbons	(PAHs)				
Anthracene	120-12-7	34221	.50	.07	Compound common in tar, diesel fuel, or crude oil			
Benzo[a]pyrene	50-32-8	34248	.50	.50	Regulated PAH, used in cancer research			
<i>p</i> -Cresol	106-44-5	62084	1.0	.20	Wood preservative and combustion byproduct			
Fluoranthene	206-44-0	34377	.50	.05	Component of coal tar and asphalt (street paving)			
Pentachlorophenol (PCP)	87-86-5	34459	2.0	.25	Wood preservative			
Phenanthrene	85-01-8	34462	.50	.05	Component of tar, diesel fuel, or crude oil			
Pyrene	129-00-0	34470	.50	.05	Component of tar, diesel fuel, or crude oil			

Table 3. Organic wastewater-indicator compounds analyzed in water samples from streams near Atlanta, GA, March 2003 to January 2006.—Continued

[CAS, Chemical Abstract Service; NWQL, USGS National Water Quality Laboratory; $\mu g/L$, microgram per liter; bold compounds are not included in the study because of excessive false positives in laboratory blanks or in blind blank samples, or they were not detected in any sample; italicized compounds are potential endocrine disruptors; —, not determined; β , beta; VOC, volatile organic compound]

Compound	CAS numberª	Parameter code ^b	NWQL reporting level (µg/L)	Study reporting level° (µg/L)	Possible uses or sources ^d			
Automotive-use compounds								
1-Methylnaphthalene ^g	90-12-0	62054	0.50	0.04	2-5 percent of gasoline, diesel fuel, or crude oil			
2-Methylnaphthalene ^g	91-57-6	62056	.50	.04	2-5 percent of gasoline, diesel fuel, or crude oil			
2,6-Dimethylnaphthalene	581-42-0	62055	.50	.04	Diesel fuel or kerosene			
5-Methyl-1H-benzotriazole	136-85-6	62063	2.0	.10	Anticorrosive used in antifreeze and deicer products			
Isopropylbenzene (cumene)	98-82-8	62078	.50	.05	Fuels, paint thinner, production of phenol and acetone			
Naphthalene	91-20-3	34443	.50	.03	Gasoline ingredient (about 10 percent), moth repellant			
Non-ionic detergent metabolites (NDMCs)								
4-Cumylphenol	599-64-4	62060	1.0	1.0	Non-ionic detergent or detergent metabolite			
<i>p-Nonylphenol (total)</i> ^g	84852-15-3	62085	5.0	.33	Non-ionic detergent			
4-Nonylphenol diethoxylate (NPEO2)	26027-38-3	62083	5.0	1.1	Detergent metabolite			
4-Octylphenol monoethoxylate (OPEO1) ^g	26636-32-8	61706	1.0	.09	Detergent metabolite			
4-Octylphenol diethoxylate (OPEO2)	26636-32-8	61705	1.0	.05	Detergent metabolite			
4-n-Octylphenol	1806-26-4	62061	1.0	1.0	Non-ionic detergent			
4- <i>tert</i> -Octylphenol ^g	140-66-9	62062	1.0	.02	Non-ionic detergent			
Flame-retardant compounds								
Tributyl phosphate (TBP)	126-73-8	62089	.50	.15	Anti-foaming agent, fire retardant			
Tris(2-butoxyethyl) phosphate (TBEP) ^g	78-51-3	62093	.50	.10	Fire retardant			
Tris(2-chloroethyl) phosphate (TCEP)	115-96-8	62087	.50	.05	Plasticizer, fire retardant			
Tris(dichloroisopropyl) phosphate (TDCPP)	13674-87-8	62088	.50	.08	Fire retardant			

^aCAS Registry Number[®] is a Registered Trademark of the American Chemical Society. CAS recommends the verification of CAS Registry Numbers through CAS Client Services at *http://www.cas.org.*

^bParameter codes provide a numeric description of chemical compounds with the analytical results for samples stored in the USGS National Water Information System (NWIS).

^cThese values are determined by the distribution frequency of compound concentrations in all water samples collected during the study. Distributions are listed in table 8.

^dCambridgeSoft Corporation (2006); National Institute of Standards and Technology (2006); Supresta Corporation, Inc. (2007); Extension Toxicology Network (1996a,b,c).

° Values re-censored because of laboratory or field blank contamination, or because of false positives in blind blank samples.

^fRemoved from lab schedule 1433 because of low recovery (Zaugg and Leiker, 2006).

^gAnalytical results are given as estimates because analytical performance was highly variable.

tetrahydronaphthalene (AHTN), and isoborneol, and methyl salicylate were removed by WWTPs with activated sludge technology at 91, 89, 99, and 99 percent efficiency, with average effluent concentrations of 1.17, 1.18, 0.023, 0.024 microgram per liter (μ g/L), respectively. Simonich and others (2000) and Lee and Rasmussen (2006) also showed that fragrances were removed more efficiently in a WWTP using activated sludge technology than one using trickling filter technology. Additionally, Matamoros and others (2007), showed that traditional WWTPs remove 99 percent of influent caffeine and 75-90 percent of HHCB and AHTN concentrations. Another personal-use compound often found in association with other fragrances is indole. Concentrated indole has a strong fecal odor and has been used as a pheromone in insect-trap baits, but it is most commonly used in the manufacture of fragrances, especially synthetic jasmine oil (U.S. National Library of Medicine, 2008).

Some fragrances also have been detected in air samples and may be a component in atmospheric deposition. In a study by Peck and Hornbuckle (2006), air samples collected in urban Cedar Rapids, IA, and in urban areas around Lake Erie contained gas-phase HHCB and AHTN at concentrations that increased along an environment gradient representing rural, suburban, and urban air masses. The concentrations were highest in air samples from the urban air mass. The study concluded that populated areas are major sources of HHCB and AHTN and that the frequency of detection and concentrations decrease in step with a decreasing population gradient.

Caffeine concentrations in treated wastewater effluent are so small that further dilution in receiving waters results in nearly undetectable concentrations (Buerge and others, 2006). Caffeine concentrations in influents to and effluents from Swiss WWTPs were 7-73 µg/L and 0.03-9.5 µg/L, respectively, resulting in a removal efficiency of 81-99.9 percent during treatment (Buerge and others, 2003). Because caffeine concentrations in untreated wastewater are orders of magnitude higher than in WWTP effluents, even a small percentage of untreated wastewater can substantially increase the load of caffeine in receiving waters. For example, untreated wastewater that comprises only 1 percent of the stream discharge delivers more than half of the caffeine load in the stream. Furthermore, when that percentage of untreated wastewater increases to 10 percent of the discharge, the wastewater delivers more than 90 percent of the total caffeine load to a stream (Buerge and others, 2006).

Atmospheric deposition probably is not a source of the antimicrobial ingredient triclosan in hand soap, because that compound has not been detected in air samples. A study by Halden and Paull (2005) showed that 96 percent of triclosan was removed by WWTPs using activated sludge technology. In addition, the study showed that 50–56 percent of the annual triclosan load to streams and lakes came from WWTPs using activated sludge technology because that technology was more common in the study watershed, while 3–5 percent of the annual triclosan load came from CSOs. The estimated half-life

of triclosan is 60 days. Triclosan and a degradation compound, methyl triclosan, can have acute and chronic detrimental effects on aquatic organisms and may bioaccumulate in fish tissue (Glaser, 2004; Institute for Environment and Health, 2005).

Disinfectant Compounds

Bromoform is the only disinfectant-derived compound addressed in this report. Chlorine is commonly used to disinfect water before it is released to a municipal drinking-water system or to disinfect treated-wastewater effluent before it's discharged to a body of water. Chlorine can oxidize bromide ions in water, creating hypobromous acid, which then reacts with endogenous organic compounds such as humic or fulvic acid to produce bromoform (Agency for Toxic Substance and Disease Registry, 2005). Between 1989 and 1993, 11 percent of treated-wastewater effluent samples in New York contained bromoform concentrations ranging from 0.2 to 12 μ g/L (Stubin and others, 1996).

Pesticide Compounds

Six pesticides are addressed in this report: three insecticides, two herbicides, and a fumigant. The insecticides include carbaryl, chlorpyrifos, and diazinon. Carbaryl is the active ingredient in the insecticide Sevin[®], which is commonly used to dust vegetable plants in home gardens, typically a warm-weather activity. Carbaryl degrades rapidly in soil and water by photolysis and microbially mediated hydrolysis. The half-life ranges from 7 to 14 days in sandy loam soil, up to 30 days in clay loam soil, and up to 10 days in water with neutral pH (Extension Toxicology Network, 1996a).

Chlorpyrifos is a broad-spectrum organophosphate insecticide originally registered for mosquito control but later was registered for termite, flea, tick, fire ant, lice, and agricultural insect control (Extension Toxicology Network, 1996a). Dursban[®] was the common trade name for the product containing chlorpyrifos available to homeowners. Chlorpyrifos is highly toxic to birds, bees, and aquatic organisms. Because of this toxicity, the sale of chlorpyrifos to homeowners ended in July 2000, and its use in residential pre-construction termite control by professionals ended on December 31, 2005 (U.S. Environmental Protection Agency, 2002); however, professional applications to crops, orchards, and golf courses, and other agricultural uses have not been banned. The persistence of chlorpyrifos in soil depends on the soil type and its organic content (Wauchope and others, 1992). Information compiled by Howard (1991) indicated that chlorpyrifos is unstable in water because it is easily hydrolyzed, especially as water temperature increases. The rate of hydrolysis decreases 2.5- to 3-fold with each 10-°C drop in water temperature. The hydrolysis of chlorpyrifos is constant in acidic to neutral waters (at pH 7.0 and 25 °C, the half-life is 35-78 days), but increases in alkaline waters.

Diazinon is an insecticide used primarily for residential pest control during the warm season. Because insects become more prevalent in warm weather, diazinon use would be expected to increase as well. Diazinon is commonly detected in urban storm runoff (U.S. Environmental Protection Agency, 1983); therefore, most of the diazinon detected in samples collected during this study was probably delivered to streams in the Atlanta area in that manner. Furthermore, diazinon commonly is detected in CSOs because a substantial percentage of the water in CSOs is urban storm runoff (U.S. Environmental Protection Agency, 1983). Diazinon is slightly water soluble and is rapidly degraded in soil (half-life is 2-4 weeks) and in acidic water (pH less than 7, half-life is 12 hours), but may persist in neutral or alkaline water (pH greater than 7, half-life is 6 months; Extension Toxicology Network, 1996b). In addition, diazinon is highly toxic to birds, bees, and aquatic life. This toxicity led the USEPA to prohibit the sale of diazinon for non-professional residential use beginning December 31, 2004 (U.S. Environmental Protection Agency, 2007); however, it probably continued to be applied until products purchased before that date were exhausted.

The herbicides addressed in this report include bromacil and prometon. Bromacil is an herbicide used throughout the year to control brush on non-crop land, and rights-of-way and in the selective control of perennial grasses and weeds (Extension Toxicology Network, 1996c). Bromacil is moderately water soluble, and its persistence in soil depends on the amount of organic matter in the soil (Wauchope and others, 1992). Bromacil's half-life in river water is about 2 months (U.S. Environmental Protection Agency, 1975). Prometon is a triazine herbicide commonly used for warm-season weed control, especially around ditches, roadway medians, and rights-of-way. Prometon is persistent and highly mobile in the environment; half-life values are on the order of 1–2 years (National Pesticide Information Center, 1994).

The fumigant 1,4-dichlorobenzene (14DCB) is the active ingredient in moth balls, an insect repellant commonly associated with the storage of clothing, and in toilet deodorizer blocks (Agency for Toxic Substances and Disease Registry, 2006); thus, 14DCB may be detected in streams receiving CSOs or affected by leaking or broken sanitary sewer pipes, especially during the cool season when its volatilization rate is lower than during the warm season.

Sterol Compounds

The four sterol compounds addressed in this report include cholesterol, 3- β -coprostanol (coprostanol), β -sitosterol (sitosterol), and β -stigmastanol (stigmastanol). Cholesterol is a plant- and animal-derived sterol and coprostanol is a human- and mammal-derived sterol (Martin and others, 1973). Although sitosterol and stigmastanol were once considered vegetation sterols, recent publications report that those sterols are also present in mammal and bird feces (Shah and others, 2007). Coprostanol was first identified as a potential indicator of fecal pollution by Goodfellow and others (1977). Since that publication, coprostanol has been used as an indicator of sewage contamination in a large number of studies, especially those in estuaries or marine environments (Pocklington and others, 1987; Grimalt and others, 1990; Leeming and Nichols, 1996; Isobe and others, 2004). Shah and others (2007) concluded that among the eight sterols investigated no single sterol was a conclusive indicator of human fecal contamination; however, sterol ratios could identify which fecal-contamination mixtures had a human contribution.

Industrial-Use Compounds

The industrial-use compounds anthraquinone, bisphenol-A, carbazole, d-limonene, tetrachloroethene (PCE), and triphenyl phosphate (TPP) are commonly used in the manufacturing industry. Anthraquinone is used to repel geese and other birds from areas where they have either become a nuisance, such as at seed storage facilities, golf courses, and parks, or a safety hazard at places such as airports (U.S. Environmental Protection Agency, 1998). This compound commonly is used in the manufacturing of dyes and as an additive in the paper pulping industry (U.S. National Library of Medicine, 2008). In the environment, anthraguinone can be produced from the photolytic and biodegradation of anthracene. In addition, the chlorination of water containing anthracene may produce anthraquinone by oxidation (U.S. National Library of Medicine, 2008). Anthraquinone can exist in the vapor phase and in a particulate phase in the atmosphere (Bidleman, 1988) and has been measured in rainwater and atmospheric deposition in Portland, OR (Ligocki and others, 1985a, 1985b). Anthraquinone was detected in exhaust particulates from vehicles with catalytic converters (4.4 micrograms per kilometer driven, $\mu g/km$) and road dust in Los Angeles, California (Rogge and others, 1993).

The compound bisphenol-A is used to make the epoxybased surface coatings used in containers, bottles, and metal cans that come in contact with food. This compound also is used to manufacture polycarbonate plastic baby bottles and water carboy containers (U.S. Environmental Protection Agency, 2006). Bisphenol-A is also an ingredient in some flame retardant formulations such as FYRflex[™], which is added to resins (Supresta Corporation, 2007). A growing concern in the health services community is that bisphenol-A is capable of disrupting endocrine systems to the detriment of gender development and metabolic health in animals and humans. Krishnan and others (1993) was among the first to show that bisphenol-A affects estrogen receptors in cells and that it can migrate out of polycarbonate plastic and into the contents of the container. McNeal and others (2000) showed that distilled water contained bisphenol-A concentrations as great as 4.7 µg/L after 39 weeks of storage in polycarbonate carboys. Ehrenberg (2008) summarizes recent research that indicates bisphenol-A suppresses a hormone in humans that protects them from heart attacks and type-2 diabetes.

Bisphenol-A is probably not a specific indicator of sewage effluent because even though it is present in food and beverage containers commonly used in most households in the United States, it is also found in common flame-retardant formulations (Supresta Corporation, 2007) and is probably a contaminant in urban runoff. Rudel and others (1998) showed that treated wastewater from Cape Cod, MA, contained bisphenol-A at an average concentration of 0.038 μ g/L; however, the bisphenol-A concentration was four times higher in untreated septic-tank effluent, indicating that wastewater treatment facilities may remove at least 75 percent of the influent concentration.

Carbazole is found in coal, petroleum, and peat and may be released to the environment through incomplete combustion of those substances (Smith and others, 1978). Furthermore, carbazole is used in the manufacturing of insecticides, rubber antioxidants, lubricants, and in odor inhibiters for detergents (Sax and Lewis, 1987, p. 216). This compound was detected in atmospheric deposition samples from Pasadena, CA, during September 1972 (Schuetzle and others, 1975).

Tetrachloroethene (PCE) is used for dry cleaning and during the processing and finishing of textiles, in cold cleaning and vapor degreasing of metals, in the synthesis of various fluorocarbon compounds, and as a heat-exchange fluid (Lewis, 1997). Because PCE is a volatile organic compound, it evaporates quickly during use and has a volatilization half-life from soil of 1.2–5.4 hours, depending on the soil organic content (Riddick and others, 1986). Once evaporated, PCE exists solely as a vapor in the atmosphere, and based on calculations using rate constants, is expected to degrade slowly (half-life of 96 days) by photochemical de-hydroxylation (Riddick and others, 1986; U.S. Environmental Protection Agency, 1981). Andelman (1985) showed that mean atmospheric PCE concentrations for seven United States cities ranged from 0.29 to 0.59 parts per billion (ppb) with a maximum concentration of 7.6 ppb. Atmospheric PCE was detected on September 1974 in the White Face Mountains of New York-one of the more remote areas of the United Statesat concentrations ranging from 0.02 to 0.19 ppb (Lillian and others, 1975). Pankow and others (1997) suggest that the urban atmosphere may be an important nonpoint source of PCE and other volatile organic compounds to shallow groundwater in urban areas.

Wastewater effluent commonly contains PCE at detectable concentrations because of intentional or inadvertent disposal in sanitary sewer systems (U.S. Environmental Protection Agency, 1981). Effluent from a wastewater treatment facility in Maryland contained PCE concentrations from 8 to 129 ppb (U.S. Environmental Protection Agency, 1981). Fifteen percent of samples from treated wastewater effluent in the Atlanta metropolitan area contained detectable concentrations of PCE with a maximum concentration of 0.53 μ g/L (Frick and Zaugg, 2003). In addition, Sando and others (2006) showed that treated wastewater effluent near Sioux Falls, SD, had a median PCE concentration of 0.087 μ g/L.

The compound TPP is an ingredient of the FYROL™ and FYRQUEL[™] family of flame-retardant formulations (Supresta Corporation, 2007). These flame retardants are used widely in phenolic and phenylene-oxide based resins used to manufacture electrical and automobile components, as a non-flammable plasticizer in cellulose acetate for photographic films, in roofing paper, and in hydraulic fluids and lubricating oils (O'Neil, 2001; World Health Organization, 1998a). In the environment, TPP has been measured in ambient air samples from rural and urban areas. In one study, urban-measured TPP concentrations were 2–10 times higher than those in rural air (World Health Organization, 1998a). Marklund and others (2005) showed that snow samples within 2 meters (6.56 ft) of road intersections in northern Sweden contained detectable concentrations of TPP ranging from 11 to 30 parts per trillion (ppt). In addition, snow samples near an airport runway and staging area contained TPP at a concentration of about 25 ppb. Based on samples of vehicle and aircraft oil, hydraulic fluid, and lubricant products commonly used in that area, Marklund and others (2005) concluded that leakage of hydraulic and transmission fluids and engine oils from vehicles and aircraft are probable sources of TPP measured at the sampled sites. This study also showed detectable amounts of TPP in air and atmospheric deposition samples.

In several studies, nearly all water samples collected downstream of urban areas contained TPP at low concentrations, even though TPP has a high soil adsorption ratio and degrades rapidly in aqueous environments. Concentrations of TPP in wastewater effluent are at least an order of magnitude lower than those in wastewater influent (World Health Organization, 1998a).

The compound *d*-limonene (limonene) is found in the environment from natural and anthropogenic sources. Limonene is one of several monoterpene compounds released to the atmosphere from certain trees and shrubs and is found in the peel of citrus fruits. Anthropogenic sources include solvents used by industry to degrease metals before painting and by the electronic and printing industries. Limonene also is used as a flavor and fragrance additive in food, household cleaning products, and perfumes (World Health Organization, 1998b).

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) have been detected in gaseous and particulate air samples by several researchers. Atmospheric removal of PAHs by condensation and deposition may limit the usefulness of PAHs as a chemical marker of wastewater contamination, especially in urban areas. In one study for example, gas-phase concentrations of PAHs were 50 times greater in an urban air mass than in a rural air mass and showed significant seasonality (Gustafson and Dickhut, 1997). Wagrowski and Hites (1997) found that vegetation was able to scavenge PAH-associated particulates from air and found that PAH burdens in urban areas were 10 times higher than those in rural areas. In that study, the PAHs phenanthrene, fluoranthene, and pyrene were found in urban and rural samples, but anthracene was found only in urban samples. In another study where urban air samples were collected from a highway tunnel, 76 percent of the total PAH mass consisted of a 2-ring compound (naphthalene), 16 percent of the mass consisted of 3-ring compounds (phenanthrene and anthracene), and 4.3 percent of the mass consisted of 4-ring compounds (fluoranthene and pyrene; Khalili and others, 1995). Furthermore, in wood smoke samples, 69 percent of the PAH mass consisted of 3-ring compounds (anthracene and phenanthrene), and 11 percent consisted of a 2-ring compound (naphthalene). Also during this study, gasoline engines released more of the 2-ring PAH (naphthalene, 55 percent), 3-ring compounds (antharcene and phenanthrene, 18 percent), and 4-ring compounds (such as fluoranthene and pyrene) than did diesel engines. Conversely, diesel engines released more of the 3-ring PAHs (56 percent) and less of the 5-ring and 4-ring PAHs than did gasoline engines (Khalili and others, 1995). Interestingly, Khalili and others (1995) reported that phenanthrene, fluoranthene, and pyrene were associated with road-salt particles (from salting roads during winter), which appear to be absorbing volatile PAH emissions from motor vehicles. In addition, oil combustion is associated with high loadings of the more volatile PAHs (fluorene, fluoranthene, and pyrene; Khalili and others, 1995).

The deposition of PAH-associated airborne particulates and aerosols onto roofs, roads, parking lots, and vegetation may contribute a large portion of the PAH load in urban storm runoff (Lopes and others, 1998). Ligocki and others (1985a, 1985b) measured anthracene, phenanthrene, pyrene, and fluoranthene in filtered and unfiltered rainwater during storms in the urban area of Portland, OR. The dissolved concentrations of these PAHs represented gaseous exchange of PAH aerosols and those associated with particulates scavenged from the atmosphere during rainfall in the urban area. These results indicate that rainfall and dry deposition probably contribute to PAH accumulation on impervious areas, which is subsequently washed off during storm runoff. Regardless of storm or dryweather origins, substantial amounts of PAHs are transported to streams and rivers in urban runoff (U.S. Environmental Protection Agency, 1983).

Automotive-Use Compounds

The chemicals naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene, isopropylbenzene, and 5-methyl-1H-benzotriazole represent the automotive-use compounds in this study. The first five chemicals are common ingredients at proportionally small amounts in automobile gasoline (Smallwood and others, 2002). The compound 5-methyl-1H-benzotriazole is an anticorrosive and antioxidant chemical in the anti-icing and de-icing fluids used on aircraft and in antifreeze products for automobile radiators (Corsi and others, 2006).

Non-ionic Detergent Metabolite Compounds

Compounds in this class include *p*-nonylphenol, the nonylphenol and octylphenol ethoxylates, and 4-*tert*-octylphenol. These compounds are suspected endocrine disruptors because their chemical structure is similar to estrogenic hormones. Research has shown that these compounds have adverse affects on gender and gonad development in fish, amphibians, reptiles, and possibly humans (Soto and others, 1991; Naylor and others, 1992; Jobling and Sumpter, 1993; White and others, 1994; Routledge and Sumpter, 1996; Routledge and others, 1998; Mitchelmore and Rice, 2006).

The compound *p*-nonylphenol is used as a non-ionic surfactant, lube oil additive, fungicide, and antioxidant for polymers (Lewis, 1997) and may be detected in the environment as the byproduct of nonyl polyethoxylate degradation (U.S. National Library of Medicine, 2008). The compound *p*-nonylphenol has a strong affinity for sediment and does not partition readily into water.

The nonylphenol and octylphenol ethoxylates are ingredients in a large number of household and industrial products. These compounds are major components of anti-icing and de-icing liquids used on aircraft at many airports across the United States (Corsi and others, 2003). The compound 4-nonylphenol diethoxylate (NPEO2) is used as a surfactant, emulsifier, and wetting agent in cosmetics, detergents, and antiseptic cleansers (O'Neil, 2001, p. 1196). Several studies have analyzed samples for non-ionic detergent metabolites in wastewater entering WWTPs and in WWTP effluents to determine the degree of removal during the treatment process. Several wastewater treatment facilities in the United States removed 93 percent of the nonylphenol and octylphenol ethoxylates from winter influent and about 99 percent from summer influent (Loyo-Rosales and others, 2007). In addition, the concentrations of nonylphenol ethoxylates in treated effluent ranged from 1.58 μ g/L in the summer to 32.3 μ g/L in the winter. Likewise, the effluent concentration of the octylphenol ethoxylates ranged from 0.005 μ g/L in the summer to $2.08 \,\mu\text{g/L}$ in the winter. Sewage effluent from residential areas had substantially higher concentrations of both ethoxylate compounds than sewage effluent from industrial or commercial areas (Loyo-Rosales and others, 2007).

Flame Retardants

The four flame-retardant compounds analyzed in the COA water samples (table 3) are considered entirely anthropogenic by the World Health Organization (World Health Organization, 1998c). Tris(2-butoxyethyl) phosphate (TBEP) is an ingredient in floor polishes and is used as a plasticizer in the manufacture of rubber and plastics. This compound is readily sorbed to soil particles and can degrade substantially within 15 days in water or soil. Marklund and others (2005) reported that snow samples within 2 meters (6.56 ft) of road intersections and in an airport parking area

of northern Sweden contained TBEP at concentrations ranging from 7 to 94 ppb and were 6–45 times greater than concentrations in samples from a reference site; however, TBEP was not detected in reference samples of automotive waste oil, automotive and aircraft hydraulic fluid, or unused engine oil. Marklund and others (2005) concluded that the source of TBEP was pedestrian traffic from the airport terminal where floor polishes and waxes were used on the floors. Wastewater treatment plant measurements and semi-continuous sludge laboratory tests have indicated that more than 80 percent of TBEP in wastewater influent is removed during treatment (World Health Organization, 1998c).

The compound tris(2-chloroethyl) phosphate (TCEP) is used to make polyester resins, polyacrylates, polyurethanes, and cellulose derivatives (World Health Organization, 1998d). Marklund and others (2005) reported that snow samples from an airport parking and runway area of northern Sweden had TCEP concentrations ranging from 29 to 39 ppb, nearly six times greater than concentrations in samples from a reference site; however, TCEP was not detected in reference samples of automotive waste oil, automotive and aircraft hydraulic fluid, or unused engine oil. In addition, TCEP was measured in dry atmospheric deposition at an average deposition rate of 550 nanograms per square meter (ng/m²), corresponding to a concentration of 87 ppb in combined wet (snowfall) and dry deposition samples. Aston and others (1996) reported that TCEP and the flame retardant tris(dichloroisopropyl) phosphate (TDCPP) were associated with particles sorbed to pine needles in the Sierra Nevada range in central California, indicating that atmospheric deposition may be a substantial source of those compounds to surface waters. The compound TCEP is one of many flame retardants found in natural waters and WWTP effluent that degrade slowly. This compound has been detected in WWTP effluents at concentrations up to 1.2 µg/L (World Health Organization, 1983).

Marklund and others (2005) reported that snow samples collected from a parking area at an airport and one of its runways in northern Sweden contained concentrations of tributyl phosphate (TBP) ranging from 2.1 to 25 parts per million (ppm). A reference sample of a commonly available hydraulic fluid used in aircraft had a TBP concentration of 190,000 ppm. Detectable amounts of TBP were measured in air and atmospheric deposition samples at the airport. Marklund and others (2005) concluded that the probable sources of TPP detected at the airport sites were hydraulic fluid leaking onto the aircraft parking areas and the condensation of volatilized hydraulic fluid onto airborne particles with subsequent deposition in the airport vicinity.

Methods of Study

Synoptic and long-term monitoring networks containing multiple sites in each watershed were established for waterquality sampling during this study (fig. 1). During March and June 2003, water-quality samples were collected at the synoptic sites under low-flow (June) and high-flow (March) conditions. The paired high- and low-flow approach may help to identify the relative effect of point (low flow) and nonpoint sources (high flow) on the water quality in Atlanta streams.

Forty-three stream sites were selected for the synoptic network. The synoptic sites were distributed among the seven study watersheds as follows: 11 sites in the South River watershed, 3 in the Intrenchment Creek watershed, 7 in the Peachtree Creek watershed, 4 in the Nancy Creek watershed, 6 in the Proctor Creek watershed, 3 in the Sandy Creek watershed, and 9 in the Utoy Creek watershed (table 1). Thirty of the 43 synoptic sites were located on tributaries to the main stream in their respective watersheds. These tributary sites were important in identifying streams that may contribute a substantial contaminant load to the mainstem stream and in establishing the most efficient location for each long-term monitoring site.

Twenty stream sites in the long-term monitoring network were established by August 2003 (fig. 1). An additional site on Woodall Creek (initially a synoptic site) was added in January 2005, bringing the long-term monitoring network to 21 sites (table 1). Thirteen sites, including Woodall Creek, were outfitted with streamgaging equipment, and 11 of those sites also were equipped with continuous water-quality monitors. The monitors consisted of a five-parameter data sonde to monitor stream temperature, dissolved oxygen, stream pH, specific conductance, and turbidity. The continuous hourly data from these sites were accessible in real time. At 11 of these 13 sites, storm samples were collected with programmable autosamplers. Of the 21 monitoring sites, 8 sites were not instrumented, and water-quality samples were collected manually once a month.

Streamflow, Meteorological, and Water-Quality Measurements

Four types of data were collected during the study period: (1) continuous streamflow at gaging stations, (2) instantaneous streamflow during sample collection at gaged and ungaged sites, (3) continuous stream-water-quality properties with an in situ five-parameter data sonde, and (4) instantaneous stream-water-quality properties. Thirteen USGS streamgaging stations were either newly established or previously existed in the study area (table 1): one in the Intrenchment Creek watershed (INT-1), two in the Nancy Creek watershed (NAN-1, NAN-3), four in the Peachtree Creek watershed (PEA-2, PEA-4, PEA-5, WOO-1), two in the Proctor Creek watershed (PRO-1, PRO-2), one in the Sandy Creek watershed (SAN-1), one in the South River watershed (SOU-1), and two in the Utoy Creek watershed (UTO-1, UTO-3). All 13 gaging stations are part of the USGS Georgia Stream-Discharge Measurement Network. Streamflow was measured in two ways during the study period. (1) Streamflow was measured manually at least six times per year at instrumented sites to develop rating curves and when samples were collected at

non-instrumented sites. Depending on flow conditions and stream clarity, a handheld velocity meter, an acoustic Doppler velocimeter, or an acoustic Doppler current profiler was used to measure and compute streamflow. (2) Streamflow was estimated continuously using a rating curve developed for each instrumented site. Streamflow measurements are made in accordance with published methods and techniques approved by the USGS Office of Surface Water (Buchanan and Somers, 1969; Rantz, 1982a,b; Kennedy, 1984; Oberg and others, 2005). Continuously measured gage heights and meteorological measurements at each gaging station were transmitted hourly by a satellite data-collection platform to the USGS Georgia Water Science Center (GAWSC) where the data were checked, the discharge was estimated from the rating curve, and the data were stored in the Automated Data Processing System database of the USGS National Water Information System (NWIS).

The only meteorological data used in this report is total daily rainfall in inches and daily maximum rainfall intensity in inches per hour. These data were calculated using 15-minute unit value measurements for the 24-hour period preceding sample collection. In addition, antecedent rainfall was calculated from rainfall data. This calculation is the number of days between sample collection and the last date that total daily rainfall exceeded 0.5 inch.

Instantaneous water-quality properties measured in the field were pH, specific conductance, dissolved oxygen, barometric pressure, water temperature, and turbidity (table 4). These properties were measured manually at all sites when samples were collected and continuously logged to a datacollection platform at all instrumented sites using a permanently installed (in situ) YSI model 6820 water-quality sonde. Continuous measurements of stream-water-quality properties were transmitted to the GAWSC hourly by satellite uplink. During the collection of water samples, stream-water-quality properties were measured directly in the stream or from composited, automatically collected samples. Periodic measurements were made at five locations along the stream cross section to determine the degree of stream mixing at each site. The water-quality sondes used for manual measurements were calibrated using published USGS protocols and procedures (Wilde, variously dated; Wilde and others, 2004). The waterquality sondes were maintained weekly and field checked for fouling, calibration loss, and drift following published USGS procedures (Wagner and others, 2006). Quality-control criteria for field equipment and measurements of stream-water-quality properties are listed in table 4.

Collection, Processing, and Quality Assurance of Water Samples

During the synoptic sampling phase of this study, only water-quality data were collected. These data included instantaneous measurements of dissolved oxygen (DO), pH, specific conductance (SC), turbidity, and water temperature using a five-parameter water-quality sonde. Water samples were analyzed at the USGS Panola Mountain Research Laboratory (PMRL) in Atlanta, GA, for turbidity, major ions, and nutrients, and at the USGS National Water Quality Laboratory (NWQL) in Denver, CO, for trace elements and OWICs. The synoptic sampling in Atlanta streams occurred during two streamflow conditions: (1) storm and non-storm high flows during March–July 2003, and (2) low-flow or base-flow conditions in late July 2003. Each synoptic site was sampled only once during the two time periods.

During the long-term monitoring phase, continuous streamflow data were collected at 13 sites, but continuous stream-water-quality properties were measured at 11 of the 13 instrumented sites. Instantaneous streamflow was measured at eight sites during sample collection. Water-quality samples were manually collected at 20 monitoring sites during highand low-flow periods from August 2003 to January 2005 and at 21 monitoring sites from January 2005 to January 2006. The study design included monthly manual sample collection at all sites during non-storm periods and automatic sampling during storm runoff at selected sites (fig. 2). The automatic samplers complimented manual sampling by allowing sample collection at discrete points at pre-selected stream stages along the storm hydrograph. Automatic samplers accomplished two purposes: (1) enabled the collection of storm samples at sites where manual sampling was impossible because of flashiness (rapid rise and fall of stream stage) of storm runoff and manpower limitations, and (2) allowed the capture of the initial increase in streamflow caused by storm runoff, commonly called the "first flush" of runoff. The "first flush" is a common phenomenon that typically contains substantial amounts of suspended sediment and chemical or bacterial constituents (Larson and others, 1999).



Figure 2. Types of samples collected for the Atlanta urban area water-quality monitoring study. [EWI, equal-width interval]

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Table 4. Summary of calibration information for water-quality instruments used to measure field water-quality properties.

[NIST, National Institute of Standards and Technology; °C, degrees Celsius; FSU, Field Services Units; %, percent; μ S/cm, microsiemens per centimeter; \leq , less than or equal to; mg/L, milligram per liter; Hg, mercury]

Parameter	Calibration method used	Acceptance criteria and response if not acceptable	Calibration frequency and location	References for calibration and use
Water temperature	NIST-certified thermister	Calibrated accuracy is within 0.2 °C, for thermistor ther- mometer, and 0.5 °C for liquid-filled thermometer. Return to manufacturer or replace.	Annual five-point calibra- tion at project lab or FSU. Additional two- point calibration checks two to three times annually.	Wilde, 2006; see manu- facturer's instructions.
Specific conductance (SC)	Standard solution with SC value greater than but close to the highest expected value.	Within 3% when values are greater than 100 μ S/cm; or within 5% when values are less than or equal to 100 μ S/cm. Clean or replace sensor. Replace calibration standards.	Onsite calibration prior to making measurement or during continuous monitor maintenance.	Radtke and others, 2005; Wagner and others, 2006; see manufac- turer's instructions.
рН	Two-point calibration, bracketing expected values. A third standard check maybe required if an alkalinity titration will be made.	Electrode slope response must be greater than or equal to 95% of theoretical response. Clean electrode, replace if necessary. Thermistor should be within \pm 0.2 °C if automatic temperature compensation feature is used.	Onsite calibration prior to making measurement or during continuous monitor maintenance.	Wagner and others, 2006; Wilde, 2006; see manu- facturer's instructions.
Dissolved oxygen (DO)	Air calibration in water or air calibration in water-saturated air (probe wrapped in wet towel). Equilibrate for 15 minutes.	Zero-DO solution check should be \leq 0.2 mg/L; meter then should be calibrated, then held steady at a constant temperature and pressure. Replace membrane electro- lyte, recalibrate, or replace sensor or meter. If DO thermistor is used to measure water temperature, see temperature criteria above.	Check operation in FSU before field trip. Onsite calibration prior to making measurements or during continuous monitor maintenance.	Wilde, 2006; Wagner and others, 2006; see manu- facturer's instructions.
Barometric pressure	Calibrate against reference barometer: NIST- certified aneroid barometer in laboratory.	Within 2 millimeters Hg, apply correction or replace.	Before each trip.	See manufacturer's instructions.
Turbidity	Two-point calibration with a midpoint standard check, or follow manufacturer's instructions.	Calibrate within ± 2 turbidity unit or $\pm 5\%$ of measured value.	Onsite calibration prior to making measurements or during continuous monitor maintenance.	Anderson, 2005; Wagner and others, 2006; See manufac- turer's instructions.

During synoptic sampling and long-term monitoring, similar methods were used to collect depth- and widthintegrated stream samples for the analysis of major ions, nutrients, and trace elements. A vertically integrated grab method was used to collect water samples for the analysis of indicator bacteria and OWICs. Samples for the analysis of indicator bacteria were collected following USGS procedures and protocols (Myers and others, 2007). The collection of water samples for the analysis of OWICs followed USGS procedures and protocols (Lewis and Zaugg, 2004). To prevent sample contamination, field personnel were instructed not to use personal-care products such as colognes, perfumes, insect repellant, sun screen, caffeinated products, or tobacco during sample collection and processing. Synoptic samples intended for major ion, nutrient, and trace element analyses were collected at the centroid of streamflow samples and depth-integrated using a weighted-bottle sampler. The sample bottle was a 1-liter (L) narrow-mouth, polyethylene bottle. The sample bottles were labeled, chilled to 4 °C, and shipped to the PMRL for analysis.

During the long-term monitoring part of this study, water samples for the analysis of major ion and nutrient constituents were collected using autosamplers (stormflow) or were manually collected composite samples (base flow, depth-integrated grab samples or depth-integrated samples using equal-widthintervals (EWI). At instrumented sites, major ion, nutrient, and trace element concentrations in point samples were compared with concentrations in manually collected composite samples (about 20 percent of all samples) to determine if point samples showed a positive or negative bias. A bias would indicate incomplete mixing at the water intake to the autosampler and data measured in those samples would not represent average conditions at the stream cross section. A number of studies have shown that EWI samples provide an unbiased measure of average chemical constituent concentrations in a stream, especially for sediment-bound constituents (Horowitz and others, 1990; Horowitz, 1991; Martin and others, 1992). Water samples were processed and quality assurance guidelines followed USGS protocols and procedures (U.S. Geological Survey, 2006).

Laboratory Analysis of Water Samples and General Methods of Laboratory Quality Control

Water samples collected during the COA synoptic study and the long-term monitoring program were analyzed by three laboratories (table 5). Two laboratories were used to analyze water samples for dissolved major ions, nutrients, and selected trace elements. The PMRL located at the GAWSC in Atlanta, GA, was used to analyze samples from March 2003 to October 2004; the NWQL was used to analyze samples from October 2004 to January 2006. The methods used by both laboratories to analyze major ions, nutrients, and select trace elements are summarized in table 5. Filtered samples were analyzed for OWICs at the NWQL using schedule SH1433 during the entire study period. A third laboratory located in the GAWSC was used for bacteria analyses in this study.

The NWQL participates in the National Environmental Laboratory Accreditation Program. Through the National Environmental Laboratory Accreditation Conference, this program establishes standards addressing all levels of laboratory quality control, quality assurance documentation, documentation of laboratory standard operating procedures, and equipment maintenance. The NWQL uses a three-tiered approach to quality control: (1) method performance, (2) data review and blind sample programs, and (3) performance evaluation studies. Maloney (2005) provides a detailed summary of data-quality management at the NWQL. Pirkey and Glodt (1998) summarize the general quality control procedures used at the NWQL.

Because organic compounds commonly are present in environmental samples at trace levels (ppt) and may be degraded by heat, light, temperature, microorganisms, and other factors, method performance for the analysis of organic compounds is evaluated differently from that used for inorganic compounds. Method performance is monitored using laboratory reagent blank samples (LRB or lab blank), samples spiked with laboratory reagent (LRS), and surrogates that are prepared and analyzed with each group of environmental samples and reference samples. In the second qualitycontrol tier, chemists from the USGS Branch of Quality Systems (BQS) monitor method performance throughout the laboratory and over time by using data from quality-control and double-blind samples. Charts are available online at http://bqs.usgs.gov/obsp/ for most of the OWICs in schedule 1433 through the Organic Blind Sample Program at the BQS. For the third tier quality control, the NWQL routinely participates in the following national performance-evaluation studies: USEPA water-pollution and water-supply studies, and National Water Research Institute of Canada (organic carbon). Performance evaluation studies by the NWQL are described in Glodt and Pirkey (1998). The results of laboratory proficiency tests for the NWQL are available at *http://nwql.usgs.gov/* Public/perf eval.shtml for the years 2002 to 2009.

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Table 5. Dissolved major ions, nutrients, and selected trace elements analyzed in water samples from streams near Atlanta, GA, March 2003 to January 2006.

[USGS, U.S. Geological Survey; MRL, method reporting limit; N, nitrogen; mg/L, milligram per liter; µg/L, microgram per liter; MPN/100 mL, most probable number per 100 milliliter; cfu, colony forming unit; DCP, direct current plasma spectroscopy; ICP-AES, inductively coupled plasma emission spectrometry; PES, plasma emission spectrometry; ICP-MS, inductively coupled plasma mass spectrometry; GF-AAS, graphite furnace atomic absorption spectrometry; ICP, inductively coupled plasma spectrometry; USEPA, U.S. Environmental Protection Agency; —, not applicable]

Parameter ^a	USGS parameter code	Units	USGS Panola Mountain Research Laboratory analytical methods, March 2003–Oct 2004 (MRL)	Method number and reference	USGS National Water Quality Laboratory analytical methods, Oct 2004–Oct 2006 (MRL)	Method reference
			Major ions			
Calcium	00915	mg/L	DCP (0.02)	I-1472-85 ^b	ICP-AES (0.02)	I-1472-87°
Magnesium	00925	mg/L	DCP (.001)	I-1472-85 ^b	ICP-AES (.014)	I-1472-87°
Potassium	00935	mg/L	DCP	I-1472-85 ^b	PES (.04)	SM 3120 ^d
Sodium	00930	mg/L	DCP (.2)	I-1472-85 ^b	ICP-AES (.20)	I-1472-87°
Silica	00955	mg/L	DCP (.009)	I-1472-85 ^b	ICP-AES (.20)	I-1472-87°
Alkalinity as cal- cium carbonate	29801	mg/L	Automated electrometric Gran titration	—	Automated electrometric titration to pH 4.5 (5.0)	I-2030-85 ^b
Chloride	00940	mg/L	Ion chromatography (.12)	SM4110C ^d	Ion chromatography (.12)	I-2057-85 ^b
Sulfate	00945	mg/L	Ion chromatography (.18)	SM4110C ^d	Ion chromatography (.18)	I-2057-85 ^b
			Nutrients			
Nitrite as N	00613	mg/L	Ion chromatography (.02)	SM4110C ^d	Colorimetric (.008)	I-2540-90°
Orthophosphate	00671	mg/L	Ion chromatography (.03)	SM4110C ^d	Phosphomolybdate, colorimetric (.006)	I-2601-90°
Nitrite plus nitrate as N	00631	mg/L	Ion chromatography	SM4110C ^d	Cadmium-reduction, colorimetric (.06)	I-2545-90°
Ammonia plus organic N	00623	mg/L	Ammonia only, automated colorimetric (.002)	SM4110C ^d	Kjeldahl digestion, colorimetric (.10)	I-2515-91°
Ammonia plus organic N, total	00625	mg/L	—	_	Unfiltered water, acidified, kjeldahl digestion, colorimetric (.10)	I-2515-91°
Phosphorus	00666	mg/L	_	_	Filtered water, colorimetric (.04)	USEPA 365.1
Phosphorus, total	00665	mg/L	Inline digestion and flow injection, colorimetric	SM4500I ^d	unfiltered water, acidified, alkaline-persulfate, colorimetric (.008)	I-4650-03 ^{fg}

Table 5.Dissolved major ions, nutrients, and selected trace elements analyzed in water samples from streams near Atlanta, GA,March 2003 to January 2006.—Continued

[USGS, U.S. Geological Survey; MRL, method reporting limit; N, nitrogen; mg/L, milligram per liter; µg/L, microgram per liter; MPN/100 mL, most probable number per 100 milliliter; cfu, colony forming unit; DCP, direct current plasma spectroscopy; ICP-AES, inductively coupled plasma emission spectrometry; PES, plasma emission spectrometry; ICP-MS, inductively coupled plasma mass spectrometry; GF-AAS, graphite furnace atomic absorption spectrometry; ICP, inductively coupled plasma spectrometry; USEPA, U.S. Environmental Protection Agency; —, not applicable]

Parameter ^a	USGS parameter code	Units	USGS Panola Mountain Research Laboratory analytical methods, March 2003–Oct 2004 (MRL)	Method number and reference	USGS National Water Quality Laboratory analytical methods, Oct 2004–Oct 2006 (MRL)	Method reference
			Trace elements	;		
Aluminum	01106	µg/L	DCP (100)	I-1472-85 ^b	ICP-MS (50)	I-2477-92 ^h
Cadmium	01025	µg/L	—	—	ICP-MS (.04)	I-2477-92 ^h
Chromium	01030	μg/L	_	—	GF-AAS, Mar 2003– Sept 2005 (.8)	I-1233-93 ^h
Chromium	01030	μg/L	_	—	Collision cell ICP, 2005 to 2006 (.12)	I-2020-05 ^{ij}
Copper	01040	µg/L	—		ICP-MS (.40)	<mark>??</mark> I-2477-92 ^{8/}
Iron	01046	µg/L	DCP (3.0)	I-1472-85 ^b	ICP-AES (6.0)	I-1472-87°
Lead	01049	µg/L	—		ICP-MS (6.0)	I-2477-92 ^h
Manganese	01056	µg/L	DCP (50)	I-1472-85 ^b	ICP-AES	I-1472-87°
Manganese	01056	µg/L	—		ICP-MS (.20)	I-2477-92 ^h
Nickel	01065	µg/L	_	_	ICP-MS (.06)	I-2477-92 ^h
Silver	01075	µg/L	—		ICP-MS (.10)	I-2477-92 ^h
Strontium	01080	µg/L	DCP (.50)	I-1472-85 ^b	_	—
Zinc	01090	µg/L	—		ICP-MS	I-2477-92 ^h
			Indicator bacteri	a ^k		
<i>Escherichia coli,</i> whole water	50468	MPN/100 mL	Colilert18®	SM9223 ^d	—	
Fecal coliform bacteria, whole water	31625	cfu/100 mL	Membrane filter	SM9222B°	_	—
 ^a Dissolved, unless indicated otherwise. ^b Fishman and Friedman, 1989. ^c Fishman, 1993. ^d Clesceri and others, 1998a. ^e Clesceri and others, 1998b. ^f Patton and Truitt (2000). 						

^gPatton and Kryskalla, 2003.

^hFaires, 1993.

ⁱMcLain, 1993.

^jGarbarino and others, 2006.

^kGeorgia Water Science Center Laboratory.

Laboratory Analysis of OWICs and Quality Assurance

In 2002, the method for SH1433 was published by the NWQL and described the analysis of 67 anthropogenic organic compounds commonly detected in domestic and industrial wastewater, and collectively called OWICs (Zaugg and others, 2002). These compounds included those associated with human-use or direct human activity such as detergents (the non-ionic surfactants of the alkylphenol ethoxylate class and their degradates), personal-care products (fragrances, cosmetics, deodorants, sun screens), fecal sterols, and food additives and antioxidants and those not directly associated with human such as flame retardants, plasticizers, industrial solvents, disinfectants, PAHs, and high-use domestic pesticides (table 3). Three organic surrogate compounds are added to each sample set to quantify analytical recoveries from the sample matrix.

Water samples intended for OWIC analysis were either filtered in the field or at the laboratory. In either case, water samples were passed through a pre-baked glass-fiber filter (0.7-micrometers, μ m, nominal pore size) under vacuum to remove suspended particulate matter, then preserved by the addition of 60 grams of sodium chloride, and stored at 4°C until extracted using solid-phase cartridges (SPE). Details of the method are described in Zaugg and others (2002). The relative standard deviation for the recovery of all compounds was \pm 7 percent. Initial method detection limits (MDL) for single-component compounds (excluding hormones and sterols) averaged 0.15 µg/L.

During the analysis of a water sample, the analytical method, which includes the analytical instrumentation, generates a signal (retention time and signal intensity) that is, ideally, specific for each compound or analyte of interest. Each analytical method used by the NWQL has a long-term method detection level (LT-MDL) and a laboratory reporting level (LRL) commonly determined by experimentation using spiked reagent blanks (Bonn, 2008). The LT-MDL is the threshold at which the signal identifying a compound emerges from the background signal generated by the analytical instrument such that the compound can be identified with 99 percent statistical certainty. Thus, the region below the LT-MDL is the area where the analytical signal that corresponds to a compound and its concentration cannot be distinguished from instrument background.

The LRL is the threshold where the instrument signal can positively identify a compound and can quantify its concentration in the sample. The LRL is greater than the LT-MDL by some multiplier that is determined by the recovery of compounds in the spiked reagent blanks used to determine the LT-MDL (Bonn, 2008). If recovery is 100 percent, then the LRL is two times the LT-MDL. If the recovery is less than 100 percent, then the LRL is greater than two times the LT-MDL (Bonn, 2008).

Schedule 1433 is an information-rich method because the mass spectrometer allows definitive identification of a

compound by comparing its chemical structure to the structure of known compounds in a data library. Information-rich methods can definitively identify a compound even if the compound concentration is not quantifiable. The following conventions are used by the NWQL to report the presence and concentration of OWICs in a water sample (Bonn, 2008). If the mass spectrometer cannot identify a compound, the compound is reported as less than the LRL (such as < 0.02, if 0.02 is the LRL), or if the mass spectrometer identifies a compound and its concentration is less than the LT-MDL, then the numeric value is reported and qualified with an "E" to indicate the compound is positively identified but not quantified, or if the compound is identified and its concentration is between the LT-MDL and the LRL, the result is reported with an "E" qualifier to indicate the concentration is an estimate with high uncertainty, or if the compound is detected with a concentration greater than the LRL, the concentration is reported without censorship or qualification.

Given that some compounds are so prevalent at trace levels in the environment and the SH1433 method can detect compounds at smaller than part-per-trillion levels, additional censoring was needed to establish study reporting levels (SRLs) before data analysis and interpretation (table 3). Censoring the data involved two steps. (1) The OWICs in water samples collected before August 2004 were censored at compound concentrations that were 10 percent greater than the 95th percentile measured in quality-control samples (Zaugg and Leiker, 2006); (2) The OWICs in water samples collected after August 2004 were censored based on the frequency distribution of compound concentrations among all samples in order to identify compound concentrations that represent background levels and, if left in the dataset, might obscure meaningful patterns in OWICs that may be present during the study period.

A laboratory audit of SH1433 released in 2006 documented several changes in the reporting of compound concentrations (Zaugg and Leiker, 2006). This audit was initiated because of persistent, low-level contamination by several organic compounds in internal laboratory blanks and in blind blank samples submitted by the BQS and analyzed using SH1433. As a result, four hormones (17-beta-estradiol, equilenin, estrone, and ethynyl estradiol) and one pesticide (dichlorvos) were removed from the schedule beginning in July 2004 because of very low recoveries from spiked samples and retroactively removed from the NWQL. Those five compounds are not included in this report. The compounds 14DCB, acetophenone, benzophenone, and phenol were identified as laboratory contaminants.

In addition, the method for reporting results was changed for four sterol and one flame-retardant compounds beginning in February 2006. The reporting methods were changed because analytical results for the continuous calibration standards used to verify method performance were highly variable and commonly fell outside of the \pm 20 percent region surrounding the most probable value. Even though the data used in this report
does not extend beyond February 1, 2006, the new reporting limits were applied retroactively to the data. Therefore, all results for 3- β -coprostanol, β -sitosterol, β -stigmastanol, cholesterol, and tris(2-butoxyethyl) phosphate were considered estimates and flagged with an "E" qualifier in this report.

The audit identified two sources of laboratory contamination: (1) exposure of SPE cartridges to ambient air in the laboratory, especially after the cartridges were cleaned, and (2) polypropylene reservoirs used to store the extraction solvent. The source or sources of blank-sample contamination by phenol and acetophenone could not be identified and are considered chronic laboratory contaminants. Phenol is not included in this study because an acceptable censoring level could not be established. The sources of contaminants in laboratory blanks were identified, and standard operating procedures were changed by August 2004. After August 2004, the frequency of contaminated laboratory blanks declined by as much as 82 percent (14DCB; Zaugg and Leiker, 2006).

Analysis of *E. coli* Bacteria and Quality Assurance

Holding-time experiments conducted as part of the COA study indicate that *E. coli* bacteria density is substantially unchanged (within the range of analytical uncertainty) over a 48-hour holding time when samples are refrigerated (mean temperature of 6 °C; Aulenbach, 2009). The methods used for the analysis of *E. coli* bacteria are those approved by the USEPA for drinking water as published in the Code of Federal Regulations (40 CFR 141.74, revision July 2000) and for ambient waters as published in the Code of Federal Regulations (40 CFR 136, revision July 2003).

Water samples were analyzed for *E. coli* density using the Enzyme Substrate Coliform Test (Clesceri and others, 1998a) with materials manufactured by the Idexx Corporation (Colilert18[®]). A number of researchers have established that the Colilert method is comparable and may be superior to the older membrane filter methods (Edberg and others, 1988; Edberg and others, 1990; Cowburn and others, 1994; Fricker and others, 1997; Chao and others, 2004).

Sample aliquots ranging from 0.1 to 50 milliliters (mL) were added to premeasured, sterile de-ionized water in 125-mL polypropylene bottles. A final volume of 100 mL is required for the Colilert method. Typically, two to three dilutions containing 0.1, 1, 10, or 50 mL of sample were needed to encompass the *E. coli* density ranges expected in the sampled streams. The Colilert reagent is contained in single-use packets, and one packet was added to each dilution, shaken, and then poured into sterile trays (Quantitray2000[®]). The trays were heat sealed, labeled, and incubated at 35 ± 0.5 °C for 20–24 hours. After incubation, the cells in the tray that were yellow and that fluoresced blue-green were counted as positive for *E. coli*. The *E. coli* density for each sample was calculated using equation 1. Because the Enzyme Substrate Coliform Test is based on statistical probabilities, results are given as the most

probable number per 100 mL (MPN/100 mL). If the value of C for a given dilution is less than 1, then C has a value of 0 in equation 1 and the sample volume (d) for that dilution is used in equation (1). Conversely, if C for a dilution was greater than 2,419.6, then the count for that dilution and its associated sample volume were not included in equation 1. Analytical methods and quality-control procedures for the analysis of *E. coli* bacteria are outlined and described in an unpublished workplan and quality-assurance manual on file in the GAWSC.

$$\frac{\sum C_{n}}{\sum d_{n}} \times 100, \qquad (1)$$

where

 C_{n} d_{n} is the count for the nth dilution, and is the sample aliquot for the nth dilution.

Data and Statistical Analysis

Sixty-three OWICs were analyzed in water samples collected during this study. These 63 compounds are apportioned among nine classes representing common sources or common uses of those compounds (table 3). For example, 17 OWICs are grouped as personal-use compounds, 9 compounds are grouped into the pesticide class, 2 compounds are grouped into the disinfectant class, 4 compounds each are grouped into the sterol and flame-retardant classes, 7 compounds each are grouped into the non-ionic detergent-metabolite (NDMCs), industrial-use, and the PAH classes, and 6 compounds are grouped into the automotive-use class. Nevertheless, 11 of the 63 OWICs analyzed in water samples collected for this study were either not detected in any water sample or failed qualitycontrol criteria and were not included in this report (table 3).

After censoring, 52 OWICs remained in the nine classes. Of these nine classes, the personal-use compounds, disinfectant (bromoform), sterols (cholesterol and coprostanol), and NDMCs are probably the most important for identifying CSOs in the Atlanta streams. Fourteen personal-use compounds were analyzed including two musk fragrances and five other fragrances, cotinine (nicotine derivative), caffeine, DEET (insect repellant), three topical analgesics (camphor, menthol, and methyl salicylate), and the antimicrobial compound triclosan. Triclosan and all NDMC compounds are considered potential endocrine disrupting compounds. The pesticide 14DCB may also be important because it is the active ingredient in toilet bowl sanitizers and deodorants. In addition, these OWIC classes were further grouped into two broad categories: (1) human-related OWICs are those often associated with human-use or human waste and consist of the personal-use, sterol, and NDMCs compounds, and (2) urban-runoff OWICs are those commonly identified in the scientific literature as components of urban runoff. This category consists of the industrial-use, automotive-use, PAH, and flame-retardant compounds.

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Percentages are commonly used in this report to show the relative distribution of OWICs among the nine OWIC classes in a given sample group, such as in all base-flow samples. Because the personal-use compound class represents a large percentage (about 25 percent) of the 52 OWICs used in this report and the other eight classes represent markedly smaller percentages, among-class percentages were calculated using standardized or weighted data for the nine OWIC classes. The calculation for standardizing the data is shown in equations 2 and 3. The class percentages in tables 9 and 10 are calculated using equations 2 and 3.

$$H_z = \frac{\sum_{n=1}^{z} D_z}{p} \quad \text{and} \tag{2}$$

$$RI = \frac{H_z}{\sum\limits_{0}^{1} H_z} \times 100 , \qquad (3)$$

where

- H_z is the number of compounds identified in an OWIC class (z),
- D is the number of compounds identified in an OWIC class (z),
- *n* is the number of samples,
- *p* is the proportion of all compounds represented within a class (z), and
- *RI* is the relative importance of an OCIC class, in percent.

Statistical analyses attempt to estimate unknown and immeasurable parameters of an identified population by taking a sample from that population. The sample, if random and unbiased, is assumed to mirror the statistical properties of the population such that any statistical measure of the sample is also the statistical measure of the population (Ott, 1988). Data analysis and statistical methods used in this report are described based on the following assumptions. The terms "measurements" and "values" are used interchangeably and identify one particular number within a set or collection of measurements or values. The term "data" is used to describe a set or collection of measurements or values from one particular property, such as turbidity. The term "dataset" is used to describe a collection of data associated by date, time, and place of sample collection. Computer-generated statistical analyses were completed on the study dataset using SPLUS (version 8.1; TIBCO Software, 2008).

Statistical analyses used for this report include nonparametric methods, linear regression, and exploratory analyses using factor analysis by principal components. Detailed descriptions of the statistical methods used for this report are given in Conover (1980), Montgomery and Peck (1982), Helsel and Hirsch (1992), and Helsel (2005). The primary nonparametric statistical methods used in this report were the Wilcoxon rank-sum test (nonparametric t-test) and the Spearman rank correlation test (Conover, 1980; Helsel and Hirsch, 1992). Regression analyses are commonly used to fulfill three objectives in this study: (1) identify relations between *E. coli* or fecal coliform bacteria and ancillary data such as stream turbidity measured in each watershed; (2) remove variation due to the influence of an exogenous measurement, such as turbidity, to better understand the variation between indicator bacteria and OWICs detected; and (3) predict the value of one measurement, such as *E. coli* density, given the value of another measurement, such as turbidity.

Exploratory data analysis is commonly used with multivariate statistical methods to identify patterns, distributions, needed data transformations, and outliers in datasets. Factor analysis by principal components (PCA) is used in this report to identify the pattern of variance in the datasets from each watershed in order to reduce the amount of complexity in the data. The PCA for this study used the same ranktransformed data used in the correlation analyses; the set of Spearman rank-correlation coefficients was the initial matrix for the PCA.

PCA provides a way to examine the interrelations in a dataset with a large number of variables and a large number of samples (Davis, 1986). Nevertheless, PCA has some limitations. The analysis can force functionally unrelated data into components, thereby leading to erroneous interpretations (Rexstad and others, 1988). Preisendorfer and others (1981) reported that a dataset of random numbers can produce seemingly relevant principal components and loadings. The correct interpretation, therefore, depends on knowledge of hydrologic, geochemical, and physical factors that may affect or govern the properties of the dataset. In this report, a statistical method called the "Rule of N" is used for identifying significant principal components. This method uses signal-to-noise theory and Chi-square statistics to split the components into those that represent relations among the actual data (signal) from those associated with random processes (noise; Preisendorfer and others, 1981).

Streamflow statistics for the study period are computed for 12 of the 13 USGS gaging stations in the study area. The gaging station at site WOO-1 had a limited period of record preventing the calculation of streamflow statistics at that site. Streamflow statistics include the median discharge, median warm- and cool-season discharge, and a flashiness and base-flow index. The term flashiness describes the frequency and rapidity of short-term changes in streamflow, especially during runoff events (Baker and others, 2004). In other words, the flashiness of a stream refers to the amount of time a stream takes to reach peak discharge and the magnitude of the peak discharge during a storm event. One method of computing flashiness is the Richardson-Baker Flashiness Index (Flashiness Index; Baker and others, 2004). The Flashiness Index is computed using equation 4.

$$\frac{\sum_{n}^{l} \left| \mathcal{Q}_{t} - \mathcal{Q}_{t-1} \right|}{\sum_{n}^{l} \mathcal{Q}_{t}} , \qquad (4)$$

where

 Q_t is the current day's mean discharge, and Q_{t-1} is the previous day's mean discharge.

In short, the Flashiness Index is a summation of the absolute values of the differences between mean daily flows for adjacent days divided by the sum of the mean daily flows for the time period, typically 1 year. The base flow of a stream is the portion of the total flow that can be attributed to groundwater discharge. Computerized base-flow separation was performed on the daily mean discharges for the instrumented sites in this study. Base-flow separation was accomplished using a FORTRAN program, which also computed a base-flow index (Wahl and Wahl, 1995). This program follows the Institute of Hydrology methods for base-flow separation. The method identifies the minimum flow during each 5-day period by dividing each water year into 5-day increments. The minimum values are then compared with adjacent minimum values to determine turning points on the base-flow hydrograph. Straight lines are then drawn between turning points to define the base-flow hydrograph. The area beneath the hydrograph is an estimate of the volume of base flow for the period. The ratio of this volume to the total volume of streamflow for the period is defined as the base-flow index. The procedure is only appropriate for unregulated streams, which tends to rule out large watersheds (Wahl and Wahl, 1995). The streams used in this analysis are neither large nor regulated; therefore, this method is appropriate.

Stream Discharge During the Study Period

The median stream discharge during the study period ranged from 1.6 ft³/s for the smallest watershed (Woodall Creek, WOO-1, fig. 1) to 67 ft³/s for the largest watershed (Peachtree Creek, PEA-1) in the study area (table 6). All gaging stations showed markedly lower discharge during the warm season, probably because evapotranspiration is at a maximum during that period. The median flashiness index for the study period is strongly related (r=0.79, *p*-value is 0.007) to the percentage of impervious surfaces in the drainage area upstream from each gaging station (fig. 3A). This relation shows that the greater the impervious area in a watershed, the quicker the stream responds to storm events. The gaging station on Proctor Creek at Hortense Way at Atlanta (PRO-2) had the highest flashiness index, and the watershed upstream had an impervious area of about 45 percent. Increases in impervious area within the study watersheds reduce the amount of base flow in the stream (r=0.70, *p*-value is 0.007; fig. 3B), which is a relation consistent with other studies in the scientific literature (Driver and Troutman, 1989; Ellis and others, 1997; Rose and Peters, 2001; Ellis and Revitt, 2008).

Occurrence of OWICs

Between March 2003 and January 2006, 863 stream samples were collected in the Atlanta urban area and analyzed for 63 OWICs. Method performance for the 63 OWICs, as measured by compound recoveries in laboratory and blindsample spikes, ranged from less than 10 percent to 180 percent (fig. 4). The compounds dichlorvos (less than 10 percent) and carbaryl (about 25 percent) had the smallest median percent recoveries, and 3-methyl-1(H)-indole (about 128 percent) had the largest. Because the recovery of dichlorvos was consistently low and the recovery of 3-methyl-1(H)-indole was consistently high, those compounds were removed from the dataset. Phenol also was removed because it was a pervasive contaminant in laboratory quality-control (QC) samples, possibly from an airborne source in the laboratory.

Before data analysis, results from other compounds found in laboratory QC samples or field equipment blanks were given additional censoring (table 3). Quality-control samples taken during the collection of stream samples (field equipment blanks) and quality-control samples from the BQS showed that water samples submitted to the NWQL were contaminated with a number of compounds that were of particular interest during the Atlanta urban study. Field personnel refrained from using personal-care items such as mosquito repellants, colognes, perfumes, caffeinated products, and cigarettes during sample collection so as not to contaminate samples; however, a small number of blank samples were contaminated with some of those compounds. Phenol, N,N-diethyl-metatoluamide (DEET), acetophenone and benzophenone were the most frequently detected compounds in field equipment blanks (table 7). Acetophenone and benzophenone are used in cosmetics and as fragrances in a variety of personal-care products and DEET is the active ingredient in personal-use insect repellants. A possible source of DEET in field blank samples might be previously used bottles or cans of repellant that were not removed from field vehicles before collection of OWIC samples.

As a result of the QC findings, an SRL was imposed on the data used in this report. The threshold for the SRL varied depending on the date of sample collection. For example, samples collected before August 2004 were censored at a concentration level that was 10 percent greater than the 95th percentile for compound concentrations in QC samples listed in Zaugg and Leiker (2006). In samples collected after August 2004, the censoring threshold for individual OWICs was determined by distributing compound concentrations into nine groups ranging from not detected to greater than 2 µg/L (table 8). The SRL was determined as the midpoint of the concentration group with the largest percentage of water samples. For example, if the concentration group $0.100-0.249 \,\mu\text{g/L}$ contained the greatest percentage of samples with caffeine, then the SRL was 0.18 µg/L and caffeine concentrations below this value represented background levels and were not tallied as detections.

Streamflow statistics for U.S. Geological Survey streamgaging stations near Atlanta, GA, March 2003 to September 2006. Table 6.

[USGS, U.S. Geological Survey; mi², square miles; \hat{t}^3/s , cubic feet per second; —, not available]

				Median s	tream discha	arge (ft³/s)	Me	dian flash	iness inde	X ^a	Me	dian base	flow index	41
Site identi- fication	USGS site identifier	USGS site name	Drainage area (mi ²)	Study period	Warm season (April to September)	Cool season (October to March)	Study period	Water year 2004	Water year 2005	Water year 2006	Study period	Water year 2004	Water year 2005	Water year 2006
NAN-1	02336410	Nancy Creek at West Wesley Road, at Atlanta	37.7	31.5	23.7	36.7	0.749	0.807	0.749	0.733	0.360	0.360	0.338	0.431
NAN-3	02336360	Nancy Creek at Rickenbacker Drive, at Atlanta	26.6	24.9	18.3	30.9	.823	.823	.815	.853	.312	.312	.277	.387
SAN-1	02336644	Sandy Creek at Bolton Road, near Atlanta	3.4	2.9	1.9	3.2	866.	866.	.994	1.05	.310	.355	.252	.310
UTO-1	02336728	Utoy Creek at Great South- west Pkwy near Atlanta	33.9	25.2	19.6	29.2	.723	.728	.723	.664	.370	.348	.370	.430
UTO-3	02336658	North Utoy Creek at Peyton Road, near Atlanta	6.4	4.3	3.4	4.7	.922	1.08	.883	.922	.303	.300	.303	.353
I-TNI	02203700	Intrenchment Creek near Atlanta	10.6	5.0	4.4	5.5	1.02	1.05	1.02	.880	.184	.184	.181	.212
PEA-2	02336300	Peachtree Creek at Atlanta ^c	86.8	67.0	60.5	72.6	.883	.892	.807	.883	.338	.338	.265	.348
PEA-4	02336120	North Fork Peachtree Creek, Buford Highway, near Atlanta	34.8	23.5	16.9	27.0	.955	1.07	.917	.955	.241	.241	.228	.281
PEA-5	02336240	South Fork Peachtree Creek, Johnson Road, near Atlanta	28.7	20.7	16.2	22.8	.933	1.09	.914	.933	.259	.259	.248	.351
W00-1	02336313	Woodall Creek at Defoors Ferry Road, at Atlanta	2.6	1.6^{d}	1.3 ^d	2.1 ^d		I		1.47				690.
PRO-1	02336526	Proctor Creek at Jackson Parkway, at Atlanta	13.4	5.7	4.8	6.7	1.21	1.21	1.08	1.29	.197	.224	.197	.164
PRO-2	02336517	Proctor Creek at Hortense Way, at Atlanta	7.2	2.5	2.2	2.8	1.31	1.31	1.23	1.31	.180	.186	.163	.180
SOU-1	02203655	South River at Forest Park Road, at Atlanta	22.5	16.2	13.8	17.8	.839	1.01	.829	.839	.313	.253	.313	.328
^a The flas	hiness of a stre	am refers to how long a stream takes to	reach peal	¢ discharge	during an eve	ent, as well as	how large th	e peak dise	charge is wl	ien compared	l with the flo	ws before a	nd after the	event.
^b This inc	lex is a dimens.	ionless measure of the base-flow volun	ie normaliz	ed to the to	tal volume of	streamflow or	ver a given ti	me period.						
° During	the drought of	1954, an instantaneous discharge of 2.3	1 ft ³ /s was	measured a	t this station o	on September	30, 1954.							

^dGaging station became operational in 2006.

Table 7.List of organic wastewater-indicator compounds detected in 20 field blanks collected betweenMarch 2003 and January 2006, and laboratory blanks sent as blind samples between 2001 and January 2006.

[USGS, U.S. Geological Survey]

Organic wastewater-	USGS	Detected in	field blanks	Detected in laboratory blind
indicator compound	parameter code	Number	Percent	sample blanks (percent)
Phenol	34466	16	80	22
N,N-diethyl-meta-toluamide (DEET)	62082	9	45	0
Acetophenone	62064	7	35	3
Benzophenone	62067	5	25	0
Menthol	62080	4	20	0
Caffeine	50305	2	10	2
Tris(2-chloroethyl) phosphate (TCEP)	62087	2	10	0
Methyl salicylate	62081	1	5	0
<i>p</i> -Nonylphenol (total)	62085	1	5	3
Triethyl citrate	62091	1	5	0



Figure 3. Relations among percentage of developed area and indices of (*A*) stream flashiness and (*B*) stream base flow at the 12 USGS streamgaging stations in the study area, near Atlanta, GA, March 2003 to January 2006.



Figure 4. Analytical recoveries of organic wastewater-indicator compounds in spiked samples sent blind between 2001 and 2006 to the USGS National Water Quality Laboratory by the USGS Branch of Quality Systems. [NS, no sample]



Figure 4. Analytical recoveries of organic wastewater-indicator compounds in spiked samples sent blind between 2001 and 2006 to the USGS National Water Quality Laboratory by the USGS Branch of Quality Systems. [NS, no sample]—Continued

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Table 8. Percentage of water samples containing organic wastewater-indicator compounds distributed among eight concentrationranges from streams near Atlanta, GA, March 2003 to January 2006.

fug/L	microgram	ner liter: <	<pre>less than ></pre>	greater than	compound	was not id	lentified in t	his concentration	ı rangel
100 -	, more Brann	per meer,	, 1000 man,	Breater than,	, compound			and concentration	ange

				Pe	ercentage	of all sam	ples				Total
a 1				Concentr	ation rang	je (µg/L)				Above study	summed
Compound	Not	0.001 to	0.010 to	0.050 to	0.100 to	0.25 to	0.50 to	1.00 to	>20	reporting levels	concen- tration ^b
	detected ^a	<0.01	0.049	0.099	0.249	0.49	0.99	2.00	× 2.0	(table 3)	(µg/L)
				Personal	l-use com	oounds					
Acetyl hexamethyl tetrahydronaph- thalene (AHTN)	67	5.4	16	9.4	1.3	< 1.0	_	_	_	11	0.7
Acetophenone	62	—	—	3.7	27	5.9	< 1.0	< 1.0	< 1.0	7	31
Benzophenone	43	< 1.0	26	22	7.8	< 1.0	< 1.0	_	_	9	4.7
Caffeine	5.3	_	5.6	13	33	23	13	4.9	2.7	61	280
Camphor	30	1.4	40	16	11	< 1.0	< 1.0	< 1.0	_	38	7.0
Cotinine	79		1.9	4.8	8.7	5.0	< 1.0	< 1.0	—	14	4.0
Hexahydro-hexamethyl cyclopenta-γ-2- benzopyran (HHCB, Galaxolide)	38	< 1.0	34	19	8.2	1.5	< 1.0	< 1.0	_	19	7.5
Indole	79	5.9	12	2.3	1.0	—	< 1.0	< 1.0	—	16	2.9
Isoborneol	96	< 1.0	1.5	< 1.0	1.5	< 1.0	< 1.0	< 1.0	—	2	5.2
Menthol	43	< 1.0	8.0	21	20	5.7	2.2	< 1.0	< 1.0	28	44
Methyl salicylate	62	3.9	25	7.9	1.3	< 1.0	—	—	—	10	.6
<i>N,N</i> -diethyl- <i>meta</i> - toluamide (DEET)	2.9	_	4.2	19	41	20	10	2.3	< 1.0	23	110
Triclosan	76	—	4.9	8.3	9.7	1.2	< 1.0	—	< 1.0	20	3.2
Triethyl citrate (ethyl citrate)	84	< 1.0	8.1	5.7	1.5	< 1.0	_	—	_	8	.5
				Disinfec	tion comp	ounds					
Tribromomethane (Bromoform)	94	< 1.0	3.0	1.3	< 1.0	< 1.0	< 1.0	_	< 1.0	6	27
				Pestici	ide compo	unds					
1,4-dichlorobenzene (14DCB)	65	9.7	11	8.0	4.8	< 1.0	< 1.0	< 1.0	< 1.0	13	14
Bromacil	57	—	< 1.0	< 1.0	4.5	11	17	4.9	4.9	42	410
Carbaryl	76	—	3.8	9.3	8.9	1.5	< 1.0	—	—	24	4.7
Chlorpyrifos	99	—	< 1.0	< 1.0	< 1.0	—	—	—	—	< 1	< 0.25
Diazinon	95	—	1.6	2.1	< 1.0	—		—	< 1.0	3	28
Prometon	95		1.0	3.0	< 1.0	< 1.0		_	< 1.0	4	2.6
				Sterc	ol compou	nds					
Cholesterol	52	_		_	_	3.1	22	18	5.6	49	330
3-β-coprostanol	69	_	—	_	1.2	8.6	13	6.4	1.2	29	100
β-sitosterol	78	—	—	—	< 1.0	3.1	10	7.6	1.4	22	120
β-stigmastanol	85	—	—	—	_	1.1	6.1	6.7	1.3	15	100

 Table 8.
 Percentage of water samples containing organic wastewater-indicator compounds distributed among eight concentration ranges from streams near Atlanta, GA, March 2003 to January 2006.—Continued

				Pe	ercentage	of all sam	ples				Total
				Concentr	ation rang	je (µg/L)				Above study	summed
Compound	Not detectedª	0.001 to <0.01	0.010 to 0.049	0.050 to 0.099	0.100 to 0.249	0.25 to 0.49	0.50 to 0.99	1.00 to 2.00	> 2.0	reporting levels (table 3)	concen- tration ^b (µg/L)
				Industria	l-use com	pounds					
Anthraquinone	41	—	3.1	12	32	9.3	2.3	< 1.0	—	9	42
Bisphenol-A	60	—	2.3	9.4	18	4.8	3.6	1.9	< 1.0	9	36
Carbazole	62	4.2	21	7.5	4.4	< 1.0	—	< 1.0	—	23	2.7
d-Limonene	83	< 1.0	11	2.5	1.3	< 1.0	< 1.0	< 1.0	—	5	7.7
Tetrachloroethene (PCE)	50	7.9	20	7.9	8.6	2.7	1.1	1.2	< 1.0	22	56
Triphenyl phosphate (TPP)	35	1.9	25	27	8.6	1.9	< 1.0	< 1.0	—	11	7.8
			Polycy	clic aroma	atic hydrod	carbons (P	AHs)				
Anthracene	73	8.5	13	4.4	1.2	_	_	_	_	5	<.25
<i>p</i> -Cresol	28	< 1.0	14	15	28	9.5	3.4	2.0	< 1.0	32	120
Fluoranthene	30	12	39	14	3.9	< 1.0	_	_	_	18	2.7
Pentachlorophenol (PCP)	71	_	< 1.0	3.7	5.0	8.8	4.2	2.9	3.4	19	100
Phenanthrene	40	11	30	12	5.8	< 1.0	< 1.0	< 1.0	_	19	8.1
Pyrene	28	11	48	10	2.2	< 1.0	< 1.0	_	_	13	1.1
				Automotiv	'e-use cor	npounds					
1-Methylnaphthalene	68	7.6	16	4.8	2.7	< 1.0	< 1.0	_	_	11	3.5
2-Methylnaphthalene	69	6.3	15	5.2	3.7	< 1.0	< 1.0	_	_	11	4.4
2,6-Dimethylnaph- thalene	85	2.3	8.0	2.2	1.5	< 1.0	—	—	—	6	1.3
5-Methyl-1H- benzotriazole	93	—	—	< 1.0	1.0	2.4	2.5	< 1.0	< 1.0	6	20
Isopropylbenzene (cumene)	94	2.5	3.4	< 1.0	—	_	_	—	—	< 1	_
Naphthalene	52	3.9	31	8.7	4.2	< 1.0	< 1.0	< 1.0	_	39	4.7
		No	on-ionic de	etergent m	etabolite (compound	s (NDMCs				
<i>p</i> -Nonylphenol (total)	60	_	_		_	3.0	12	17	7.8	38	120
4-Nonylphenol dieth- oxylate (NPEO2)	65	—	—	—	—	—	1.3	13	21	32	720
4-Octylphenol mono- ethoxylate (OPEO1)	83	—	< 1.0	4.4	4.9	2.1	3.8	1.0	< 1.0	13	37
4-Octylphenol dieth- oxylate (OPEO2)	73	—	< 1.0	7.4	16	2.3	< 1.0	_	—	26	3.4
4-tert-octylphenol	84	< 1.0	5.4	5.1	3.6	1.5	< 1.0	_	_	14	3.0

 $[\mu g/L, microgram per liter; <, less than; >, greater than; --, compound was not identified in this concentration range]$

 Table 8.
 Percentage of water samples containing organic wastewater-indicator compounds distributed among eight concentration ranges from streams near Atlanta, GA, March 2003 to January 2006.—Continued

				Pe	ercentage	of all sam	ples				Total
. .				Concentr	ation rang	e (µg/L)				Above study	summed
Compound	Not detectedª	0.001 to <0.01	0.010 to 0.049	0.050 to 0.099	0.100 to 0.249	0.25 to 0.49	0.50 to 0.99	1.00 to 2.00	> 2.0	reporting levels (table 3)	concen- tration ^b (µg/L)
				Flame reta	ardant com	pounds					
Tributyl phosphate (TBP)	32	_	13	16	29	5.2	2.4	< 1.0	< 1.0	63	64
Tris(2-butoxyethyl) phosphate (TBEP)	23	—	< 1.0	< 1.0	9.5	21	23	12	10	75	800
Tris(2-chloroethyl) phosphate (TCEP)	29	—	9.7	29	26	3.9	1.7	< 1.0	< 1.0	60	30
Tris(dichloroisopropyl)	31		9.0	27	27	5.3	< 1.0	< 1.0	—	46	23

 $[\mu g/L, microgram per liter; <, less than; >, greater than; --, compound was not identified in this concentration range]$

^aIn the context of the information-rich analytical methods used, not detected means the compound's molecular signature was not found by mass spectrometry.

^bOnly compound concentrations greater than the study quantitation level (SQLL) are summed. The SQLL is one-half the laboratory reporting level (table 3).

Fifty-two OWICS were detected in at least one sample collected during the study period. Eleven compounds in the laboratory schedule (table 3) were not included in the dataset used for this report because they either were not detected in any sample or failed QC criteria. The eight OWICS not detected were BHA, isophorone, isoquinoline, metolachlor, metalaxyl, and 4-*n*-octylphenol. Compounds that failed QC criteria were 3-methyl-1(H)-indole (skatol), phenol, and dichlorvos.

In the initial, uncensored dataset, 97 and 94 percent of all water samples contained DEET and caffeine, respectively (fig. 5*A*). Furthermore, 50 percent of the samples contained all 4 of the flame retardants, 4 of the 6 PAHs, 6 of the 14 personal-use compounds, and 3 of the 6 industrial-use compounds. Upon censoring the dataset using the SRLs listed in table 3, the flame retardants TBEP and TCEP were the most frequently identified compounds (67 and 54 percent of all water samples, respectively; fig. 5*B*). Censoring markedly reduced the relative importance of the personal-use compounds, PAHs, and industrial-use compounds in the dataset, but increased the relative importance of the flame retardant, pesticide, sterol, and NDMCs (fig. 5*A*,*B*). The dominant

OWICs in this study are similar to those reported in other parts of the United States (Kolpin and others, 2002; Wilkison and others, 2002, 2006; Galloway and others, 2005; Sando and others, 2005, 2006).

Detection frequencies and total concentrations of OWICs in water samples varied depending on flow conditions during sample collection; however, regardless of flow condition, the total OWIC concentrations were strongly related to the numbers of OWICs detected in these samples (Spearman's rho=0.77, *p*-value is less than 0.0001; fig. 6). When 16 or fewer OWICs were detected in a sample, the relation between the number of OWICs and the total concentrations was linear. This relation indicates that the total OWIC concentrations consistently increase with the addition of different compounds at low concentrations. In contrast, the relation between the number of OWICs and the total OWIC concentrations increased at an exponential rate when more than 13 OWICs were detected in a sample. This relation indicates that as the number of OWICs in a sample exceeds about 16 the incremental addition of different compounds is associated with markedly higher compound concentrations.



censoring levels, and (B) study censoring levels (table 3), March 2003 to January 2006.

Percentage of water samples containing OWICs



Figure 6. Relation between the number and the total concentration of organic wastewater-indicator compounds identified at concentrations greater than the study reporting and study quantitation levels (table 3) in water samples from streams near Atlanta, GA, March 2003 to January 2006.

Number of organic wastewater-indicator compounds (OWICs)

detected per sample

The median number of detectable OWICs and total OWIC concentrations increased as the developed area and Flashiness Index increased in the study area (fig. 7). At the 12 instrumented sites, the median number of OWICs and the median total OWIC concentration indicate statistically positive associations with the percentage of developed area in a watershed (Spearman's rho equals 0.75, p-value is 0.014, fig. 7A; Spearman's rho equals 0.60, p-value is 0.048, fig. 7*B*, respectively). Therefore, the median number and total concentration of OWICs tended to be smaller in water samples from watersheds with relatively smaller amounts of developed area (NAN, SAN, and UTO watersheds) than in samples from watersheds with higher amounts of developed area (INT, PEA, PRO, and SOU watersheds). The median number of OWICs increased slightly as the Flashiness Index increased, but this trend was not statistically significant (Spearman's rho equals 0.41, *p*-value is 0.18, fig. 7*C*). The median number of OWICs detected in samples, therefore, may not be governed by the speed at which storm runoff reaches the stream channel.



Figure 7. Relations between (*A*) impervious area and the numbers of organic wastewater-indicator compounds (OWICs) detected above study reporting levels, (*B*) impervious area and total OWIC concentration, and (C) the numbers of OWIC detected above study reporting levels and flashiness index at sampling sites near Atlanta, GA, March 2003 to January 2006.

Seasonal Variation in OWICs

In order to discern seasonal patterns in the numbers and concentrations of OWICs detected in each sample, samples were split into two seasonal groups characteristic of Atlanta's climate—cool season (November-March) and warm season (April-October)— according to the month in which they were collected. In principle, the number of OWICs identified and their concentrations in water samples should mirror their seasonal-use patterns. For example, products containing sun screen may be used more frequently during the warm season; therefore, compounds found in sun screens, such as methyl salicylate, camphor, and fragrance compounds, should be detected more frequently in warm-season samples from streams containing wastewater effluent. In contrast, the occurrence frequency and concentrations of compounds that are either used or may be present in sewage effluent year-round, such as caffeine, cotinine, and fecal sterols, should, in theory, be similar in water samples from streams regardless of season; however, concentrations may be greater during the cool season because the warm season brings higher water temperatures, greater microbial activity, and higher degradation rates.

Disinfection and Personal-Use Compounds

Seasonally, the lone disinfection compound, bromoform, was detected with similar frequency in warm- and cool-season samples (fig. 8). This result is not unexpected because few samples collectively contained bromoform concentrations above the SRL. The detection frequency and concentrations of several personal-use compounds were different, some markedly so, between warm- and cool-season samples collected during the study period. Ten of the 14 personal-use compounds were detected with similar frequency (\pm 5 percent) in warm- and cool-season samples. Three personal-use compounds-caffeine, camphor, menthol-were detected more frequently in cool- than in warm-season samples. The seasonal differences in those three compounds are difficult to explain because products that contain those compounds are used throughout the year, but during the warm season those compounds may degrade more rapidly than during the cool season. Because caffeinated beverages are consumed and excess beverages are disposed year-round, caffeine is expected in wastewater effluent year-round. As previously mentioned, more than 99 percent of caffeine that enters wastewater treatment plants is removed by the treatment process (Buerge and

others, 2006). Therefore, samples with elevated concentrations of caffeine may indicate that untreated wastewater, wet- or dry-weather urban runoff, CSOs, or runoff from large parking lots is the source of caffeine in water samples collected from streams near Atlanta. As a result, caffeine is probably a poor tracer of CSOs in the Atlanta area.

Of the personal-use compounds, only DEET—the ingredient in insect repellant—was detected in more warmthan cool-season samples. Although the increase in samples containing DEET mirrors its use during the warm season, 8 percent of the cool-season samples contained DEET at a median concentration less than the SRL ($0.34 \mu g/L$). The maximum concentration in the cool-season samples was $1.4 \mu g/L$. Because most people, including the field personnel in this study, are not likely to wear mosquito repellant during the cool season, water samples should not have contained DEET; however, these cool-season detections may represent environmental persistence or sample contamination.

Few studies have focused on the fate and stability of DEET in the environment, especially in relation to degradation in streams or its presence in groundwater. The DEET compound is not soluble in water (less than 1 gram per 100 mL) and is not degraded by hydrolysis in the environment (U.S. Environmental Protection Agency, 1998); however, certain bacteria and fungi common in soil can degrade DEET (Seo and others, 2005; Rivera-Cancel and others, 2007). Another possible explanation for the cool-season DEET detections is that cool- and warm-season samples were contaminated with DEET from the ambient air within field vehicles. Bottles of mosquito repellant containing DEET may have been left inadvertently in field vehicles during sampling, resulting in a high concentration of DEET vapors within the vehicle interior and contaminating samples. Given that scenario, cool-season detections may represent vaporized DEET in the ambient air within field vehicles regardless of season. The concentration of DEET vapors may be relatively high within a vehicle because the windows in field vehicles commonly are closed during cold weather when the heater is typically on and in hot, humid weather when the air conditioner is commonly running. With the windows closed, a limited exchange of air occurs between the vehicle interior and the ambient air outside, thereby facilitating sample contamination; however, trip samples, which could have identified such contamination, were not included among water samples sent to the laboratory for analysis during the study.





Pesticide Compounds

Studies of pesticides in surface water have shown that, typically, pesticides are detected in water samples with the greatest frequency after land application, and especially when rainfall occurs after application (Gilliom and others, 2006). In urban areas, the application of some pesticides tends to be greatest during the warm season (Sprague and others, 2007). During the study period, the pesticides carbaryl and prometon were detected in greater percentages of warm- than coolseason samples (fig. 8). In contrast, 14DCB was detected with slightly greater frequency in cool- than warm-season samples; whereas, bromacil and diazinon were detected with similar frequency during both seasons. The detection frequencies for carbaryl may be conservative because about 75 percent of laboratory blanks spiked with carbaryl had recovery rates of less than 40 percent (fig. 4).

Sterol Compounds

The sterols cholesterol and sitosterol were detected in about 10 percent more warm- than cool-season samples (fig. 8). Coprostanol was detected in slightly more (6 percent) cool- than warm-season samples. The higher number of samples containing cholesterol and sitosterol during the warm-season coincides with the greater vegetation growth and decomposition during warm weather. The seasonal difference between coprostanol and the other three sterols may be related to their different sources and the reduced decomposition of source material during the cool season. The warm season accelerates the decomposition of fecal material, resulting in the reduction of the coprostanol source and concomitantly increasing the decomposition of plant material, which is typically the source of cholesterol, sitosterol, and stigmastanol in the Atlanta streams.

Industrial-Use Compounds

Of the six industrial-use compounds analyzed during the study period, only *d*-limonene showed slight seasonal differences (fig. 8). The compound *d*-limonene was detected in about 5 percent more cool- than warm-season samples. In past years, *d*-limonene was used primarily as an insect repellant and dog or cat repellant (Kegley and others, 2008); however, in recent years its use as a degreasing substitute for chlorinated solvents, such as PCE, has increased steadily (Florida Chemical Company, 2008). The number of samples containing *d*-limonene may be higher during the cool season because degradation rates of organic compounds typically decrease as temperature decreases, enabling *d*-limonene to persist until temperatures increase and biodegradation rates increase.

Polycyclic Aromatic Hydrocarbon Compounds

Of the six PAH compounds analyzed, only twophenanthrene and *p*-cresol—showed seasonal detection patterns (fig. 8). These two compounds were detected in 7–9 percent more cool- than warm-season samples. Potential sources of PAHs in urban runoff are numerous (Yunker and others, 2002). Atmospheric inversions coupled with the increase in wood burning during the cool season and vehicle exhaust may increase the concentration of p-cresol and phenanthrene in the urban air mass during the cool season. Furthermore, regardless of season, *p*-cresol and phenanthrene may enter urban streams in Atlanta as atmospheric particulates that are deposited onto impervious surfaces (Ligocki and others, 1985a, b; Lopes and others, 1998) with subsequent wash off during rain storms as urban runoff. Fresh asphalt and asphalt seal coats can be substantial sources of fluoranthene and pyrene to urban runoff (Van Metre and others, 2009). Identifying specific sources of PAHs is complex and site specific, and is a task that is beyond the scope of this report.

Automotive-Use Compounds

Three of the six automotive-use compounds (naphthalene and 1- and 2-methylnaphthalene) were detected in 8-14 percent more cool- than warm-season samples (fig. 8). The compounds 2,6-dimethylnaphthalene, 5-methyl-1Hbenzotriazole, and isopropylbenzene were detected with similar frequency (within \pm 5 percent) in samples collected during both seasons. The similar detection frequency of 5-methyl-1H-benzotriazole in samples from both seasons is unexpected because this compound is typically a component of antifreeze solutions in vehicle radiators. During hot weather, radiator contents commonly expand, and the liquid overflows onto roadways and parking lots. The presence of the naphthalene compounds in more cool-season samples may be related to greater evaporation into the atmosphere during the warm season or slower degradation rates during cool weather (Gustafson and Dickhut, 1997).

Non-ionic Detergent Metabolites and Flame-Retardant Compounds

Seasonal variation in the numbers varied widely among the NDMCs (fig. 8). The compounds NPEO2 and 4-Octylphenol diethoxylate (OPEO2) were detected in 6–7 percent more warm- than cool-season samples; however the compounds *p*-nonylphenol, 4-Octylphenol monoethoxylate (OPEO1), and 4-*tert*-octylphenol were detected with similar frequency in samples from both seasons. The flame-retardant compounds TBEP, TCEP, and TDCPP were detected in 6–18 percent more warm- than cool-season samples during the study period. Tributyl phosphate was detected with similar frequency in both seasons.

Variation During Base Flow and Stormflow

During periods of dry weather, base flow consists of groundwater discharge and runoff from outdoor water use. Stormflow is generated by rainfall that flows overland and within shallow soil horizons and discharges to a stream channel during periods of wet weather. In urban areas, this flow is called urban runoff. The number of OWICs detected in any one base-flow sample ranged from zero in all watersheds, except for Intrenchment Creek, to a high of 36 in one South River sample (fig. 9). The median number of OWICs identified in base-flow samples ranged from 3 in control-basin samples to 14 and 16 in upstream and downstream base-flow samples, respectively. Stormflow samples from all watersheds contained substantially higher numbers of detectable OWICs than did base-flow samples. The median number of OWICs in stormflow samples ranged from 7 to 9 in control-basin samples, from 13 to 17 in upstream samples, and 10 to 19 in downstream samples.

Personal-Use Compounds

At least one personal-use compound was detected in 11 percent of all base-flow samples (table 9) and 14 percent of all stormflow samples collected during the study (table 10). The six most frequently detected compounds in base-flow samples were caffeine, triclosan, HHCB, indole, menthol, and DEET, in that order. In stormflow samples, however, the four most frequently detected compounds were caffeine, camphor, menthol, and DEET, in that order. Among all samples collected during the study period, triclosan, HHCB, indole, AHTN, and cotinine were detected more frequently in base-flow than stormflow samples (fig. 10). Conversely, acetophenone, DEET, menthol, camphor, and caffeine were detected in 7–39 percent more stormflow than base-flow samples during the study period. The other personal-use compounds, such as benzophenone, methyl salicylate, triethyl citrate, and isoborneol were detected at similar frequencies (within \pm 5 percent) in base-flow and stormflow samples.

Concentrations of individual personal-use compounds exceeded their respective SRLs in 2 (isoborneol) to 61 percent (caffeine) of samples collected during the study (tables 3, 8). The maximum concentrations of 7 of the 14 personal-use compounds were measured in a single base-flow sample from an upstream site (PRO-3) in the PRO watershed (table 11). These compounds include caffeine (11 μ g/L), menthol (8.6 μ g/L), and triclosan (2.2 μ g/L). In addition, a base-flow sample from one of the synoptic sites in the SOU watershed contained the highest concentrations of benzophenone $(0.87 \ \mu g/L)$ and camphor $(1.8 \ \mu g/L)$ measured during the study. The highest concentrations of DEET (6.0 μ g/L) and bromoform (19 µg/L) were measured in base-flow samples from downstream sites in the INT watershed. Among stormflow samples, the highest concentrations of acetophenone $(3.5 \ \mu g/L)$ and methyl salicylate $(0.33 \ \mu g/L)$ were detected at downstream sites in the SOU watershed (table 12).



Figure 9. Distribution in the numbers of organic wastewater-indicator compounds (OWICS) per sample above study reporting levels (table 3) in base-flow and stormflow samples from streams in the Nancy Creek (NAN), Sandy Creek (SAN), Utoy Creek (UTO), Intrenchment Creek (INT), Peachtree Creek (PEA), Proctor Creek (PRO), and South River (SOU) watersheds near Atlanta, GA, March 2003 to January 2006.



Relative difference in the percentage of base-flow



Pesticide Compounds

Collectively, pesticide compounds were detected with similar frequency (12 and 15 percent) in base-flow and stormflow samples (tables 9, 10). About 42 percent of all samples contained bromacil at concentrations greater than the SRL of 0.1 μ g/L (table 8). Bromacil was the most frequently detected pesticide in base-flow samples during the study and was detected in about 27 percent more base-flow than stormflow samples, indicating that stormflow dilutes bromacil concentrations (table 9, fig. 10). This difference implies that bromacil is entering Atlanta streams by either dry-weather runoff or groundwater discharge.

Among all stormflow samples, carbaryl and bromacil were the most frequently detected pesticides (table 10). Carbaryl and bromacil were detected in 41 and 27 percent, respectively, of stormflow samples collected during the study. Carbaryl was detected in about 32 percent more stormflow than base-flow samples during the study period, indicating runoff from landscaped areas is a possible source of this pesticide (fig. 10). Diazinon and prometon were detected in slightly more stormflow (5 percent more) than base-flow samples.

Less than 1–42 percent of all samples collected during the study contained individual pesticides at concentrations that exceeded their respective SRLs (tables 3, 8). The highest bromacil concentration in the study (29 μ g/L) was measured in a base-flow sample from an upstream site in the PEA watershed (table 11). The maximum carbaryl concentration, 0.98 μ g/L, was measured in a stormflow sample from the NAN watershed (table 12). The maximum 14DCB and prometon concentrations (5.0 and 2.1 μ g/L, respectively) were measured in stormflow samples from downstream sites in the PRO and SOU watersheds, respectively. Although diazinon was detected in slightly more stormflow than base-flow samples, the maximum concentration measured during the study period was 28 μ g/L in an upstream, base-flow sample from the PEA watershed (table 11).

Sterol Compounds

Sterol compounds were detected in 24 percent of all base-flow samples and in 30 percent of all stormflow samples collected during the study (tables 9, 10). Cholesterol and coprostanol were the most frequently detected sterol compounds in base-flow and stormflow samples; however, sitosterol and cholesterol were detected in 10 and 7 percent, respectively, more stormflow than base-flow samples (fig. 10). Coprostanol and stigmastanol were detected with similar frequency (within \pm 5 percent) in base-flow and stormflow samples.

Fifteen to 49 percent of all samples contained sterol compounds at concentrations that exceeded their respective SRLs (tables 3, 8). One base-flow sample collected at an upstream site in the PRO watershed (PRO-3) on March 31, 2004, contained the highest concentrations of cholesterol (16 μ g/L), coprostanol (7.5 μ g/L), and sitosterol (4.1 μ g/L) measured during the study period (tables 11, 12). A base-flow sample from a downstream site in the PRO watershed contained the highest concentration of stigmastanol (4.1 μ g/L).

Industrial-Use Compounds

The industrial-use compounds were detected in about 9 and 18 percent of base-flow and stormflow samples, respectively during the study (tables 9, 10). Tetrachloroethene (PCE, 28 percent) was the most frequently detected industrialuse compound in base-flow samples (table 9). In contrast, carbazole, and *d*-limonene were the most frequently detected industrial-use compounds in stormflow samples (table 10).

Four of the six industrial-use compounds were detected in more stormflow than base-flow samples (fig. 10). In decreasing order, carbazole, anthraquinone, TPP, and *d*-limonene were detected in 36 to 11 percent more stormflow than base-flow samples. In contrast, PCE was detected in about 12 percent more base-flow samples and bisphenol-A was detected with similar frequency in base-flow and stormflow samples. Dry-weather runoff or groundwater discharge may be the source of PCE to streams in the study area, which is diluted during stormflow.

Five (*d*-limonene) to 23 (carbazole) percent of all samples collected during the study contained industrial-use compounds at concentrations that exceeded their respective SRLs (tables 3, 8). A downstream base-flow sample from the SOU watershed contained the highest PCE concentration (8.0 μ g/L) measured during the study period (tables 11, 12). The maximum concentrations of bisphenol-A (2.2 μ g/L) and TPP (1.0 μ g/L) were measured in upstream stormflow samples from the SOU watershed. The maximum concentrations of anthraquinone (1.6 μ g/L) and carbazole (1.2 μ g/L) were measured in base-flow samples from the UTO and NAN watersheds, respectively (tables 11, 12). An upstream stormflow sample from the PEA watershed contained the maximum concentration of *d*-limonene (1.9 μ g/L).

Polycyclic Aromatic Hydrocarbon Compounds

The PAH compounds were detected in about 6 percent of all base-flow and 22 percent of all stormflow samples collected during the study (tables 9, 10). In base-flow samples, *p*-cresol was the most frequently detected PAH; whereas, fluoranthene and phenanthrene were the most frequently detected PAHs in stormflow samples. Except for anthracene, the PAH compounds were detected in 12–33 percent more stormflow than base-flow samples (fig. 10). Anthracene was detected with similar frequency in base-flow and stormflow samples.

Five (anthracene) to 32 (*p*-cresol) percent of all samples collected during the study contained PAHs at concentrations that exceeded their respective SRLs (tables 3, 8). A base-flow sample from an upstream site in the PEA watershed contained the highest *p*-cresol concentration (24 μ g/L) measured during the study (table 11). In addition, the highest *p*-cresol concentration (18 μ g/L) in stormflow samples was measured at a downstream site in the PRO watershed (table 12). The highest PCP concentrations in base-flow and stormflow samples (3.9 and 7.2 μ g/L, respectively) were measured from sites in the UTO watershed (tables 11, 12). Stormflow samples from the UTO and NAN watersheds contained the highest

concentration of fluoranthene (0.42 μ g/L) measured during the study. In addition, a stormflow sample from the UTO watershed contained the highest phenanthrene concentration (1.3 μ g/L) measured during the study. A base-flow sample from a downstream site in the PRO watershed contained the highest pyrene concentration (0.50 μ g/L) measured during the study (table 11).

Automotive-Use Compounds

As a class, the automotive-use compounds were typically detected with the lowest frequency in base-flow and stormflow samples during the study period (tables 9, 10). Only about 5.1 percent of base-flow samples and 16 percent of stormflow samples contained at least one detectable automotive-use compound. Naphthalene was the most frequently detected automotive-use compound in all base-flow and stormflow samples (14 and 30 percent, respectively). Four of the six automotive-use compounds were detected in 11–18 percent more stormflow than base-flow samples (fig. 10). The compound 5-methyl-1H-benzotriazole (an anti-corrosive compound) and isopropylbenzene were detected at similar frequencies in base-flow and stormflow samples.

Less than 1 (isopropylbenzene) to 39 (naphthalene) percent of the automotive-use compounds were detected at concentrations that exceeded their respective SRLs (tables 3, 8). Except for 5-methyl-1H-benzotriazole, the highest concentrations of the automotive-use compounds were measured in stormflow samples (tables 11, 12). The highest concentration of 1-methylnaphthalene (0.72 μ g/L) was measured in a downstream stormflow sample from the PRO watershed; whereas, the highest concentrations of 2-methylnaphthalene and 2,6-dimethylnaphthalene (0.8 and $0.4 \mu g/L$, respectively) were measured in stormflow samples from upstream sites in the PEA watershed. Among stormflow samples, the highest concentration of naphthalene (1.2 μ g/L) was measured at a site in the UTO watershed (table 12). The highest concentrations of 5-methyl-1H-benzotriazole were measured in an upstream base-flow sample (6.1 μ g/L) and a downstream stormflow sample (5.1 μ g/L) from the SOU watershed (tables 10, 11).

Detection frequencies of organic wastewater-indicator compounds in base-flow samples collected from streams in the control basins (Nancy Creek, Sandy Creek, and Utoy Creek), and at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006. Table 9.

[NAN, Nancy Creek: SAN, Sandy Creek; UTO, Utoy Creek; INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek watershed; SOU, South River; ---, less than 1 percent]

						Dete	sction free	luency (pu	ercent)						
			Control	basin		'n	ostream w	ratershed				Downstr	eam wate	rshed	
Compound	All basins	All control	NAN	SAN	UTO	All upstream	INT	PEA	PRO	SOU	All downstream	INT	PEA	PRO	SOU
Number of samples	475	sampres 156	57	21	78	167	1a	85	32	49	152	26	54	45	27
-						Parconal-lica		shr							
AHTN, tonalide	14	=	=	14	10	14	0/1	7.1	28	18	16	31	3.7	18	26
Acetophenone	4.2					4.8	0/1	1.2		14	7.9	19		13	3.7
Benzophenone	9.1	3.8	5.3	9.5	1.3	13	0/1	7.1	16	22	10	27	1.9	8.9	11
Caffeine	39	20	25	19	17	41	1/1	37	22	61	55	81	50	44	56
Camphor	13	8.3	3.5	24	7.7	19	0/1	8.2	25	33	11	19	1.9	16	11
Cotinine	16	5.1	1.8	9.5	6.4	18	0/1	7.1	19	37	26	50	3.7	36	33
HHCB, galaxolide	21	14	11	19	15	25	0/1	7.1	56	37	22	69	1.9	20	22
Indole	20	14	1.8	29	18	23	1/1	8.2	38	39	23	39	5.6	31	30
Isoborneol	2.5				1.3	3.6	0/1		3.1	10	3.3	3.8		6.7	3.7
Menthol	20	15	11	24	15	21	0/1	8.2	25	41	26	39	7.4	36	33
Methyl salicylate	10	9.6	8.8	19	7.7	8.4	0/1	1.2	13	18	13	15	7.4	8.9	26
DEET	18	10	5.3	14	13	23	0/1	18	22	35	20	62	7.4	11	22
Triclosan	26	22	14	24	27	24	0/1	8.2	47	37	31	62	9.3	40	30
Triethyl citrate	9.3	6.4	3.5	14	6.4	13	0/1	5.9	13	27	7.9	23		6.7	11
Class percentage ^b	11	7.3	5.2	11	8	13		6.4	17	22	14	28	5.2	15	17
						Disinfection	compoun	ds							
Bromoform	6.5	1.3	1.8		1.3	15	0/1	5.9		41	2.6	11			3.7

						Det	ection fre	d) house the	ercent)			·			
			Control	basin			pstream v	vatershed				Downstr	eam wate	ershed	
Compound	All	AII				AII					AII				
	basins	control samples	NAN	SAN	UTO	upstream samples	IN	PEA	PRO	SOU	downstream samples	INT	PEA	PRO	SOU
						Pesticide o	punoduoc	s							
1,4-Dichlorobenzene (14DCB)	13	4.5	5.3	10	2.6	10	0/1	9.4	19	6.1	24	35	=	38	19
Bromacil	54	37	11	14	63	64	1/1	45	75	06	61	31	39	89	85
Carbaryl	10	9.0	8.8	4.8	10	10	0/1	7.1	3.1	20	9.2	12	3.7	13	11
Chlorpyrifos	I						0/1		3.1		1.3			4.4	
Diazinon	2.7	I			1.3	4.2	0/1	4.7	6.3	2.0	3.3		3.7	4.4	3.7
Prometon	3.2	1.3			2.6	4.2	0/1	4.7	6.3	2.0	3.9	3.8	5.6		7.4
Class percentage ^{b}	12	7.7	3.6	4.2	12	14	I	10	17	18	15	12	9.3	22	19
						Sterol co	spunodu								
Cholesterol	45	32	28	19	39	44	0/1	35	99	47	60	LT	46	64	63
3-β-Coprostanol	28	15	11	14	19	26	0/1	17	38	35	43	LL	26	49	33
β-sitosterol	17	10	8.8	4.8	13	14	0/1	9.4	19	20	27	39	18	33	22
β-stigmastanol	14	8.3	8.8		10	11	0/1	9.4	6.3	16	23	23	18	29	22
Class percentage ^b	24	15	13	6	19	22	I	16	30	27	35	50	25	41	33
						Industrial-us	e compou	spu							
Anthraquinone	2.5	2.6	1.8	4.8	2.6		0/1		3.1		4.6	15		6.7	
Bisphenol-A	5.5	1.9		4.8	2.6	7.2	0/1	3.5	6.3	14	7.2	12	3.7	6.7	11
Carbazole	6.3	4.5	5.3		5.1	5.4	0/1	3.5	3.1	10	9.2	15	5.6	11	7.4
d-Limonene	12	8.3	3.5	14	10	16	0/1	9.4	25	22	13	15	5.6	13	22
Tetrachloroethylene (PCE)	28	14	37	4.8		50	1/1	36	81	53	17	3.8	17	27	15
Triphenyl phos- phate (TPP)	5.1	1.3			2.6	7.8	0/1		6.3	22	5.9	12	I	11	3.7
Class percentage ^b	8.8	4.8	7.0	4.2	3.4	13		7.8	18	18	8.3	11	4.6	11	8.7

Table 9. Detection frequencies of organic wastewater-indicator compounds in base-flow samples collected from streams in the control basins (Nancy Creek, Sandy Creek, and Utoy Creek), and Utoy Creek), and at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek, and South River Wasterback on Alastic 20, March 2003 to London 2006. Continued

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Occurrence of OWICs

Detection frequencies of organic wastewater-indicator compounds in base-flow samples collected from streams in the control basins (Nancy Creek, Sandy Creek, and Utoy Creek), and at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.—Continued Table 9.

[NAN, Nancy Creek; SAN, Sandy Creek; UTO, Utoy Creek; INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek watershed; SOU, South River; ---, less than 1 percent]

						Dete	ection fre	tuency (pe	ercent)						
			Control	basin		ī	pstream v	/atershed				Downstre	eam wate	rshed	
Compound	All basins	AII control samples	NAN	SAN	UTO	All upstream samples	INT	PEA	PRO	SOU	All downstream samples	INT	PEA	PRO	SOU
					Polycyc	lic aromatic h	hydrocarb	ons (PAHs							
Anthracene	1.7		1.8			1.2	0/1	1.2		2.0	3.3			11	
<i>p</i> -Cresol	15	6.4		19	7.7	22	1/1	4.7	19	53	16	39	1.9	22	15
Fluoranthene	5.5	3.2	5.3		2.6	6.0	1/1	2.4	6.3	10	7.2	11	5.6	11	
Pentachlorophenol (PCP)	7.2	10		4.8	18	3.6	0/1		3.1	10	8.6		3.7	16	15
Phenanthrene	4.8	2.6	3.5		2.6	4.8	0/1		6.3	12	7.2	19	1.9	8.9	3.7
Pyrene	6.7	5.8	8.8		5.1	7.8	0/1	3.5	6.3	16	9.9	7.7	3.7	11	3.7
Class percentage ^b	6.1	4.2	2.8	3.5	5.3	6.7		1.7	6.0	15	7.3	11	2.5	12	5.5
					A	utomotive-us	se compor	spur							
1-Methylnaph- thalene	2.9	1.9	3.5		1.3	3.6	0/1			12	3.3	3.8		4.4	7.4
2-Methylnaph- thalene	3.4	1.3	3.5			4.2	0/1		I	14	4.6	<i>T.T</i>		6.7	7.4
2,6-Dimethyl naphthalene	1.3		1.8			1.8	0/1			6.1	1.3			2.2	3.7
5-Methyl-1H- benzotriazole	6.5	1.9	1.8		2.6	6.6	1/1	5.9		10	11	3.8	15	11	11
Isopropylbenzene	I					I	0/1				I			2.2	
Naphthalene	14	13	5.3	10	19	15	0/1	1.2	25	33	14	15	7.4	20	15
Class percentage ^b	5.1	3.4	2.9	1.7	4.2	5.6		1.3	4.5	14	6.3	5.6	4.0	8.4	8.0
					Non-ion	c detergent r	netabolite	s (NDMC	(\$						
<i>p</i> -Nonylphenol (total)	32	23	25	38	18	31	0/1	18	25	57	44	62	28	40	67

Detection frequencies of organic wastewater-indicator compounds in base-flow samples collected from streams in the control basins (Nancy Creek, Sandy Creek, and Utoy Creek), and at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.—Continued Table 9.

Control hasin4.0000001141.94.55.34.83.81.31.00.14.0000001141.91.84.81.31.00.10.10.000001141.91.84.81.31.70.10.00001141.91.84.81.31.70.10.00001141.91.81.31.70.10.10.00001141.91.81.3		Detection	n frequency (percent)						
CompoundAll basinsAll controlAll upstreamAll upstream4-Nonylphenol3215181015340/14-Nonylphenol3215181015340/14-Ocylphenol11 4.5 5.3 4.8 3.8120/14-Ocylphenol19 8.3 7.0 $$ 12230/14-Ocylphenol19 8.3 7.0 $$ 12230/14-Ocylphenol141.9 8.3 7.0 $$ 1220 $-$ 4-Crylphenol19 8.3 7.0 $$ 12230/14-cr/Ocylphenol141.9 1.9 8.3 7.0 $$ 1220 $$ 4-terr-Ocylphenol141.9 8.3 7.0 $$ 12 23 $0/1$ 10FO2)1119 8.3 7.0 $$ 12 23 $0/1$ 1111 1.9 8.3 4.8 1.3 10 $0/1$ 111118 $$ 1.3 17 $0/1$ 111118 $$ 1.3 17 $0/1$ 111118 $$ 1.3 17 $0/1$ 111118 $$ 1.3 17 $0/1$ 111118 $$ 1.3 17 $0/1$ 111118 $$ 1.3 17 $0/1$ 11 <th>Control basin</th> <th>Upstre</th> <th>am watershe</th> <th>q</th> <th></th> <th></th> <th>Downsti</th> <th>ream wate</th> <th>ershed</th> <th></th>	Control basin	Upstre	am watershe	q			Downsti	ream wate	ershed	
Anticipation	NAN NAN	All	, L	6	100	All	H		G	100
4-Nonylphenol 32 15 18 10 15 34 01 diethoxylate (NPE02) 11 4.5 5.3 4.8 3.8 12 01 4-Octylphenol 11 4.5 5.3 4.8 3.8 12 01 4-Octylphenol 19 8.3 7.0 - 12 23 01 4-Octylphenol 19 8.3 7.0 - 12 23 01 diethoxylate 19 8.3 7.0 - 12 23 01 diethoxylate 19 8.3 7.0 - 12 23 01 diethoxylate 19 1.9 1.8 4.8 1.3 10 01 A-tert-Octylphenol 14 1.9 1.8 4.8 1.3 10 01 A-tert-Octylphenol 14 1.9 1.8 0.9 0 0 0 Class percentage 20 0.1 10 0 0 0 0 0 0 0 0 0<	NAN SAN ULU	upstream IN samples	rea	rku	nne	aownstream samples	2	PEA	LKU	nne
	18 10 15	34 0/1	1 19	31	63	46	81	28	42	56
	5.3 4.8 3.8	12 0/1	9.4	13	16	17	27	11	22	11
4-terr-Octylphenol 14 1.9 1.8 4.8 1.3 10 $0/1$ Class percentage ^b 20 9.6 10 10 9.0 20 20 $0/1$ Class percentage ^b 20 9.6 10 10 9.0 20 $0/1$ Tributyl phosphate 16 7.1 18 -1 1.3 17 $0/1$ Tributyl phosphate 16 7.1 18 -1 1.3 17 $0/1$ Trist2-butoxyethyl) 64 46 33 43 55 62 $1/1$ Phosphate (TBEP) 71 18 -1 1.3 73 55 $0/1$ Trist2-butoxyethyl) 52 36 56 29 23 55 $0/1$ Phosphate (TDEP) 37 15 18 14 13 43 $0/1$ Trist(dichloroiso- 37 15 18 14 13 43 $0/1$ Propp/l phote- 90 91 91 91 91 91 91	7.0 — 12	23 0/1	1 18	28	29	27	46	13	29	33
Class percentage ^b 20 9.6 10 10 9.0 20 - Tributyl phosphate 16 7.1 18 - 1.3 17 0/1 Tributyl phosphate 16 7.1 18 - 1.3 17 0/1 Tributyl phosphate 16 7.1 18 - 1.3 17 0/1 Tris(2-butoxyethyl) 64 46 33 43 55 62 1/1 phosphate (TBEP) 52 36 56 29 23 55 0/1 Tris(2-chloroethyl) 52 36 56 29 23 55 0/1 Tris(dichloroiso- 37 15 18 14 13 43 0/1 Tris(dichloroiso- 37 15 18 14 13 43 0/1	1.8 4.8 1.3	10 0/	1 7.1	9.4	16	31	31	7.4	69	15
Tributyl phosphate 16 7.1 18 1.3 17 0/1 (TBP) (TBP) 64 46 33 43 55 62 1/1 Tris(2-butoxyethyl) 64 46 33 43 55 62 1/1 Phosphate (TBEP) 7.1 18 1.3 17 0/1 Tris(2-butoxyethyl) 52 36 56 29 23 55 0/1 Tris(2-chloroethyl) 52 36 56 29 23 55 0/1 Tris(dichloroiso- 37 15 18 14 13 43 0/1 Propyl) phos- 57 15 18 14 13 43 0/1	10 10 9.0	20	- 13	19	33	30	45	16	37	33
Tributyl phosphate 16 7.1 18 - 1.3 17 0/1 (TBP) (TBP) 5 5 5 5 13 14 13 17 0/1 Tris(2-butoxyethyl) 64 46 33 43 55 62 1/1 phosphate (TBEP) 5 36 56 29 23 55 0/1 Tris(2-chloroethyl) 52 36 56 29 23 55 0/1 Tris(2-chloroethyl) 51 15 18 14 13 43 0/1 Tris(dichloroiso- 37 15 18 14 13 43 0/1 propyl) phos- phote (TDCPP) 7 7 15 18 14 13 43 0/1	Fla	me-retardant coi	spunodu							
Tris(2-butoxyethyl) 64 46 33 43 55 62 1/1 phosphate (TBEP)	18 — 1.3	17 0/1	1	19	26	24	85	5.6	16	19
Tris(2-chloroethyl) 52 36 56 29 23 55 0/1 phosphate (TCEP) 3 3 3 3 3 3 3 3 3 3 1 3 1 1	33 43 55	62 1/1	1 51	59	82	85	100	72	84	100
Tris(dichloroiso- 37 15 18 14 13 43 0/1 propyl) phos- phate (TDCPP) phate (TDCPP) <td< td=""><td>56 29 23</td><td>55 0/:</td><td>1 45</td><td>47</td><td>80</td><td>66</td><td>92</td><td>46</td><td>62</td><td>85</td></td<>	56 29 23	55 0/:	1 45	47	80	66	92	46	62	85
	18 14 13	43 0/1	1 20	34	88	54	85	35	42	82
Class percentage ^b 39 24 29 20 21 41 —	29 20 21	41 —	- 29	37	64	53	83	37	47	99
^a For sample sizes less than 10, the number of samples containing the compound is given instead of a percentag ^b Weiohted value based on the nercentage of communds detected within its associated commund class	es containing the compound is given	instead of a percer	ntage.							

less than 1 nercent1 chment Creek: DEA Deachtree Creek: DRO Proctor Creek watershed: SOU South River INAN Nancy Creek: SAN, Sandy Creek: UTO, Utoy Creek: INT, Intr Table 10. Detection frequencies of organic wastewater-indicator compounds in stormflow samples collected from streams in the control basins (Nancy Creek, Sandy Creek, and Utoy Creek), and at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.

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						ā	etection f	requency (percent)						
			Control	basin			Ups	tream basi	=			Downs	tream bas	.=	
Compound	AII basins	AII control	NAN	SAN	UTO	All upstream	INT	PEA	PRO	SOU	AII downstream	INT	PEA	PRO	SOU
		samples				samples					samples				
Number of samples	388	144	71	17	56	108	2^{a}	71	8^{a}	27	136	19	59	33	25
						Personal-u	se compo	spun							
AHTN	7.2	5.6	4.2	18	3.6	6.5	2/2			19	9.6	21	5.1	9.1	12
Acetophenone	11	2.1		Ι	5.4	15	0/2	16	3/8	7.4	16	37	8.5	18	16
Benzophenone	8.2			5.9		8.3	0/2	9.9	1/8	3.7	16	74	5.1	6.1	12
Caffeine	LL	63	89	24	41	81	2/2	90	5/8	59	89	100	83	88	96
Camphor	48	47	55	35	41	48	2/2	55	4/8	26	49	74	27	58	68
Cotinine	11		1.4	I		10	2/2	4.2	4/8	7.4	23	32	15	18	40
HHCB, Galaxolide	9.0	4.2	4.2		5.4	9.3	2/2		5/8	11	14	37	1.7	24	12
Indole	13	10	8.5	18	11	17	2/2	4.2	5/8	30	13	16	8.5	27	4.0
Isoborneol	2.1					4.6	0/2	5.6		3.7	2.2	5.3		3.0	4.0
Menthol	37	23	24	29	20	38	2/2	38	5/8	26	51	63	30	67	68
Methyl salicylate	8.5			I	3.6	13	0/2	8.5	3/8	19	13	32	5.1	15	12
DEET	28	21	11	24	32	35	1/2	39	5/8	15	30	58	20	21	44
Triclosan	12	10	13	18	5.4	18	2/2	5.6	6/8	26	10	16	3.4	18	8.0
Triethyl citrate	4.9	2.8	2.8	I	3.6	5.6	1/2	2.8	2/8	3.7	6.6	11	6.8	6.1	4.0
Class percentage ^b	14	10	11	8.9	8.9	16	I	15	31	13	18	30	12	20	21
						Disinfectio	и сотрог	spu							
Bromoform	4.6				1.8	7.4	0/2	1.4		26	6.6	16	3.4		16

Table 10. Detection frequencies of organic wastewater-indicator compounds in stormflow samples collected from streams in the control basins (Nancy Creek, Sandy Creek, and Utoy Creek), and at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006 — Continued

[NAN, Nancy Creek; SAN, Sandy Creek; UTO, Utoy Creek; INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek; SOU, South River; --, less than 1 percent]

						ă	stection fr	equency (r	ercent)						
			Control 1	basin			Upst	ream basi				Downs	tream basi	.=	
Compound	AII	AII				AII					AII				
	basins	control samples	NAN	SAN	UTO	upstream samples	INT	PEA	PR0	SOU	downstream samples	INT	PEA	PR0	SOU
						Pesticide	compoun	ds							
1,4-Dichlorobenzene (14DCB)	16	6.9	1.4	5.9	14	4.6	2/2	1.4		7.4	35	79	12	70	8.0
Bromacil	27	6.9	1.4	5.9	14	48	1/2	37	4/8	78	32	5.3	17	76	32
Carbaryl	41	31	20	41	41	47	2/2	47	4/8	44	47	74	58	9.1	52
Chlorpyrifos	1.0	1.4	2.8			1.9	0/2	2.8			I				
Diazinon	7.0	5.6	2.8	12	7.1	7.4	2/2	1.4	2/8	11	8.1		6.8	12	12
Prometon	7.7	4.2	1.4	5.9	7.1	6.5	0/2	8.5	1/8	I	12	21	14		20
Class percentage ^b	15	8.2	4.4	10	12	17		14	20	21	20	26	16	25	18
						Sterol c	ompound:								
Cholesterol	52	42	45	47	36	63	0/2	65	6/8	59	55	63	54	55	52
3-β-Coprostanol	31	23	30	24	14	33	0/2	25	4/8	52	39	47	34	42	40
β-sitosterol	29	20	23	24	16	36	0/2	37	4/8	33	32	37	31	24	40
β-stigmastanol	16	13	17	12	7.1	17	0/2	11		37	20	42	17	6.1	28
Class percentage ^b	30	22	26	24	17	34	I	32	40	42	34	44	31	29	37
						Industrial-u	se compo	spur							
Anthraquinone	14	9.0	13		7.1	31	0/2	39		19	6.6	16	8.5	3.0	
Bisphenol-A	8.8	5.6	11			14	0/2	8.5		33	8.1	5.3	10	6.1	8.0
Carbazole	42	42	45	24	43	46	1/2	51		48	39	26	42	27	56
<i>d</i> -Limonene	23	15	21	12	8.9	32	2/2	34	4/8	19	24	21	15	36	28
Tetrachloroethene (PCE)	15	6.3	9.9	12		32	2/2	20	6/8	44	11	21	3.4	18	12
Triphenyl phosphate (TPP)	18	7.6	1.4	12	14	32	0/2	20	3/8	63	18	47	5.1	18	24
Class percentage ^{b}	18	13	15	8.7	11	27		25	24	33	16	20	13	16	19

Table 10. Detection frequencies of organic wastewater-indicator compounds in stormflow samples collected from streams in the control basins (Nancy Creek, Sandy Creek, and Utoy Creek), and at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.—Continued

[NAN, Nancy Creek; SAN, Sandy Creek; UTO, Utoy Creek; INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek; SOU, South River; ---, less than 1 percent]

						Ď	stection f	,equency (percent)						
I			Control	basin			Upsi	tream basi	=			Downs	tream bas	. <u></u>	
Compound	AII basins	AII control samples	NAN	SAN	UTO	AII upstream samples	IN	PEA	PRO	SOU	All downstream samples	IN	PEA	PRO	SOU
					Polycy	clic aromatic	hydrocar	bons (PAH	ls)						
Anthracene	3.6	4.2	4.2		5.4	5.6	0/2	4.2		11	1.5			6.1	
<i>p</i> -Cresol	28	23	11	24	38	28	0/2	18	4/8	48	35	58	6.8	64	44
Fluoranthene	36	37	32	5.9	52	38	1/2	37		52	34	5.3	24	61	44
Pentachlorophenol (PCP)	22	22	8.5	12	43	30	0/2	25		52	15	21	17	6.1	20
Phenanthrene	37	39	38	18	46	32	0/2	31		44	40	58	17	70	40
Pyrene	20	17	8.5	I	32	24	0/2	21	I	41	21	Ι	8.5	49	32
Class percentage ^b	22	21	15	8.7	32	23	Ι	20	7.4	37	22	21	11	38	27
						Automotive-ι	nse comp	spunc							
1-Methylnaphthalene	20	11	1.4	18	21	15	0/2	9.9		33	33	53	5.1	64	44
2-Methylnaphthalene	21	11	1.4	18	21	18	1/2	11		37	35	58	8.5	64	40
2,6-Dimethyl naph- thalene	12	4.9	1.4	18	5.4	10	0/2	5.6		26	20	32	5.1	36	24
5-Methyl-1H-benzo- triazole	6.2	2.1	2.8	5.9		10	0/2	9.9	2/8	7.4	7.4		6.8	9.1	12
Isopropylbenzene							0/2				I		1.7		
Naphthalene	30	25	10	23	45	19	1/2	18		26	44	74	15	70	56
Class percentage ^b	16	9.8	3.1	15	17	13	I	9.9	4.5	23	25	39	T.T	44	32

Table 10. Detection frequencies of organic wastewater-indicator compounds in stormflow samples collected from streams in the control basins (Nancy Creek, Sandy Creek, and Utoy Creek), and at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.—Continued

[NAN, Nancy Creek; SAN, Sandy Creek; UTO, Utoy Creek; INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek; SOU, South River; ---, less than 1 percent]

						ă	etection f	equency (percent)						
			Control	basin			Upst	tream basi	i			Downst	tream bas	i	
Compound	AII	AII				AII					AII				
	basins	control samples	NAN	SAN	UTO	upstream samples	INT	PEA	PRO	SOU	downstream samples	INT	PEA	PRO	SOU
					Non-io	nic detergent	t metaboli	tes (NDM(Cs)						
<i>p</i> -Nonylphenol (total)	50	42	47	53	32	48	1/2	48	4/8	48	59	95	46	39	88
4-Nonylphenol diethoxylate (NPEO2)	34	18	16	41	14	44	1/2	44	2/8	48	43	74	24	36	76
4-Octylphenol monoethoxylate (OPE01)	16	6.9	10	12	1.8	17	0/2	11	1/8	33	24	26	15	27	36
4-Octylphenol diethoxylate (OPEO2)	34	21	30	18	11	40	0/2	30	7/8	56	43	68	34	33	56
4-tert-Octylphenol	18	10	17	5.9	3.6	14	0/2	18		7.4	30	5.3	14	64	44
Class percentage ^b	27	18	21	23	11	29	Ι	27	32	35	36	49	24	36	54
						Flame-retard	ant comp	spunc							
Tributyl phosphate (TBP)	27	10	14	12	3.6	33	0/2	34		44	40	95	20	33	52
Tris(2-butoxyethyl) phosphate (TBEP)	91	85	86	94	80	93	2/2	96	7/8	85	96	100	92	100	96
Tris(2-chloroethyl) phosphate (TCEP)	71	55	56	88	43	82	2/2	79	7/8	85	81	95	81	64	92
Tris(dichloroiso- propyl) phosphate (TDCPP)	54	29	27	35	30	66	1/2	58	4/8	93	71	95	76	33	92
Class percentage ^b	56	41	42	53	36	63		61	52	71	99	89	62	53	77
^a For sample sizes less tl	han 10, the nu	umber of samp	oles contain	ning the cor	mpound is giv	ven instead of a	a percentag	e.							

^b Weighted value based on the proportion of compounds detected within its organic wasterwater-indicator compound (OWIC) class.

Table 11. Maximum and 75th percentile concentrations for organic wastewater-indicator compounds in base-flow samples collected from streams in the control basins (Nancy Creek, Sandy Creek, and Utoy Creek), and at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006. [CSO, combined sewer overflow; µg/L, microgram per liter; NAN, Nancy Creek; SAN, Sandy Creek; UTO, Utoy Creek; INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek; SOU, South River < less than hold font indicates 75th percentile values above the study quantitation level (SRL), shaded cell indicates maximum concentration values are study-period maximums for all samples]

		Control b	asin		Upstream	watershe	ed from C	SO outfal	ls	Downstrea	am waters	shed from	CSO outfa	lls
Compound	Maximum concentration	75th perc	entile conce (μg/L)	ntration	Maximum concentration	75th pe	rcentile ((µg/	concentra L)	ation	Maximum concentration	75th pe	ercentile (µg/	concentra L)	tion
	(hg/L)	NAN	SAN	UTO	(hg/L)	INT	PEA	PRO	SOU	(hg/L)	INT	PEA	PRO	SOU
					Personal-use c	ounodwo:	s							
AHTN	<0.25	<0.25	<0.25	<0.25	0.40^{a}	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Acetophenone	<.25	< .25	< .25	< .25	1.8 ^b	< .25	< .25	< .25	< .25	.58ª	<0.25	< .25	< .25	< .25
Benzophenone	<.25	< .25	< .25	< .25	.87 ^{c,d}	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25
Caffeine	1.7 ^e	< .25	< .25	< .25	11a,f	< .25	< .25	< .25	.55	$10^{\rm a,g}$.65	.27	.35	.37
Camphor	<.25	< .25	< .25	< .25	1.8 ^{c,d}	< .25	< .25	< .25	< .25	.33ª	< .25	< .25	< .25	< .25
Cotinine	<.50	< .50	<.50	< .50	$1.4^{\rm a,f}$	<.50	<.50	< .50	< .50	.63 ^g	< .25	<.50	<.50	<.50
HHCB, Galaxolide	.35°	<.25	<.25	<.25	$1.6^{\rm a,f}$	<.25	<.25	<.25	<.25	.56 ^a	<.25	<.25	<.25	< .25
Indole	<.25	<.25	<.25	<.25	1.9 ^{a,f}	<.25	<.25	<.25	<.25	<.25	<.25	<.25	<.25	<.25
Isoborneol	<.25	< .25	< .25	< .25	.75°,d	<.25	< .25	< .25	< .25	.28ª	< .25	< .25	< .25	< .25
Menthol	1.7°	< .25	< .25	< .25	$8.6^{a,f}$	< .25	< .25	< .25	< .25	2.0^{a}	< .25	< .25	< .25	< .25
Methyl salicylate	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25	.33 ^{a,f}	< .25	< .25	< .25	< .25
DEET	.76 ^e	< .34	< .34	< .34	2.4 ^{c,d}	<.34	< .34	< .34	.40	6.0 ^g	.72	< .34	< .34	< .34
Triclosan	<.50	< .50	<.50	< .50	$2.2^{\rm a,f}$	<.50	<.50	< .50	<.50	.53 ^a	< .50	< .50	< .50	< .50
Triethyl citrate	< .25	< .25	< .25	< .25	.31 ^{a,f}	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25
					Disinfection c	;punodmo	6							
Bromoform	.51 ^h	< .25	< .25	< .25	.30°	< .25	< .25	< .25	< .25	19 ^g	< .25	< .25	< .25	< .25

Table 11. Maximum and 75th percentile concentrations for organic wastewater-indicator compounds in base-flow samples collected from streams in the control basins (Nancy Creek, Sandy Creek, and Utoy Creek), and at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.—Continued [CSO, combined sewer overflow; µg/L, microgram per liter; NAN, Nancy Creek; SAN, Sandy Creek; UTO, Utoy Creek; INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek; SOU, South River; <, less than; bold font indicates 75th percentile values above the study quantitation level (SRL); shaded cell indicates maximum concentration values are study-period maximums for all samples]

				•										,
		Control b	asin		Upstream	n watershe	ed from C	SO outfa	lls	Downstree	am waters	shed from	CSO outf	alls
Compound	Maximum concentration	75th perc	entile conce (μg/L)	ntration	Maximum concentration	75th pe	ercentile (µg/	concentr L)	ation	Maximum concentration	75th pe	ercentile (µg/	concentra L)	ation
	(hg/L)	NAN	SAN	UTO	(hg/L)	INT	PEA	PRO	SOU	(µg/L)	INT	PEA	PRO	SOU
					Pesticide co	spunodu								
1,4-Dichlorobenzene (14DCB)	<0.25	<0.25	<0.25	<0.25	1.6	<0.25	<0.25	<0.25	<0.25	.63ª	<0.25	<0.25	<0.25	<0.25
Bromacil	$3.2^{\rm h}$	<0.25	< .25	.47	29^{b}	< .25	.41	.62	1.0	8.7^{a}	.31	.42	.87	.81
Carbaryl	<.50	< .50	<.50	< .50	<.50	<.50	<.50	< .50	< .50	.78ª	< .50	< .50	< .50	<.50
Chlorpyrifos	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25
Diazinon	< .25	< .25	< .25	< .25	28^{b}	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25
Prometon	< .25	< .25	< .25	< .25	<.25	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25
					Sterol com	spunodu								
Cholesterol	5.6°	< 1.0	< 1.0	< 1.0	16 ^{a,f}	< 1.0	< 1.0	1.2	1.0	7.5ª	2.0	88.	1.0	1.3
3-β-Coprostanol	2.7°	< 1.0	< 1.0	< 1.0	$7.5^{\rm a,f}$	< 1.0	< 1.0	< 1.0	< 1.0	3.8ª	1.3	< 1.0	< 1.0	< 1.0
β-sitosterol	$1.4^{\rm h}$	< 1.0	< 1.0	< 1.0	4.1 ^{a,f}	< 1.0	< 1.0	< 1.0	< 1.0	3.8ª	< 1.0	< 1.0	< 1.0	< 1.0
β-stigmastanol	$1.3^{\rm h}$	< 1.0	< 1.0	< 1.0	$2.5^{c,d}$	< 1.0	< 1.0	< 1.0	< 1.0	4.1 ^a	< 1.0	< 1.0	< 1.0	< 1.0
					Industrial-use	compound	s							
Anthraquinone	1.6 ⁱ	< .25	<.25	<.25	.54ª	< .25	< .25	< .25	< .25	.68ª	< .25	< .25	< .25	< .25
Bisphenol-A	<.50	< .50	<.50	< .50	2.0^{a}	<.50	<.50	< .50	< .50	1.7^{b}	< .50	< .50	< .50	<.50
Carbazole	1.2 ^h	< .25	< .25	< .25	<.25	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25
d-Limonene	< .25	< .25	<.25	< .25	<.25	< .25	< .25	< .25	< .25	.43ª	< .25	< .25	< .25	< .25
Tetrachlorethene (PCE)	1.1e	<.25	<.25	<.25	2.8ª	< .25	< .25	.60	< .25	8.0°	< .25	< .25	< .25	< .25
Triphenyl phosphate (TPP)	< .25	< .25	< .25	< .25	.51°	< .25	<.25	< .25	< .25	.26 ^g	< .25	< .25	< .25	< .25

Table 11. Maximum and 75th percentile concentrations for organic wastewater-indicator compounds in base-flow samples collected from streams in the control basins (Nancy Creek, Sandy Creek, and Utoy Creek), and at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.—Continued [CSO, combined sewer overflow; µg/L, microgram per liter; NAN, Nancy Creek; SAN, Sandy Creek; UTO, Utoy Creek; INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek; SOU, South River; <, less than; bold font indicates 75th percentile values above the study quantitation level (SRL); shaded cell indicates maximum concentration values are study-period maximums for all samples]

	1									•			-	
		Control b	asin		Upstream	watershe	od from C	SO outfal	s	Downstree	am waters	shed from	CSO outfa	ılls
Compound	Maximum concentration	75th perc	entile conce (µg/L)	ntration	Maximum concentration	75th pe	rcentile ((µg/l	concentra .)	ation	Maximum concentration	75th p	ercentile ((µg/	concentra L)	tion
	(µg/L)	NAN	SAN	UTO	(hg/L)	INT	PEA	PR0	SOU	(hg/L)	INT	PEA	PRO	SOU
				Polycy	clic aromatic hy	drocarboi	ns (PAHs)							
Anthracene	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	< .25	<0.25	<0.25	<0.25	<0.25
<i>p</i> -Cresol	.63°	< .50	<.50	< .50	24^{b}	<.50	<.50	< .50	< .50	$2.4^{\rm a}$	< .50	< .50	< .50	< .50
Fluoranthene	< .25	< .25	<.25	< .25	<.25	< .25	< .25	< .25	< .25	.40ª	< .25	< .25	< .25	< .25
Pentachlorophenol (PCP)	3.9 ⁱ	< 1.0	< 1.0	< 1.0	.90 ^d	< 1.0	< 1.0	< 1.0	< 1.0	3.6ª	< 1.0	< 1.0	< 1.0	< 1.0
Phenanthrene	$1.1^{ m h}$	< .25	<.25	< .25	<.25	< .25	< .25	< .25	< .25	.29ª	< .25	< .25	< .25	< .25
Pyrene	<.25	< .25	< .25	< .25	<.25	< .25	< .25	< .25	< .25	.50 ^a	< .25	< .25	< .25	< .25
					Automotive-use	compoun	ds							
1-Methylnaphtha- lene	< .25	< .25	<.25	< .25	<.25	< .25	< .25	< .25	< .25	.41ª	< .25	< .25	< .25	< .25
2-Methylnaphtha- lene	< .25	< .25	<.25	< .25	.30 ^d	< .25	< .25	< .25	< .25	.60 ^a	< .25	< .25	< .25	< .25
2,6-Dimethyl naphthalene	< .25	< .25	<.25	< .25	< .25	< .25	< .25	< .25	< .25	<.25	< .25	< .25	< .25	< .25
5-Methyl-1H- benzotriazole	2.8∘	<1.0	<1.0	<1.0	6.1 ^d	<1.0	<1.0	<1.0	<1.0	1.1 ^a	< .25	<1.0	<1.0	<1.0
Isopropylbenzene	<.25	< .25	<.25	< .25	< .25	<.25	<.25	< .25	< .25	< .25	< .25	< .25	< .25	< .25
Naphthalene	<.25	< .25	< .25	< .25	.25 ^d	< .25	<.25	< .25	< .25	.79ª	< .25	< .25	< .25	< .25

Table 11. Maximum and 75th percentile concentrations for organic wastewater-indicator compounds in base-flow samples collected from streams in the control basins (Nancy Creek, Sandy Creek, and Utoy Creek), and at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.—Continued [CSO, combined sewer overflow, µg/L, microgram per liter; NAN, Nancy Creek; SAN, Sandy Creek; UTO, Utoy Creek; INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek; SOU, South River: <. less than: bold font indicates 75th percentile values above the study quantitation level (SRL); shaded cell indicates maximum concentration values are study-period maximums for all samples]

		Control b	asin		Upstream	ı watershe	ed from C	SO outfa	lls	Downstre	am water:	shed from	CSO outf	alls
Compound	Maximum concentration	75th perc	:entile conce (μg/L)	entration	Maximum concentration	75th pe	rcentile ((µg/	concentr L)	ation	Maximum concentration	75th p	ercentile (µg.	concentr. /L)	ation
	(hg/L)	NAN	SAN	UTO	(hg/L)	IN	PEA	PRO	SOU	(hg/L)	INT	PEA	PRO	SOU
				Non-i	onic detergent m	etabolites	(NDMCs							
<i>p</i> -Nonylphenol (total)	3.1	<2.5	<2.5	<2.5	10 ^d	2.5	2.5	<2.5	<2.5	3.6 ^d	<2.5	<2.5	<2.5	<2.5
4-Nonylphenol dieth- oxylate (NPEO2)	4.1 ⁱ	<2.5	<2.5	<2.5	48 ^d	2.5	2.5	<2.5	4.9	18 ^{a,g}	4.4	<2.5	<2.5	4.3
4-Octylphenol mono- ethoxylate (OPEO1)	<.50	< .50	<.50	<.50	1.6ª	<.50	<.50	<.50	<.50	2.5ª	<.50	< .50	< .50	< .50
4-Octylphenol dieth- oxylate (OPEO2)	<.50	< .50	<.50	< .50	.56°	<.50	<.50	<.50	<.50	.68ª	< .50	< .50	< .50	< .50
4-tert-Octylphenol	<.50	< .50	<.50	< .50	.52ª	<.50	< .50	< .50	<.50	.56ª	< .50	< .50	< .50	< .50
					Flame-retardan	t compour	lds							
Tributyl phosphate (TBP)	4.3 ^h	<0.25	<0.25	<0.25	.75ª	<0.25	<0.25	<0.25	<0.25	2.9 ^g	.34	<0.25	<0.25	<0.25
Tris(2-butoxyethyl) phosphate (TBEP)	4.6 ^h	.25	.34	.30	9.3 ^b	<.25	.39	.53	.95	70^{a}	2.4	.48	1.5	.94
Tris(2-chloroethyl) phosphate (TCEP)	.49°	< .25	< .25	< .25	2.0°	<.25	< .25	< .25	< .25	.52 ^g	< .25	< .25	< .25	< .25
Tris(dichloroisopropyl) phosphate (TDCPP)	<.25	<.25	<.25	< .25	1.5°	<.25	< .25	< .25	.27	.37°	< .25	< .25	< .25	< .25
^a Proctor Creek waters ^b ^b Peachtree Creek wate	hed. rshed													

South River watershed.

⁴Measured in one sample collected at synoptic site 4 in the SOU watershed on July 14, 2003.

^e Sandy Creek watershed.

Measured in one sample collected at site PRO-3 on May 13, 2004.

³ Intrenchment Creek watershed.

ⁿNancy Creek watershed. ⁱUtoy Creek watershed. Table 12. Maximum and 75th percentile concentrations for organic wastewater-indicator compounds in stormflow samples collected from streams in the control basins (Nancy Creek, Sandy Creek, and Utoy Creek), and at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.

[CSO, combined sewer overflows; µg/L, microgram per liter; NAN, Nancy Creek; SAN, Sandy Creek; UTO, Utoy Creek; INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek; SOU, South River; <, less than; —, insufficient sample size; bold font indicates 75th percentile values above the study quantitation level (SRL); shaded cell indicates maximum concentration values are the maximum concentrations for all samples in the study period

		Control b	asin		Upstream	watersh	ned from C	SO outfa	lls	Downstree	am waters	shed from	CSO outfa	alls
Compound	Maximum concentration	75th perc	entile conce (μg/L)	ntration	Maximum concentration	75th p	ercentile (µg/	concentr L)	ation	Maximum concentration	75th pe	ercentile (µg/	concentra L)	tion
	(hg/L)	NAN	SAN	UTO	(hg/L)	INT	PEA	PR0	SOU	(hg/L)	INT	PEA	PRO	SOU
					Personal-use c	unoduo	ds							
AHTN, tonalide	<0.25	<0.25	<0.25	<0.25	<0.25		<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
Acetophenone	$.38^{a}$	< .25	< .25	< .25	.59 ^b		< .25	.48	< .25	$3.5^{\rm b}$.41	<.25	< .25	< .25
Benzophenone	< .25	< .25	< .25	< .25	.43 ^d		< .25	< .25	< .25	.36°	< .25	< .25	< .25	< .25
Caffeine	3.0°	99.	< .25	< .25	3.5 ^b		.64	.80	.81	2.8 ^{c,d}	88.	.38	.74	.67
Camphor	.50 ^e	< .25	< .25	< .25	.73 ^d		< .25	< .25	< .25	.53 ^b	< .25	< .25	< .25	< .25
Cotinine	<.50	< .50	<.50	< .50	< .50		< .50	<.50	< .50	< .50	< .50	<.50	<.50	<.50
HHCB, Galaxolide	< .25	< .25	< .25	< .25	.32 ^f		< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25
Indole	.75ª	< .25	< .25	< .25	< .25		< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25
Isoborneol	< .25	< .25	< .25	< .25	1.9 ^d		< .25	< .25	<.25	< .25	< .25	<.25	<.25	<.25
Menthol	.31 ^a	< .25	< .25	< .25	.62 ^f		< .25	.32	< .25	.77°	.30	<.25	.32	< .25
Methyl salicylate	< .25	< .25	< .25	< .25	< .25		< .25	< .25	< .25	.33 ^b	<.25	<.25	< .25	< .25
DEET	.87 ^a	< .34	< .34	.45	2.3^d		.50	1.3	1.6	1.0^{d}	.52	<.34	< .34	.63
Triclosan	< .50	< .50	< .50	< .50	< .50	I	< .50	<.50	<.50	< .50	<.50	<.50	<.50	<.50
Triethyl citrate	< .25	< .25	< .25	< .25	< .25		< .25	< .25	< .25	< .25	< .25	< .25	< .25	< .25
					Disinfection co	ounoduuc	s							
Bromoform	< .25	< .25	< .25	< .25	.36		< .25	< .25	< .25	6.1°	< .25	< .25	< .25	<.25

Table 12. Maximum and 75th percentile concentrations for organic wastewater-indicator compounds in stormflow samples collected from streams in the control basins (Nancy Creek, Sandy Creek, and Utoy Creek), and at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.—Continued

[CSO, combined sewer overflows; µg/L, microgram per liter; NAN, Nancy Creek; SAN, Sandy Creek; UTO, Utoy Creek; INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek; SOU, South River; <, less than; —, insufficient sample size; bold font indicates 75th percentile values above the study quantitation level (SRL); shaded cell indicates maximum concentration values are the maximum concentrations for all samples in the study period]

	-	_												
		Control ba	asin		Upstream	watersh	ed from C	SO outfal	s	Downstre	am water	shed from	CSO outf	alls
Compound	Maximum concentration	75th perce	entile concer (µg/L)	ntration	Maximum concentration	75th pe	ercentile (µg/l	concentra L)	ation	Maximum concentration	75th p	ercentile ((µg/	concentra L)	tion
	(µg/L)	NAN	SAN	UTO	(hg/L)	INT	PEA	PRO	SOU	(hg/L)	INT	PEA	PRO	SOU
					Pesticide cor	spunodu								
1,4-Dichlorobenzene (14DCB)	<.25	< .25	< .25	< .25	< .25	I	< .25	< .25	<.25	5.0 ^f	< .25	< .25	< .25	< .25
Bromacil	.75 ^a	< .25	<.25	<.25	12^{d}		.30	2.2	1.6	$21^{\rm f}$	< .25	< .25	2.3	.44
Carbaryl	.98°	< .50	< .50	< .50	.87 ^b		<.50	<.50	<.50	.54 ^f	< .50	< .50	< .50	< .50
Chlorpyrifos	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25		< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
Diazinon	< .25	< .25	<.25	<.25	< .25		<.25	<.25	< .25	< .25	< .25	< .25	< .25	< .25
Prometon	.25 ^a	< .25	<.25	< .25	< .25		<.25	<.25	< .25	2.1 ^b	< .25	< .25	< .25	< .25
					Sterol com	spunoc								
Cholesterol	2.3ª	<1.0	<1.0	<1.0	2.8 ^b		<1.0	1.2	1.6	3.6 ^d	1.3	<1.0	1.3	1.2
3-β-Coprostanol	1.4 ^e	<1.0	<1.0	<1.0	2.5 ^b		<1.0	<1.0	1.0	$2.2^{\rm f}$	<1.0	<1.0	<1.0	<1.0
β-sitosterol	1.7 ^{a,e}	<1.0	<1.0	<1.0	1.9 ^b		<1.0	<1.0	1.0	2.3 ^b	<1.0	<1.0	<1.0	<1.0
β-stigmastanol	2.0 ^g	<1.0	<1.0	<1.0	1.8 ^b		<1.0	<1.0	<1.0	2.2 ^b	<1.0	<1.0	<1.0	<1.0
					Industrial-use c	ounoduuo	s							
Anthraquinone	.73ª	< .25	<.25	<.25	1.2 ^b		.35	< .25	< .25	.60 ^d	.25	< .25	< .25	< .25
Bisphenol-A	.86 ^e	< .50	<.50	<.50	2.2 ^b		<.50	<.50	-54	1.3 ^b	< .50	<.50	< .50	< .50
Carbazole	1.2 ^e	< .25	< .25	<.25	.28 ^d		< .25	< .25	<.25	< .25	< .25	< .25	< .25	< .25
<i>d</i> -Limonene	< .25	< .25	< .25	< .25	1.9 ^d		< .25	< .25	<.25	.62 ^d	< .25	< .25	< .25	< .25
Tetrachlorethene (PCE)	< .25	< .25	< .25	<.25	2.8 ^d		< .25	< .25	<.25	.25 ^b	< .25	< .25	< .25	< .25
Triphenyl phosphate (TPP)	.28ª	< .25	< .25	< .25	1.0 ^b	I	<.25	<.25	.27	.48°	< .25	< .25	< .25	< .25

trations for organic wastewater-indicator compounds in stormflow samples collected from streams in the control basins	at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek,	Atlanta, GA, March 2003 to January 2006.—Continued
Maximum and 75th percentile concentrations for organic was	ek, Sandy Creek, and Utoy Creek), and at sites upstream and d	ek, and South River watersheds near Atlanta, GA, March 2003
Table 12.	(Nancy Cree	Proctor Crei

[CSO, combined sewer overflows; µg/L, microgram per liter; NAN, Nancy Creek; SAN, Sandy Creek; UTO, Utoy Creek; INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek;

		Control b	asin		Upstream	watersh	led from C	SO outfa	lls	Downstre	eam water	shed from	CSO out	alls
Compound	Maximum concentration	75th perce	entile concen (µg/L)	itration	Maximum concentration	75th p	ercentile ((µg/	concentr L)	ation	Maximum concentration	75th p	ercentile (µg/	concentra 'L)	ation
	(hg/L)	NAN	SAN	UTO	(Hg/L)	INT	PEA	PR0	SOU	(hg/L)	INT	PEA	PR0	SOU
				Polycy	clic aromatic hyo	drocarbo	ins (PAHs)							
Anthracene	< .25	< .25	< .25	< .25	< .25		< .25	< .25	<.25	< .25	<.25	< .25	< .25	<.25
<i>p</i> -Cresol	1.8ª	< .50	< .50	< .50	1.2 ^b		< .50	<.50	<.50	18^{f}	.52	<.50	.74	<.50
Fluoranthene	.42 ^{a,e}	< .25	< .25	< .25	< .25		< .25	< .25	< .25	.34 ^d	< .25	< .25	< .25	<.25
Pentachlorophenol (PCP)	7.2ª	<1.0	<1.0	2.4	3.8 ^b		<1.0	<1.0	1.0	1.1 ^{d,f}	<1.0	<1.0	<1.0	<1.0
Phenanthrene	1.3ª	< .25	< .25	< .25	.33 ^d		< .25	<.25	< .25	.41 ^f	< .25	< .25	< .25	<.25
Pyrene	.32°	< .25	< .25	< .25	< .25	I	< .25	< .25	< .25	.28 ^d	< .25	< .25	< .25	< .25
					Automotive-use	compoul	spu							
1-Methylnaph- thalene	.48ª	<0.25	<0.25	<0.25	.61 ^d		< .25	< .25	< .25	.72 ^f	<0.25	<0.25	<0.25	<0.25
2-Methylnaphthalene	.52 ^a	< .25	< .25	< .25	.80 ^d		< .25	< .25	< .25	.80 ^f	< .25	< .25	< .25	<.25
2,6-Dimethyl naphthalene	.30 ^g	< .25	< .25	< .25	.40 ^d		< .25	<.25	<.25	.34 ^f	<.25	<.25	<.25	<.25
5-Methyl-1H- benzotriazole	2.8 ^g	<1.0	<1.0	<1.0	.61 ^b		<1.0	<1.0	<1.0	5.1 ^b	<1.0	<1.0	<1.0	<1.0
Isopropylbenzene	< .25	< .25	< .25	< .25	< .25		< .25	<.25	<.25	< .25	< .25	<.25	< .25	<.25
Naphthalene	1.2 ^a	< .25	< .25	< .25	.54 ^d		< .25	< .25	< .25	< .25	< .25	<.25	< .25	<.25

Table 12. Maximum and 75th percentile concentrations for organic wastewater-indicator compounds in stormflow samples collected from streams in the control basins (Nancy Creek, Sandy Creek, and Utoy Creek), and at sites upstream and downstream from known combined sewer outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.—Continued

[CSO, combined sewer overflows; µg/L, microgram per liter; NAN, Nancy Creek; SAN, Sandy Creek; UTO, Utoy Creek; INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek; SOU, South River; <, less than; --, insufficient sample size; bold font indicates 75th percentile values above the study quantitation level (SRL); shaded cell indicates maximum concentration values are the maximum concentrations for all samples in the study period]

		Control b	asin		Upstream	watersh	ed from C	SO outfal	s	Downstre	am water:	shed from	CSO outf	alls
Compound	Maximum concentration	75th perc	entile conce. (µg/L)	ntration	Maximum concentration	75th p	ercentile (µg/	concentra L)	ation	Maximum concentration	75th p	ercentile (μg/	concentra L)	ntion
	(hg/L)	NAN	SAN	UTO	(hg/L)	INT	PEA	PR0	SOU	(hg/L)	INT	PEA	PRO	SOU
				Non-ic	onic detergent me	etabolites	(NDMCs)							
<i>p</i> -Nonylphenol (total)	4.0	<2.5	<2.5	<2.5	3.4 ^b		<2.5	<2.5	<2.5	6.3°	2.5	<2.5	<2.5	<2.5
4-Nonylphenol dieth- oxylate (NPEO2)	65	<2.5	<2.5	<2.5	14 ^b		<2.5	<2.5	3.0	9.2 ^f	2.8	<2.5	<2.5	3.0
4-Octylphenol mono- ethoxylate (OPEO1)	1.7	< .50	< .50	< .50	1.0 ^b		< .50	< .50	< .50	1.2 ^f	<.50	< .50	< .50	< .50
4-Octylphenol dieth- oxylate (OPEO2)	.60	< .50	< .50	< .50	< .50		< .50	< .50	< .50	<.50	<.50	< .50	< .50	< .50
4-tert-Octylphenol	< .50	< .50	< .50	< .50	< .50		< .50	<.50	<.50	.89 ^b	<.50	<.50	<.50	<.50
					Flame-retardant	compoul	spu							
Tributyl phosphate (TBP)	.88°	< .25	< .25	< .25	2.1 ^d		< .25	< .25	.50	9.9°	.72	< .25	< .25	< .25
Tris(2-butoxyethyl) phosphate (TBEP	7.0 ^a	.74	.55	.72	20^{d}		1.1	3.4	1.0	18	3.3	1.2	2.3	1.2
Tris(2-chloroethyl) phosphate (TCEP)	.39°	< .25	< .25	< .25	1.2 ^b		< .25	< .25	.57	.74°	.30	< .25	< .25	.25
Tris(dichloroisopropyl) phosphate (TDCPP)	.26 ^g	< .25	< .25	< .25	ρ <i>LL</i> .		< .25	< .25	.43	.55 ^b	< .25	< .25	< .25	< .25
^a Utoy Creek watershee	ਜ													
^b South River watershe	.d.													
° Intrenchment Creek w	vatershed.													
^d Peachtree Creek wate	rshed.													
^e Nancy Creek watersh	ed.													

⁸ Proctor Creek watershed. ⁸ Sandy Creek watershed.

Non-ionic Detergent Metabolite Compounds

As a class, the NDMCs were detected in 20 and 27 percent of base-flow and stormflow samples, respectively (tables 9, 10). In base-flow samples, *p*-nonylphenol and NPEO2 (32 percent each) were detected with the greatest frequency; whereas, *p*-nonylphenol (50 percent), and NPEO2 and OPEO2 (34 percent each) were detected with the greatest frequency in stormflow samples. The compounds *p*-nonylphenol and OPEO2 were detected in 18 and 14 percent, respectively, more stormflow than base-flow samples during the study (fig. 10). The compounds 4-*tert*-octylphenol, OPEO1, and NPEO2 were detected with similar frequency (within \pm 5 percent) in base-flow and stormflow samples.

Only 13 to 38 percent of the NDMCs were detected at concentrations that exceeded SRLs (tables 3, 8). The highest concentration of *p*-nonylphenol (10 μ g/L) seen in the study was measured in a base-flow sample from an upstream site in the SOU watershed (table 11). The highest concentrations of OPEO1 (2.5 μ g/L) and OPEO2 (0.68 μ g/L) were measured in base-flow samples from downstream sites in the PRO watershed. In addition, the highest NPEO2 concentration (65 μ g/L) in the study was measured in a stormflow sample from the UTO watershed and the highest concentration of 4-*tert*-octylphenol (0.89 μ g/L) was measured in a stormflow sample from a downstream site in the SOU watershed (table 12).

Flame-Retardant Compounds

The flame retardants were detected in more base-flow (39 percent) and stormflow (56 percent) samples than any other OWIC class during the study period (tables 10, 11). All four of the flame-retardant compounds were detected in a 10–26 percent more stormflow than base-flow samples (fig. 10). The compounds TBEP and TCEP were the most frequently detected flame retardant in base-flow and stormflow samples. Tributyl phosphate was detected in the fewest base-flow and stormflow samples during the study.

The concentrations of individual flame retardants exceeded their respective SRLs in 46 (TDCPP) to 75 percent (TBEP) of all samples collected during the study (tables 3, 8). Even though the flame retardants were detected in more stormflow than base-flow samples, base-flow samples contained the highest measured concentrations for three of the four flame retardants (tables 11, 12). The highest TBEP concentration observed in the study (70 μ g/L) was measured in a base-flow sample from a downstream site in the PRO watershed, and the highest TCEP and TDCPP concentrations (2.0 and 1.5 μ g/L, respectively) were measured at upstream sites in the SOU watershed (table 11). The highest TBP concentration (9.9 μ g/L) was measured in a stormflow sample from a downstream site in the INT watershed (table 12).

OWICs in the Nancy Creek, Sandy Creek, and Utoy Creek Watersheds

Because neither CSOs nor other known point discharges were present in the NAN, SAN, and UTO watersheds, the occurrence, distribution, and concentrations of OWICs in these watersheds most likely represent "urban background." For this reason, the NAN, SAN, and UTO watersheds are collectively referred to here as the "control basins" for comparisons with samples collected upstream and downstream from CSO outfalls in the other four watersheds within the study area. Although streams in the control basins were not affected by CSOs during the study period, SSOs occurred intermittently as a result of blockages in the sewer lines or broken pipes (City of Atlanta study, technical advisory committee, oral commun., June 2008).

The predominant land uses in the NAN watershed are residential and commercial. In the SAN and UTO watersheds, residential and woodland/parks are the dominant land uses (table 2; Atlanta Regional Commission, 2005). Developed areas encompass 61–77 percent and impervious areas 17–27 percent of the drainage areas in these three watersheds. The NAN watershed has about 10 percent more of its watershed designated as commercial development and slightly more industrial and industrial/commercial development than either the SAN or UTO watersheds. The SAN and UTO watersheds have about three times more wetlands (lakes or ponds) and parks than the NAN watershed.
Among all samples collected from the control-basin sites, the pattern of OWIC detections (fig. 11) were typically similar to the pattern seen among all samples collected during the study period (fig. 5*B*). In contrast, substantial seasonal and hydrologic differences were seen in the detection frequencies between control-basin samples and samples collected at sites upstream and downstream from CSOs.

Seasonal Variation

Typically, the seasonal differences in the percentage of OWICs among cool- and warm-season samples from the control basins was similar to the seasonal pattern observed in all samples collected during the study period (figs. 8, 12). In control-basin samples, DEET, carbaryl, TDCPP, pyrene, TCEP, anthracene, sitosterol, and prometon were detected in more warm- than cool-season samples. Conversely caffeine, camphor, menthol, *p*-cresol, OPEO2, *p*-nonylphenol, naphthalene, AHTN, phenanthrene, coprostanol, carbazole, 4-*tert*-octylphenol, 14DCB, TBP, triclosan, and OPEO1 were detected in more cool- than warm-season samples from the control basins. In samples collected from the control basins, 28 compounds (54 percent) were detected with similar frequency (within \pm 5 percent) during both seasons.

In some instances, the seasonal patterns for individual control-basin watersheds differed markedly from the seasonal pattern seen for the control-basin samples collectively. For example, camphor and triclosan were detected with similar frequency in SAN samples collected (table 13) in both seasons, but among NAN and UTO samples those compounds were detected in substantially more cool-season samples. In addition, carbaryl was detected in NAN samples with similar frequency during both seasons, but was detected in substantially more warm-season samples among SAN and UTO samples. Among all control-basin sites, bromacil was detected with similar frequency in both seasons, but was detected with greater frequency in warm-season samples from the NAN and SAN watersheds. In contrast, bromacil was detected in more cool-season samples from the UTO watershed. Among the sterols, cholesterol and sitosterol were detected in the NAN watershed with similar frequency during both seasons; whereas, cholesterol was detected in slightly more cool-season samples from the SAN watershed, but was detected in substantially more warm-season samples from the UTO watershed. Sitosterol was detected with similar frequency in the SAN and UTO watersheds during both seasons.

Variation During Base Flow and Stormflow

Although similarities in the dominant OWIC classes exist among base-flow and stormflow samples from the NAN, SAN, and UTO watersheds, detection frequencies and maximum concentrations of individual compounds were different. The median numbers of OWICs per base-flow sample (three to four compounds) were statistically similar among samples from the NAN, SAN, and UTO watersheds (*p*-value greater than 0.05), but all were statistically lower than the median numbers (seven to nine) in stormflow samples from their respective watersheds (p-value less than 0.05, fig. 9). The median numbers of OWICs detected per stormflow sample were statistically similar among NAN, SAN, and UTO watersheds (*p*-value greater than 0.05). A base-flow and stormflow sample from the UTO watershed contained 24 and 21 compounds; the highest numbers of OWICs detected in one sample from the control-basin watersheds during the study period.

Thirty-three of the 52 OWICs analyzed were detected in less than 10 percent of the base-flow samples, and 7 of those acetophenone, isoborneol, chlorpyrifos, diazinon, anthracene, 2,6-dimethylnaphthalene, and isopropylbenzene—were detected in less than 1 percent of the control-basin samples (table 9). In contrast, 23 of the 52 OWICs analyzed were detected in less than 10 percent of the stormflow samples, and 6 of those—benzophenone, cotinine, isoborneol, methyl salicylate, bromoform, and isopropylbenzene—were detected in less than 1 percent of the control-basin samples (table 10).

The detection frequencies of most of the OWICs were typically higher in stormflow than base-flow samples from the control basins (fig. 13). Nineteen compounds were detected with similar frequency in base-flow and stormflow samples from the control basin sites and five compounds were detected in a greater percentage of base-flow than stormflow samples. Nine compounds were detected in 20-43 percent more stormflow than base-flow samples from the control basins. Among these were caffeine, TBEP, camphor, carbazole, carbaryl, phenanthrene, fluoranthene, TCEP, and *p*-nonylphenol. In contrast, bromacil was detected in 30 percent more base-flow than stormflow samples from the control basins. Furthermore, PCE, triclosan, HHCB, and methyl salicylate were detected in 7-11 percent more base-flow than stormflow samples. Compounds that were detected with similar frequency in base-flow and stormflow samples include bromoform, TBP, 14DCB, stigmastanol, NPEO2, OPEO1, prometon, 5-methyl-1H-benzotriazole, and bisphenol-A.









64 Occurrence of Organic Wastewater-Indicator Compounds in Urban Streams of the Atlanta Area, Georgia, 2003–2006

Table 13. Detection frequencies by season for individual organic wastewater-indicator compounds in water samples from the Nancy Creek, Sandy Creek, and Utoy Creek watersheds near Atlanta, GA, March 2003 to January 2006.

[NAN, Nancy Creek; SAN, Sandy Creek; UTO, Utoy Creek; Cool, cool season (October–April); Warm, warm season (April–October); ---, not detected above study reporting levels]

	Detection frequency (percent)										
Compound	Control ba	sins (total)	N	AN	S	AN	U	٥٦			
	Cool	Warm	Cool	Warm	Cool	Warm	Cool	Warm			
Number of samples	162	135	86	42	14	24	62	69			
Personal-use compounds											
AHTN, tonalide	13	2.2	11	—	36	4.2	13	2.9			
Acetophenone	—	2.2	—	—	—	—	0	4.3			
Benzophenone	2.4	2.2	1.2	4.8	14	4.2	1.6	0			
Caffeine	58	19	76	29	43	8.3	40	16			
Camphor	36	16	45	4.8	29	29	27	17			
Cotinine	4.2	1.5	1.2	2.4	7.1	4.2	8.1	0			
HHCB, galaxolide	9.1	9.6	5.8	9.5	7.1	13	15	8.7			
Indole	12	13	7.0	2.4	21	25	16	15			
Isoborneol	—	—	—	—	—	—	0	1.4			
Menthol	26	9.6	21	12	50	13	29	7.2			
Methyl salicylate	4.8	6.7	2.3	7.1	7.1	13	8.1	4.3			
DEET	1.8	32	1.2	24	—	29	3.2	38			
Triclosan	19	13	16	7.1	21	21	23	15			
Triethyl citrate	3.6	5.9	3.5	2.4	7.1	8.3	3.2	7.2			
Class percentage ^a	14	9.5	14	7.5	17	12	13	10			
		Disi	infection co	mpounds							
Bromoform		2.2	—	2.4	_	—	_	2.9			
		Pe	esticide com	pounds							
1,4-Dichlorobenzene (14DCB)	8.5	2.2	4.7	—	7.1	8.3	15	1.4			
Bromacil	21	24	2.3	12	7.1	13	52	36			
Carbaryl	11	30	14	17	7.1	29	8.1	38			
Chlorpyrifos	1.2	—	2.3	—	—	—	—	—			
Diazinon	3.0	3.0	1.2	2.4	7.1	4.2	4.8	2.9			
Prometon	_	5.2	_	2.4	_	4.2	1.6	7.2			
Class percentage	7.7	11	4.1	5.6	4.8	9.7	13	14			
		:	Sterol comp	ounds							
Cholesterol	35	39	38	36	36	29	32	44			
3-β-Coprostanol	23	14	27	9.5	29	13	18	17			
β-sitosterol	13	18	17	14	7.1	17	8.1	20			
β-stigmastanol	12	8.1	16	7.1	7.1	4.2	8.1	10			
Class percentage	21	20	25	17	20	16	16	23			
		Indu	strial-use co	ompounds							
Anthraquinone	6.1	5.2	8.1	7.1	7.1	—	3.2	5.8			
Bisphenol-A	3.6	3.7	7.0	4.8	—	4.2	—	2.9			
Carbazole	26	19	30	21	14	8.3	23	20			

 Table 13.
 Detection frequencies by season for individual organic wastewater-indicator compounds in water samples from

 the Nancy Creek, Sandy Creek, and Utoy Creek watersheds near Atlanta, GA, March 2003 to January 2006.—Continued

[NAN, Nancy Creek; SAN, Sandy Creek; UTO, Utoy Creek; Cool, cool season (October–April); Warm, warm season (April–October); —, not detected above study reporting levels]

	Detection frequency (percent)										
Compound	Control ba	sins (total)	N	AN	SA	\N	UT	0			
	Cool	Warm	Cool	Warm	Cool	Warm	Cool	Warm			
		Industrial-u	use compou	nds—Continu	beu						
<i>d</i> -Limonene	13	10	17	4.8	14	13	6.5	13			
Tetrachloroethene (PCE)	10	10	20	26	_	13	_	—			
Triphenyl phosphate (TPP)	5.5	3.0	1.2	—	14	_	9.7	5.8			
Class percentage	11	8.5	14	11	8.3	6.2	7.0	8.0			
		Polycyclic a	romatic hyd	rocarbons (P	AHs)						
Anthracene	—	5.2	—	9.5	—	—	—	4.3			
<i>p</i> -Cresol	21	5.9	9.3	0	36	13	36	7.2			
Fluoranthene	21	17	20	21	7.1	—	27	20			
Pentachlorophenol (PCP)	18	13	5.8	2.4	14	4.2	36	23			
Phenanthrene	25	14	27	14	14	4.2	26	17			
Pyrene	6.7	16	2.3	21	_	_	15	19			
Class percentage	15	12	11	11	12	3.5	23	15			
Automotive-use compounds											
1-Methylnaphthalene	8.5	3.7	3.5	—	14	4.2	15	5.8			
2-Methylnaphthalene	7.9	3.7	3.5	_	14	4.2	13	5.8			
2,6-Dimethylnaphthalene	2.4	3.0	2.3	_	14	4.2	_	4.3			
5-Methyl-1H-benzotriazole	—	4.4	_	7.1	_	4.2	_	2.9			
Isopropylbenzene	—	—	_	—	_	_	_	—			
Naphthalene	24	13	9.3	4.8	29	8.3	44	19			
Class percentage	7.2	4.6	3.1	2.0	12	4.2	12	6.3			
		Nonionic de	tergent met	abolites (NDN	MCs)						
<i>p</i> -Nonylphenol (total)	37	26	43	24	64	33	24	25			
4-Nonylphenol diethoxylate (NPEO2)	16	18	16	17	21	25	15	16			
4-Octylphenol monoethoxyl- ate (OPEO1)	7.9	3.0	12	_	7.1	8.3	3.2	2.9			
4-Octylphenol diethoxylate (OPEO2)	20	7.4	26	7.1	14	4.2	15	8.7			
4-tert-Octylphenol	9.1	2.2	12	7.1	14	_	4.8	—			
Class percentage	18	11	22	11	24	14	12	10			
		Flame	e-retardant o	compounds							
Tributyl phosphate (TBP)	11	5.2	15	17	14	_	4.8				
Tris(2-butoxyethyl) phosphate (TBEP)	63	66	66	55	64	67	61	73			
Tris(2-chloroethyl) phosphate (TCEP)	41	50	48	74	57	54	31	33			
Tris(dichloroisopropyl) phos- phate (TDCPP)	16	28	12	45	36	17	19	22			
Class percentage	33	37	35	48	43	34	29	32			

^a Weighted value based on the percentage of compounds detected within its associated compound class.





Among the control basins, a greater percentage of base-flow samples from the SAN than from the NAN or UTO watersheds contained benzophenone, camphor, HHCB, indole, menthol, methyl salicylate, triethyl citrate, 14DCB, *d*-limonene, *p*-cresol, and *p*-nonylphenol (table 9). These compounds may indicate sewage-contaminated groundwater from broken or leaking sanitary sewer pipes was entering SAN streams during base flow (Daughton, 2004). Caffeine was detected in substantially more base-flow samples from the NAN than SAN or UTO watersheds. In contrast to base-flow samples, the personal-use compounds collectively were detected with similar frequency in stormflow samples from the NAN, SAN, and UTO watersheds. Nevertheless, caffeine and camphor were detected in a greater percentage of stormflow samples from the NAN watershed, while the fragrances AHTN, benzophenone, indole, and menthol, and triclosan were detected in a greater percentage of stormflow samples from the SAN watershed. In addition, DEET was detected in a greater percentage of stormflow samples from the UTO watershed.

Collectively, the pesticide compounds were detected in about 8 percent of base-flow and stormflow samples from the control basins (tables 9, 10). Pesticides were detected in about three times more base-flow samples from the UTO than the NAN or SAN watersheds, primarily because bromacil was detected in 63 percent of UTO base-flow samples (table 9). During base flow, 14DCB was detected in a slightly higher percentage of samples from the SAN than the NAN or UTO watersheds.

Collectively, the pesticides were detected with greater frequency in stormflow samples from the SAN and UTO than the NAN watersheds, primarily because carbaryl was detected in 41 percent of the SAN and UTO stormflow samples (table 10). The compounds 14DCB and bromacil were detected in 2–10 times more stormflow samples from the UTO than from the SAN and NAN watersheds, respectively. Diazinon was detected with slightly greater frequency in stormflow samples from the SAN than from the NAN or UTO watersheds.

Cholesterol was the dominant sterol in base-flow (32 percent) and stormflow (42 percent) samples from control-basin sites during the study (tables 9, 10). Cholesterol, coprostanol, and sitosterol were detected in 8–10 percent more stormflow than base-flow samples from control-basin sites (fig. 13). During base flow, the sterols in general and cholesterol in particular, were detected with greater frequency in samples from the UTO than from the NAN or SAN watersheds; however, the sterols were detected with similar frequency in base-flow and stormflow samples from the UTO watershed. Conversely, the sterols were detected in substantially more stormflow than base-flow samples from the NAN and SAN watersheds. A similar percentage of stormflow samples from the NAN and SAN watersheds contained sterols.

Typically, the industrial-use, PAH, automotive-use, and NDMCs were detected with similar frequency in base-flow samples from the NAN, SAN, and UTO watersheds (table 9),

but were more variable during stormflow (table 10). Nevertheless, compounds with the greatest detection frequency among base-flow samples from the control basins include: PCE from the NAN sites; *d*-limonene, *p*-cresol, and *p*-nonylphenol from SAN sites; and PCP, naphthalene, and OPEO2 from UTO sites. During stormflow, industrial-use and PAH compounds were detected in the lowest percentage of stormflow samples from the SAN watershed; however, the industrial-use compounds were detected in a similar percentage of samples from the NAN and UTO watersheds. Carbazole was the most frequently detected industrial-use compound in stormflow samples from the NAN and UTO watersheds. The PAH compounds were detected with the greatest frequency (32 percent) in samples from the UTO watershed; a detection frequency that was two to four times higher than samples from the NAN and SAN watersheds, respectively. Fluoranthene and phenanthrene were the most frequently detected PAHs in NAN and UTO samples. Automotive-use compounds were detected in the lowest percentage of stormflow samples from the NAN watershed, but in a similar percentage of stormflow samples from the SAN and UTO watersheds. Naphthalene was the dominant automotive-use compounds in stormflow samples from all three of the control-basin watersheds.

The NDMCs were detected in a similar percentage of stormflow samples from the NAN and SAN watersheds, but 10–12 percent higher than stormflow samples from the UTO watershed (table 10). Among the NDMCs, *p*-nonylphenol was the dominant compound detected in stormflow samples from all three control-basin watersheds. In addition, *p*-nonylphenol and NPEO2 were detected in a substantially higher percentage of stormflow samples from the SAN watershed.

Typically, the flame retardants were detected in about twice as many stormflow than base-flow samples from controlbasin sites during the study (tables 9, 10). Among the baseflow samples, a greater percentage of NAN than SAN or UTO samples contained flame retardants. In these NAN samples, TBEP and TCEP were detected with the greatest frequency among control-basin samples; whereas, TBEP was detected with the greatest frequency in base-flow samples from UTO sites. In contrast, flame-retardant compounds were detected with the greatest frequency in stormflow samples from the SAN watershed at a percentage that was 11–17 percent higher than in NAN and UTO samples (table 10). The compounds TBEP and TCEP were the dominant flame retardants in stormflow samples from all three control-basin watersheds.

Among the 52 OWICs detected during the study, the 75th percentile concentrations of only 2 (bromacil and TBEP) exceeded SRLs in base-flow samples, while the 75th percentile concentrations of 4 compounds (caffeine, DEET, PCP, and TBEP) exceeded SRLs in stormflow samples from the control basins (tables 11, 12). Among the base-flow samples from the control-basins those from the NAN watershed contained the highest concentrations of bromoform, bromacil, sitosterol, stigmastanol, carbazole, phenanthrene, TBP, and TBEP; those from the SAN watershed contained the highest concentrations of caffeine, HHCB, menthol, DEET, cholesterol, coprostanol, PCE, *p*-cresol, 5-methyl-1H-benzotriazole, and TCEP among base-flow samples from the control basins; and those from the UTO watershed contained the highest concentrations of anthraquinone, PCP, *p*-nonylphenol, and NPEO2 (table 11).

Conversely, among stormflow samples from the control basins, those from the NAN watershed contained the highest concentrations of 11 compounds: caffeine, camphor, carbaryl, coprostanol, sitosterol, bisphenol-A, carbazole, fluoranthene, pyrene, TBP, and TCEP; those from SAN watershed contained the highest concentrations of 5 compounds: stigmastanol, 2,6-dimethylnaphthalene, 5-Methyl-1H-benzotriazole, OPEO1, and TDCPP; and those from the UTO watershed contained the highest concentrations of 21 compounds: 4 personal-use and PAH compounds each, 2 pesticide, sterol, and industrial-use compounds each, 3 automotive-use and NDMCs each, and 1 flame-retardant compound (table 12). Water samples collected from control-basin sites contained maximum compound concentrations that were similar to those reported by Kolpin and others (2004).

Relations Among OWICs and Selected Water-Quality Constituents and Properties

The PCA of samples collected from the control basins yielded six components that explained about 56 percent of the data variability (table 14); however, only three components were significant enough to be considered the principal components of the dataset. These three components explained about 46 percent of the data variability. The first component (PC1) explained about 29 percent of the data variability and indicates moderate, positive associations among aluminum concentrations, turbidity, streamflow, dissolved copper and lead concentrations, and the number of urban-runoff-related OWICs per sample. Furthermore, PC1 also indicates a strong, but negative, association among major ions (field specific conductance, chloride and acid-neutralizing capacity concentrations). These associations indicate that when major ions were elevated, streamflow, turbidity, dissolved aluminum, copper and lead concentrations, and the numbers of urban-runoff-related OWICs per sample were low. The scores for individual samples (PC1 scores) indicate that base-flow samples were strongly represented by the negative associations in PC1 and that stormflow samples were strongly represented by the positive associations in PC1. Based on the parameter associations with PC1, major ion concentrations are higher, and aluminum, turbidity, and the number of urban OWICs per sample were lower during base flow; however, this trend reverses as streamflow increases during storm runoff. This component appears to describe the classic water quality of an urban stream not affected by wastewater effluent, but receiving varying amounts of dry-weather and storm-related urban runoff.

OWICs in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River Watersheds

Although the predominant land use is residential in the INT, PEA, PRO, and SOU watersheds, industrial and commercial land uses are more extensive than in the control basins (table 2; Atlanta Regional Commission, 2005). In the INT, PEA, PRO, and SOU watersheds, 76–93 percent of the drainage areas are developed (Atlanta Regional Commission, 2005). Sampling sites within the INT, PEA, PRO, and SOU watersheds were parsed into sites upstream (these include sites on tributaries not affected by CSOs) and sites downstream from known CSO outfalls. The OWICs were analyzed in samples collected at 27 sites either upstream from or not affected by CSOs and at 14 sites downstream from CSO outfalls (fig. 1, table 1). Because only two samples were collected upstream of CSO outfalls in the INT watershed, comparative analyses of those samples to other upstream samples were not possible.

OWICs at Sites Upstream from Combined Sewer Overflow Outfalls

In water samples from upstream sites, the OWICs detected in the highest and lowest percentage of samples was similar to the pattern for all samples collected during the study period (fig. 5*B*). When compared with the control-basin samples, 29 OWICs were detected in up to 34 percent more upstream samples (fig. 14). The remaining 23 OWICs were detected with similar frequency in control-basin and upstream samples, including all of the automotive-use compounds. The 10 compounds that were detected in a greater percentage of upstream than control-basin samples are bromacil (34 percent), TDCPP (31 percent), PCE (26 percent), NPEO2 (24 percent), TCEP (23 percent), caffeine (20 percent), TBP (17 percent), OPEO2 (13 percent), and TPP and bromoform (12 percent each).

Seasonal Variation

Typically, seasonal differences in the percentage of cooland warm-season upstream samples containing OWICs were similar to the seasonal pattern observed in all samples collected during the study period (fig. 8, table 15). Nevertheless, the seasonal pattern in several OWICs at upstream sites in the PEA, PRO, and SOU watersheds differed from the seasonal pattern of OWICs detected among control-basin samples collected during the study (tables 13, 15).

Except for the sterol, automotive-use, and flame-retardant compounds, OWICs were detected with similar frequency in cool- and warm-season samples (table 15). The sterol and flame-retardant compounds were detected in 5–7 percent more warm- than cool-season samples, and the automotive-use compounds in a greater percentage of cool-season samples. Typically, the percentages of OWICs in cool- and warmseason samples were markedly greater from upstream SOU than upstream PEA and PRO sites.

Table 14. Results of a principal components analysis on 16 parameters associated with base-flow and stormflow samples from the control basins (Nancy Creek, Sandy Creek, and Utoy Creek) near Atlanta, GA, March 2003 to January 2006.

[PC, principal component, which is a group of correlated parameters whose variance explains some proportion of the data variability in a dataset; loading, a value indicating how important the variability of a parameter is to the total variance of the component, analogous to a correlation coefficient; ft^3/s , cubic feet per second; FNU, formazin nephelometric unit; MPN per 100 mL, most probable number per 100 milliliters; SC, specific conductance at 25 degrees Celsius; μ S/cm, microsiemens per centimeter; mg/L, milligram per liter; μ g/L, microgram per liter; OWICs, organic wastewater-indicator compounds; —, not significant, loading less than 0.400]

Dovometor	Principal co	Communality		
rarameter —	PC1	PC2	PC3	— Communanty [®]
Streamflow (ft ³ /s)	0.625			0.700
Turbidity (FNU)	.669			.584
<i>Escherichia coli</i> density (MPN per 100 mL)	—	—	_	.276
Field SC (µS/cm)	842	—	—	.854
Acid-neutralizing capacity (mg/L)	877	—	_	.883
Chloride (mg/L)	687			.590
Aluminum (µg/L)	.680			.554
Cadmium (µg/L)		0.517		.317
Copper (µg/L)	.469	.737		.785
Lead (µg/L)	.515	.535		.585
Manganese (µg/L)	511		0.605	.729
Nickel (µg/L)		.641		.522
Zinc (µg/L)			.434	.401
Number of human-associated OWICs per sample ^b	_	_	_	.340
Number of urban-runoff OWICs per sample ^c	.630	_	—	.686
Number of pesticides detected per sample	—	_	—	.233
Proportion of variance explained by component	.290	.116	.062	
Cumulative variance for each added component ^d	.290	.406	.468	

^aCommunality is a measure of a parameter's importance in explaining the variability in the dataset. The higher the number, the greater the importance.

^b Sum of personal-use, sterol, and nonionic detergent compounds per sample.

° Sum of polycyclic aromatic hydrocarbon, industrial-use, automotive-use, and flame retardant compounds per sample.

^d Total variance explained by six components is 0.565.



Among the personal-use compounds in upstream samples, four compounds were detected with greater frequency in cool-season samples, six with equal frequency in both seasons, and four with greater frequency in warmseason samples. Except for DEET and methyl salicylate, the personal-use compounds were detected in a greater percentage of cool- than warm-season samples from upstream SOU sites. The cool-season samples from upstream SOU sites contained 17-28 percent more personal-use compounds than did cooland warm-season samples from upstream PEA and PRO sites, and control-basin sites. A slightly higher percentage of warmthan cool-season samples from upstream PEA and PRO sites contained personal-use compounds. The seasonal distribution of personal-use compounds in samples from upstream PEA sites was similar to that seen among the control-basin sites (tables 13, 15). During the cool season, the dominant personaluse compounds in upstream SOU samples were caffeine and menthol; whereas during both seasons caffeine was dominant in upstream PEA samples, and caffeine and triclosan were dominant in upstream PRO samples. In the upstream SOU samples, bromoform was detected with markedly greater frequency in cool- than warm-season samples, contrary to the pattern for all other samples in the study in which bromoform was detected with similar frequency (less than 5 percent) during both seasons.

Although the pesticides were collectively detected with greater frequency during both seasons at upstream than at control-basin sites, 14DCB, chlorpyrifos, and diazinon were detected with similar frequency among control-basin, upstream PEA, and upstream SOU samples (tables 13, 15). At upstream PEA sites, bromacil was detected with similar frequency during both seasons, but carbaryl and prometon were detected with greater frequency in warm-season samples. Conversely, bromacil was detected in about 16 percent more cool- than warm-season samples at upstream SOU sites; whereas, carbaryl was detected in slightly more warm-season samples. At upstream PRO sites, 14DCB and bromacil were detected in 14-19 percent more cool- than warm-season samples; however, bromacil was detected with greater frequency during both seasons at upstream SOU sites (table 15). In addition, the pesticides carbaryl, diazinon, and prometon were detected in greater percentages of warm- than cool-season samples from upstream PRO sites.

The seasonal distribution of the sterol compounds in upstream samples from the PEA, PRO, and SOU watersheds typically mirrored the seasonal pattern among all samples collected during the study (fig. 8, table 15). All four sterols were detected in a similar percentage of cool-season samples from control-basin and upstream PEA sites; whereas, only coprostanol and stigmastanol from those sites had similar detection frequencies during the warm season (tables 13, 15). All four sterols were detected in a substantially greater percentage of cool-season samples from upstream SOU sites than from upstream sites in the other watersheds. Nevertheless, cholesterol was detected with similar frequency in upstream PRO samples during both seasons, in contrast to the greater percentage of warm-season samples for the PEA and SOU watersheds and for all samples collected during the study.

Among upstream samples collected during the study, the industrial-use compounds were detected with similar frequency during both seasons (table 15), but in 9-13 percent more cool- and warm-season samples than at control-basin sites (table 13). Although collectively the industrial-use compounds were detected with similar frequency in both seasons, anthraquinone, carbazole, and TPP were detected in more warm-season samples and *d*-limonene in more cool-season samples (table 15). In contrast to the greater detection frequency of anthraquinone, carbazole, and PCE in warm-season samples from upstream PEA sites, anthraquinone and carbazole were detected with similar frequencies during both seasons and PCE with greater frequency in warm-season samples from upstream PRO and SOU sites. At upstream PRO sites, PCE was detected in 92 and 75 percent of cool- and warm-season samples, respectively. Furthermore, bisphenol-A and *d*-limonene were detected in a greater percentage of coolseason samples from upstream PEA sites. In contrast, a greater percentage of upstream PRO and SOU samples contained bisphenol-A during the warm season and PCE during the cool-season.

Typically the seasonal distribution of the PAH compounds in upstream samples paralleled the pattern seen among all samples collected during the study period and the detection frequencies during both seasons were similar to those for control-basins sites (fig. 8). Except for anthracene, the seasonal distribution of individual PAH compounds differed substantially among samples collected from upstream sites (table 15). Anthracene was detected at all upstream sites with similar frequency during both seasons, p-cresol with greater frequency in cool-season samples, and fluoranthene and pyrene with greater frequency in warm-season samples. Five PAHs were detected with substantially greater frequency in cool- and warm-season samples from upstream SOU than upstream PEA and PRO sites, and control-basin sites (tables 13, 15). The compounds fluoranthene, PCP, and phenanthrene were detected with greater frequency in cool-season samples from the control-basin sites than from upstream PEA and PRO sites; however, p-cresol was detected with greater frequency in coolseason samples from upstream PRO and control-basin sites than from upstream PEA sites. In contrast, all six PAHs were detected with similar frequency in warm-season samples from control-basin and upstream PEA sites and, except for p-cresol, with substantially greater frequency than warm-season samples from upstream PRO sites.

Except for 2,6-dimethylnaphthalene, the seasonal distribution of automotive-use compounds in upstream samples was similar to the distribution for all samples in the study and control-basin samples (fig. 8, tables 13, 15). The compound 2,6-dimethylnaphthalene was detected with greater frequency in cool- than warm-season samples from upstream sites, contrary to the similar distribution in both

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Table 15. Detection frequencies by season for individual organic wastewater-indicator compounds in water samples at sites upstream from combined sewer overflow outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.

[INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek; SOU, South River; Cool, cool season (October–April); Warm, warm season (April–October); —, not detected above study detection levels]

	Detection frequency (percent)									
Compound	All sites INT PEA PRO					RO	S	ງບ		
-	Cool	Warm	Warm	Cool	Warm	Cool	Warm	Cool	Warm	
Number of samples	105	170	3ª	66	90	12	28	27	49	
			Personal-u	se compou	ınds					
AHTN, tonalide	12	10.6	2/3	3.0	4.4	17	25	33	10	
Acetophenone	6.7	10.0	—	3.0	11	—	11	19	8.2	
Benzophenone	11	12	—	7.6	8.9	—	21	22	12	
Caffeine	60	55	3/3	58	63	8.3	39	89	45	
Camphor	34	28	2/3	29	30	33	29	48	20	
Cotinine	13	16	2/3	6.1	5.6	8.3	32	33	22	
HHCB, galaxolide	19	19	2/3	1.5	5.6	58	57	44	18	
Indole	17	23	3/3	3.0	8.9	33	46	44	31	
Isoborneol	7.6	1.8	—	6.1		—	3.6	15	4.1	
Menthol	31	25	2/3	17	26	25	36	70	16	
Methyl salicylate	4.8	14		_	7.8		25	19	18	
DEET	8.6	40	1/3	3.0	46		43	26	29	
Triclosan	24	20	2/3	7.6	6.7	58	50	48	25	
Triethyl citrate	6.7	12	1/3	1.5	6.7	_	21	22	16	
Class percentage ^b	18	19	_	10	16	17	21	38	20	
			Disinfectio	on compou	nds				-	
Bromoform	14	11	_	3.8	4.4		_	48	29	
		·	Pesticide	e compound	ds		·			
1,4-Dichlorobenzene (14DCB)	8.6	7.6	2/3	6.1	5.6	25	11	7.4	6.1	
Bromacil	59	57	2/3	39	42	83	64	96	80	
Carbaryl	15	31	2/3	14	33	_	18	26	31	
Chlorpyrifos		1.8	_		2.2	_	3.6	_	_	
Diazinon	2.9	7.1	2/3	3.0	3.3	_	14	3.7	6.1	
Prometon	1.9	7.1	_	1.5	10	_	11	3.7	_	
Class percentage	14	17		11	16	18	17	23	20	
			Sterol o	compounds	;					
Cholesterol	40	59		32	61	67	68	48	53	
3-β-Coprostanol	32	27		26	17	42	39	44	39	
β-sitosterol	12	29	_	11	30	8.3	32	19	29	
β-stigmastanol	11	15	_	9.1	11	_	7.1	19	27	
Class percentage	24	31	_	19	30	29	26	32	37	
			Industrial-u	ise compoi	unds					
Anthraquinone	7.6	15		9.1	24		3.6	7.4	6.1	
Bisphenol-A	10	10		9.1	3.3	—	7.1	15	25	
Carbazole	16	25	1/3	15	32		3.6	26	22	

Table 15.Detection frequencies by season for individual organic wastewater-indicator compounds in water samples at
sites upstream from combined sewer overflow outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and
South River watersheds near Atlanta, GA, March 2003 to January 2006.—Continued

[INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek; SOU, South River; Cool, cool season (October–April); Warm, warm season (April–October); —, not detected above study detection levels]

	Detection frequency (percent)										
Compound	Alls	sites	INT	P	EA	PI	RO	S	SOU		
-	Cool	Warm	Warm	Cool	Warm	Cool	Warm	Cool	Warm		
		Indus	strial-use co	mpounds—	-Continued						
<i>d</i> -Limonene	27	20	2/3	27	16	33	29	22	20		
Tetrachloroethene (PCE)	44	42	3/3	26	31	92	75	67	41		
Triphenyl phosphate (TPP)	14	19	_	7.6	10	_	18	37	37		
Class percentage	20	21	—	16	19	21	16	29	25		
		Polycy	clic aromati	c hydrocarl	bons (PAHs)						
Anthracene	2.9	2.9	_	3.0	2.2	_	_	3.7	6.1		
p-Cresol	35	18	1/3	15	7.8	33	21	85	33		
Fluoranthene	13	22	2/3	14	21	_	7.1	19	29		
Pentachlorophenol (PCP)	8.6	17	_	4.5	17	8.3	_	19	29		
Phenanthrene	11	18	_	7.6	19	—	7.1	22	25		
Pyrene	10	17	_	7.6	14	—	7.1	19	29		
Class percentage	13	15	_	8.6	13	6.9	4.8	28	25		
Automotive-use compounds											
1-Methylnaphthalene	12	5.3		9.1	1.1	_	_	26	16		
2-Methylnaphthalene	13	7.1	1/3	9.1	2.2	_	_	30	18		
2,6-Dimethylnaphthalene	10	2.4	_	6.1	—	—	_	22	8.2		
5-Methyl-1H-benzotriazole	8.6	7.6	1/3	11	5.6	_	7.1	7.4	10		
Isopropylbenzene		_	_			_	_		_		
Naphthalene	22	14	1/3	6.1	11	33	14	56	16		
Class percentage	11	6.0	_	6.8	3.3	5.5	3.6	23	11		
		Nonior	nic detergen	t metabolit	es (NDMCs)						
<i>p</i> -Nonylphenol (total)	36	38	1/3	24	37	17	36	74	43		
4-Nonylphenol diethoxyl- ate (NPEO2)	38	38	1/3	30	30	—	43	74	49		
4-Octylphenol monoethox- ylate (OPEO1)	11	16	—	6.1	13	8.3	14	22	22		
4-Octylphenol diethoxylate (OPEO2)	23	34	—	17	28	25	46	37	39		
4-tert-Octylphenol	8.6	14	_	12	12		11	3.7	18		
Class percentage	23	27	—	18	24	10	24	42	34		
			Flame-retar	dant compo	ounds						
Tributyl phosphate (TBP)	29	20		2.7	17	83	18	41	2.9		
Tris(2-butoxyethyl)	67	78	3/3	64	77	50	71	82	84		
phosphate (TBEP)											
Tris(2-chloroethyl) phosphate (TCEP)	56	71	2/3	49	69	25	68	89	78		
Tris(dichloroisopropyl) phosphate (TDCPP)	46	55	1/3	32	41	8.3	50	96	86		
Class percentage	49	54	_	43	51	23	41	77	69		

^a For sample sizes less than 10, the number of compound detections out of the all samples collected in a watershed is given instead of a percentage. ^b Weighted value based on the percentage of compounds detected within its associated compound class. seasons for all samples and control-basin samples. In general, the automotive-use compounds were detected in the greatest percentage of cool- and warm-season samples from upstream SOU than upstream PEA and PRO, and control-basin sites. Only naphthalene and the corrosion-inhibiter 5-methyl-1Hbenzotriazole were detected in upstream PRO samples. The automotive-use compounds were typically detected with similar frequency in samples from control-basin and upstream PEA sites during both seasons.

The seasonal distribution of the NDMCs detected in upstream samples differs from the seasonal distribution seen among all samples collected during the study period (fig. 8; table 15). Among all samples collected during the study, NPEO2 and OPEO2 were detected in more warm- than cool-season samples, and *p*-nonylphenol, OPEO1, and 4-tert-octylphenol were detected with similar frequency during both seasons. With some exceptions, NDMCs were detected with substantially greater frequency in samples collected from upstream SOU sites than from upstream PEA and PRO sites, and from control-basin sites during both seasons (tables 13, 15). The compound *p*-nonylphenol was detected in a greater percentage of cool-season samples from controlbasin sites than from upstream PEA and PRO sites; however, all of the NDMCs were detected in a greater percentage of warm-season samples from upstream PEA and PRO than control-basin sites. The compounds NPEO2 and 4-tertoctylphenol were detected with similar frequency in samples from upstream PEA sites during both seasons (table 15). The compounds OPEO1 and OPEO2 were detected in upstream SOU samples with similar frequency (within \pm 5 percent) during both seasons.

Typically the seasonal distribution of the flame-retardant compounds in upstream samples paralleled the pattern seen among all samples collected during the study period (fig. 8, table 15). The flame retardants collectively were detected in a greater percentage of cool- and warm-season samples from upstream than control-basin sites. During both seasons, all four flame retardants were detected in substantially greater percentages of samples from upstream SOU sites than from upstream PEA and PRO sites, and from control-basin sites (tables 13, 15). The flame retardants were detected in 41-96 percent of cool-season samples and 29-86 percent of warm-season samples from upstream SOU sites (table 15). During both seasons, TDCPP was the most frequently detected flame retardant in samples from upstream SOU sites; whereas, TBEP was detected with the greatest frequency in samples from all other sites during both seasons. In addition, TCEP was detected with similar frequency in upstream SOU samples in both seasons. Among cool- and warm-season samples, flame retardants were detected with the lowest frequency at upstream PRO sites.

Variation During Base Flow

Typically, the numbers of detectable OWICs per sample were markedly higher in stormflow than base-flow samples from upstream sites. The median numbers of OWICs detected in upstream base-flow samples from the PEA, PRO, and SOU watersheds were 4, 8, and 14, respectively, and were statistically lower than the medians in stormflow samples from the PEA, PRO, and SOU watersheds (13, 17, 17, respectively; *p*-value less than 0.05; fig. 9). The median number of OWICs detected in upstream base-flow samples from the PEA, PRO, and SOU watersheds were statistically different among the three watersheds (*p*-value less than 0.05; fig. 9). In general, the detection frequencies in base-flow samples from the upstream sites (table 9) paralleled the pattern depicted in figure 5*B* for all samples collected during the study.

At least one compound from seven of the nine OWIC classes was detected in 6-17 percent more base-flow samples from upstream than control-basin sites (table 9). In contrast, the PAH and automotive-use compounds were detected in a similar percentage of base-flow samples from upstream and control-basin sites. Among upstream samples, a greater percentage of base-flow than stormflow samples contained PCE, bromacil, the personal-use compounds HHCB, triethyl citrate, cotinine, indole, and triclosan; and bromoform (fig. 15). Fifteen compounds were detected with similar frequency during base flow and stormflow. When compared to controlbasin samples, 15 OWICs were detected in 5-23 percent more base-flow samples from upstream sites (fig. 16A). Among the 15 OWICs, the compounds PCE, TDCPP, caffeine, bromacil, bromoform, and p-cresol were detected in at least 10 percent more base-flow samples from the upstream sites. Only PCP, triclosan, and carbaryl were detected in a greater percentage (6-8 percent) of base-flow samples from control-basin sites than from upstream sites. Thirty-four compounds were detected with similar frequency in base-flow samples from upstream and control-basin sites.

Among base-flow samples, OWICs were detected in the smallest percentage of samples from upstream PEA than upstream PRO or SOU sites, but with similar frequency in samples from control-basin sites. The personal-use, bromoform, PAH, automotive-use, NDMCs, and flame-retardant compounds were detected in substantially more base-flow samples from upstream SOU than upstream PEA and PRO sites, and control-basin sites (table 9). Among the personal-use compounds, HHCB, indole, menthol, methyl salicylate, and triclosan were detected with greater frequency in base-flow samples from control-basin than from upstream PEA sites; moreover, only caffeine and DEET were detected with greater frequency in base-flow samples from upstream PEA than from control-basin sites. In addition, AHTN, HHCB, and triclosan were detected with greater frequency in base-flow samples





Relative difference in the percentage of upstream samples containing OWICs



to January 2006.

Relative difference in the percentage of samples containing OWICs

from upstream PRO than upstream SOU sites. Bromoform was detected in nearly 6 percent of samples from upstream PEA sites and in 41 percent of samples from upstream SOU sites. These percentages are markedly higher than those for baseflow samples from the upstream PRO or control-basin sites.

Collectively, the pesticide, sterol, and industrial-use compounds were detected in a similar percentage of base-flow samples from upstream sites in the PRO and SOU watersheds and with substantially greater frequency than samples from upstream PEA sites (table 9). Nevertheless, 10-13 percent more samples from upstream PRO sites contained 14DCB than those from upstream PEA and SOU sites, respectively. Bromacil and carbaryl were detected in 13-45 percent more base-flow samples from upstream SOU than upstream PEA and PRO sites. The pesticides 14DCB and bromacil were detected in about 5-8 percent, respectively, more base-flow samples from upstream PEA than from control-basin sites. A greater percentage of upstream base-flow samples from the PRO than SOU watersheds contained cholesterol; whereas, coprostanol and sitosterol were detected with similar frequency in base-flow samples from the PRO and SOU watersheds. Collectively, the sterols and industrial-use compounds were detected with similar frequency in baseflow samples from upstream PEA and control-basin sites; however, the detection frequency of PCE in base-flow samples from upstream PEA sites was 31-35 percent higher than for base-flow samples from SAN and UTO sites, but similar to the frequency in base-flow samples from the NAN watershed. Among the industrial-use compounds, bisphenol-A, carbazole, and TPP were detected in 7-16 percent more base-flow samples from upstream SOU than PRO sites. In contrast, PCE was detected in 81 percent of base-flow samples from upstream PRO sites, 28 and 45 percent higher than at upstream SOU and PEA sites.

Typically, the PAH and automotive-use compounds were detected with similar frequency in base-flow samples from upstream and control-basin sites (table 9). The PAH and automotive-use compounds were each detected in 9–13 percent more base-flow samples from upstream SOU than upstream PRO and PEA sites, respectively, during the study. Except for naphthalene, compounds in the automotiveuse class were detected in less than 1 percent of base-flow samples at upstream PRO sites. Among base-flow samples, naphthalene was the dominant automotive-use compound at upstream PRO and SOU sites, while 5-methyl-1H-benzotriazole was dominant in base-flow samples from upstream PEA sites. The automotive-use and PAH compounds were detected with similar frequency in base-flow samples from sites in the control basins and upstream PEA and PRO watersheds.

Collectively, the NDMCs and flame-retardant compounds were detected in 10 and 17 percent, respectively, more baseflow samples from upstream than control-basin sites (table 9). Except for OPEO1 and OPEO2, the NDMCs were detected in 14–35 percent more base-flow samples from upstream SOU than upstream PEA or PRO sites. The compounds OPEO1 and OPEO2 were detected with similar frequency in base-flow samples from upstream SOU and PRO sites. The compound *p*-nonylphenol was detected in about 5 percent more base-flow samples from control-basin than from upstream PEA sites, but OPEO1, OPEO2 and 4-*tert*-octylphenol were detected with greater frequency in upstream PEA samples.

Eighty to 88 percent of base-flow samples from upstream SOU sites contained the flame retardants TBEP, TCEP, and TDCPP; these percentages were 24–40 percent greater than for base-flow samples from upstream PEA and PRO sites, or control-basin sites. A slightly greater percentage of base-flow samples from upstream PEA than control-basin sites contained the flame retardants TBEP, TCEP, and TDCPP, while TBP was detected with similar frequency at those sites.

In upstream base-flow samples, the 75th percentile concentrations for eight compounds exceeded the SRL (table 11). These compounds include caffeine, DEET, bromacil, cholesterol, NPEO2, TBEP, and TDCPP in upstream SOU samples; bromacil and TBEP in upstream PEA samples; bromacil, cholesterol, PCE, and TBEP at upstream PRO samples. Although the 75th percentile concentrations in 12 of the 14 personal-use compounds in upstream base-flow samples did not exceed SRLs, the highest study-period concentrations of several compounds were measured in upstream samples. A water sample collected under base-flow conditions from site PRO-3 on March 31, 2004, contained the highest concentrations for 7 of the 14 personal-use compounds (caffeine, $11 \mu g/L$; cotinine, 1.4 μ g/L; HHCB, 1.6 μ g/L; indole, 1.9 μ g/L; menthol, 8.6 µg/L; triclosan, 2.2 µg/L; and triethyl citrate, $0.31 \,\mu g/L$) measured during the study. The concentrations for menthol, cotinine, triethyl citrate, indole, and triclosan in this one sample accounted for 20-69 percent of the total OWIC concentrations measured in all samples collected during the study period (table 8). These concentrations were unusual because this site is on a small tributary to Proctor Creek that was not affected by CSOs and whose watershed had the fourth highest percentage of woodland and parks in the study area (table 2). Furthermore, the sample was collected during base flow and had an E. coli density of 1,000 MPN/100 mL, which is typical for residential areas during base flow. Another base-flow sample from an upstream PRO site contained the highest AHTN concentration (0.40 μ g/L, 57 percent of the total summed AHTN concentration for all samples) measured during the study (table 11).

The exceptionally high concentrations of personal-use compounds in the May 13, 2004, sample from site PRO-3 are substantially higher than concentrations measured in treated wastewater effluent in Sioux Falls, SD (Sando and others, 2005, 2006), but similar to concentrations in wastewater effluent from septic systems in Oregon (Hinkle and others, 2005). One upstream base-flow sample from the SOU water-shed (synoptic site 4, fig. 1) collected on July 14, 2004, contained the highest concentrations of benzophenone (0.87 µg/L)

and camphor (1.8 μ g/L) measured during the study period. In addition, the highest isoborneol (0.75 μ g/L) and DEET (2.4 μ g/L) concentrations among base-flow samples were measured at upstream sites in the SOU watershed.

The 75th percentile bromacil concentration in base-flow samples was highest at upstream SOU sites $(1.0 \ \mu g/L)$ and lowest at upstream PEA sites $(0.41 \ \mu g/L)$; table 11). The 75th percentile concentrations for bromacil in upstream PRO and SOU samples were 40 to nearly 100 percent higher than the concentrations in base-flow samples from the control basins. The 75th percentile bromacil concentration in baseflow samples from the UTO watershed was similar to the concentration in base-flow samples from upstream PEA sites. Upstream base-flow samples from the PEA watershed contained the highest bromacil (29 $\mu g/L$) and diazinon (28 $\mu g/L$) concentrations measured during the study period. In addition, a base-flow sample from an upstream PRO site contained the highest 14DCB concentration (1.6 $\mu g/L$) measured in baseflow samples during the study period.

Except for cholesterol in base-flow samples from upstream PRO sites, the 75th percentile concentrations of all sterols in upstream base-flow samples were below SRLs (table 11). The PRO-3 base-flow sample described earlier contained the highest concentrations of cholesterol (16 μ g/L), coprostanol (7.5 μ g/L), and sitosterol (4.0 μ g/L) measured in all samples during the study period. An upstream base-flow sample from the SOU watershed contained the highest concentration of stigmastanol (2.5 μ g/L) measured in base-flow samples during the study period.

Except for PCE from upstream PRO sites, the 75th percentile concentrations for the industrial-use compounds were below SRLs in upstream base-flow samples (table 11). Nevertheless, among upstream base-flow samples, those from the PRO watershed contained the highest concentrations of anthraquinone (0.54 μ g/L), bisphenol-A (2.0 μ g/L), and PCE (2.8 μ g/L), while those from the SOU watershed had the highest concentration of TPP (0.51 μ g/L).

Even though the 75th percentile concentrations for the PAH and automotive-use compounds in upstream base-flow samples were below SRLs, upstream base-flow samples from the PEA watershed contained the highest concentration of *p*-cresol (24 μ g/L) measured among all samples collected during the study period (table 11). Among upstream base-flow samples, the highest PCP (0.91 μ g/L), 2-methylnaphthalene (0.30 μ g/L), and naphthalene (0.25 μ g/L) concentrations were measured from the SOU watershed. Among all samples collected during the study, the highest concentration of the automotive-use compound 5-methyl-1H-benzotriazole (6.1 μ g/L) was measured in an upstream base-flow sample from the SOU watershed.

Except for NPEO2 in an upstream base-flow sample from the SOU watershed, the 75th percentile concentrations for the NDMCs were below SRLs in upstream base-flow samples (table 11). The highest concentration of *p*-nonylphenol (10 μ g/L) observed among all samples collected during the study period was measured in an upstream base-flow sample from the SOU watershed (tables 11, 12). The highest NPEO2 concentration (48 μ g/L) among base-flow and stormflow samples from upstream and downstream sites, and stormflow samples from control-basin sites was measured in an upstream base-flow sample from the SOU watershed. In addition, the highest concentration of OPEO1 (1.6 μ g/L) and OPEO2 (0.56 μ g/L) in base-flow samples from control-basin and upstream sites and stormflow samples from upstream and downstream sites were measured at an upstream PRO and upstream SOU site, respectively. The highest 4-*tert*-octylphenol concentration (0.52 μ g/L) among base-flow and stormflow samples from control-basin and upstream sites was measured in a base-flow sample from an upstream PRO site.

Except for TBEP and TDCPP, the 75th percentile concentrations for the flame retardants were below the SRL in base-flow samples from all upstream sites (table 11). Only the 75th percentile TBEP concentration exceeded the SRL in base-flow samples from all upstream sites, while the 75th percentile TDCPP concentration exceeded the SRL in base-flow samples from upstream SOU sites. The 75th percentile TBEP concentration in base-flow samples was highest at upstream SOU sites (0.95 µg/L) and lowest at upstream PEA sites (0.39 µg/L), but substantially higher than the 75th percentile concentrations in base-flow samples from the control basins and from upstream PRO sites. The 75th percentile TBEP concentration in upstream base-flow samples from the PEA watershed (0.39 μ g/L) was similar to the concentrations measured in the SAN, and UTO basins. Among upstream base-flow samples, the highest concentration of TBP (0.75 µg/L) was measured at a PRO site, the highest TBEP concentration was measured in a base-flow sample from an upstream PEA site, and the highest concentrations of TCEP $(2.0 \ \mu g/L)$ and TDCPP $(1.5 \ \mu g/L)$ in the study period were measured in a base-flow sample from an upstream from SOU site (table 11).

Relations Among OWICs and Selected Water-Quality Constituents and Properties

A PCA of base-flow samples collected at upstream sites in the INT, PEA, PRO, and SOU watersheds revealed some notable relations with 15 inorganic constituents, water-quality properties, and OWICs (table 16). In upstream base-flow samples, about 75 percent of the total variability in the 15 variables data was explained by six components, but only three were considered principal components. The PC1 explains about 39 percent of the variability in upstream base-flow samples and has high loadings (greater than 0.7) and strong associations (loadings with similar magnitudes) with zinc, cadmium, copper, manganese, lead, and aluminum (the trace metals common in urban areas), and moderate loadings (0.5–0.7) and associations with the total number of OWICs related to urban runoff. The *E. coli* density associated with samples that scored high on this component ranged from 10 to 140 MPN/100 mL. Base-flow samples from SOU-3 scored the highest on this component. Therefore, PC1 appears to describe constituents and parameters associated with dry-weather urban runoff or groundwater discharge with very low *E. coli* density.

The second principal component (PC2) explains nearly 15 percent of the total variability in upstream base-flow

samples (table 16). This component has high loadings with specific conductance and moderate loadings with acidneutralizing capacity, chloride concentration, and the number of human-associated OWICs per sample. Therefore, PC2 describes samples with elevated major ion concentrations that tend to have elevated numbers human-associated OWICs. Although *E. coli* density did not have a significant loading

Table 16.Results of a principal components analysis on 15 parameters associated with base-flow samplescollected at sites upstream from combined sewer overflow outfalls in the Intrenchment Creek, Peachtree Creek,Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.

[PC, principal component, which is a group of correlated parameters whose variance explains some proportion of the data variability in a dataset; loading, a value indicating how important the variability of a parameter is to the total variance of the component, analogous to a correlation coefficient; ft^3 /s, cubic feet per second; FNU, formazin nephelometric unit; MPN per 100 mL, most probable number per 100 milliliters; SC, specific conductance at 25 degrees Celsius; μ S/cm, microsiemens per centimeter; mg/L, milligram per liter; μ g/L, microgram per liter; OWICs, organic wastewater-indicator compounds; —, not significant, loading less than 0.400]

Devementer	Principal con	Communalitua		
Farameter —	PC1	PC2	PC3	– communanty"
Turbidity (FNU)	_	_	0.536	0.516
<i>Escherichia coli</i> density (MPN per 100 mL)	—	—	_	.377
Field SC (µS/cm)	0.495	0.768	439	1.000
Acid-neutralizing capacity (mg/L)	_	.686	_	.775
Chloride (mg/L)	—	.584		.583
Aluminum (µg/L)	.775	—	_	.800
Cadmium (µg/L)	.914			.884
Copper (µg/L)	.891			.872
Lead (µg/L)	.853			.960
Manganese (µg/L)	.888			.837
Nickel (µg/L)	.643			.556
Zinc (µg/L)	.943			.965
Number of human-associated OWICs per sample ^b	—	.482	.575	.783
Number of urban-runoff OWICs per sample ^c	.537	_	.517	.755
Number of pesticides detected per sample	_	—	.434	.552
Proportion of variance explained by component	.389	.145	.115	
Cumulative variance for each added component ^d	.389	.534	.649	

^aCommunality is a measure of a parameter's importance in explaining the variability in the dataset. The higher the number, the greater the importance.

^b Sum of personal-use, sterol, and nonionic detergent compounds per sample.

° Sum of polycyclic aromatic hydrocarbon, industrial-use, automotive-use, and flame retardant compounds per sample.

^dTotal variance explained by six components is 0.750.

on this component, E. coli densities also tend to be elevated in samples that scored high on this component. Twenty-six upstream base-flow samples scored high on PC2: 12 from WOO-1 and 2 from LUL-1 in the PEA watershed; 5 from PRO-3 and a synoptic site in the PRO watershed; and 3 from SOU-3, 2 from SOU-2, and 1 from a synoptic site in the SOU watershed. The median number of human-associated OWICs in these samples is 7.5, with a maximum of 20, the median specific conductance is $329 \,\mu\text{S/cm}$ at $25 \,^{\circ}\text{C}$. with a maximum of 940 µS/cm at 25 °C; and the median E. coli density is 2,100 MPN/100 mL, with a maximum of 105,000 MPN/100 mL. Some of these samples clearly captured water from dry-weather runoff affected by human or animal waste or sewage-affected groundwater discharge; however, the associations with elevated major ion concentrations, number of human-associated OWICs, and E. coli densities were not consistent. For example, sewage fungi (Sphaerotilus nathans) was observed growing on the bottom sediments of Woodall Creek upstream from the WOO-1 site, but only three base-flow samples from WOO-1 contained more than six human-associated OWICs and had E. coli densities greater than 1,100 MPN/100 mL.

Principal component 3 (PC3) explained about 11 percent of the total variability in upstream base-flow samples (table 16). The number of human-associated OWICs, turbidity, and the number of urban-runoff OWICs had moderate loadings on PC3 and were moderately associated with each other. This component describes the increase in the number of human- and urban-runoff-associated OWICs as stream turbidity increases and may indicate a different source of dry-weather runoff than that indicated by sample associations with PC2.

Cluster analysis on E. coli density and the three principal components identified eight different groups of upstream base-flow samples. One group of 71 samples, primarily from upstream sites in the PEA and PRO watersheds, contained the lowest combination of total OWICs per sample, E. coli density, and specific conductance of any cluster group. The median values for total OWICs per sample, E. coli density, and specific conductance were 3 OWICs, 465 MPN/100 mL, and 152 µS/cm at 25 °C, respectively. This sample group probably describes groundwater-dominated base flow minimally affected by dry-weather runoff. Another group of seven samples from site SOU-3 contained milligram-per-liter levels of aluminum, manganese, and zinc; elevated specific conductance, turbidity, OWICs, and sulfate concentrations; and E. coli densities less than 80 MPN/100 mL. These samples probably represent dry-weather runoff from areas where metals may accumulate on impervious surfaces, such as industrial areas or truck stops, especially areas where vehicles are repaired or washed. Six samples from the PRO-3, SOU-2, and WOO-1 sites comprise a group with high numbers of OWICs per sample and high E. coli densities, but with major ion concentrations that were similar to most of the other cluster groups. The median number of human-associated OWICs and E. coli densities in this sample group was

10 and 17,000 MPN/100 mL, respectively. These samples seem to have captured stream water affected by sewage effluent, either through leaking sewer lines or intermittent breaks in those lines. Fourteen base-flow samples from WOO-1, LUL-1, and SOU-2 comprise a group with low numbers of OWICs (less than 10) per sample, elevated major ion concentrations, and low-to-moderate E. coli densities. The median number of human- and urban-runoff-associated OWICs in these samples was four and the median specific conductance was 376 µS/cm at 25 °C. The median E. coli density, however, was 345 MPN/100 mL for the SOU-2 and LUL-1 samples, and one WOO-1 sample, but 1,300 MPN/100 mL for the other 9 WOO-1 samples. This group of samples probably represents dry-weather runoff in a densely urban, small watershed setting. The drainage areas of these three watersheds are less than 5 mi².

In general, the PCA did not identify a definitive pattern in the data related to sewage contamination during base flow at sites upstream from CSO outfalls. Probably the most important source of OWICs in these watersheds is random dry-weather runoff from landscape watering, runoff from municipal water on impervious surfaces as a result of vehicle or pavement washing; however, the data do indicate that leaking sanitary-sewer lines or discharges that are either not permitted or permitted but out of compliance may exist in a small portion of the areas represented by upstream sites in the INT, PEA, PRO, and SOU watersheds.

Variation During Stormflow

Typically, OWICs were detected more frequently in stormflow than in base-flow samples from upstream sites. The median numbers of OWICs per sample in upstream stormflow samples ranged from 13 in samples from the PEA watershed to 17 in samples from the PRO and SOU watersheds (fig. 9). The median numbers of OWICs per stormflow sample were statistically similar between upstream PRO and SOU sites and both sites were statistically higher than the median number of OWICs from upstream PEA sites (*p*-value greater than 0.05). An upstream stormflow sample from the SOU watershed contained 33 compounds, a number only exceeded during the study period by a base-flow sample from an upstream SOU site. During stormflow, the median number of OWICs per sample at upstream PEA sites was statistically higher than those from control-basin sites (*p*-value less than 0.05). Because only eight upstream stormflow samples were collected from the PRO watershed, statistical comparisons with other basins are tentative.

Thirty OWICs were detected in 5–41 percent more stormflow than base-flow samples from upstream sites during the study; whereas, 13 OWICs were detected with similar frequency in stormflow and base-flow samples (fig. 15). Compared to stormflow samples from control-basin sites, 31 OWICs were detected in 5–41 percent more stormflow samples from upstream sites, while 18 compounds were detected with similar frequency at both sites and 3 compounds were detected with greater frequency at control-basin sites (fig. 16*B*). Only camphor, phenanthrene, and naphthalene were detected in a greater proportion of stormflow samples from control-basin than upstream sites.

Collectively, the personal-use compounds were detected in a greater percentage of stormflow samples from upstream than from control-basin sites (table 10). Among the personaluse compounds, DEET, acetophenone, methyl salicylate, menthol, caffeine, and benzophenone were detected with the greatest frequency in upstream than control-basin stormflow samples. About twice as many stormflow samples from upstream PRO than PEA and SOU sites contained detectable personal-use compounds. Although personal-use compounds were collectively detected with similar frequency in stormflow samples from upstream PEA and SOU sites, a greater percentage of samples from the PEA site contained acetophenone, benzophenone, caffeine, camphor, menthol, and DEET and a greater percentage of samples from the SOU site contained AHTN, HHCB, indole, methyl salicylate, and triclosan. Bromoform was detected in about 25 percent more stormflow samples from upstream SOU sites than from upstream PEA and PRO sites, and control-basin sites.

Collectively, the pesticides were detected in about 9 percent more stormflow samples from upstream than from control-basin sites (table 10). Among the pesticides, bromacil and carbaryl were detected in a greater percentage of stormflow samples from upstream than control-basin sites, whereas 14DCB, diazinon, chlorpyrifos, and prometon were detected with similar frequency in stormflow samples from upstream and control-basin sites. The pesticides were detected with similar frequency in stormflow samples from upstream PRO and SOU sites, but with the lowest frequency in stormflow samples from upstream PEA sites. Bromacil, 14DCB and diazinon were detected in a greater percentage of stormflow samples from upstream SOU than upstream PEA and PRO sites. Conversely, carbaryl was detected with similar frequency in stormflow samples from upstream PEA, PRO, and SOU sites, whereas prometon was detected in more upstream PEA samples. The percentage of stormflow samples containing pesticides was similar among upstream sites in the PEA, SAN, and UTO watersheds.

The sterol, industrial-use, non-ionic detergent metabolites, and the flame-retardant compounds were detected in a greater percentage of stormflow samples from upstream than control-basin sites (table 10). Moreover, the sterol, industrialuse, PAH, automotive-use, non-ionic detergent metabolites, and the flame-retardant compounds were detected in a greater percentage of stormflow samples from upstream SOU than upstream PEA sites. Nevertheless, a greater percentage of stormflow samples from upstream PEA than SOU sites contained cholesterol, anthraquinone, *d*-limonene, 4-*tert*octylphenol, and TBEP. The industrial-use, PAH, automotiveuse, and flame retardants were detected with greater frequency in stormflow samples from upstream SOU than PRO sites. In addition, sitosterol, carbazole, 5-methyl-1H-benzotriazole, *p*-nonylphenol, and NPEO2 were detected with similar frequency in stormflow samples from upstream SOU and upstream PEA sites.

The 75th percentile concentrations for 17 of the 52 OWICs in upstream stormflow samples exceeded SRLs (table 12). Among the 17 OWICs, two personal-use compounds, caffeine and DEET, exceeded SRLs in upstream stormflow samples from the PEA, PRO, and SOU watersheds. In addition, the 75th percentile acetophenone and menthol concentrations in upstream PRO samples exceeded SRLs. The 75th percentile caffeine and DEET concentrations in stormflow samples from the upstream PRO (0.80 and 1.3 μ g/L, respectively) and upstream SOU sites (0.81 and 1.6 μ g/L, respectively) were markedly higher than those for upstream PEA samples (0.64 and 0.50 μ g/L, respectively), and control-basin samples.

Among stormflow samples from upstream and controlbasin sites, those from PEA sites contained the highest concentrations of benzophenone (0.43 µg/L), camphor (0.73 µg/L), isoborneol (1.9 µg/L), and DEET (2.3 µg/L); those from the SOU watershed contained the highest concentrations of acetophenone (0.59 µg/L), caffeine (3.5 µg/L), and bromoform (0.36 µg/L); and those from the PRO watershed contained the highest concentrations of HHCB (0.32 µg/L) and menthol (0.62 µg/L). Among all samples, however, stormflow samples from upstream sites in the PEA and SOU watersheds contained the highest concentrations of isoborneol (1.9 µg/L; tables 11, 12).

The 75th percentile concentrations for all pesticides except bromacil in upstream stormflow samples were below SRLs (table 12). The 75th percentile bromacil concentrations were 0.30, 2.2, and 1.6 μ g/L, respectively, in samples from the PEA, PRO, and SOU watersheds. The highest bromacil concentration (12 μ g/L) among stormflow samples from upstream and control-basin sites was measured at an upstream PEA site. Among upstream stormflow samples, the highest concentration of carbaryl (0.87 μ g/L) was measured in samples from the SOU watershed.

The 75th percentile concentrations for three of the four sterol compounds exceeded SRLs in upstream stormflow samples from the SOU watershed (table 12). The 75th percentile concentrations for cholesterol were 1.2 and 1.6 μ g/L in upstream stormflow samples from the PRO and SOU watersheds, respectively. Only upstream samples from the SOU watershed contained coprostanol and sitosterol at 75th percentile concentrations that exceeded SRLs. Among stormflow samples from the control basins and from upstream sites, those from upstream SOU sites contained the highest concentrations of cholesterol (2.8 μ g/L), coprostanol (2.5 μ g/L), and sitosterol (1.8 μ g/L).

Except for anthraquinone in stormflow samples from upstream PEA sites and bisphenol-A and TPP in stormflow samples from upstream SOU sites, the 75th percentile concentrations for the industrial-use compounds were below SRLs (table 12). Among stormflow samples from the control basins and from the upstream sites, those from upstream SOU sites contained the highest concentrations of anthraquinone (1.2 µg/L), bisphenol-A (2.2 µg/L), and TPP (1.0 µg/L). These bisphenol-A and TPP concentrations also were the highest concentrations measured among all samples collected during the study period (tables 11, 12). An upstream stormflow sample from the PEA watershed contained the highest concentration of *d*-limonene (1.9 µg/L) in the study, and among stormflow samples from upstream and control-basin sites, the highest concentration of PCE (2.8 µg/L).

Except for PCP in stormflow samples from upstream SOU sites, the 75th percentile concentrations for the PAHs in all upstream stormflow samples were below SRLs (table 12). The 75th percentile concentration for PCP in SOU samples was 1.0 μ g/L. Among upstream stormflow samples, those from the SOU watershed contained the highest concentrations of *p*-cresol (1.2 μ g/L) and PCP (3.8 μ g/L), and an upstream sample from the PEA watershed contained the highest concentration of phenanthrene (0.33 μ g/L).

The 75th percentile concentrations were below SRLs for all automotive-use compounds in upstream stormflow samples (table 12). Nevertheless, the highest concentrations of 1-methylnaphthalene (0.61 μ g/L), 2-methylnaphthalene (0.80 μ g/L), 2,6-dimethylnaphthalene (0.40 μ g/L), and naphthalene (0.54 μ g/L) in stormflow samples from upstream and control-basin sites were measured from an upstream PEA site. In addition, these 2-methylnaphthalene and 2,6-dimethylnaphthalene concentrations were the highest measured in all samples collected during the study period. Among stormflow samples from upstream sites, a sample from a SOU site contained the highest concentration of 5-methyl-1H-benzotriazole (0.61 μ g/L).

Except for NPEO2 in upstream stormflow samples from the SOU watershed, the 75th percentile concentrations of all non-ionic detergent compounds were below SRLs (table 12). Among stormflow samples from the control-basin and upstream sites, a sample from an upstream SOU site contained the highest concentration of *p*-nonylphenol ($3.4 \mu g/L$; tables 11, 12). In addition, the highest concentration of NPEO2 ($14 \mu g/L$) in stormflow samples from upstream sites was measured at a SOU site. An upstream stormflow sample from the SOU watershed also contained the highest OPEO1 concentration ($1.0 \mu g/L$) measured among upstream stormflow samples collected during the study period.

Except for TBEP, the 75th percentile concentrations of all flame-retardant compounds were below SRLs in upstream stormflow samples from the PEA and PRO watersheds; however, the 75th percentile concentrations of all flame-retardant compounds exceeded SRLs in stormflow samples from upstream SOU sites (table 12). The 75th percentile TBEP concentration in upstream stormflow samples from the PEA watershed was similar to the concentration in stormflow samples from upstream SOU sites and among base-flow samples from all sites in the SOU watershed, but 0.3 to 0.7 μ g/L higher than in all samples from the control

basins and in base-flow samples from upstream PEA and PRO sites (tables 11, 12). Among stormflow samples from controlbasin and upstream sites, the highest concentrations of TBP ($2.1 \mu g/L$), TBEP ($20 \mu g/L$), and TDCPP ($0.77 \mu g/L$) were measured at upstream SOU sites.

Relations Among OWICs and Selected Water-Quality Constituents and Properties

A principal components analysis (PCA) of 15 waterquality properties and chemical and bacterial constituents in stormflow samples collected from upstream sites in the INT, PEA, PRO, and SOU watersheds revealed six components that explained about 77 percent of the total variability in the data; however, only four were considered principal components (table 17). The PC1 explains about 46 percent of the variability in upstream stormflow samples. This component shows high loadings (greater than 0.7) and strong associations (loadings with similar magnitudes) among zinc, manganese, nickel, copper, aluminum, lead, and cadmium (typically the trace metals common in urban areas), and specific conductance. Notably lacking in PC1 is an association with turbidity, because stormflow typically has high turbidity. The loadings on PC1 indicate that specific conductance tended to be elevated when trace metals were elevated. Typically, storm runoff causes a decrease in specific conductance. Therefore, PC1 appears to describe elevated major-ion and trace-metal concentrations in urban storm runoff, perhaps from industrial areas or over-flowing sanitary sewers.

The PC2, PC3, and fourth (PC4) principal components explain 14, 9, and 5 percent, respectively, of the total variability in upstream stormflow samples (table 17). The PC2 shows a high negative loading with acid-neutralizing capacity and moderate (between 0.5 and 0.7), inverse associations with turbidity and specific conductance. The PC3 indicates a high loading with the number of human-associated OWICs and a moderate loading with the number of urban-runoff related OWICs. The PC4 component has a moderate loading with *E. coli* density.

An agglomerative hierarchical cluster analysis produced 10 clusters using the ranks of the principal component scores for PC1, PC2, PC3, and PC4. The cluster analysis indicated three general groups of samples: (1) samples that scored high on PC1 and PC3 indicating elevated trace metal concentrations and urban-runoff related OWICs, (2) samples that did not score high on PC1, but scored high on PC2, and (3) samples that scored high on PC3 and PC4, indicating elevated human-related OWICs and *E. coli* densities. Stormflow samples from three sites (PRO-3, LUL-1, and INT-synoptic) representing four storms scored high on PC3 and PC4, indicating possible sewage contamination. In these samples, the number of human-related OWICs ranged from 10 to 16, with a median of 14, and *E. coli* densities ranged from 37,000 to 172,000 MPN/100 mL, with a median of 77,000 MPN/100 mL.

Table 17. Results of a principal components analysis on 15 parameters associated with stormflow samples collected at sites upstream from combined sewer overflow outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.

[PC, principal component, which is a group of correlated parameters whose variance explains some proportion of the data variability in a dataset; loading, a value indicating how important the variability of a parameter is to the total variance of the component, analogous to a correlation coefficient; ft^3 /s, cubic feet per second; FNU, formazin nephelometric unit; MPN per 100 mL, most probable number per 100 milliliters; SC, specific conductance at 25 degrees Celsius; μ S/cm, microsiemens per centimeter; mg/L, milligram per liter; μ g/L, microgram per liter; OWICs, organic wastewater-indicator compounds; —, not significant, loading less than 0.400]

Devemeter	Pri	Communality			
rarameter —	PC1	PC2	PC3	PC4	— communanty"
Turbidity (FNU)		0.530			0.439
Escherichia coli density (MPN per 100 mL)	—	—	—	0.678	.648
Field SC (µS/cm)	0.725	592	_		.988
Acid-neutralizing capacity (mg/L)	—	796	—	—	.710
Chloride (mg/L)	.508	660	_		.721
Aluminum (µg/L)	.902	_	_	—	.922
Cadmium (µg/L)	.840	_	—	—	.796
Copper (µg/L)	.929	_	_	—	.928
Lead (µg/L)	.886	_	—	_	.922
Manganese (µg/L)	.963	—	—	—	.971
Nickel (µg/L)	.961	_	—	_	.953
Zinc (µg/L)	.983	_	—	_	.994
Number of human-associated OWICs per sample ^b	—	—	.752	—	.640
Number of urban-runoff OWICs per sample ^c	—	.454	.513	422	.674
Number of pesticides detected per sample	—	—	_	—	.223
Proportion of variance explained by component	.459	.141	.088	.051	
Cumulative variance for each added component ^d	.459	.600	.688	.739	

^a Communality is a measure of a parameter's importance in explaining the variability in the dataset. The higher the number, the greater the importance.

^b Sum of personal-use, sterol, and nonionic detergent compounds per sample.

^e Sum of polycyclic aromatic hydrocarbon, industrial-use, automotive-use, and flame retardant compounds per sample.

^d Total variance explained by six components is 0.769.

OWICs at Sites Downstream from Combined Sewer Overflow Outfalls

Fourteen sites in the INT, PEA, PRO, and SOU watersheds were downstream from CSO outfalls and commonly were affected by CSOs during moderate to large storms during the study period. The variations in the distribution of OWICs in downstream samples by season and by flow event were markedly different from the variations in control-basin and upstream samples. In water samples from downstream sites, the OWICs detected in the highest and lowest percentage of samples was similar to the pattern for all samples collected during the study period (fig. 5*B*).

Seasonal Variation

Typically, seasonal differences in the percentage of cool- and warm-season samples containing OWICs at downstream sites, collectively, were similar to the seasonal pattern observed for all samples collected during the study period (fig. 8, table 18). Nevertheless, when the seasonal pattern of OWICs detected in downstream samples is considered for the individual INT, PEA, PRO, and SOU watersheds, those patterns typically differed from the seasonal pattern of OWICs detected among all samples collected during the study. The personal-use, disinfection, pesticide, sterol, and industrial-use classes were detected with similar frequency in cool-and warm-season samples from downstream sites. The PAH and automotive-use classes were detected more frequently in coolseason samples, while the NDMCs and flame-retardant classes were detected in slightly more warm-season samples.

Seven personal-use compounds were detected in a greater percentage of cool-season samples from both downstream and upstream sites than from control-basin sites; only AHTN, camphor, isoborneol, and triethyl citrate were detected with similar frequency in cool-season samples from control-basin and downstream sites (tables 13, 15, 18). The percentage of downstream INT samples from both seasons that contained detectable personal-use compounds was markedly higher than the percentage of samples from the PEA, PRO, and SOU sites. In cool-season samples, 11 personal-use compounds were detected with greater frequency at downstream INT sites than at downstream PEA, PRO, and SOU sites; however, caffeine camphor, and menthol were detected with similar or slightly higher percentages of cool-season samples from downstream SOU than INT sites. The personal-use compounds were detected with the lowest frequency in cool-season samples from downstream PEA sites; however, four compounds were detected with greater frequency in cool-season samples from downstream than upstream PEA sites and three (benzophenone, camphor, and isoborneol) were detected in a greater percentage of upstream PEA samples (tables 15, 18). In coolseason samples, nine personal-use compounds were detected with greater frequency at downstream than at upstream PRO sites; however, HHCB and triclosan were detected in a greater

percentage of cool-season samples from upstream PRO sites. Among SOU sites, 11 personal-use compounds were detected with greater frequency in cool-season samples from upstream than from downstream sites; moreover, caffeine, camphor, and methyl salicylate were detected with similar frequency in coolseason samples from upstream and downstream SOU sites.

Typically, personal-use compounds were detected with greater frequency in warm-season samples from downstream sites than from control-basin or upstream sites (tables 13, 15, 18). Nine of 14 compounds were detected with greater frequency in warm-season samples from downstream than upstream sites, while 5 compounds were detected with similar frequency. Seven personal-use compounds were detected with greater frequency in warm-season samples from downstream INT than all PEA and SOU sites, and downstream PRO sites. In the PEA watershed, camphor, indole, menthol, and DEET were detected in a greater percentage of warm-season samples from upstream than downstream sites (tables 15, 18). Conversely, the other 10 compounds were detected in a similar percentage of warm-season samples from downstream and upstream PEA sites. In the PRO watershed, only caffeine was detected in a greater percentage of warm-season samples from downstream than upstream sites; however, benzophenone, HHCB, indole, and triethyl citrate were detected with greater frequency at upstream sites during the warm season. Conversely, the other 10 personal-use compounds were detected in a similar percentage of warm-season samples from downstream and upstream PRO sites. In the SOU watershed, eight personal-use compounds were detected in a greater percentage of warm-season samples from downstream than upstream sites; however, indole, triclosan, and triethyl citrate were detected with greater frequency at upstream sites.

Except for bromacil, the seasonal distribution of pesticides in downstream samples, collectively, was similar to the seasonal distribution observed among all samples collected during the study period (fig. 8, table 18). During both seasons, bromacil was detected with greater frequency at upstream than control-basin and downstream sites; 14DCB was detected with the greatest frequency at downstream sites. In addition, 14DCB was detected in a greater percentage of warm-season samples from downstream INT and SOU sites, contrary to the similar detection frequency during both seasons for all samples collected in the study. In the PEA watershed, carbaryl was detected with similar frequency in cool-season samples from upstream and downstream sites, but with greater frequency in warm-season samples from downstream sites. In the PRO and SOU watersheds, carbaryl was detected with similar frequency in warm-season samples from upstream and downstream sites, but a slightly greater percentage of cool-season samples contained carbaryl at downstream PRO and SOU sites. Carbaryl was detected in a markedly higher frequency in cool- and warm-season samples from downstream SOU than PRO sites. Typically, diazinon was detected with similar frequency at all sites during both seasons; however, warm-season samples from upstream PRO sites

contained diazinon in a slightly greater percentage than in cool- and warm-season samples from the INT, PEA, and SOU sites. Prometon was detected with similar frequency in warm-season samples from downstream INT, PEA, and SOU sites; however, in the SOU watershed, prometon was detected in a slightly greater percentage of samples from upstream sites during both seasons.

The seasonal distribution of the sterol compounds in downstream samples mirrored the seasonal pattern among all samples collected during the study (fig. 8, table 18). In addition, the sterols collectively were detected in a greater percentage of samples from downstream than upstream and control-basin sites during both seasons (tables 13, 15, 18). Cholesterol, coprostanol, and stigmastanol were detected with greater frequency in samples from downstream INT sites than from downstream PEA, PRO, and SOU sites during both seasons. The sterols were detected with similar frequency in downstream PEA samples during both seasons, but in a greater percentage of cool-season samples from downstream than upstream PEA sites. Furthermore, coprostanol was detected with similar frequency in downstream PEA and SOU samples during both seasons, and sitosterol in slightly more cool- than warm-season samples from downstream PEA sites, in contrast to the seasonal pattern among all samples during the study.

Among all samples collected during the study, the industrial-use compounds were detected with similar frequency during both seasons (fig. 8), and the detection frequencies for anthraquinone, bisphenol-A, carbazole, and TPP in downstream samples mirror that pattern (table 18). During the cool-season, anthraquinone, bisphenol-A, d-limonene, and TPP were detected in a similar percentage of samples from downstream, upstream, and control-basin sites (tables 13, 15, 18). In addition, a greater percentage of cool-season samples from downstream than upstream sites contained carbazole, while a greater percentage of cool-season samples from upstream sites contained PCE than either downstream or control-basin sites. Among downstream sites, d-limonene and PCE were detected in slightly greater percentages of cool- than warm-season samples. Nevertheless, PCE was detected with similar frequency in samples collected from downstream INT and PRO sites during both seasons, with greater frequency in cool-season samples from downstream PEA sites, and with greater frequency in warm-season samples from downstream SOU sites.

The seasonal distribution of PAHs in downstream samples differed substantially from the pattern seen among all samples collected during the study (fig. 8, table 18). During both seasons, anthracene was detected with similar frequency at all sites (tables 13, 15, 18). During the cool-season, fluoranthene and phenanthrene were detected with similar frequency at downstream and control-basin sites, but at twice the frequency for upstream sites. A similar percentage of cool-season samples from downstream and upstream sites contained *p*-cresol, but PCP was detected in a smaller percentage of cool-season samples from downstream sites than from control-basin sites. The compounds *p*-cresol, fluoranthene, and phenanthrene were detected with the greatest frequency in cool-season samples from downstream PRO sites. During the warm season, the PAHs typically were detected in a smaller percentage of samples from downstream than upstream or control-basin sites. Among downstream sites, a greater percentage of warm-season samples from the INT than PEA, PRO or SOU watersheds contained *p*-cresol and phenanthrene; whereas, PCP was detected with the greatest frequency in warm-season samples from downstream SOU sites (table 18).

Except for 2,6-dimethylnaphthalene, the seasonal distribution of automotive-use compounds in downstream samples, collectively, was similar to the distribution for all samples in the study and control-basin samples (table 18, fig. 8). The compound 2,6-dimethylnaphthalene was detected with greater frequency in cool- than warm-season samples from downstream sites, contrary to the similar distribution in both seasons for all samples and control-basin samples (tables 13, 15, 18). During the cool-season, the automotive-use compounds typically were detected with greater frequency in downstream samples than upstream or control-basin samples. During the warm season, however, the automotive-use compounds were detected in similar percentage of samples from downstream, upstream, and control-basin sites. A greater percentage of cool-season samples from downstream PRO sites contained naphthalene and the three methylnaphthalene compounds than did downstream samples from the INT, PEA, and SOU sites (table 18). The corrosion-inhibitor 5-methyl-1H-benzotriazole was detected with the greatest frequency in warm-season samples from downstream SOU sites, followed by cool- and warm-season samples from downstream PEA sites. The automotive-use compounds tended to be detected with greater frequency in cool-season samples from upstream SOU than downstream SOU sites, but with greater frequency in warm-season samples from downstream SOU sites.

Except for 4-tert-octylphenol, the seasonal distribution of NDMCs detected in downstream samples mirrored the seasonal distribution seen among all samples collected during the study period (fig. 8; table 18). During the cool season, p-nonylphenol, OPEO1, and 4-tert-octylphenol were detected with greater frequency in downstream than in upstream or control-basin samples (tables 13, 15, 18). In addition, NPEO2 and OPEO2 were detected with similar frequency in cool-season samples from downstream and upstream sites. Except for 4-tert-octylphenol, the NDMCs were detected with greater frequency in cool-season samples from downstream INT than from downstream PEA and PRO sites (table 18). The NDMCs were detected with the lowest frequency in cool-season samples from downstream PEA sites, and except for *p*-nonylphenol, with similar frequency in cool-season samples from upstream PEA sites (tables 15, 18). Furthermore, cool-season samples from downstream sites in the PEA watershed contained *p*-nonylphenol at a greater frequency than in samples from upstream sites.

86 Occurrence of Organic Wastewater-Indicator Compounds in Urban Streams of the Atlanta Area, Georgia, 2003–2006

Table 18. Detection frequencies by season for individual organic wastewater-indicator compounds in water samples at sites downstream from combined sewer overflow outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.

[INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek; SOU, South River; Cool, cool season (October–April); Warm, warm season (April–October); —, not detected above study detection levels]

	Detection frequency (percent)										
Compound	Alls	sites	11	NT	P	EA	P	RO	SC	U	
	Cool	Warm	Cool	Warm	Cool	Warm	Cool	Warm	Cool	Warm	
Number of samples	147	173	17	28	50	63	58	52	22	30	
Personal-use compounds											
AHTN, tonalide	14	15	29	25	8.0	1.6	14	23	18	20	
Acetophenone	8.2	15	18	32		7.9	12	15	9.1	10	
Benzophenone	7.5	18	35	54	2.0	4.8	5.2	15	4.5	17	
Caffeine	75	61	88	89	76	60	66	44	86	67	
Camphor	35	24	41	43	20	11	43	25	46	33	
Cotinine	25	25	53	36	14.0	6.3	24	31	27	43	
HHCB, galaxolide	21	26	59	54	2.0	1.6	31	42	9.1	23	
Indole	22	20	41	21	8.0	6.3	29	39	18	17	
Isoborneol	2.7	2.9	12	_	_	_	3.4	5.8	0.0	6.7	
Menthol	44	32	59	43	20	19	53	39	64	40	
Methyl salicylate	10	16	12	29	6.0	6.3	8.6	21	23	17	
DEET	4.1	45	29	79	2.0	24	_	44	_	57	
Triclosan	25	26	53	36	4.0	7.9	36	46	18	20	
Triethyl citrate	6.8	10	18	18	4.0	3.2	5.2	15	9.1	6.7	
Class percentage ^a	20	21	39	40	12	11	20	18	24	27	
	Disinfection compounds										
Bromoform	5.4	2.9	18	11	4.0	_	—	—	14	6.7	
			Pe	sticide com	pounds						
1,4-Dichlorobenzene (14DCB)	34	23	41	61	16	7.9	59	21	4.5	20	
Bromacil	52	46	29	14	22	32	79	77	68	53	
Carbaryl	13	37	—	61	16	44	6.9	19	32	30	
Chlorpyrifos			_	_	_	—	1.7	1.9	_	—	
Diazinon	4.1	5.8	_	_	8.0	3.2	1.7	9.6	4.5	10	
Prometon		13	_	18	_	18	—	_	4.5	20	
Class percentage	16	20	12	26	10	17	21	18	19	22	
			5	Sterol comp	ounds						
Cholesterol	56	63	65	75	50	51	60	71	50	63	
3-β-Coprostanol	44	40	77	57	30	30	50	44	36	37	
β-sitosterol	25	33	24	46	28	22	21	39	27	33	
β-stigmastanol	16	23	29	32	16	19	10	19	23	27	
Class percentage	33	36	48	53	31	30	29	31	34	40	
			Indu	strial-use c	ompounds						
Anthraquinone	5.4	5.2	29	7.1	2.0	6.3	3.4	5.8			
Bisphenol-A	6.1	8.1	5.9	11	12	3.2	3.4	7.7	—	17	
Carbazole	22	20	24	18	28	22	16	12	27	33	

Table 18.Detection frequencies by season for individual organic wastewater-indicator compounds in water samples at sitesdownstream from combined sewer overflow outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South Riverwatersheds near Atlanta, GA, March 2003 to January 2006.—Continued

[INT, Intrenchment Creek; PEA, Peachtree Creek; PRO, Proctor Creek; SOU, South River; Cool, cool season (October–April); Warm, warm season (April–October); —, not detected above study detection levels]

	Detection frequency (percent)									
Compound	All s	sites	II	IT	P	EA	P	PRO SOU		
-	Cool	Warm	Cool	Warm	Cool	Warm	Cool	Warm	Cool	Warm
Industrial-use compounds—Continued										
<i>d</i> -Limonene	23	16	24	14	10	11	31	21	32	20
Tetrachloroethene (PCE)	25	20	12	11	16	4.8	43	46	9.1	17
Triphenyl phosphate (TPP)	10	14	29	25	2.0	3.2	12	17	4.5	20
Class percentage	14	12	20	14	12	8.5	14	11	12	18
		P	olycyclic ai	romatic hyd	Irocarbons	(PAHs)				
Anthracene	—	3.5	—	—	—	—	1.7	12	—	—
p-Cresol	39	15	53	43	10	—	57	15	46	17
Fluoranthene	23	15	5.9	11	20	11	31	17	23	20
Pentachlorophenol (PCP)	9.5	12	—	14	14	7.9	8.6	10	9.1	23
Phenanthrene	27	16	29	39	18	3.2	40	12	14	27
Pyrene	16	10	5.9	3.6	4.0	7.9	28	14	18	17
Class percentage	19	11	16	18	11	5.0	26	11	18	17
Automotive-use compounds										
1-Methylnaphthalene	22	9.8	12	32	6.0	—	40	—	23	27
2-Methylnaphthalene	25	10	18	36	8.0	1.6	41	—	23	23
2,6-Dimethylnaphthalene	13	5.8	—	21	6.0	—	22	—	14	13
5-Methyl-1H-benzotriazole	7.5	9.2	—	3.6	10	11	8.6	5.8	4.5	17
Isopropylbenzene	1.4	_	_	_	2.0	—	1.7	—	—	_
Naphthalene	40	17	29	46	22	3.2	59	9.6	36	33
Class percentage	18	8.5	9.8	23	9.0	2.6	28	1.6	17	19
		Ν	onionic de	tergent met	abolites (N	DMCs)				
p-Nonylphenol (total)	46	51	77	75	38	37	33	40	77	77
4-Nonylphenol dieth- oxylate (NPEO2)	37	46	77	79	26	25	26	40	59	70
4-Octylphenol mono- ethoxylate (OPEO1)	18	21	24	29	18	9.5	19	25	14	30
4-Octylphenol diethoxylate (OPEO2)	25	44	53	57	16	30	21	48	32	53
4-tert-Octylphenol	31	26	24	18	10	11	53	44	23	33
Class percentage	30	35	51	51	22	23	28	32	41	53
			Flame	-retardant	compounds	;				
Tributyl phosphate (TBP)	30	30	88	89	18	9.5	22	19	32	37
Tris(2-butoxyethyl) phosphate (TBEP)	86	89	100	100	74	89	88	79	100	97
Tris(2-chloroethyl) phosphate (TCEP)	62	78	94	93	50	76	53	65	86	90
Tris(dichloroisopropyl) phosphate (TDCPP)	52	68	88	89	46	65	31	50	91	83
Class percentage	56	61	93	93	47	60	44	37	77	77

^a Weighted value based on the percentage of compounds detected within its associated compound class.

The percentages of samples containing *p*-nonylphenol and NPEO2 were similar during both seasons at downstream INT and PEA sites; *p*-nonylphenol was detected with similar frequency during both seasons at downstream SOU sites (table 18). The percentage of samples containing all five NDMCs was similar in downstream and upstream PEA samples during both seasons (tables 15, 18). In the PRO watershed, a greater percentage of warm-season samples from downstream than upstream sites contained OPEO1 and 4-*tert*-octylphenol. In addition, all five NDMCs were detected with greater frequency in warm-season samples from downstream than upstream SOU sites.

Among all samples collected during the study, the flame retardants TDCPP, TCEP, and TBEP were detected in greater percentages of warm- than cool-season samples; TBP was detected with similar frequency during both seasons (fig. 8). This seasonal pattern was notably different from the seasonal pattern for TBP and TBEP detected in downstream samples (table 18). At downstream INT and SOU sites, TBP, TBEP, and TCEP were detected with similar frequency in samples from both seasons. In addition, TDCPP was detected with similar frequency in downstream INT samples, but at a greater frequency in cool-season samples from downstream SOU sites. Except for TBP and TBEP, downstream PEA samples mirrored the seasonal pattern for all samples. At downstream PEA sites, TBP and were detected with greater frequency in cool-season samples, while TBEP, TCEP, TDCPP were detected with greater frequency in warm-season samples.

During the cool season, all four flame retardants were detected with greater frequency in samples from downstream than upstream or control-basin sites (tables 13, 15, 18). In the PEA watershed, TBEP and TDCPP were detected with greater frequency in cool-season samples from downstream sites, TBP with greater frequency in cool- and warm-season samples from upstream sites, and TCEP with similar frequencies in samples from upstream and downstream sites. Among warm-season samples from the PEA watershed, TBEP, TCEP, and TDCPP were detected with greater frequency at downstream than at upstream sites. In the PRO watershed, all flame retardants were detected with greater frequency in cool-season samples from downstream than from upstream sites; however, during the warm season only TBEP was detected with greater frequency at downstream than upstream PRO sites. In the SOU watershed, TBP was detected with greater frequency in cool-season samples from upstream sites, TBEP with greater frequency in cool-season samples from downstream sites, and TCEP and TDCPP with similar frequency in samples from downstream and upstream sites. Among warm-season samples from the SOU watershed, all but TDCPP were detected with greater frequency at downstream than upstream sites; TDCPP was detected with similar frequency in warm-season samples from downstream and upstream SOU sites.

Variation During Base Flow

The median numbers of OWICs per sample in downstream base-flow samples (6-16) were statistically different among the INT, PEA, PRO, and SOU watersheds (p-value less than 0.05; fig. 9). Among downstream base-flow samples, median number of OWICs per sample from the INT watershed was statistically higher than the medians in samples from the PEA, PRO, and SOU sites, and control-basin sites. The median number of OWICs per sample in downstream base-flow samples from the SOU watershed was statistically higher than the medians for base-flow and stormflow samples from control-basin sites, base-flow samples from upstream and downstream PEA sites, base-flow samples from upstream and downstream PRO sites (p-value less than 0.05), but statistically similar to the medians in upstream base-flow samples from SOU sites, and upstream stormflow samples from the PEA watershed (p-value greater than 0.05). Among downstream sites in the PEA watershed, the median number of OWICs per sample in base-flow samples was statistically similar to the medians for base-flow samples from the control basins and for upstream base-flow samples from the PEA watershed (p-value less than 0.05). The median number of OWICs per sample in downstream base-flow samples from the PRO watershed was statistically higher than the median number for base-flow samples from the control-basin sites, and from upstream and downstream PEA sites, but was statistically similar to the median numbers for stormflow samples from the control basins and downstream PEA sites (p-value greater than 0.05).

The OWIC classes ranked from the highest to the lowest detection frequencies in downstream base-flow samples are the flame retardant (53 percent), sterol (35 percent), NDMCs (30 percent), pesticide (15 percent), personal-use (14 percent), industrial-use (8.3 percent), PAH (7.3 percent), and automotive-use compounds (6.3 percent; table 9). Typically, a greater percentage of base-flow than stormflow samples from downstream sites contained bromacil, triclosan, indole, HHCB, AHTN, and PCE (fig. 17). The personal-use, bromoform, sterol, NDMCs, and flame-retardant compounds were detected in a greater percentage of base-flow samples from downstream INT than PEA, PRO, or SOU sites. Pesticides were detected with similar frequency in base-flow samples from downstream INT and PEA sites, but with the greatest frequency in downstream PRO and SOU sites. Compounds from all nine OWIC classes were detected with the lowest frequency in base-flow samples from downstream PEA sites. Except for the sterol, PAH, and flame-retardant compounds, OWICs were detected with similar frequency in base-flow samples from downstream PRO and SOU sites. The sterol and PAH compounds were detected in greater percentages of baseflow samples from downstream PRO than SOU sites; however, a greater percentage of flame-retardant compounds were detected in base-flow samples from downstream SOU than PRO sites. The industrial-use and automotive-use compounds were detected with similar frequency in base-flow samples from all downstream sites.





Twenty-six OWICs were detected in 5–40 percent more base-flow samples from downstream sites than from the control-basin sites and 26 OWICs were detected with similar frequency at those sites (fig. 18*A*). All of the sterol, NDMCs, and flame-retardant compounds were detected in 12–40 percent more base-flow samples from downstream than control-basin sites. Among the personal-use compounds, caffeine, cotinine, menthol, DEET, indole, triclosan, HHCB, and acetophenone were detected in a greater percentage of base-flow samples from downstream than control-basin sites. In addition, bromacil, 14DCB, *p*-cresol, and 5-methyl-1Hbenzotriazole were detected with greater frequency in baseflow samples from downstream than control-basin sites.

In addition, 15 compounds were detected in 5–22 percent more base-flow samples from downstream sites than from upstream sites (fig. 19*A*); however, PCE, bromoform, camphor, *p*-cresol, and triethyl citrate were detected in more base-flow samples from upstream sites. Thirty-two compounds were detected with similar frequency in base-flow samples from downstream and upstream sites. A greater percentage of downstream than upstream samples contained all four sterol, four of the five NDMCs, and all four flame-retardant compounds. Moreover, among the personal-use and pesticide compounds, only caffeine, cotinine, triclosan, and 14DCB were detected with greater frequency in base-flow samples from downstream than upstream sites.

The 75th percentile concentrations of only eight compounds exceeded SRLs in base-flow samples from downstream sites (table 11). The 75th percentile concentrations for caffeine, bromacil, cholesterol, and TBEP exceeded SRLs in all downstream base-flow samples from the INT, PEA, PRO, and SOU watersheds. Except for bromacil, the 75th percentile concentrations for caffeine, cholesterol, and TBP were highest from the INT watershed. The 75th percentile cholesterol concentration in the SOU samples $(1.3 \mu g/L)$ was slightly lower than the concentration in the INT samples $(2.0 \ \mu g/L)$ and in upstream stormflow samples from the SOU watershed $(1.6 \mu g/L; tables 11, 12)$. The 75th percentile concentration for bromacil was highest in base-flow samples from downstream PRO and SOU sites. Downstream base-flow samples from the INT watershed contained DEET, coprostanol, and TBP at 75th percentile concentrations that exceeded SRLs. In addition, downstream base-flow samples from the INT and SOU watersheds contained NPEO2 at similar 75th percentile concentrations that exceeded the SRL.

Among base-flow and stormflow samples from the control basins and downstream sites, the highest acetophenone, HHCB, isoborneol, menthol, methyl salicylate, and triclosan concentrations were measured in base-flow samples from downstream PRO sites (tables 11, 12); the highest caffeine concentration (10 μ g/L) was measured in a base-flow sample from an INT and PRO site, and the highest cotinine concentration (0.63 μ g/L) was measured in a base-flow sample from a downstream INT site. Buerge and others (2006) showed that average caffeine concentrations in untreated

wastewater ranged from 7.0 to 7.3 μ g/L with a maximum of 11 μ g/L. The highest concentration of DEET (6.0 μ g/L) measured during the study period was in a downstream base-flow sample from the INT watershed.

Among all samples from the control basins and downstream base-flow samples, the highest concentration of 14DCB (0.63 µg/L) was measured in a sample from the PRO watershed (tables 11, 12). A downstream base-flow sample from the PRO watershed had concentrations of bromacil ($8.7 \mu g/L$) and carbaryl (0.78 µg/L) that were the highest measured among base-flow samples from the control basins and from downstream sites. This bromacil concentration also was the highest among stormflow samples from the control basins, and the carbaryl concentration also was the highest among upstream base-flow samples. Among base-flow samples from controlbasin and downstream sites, a base-flow sample collected at PRO-2 contained the highest concentrations of cholesterol (7.5 µg/L), coprostanol (3.8 µg/L), and sitosterol (3.8 µg/L), and the highest stigmastanol (4.1 µg/L).

The 75th percentile concentrations for all industrialuse, PAH, and automotive-use compounds in downstream base-flow samples were below the SRL (table 11). Among downstream base-flow samples, those from the INT watershed contained the highest concentration of triphenyl phosphate $(0.26 \,\mu\text{g/L})$, those from the PRO watershed contained the highest concentrations of anthraquinone (0.68 μ g/L), d-limonene (0.43 μ g/L), p-cresol (2.4 μ g/L), fluoranthene $(0.40 \ \mu g/L)$, PCP $(3.6 \ \mu g/L)$, phenanthrene $(0.29 \ \mu g/L)$, pyrene $(0.50 \ \mu g/L)$, 1-methylnaphthalene $(0.41 \ \mu g/L)$, 2-methylnaphthalene (0.60 μ g/L), 5-methyl-1H-benzotriazole (1.1 μ g/L), and naphthalene (0.79 μ g/L). The highest PCE concentration $(8.0 \ \mu g/L)$ measured during the study was detected in a downstream base-flow sample from the SOU watershed. Among all samples from control-basin and downstream sites, a downstream base-flow sample from the PEA watershed contained the highest bisphenol-A concentration (1.7 μ g/L).

Except for NPEO2, TBP, and TBEP, the 75th percentile concentrations for the NDMCs and flame-retardant compounds in downstream base-flow samples were below the SRL (table 11). The 75th percentile concentrations for NPEO2 were similar in base-flow samples from downstream INT and SOU sites, but below the SRL in base-flow samples from downstream PEA and PRO sites. The 75th percentile concentrations for TBEP were highest in base-flow samples from downstream INT samples (2.4 µg/L) and lowest from downstream PEA samples (0.48 µg/L). Among all samples collected during the study, the highest concentrations of OPEO1 (2.5 µg/L), OPEO2 $(0.68 \mu g/L)$, and TBEP (70 $\mu g/L$) were measured in downstream base-flow samples from the PRO watershed. Among base-flow samples from control-basin and downstream sites and stormflow samples from upstream and downstream sites, a downstream base-flow sample from the INT and PRO watersheds contained the highest concentration of NPEO2 (18 µg/L). Except for downstream stormflow samples, the highest 4-tert-octylphenol concentration (0.56 μ g/L) was measured in a downstream



of combined sewer overflow (CSO) outfalls and control-basin sites near Atlanta, GA, in (A) base-flow samples and (B) stormflow samples, March 2003 to January 2006.



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base-flow sample from the PRO watershed. In addition, the highest *p*-nonylphenol concentration (3.6 μ g/L) among base-flow samples from control-basin and downstream sites and upstream stormflow samples was measured in a downstream base-flow sample from the SOU watershed.

Among the samples collected from upstream sites, stormflow samples from control-basin sites, and downstream base-flow samples, the highest TBP concentration $(2.9 \ \mu g/L)$ was measured in a base-flow sample from a downstream INT (tables 11, 12). Among the samples collected from control-basin sites and downstream base-flow samples, the highest TCEP concentration $(0.52 \ \mu g/L)$ was measured in a downstream base-flow sample from the INT watershed, and the highest TDCPP concentration $(0.37 \ \mu g/L)$ was measured in a downstream base-flow sample from the SOU watershed.

Relations Among OWICs and Select Water-Quality Parameters and Constituents

A PCA of base-flow samples collected at downstream sites in the INT, PEA, PRO, and SOU watersheds revealed that six components explained about 69 percent of the total variability in 15 chemical and bacterial constituents, and water-quality properties (table 19). About 64 percent of the total variability was explained by five principal components. The PC1 explains about 17 percent of the variability in these samples. This component has high loadings (greater than 0.7) and strong associations (loadings with similar magnitudes) with specific conductance and ANC, indicating an association with major ions in the data. The PC1 appears to describe the affect of groundwater chemistry on the chemistry of base flow because groundwater tends to have higher concentrations of major ions. The PC2 explains about 13 percent of the variability in downstream base-flow samples. This component has high loadings and strong associations with nickel and zinc concentrations and indicates a source (perhaps dry-weather runoff) of nickel and zinc to these streams. The PC3 explains about 12 percent of the total variability and has a high loading with the number of urban runoff-related OWICs per sample and a moderate (0.5-0.7) loading with turbidity and the number of human-related OWICs per sample. The PC4 explains about 12 percent of the total variability and has high loadings with copper and cadmium. The fifth principal component (PC5) explains about 10 percent of the total variability and has high loadings with aluminum and manganese. The E. coli density is notably absent as an important parameter among these principal components, even though E. coli densities as high as 242,000 MPN/100 mL have been measured in some downstream base-flow samples.

An agglomerative hierarchical cluster analysis produced eight clusters using the ranks of the principal component scores for PC1, PC2, PC3, PC4, and PC5. One cluster consisted of samples from INT-1, PRO-1, and PRO-2 that scored high on PC3 and in some cases PC1. These samples also contained *E. coli* densities that ranged from 1 to 24,000 MPN/100 mL. Because about 50 percent of *E. coli* densities in these samples are less than about 800 MPN/100 mL and sampling sites are downstream from CSO outfalls, CSO treatment facilities may have discharged chlorinated effluent to Intrenchment and Proctor Creeks. The cluster analysis also indicated that various sources of trace metals entered Intrenchment and Proctor Creeks, and, especially, the South River downstream from CSO outfalls during base flow.

Variation During Stormflow

The median numbers of OWICs per sample detected in downstream stormflow samples ranged from 10 in the PEA watershed to 19 in the INT and SOU watersheds (fig. 9). The median numbers of OWICs per sample were statistically similar among base-flow and stormflow samples from downstream sites in the INT, upstream and downstream stormflow samples from the PRO and SOU watersheds (*p*-value greater than 0.05); however, median numbers of OWICs per sample in these samples were statistically higher than those in base-flow and stormflow samples from the control basins and from upstream and downstream sites in the PEA watershed, in base-flow samples from upstream and downstream sites in the PRO watershed, and base-flow samples from all SOU sites.

Twenty-eight compounds from seven of the nine OWIC classes were detected in 5–39 percent more stormflow than base-flow samples from downstream sites, and 18 compounds were detected with similar frequency in base-flow and storm-flow samples (fig. 17). The most frequently detected OWIC classes in downstream stormflow samples were the flame retardants (66 percent), the non-ionic detergents (36 percent), and the sterols (34 percent; table 10).

Thirty-four compounds were detected in 5-43 percent more stormflow samples from downstream than control-basin sites, and 17 compounds were detected with similar frequency in stormflow samples from downstream and control-basin sites (fig. 18B). Only PCP was detected in more stormflow samples from control-basin than downstream sites. In addition, 18 compounds were detected with greater frequency in stormflow samples from downstream than upstream sites (fig. 19B). These compounds include the personal-use compounds menthol, cotinine, caffeine, and benzophenone; the pesticides 14DCB and prometon; coprostanol; four of the six automotive-use compounds; the PAHs phenanthrene and *p*-cresol; three of the five non-ionic detergent metabolites; and the flame retardants TBP and TDCPP. In contrast, all of the industrial-use compounds, PCP, bromacil, triclosan, and cholesterol were detected with greater frequency in stormflow samples from upstream than downstream sites.

Typically, the sterol compounds were detected with similar frequency in base-flow and stormflow samples from downstream sites (tables 9, 10). In contrast, the personal-use and pesticides were detected in slightly greater percentages, while the industrial-use, PAHs, automotive-use, NDMCs, and flame retardants were detected in substantially higher percentages of stormflow than base-flow samples from downstream sites. Among stormflow samples, the personal-use, pesticide, sterol, Table 19.Results of a principal components analysis on 15 parameters associated with base-flow samples collected at sitesdownstream from combined sewer overflow outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South Riverwatersheds near Atlanta, GA, March 2003 to January 2006.

[PC, principal component, which is a group of correlated parameters whose variance explains some proportion of the data variability in a dataset; loading, a value indicating how important the variability of a parameter is to the total variance of the component, analogous to a correlation coefficient; ft^3 /s, cubic feet per second; FNU, formazin nephelometric unit; MPN per 100 mL, most probable number per 100 milliliters; SC, specific conductance at 25 degrees Celsius; μ S/cm, microsiemens per centimeter; mg/L, milligram per liter; μ g/L, microgram per liter; OWICs, organic wastewater-indicator compounds; —, not significant, loading less than 0.400]

Devenueten		0				
Farameter —	PC1	PC2	PC3	PC4	PC5	— communanty ^a
Turbidity (FNU)	—	—	0.694	—	—	0.524
Escherichia coli density (MPN per 100 mL)	—		_	—	—	.147
Field SC (µS/cm)	0.938	_		_	_	.934
Acid-neutralizing capacity (mg/L)	.831	—	—	—	—	.842
Chloride (mg/L)	.691	—		—	_	.600
Aluminum (µg/L)	_	—		—	0.859	.756
Cadmium (µg/L)	_	_	—	0.817	_	.817
Copper (µg/L)	_	—		.955	_	.929
Lead (µg/L)	.567	—	—	—	—	.554
Manganese (µg/L)	_	—		—	.832	.836
Nickel (µg/L)	_	0.816		—	_	.772
Zinc (µg/L)	_	.908		—	_	.847
Number of human-associated OWICs per sample ^b	—	—	.588	—	—	.613
Number of urban-runoff OWICs per sample ^c	—	_	.790	_	—	.783
Number of pesticides detected per sample	_	—	_	_	—	.435
Proportion of variance explained by component	.169	.128	.124	.117	.101	
Cumulative variance for each added component ^d	.169	.297	.421	.538	.639	

^a Communality is a measure of a parameter's importance in explaining the variability in the dataset. The higher the number, the greater the importance.

^b Sum of personal-use, sterol, and nonionic detergent compounds per sample.

^cSum of polycyclic aromatic hydrocarbon, industrial-use, automotive-use, and flame retardant compounds per sample.

^d Total variance explained by six components is 0.692.

PAH, and flame-retardant compounds were detected in similar percentages of samples from downstream and upstream sites. In addition, the PAHs and industrial-use compounds were detected with similar frequency in stormflow samples from downstream and control-basin sites, but compounds in the other seven OWIC classes were detected in a markedly higher proportion of stormflow samples from downstream than control-basin sites.

The personal-use, bromoform, sterol, and flame-retardant compounds were detected in a greater percentage of stormflow samples from downstream INT than downstream PEA, PRO, or SOU sites (table 10). In contrast, personal-use, industrialuse, PAH, automotive-use, and NDMCs were detected in the lowest percentage of stormflow samples from downstream PEA sites. The compounds caffeine (89 percent), carbaryl (47 percent), cholesterol (55 percent), carbazole (39 percent), p-cresol and phenanthrene (58 percent), naphthalene (44 percent), *p*-nonylphenol (59 percent), and TBEP (96 percent) were the most frequently detected compounds in their respective OWICs classes among downstream stormflow samples. Sixteen percent of stormflow samples from downstream INT and SOU sites contained bromoform; a percentage that was about 5-10 percent higher than the percentage in base-flow samples from those sites (table 9), but 10-25 percent lower than base-flow and stormflow samples from upstream SOU sites. Downstream stormflow samples from the INT watershed contained the highest bromoform concentration (6.1 μ g/L) measured among stormflow samples from control-basin sites and upstream and downstream sites (table 12).

Collectively, the pesticides were detected in a similar percentage of stormflow samples from downstream INT and PRO sites, a percentage that was 7–10 percent higher than the percentages for stormflow samples from downstream PEA and SOU sites (table 10). The pesticide 14DCB was detected in 62-71 percent more stormflow samples from downstream INT and PRO than PEA and SOU sites; bromacil was detected in 44-71 percent more stormflow samples from downstream PRO than INT, PEA, or SOU sites. Carbaryl was detected in 41-62 percent more stormflow than base-flow samples from downstream INT, PEA, and SOU sites, but was detected with similar frequency in stormflow and base-flow samples from downstream PRO sites. During stormflow, 74 percent of downstream samples from INT sites contained carbaryl, 16-22 percent more than stormflow samples from downstream PEA and SOU sites.

Collectively, the sterol compounds were detected in a similar percentage of stormflow and base-flow samples from downstream sites (table 10, fig. 17). Nevertheless, a greater percentage of base-flow than stormflow samples contained sterols at downstream INT and PRO sites; whereas, a slightly greater percentage of stormflow than base-flow samples contained sterol compounds at downstream PEA and SOU sites. The sterol compounds were detected with greater frequency in stormflow samples from downstream INT than downstream PEA, PRO, or SOU sites. Cholesterol was detected with similar frequency in samples from downstream PEA, PRO, and SOU

sites. A similar percentage of stormflow samples from downstream PRO and SOU sites contained coprostanol. In addition, a similar percentage of stormflow samples from downstream INT and SOU sites contained sitosterol.

The industrial-use compounds collectively were detected in twice as many downstream stormflow than base-flow samples during the study (tables 9, 10). During stormflow, the industrial-use compounds were detected with similar frequency in samples from upstream and downstream PRO sites, and with similar frequency at downstream and upstream sites in the INT, PEA, and SOU watersheds. Although collectively the industrial-use compounds were detected with similar frequency in stormflow samples from downstream sites, anthraquinone and TPP were detected in a greater percentage of samples from downstream INT sites (table 10). Moreover, carbazole was detected with greater frequency in stormflow samples from downstream SOU sites and *d*-limonene was detected with greater frequency at downstream PRO sites. A similar percentage of stormflow samples from downstream INT and PRO sites contained PCE.

Typically, the PAH and automotive-use compounds were detected with the greatest frequency in stormflow than base-flow samples from all downstream sites (tables 9, 10). The PAH compounds were detected in a greater percentage of stormflow samples from downstream sites than from upstream and control-basin sites (table 10). Except for PCP, than PAH compounds were detected with greatest frequency in stormflow samples from downstream PRO than downstream INT, PEA, and SOU sites. The compound PCP was detected in a similar percentage of stormflow samples (within \pm 5 percent) from downstream INT, PEA, and SOU sites. Collectively, the automotive-use compounds were detected in a greater percentage of stormflow samples from downstream PRO than downstream INT, PEA, and SOU sites. Among all downstream stormflow samples, naphthalene was detected with the greatest frequency at all sites. The corrosion inhibitor 5-methyl-1H-benzotriazole was detected with similar frequency in stormflow samples from downstream PEA, PRO, and SOU sites, but was detected in less than 1 percent of samples from downstream INT sites.

Collectively, the NDMCs were detected in a greater percentage of stormflow samples from downstream than upstream and control-basin sites; however, the NDMCs were detected with similar frequency in stormflow samples from upstream and downstream sites in the PEA and PRO watersheds (table 10). Collectively, the NDMCs were detected in 5–30 percent more stormflow samples from downstream SOU than INT, PEA, or PRO sites. Nevertheless, *p*-nonylphenol and OPEO2 were detected in a greater percentage of the INT samples. In addition, NPEO2 was detected with the highest frequency in stormflow samples from downstream INT and SOU sites and 4-*tert*octylphenol was detected in a higher percentage of samples from downstream PRO than downstream INT, PEA, or SOU sites.

Collectively, the flame-retardant compounds were detected with similar frequency in stormflow samples from downstream and upstream sites, but with substantially greater frequency than at control-basin sites (table 10). Collectively, the flame-retardant compounds were detected in 12–36 percent more stormflow samples from downstream INT sites than from downstream PEA, PRO, or SOU sites. The compound TBEP was detected in 92–100 percent of stormflow samples from all downstream sites. The compounds TCEP and TDCPP were detected with similar frequency in stormflow samples from downstream INT and SOU sites.

Thirteen of the 52 OWICs analyzed in stormflow samples from downstream sites had 75th percentile concentrations that exceeded SRLs during the study period (table 12). Among the personal-use compounds, only acetophenone, caffeine, menthol, and DEET had 75th percentile concentrations that exceeded SRLs in stormflow samples from the downstream sites. In addition, only stormflow samples from downstream INT sites had a 75th percentile acetophenone concentration $(0.41 \,\mu\text{g/L})$ above the SRL. Among downstream stormflow samples, those from INT sites had the highest 75th percentile caffeine concentration (0.88 μ g/L). The 75th percentile menthol concentration was similar in samples from the INT $(0.30 \ \mu g/L)$ and PRO watersheds $(0.32 \ \mu g/L)$. The 75th percentile DEET concentration was slightly higher in samples from the SOU watershed (0.63 μ g/L) than in samples from downstream INT sites (0.52 µg/L). Among stormflow samples from downstream sites, a sample from the INT watershed contained the highest concentrations of benzophenone $(0.36 \ \mu g/L)$, caffeine (also from the PEA watershed, 2.8 $\mu g/L)$, and menthol (0.77 μ g/L). Among downstream stormflow samples, those from PEA sites contained the highest DEET concentration (1.0 μ g/L), while stormflow samples from downstream PRO sites contained the highest concentrations of acetophenone (3.5 μ g/L), camphor (0.53 μ g/L), and methyl salicylate (0.33 μ g/L). These acetophenone and methyl salicylate concentrations were the highest measured among all samples collected during the study.

Except for bromacil in stormflow samples from downstream INT and PRO sites, the 75th percentile concentrations of all pesticide compounds were less than SRLs; however, only among stormflow samples from downstream PRO and SOU sites, were the 75th percentile bromacil concentrations greater than the SRL (table 12). The 75th percentile bromacil concentration in stormflow samples from downstream PRO sites was 2.3 μ g/L, a concentration that was about 0.7 to 2 μ g/L higher than in stormflow samples from upstream and downstream PEA and SOU sites, and control-basin sites, and in base-flow samples from all sites (tables 11, 12).

Among all samples collected during the study period, downstream stormflow samples from the PRO watershed contained the highest concentration of 14DCB (5.0 µg/L; tables 11, 12). In addition, these samples from the PRO watershed contained the highest bromacil concentration (21 µg/L) among all stormflow samples and base-flow samples from the control-basin and downstream sites, and contained the highest carbaryl concentration (0.54 µg/L) among downstream stormflow samples (table 12). The highest prometon concentration in all samples collected during the study was measured in a stormflow sample from a downstream SOU site (tables 11, 12).

Except for cholesterol, the 75th percentile concentrations of all sterol compounds were below SRLs in stormflow samples from downstream sites (table 12). The 75th percentile concentration for cholesterol exceeded the SRL and was similar among stormflow samples from downstream INT, PRO and SOU sites. Nevertheless, the highest cholesterol concentration (3.6 µg/L) among stormflow samples was measured in a downstream sample from the PEA watershed. This concentration was 2-5 times lower than the highest concentrations measured among base-flow samples (tables 11, 12). The highest concentration of coprostanol among stormflow samples from control-basin and downstream sites was measured in a downstream stormflow sample from the PRO watershed (2.2 μ g/L). In addition, downstream stormflow samples from the SOU watershed contained the highest concentrations of sitosterol and stigmastanol among base-flow samples from control-basin sites and all stormflow samples.

Except for anthraquinone, the 75th percentile concentrations for all industrial-use compounds were below SRLs in stormflow samples from downstream sites (table 12). The 75th percentile anthraquinone concentration exceeded the SRL only in stormflow samples from downstream INT sites. Nevertheless, the highest concentrations anthraquinone (0.60 μ g/L) and *d*-limonene (0.62 μ g/L) among downstream stormflow samples were measured in the PEA watershed. In addition, the highest concentration of bisphenol-A (1.3 μ g/L) among all control-basin samples and downstream stormflow samples was measured in a stormflow sample from a downstream SOU site. The highest TPP concentration (0.48 μ g/L) among controlbasin samples, upstream base-flow samples, and downstream stormflow samples was measured in a downstream stormflow sample from the INT watershed (tables 11, 12).

Except for *p*-cresol in samples from the INT and PRO watersheds, the 75th percentile concentrations for all PAHs in downstream stormflow samples were below SRLs (table 12). The 75th percentile *p*-cresol concentration among stormflow samples exceeded the SRL at downstream INT and PRO sites and was highest at downstream PRO sites. Among all samples from control-basin and downstream sites, and upstream baseflow samples, a stormflow sample from a downstream PRO site contained the highest *p*-cresol concentration (18 μ g/L). Furthermore, among upstream base-flow and downstream stormflow samples, a stormflow sample from a downstream PRO site contained the highest phenanthrene concentration $(0.41 \ \mu g/L)$. Downstream stormflow samples from the PEA watershed contained the highest concentrations of fluoranthene $(0.34 \ \mu g/L)$ and pyrene $(0.28 \ \mu g/L)$ among base-flow samples from control basins, all upstream samples, and downstream stormflow samples. Downstream stormflow samples from the PEA and PRO watersheds contained the highest PCP concentration (1.1 μ g/L) measured in base-flow samples from control-basin sites and downstream stormflow samples.

The 75th percentile concentrations for all automotive-use compounds in downstream stormflow samples were below
SRLs (table 12). Nevertheless, the highest concentrations of 1- and 2-methylnaphthalene (0.72 and 0.80 μ g/L, respectively) among all samples were measured in a stormflow sample from a downstream PRO site (tables 11, 12). In addition, among all samples from control-basin and downstream sites, the highest concentration of 2,6-dimethylnaphthalene (0.34 μ g/L) was measured in a downstream stormflow sample from the PRO watershed. The highest concentration of 5-methyl-1H-benz-otriazole (5.1 μ g/L) among all control-basin and downstream sites, and upstream stormflow samples was measured in a downstream stormflow sample from the SOU watershed.

Except for *p*-nonylphenol and NPEO2 in stormflow samples from downstream INT sites and NPEO2 in stormflow samples from downstream SOU sites, the 75th percentile concentrations for all non-ionic detergent compounds in downstream stormflow samples were less than SRLs (table 12). In the INT samples, the 75th percentile concentrations for *p*-nonylphenol and NPEO2 were 2.5 and 2.8 µg/L, respectively. The 75th percentile NPEO2 concentration in the SOU stormflow samples was 3.0 µg/L. Among stormflow samples, the highest concentration of *p*-nonylphenol (6.3 μ g/L) was measured at a downstream INT site (tables 11, 12). Among base-flow samples from control-basin sites and downstream stormflow samples, the highest NPEO2 concentration (9.2 μ g/L) was measured at a downstream PRO site. Among base-flow samples from control-basin sites and stormflow samples from all sites, a stormflow sample from a downstream PRO site contained the highest concentration of OPEO1 (1.2 μ g/L). The highest concentration of 4-tert-octyphenol (0.89 µg/L) among all samples collected during the study period was measured in a stormflow sample from a downstream SOU site.

Except for TDCPP, the 75th percentile concentrations for the flame retardants in downstream stormflow samples from the INT watershed were above the SRL (table 12). In the INT samples, the 75th percentile concentrations for TBP, TBEP, and TCEP were 0.72, 3.3, and 0.30 µg/L, respectively. Only TBEP had 75th percentile concentrations (1.2, 2.3, and $1.2 \mu g/L$, respectively) greater than the SRL in stormflow samples from downstream PEA, PRO, and SOU sites. Among all samples collected during the study period, the highest TBP concentration (9.9 μ g/L) was measured in a stormflow sample from a downstream INT site (tables 11, 12). In addition, the highest TBEP (18 μ g/L) and TCEP (0.74 μ g/L) concentrations among downstream stormflow samples were measured in samples from the PRO and INT watersheds, respectively (table 12). The highest TDCPP concentration (0.55 μ g/L) among control-basin and downstream samples was measured in a downstream stormflow sample from the SOU watershed.

Relations Among OWICs and Select Water-Quality Parameters and Constituents

A PCA was completed on 15 chemical constituents and water-quality properties measured in 89 stormflow samples from downstream sites (table 20). Six components were

generated that explained about 65 percent of the total variability in the data; however, only the first four components are statistically meaningful and were considered the principal components. The PC1, which explains about 27 percent of the variability in the dataset, has a strong (loading greater than 0.7) positive association with field specific conductance and ANC, and a moderate (loading between 0.5 to 0.7) positive association with manganese, chloride, the number of humanrelated OWICs, nickel, and zinc (common urban trace metals). This component describes the relations among major ions, select trace metals, and human-related OWICs. The PC2, which explains about 16 percent of the data variability, has a strong, positive association with dissolved copper and lead concentrations, which are common urban trace metals. This component, therefore, describes storm runoff that contains elevated copper and lead concentrations, either from a different source of runoff than described by PC1 or runoff that is particular to a specific watershed. The PC3, which explains about 9 percent of the variability in downstream stormflow samples, has a moderate association with E. coli density. This component describes elevated E. coli densities in storm runoff. The PC4, which explains about 6 percent of the variability in downstream stormflow samples, has a relatively low, but negative association with zinc and manganese concentrations.

A total of 26 downstream stormflow samples scored high (greater than 0.75) on PC1, indicating that as specific conductance increased, the number of human-related OWICs also increased. This number includes samples that represent 50, 2, 50, and 64 percent of stormflow samples from downstream sites in the INT, PEA, PRO, and SOU watersheds, respectively. Nearly 86 percent of downstream stormflow samples from the PEA watershed and 2 percent each of those samples from the PRO and SOU watersheds contained relatively low specific conductance values and numbers of human-related OWICs. Depending on the volume of effluent during a storm, an increase in specific conductance may be an indication of CSOs to a stream. Because the screening and disinfection of CSOs is the required treatment before discharge to a stream under provisions of the National Pollutant Discharge Elimination System, E. coli bacteria densities should be low in samples collected downstream from the discharge of CSOs. Among samples that scored high on PC1, one PEA sample and all of the INT samples contained E. coli bacteria densities that were at or less than the detection limit of 1 MPN/100 mL. In addition, three PRO and one SOU samples contained E. coli densities that were less than the 20th percentile density in stormflow samples from downstream sites in those watersheds, which may also indicate the influence of CSOs. The number of human-related OWICs did not consistently increase as specific conductance increased or as E. coli densities changed. In some cases, these samples scored high on PC1 but had relatively low numbers of human-related OWICs and E. coli densities. This phenomenon can result because the chlorine added to CSO effluent can oxidize and degrade OWICs and render OWICs undetectable (Zaugg and others, 2002).

Table 20. Results of a principal components analysis on 15 parameters associated with stormflow samples collected at sites downstream from combined sewer overflow outfalls in the Intrenchment Creek, Peachtree Creek, Proctor Creek, and South River watersheds near Atlanta, GA, March 2003 to January 2006.

[PC, principal component, which is a group of correlated parameters whose variance explains some proportion of the data variability in a dataset; loading, a value indicating how important the variability of a parameter is to the total variance of the component, analogous to a correlation coefficient; ft³/s, cubic feet per second; FNU, formazin nephelometric unit; MPN per 100 mL, most probable number per 100 milliliters; SC, specific conductance at 25 degrees Celsius; μ S/cm, microsiemens per centimeter; mg/L, milligram per liter; μ g/L, microgram per liter; OWICs, organic wastewater-indicator compounds; —, not significant, loading less than 0.400]

Parameter —	Principal component loading (without rotation)				Communalitud
	PC1	PC2	PC3	PC4	— communanty"
Turbidity (FNU)	-0.408	_		_	0.379
Escherichia coli density (MPN per 100 mL)	—	_	0.615	_	.591
Field SC (µS/cm)	.897	_	_	_	1.000
Acid-neutralizing capacity (mg/L)	.713	-0.425	_	_	.811
Chloride (mg/L)	.613	_	_	_	.448
Aluminum (µg/L)	429	.453	_	_	.522
Cadmium (µg/L)	.470	_	_	_	.508
Copper (µg/L)	—	.832	_	_	.855
Lead (µg/L)	—	.753	_	_	.877
Manganese (µg/L)	.687	_	_	-0.417	.739
Nickel (µg/L)	.518	_	_	_	.735
Zinc (µg/L)	.554	_	_	530	.740
Number of human-associated OWICs per sample ^b	.579	_	.464	—	.657
Number of urban-runoff OWICs per sample ^c	.447	_	.407	—	.585
Number of pesticides detected per sample	.405	_	_	—	.326
Proportion of variance explained by component	.269	.156	.093	.063	
Cumulative variance for each added component ^d	.269	.425	.518	.581	

^aCommunality is a measure of a parameter's importance in explaining the variability in the dataset. The higher the number, the greater the importance.

^b Sum of personal-use, sterol, and nonionic detergent compounds per sample.

^cSum of polycyclic aromatic hydrocarbon, industrial-use, automotive-use, and flame retardant compounds per sample.

^d Total variance explained by six components is 0.652.

In an effort to document contaminants of emerging concern in Atlanta-area streams, 863 water samples were collected by the USGS, in cooperation with the City of Atlanta, between 2003 and 2006. This sampling effort was intended to determine if specific organic compounds or their detection patterns could be used to identify sewage contamination in streams within an urban environment, especially in streams receiving CSOs. These overflows enter streams at points commonly called "outfalls."

Water samples were collected from streams in seven watersheds within the Atlanta area and analyzed for 52 organic compounds commonly detected in wastewater effluent. These samples were analyzed at the USGS NWQL in Denver, CO. Because of the association with wastewater effluent, these compounds are commonly called OWICs, many of which are considered chemicals of emerging concern.

Sixty-three sampling sites representing three site types were established in the seven study watersheds. The first site type consisted of 23 sites within the Nancy Creek (NAN), Sandy Creek (SAN), and Utoy Creek (UTO) watersheds, which are watersheds without combined sewer outfalls and, therefore, not affected by CSOs. These watersheds were designated as "control basins" because OWIC concentrations in their streams probably were representative of urban background. Developed areas compose 60-77 percent of the combined drainage area in the control basins. The second and third site types were located in Intrenchment Creek (INT), Peachtree Creek (PEA), Proctor Creek (PRO), and South River (SOU) watersheds, which are watersheds with combined sewer outfalls. Although the predominant land use is residential in these watersheds, industrial and commercial land uses are more extensive than in the control basins. Developed land covers 76–93 percent of the area upstream from sampling sites in the INT, PEA, PRO, and SOU watersheds, with the amount of impervious area ranging from 24-51 percent. The second site type, designated "upstream sites," consisted of 27 sites located either upstream from combined sewer outfalls or in tributary basins without outfalls and, therefore, not affected by CSOs. In the INT watershed, only one site was upstream from a CSO outfall. The third site type designated as "downstream sites" consisted of 14 sites located downstream from combined sewer outfalls and was commonly affected by CSOs during moderate to large storms.

Although anecdotal information indicates that sanitarysewer overflows occurred intermittently in all seven watersheds as a result of blockages or breaks in the sewer lines, specific occurrences were not documented. During the study period, all streams within the study area were on Georgia's 303d list of impaired streams within the State (Georgia Environmental Protection Division, 2006). These streams were impaired because of high fecal coliform bacteria density as a result of urban runoff and combined sewer overflows.

Of the 60 OWICs analyzed in water samples collected between March 2003 and January 2006, 52 were detected

above SRLs. The compounds BHA, isophorone, isoquinoline, metolachlor, metalaxyl, and 4-octylphenol were not detected in any sample collected during the study. The 52 OWICs were grouped into 9 classes based on similar chemistry, sources, or usage. Of these nine classes, the personal-use compounds, sterols (cholesterol and coprostanol), and non-ionic detergent metabolites are probably the most important for identifying CSOs in the Atlanta-area streams. The antimicrobial compound triclosan and all NDMCs are considered potential endocrine disrupting compounds. In addition, stream samples collected during the study were analyzed for major ions, nutrients, trace metals, and *Escherichia coli* density. Four compounds—TBEP, TCEP, bromacil, and cholesterol—were detected above SRLs in at least 45 percent of all samples collected during the study.

Although the median numbers of OWICs per base-flow sample (four compounds) were statistically similar among samples from the NAN, SAN, and UTO watersheds, all were statistically lower than the medians (six to nine) in stormflow samples from their respective watersheds.

Seasonal Variation

The seasonal distributions of OWICs detected among all samples collected during the study period were consistent with seasonal- or urban-usage patterns; however, within specific watersheds and site types, the seasonal distribution of some OWICs was commonly different and more variable than the seasonal distribution seen among all samples. During both seasons, OWICs were detected in the smallest percentage of samples from control-basin than from upstream or downstream sites. Typically, the personal-use and pesticide compounds were detected with similar frequency in cool- and warm-season samples from upstream and downstream sites; whereas, bromoform and the industrial-use compounds were detected with the greatest frequency in samples from upstream sites.

Among the personal-use compounds, caffeine, camphor, and menthol were detected with greater frequency in coolthan warm-season samples from all sites, while DEET was detected more frequently in warm-season samples. About 8 percent of cool-season samples contained DEET with a maximum concentration of 1.4 μ g/L. These detections indicate possible contamination by an unknown source of DEET during the cool season.

Among the pesticides, carbaryl and prometon were detected in greater percentages of warm- than cool-season samples, while 14DCB was detected with greater frequency in cool-season samples and bromacil with similar frequency during both seasons. Collectively the pesticides were detected in a similar percentage of samples from upstream and downstream sites during both seasons. Nevertheless, bromacil was detected with the greatest frequency in upstream SOU and downstream PRO sites during both seasons, while carbaryl and 14DCB were detected with the greatest frequency in warm-season samples from downstream INT sites. Typically, bromoform and the industrial-use compounds were detected with similar frequency in warm- and coolseason samples collected during the study. During both seasons, bromoform and industrial-use compounds were detected in a greater percentage of samples from upstream sites, especially samples from upstream SOU sites, than from downstream sites.

The sterol, PAH, automotive-use, NDMCs, and flameretardant compounds were detected in the greatest percentage of samples from both seasons at downstream rather than upstream sites. In general, the sterol compounds cholesterol and sitosterol were detected in greater percentages of warmthan cool-season samples, while coprostanol was detected with greater frequency in cool-season samples. A greater percentage of downstream than upstream samples contained sterol compounds in both seasons, especially samples from downstream INT sites. Among the PAH compounds, p-cresol and phenanthrene were detected in a greater percentage of cool- than warm-season samples, while the other four compounds were detected with similar frequency during both seasons. The PAH compounds were detected with the greatest frequency in cool- and warm-season samples from upstream SOU sites and cool-season samples from downstream PRO sites. The automotive-use compounds naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene were detected in greater percentages of cool- than warm-season samples, while the NDMCs OPEO2 and NPEO2, and flame retardants TDCPP, TCEP, and TBEP, were detected with the greatest frequency in warm-season samples. The automotive-use compounds were detected with the greatest frequency in cool-season samples from downstream PRO sites. A greater percentage of samples from both seasons contained NDMCs and flame retardants at downstream INT and SOU sites than at other sites in the study area.

Variation During Base Flow

During periods of dry weather, base flow primarily consists of groundwater discharge and runoff from outdoor water use (dry-weather runoff). Except for the PAH and automotiveuse compounds, compounds in the other seven OWIC classes were detected with the lowest frequency in base-flow samples from control-basin than from upstream or downstream sites. The PAH and automotive-use compounds were detected with similar frequency in base-flow samples from all three site types. A greater percentage of base-flow samples from the SAN watershed contained personal-use compounds and the NDMCs *p*-nonylphenol than those from the NAN or UTO watersheds. Bromacil, PCP, and the flame retardant TBEP were detected in more base-flow samples from the UTO than from the NAN or SAN watersheds; whereas, caffeine, PCE, and the flame retardants TBP and TCEP were detected with the greatest frequency in base-flow samples from the NAN watershed. In addition, all nine OWIC classes were detected in a similar

percentage of base-flow samples from upstream PEA and control-basin sites. In addition, except for the sterol and flameretardant compounds, compounds in the other OWIC classes were detected with similar frequency in base-flow samples from control-basin sites and upstream and downstream PEA sites. The sterol and flame-retardant compounds were detected in a greater percentage of base-flow samples from downstream PEA than upstream PEA and control-basin sites.

Among upstream samples, a greater percentage of base-flow than stormflow samples contained the personal-use compounds AHTN, benzophenone, cotinine, HHCB, indole, triclosan, and triethyl citrate; 14DCB, bromacil, and PCE. Furthermore, the personal use, bromoform, PAH, automotive use, NDMCs, and flame retardants were detected in a greater percentage of upstream base-flow samples from SOU than PEA or PRO sites. The pesticide, sterol, and industrial-use compounds were detected with similar frequency in base-flow samples from upstream PRO and SOU sites.

Collectively, the personal-use and pesticide compounds were detected in a slightly greater percentage of base-flow than stormflow samples during the study period. The personaluse compounds AHTN, cotinine, HHCB, indole, and triclosan were detected in up to three times more base-flow than stormflow samples. The detection frequencies of these five compounds were particularly high in base-flow samples from downstream sites, especially those from the INT watershed. Because many household soaps and detergents contain triclosan and a variety of fragrances, the compounds triclosan, HHCB, indole, and AHTN may be found in dry-weather runoff entering streams when soaps or detergents are used outdoors; however, because these compounds also are present in sewage effluent, they may exist in groundwater that has intercepted sewage effluent from leaking sanitary-sewer pipes or septic systems.

Bromoform was detected with the highest frequency in base-flow samples from upstream SOU and downstream INT sites. The presence of bromoform in these samples indicates that stream reaches not affected by CSOs in the South River watershed received water that was disinfected with either chlorine or a chlorine-containing compound, the source of which is unknown. The chlorine in chlorinated municipal water or chlorine-disinfected sewage or CSO effluent reacts with bromide ions to create bromoform.

Among the pesticides, bromacil was detected with greater frequency in base-flow than stormflow samples at all sites, and carbaryl was detected with the greatest frequency in stormflow samples. Furthermore, bromacil was detected with the greatest frequency in base-flow samples from upstream and downstream sites in the PRO and SOU watersheds, and carbaryl in stormflow samples from downstream INT and PEA sites. Bromacil may exist in base flow through dry-weather runoff from irrigated landscaped areas or through contaminated groundwater.

Although collectively the sterol, industrial-use, and automotive-use compounds were each detected in more stormflow than base-flow samples, several compounds in these classes did not follow that pattern. For example, the sterol stigmastanol and the automotive-use compound 5-methyl-1Hbenzotriazole were detected with similar frequency in baseflow and stormflow samples. In addition, PCE was detected in nearly twice as many base-flow as stormflow samples at all sites. More specifically, PCE was detected with the highest frequency in base-flow samples from the upstream sites, particularly those from the PRO watershed. Because PCE is a common contaminant in urban groundwater, it may exist in groundwater contributions to base flow.

Variation During Stormflow

Stormflow is streamflow generated by rainfall that flows overland and within shallow soil horizons and discharges to a stream channel during periods of wet weather. In urban areas, this flow is called urban runoff. Collectively, compounds from six of the nine OWIC classes were detected with greater frequency in stormflow than base-flow samples from the study watersheds. Although typically personal-use compounds were detected with slightly greater frequency in base-flow samples, a greater percentage of stormflow samples from all sites contained acetophenone, caffeine, camphor, menthol, and DEET. In addition, the pesticide carbaryl; the sterols cholesterol, coprostanol, and sitosterol; the industrial-use compounds anthraquinone, carbazole, triphenyl phosphate, and d-limonene; all PAH compounds; four of the siz automotiveuse compounds; the NDMCs p-nonylphenol, OPEO1, OPEO2, and 4-tert-octylphenol; and all four flame-retardant compounds were detected with greater frequency in stormflow samples.

Although collectively the personal-use compounds were detected with similar frequency in stormflow samples from the NAN, SAN, and UTO watersheds, caffeine and camphor were detected in more NAN samples, several fragrances and menthol in more SAN samples, and DEET in more UTO samples. In addition, the industrial-use compounds were detected with the highest frequency in NAN samples. The sterol and NDMCs were detected in a similar percentage of stormflow samples from the NAN and SAN watersheds; whereas, the pesticide, industrial-use, and automotive-use compounds were detected in a similar percentage of stormflow samples from the SAN and UTO watersheds. The flame-retardant compounds were detected with the greatest frequency in stormflow samples from the SAN watershed. Conversely, PAHs were detected with the greatest frequency in stormflow samples from the UTO watershed.

Based on a PCA, major ion concentrations are higher, and aluminum, turbidity, and the number of OWICs per sample were lower during base flow; however, this trend reverses as streamflow increases during storm runoff. The PCA indicates the water quality at control-basin sites is characteristic of water quality in an urban stream that is not affected by wastewater effluent, but receives varying amounts of dry-weather runoff and groundwater during base flow, and urban storm runoff during wet weather.

The median numbers of OWICs per stormflow sample ranged from 15 to 19 compounds and were statistically similar at upstream and downstream sites in the PRO and SOU watersheds. Because only eight stormflow samples were collected from the upstream PRO sites, those results were not compared to the other site types. Typically, the numbers of detectable OWICs per sample were markedly higher in stormflow than base-flow samples from upstream sites. The median numbers of OWICs detected in upstream base-flow samples from the PEA, PRO, and SOU watersheds were 4, 7, and 14, respectively, and were statistically lower than the medians in stormflow samples from the PEA, PRO, and SOU watersheds (13, 17, 17, respectively). During stormflow, the personal-use, pesticide, sterol, PAH, and flame-retardant compounds were detected in a similar percentage of upstream and downstream samples during the study period. In addition, the industrialuse compounds were detected in a greater percentage of stormflow samples from upstream than downstream sites, but the automotive-use and NDMCs were detected with greater frequency in stormflow samples from downstream sites.

Most OWICs were detected with greater frequency in stormflow than base-flow samples from upstream and downstream sites in the PEA watershed. Except for the industrialuse and PAH compounds, OWIC classes were detected with similar frequency in stormflow samples from upstream and downstream PEA sites. Bromoform was detected with greater frequency in stormflow samples from downstream than upstream PEA sites. Typically, the industrial-use and PAH compounds were detected in a larger percentage of stormflow samples from upstream than from downstream PEA sites.

Collectively, compounds in the personal-use and pesticide classes were detected with similar frequency in base-flow and stormflow samples from upstream sites, while at downstream sites, the personal-use and sterol compounds were detected with similar frequency during the two flow conditions. A markedly higher percentage of stormflow than base-flow samples from downstream INT sites contained pesticide, PAH, and automotiveuse compounds; whereas, only a slightly higher percentage of stormflow samples contained bromoform, industrial-use, and flame-retardant compounds from those sites. Furthermore, the percentage of samples from downstream INT sites that contained personal-use compounds and NDMCs differed little under baseflow and stormflow conditions. In contrast, the sterol compounds were detected in fewer stormflow than base-flow samples from downstream INT sites. The pesticide compounds were detected with similar frequency in downstream stormflow samples from the INT and PRO sites and in downstream PEA and SOU sites. The industrial-use compounds in stormflow samples were detected with similar frequency at downstream INT, PRO, and SOU sites. In addition, PAHs in stormflow samples were detected with greater frequency at downstream PRO and all SOU sites than at downstream INT sites.

Typically, the 75th percentile concentrations of OWICs analyzed in water samples exceeded SRLs in 7 percent of base-flow samples and up to 25 percent of stormflow samples collected during the study period. The most common of these OWICs were caffeine, bromacil, cholesterol, and TBEP. In general, the highest OWIC concentrations observed during the study period were measured in relatively few samples. The maximum and 75th percentile concentrations of several OWICs measured in stream samples during the current study were commonly greater than those measured in other studies across the United States. Concentrations for 11 of the 14 personal-use compounds, 4 of the 6 pesticide compounds, all 4 sterol compounds, 4 of the 6 industrial-use compounds, 3 of the 6 PAH compounds, 5 of the 6 automotive-use compounds, 3 of the 5 non-ionic detergent metabolites, and all 4 flame-retardant compounds were greater in this current study than the concentrations reported by Kolpin and others (2002), Galloway and others (2005), and Sando and others (2005, 2006). The maximum caffeine (11 μ g/L) and DEET (6 μ g/L) concentrations in this current study exceed the maximum concentrations summarized by Kolpin and others (2004). The OWIC concentrations measured in the current study generally were similar to those measured in stream samples reported by Wilkison and others (2002, 2006); however, maximum concentrations for the compounds AHTN, cotinine, triclosan, triethyl citrate, chlorpyrifos, diazinon, prometon, cholesterol, coprostanol, sitosterol, anthracene, fluoranthene, phenanthrene, pyrene, naphthalene, 2,6-methylnaphthalene, and OPEO2 were substantially higher in the studies by Wilkison and others (2002, 2006) in the Blue River basin of Kansas and Missouri.

Conclusions

A large number of factors control the occurrence and concentrations of organic wastewater-indicator compounds (OWICs) in urban streams near Atlanta, GA. Factors that may affect the occurrences and concentrations of OWICs include the presence and timing of combined sewer overflows (CSOs), flow condition (base flow or stormflow), timing of sample collection (rising or falling limb of storm hydrograph), amount of impervious area, and land uses in the watershed. Clearly, season (cold or warm) and flow condition are two factors that influence OWICs in these streams. The elevated number of OWICs in base-flow samples collected upstream from CSO outfalls may be caused by contributions from many potential sources in these watersheds. These sources may include dryweather urban runoff from landscape watering and the washing of vehicles or machinery on impervious surfaces, leaking sanitary sewer lines, and either non-permitted discharges or permitted but out-of-compliance discharges to the streams. Compounds such as *N*,*N*-diethyl-*meta*-toluamide (DEET), diazinon, and carbaryl were detected more frequently during the warm season when insect repellants and pesticide use is highest. In contrast, wood burning occurs more frequently during the cool season; therefore, compounds such as p-cresol and phenanthrene were detected, as expected, more frequently in cool-season samples. The similarity in the pattern and distribution of OWICs detected in base-flow and stormflow samples collected at sites upstream and downstream from known CSO outfalls indicates that CSOs were not the only source of OWICs during the study period. The 52 OWICs identified in this current study may be better suited for identifying sewagecontaminated groundwater than sewage-contaminated surface water because groundwater is not typically affected by the OWICs that are common in urban runoff.

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Appendix

History of Combined Sewer Systems in the United States

Before 1858, centralized sewage disposal systems did not exist in the United States (U.S. Environmental Protection Agency, 2004). By 1890, however, most large cities had a central system of pipelines that collected and transported human waste and, inadvertently, storm runoff to a receiving water body, usually a river or stream. Until about 1950, these combined sewer systems (CSSs) were a common form of wastewater management for major metropolitan areas in the United States. Most CSSs discharged untreated effluent into rivers and streams relying on dilution and natural processes within the stream to treat the effluent (U.S. Environmental Protection Agency, 2004). Although CSSs were efficient and cost-effective in metropolitan areas with low to moderate rainfall and limited population growth, they were quickly overwhelmed in areas, such as Atlanta, with moderate to high rainfall and rapid population growth (U.S. Environmental Protection Agency, 2004). By 1960, the aesthetic and water quality of rivers and streams in many metropolitan areas declined because rivers and streams could not rapidly assimilate the ever-increasing amounts of CSS effluent as populations increased. Therefore, during the early 1960s, most large cities began constructing separate sanitary sewer systems (SSS) that included simple treatment facilities. In addition, effluent from the older CSS was conveyed to those treatment facilities.

These early wastewater treatment plants (WWTPs) were designed to remove solids from the influent wastewater in settling basins (primary treatment) before discharge into the rivers and streams in the area by way of pipes or canals. Any discharge to a water body by way of pipe, ditch, canal, or other physical structure is commonly known as a point-source discharge (U.S. Environmental Protection Agency, 2004). By separating the stormwater system from the sanitary system, the separate stormwater system only conveyed and discharged urban runoff to the receiving waters. For those cities that added treatment facilities to their CSSs, it was soon apparent that those facilities were substantially under designed and could not keep up with a growing population. As a result, the treatment capacity of those facilities was commonly exceeded during times of heavy rain. Once the treatment facility reached capacity, the excess influent (sanitary and stormwater) bypassed most of the treatment system and was discharged into the receiving stream. These overflows-consisting of untreated sewage effluent and urban runoff-were screened to remove large items, disinfected, and discharged into nearby streams. The discharged effluent not only violated National Pollutant Discharge Elimination System (NPDES) permit stipulations, but also violated stream water-quality standards promulgated by the Federal Clean Water Act and enforced by State environmental agencies. In an effort to meet water-quality standards in receiving streams, many cities subsequently opted to construct separate sanitary systems to support newly developed areas and to increase the capacity to treat the influents going to the remaining CSSs.

Historical Influence of Combined Sewer Overflows and Urban Runoff on Stream-Water Quality

The Federal Water Pollution Control Act of 1948 (Public Law 80-845) was the first Federal regulation specifically addressing water pollution in the United States. Although this law provided technical-assistance funds to State and local agencies, it affirmed that State and local governments were the proper entities for establishing and enforcing water pollution laws in their respective jurisdictions (Copeland, 2006). Between 1948 and 1965, three amendments to the 1948 law were promulgated: (1) Water Pollution Control Act of 1956 (Public Law 84–660), (2) Federal Water Pollution Control Act Amendments (1961, Public Law 87–88), and (3) Water Quality Act of 1965 (Public law 89–234; Copeland, 2006). The 1965 law was the first to require States to establish water-quality standards to determine pollution levels, pollutant control goals, and provide a basis for enforcement.

Before 1965, many water-quality studies in the United States focused on point-source discharges and their effect on the aesthetic and chemical qualities of the Nation's rivers and streams (U.S. Environmental Protection Agency, 1983). The majority of point-source discharges were typically effluents from WWTPs and from various types of industries. Those early studies concluded that point-source discharges were the source of river and stream degradation. These findings ultimately led to the Water Quality Control Act of 1965 (Public Law 89–234) and the Federal Water Pollution Control Act of 1972 (Public Law 92–500). These laws and their later amendments under the Clean Water Act provided local and State governments with the legal mandates and monetary support needed to reduce or eliminate the contaminants in sewage and industrial effluent discharged to rivers and streams.

Because of the Water Quality Control and the Federal Water Pollution Control Acts, the water quality of point-source discharges improved substantially between 1965 and 1975. This improvement came as WWTPs and industrial dischargers retooled and upgraded their facilities to provide secondary treatment of sanitary and industrial wastes (U.S. Environmental Protection Agency, 1983). As primary treatment of sewage effluent became widespread during the 1960s, the water quality of rivers and streams improved. Moreover, the advent of secondary treatment of sewage effluent beginning in the 1970s and enforcement of discharge permits under the NPDES further improved the water quality of receiving waters. Nevertheless, as the quality of effluents improved, water-quality studies showed that undefined sources of contaminants also entered rivers and streams through storm runoff, particularly runoff from urban areas. These findings sparked the interest of the U.S. Government and facilitated the start of several urban runoff studies by Federal agencies (U.S. Environmental Protection Agency, 1983).

Several large studies in the mid- to late-1970s showed that urban storm runoff contained substantial numbers of contaminants at concentrations that could affect public health (U.S. Environmental Protection Agency, 1980). One study in Atlanta by the U.S. Environmental Protection Agency (USEPA) showed that 64 percent of the 5-day biochemical oxygen demand (BOD_c) load to urban streams came from separate storm sewers (urban runoff), 19 percent from CSSs, and 17 percent from wastewater treatment plants (U.S. Environmental Protection Agency, 1983). Other studies showed that BOD₅ levels in stormwater, which commonly infiltrated into SSSs, were equal to or greater than those measured in secondary-treated domestic sewage (U.S. Environmental Protection Agency, 1983). These studies attributed the waterquality degradation in urban streams to undefined, nonpoint sources of contaminants (U.S. Environmental Protection Agency, 1983). Furthermore, many of those studies concluded that future efforts to improve the water quality of urban rivers and streams in the United States would be hampered by nonpoint-source contaminants carried in storm runoff. Because nonpoint sources of contaminants are commonly undefined, their mitigation would be more difficult and more costly than the efforts used to mitigate contaminants from point sources (U.S. Environmental Protection Agency, 1983).

Because these studies implicated urban runoff as a substantial source of contaminants to rivers and streams, the USEPA extensively reviewed urban water-quality data generated from urban studies across the United States (U.S. Environmental Protection Agency, 1980). The review encompassed studies from the academic community and water-quality data collected by local and State agencies under section 208 of the Federal Water Pollution Control Act. This review concluded that the water quality of rivers and streams in the Nation's urban areas was probably degraded by urban storm-water runoff. This conclusion, however, was tempered because the data represented water samples that were not collected, processed, or analyzed using similar or consistent methods and procedures. These inconsistencies introduced ambiguity and uncertainty in the data, and precluded the definitive conclusions needed to establish new regulations (U.S. Environmental Protection Agency, 1983). As a result, the USEPA sponsored a Nationwide Urban Runoff Program (NURP) in the late 1970s consisting of individual waterquality studies in 28 urban areas across the United States. The purpose of the program was to develop a database containing nationally consistent water-quality data from urban streams (U.S. Environmental Protection Agency, 1983).

Results from the NURP studies indicated that several constituent concentrations in urban streams were markedly higher than those from non-urban streams. In these studies, 60 percent of the USEPA-listed organic priority pollutants, mainly pesticides, were detected in urban stream samples. In addition, fecal coliform bacteria counts were high in urban streams and commonly exceeded the USEPA criterion for body-contact recreation and violated water-quality standards in many States. Fecal coliform levels as high as 1 million colonies per 100 milliliters (col/100 mL) were measured in urban areas where untreated sewage effluent mixed with storm runoff in CSOs. The median fecal coliform level for all studies was 21,000 col/100 mL (U.S. Environmental Protection Agency, 1983). The NURP studies did show that nonpoint source contaminants in urban runoff pose a substantial threat to the water quality in the Nation's urban streams (including Atlanta), particularly when runoff included CSOs. Although Atlanta's NURP study showed that urban runoff appeared to degrade the water-quality of Atlanta's urban streams, CSOs from Atlanta's overburdened CSS further increased waterquality degradation in those streams (U.S. Environmental Protection Agency, 1983).

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