

**National Water-Quality Assessment Program**

**Use of Chemical Analysis and Assays of Semipermeable Membrane Devices Extracts to Assess the Response of Bioavailable Organic Pollutants in Streams to Urbanization in Six Metropolitan Areas of the United States**



Scientific Investigations Report 2007–5113

**Cover.**

Left — Semipermeable membrane devices deployed in Auchumpkee Creek at Allen Road near Roberta, Georgia (*Photograph by Mark Gregory, U.S. Geological Survey*).

Center — Urban creek near Birmingham, Alabama (*Photograph by Humbert Zappia, formerly with the U.S. Geological Survey*).

Right — Deploying semipermeable membrane devices in Bear Creek below Estes Road in Lakewood, Colorado (*Photograph by Stephen Porter, U.S. Geological Survey*).

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By Wade L. Bryant, Steve L. Goodbred, Thomas L. Leiker, Laura Inouye,  
and B. Thomas Johnson

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

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

The U.S. Geological Survey (USGS) is committed to serve the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (<http://www.usgs.gov/>). Information on the quality of the Nation's water resources is of critical interest to USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for multiple water uses make water availability, now measured in terms of quantity and quality, even more critical to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy (<http://water.usgs.gov/nawqa/>). Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management strategies that protect and restore water quality.

Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifer systems, referred to as Study Units (<http://water.usgs.gov/nawqa/studyu.html>). Collectively, these Study Units account for more than 60 percent of the overall water use and population served by public water supply, and are representative of the Nation's major hydrologic landscapes, priority ecological resources, and agricultural, urban, and natural sources of contamination.

Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local knowledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally and nationally. The consistent, multi-scale approach helps to determine if certain types of water-quality issues are isolated or pervasive, and allows direct comparisons of how human activities and natural processes affect water quality and ecological health in the Nation's diverse geographic and environmental settings. Comprehensive assessments on pesticides, nutrients, volatile organic compounds, trace metals, and aquatic ecology are developed at the national scale through comparative analysis of the Study-Unit findings (<http://water.usgs.gov/nawqa/natsyn.html>).

The USGS places high value on the communication and dissemination of credible, timely, and relevant science so that the most recent and available knowledge about water resources can be applied in management and policy decisions. We hope this NAWQA publication will provide you

the needed insights and information to meet your needs, and thereby foster increased awareness and involvement in the protection and restoration of our Nation's waters.

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

Robert M. Hirsch  
Associate Director for Water

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## Conversion Factors

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Area		
square meter (m <sup>2</sup> )	0.0002471	acre
square kilometer (km <sup>2</sup> )	0.3861	square mile (mi <sup>2</sup> )
Volume		
liter (L)	0.2642	gallon (gal)
cubic meter (m <sup>3</sup> )	0.0002642	million gallons (Mgal)
Flow rate		
meter per second (m/s)	3.281	foot per second (ft/s)
cubic meter per second (m <sup>3</sup> /s)	35.31	cubic foot per second (ft <sup>3</sup> /s)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)

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

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

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

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



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## Abstract

Studies to assess the effects of urbanization on stream ecosystems are being conducted as part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program. The overall objectives of these studies are to (1) determine how hydrologic, geomorphic, water quality, habitat, and biological characteristics respond to land-use changes associated with urbanization in specific environmental settings, and (2) compare these responses across environmental settings. As part of an integrated assessment, semipermeable membrane devices (SPMDs) were deployed in streams along a gradient of urban land-use intensity in and around Atlanta, Georgia; Raleigh-Durham, North Carolina; and Denver-Fort Collins, Colorado, in 2003; and Dallas-Fort Worth, Texas; Milwaukee-Green Bay, Wisconsin; and Portland, Oregon, in 2004. Sites were selected to avoid point-source discharge and to minimize natural variability within each of the six metropolitan areas. In addition to standard chemical analysis for hydrophobic organic contaminants, three assays were used to address mixtures and potential toxicity: (1) Fluoroscan provides an estimate of the total concentration of polycyclic aromatic hydrocarbons (PAHs); (2) the P450RGS assay indicates the presence and levels of aryl hydrocarbon receptor agonists; and (3) Microtox® measures toxicological effects on photo-luminescent bacteria.

Of the 140 compounds targeted or identified by gas chromatography/mass spectrometry analysis in this study, 67 were not detected. In terms of numbers and types of compounds, the following were detected: 2 wood preservatives, 6 insecticides (parent compounds), 5 herbicides, 22 polycyclic aromatic hydrocarbons, 2 dibenzofurans, 4 polychlorinated biphenyls, 7 compounds associated with fragrances or personal care

products, 4 steroids associated with wastewater, 5 poly-dibromated diphenyl ethers (flame retardants), 3 plasticizers, 3 antimicrobials/disinfectants, and 3 detergent metabolites.

Of the 73 compounds detected and three assays utilized, 29 were detected in 25 percent or more of the streams and were strongly related to increases in urban intensity (defined as having a Spearman's rho  $\geq 0.5$  with percent urban land cover) in at least one of the six metropolitan areas investigated. These 29 endpoints included 16 PAHs, a wood preservative (pentachloroanisole), 2 insecticides (chlorpyrifos and chlordane), 3 herbicides (benfluralin, trifluralin, and dacthal), a synthetic musk (hexahydrohexamethylcyclopentabenzopyran, HHCB), 2 furans (methyl dibenzofuran and benzo[*b*]naphtho[2,3-*d*]furan), and a flame retardant (BDE 47). In addition, the number of compounds detected and results of the Fluoroscan and P450RGS assays were strongly related to urban intensity.

Average water concentrations estimated from SPMDs were compared to screening benchmarks for the protection of human health and aquatic life; of the 14 compounds with available benchmarks, 3 compounds (anthracene, dieldrin, and diazinon) exceeded those levels in one or more streams. Both dieldrin and anthracene exceeded their respective benchmarks in seven streams, and diazinon in only one stream. There were more exceedances in Milwaukee-Green Bay and Raleigh-Durham than in the other metropolitan areas, and there were no exceedances in Dallas-Fort Worth.

The six metropolitan areas studied differed in the number and types of endpoints related to urban intensity, probably from a combination of factors governing source strength, transport, and fate of hydrophobic compounds. The number of endpoints strongly related to urban intensity ranged from 3 in Dallas-Fort Worth and Portland to 21 in Raleigh-Durham. High frequencies of detection and strong correlations with

urban land cover for pyrogenic PAHs (such as unsubstituted 4-ringed PAHs) in all six metropolitan areas indicate that these compounds are an important component of urbanization, regardless of location. Pentachloroanisole, dibenzofurans, and petrogenic PAHs (alkylated PAHs and heterocyclic dibenzothiophenes) were frequently detected and strongly related to urban intensity in Atlanta, Raleigh-Durham, Milwaukee-Green Bay, and Denver-Fort Collins. Two insecticides were related to urban intensity: chlorpyrifos in Atlanta, Raleigh-Durham, and Dallas-Fort Worth; and chlordane in Raleigh-Durham. Three herbicides were strongly related to urban intensity: trifluralin in Atlanta and Raleigh-Durham; benfluralin in Atlanta, and dacthal in Denver-Fort Collins. The detection frequencies for most wastewater indicator compounds were too low to establish relations with urban intensity. Of the wastewater compounds analyzed, HHCB in Raleigh-Durham and Denver-Fort Collins, and BDE 47 in Denver-Fort Collins and Dallas-Forth Worth, had the strongest relations with urban intensity.

In addition to pyrogenic PAHs, levels of aryl hydrocarbon receptor agonists (as measured by the P450RGS assay) were strongly related to increasing urban intensity in all six metropolitan areas. PAHs were the only group of aryl hydrocarbon agonists consistently detected and related with urban intensity in all six metropolitan areas. It is unknown which compounds in the SPMDs caused the increased response in the P450RGS assay because the SPMDs likely contained many aryl hydrocarbon receptor agonists not quantified by chemical analysis. It is clear that bioavailable, aryl hydrocarbon receptor agonists increase in streams with increasing urban intensity in the basin. Potential toxicity mediated by this metabolic pathway should be considered in integrated assessments of the response of aquatic biota to urbanization.

## Introduction

Rapid growth in urban areas of the United States has caused concern about the effects of urbanization on water quality of streams. Although urban land is a small component of the landscape in the United States, these lands have a disproportionate effect on stream condition (U.S. Environmental Protection Agency, 2000c). It is estimated that 1 square kilometer (km<sup>2</sup>) of urbanized basin impairs three times the length of stream that would be impaired by a similar amount of agricultural land (National Resources Conservation Service, 2000; U.S. Environmental Protection Agency, 2000c). With the population of the United States projected to increase from 283 million in 2000 to 420 million in 2050 (U.S. Census Bureau, 2004), urbanization is a significant source of stream impairment that will be increasing for the foreseeable future.

Although a number of studies have assessed the health of ecological communities in urban streams, it is difficult for water-quality managers and regulators to develop specific strategies for mitigation and restoration because urbanization

can affect streams by altering many interrelated physical, chemical, and biological factors. With limited resources, most government agencies cannot afford to conduct comprehensive urban stream studies using consistent designs and methods that assess all factors that might impair streams. This makes it difficult to compare responses between metropolitan areas or to extrapolate results from one area of the country to another. Studies of multiple metropolitan areas using a common design and method could help provide a comprehensive understanding of regional responses to urbanization that are comparable in diverse environmental settings.

Comparing responses to increasing urban land-use intensity across environmental settings and examining patterns in relations between stressors (factors associated with urbanization) and receptors (physical, chemical, and biological) will allow evaluation of policy, management, and restoration alternatives at regional and national scales. For example, how does the hydrologic and chemical character of streams change with increasing impervious surfaces in humid as opposed to dry settings, and are the same landscape features associated with responses in both settings? An understanding of how urban land-use intensity influences stream ecosystems can help determine management and legislative strategies for the protection of surface-water resources, and provide guidance for cost-effective restoration of damaged ecosystems.

In 1999, the U.S. Geological Survey (USGS) began a series of studies, based on a common design and using consistent methods, to examine the effects of urbanization on aquatic assemblages, physical habitat, and water chemistry in selected metropolitan areas of the United States. These studies, collectively referred to as the "Effects of Urbanization on Stream Ecosystems" (EUSE), are designed to address two major questions: (1) How do the hydrologic, geomorphic, chemical, and biological characteristics of stream ecosystems respond to land-use changes associated with urbanization, and (2) How do these responses vary across environmental settings? An overview of these studies can be found in Tate and others (2005) and U.S. Geological Survey (2006).

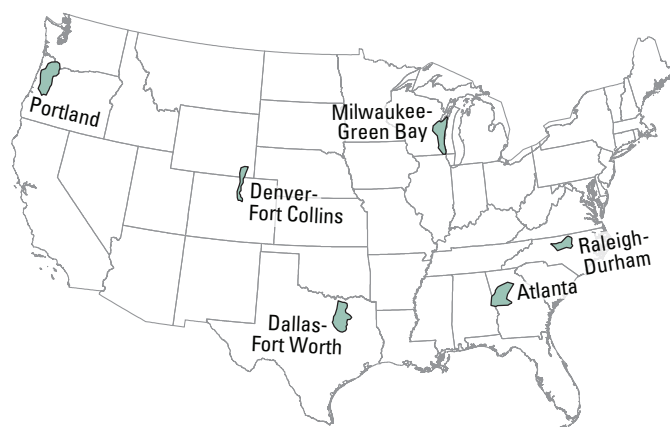
## Purpose and Scope

The purposes of this study were to (1) assess the occurrence and distribution of selected hydrophobic contaminants in streams across a range of urban land-use conditions not having the influence of large point-source discharges, (2) determine if the concentrations of hydrophobic organic contaminants (HOCs) and their potential toxicity to aquatic biota responded along a gradient of urbanization within each metropolitan area, and (3) compare these responses among the six metropolitan areas studied. This report describes the results of chemical analysis and bioassays of extracts of semipermeable membrane devices (SPMDs) deployed in streams in and around six major metropolitan areas: Atlanta, Georgia; Raleigh-Durham, North Carolina; Denver-Fort Collins, Colorado; Dallas-Fort

Worth, Texas; Portland, Oregon, and Milwaukee-Green Bay, Wisconsin.

## Methods

Semipermeable membrane devices were deployed in streams selected to cover the range of urban land-use intensity in and around six metropolitan areas (fig. 1). The distribution of the basins sampled in relation to ecoregion and land use in each metropolitan area is shown in figures 2–7. Extracts of SPMDs were analyzed to determine concentrations of hydrophobic organic contaminants. In addition to analysis of hydrophobic compounds, three assays were used to address mixtures and potential toxicity: (1) Fluoroscanner provides an estimate of the total concentration of polycyclic aromatic hydrocarbons (PAHs); (2) the P450RGS assay indicates the presence and levels of aryl hydrocarbon receptor agonists, such as PAHs, planar polychlorinated biphenyls (PCBs), chlorinated dibenzo-*p*-dioxins, and chlorinated dibenzofurans; and (3) Microtox® measures toxicological effects on photoluminescent bacteria.

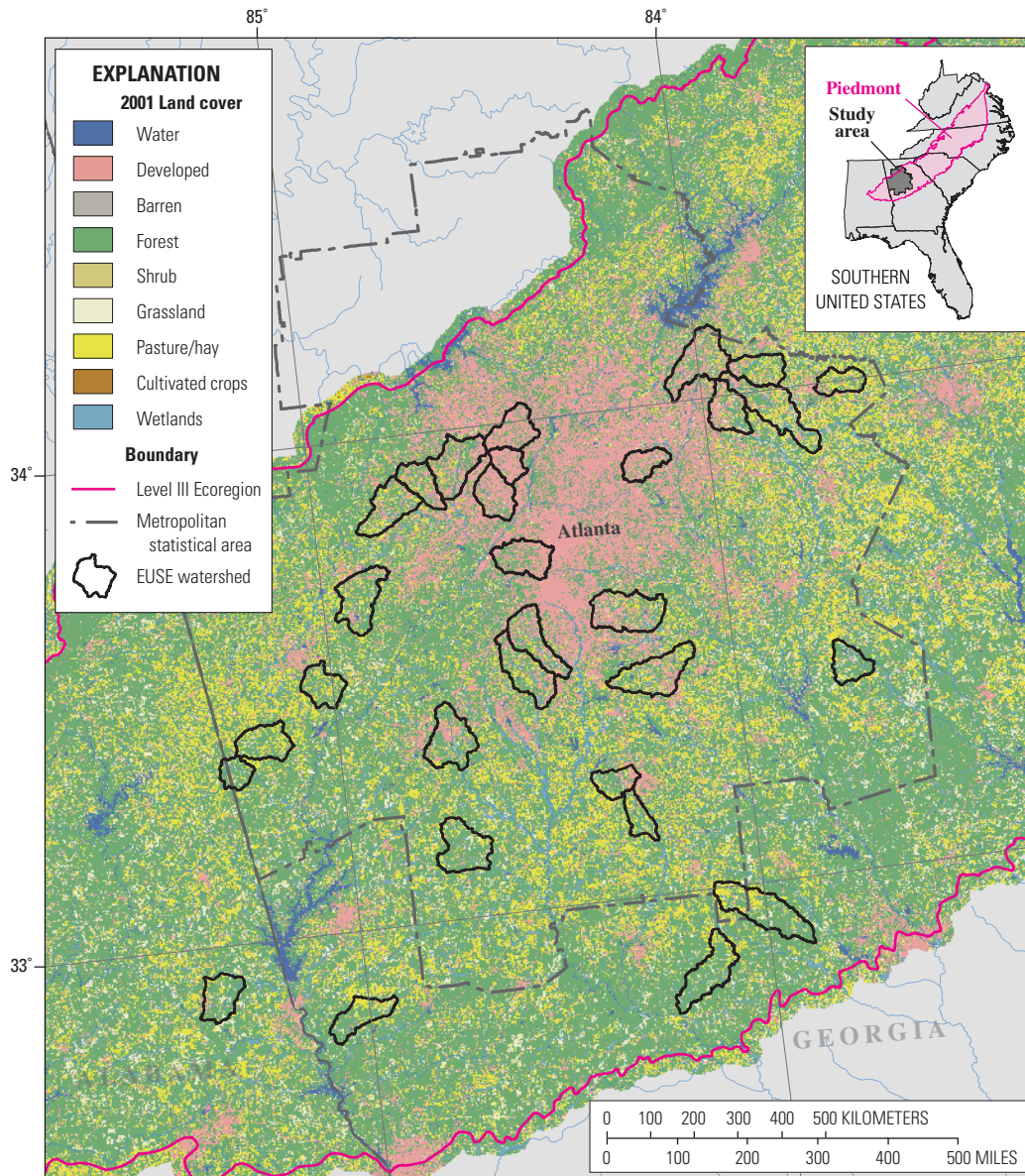


**Figure 1.** Locations of metropolitan areas sampled in the United States.

## Site Selection

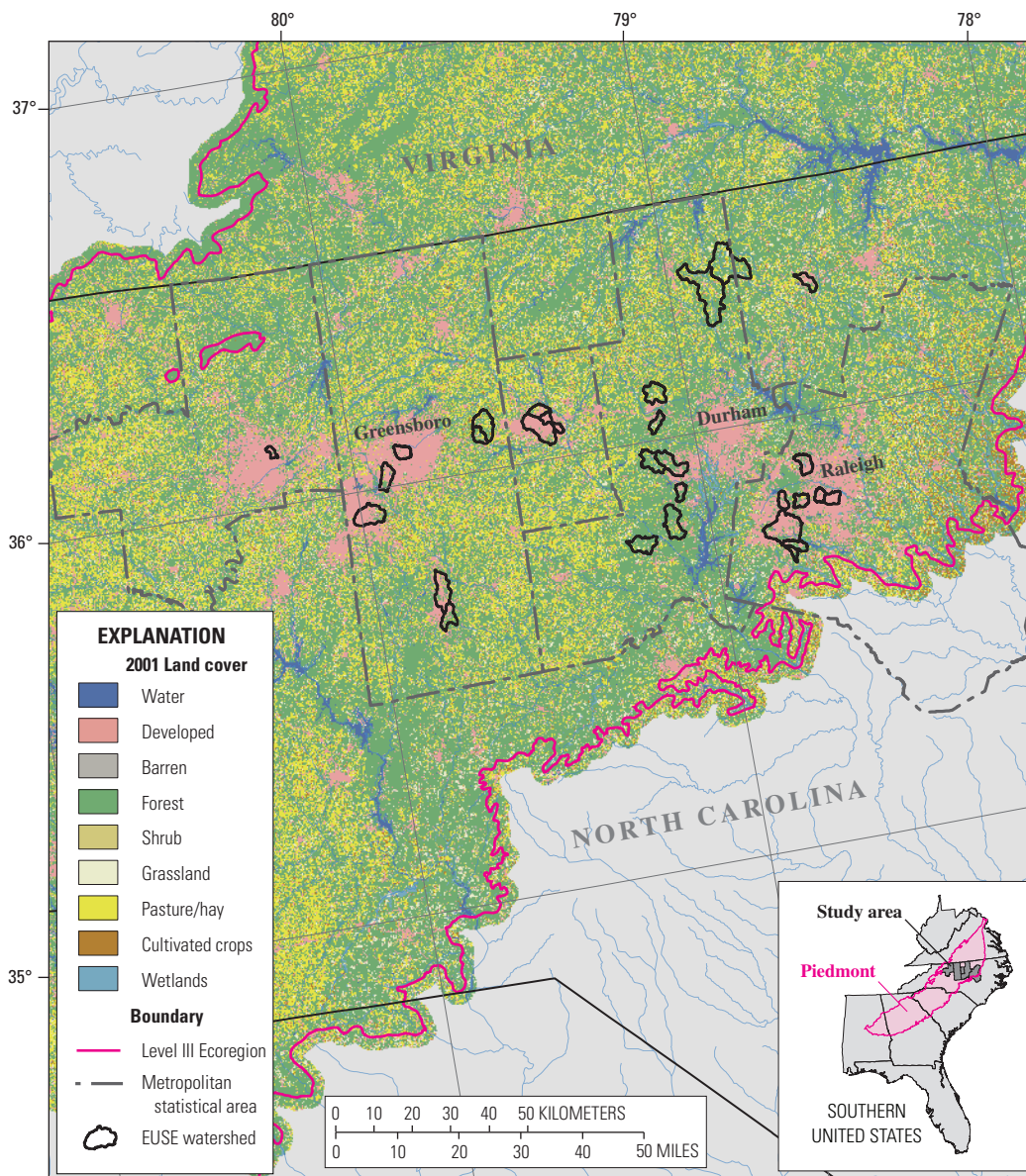
Previous studies have demonstrated that land cover alone does not adequately represent the degree of urbanization (Grove and Burch, 1997; McMahon and Cuffney, 2000). In this study, land cover, infrastructure, population, and socioeconomic variables were integrated into a multimetric index of urban intensity in the study area (UIISU) following the procedures outlined in McMahon and Cuffney (2000) and Tate and others (2005). A complete description of the data sources and methods used to characterize urbanization in these six metropolitan areas along with comparisons of the environmental settings and key features of urbanization can be found in Falcone and others (2006). A population of candidate basins (2<sup>nd</sup>–5<sup>th</sup> order streams) was developed using 30-meter (m) digital elevation models. From the candidate list, sites were selected after field reconnaissance to: (1) avoid point discharges, such as sewage treatment plants or industrial discharges; (2) minimize natural variability due to factors such as ecoregion, slope, basin size, canopy closure, and bed substrate; and (3) cover the range of urban land-use intensity in each metropolitan area as measured by the UIISU. After site selection, the UIISU variables were range-standardized to provide a UIISU score from 0–100 for each basin sampled within a metropolitan area.

Judgment was used to select variables to calculate the UIISU, which allowed locally important factors and urbanization patterns to be included to maximize the coverage of urban conditions within a particular metropolitan area. This approach resulted in a unique set of variables used to develop the UIISU in each metropolitan area. Therefore, the UIISU is not comparable across metropolitan areas. For example, 15 component variables were used in Denver-Fort Collins and 5 component variables were used in Raleigh-Durham (Falcone and others, 2006). Because the derivation of the UIISU is unique to each metropolitan area, the percent urban land cover (P\_NLCD1\_2) was used to compare urban intensity and to assess patterns of responses in the endpoints measured to urbanization across metropolitan areas. Percent urban land cover, as used in this report, is the aggregated National Land Cover Database (NLCD) 2001 level 1 “developed” category, including developed open space and low-, medium-, and high-intensity development. This variable was chosen because of the accessibility of the 2001 National Land Cover Database (U.S. Geological Survey, 2005) and the strong correlation with the UIISU in each of the metropolitan areas (Spearman’s rho 0.79–0.98).



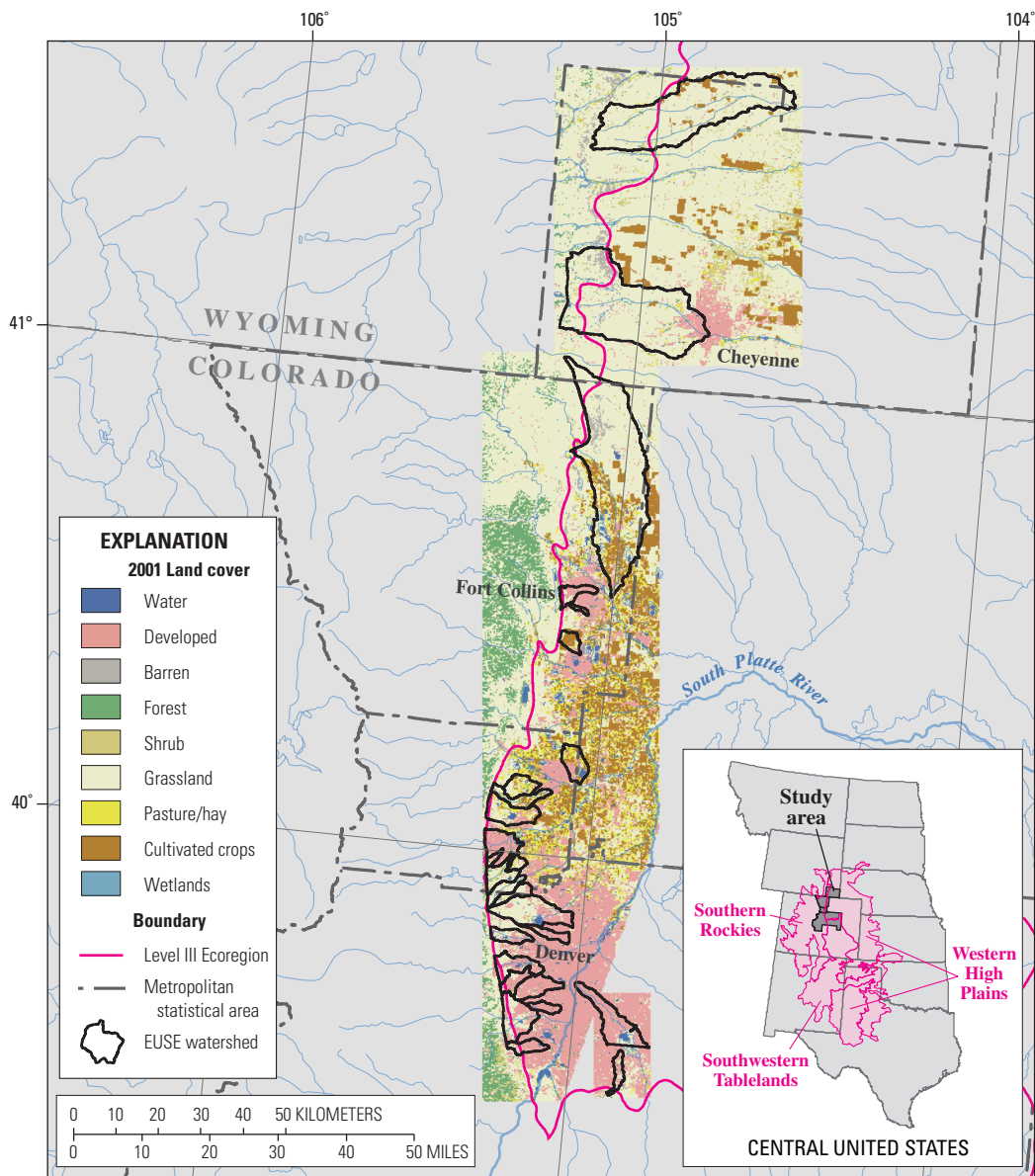
Base from U.S. Geological Survey digital files  
 U.S. Geological Survey National land cover database, 2001  
 accessed December 2005 at <http://www.mrls.gov/mrlc2k.nlcd.asp>

**Figure 2.** Distribution of basins sampled near Atlanta, Georgia, in relation to ecoregion and land use. [EUSE, effects of urbanization on stream ecosystems]



Base from U.S. Geological Survey digital files  
 U.S. Geological Survey National land cover database, 2001  
 accessed December 2005 at <http://www.mrls.gov/mrlc2k.nlcd.asp>

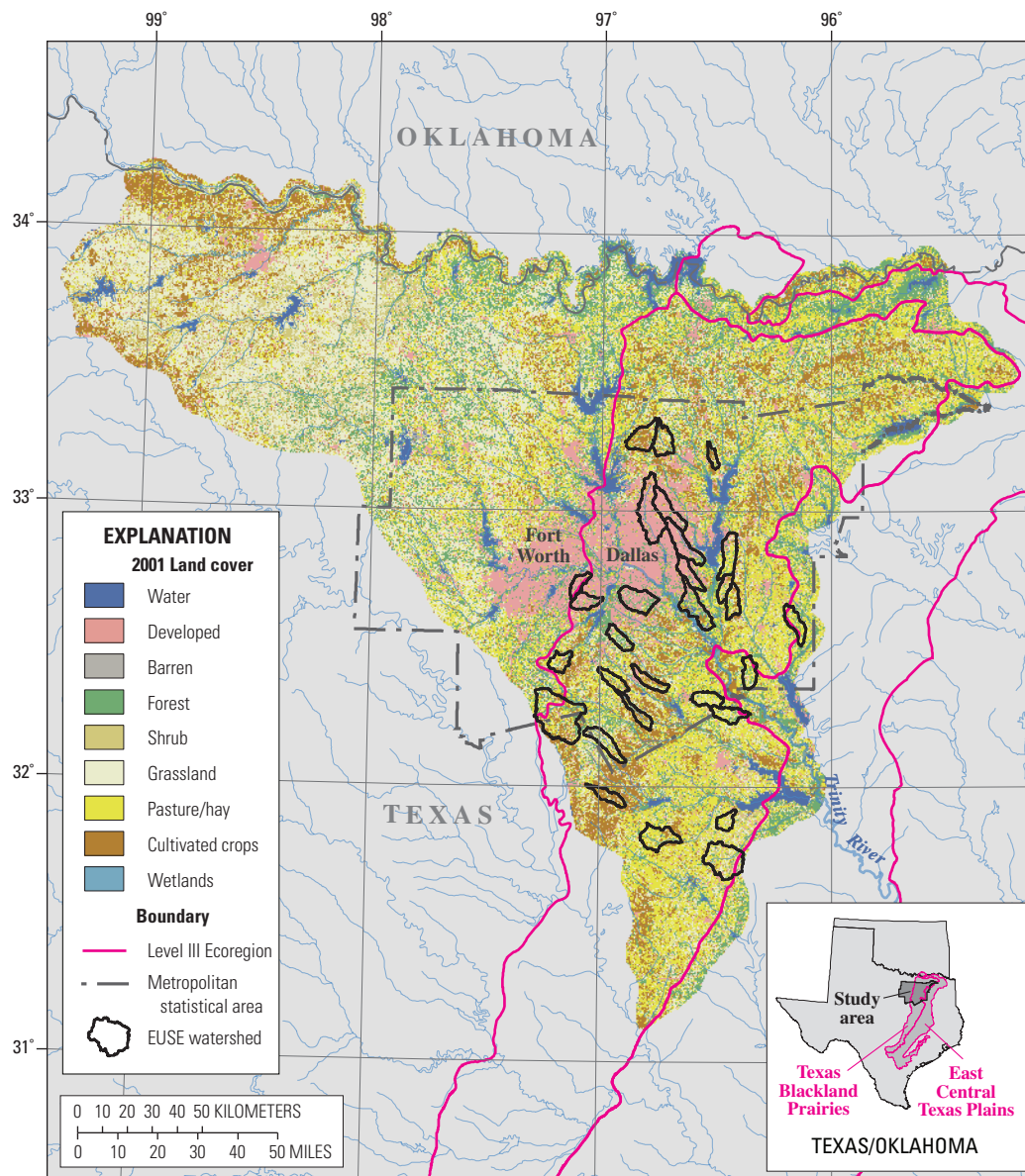
**Figure 3.** Distribution of basins sampled near Raleigh-Durham, North Carolina, in relation to ecoregion and land use. [EUSE, effects of urbanization on stream ecosystems]



Base from U.S. Geological Survey digital files  
U.S. Geological Survey National land cover database, 2001  
accessed December 2005 at <http://www.mrls.gov/mrlc2k.nlcd.asp>

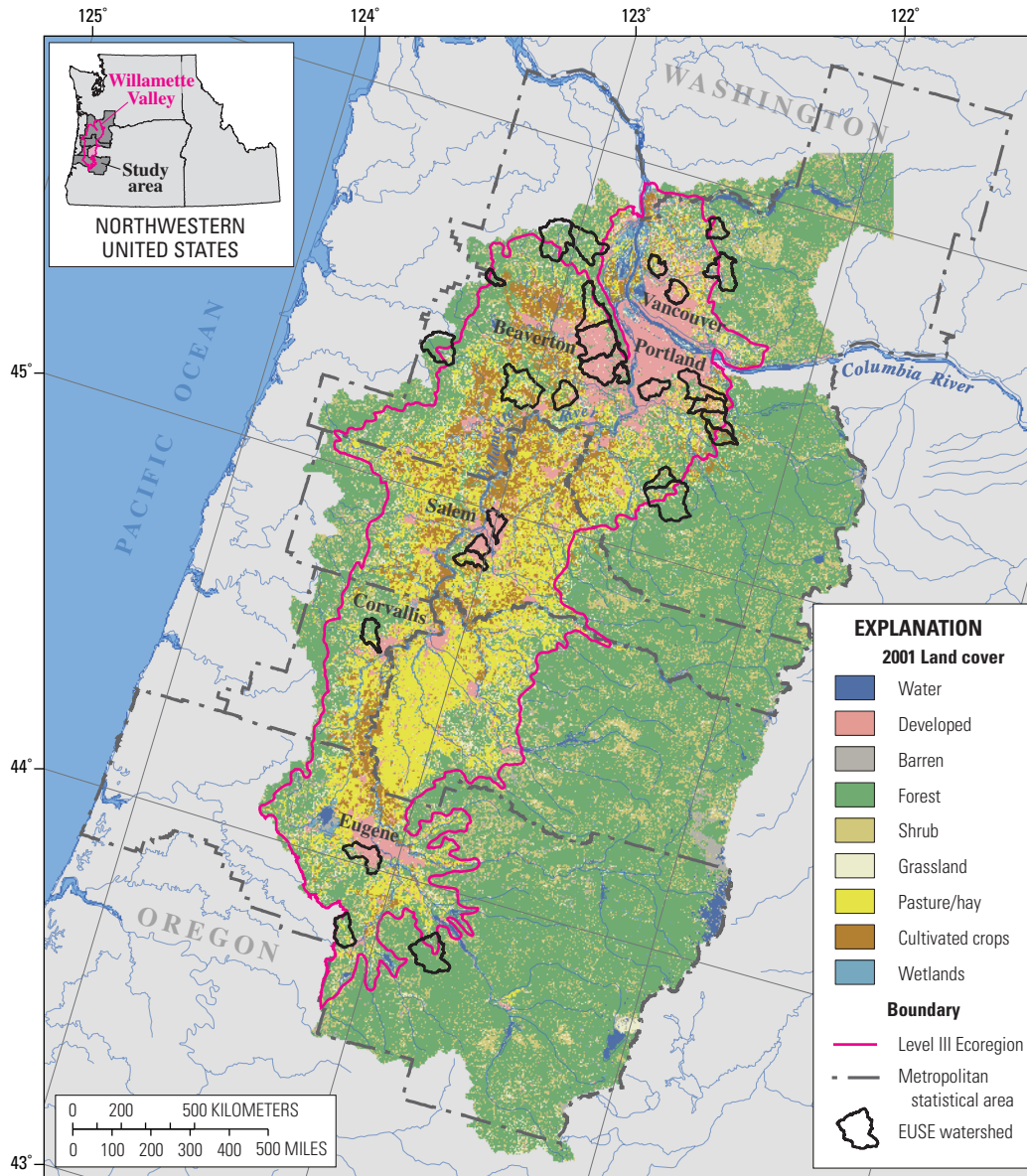
**Figure 4.** Distribution of basins sampled near Denver-Fort Collins, Colorado, in relation to ecoregion and land use. [EUSE, effects of urbanization on stream ecosystems]





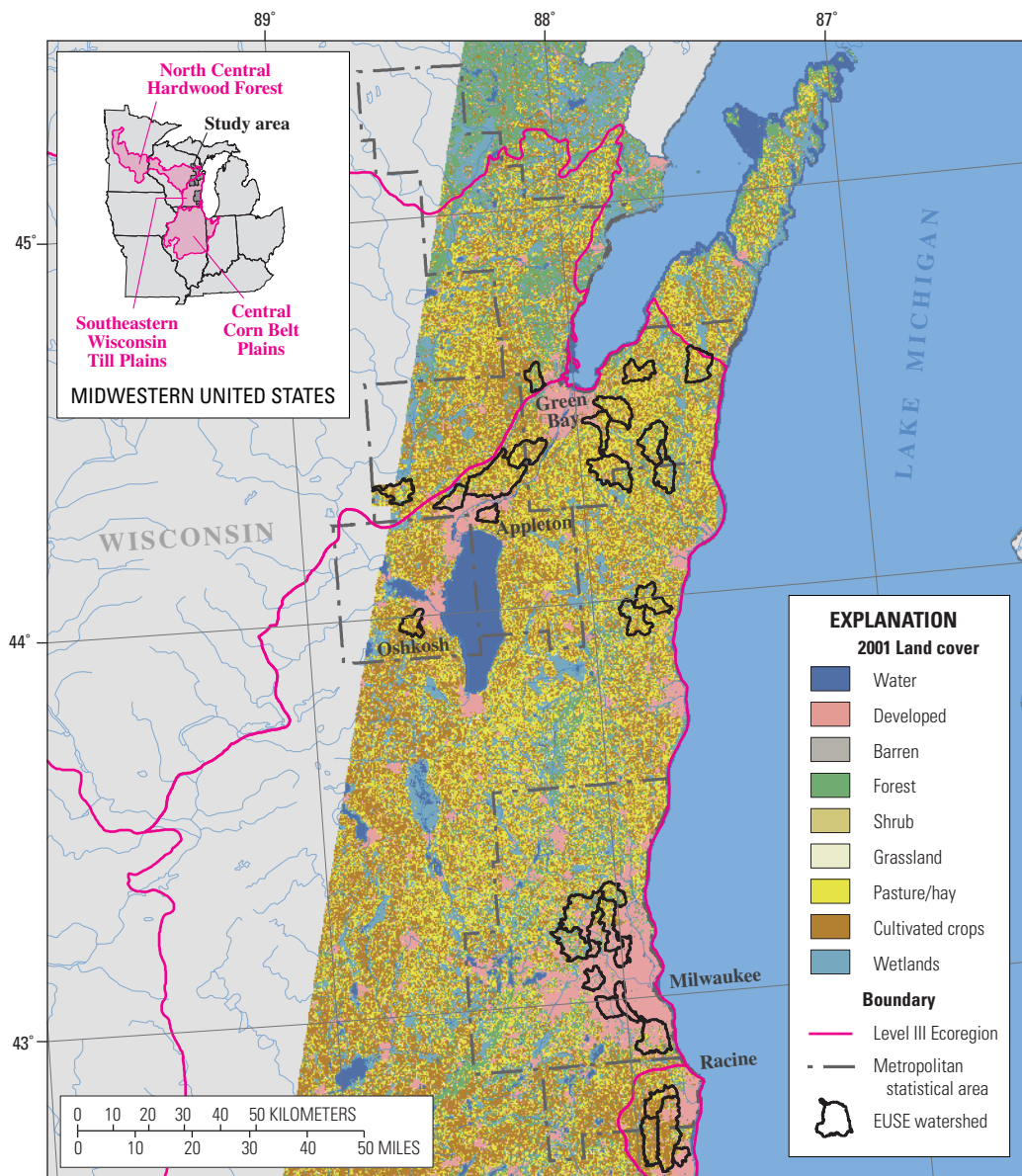
Base from U.S. Geological Survey digital files  
 U.S. Geological Survey National land cover database, 2001  
 accessed December 2005 at <http://www.mrls.gov/mrlc2k.nlcd.asp>

**Figure 5.** Distribution of basins sampled near Dallas-Fort Worth, Texas, in relation to ecoregion and land use. [EUSE, effects of urbanization on stream ecosystems]



Base from U.S. Geological Survey digital files  
 U.S. Geological Survey National land cover database, 2001  
 accessed December 2005 at <http://www.mrls.gov/mrlc2k.nlcd.asp>

**Figure 6.** Distribution of basins sampled near Portland, Oregon, in relation to ecoregion and land use. [EUSE, effects of urbanization on stream ecosystems]



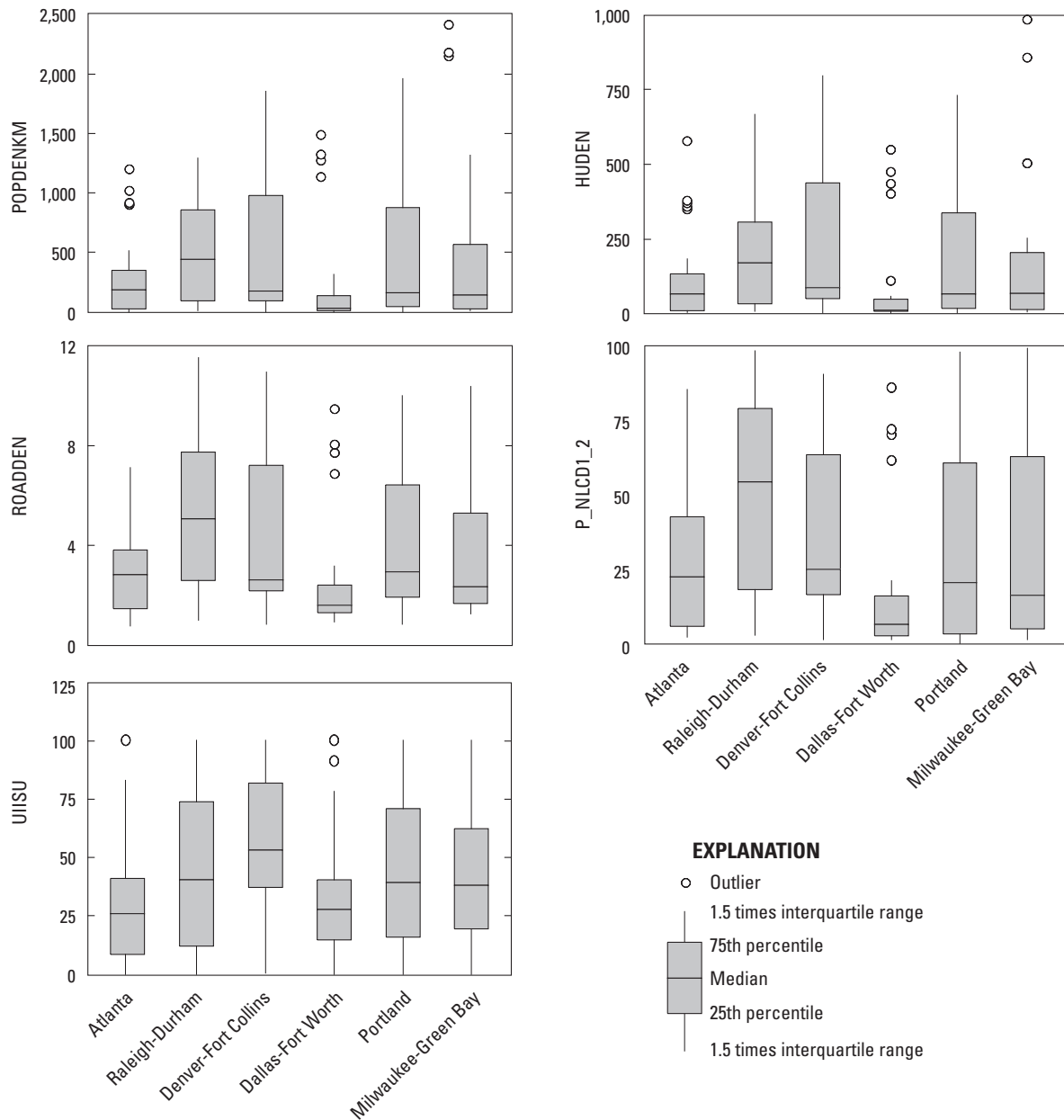
Base from U.S. Geological Survey digital files  
 U.S. Geological Survey National land cover database, 2001  
 accessed December 2005 at <http://www.mrls.gov/mrlc2k.nlcd.asp>

**Figure 7.** Distribution of basins sampled near Milwaukee-Green Bay, Wisconsin, in relation to ecoregion and land use. [EUSE, effects of urbanization on stream ecosystems]

Compared to the other metropolitan areas, streams sampled in Dallas-Fort Worth had the lowest median values and streams sampled in Raleigh-Durham had the highest median values for percent urban land cover (fig. 8). The median value for percent urban land cover in Raleigh-Durham (54.4) was almost 9 times the value in Dallas-Fort Worth (6.8). Even though streams selected in the Raleigh-Durham metropolitan area were evenly distributed along the defined gradient (UII), the overall design was skewed toward basins that were more urban compared to the other metropolitan areas not only based on 2001 land-cover data but also in terms of population

density, housing unit density, and road density (fig. 8). Falcone and others (2006) reported similar patterns for all of the streams selected for the urban gradient studies, so the loss of SPMDs during deployment (8 of 29 sites) in Denver-Fort Collins did not skew the overall design (sites where SPMDs were lost are not shown in figure 8).

Before investigating any patterns in the response variables, it is important not only to understand the urban gradient in terms of the features/patterns associated with urbanization (for example, population density, road density) but also the backdrop of existing land use over which urbanization is



**Figure 8.** Distribution of population density (POPDENKM, people per square kilometer), housing unit density (HUDEN, housing units per square kilometer), road density (ROADDEN, kilometers of road per square kilometer), percent urban land cover (P\_NLCD1\_2), and study unit index (UIISU) for basins where SPMDs were retrieved.

occurring. This is especially important because the presence and concentration of many of the hydrophobic compounds analyzed are known to be influenced by other land uses (for example, pesticides and agriculture). Even though the focus of this study was on the effects of urbanization, streams from a wide range of land-use conditions were sampled because the gradient design covered a range of urban land-use intensity in each of the six metropolitan areas and the fact that urbanization is occurring over a backdrop of different existing land uses in the metropolitan areas studied. In a detailed analysis of the streams sampled in this study, Falcone and others (2006) reported that urbanization is generally displacing shrub/grasslands in Denver-Fort Collins, agricultural land in Milwaukee-Green Bay, and forested land in Atlanta, Raleigh-Durham, Dallas-Fort Worth, and Portland.

## Assessment Approaches for Hydrophobic Contaminants in Streams

Hydrophobic contaminants at high enough concentrations in streams can result in harmful effects to aquatic biota, such as anomalies in fish, chronic and acute toxicity, and endocrine disruption (Klein, 1979; Pitt and others, 1995; Kime, 1998; McLachlan, 2001; Ma and others, 2005). Thus, the assessment of hydrophobic contaminants may be important in understanding stream responses to urbanization. Evaluation of contaminants in urban streams traditionally has been done through discrete sampling of the water column, bed sediments, and(or) biological tissues. Each approach has advantages and disadvantages, and the compounds of interest and goals of the study or assessment typically drive selection of sampling media.

Many compounds may be present in water at ultra-trace levels, which often are below the limits of detection for standard analytical methods. To detect such compounds would require solvent extraction of a large volume of water, which can be cumbersome and expensive. In addition, discrete samples of the water column provide “instantaneous” conditions and could miss significant changes in water quality that may occur over relatively short time intervals. This is especially pertinent in urban settings where events, such as spills, stormwater runoff, or pesticide applications, can be difficult to predict, and peak concentrations are likely to be missed by periodic or occasional sampling. In addition, the fraction of chemical bound to organic carbon in the water column may be the largest portion when whole water is analyzed, and aquatic biota do not readily take up this portion.

Determination of contaminant concentrations in bed sediment is a widely used approach in monitoring and assessing hydrophobic contaminant distributions in streams (Wong and others, 2000; Lopes and Furlong, 2001). In urban settings, care must be taken to sample sediment that is representative of recent transport and not affected by local sources, such as construction sites or bank erosion. This can be difficult in urban settings that are “flashy” due to impervious surfaces in

the basin. In addition, chemical analysis of bed sediment does not address questions related to bioavailability and, therefore, may not be related to ecological effects (Paine and others, 1996).

Some studies have monitored concentrations of hydrophobic organic compounds using suspended sediment sampling of urban streams (Mahler and Van Metre, 2003; Van Metre and Mahler, 2004). This approach has the advantages of directly sampling contaminants in transport and allowing computation of loads of trace contaminants in stormwater runoff (Mahler and Van Metre, 2003). Like other sediment analysis, this approach does not directly address questions related to bioavailability or ecological impacts; however, as with bed sediments, there are generally accepted sediment-quality guidelines (MacDonald and others, 2000) to which these data can be compared.

The use of biological tissue as a medium for chemical analysis can be hampered by the lack of a common aquatic species at all sampling sites or the lack of target organisms due to toxicity or other environmental conditions, such as high or low temperature. In addition, organisms move in response to stressors, and uptake and feeding rates vary due to factors such as water temperature or reproductive cycle. More importantly, aquatic organisms metabolize some commonly targeted compounds, such as PAHs.

SPMDs were used to concentrate hydrophobic organic contaminants as an alternative to sampling water, bed sediment, or biological tissues. SPMDs were developed by Huckins and others (1990) as a passive in-situ sampler to concentrate organics for subsequent chemical analysis. SPMDs have been deployed for more than a decade and have been used to show the presence, bioavailability, and bioconcentration potential of many organic compounds in water, sediment, and air (Huckins and others, 1990, 1993, 1996, 2006; Petty and others, 1995, 2000). These devices consist of a thin film of triolein, a neutral triglyceride found in many aquatic organisms, sealed inside a thin-walled tube of low-density polyethylene. Freely dissolved chemicals, of neutral polarity, diffuse through the membrane into the triolein. The permeability of the membrane is similar to fish gills in terms of selectivity. SPMDs concentrate dissolved neutral hydrophobic organic molecules, the fraction that is typically bioavailable. Accumulation of a compound in the SPMD is related to its molecular size and *n*-octanol-water partitioning coefficient ( $K_{ow}$ ). Compounds accumulated by SPMDs include PAHs, PCBs, dioxins, furans, certain pesticides, and other compounds with  $\log K_{ow}$  greater than 3.0.

SPMDs are stationary, give reproducible results, are durable in severe environments, and do not metabolize or deplete the sequestered compounds. SPMDs provide a distinct advantage over sampling other media by accumulating the bioavailable fraction of waterborne hydrophobic organic contaminants providing data relevant for assessment of exposure and potential toxicity (Gourlay and others, 2005; Huckins and others, 2006; Rosen and others, 2006). As with any methodology, however, there are limitations using

SPMDs. For example, they sample only nonpolar hydrophobic compounds (Huckins and others, 2006), which may not include other potentially toxic compounds present in urban streams. In addition, they can be contaminated during fabrication, handling, and processing because they are efficient at sequestering hydrophobic compounds.

For many compounds, SPMD concentrations can be used to backcalculate average water concentrations over the period of deployment using laboratory-determined sampling rates and equations and then compared to water-quality criteria or toxicity benchmarks (Huckins and others, 1993; Huggins, 1999; Booij and others, 2003). Data from the diffusion of performance reference compounds (PCRs), spiked into SPMDs prior to deployment, can be used to adjust for differences in exposure conditions that cause sampling rates to be shifted (from experimentally determined values) by a constant factor for all compounds (Huckins and others, 2002). PCRs were not used in SPMDs in this study, however, because they may cause response in the assays used.

## SPMD Deployment, Retrieval, and Extraction

SPMDs were deployed 4 to 6 weeks prior to sampling invertebrate, algae, and fish communities at each site. Some SPMDs were lost due to high flows and the inability to secure the devices to stable substrates (shifting sand). Two 15-centimeter (cm)-long SPMDs were constructed by Environmental Sampling Technologies (EST) Laboratory (St. Joseph, MO), placed around a stainless steel carrier inside a protective metal deployment device, sealed in airtight cans, and shipped overnight. The cans were kept frozen until the day of deployment and brought chilled to the field in coolers. In order to assess contamination during fabrication and shipping, one SPMD (fabrication blank) was shipped to and from EST with the batch for each metropolitan area, but remained sealed in the airtight can until cleanup and extraction. To assess potential contamination from the atmosphere during deployment and retrieval, one SPMD (trip blank) was exposed to air while SPMDs were being deployed and retrieved from the stream. A single trip blank was used for 5 to 10 sites. Replicate SPMDs were placed at three sites per metropolitan area.

Each site was assessed for proper placement of the SPMD. The ideal location had (1) at least 3 centimeters per second (cm/sec) of velocity but not so much current that floating debris could cause damage; (2) enough water depth that if streamflow decreased during the deployment period, the SPMD would not be exposed to air; and (3) minimal chances of vandalism. Once a location was found, a section of rebar 1 cm in diameter was driven into the substrate. A trip blank then was opened, exposing an SPMD to the atmosphere, and the SPMD for deployment was taken out of its sealed container, placed quickly underwater, and attached to the rebar with a plastic tie. Latex gloves were worn during all handling of SPMDs. Time of deployment was noted, and then the trip blank was sealed back in its can. Depth below the surface and

distance above the streambed were measured with a stadia rod. Point stream velocity was measured directly upstream from the SPMD by using a pygmy flowmeter. Field measurements of dissolved oxygen, pH, specific conductance, and water temperature were made using hand-held and calibrated meters in the general location of the SPMD.

During retrieval, the can with the trip blank SPMD was opened, the plastic tie was cut, and the SPMD was removed and cleaned of sediment and debris, then quickly placed back in its can, sealed, and chilled in a cooler. Time of retrieval was noted. Point velocity, depth below the surface, distance above the streambed, and field water-quality measurements were made.

Trip blanks and deployed SPMDs were brought back to the laboratory and frozen until their shipment to the EST Laboratory for extraction. Contaminant residues concentrated in the SPMDs were recovered and separated from the lipid by dialysis, following methods described by Huckins and others (1990). At the EST Laboratory, each SPMD was removed from the carrier and rinsed by immersion in 100 milliliters (mL) of hexane. Next, each SPMD was placed in a stainless steel pan, washed with tap water, and lightly brushed to remove material adhering to the surface. After washing, each SPMD was immersed in 1 normal HCL for 30 seconds, rinsed with tap water followed by acetone, and allowed to air dry. The SPMDs were then put in clean jars with at least 180 mL of hexane in an incubator at 18 degrees Celsius (°C) for 24 hours. The hexane was then decanted into another jar, the first jar was filled again with hexane, and both were further incubated for 8 hours, after which the contents were combined. The combined sample was then concentrated with a Kudern-Danish flask and further concentrated with nitrogen gas to approximately 1 mL and put into amber ampules. Extracts were placed into iso-octane for the chemical analysis and the P450RGS assay or dimethyl sulfoxide for Fluorocan and Microtox® analyses.

## Chemical Analysis

A portion of each SPMD dialysate in iso-octane solvent was chemically analyzed for hydrophobic compounds. Extracts from each site were shipped to the U.S. Geological Survey's National Water Quality Laboratory for identification and quantification by gas chromatography/mass spectrometry (GC/MS) analysis under two different ionization conditions. First, electron-capture negative ionization (ECNI) was used to measure halogenated compounds (organochlorine pesticides, PCBs, and brominated diphenyl ethers). The ECNI scan range was for compounds with 35 to 600 Daltons, the scan cycle rate was 1.3 seconds, the modifying gas was methane, and the source pressure was  $4.2 \times 10^{-4}$  torr. Samples were spiked with decafluorobiphenyl, alpha-HCH-d6, *p,p*-DDT-d8, and nonachlorobiphenyl for calculation of the percentage of recoveries. Second, electron ionization (EI), the conventional method for analyzing organic compounds by mass spectrometry, was

used to measure PAHs, alkyl phenols, polycyclic musks, and plant and fecal steroids. The EI scan range also was 35 to 600 Daltons, the scan cycle rate also was 1.3 seconds, but the source pressure was lower,  $2 \times 10^{-5}$  torr. Prior to the EI scan, samples were spiked with decafluorobiphenyl to calculate the percentage of recovery. Identification of target compounds was established by comparing the mass spectra and retention times for individual target compounds in sample extracts with these compounds in authentic standards. A six-point linear calibration curve was used for quantitation. Identification of unknown compounds was established by comparing the mass spectrum of the compound detected in the extract with

a library of mass spectra. Because authentic standards for the unknown compounds were not available, the quantification of an unknown compound is an estimate based on the response of the internal injection standard used for the quantification of the target compounds. Although the reported concentrations of unknown compounds are estimates, the data may still be used to compare relative concentrations over time or among sites, or to establish associations with various assays. A complete list of compounds analyzed, their Chemical Abstract Service (CAS) numbers, and reporting levels are given in table 1. Raw data are reported as nanograms of compound per SPMD.

**Table 1.** List of compounds analyzed in SPMD extracts.

[bold, not detected; CAS, Chemistry Abstracts Service Registry Number; na, not applicable; ng, nanograms; SPMD, semipermeable membrane device; g/mole, grams per mole; logKow, log octanol-water partition coefficient; \*, more than one isomer. Synonyms listed in parentheses under compound name are used in subsequent tables in this report]

Compound name	CAS number	Class/Use	Reporting level (ng/SPMD)	Molecular weight (g/mole)	logKow
1,2,3,4-tetramethylnaphthalene	103203-58-3	polycyclic aromatic hydrocarbon	1	188.31	
1,4-dichlorobenzene	106-46-7	deodorizer / moth repellent	100	147.00	3.28
1-methylnaphthalene	90-12-0	polycyclic aromatic hydrocarbon	25	142.20	3.87
1-methylpyrene	2381-21-7	polycyclic aromatic hydrocarbon	1	216.28	5.72
2,2',4,4'-tetrabromodiphenyl ether (BDE 47)	40088-47-9	fire retardant	2	485.80	6.05
2,2',4,4',5,5'-hexabromodiphenyl ether (BDE 153)	68631-49-2	fire retardant	2	643.60	7.90
2,2',4,4',5,6'-hexabromodiphenyl ether (BDE 154)	207122-15-4	fire retardant	2	643.60	7.82
2,2',4,4',5-pentabromodiphenyl ether (BDE 99)	32534-81-9	fire retardant	2	564.70	6.84
2,2',4,4',6-pentabromodiphenyl ether (BDE 100)	189084-64-8	fire retardant	2	564.80	7.24
2,6-dimethylnaphthalene	581-42-0	polycyclic aromatic hydrocarbon	25	156.23	4.31
2-heptadecanone	2922-51-2	fragrance	1	254.46	6.64
2-methylbenzothiophene	1195-14-8	s - polycyclic aromatic hydrocarbon	100	148.23	3.71
2-methylnaphthalene	91-57-6	polycyclic aromatic hydrocarbon	25	142.20	3.86
3-(4-methoxy phenyl)-2-2-propanoic acid (MPAA)	1929-29-9	personal care product (sunscreen)	1	250.30	2.65
3,4-dichlorophenyl isocyanate	102-36-3	plasticizer	200	188.01	3.88
3,5-diphenylpyrazole	1145-01-3	anti inflammatory	25	220.28	3.59
3-beta-coprostanol	360-68-9	fecal steroid	1,000	388.67	8.82
3-methyl-1H-indole (skatole)	83-34-1	fragrance	50	31.18	2.60
3-tert-butyl-4-hydroxyanisole (BHA)	25013-16-5	antioxidant	250	360.50	3.50
4-cumylphenol	599-64-4	nonionic detergent metabolite	100	212.29	4.12
4H-cyclopenta[def]phenanthrene	203-64-5	polycyclic aromatic hydrocarbon	1	190.24	4.60
4-n-octylphenol	1806-26-4	nonionic detergent metabolite	250	206.32	4.12
4-tert-octylphenol	140-66-9	nonionic detergent metabolite	250	206.32	4.12
5-methyl-1H-benzotriazole	136-85-6	anticorrosive	8,000	133.15	1.44
7H-benz[de]anthracen-7-one	82-05-3	polycyclic aromatic hydrocarbon	1	230.27	4.81
acetophenone	98-86-2	fragrance	100	120.15	1.58
acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	21145-77-7	fragrance	100	258.40	5.70
aldrin	309-00-2	organochlorine insecticide	4	364.92	6.50
alpha-HCH	319-84-6	organochlorine insecticide	16	290.83	3.80
anthracene	120-12-7	polycyclic aromatic hydrocarbon	100	178.23	4.61
anthraquinone	84-65-1	bird repellent on seeds	500	208.22	3.39
atrazine	1912-24-9	triazine herbicide	250	215.69	2.61

**Table 1.** List of compounds analyzed in SPMD extracts. — Continued

[bold, not detected; CAS, Chemistry Abstracts Service Registry Number; na, not applicable; ng, nanograms; SPMD, semipermeable membrane device; g/mole, grams per mole; logKow, log octanol-water partition coefficient; \*, more than one isomer. Synonyms listed in parentheses under compound name are used in subsequent tables in this report]

Compound name	CAS number	Class/Use	Reporting level (ng/SPMD)	Molecular weight (g/mole)	logKow
benfluralin	1861-40-1	dinitroaniline herbicide	2	335.29	5.29
benz[a]anthracene	56-55-3	polycyclic aromatic hydrocarbon	1	228.30	5.81
benz[c]acridine	225-51-4	n - polycyclic aromatic hydrocarbon	1	229.28	4.49
benzo[a]pyrene	50-32-8	polycyclic aromatic hydrocarbon	1	252.31	6.11
benzo[b]naphtho[2,1]thiophene	239-35-0	s - polycyclic aromatic hydrocarbon	1	234.32	5.34
benzo[b]naphtho[2,3-d]furan	243-42-5	furan	1	218.26	5.05
benzophenone	119-61-9	plasticizer / photoinhibitor	250	182.22	3.18
beta-HCH	319-85-7	organochlorine insecticide	64	290.83	3.80
beta-sitosterol	83-46-5	plant steroid	1,000	414.72	9.65
bis(2-ethylhexyl) phthalate (DEHP)	117-81-7	plasticizer	25	390.57	7.60
bisphenol A	80-05-7	plasticizer	500	228.29	3.40
bromacil	314-40-9	uracil herbicide	250	261.12	2.11
bromoform	75-25-2	antimicrobial / disinfectant	25	252.73	2.35
butyl citrate	77-94-1	plasticizer	1	360.44	3.28
caffeine	58-08-2	stimulant	250	194.19	0.01
camphor	76-22-2	flavorant	25	152.24	2.38
carbaryl	63-25-2	carbamate insecticide	500	201.23	2.36
carbazole	86-74-8	n - polycyclic aromatic hydrocarbon	250	167.21	3.72
chlorpyrifos	2921-88-2	organophosphate insecticide	4	350.59	4.96
cholesterol	57-88-5	plant/animal steroid	1,000	386.67	8.74
cis-chlordane	5103-71-9	organochlorine insecticide	8	409.78	5.38
cis-nonachlor	5103-73-1	organochlorine insecticide	8	444.23	6.20
cotinine	486-56-6	nicotine metabolite	250	176.22	0.07
cumene	98-82-8	solvent	50	120.20	3.66
dacthal (DCPA)	1861-32-1	chlorobenzoic acid ester herbicide	2	331.96	4.28
delta-HCH	319-86-8	organochlorine insecticide	32	290.83	4.10
diazinon	333-41-5	organothiophosphate insecticide	250	304.35	3.81
dibenzothiophene	132-65-0	s - polycyclic aromatic hydrocarbon	1	184.26	4.38
dieldrin	60-57-1	organochlorine insecticide	32	380.91	5.40
diethyl phthalate	84-66-2	plasticizer	25	222.24	2.42
diethyltoluamide (DEET)	134-62-3	insect repellent	250	191.27	2.02
d-limonene	5989-27-5	fragrance	25	136.23	4.23
endosulfan I	000959-98-8	organochlorine insecticide	8	406.93	3.83
endosulfan II	033213-65-9	organochlorine insecticide	8	406.93	3.83
endosulfan sulfate	1031-07-8	organochlorine insecticide	4	422.93	3.66
endrin	000072-20-8	organochlorine insecticide	128	380.91	5.20
endrin aldehyde	7421-93-4	organochlorine insecticide	32	380.91	4.80
endrin ketone	53494-70-5	organochlorine insecticide	4	380.91	4.99
ethyl citrate	77-93-0	plasticizer	250	402.50	4.92
fipronil	120068-37-3	phenyl pyrazole insecticide	8	437.15	4.00
fluoranthene	206-44-0	polycyclic aromatic hydrocarbon	50	202.25	4.93
fluorene	86-73-7	polycyclic aromatic hydrocarbon	1	166.20	4.18
gamma-HCH	58-89-9	organochlorine insecticide	16	290.83	3.72
heptachlor epoxide	1024-57-3	organochlorine insecticide	16	389.32	4.98



**Table 1.** List of compounds analyzed in SPMD extracts. — Continued

[bold, not detected; CAS, Chemistry Abstracts Service Registry Number; na, not applicable; ng, nanograms; SPMD, semipermeable membrane device; g/mole, grams per mole; logKow, log octanol-water partition coefficient; \*, more than one isomer. Synonyms listed in parentheses under compound name are used in subsequent tables in this report]

Compound name	CAS number	Class/Use	Reporting level (ng/SPMD)	Molecular weight (g/mole)	logKow
hexachlorobenzene (HCB)	118-74-1	organochlorine insecticide	4	284.78	5.73
hexahydrohexamethylcyclopentabenzopyran (HHCB)	1222-05-5	fragrance	100	258.40	5.90
indole	120-72-9	animal repellent	50	117.15	2.14
isoborneol	124-76-5	fragrance	100	154.25	3.24
isophorone	78-59-1	solvent	25	138.21	1.70
isoquinoline	119-65-3	fragrance	25	129.16	2.08
menthol	89-78-1	flavorant	100	156.27	3.38
metalaxyl	57837-19-1	benzenoid fungicide	250	279.34	1.65
methylanthracene*	610-48-0	polycyclic aromatic hydrocarbon	1	192.26	5.07
methyldibenzofuran*	60826-62-2	furan	1	132.16	3.22
methyl salicylate	119-36-8	liniment / flavorant	250	152.15	2.55
methyl triclosan	4640-01-1	antimicrobial / disinfectant	1	166.15	5.00
methyl-9H-fluorene*	1730-37-6	polycyclic aromatic hydrocarbon	1	180.25	4.15
metolachlor	51218-45-2	acetanilide herbicide	100	283.80	3.13
mirex	2385-85-5	organochlorine insecticide	4	545.55	6.89
naphthalene	91-20-3	polycyclic aromatic hydrocarbon	25	128.18	3.30
npeo1-total	26027-38-2	nonionic detergent metabolite	1,500	na	5.60
npeo2-total	26027-38-2	nonionic detergent metabolite	2,000	na	5.60
o,p'-DDD	53-19-0	organochlorine insecticide	64	320.05	6.02
o,p'-DDE	3424-82-6	organochlorine insecticide	16	318.03	6.00
o,p'-DDT	789-02-6	organochlorine insecticide	64	354.49	6.79
octachlorostyrene	29082-74-4	organochlorine / industrial by product	2,500	379.10	7.46
opeo-1	26636-32-8	nonionic detergent metabolite	100	na	5.50
opeo-2	26636-32-8	nonionic detergent metabolite	250	na	5.50
oxadiazon	19666-30-9	oxadiazolone herbicide	1	345.22	4.80
oxychlorodane	27304-13-8	organochlorine insecticide	4	423.77	5.48
p,p'-DDD	72-54-8	organochlorine insecticide	64	320.05	6.02
p,p'-DDE	72-55-9	organochlorine insecticide	64	318.03	6.51
p,p'-DDT	50-29-3	organochlorine insecticide	64	354.49	6.91
para-cresol	106-44-5	wood preservative	250	108.94	1.94
para-nonylphenol (total)	84852-15-3	nonionic detergent metabolite	25	na	5.60
PCB 101	37680-73-2	polychlorinated biphenyl	32	326.44	6.80
PCB 110	38380-03-9	polychlorinated biphenyl	32	326.44	6.22
PCB 118	31508-00-6	polychlorinated biphenyl	32	326.44	7.12
PCB 138	35065-28-2	polychlorinated biphenyl	4	360.88	7.44
PCB 146	51908-16-8	polychlorinated biphenyl	2	360.88	7.12
PCB 149	38380-04-0	polychlorinated biphenyl	16	360.88	7.28
PCB 151	51908-16-8	polychlorinated biphenyl	4	360.88	7.12
PCB 170	35065-30-6	polychlorinated biphenyl	2	395.33	8.27
PCB 174	38411-25-5	polychlorinated biphenyl	2	395.33	8.27
PCB 177	52663-70-4	polychlorinated biphenyl	2	395.33	8.27
PCB 180	35065-29-3	polychlorinated biphenyl	2	395.33	8.27

**Table 1.** List of compounds analyzed in SPMD extracts. — Continued

[bold, not detected; CAS, Chemistry Abstracts Service Registry Number; na, not applicable; ng, nanograms; SPMD, semipermeable membrane device; g/mole, grams per mole; logKow, log octanol-water partition coefficient; \*, more than one isomer. Synonyms listed in parentheses under compound name are used in subsequent tables in this report]

Compound name	CAS number	Class/Use	Reporting level (ng/SPMD)	Molecular weight (g/mole)	logKow
PCB 183	52663-69-1	polychlorinated biphenyl	2	395.33	8.27
PCB 187	52663-68-0	polychlorinated biphenyl	2	395.33	8.27
PCB 194	35694-08-7	polychlorinated biphenyl	2	429.77	8.68
PCB 206	40186-72-9	polychlorinated biphenyl	2	464.22	9.14
PCB70	32598-11-1	polychlorinated biphenyl	32	291.99	6.23
pentachloroanisole (PCA)	1825-21-4	wood preservative (organochlorine)	2	280.37	5.45
phenanthrene	85-01-8	polycyclic aromatic hydrocarbon	50	178.24	4.46
phenol	108-95-2	antimicrobial / disinfectant	100	94.12	1.46
prometon	1610-18-0	triazine herbicide	250	225.00	4.92
pyrene	129-00-0	polycyclic aromatic hydrocarbon	25	202.26	4.88
stigmasterol	19466-47-8	plant steroid	1,000	416.74	9.73
toxaphene*	8001-35-2	organochlorine insecticide	4	448.26	5.90
trans-chlordane	005103-74-2	organochlorine insecticide	8	409.78	6.10
trans-nonachlor	39765-80-5	organochlorine insecticide	16	444.23	6.08
tri(2-butoxyethyl) phosphate	78-51-3	fire retardant / plasticizer	250	398.48	3.75
tri(2-chloroethyl)phosphate	115-96-8	fire retardant / plasticizer	250	269.49	1.51
tri(dichloroisopropyl)phosphate	13674-87-8	fire retardant / plasticizer	250	430.91	3.76
tributyl phosphate	126-73-8	solvent / plasticizer	500	266.32	4.00
triclosan	3380-34-5	antimicrobial / disinfectant	500	289.55	4.76
trifluralin	1582-09-8	dinitroaniline herbicide	2	335.29	5.34
trimethylnaphthalene*	2245-38-7	polycyclic aromatic hydrocarbon	1	176.20	5.00
triphenyl phosphate	115-86-6	fire retardant / plasticizer	250	266.32	4.00

## Fluoroscan Assay

SPMD extracts were exposed to ultraviolet light at 280 nanometers (nm) wavelength to determine the presence of PAH compounds using the Fluoroscan method developed by Johnson and others (2004). These tests were conducted at the U.S. Geological Survey's Columbia Environmental Research Center in Columbia, MO. A fluorometer was used to measure the fluorescence of the extract from each site and compared to a standard curve for pyrene. Samples were run in duplicate, and quality-control (QC) samples included solvent, fabrication, and trip blanks. Average values of the duplicates are reported in appendix 1. The value for each site was reported as the equivalent number of micrograms of pyrene per milliliter of SPMD extract (PYR-EQ) that would produce the same fluorescence as the sample. Because many PAHs can fluoresce and maximum excitation wavelength varies by compound, fluorescence, in general, and this method, in particular (single 280 nm excitation), is not able to quantify individual PAHs but can serve as a screen for environmental samples (sediment, fish bile, SPMD extracts). Various adaptations of fluorescent

assays, using single and multiple excitation wavelengths, have been used to measure relative amounts of PAHs in environmental samples (Johnson and others, 2004; Lee and Anderson, 2005).

## Microtox® Assay

The Microtox® bioassay measures the light production of photo-luminescent bacteria when exposed to SPMD extracts. The biochemical pathway for light production is inhibited by a wide range of compounds that are sequestered by the SPMDs if present in the water column. Microtox® bioassays were conducted according to the standard protocol for the basic test described in Johnson (1998) and Johnson and others (2004). Suspensions of a selected strain of the luminescent bacteria (*Vibrio fischeri*, Azur Environmental, Inc., Carlsbad, CA) were exposed to SPMD extract in a standard four-tube 1:2 dilution series with controls. Samples were incubated at 17 °C in a temperature-controlled incubator, and light emissions were measured after 5 minutes with a luminometer (Azur Analyzer 500). Phenol and dimethyl sulfoxide (DMSO) were used as the

assay's standard positive and negative controls, respectively, and the carrier solvent did not exceed 5 percent of the sample volume. Samples were run in triplicate and QC samples included fabrication blanks, trip blanks, phenol control (positive), and DMSO solvent. Microtox® results are reported as the effective concentration in milligram equivalents SPMD/milliliter carrier solvent that reduces light output by 50 percent (EC50).

## P450RGS Assay

Many of the more highly toxic compounds found in stormwater runoff are capable of inducing cytochrome P450 enzyme activity (Villeneuve and others, 1997). The cytochrome P450 enzyme system is the major cellular pathway for the metabolism of xenobiotic compounds. Bioassays based on the cytochrome P450 family of enzymes have been used as biomarkers of exposure to PAHs, planar PCBs, chlorinated dibenzo-*p*-dioxins, chlorinated dibenzofurans, chlorodiphenyl ethers, chlorinated naphthalenes, and plant flavones (Safe, 1990; Drastichova, 2004). Many of these compounds are highly toxic, and increases in P450 activity in fish have been associated with changes in reproduction, growth, pathology, and physiology (Parrott and Tillitt, 1997).

The same biochemical pathway (aryl hydrocarbon receptor) responsible for the toxicity of dioxin and dioxin-like chemicals in whole organisms is used in the P450RGS assay. The P450RGS assay responds to a wide variety of compounds and offers a cost-effective alternative to traditional whole animal tests with fish (Ang and others, 2000). Given that no single species of fish was available across the six metropolitan areas, SPMDs provide a mechanism to concentrate aryl hydrocarbon receptor agonists from the water column.

The P450RGS assays were conducted at the U.S. Army Corps of Engineers Research and Development Center in Vicksburg, MS. The assay employs human hepatoma cells that are stably transfected with a plasmid containing the human CYP1A promoter sequence fused to the firefly luciferase gene, which is used as a reporter. The induction of the CYP1A1 gene results in the production of luciferase, and the light produced responds to the presence of compounds that bind to the aryl hydrocarbon receptor (AhR) in a quantitative fashion. Details of the protocols can be found in Ang and others (2000). The assay conforms to American Public Health Association Standard Method 8070 (American Public Health Association, 1996), American Society for Testing and Materials Standard Guide E-1853 (American Society for Testing and Materials, 1997), and U.S. Environmental Protection Agency (USEPA) Method 4425 (U.S. Environmental Protection Agency, 2000b). Samples were run in triplicate, and QC samples included the standard reference material NIST NY/NJ 1944, fabrication blanks, trip blanks, and isoctane solvent. The standard reference material for the P450RGS assay was 2.5 grams of NIST NY/NJ dissolved in 0.2 mL of isoctane. This standard reference sediment includes 24 PAHs

ranging from 0.3 to 9 milligrams per kilogram (mg/kg) dry weight (DW), 35 PCBs ranging from 3 to 80 micrograms per kilogram ( $\mu\text{g}/\text{kg}$ ) DW, 11 chlorinated pesticides ranging from 6 to 120  $\mu\text{g}/\text{kg}$  DW, and 17 dioxins/furans ranging from 0.04 to 6  $\mu\text{g}/\text{kg}$  DW. Results from the laboratory are reported in toxic equivalents (TEQs), which are the number of picograms of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) in 1 mL of SPMD extract that would cause the same response as the sample.

## Quality Assurance

Spike recoveries for GC/MS analysis ranged from 80.4 to 136 percent (appendix 1). Analysis of variance showed no difference in spike recoveries among metropolitan areas ( $p < 0.01$ ). Regression analysis showed no relation ( $p < 0.01$ ) between the percentage of recovery and the amount of urbanization in the basins (UIISU and P\_NLCD1\_2) in any metropolitan area. No corrections to data were made based on spike recoveries.

Duplicate SPMDs were deployed at three sites per metropolitan area. Duplicate values above the method reporting limit differed by no more than 20 percent for any chemical concentration or assay when measured above the reporting limit in both replicates. In the few cases where compounds were detected in only one of the duplicates, the maximum value for chemical concentration and assays were used for all subsequent analyses.

Twenty-eight compounds were detected in solvent, fabrication, or trip blanks (table 2). For the purposes of this report, all values of field samples were considered nondetections if they were less than the maximum value reported for any solvent, fabrication, or trip blank from that study area. Values of field samples greater than QC samples were corrected by subtracting the maximum value of the solvent, fabrication, or trip blank for each sample. The concentrations used for corrections and the percentage of samples above the reporting level prior to corrections but below the censoring value are shown in table 2.

## Normalizing for Time of Exposure

SPMDs were not deployed for the same amount of time at all sites. In Denver-Fort Collins, SPMDs at eight sites were lost after approximately 5 weeks due to high flows and unstable bed substrates (shifting sand). At that time, the decision was made to remove the remaining SPMDs in Denver-Fort Collins. To adjust for differences in exposure time, values for chemical concentrations and assays, after corrections for blank contamination, were normalized to a 45-day exposure. All subsequent analyses used blank corrected/time normalized data. Appendix 1 contains the chemical concentration and assay data used for data analysis (blank corrected, time normalized), along with latitude/longitude, deployment date, retrieval date, drainage area, urban index (UIISU), percent

**Table 2.** List of compounds detected in SPMD quality-control (QC) samples (trip blanks, fabrication blanks, solvent blanks) applicable to each metropolitan area, concentration used for correction based on QC sample, and percent of samples above reporting level but below concentration in QC sample.

Compound name	Atlanta		Raleigh-Durham		Denver-Fort Collins		Dallas-Fort Worth		Portland		Milwaukee-Green Bay	
	Conc.	Percent	Conc.	Percent	Conc.	Percent	Conc.	Percent	Conc.	Percent	Conc.	Percent
1-methylnaphthalene			36.1	13	116.0	100	32.1					
2,6-dimethylnaphthalene	30.7	7	56.2	20	153.0	100	60.1	21				
2-methylbenzothiophene	465.0	71										
2-methylnaphthalene	29.3		49.0	33	52.7	57	66.1	83	36.9	68	38.4	31
7H-benz[de]anthracen-7-one			1.2						3.9			
acetophenone	58.3		49.1		65.5	29						
AHTN	14.1											
anthracene	4.2											
BDE 153											0.5	
BDE 47					0.2		0.5					
BDE 99							0.2					
benzophenone	53.6		92.6		215	24						
butyl citrate											8.42	
cholesterol	1,130.0	7	3,110.0	80	3,720.0	100					1,744.0	76
DEHP	2,700.0	79	3,890.0	97	1,980.0	100	2,010.0	96	584.0	43	879.0	69
dibenzothiophene	30.1											
diethyl phthalate	572.0	89	187.0	13	291.0	76	344.0	92	194.0	57	295.0	83
d-limonene	102.0	43	58.2	27								
fluoranthene	1.4		5.3									
fluorene	22.8											
isoquinoline							41.6					
methylanthracene	1,618.3	25										
methyl dibenzofuran	76.7											
MPAA	5,487.4	82	26.7	27	18.6	81			46.8	39		
naphthalene			2.0		3.1		2.4					
phenanthrene	3.8		5.2	3	3.5	10						
pyrene	1.0		5.8									
trimethylnaphthalene	2,438.0	32					17.8	13				

urban land cover (P\_NLCD1\_2), road density (ROADDEN), population density (POPDENKM), and housing unit density (HUDEN) for basins where SPMDs were retrieved.

## Data Analysis

Average water concentrations during the period of deployment for 14 hydrophobic compounds were calculated by using published calibration data (Huckins and others, 2006) and an Excel-based water concentration calculator (Dave Alvarez, U.S. Geological Survey, written commun., 2006). An estimated water temperature of 18 °C was used in the model at all sites for all compounds, which was close to actual stream temperatures based on deployed temperature recorders. The compounds were selected on the basis of having published calibration data and water-quality benchmarks. These calculated water concentrations were compared with published values for aquatic protection or human-health benchmarks, whichever was the lowest, to assess the potential toxicity for these 14 compounds.

An important step to evaluating the risk posed by environmental contaminants in streams is a screening process that compares chemical concentrations to toxicological benchmarks or concentrations that are not hazardous (Suter, 1996). The greatest number of relevant toxicological benchmarks are the U.S. National Ambient Water Quality Criteria for Protection of Aquatic Life (U.S. Environmental Protection Agency, 2006a), but these benchmarks were established as regulatory values that are designed to protect most aquatic species most of the time (Stephan and others, 1985). Other benchmarks for drinking water have been established to protect human health (Toccalino and others, 2006; U.S. Environmental Protection Agency, 2006b). In order to minimize the likelihood of screening out a potentially toxic compound, it is best to be conservative and use more protective benchmarks whenever available (Suter, 1996). Therefore, the lowest available benchmarks were used for comparison with calculated water concentrations in this study. Exceedance of any of these benchmarks, however, does not necessarily indicate that toxicity is occurring. Many urban streams have more tolerant taxa that are less sensitive to toxicity and environmental contaminants. In addition, the health-based screening levels from Toccalino and others (2006) were developed assuming a life-time exposure of the measured concentration through drinking water; however, small urban streams are not used as drinking-water sources. Even so, the comparisons of estimated water concentrations to these benchmarks were used as a screening-level assessment to provide a perspective on the potential for adverse effects, as well as a framework for comparing relative toxicity among compounds or sites. Two highly urbanized sites in Atlanta—Rottenwood Creek Interstate North Parkway near Symrna, GA (85 percent urban land cover) and Jackson Creek at Lester Road near Lilburn, GA (67 percent urban land cover)—were not included in the

analysis because of missing data. Table 3 contains a list of compounds and benchmarks used in this analysis.

Spearman's rank correlation coefficients ( $\rho$  values) were calculated to measure the strength of monotonic relations between each SPMD endpoint (chemical and assays) with urban intensity as measured by the percent urban land cover (P\_NLCD1\_2). In addition, scatterplots with LOWESS smoothing were used to examine potential patterns (for example, linear as opposed to threshold response) in the relations between each SPMD endpoint and the percent of urban land cover.

Because of the high number of nondetections for many of the target compounds, descriptive statistics for chemical concentrations were calculated (median, 25<sup>th</sup> and 75<sup>th</sup> percentiles) using the robust log-probability regression method (ROS) as described in Helsel (2005). Summary statistics were calculated for variables with percent detections greater than 25 percent using the USGS left-censored data analysis library (Slack and others, 2003) for SPLUS 7.0.

## Results

Stage and water temperature were measured continuously during the period SPMDs were deployed. These records were examined to determine if the number of storm events and(or) water temperatures would be expected to affect the ability to relate the endpoints to urban land-use intensity within each metropolitan area and to compare responses among the six metropolitan areas studied. Based on examination of in-stream stage and local rainfall records, there were at least two and as many as seven rainfall events in every basin to cause surface runoff during the period SPMDs were deployed. Although the number and magnitude of storm events varied, the ability to relate the endpoints to urban land-use intensity was determined not to be affected. SPMD uptake rates are influenced by water temperature, but based on the in-stream temperature measurements, the differences between the sites were not enough to affect the observed differences in the endpoints measured within and(or) the patterns of responses among metropolitan areas.

### Occurrence and Distribution of Hydrophobic Organic Contaminants

In this study, 140 compounds were targeted or identified by GC/MS analysis; of these, 67 were not detected (table 1). In theory, SPMDs are well suited for neutral organic compounds with log octanol-water partition coefficients ( $K_{ow}$ )  $\geq 3.0$ . Noteworthy compounds with  $\log K_{ow} > 3.0$  that were not detected include DDT, DDD, DDE, several PCB congeners, and several organochlorine insecticides. These are noteworthy because of their known toxicity to aquatic organisms and(or) known AhR activity (induction in the P450RGS assay). Several compounds with  $\log K_{ow} < 3.0$  were detected.

**Table 3.** Summary of potential toxicity for 14 hydrophobic compounds based on the highest calculated average water concentration during the deployment period for sites sampled in six metropolitan areas of the United States.

[ $\mu\text{g/L}$ , micrograms per liter; BHC, benzene hexachloride; DCPA (dacthal), dimethyl tetrachloroterephthalate; PCB, polychlorinated biphenyl]

Compound	Lowest screening value <sup>a</sup> (in $\mu\text{g/L}$ )	Highest average water concentration <sup>b</sup> (in $\mu\text{g/L}$ )	Potential toxicity in the water column?
Anthracene	0.0013 <sup>c</sup> (Chronic, Biota)	0.0132	Yes
Benzo (a) pyrene	0.014 <sup>c</sup> (Chronic, Biota)	0.002	No
BHC (Lindane)	0.08 <sup>c</sup> (Chronic, Biota)	Not detected	? <sup>d</sup>
Chlordane	0.0043 <sup>c</sup> (Chronic, Biota)	0.0004	No
Chlorpyrifos	0.041 <sup>c</sup> (Chronic, Biota)	0.028	No
DCPA	70 <sup>f</sup> (Human Health)	0.0005	No
Diazinon	0.043 <sup>c</sup> (Chronic, Biota)	0.301	Yes
	0.17 <sup>c</sup> (Acute, Biota)		Yes
Dieldrin	0.002 <sup>f</sup> (Human Health)	0.005	Yes
Fluoranthene	6.16 <sup>c</sup> (Chronic, Biota)	0.086	No
Fluorene	3.9 <sup>c</sup> (Chronic, Biota)	1.426	No
Heptachlor epoxide	0.0038 <sup>c</sup> (Chronic, Biota)	0.0008	No
Naphthalene	23.4 <sup>c</sup> (Chronic, Biota)	0.967	No
Total PCBs	0.014 <sup>c</sup> (Chronic, Biota)	0.0002	No
Phenanthrene	3.23 <sup>c</sup> (Chronic, Biota)	0.084	No

<sup>a</sup> Toxicological benchmark values for screening potential contaminants of concern for effects on aquatic life or human health.

<sup>b</sup> Average water concentration for duration of SPMD deployment calculated using the highest SPMD extract concentration of all sites sampled. Calculated with Water Estimator Model provided by D. Alvarez (Columbia, MO). Water concentrations calculated assuming 18 degrees Celsius water temperature, except total PCBs, which assumed 10 degrees Celsius.

<sup>c</sup> Suter (1996).

<sup>d</sup> The reporting limit is above the screening value; therefore, it is possible that Lindane was present in some streams above the screening value.

<sup>e</sup> U.S. Environmental Protection Agency (2006).

<sup>f</sup> Toccalino (2006).

A breakdown of detection frequencies by compound and metropolitan area is given in appendix 2. In order to compare compounds with similar environmental chemistries or sources, compounds are grouped by chemical class or use. The following compounds were detected: 2 wood preservatives, 6 insecticides (parent compounds), 5 herbicides, 22 polycyclic aromatic hydrocarbons, 2 dibenzofurans, 4 PCB congeners, 7 compounds associated with fragrances or personal care products, 4 steroids associated with wastewater, 5 polydibromated diphenyl ethers (flame retardants), 3 plasticizers, 3 antimicrobials/disinfectants, and 3 detergent metabolites (appendix 2).

The most frequently detected compound was pentachloroanisole. It was detected in 71 percent of the streams sampled in the six metropolitan areas combined (appendix 2). Pentachloroanisole is a microbial breakdown product of the wood

preservative pentachlorophenol. In addition to pentachloroanisole, five PAH compounds—methyl anthracene, fluoranthene, pyrene, phenanthrene, and benz[*a*]anthracene—were detected in more than half the streams sampled. Fluoranthene and pyrene were measured above the reporting level in every stream sampled in Raleigh-Durham. Naphthalene was detected in every stream sampled in Denver-Fort Collins.

Of the 73 compounds detected, 49 were detected in Raleigh-Durham, 48 in Atlanta and Milwaukee-Green Bay, 40 in Denver-Fort Collins, 39 in Portland, and 36 in Dallas-Fort Worth. There were no compounds detected at only one site in the six metropolitan areas studied (Tehuacana Ck at Rural Rd 27 Nr Wortham, Texas—P\_NLCD1\_2 = 6.9). The highest number of compounds detected at any one site was 32 (Pigeon House Br at Crabtree Blvd at Raleigh, North

Carolina—P\_NLCD1\_2 = 98.4). Raleigh-Durham (13) and Atlanta (10) had the most number of streams sampled with more than 20 compounds detected.

## Calculated Water Concentrations Compared to Benchmarks

Three of 14 hydrophobic organic compounds examined (21 percent) had calculated average water column concentrations from SPMD extracts above toxicological screening benchmarks at one or more sites in the six metropolitan areas (table 3). Of these three compounds, aquatic-life benchmarks were exceeded by one PAH (anthracene) and one organophosphate insecticide (diazinon); human-health benchmarks were exceeded only by the organochlorine insecticide dieldrin. Technically, the human-health benchmark for dieldrin applies to drinking water and assumes lifetime consumption at these concentrations. Water concentrations for the other 11 hydrophobic compounds were considerably lower than toxicological benchmarks although the highest chlorpyrifos concentration was relatively close (68 percent) to the published chronic value.

Of the 163 streams examined, 15 (9.2 percent) had calculated average water concentrations above one or more

benchmark values (table 4). Comparisons between metropolitan areas show that Raleigh-Durham and Milwaukee-Green Bay had the most streams with calculated water concentrations above screening benchmarks (5), followed by Denver-Fort Collins (2), Portland (2), and Atlanta (1). None of the streams sampled in the Dallas-Fort Worth metropolitan area had concentrations above benchmark values for any of the 14 compounds examined. Ratios of calculated water concentrations to screening benchmarks (toxicity ratio, TR) ranged from 1.50 in North Fork Deep Creek in Barton, Oregon (dieldrin) to 10.0 at the Little Menomonee River at Milwaukee, Wisconsin (anthracene). Anthracene had the highest mean TR of 7.2, followed by diazinon (6.9) and dieldrin (1.8). Calculated water concentration for both anthracene and dieldrin exceeded screening benchmarks in seven streams, whereas diazinon was exceeded only in one stream, Lena Gulch at Wheat Ridge, Colorado. Calculated diazinon water concentration was not only higher than the chronic aquatic-life benchmark, but also well above the acute benchmark. The percent of urban land cover for basins where calculated water concentrations were above screening benchmarks generally was high, and no streams in basins below 27 percent urban land cover were found to exceed benchmark values.

**Table 4.** Streams with one or more calculated average water concentrations above threshold values. Ratio of calculated value to threshold value (if greater than 1) shown.

[P\_NLCD1\_2, percent urban land cover]

Metropolitan area	Site name	P_NLCD1_2	Anthracene	Dieldrin	Diazinon
Atlanta	Nickajack Creek at U.S. 78/278 near Mableton, GA	66.17		1.61	
Raleigh-Durham	SW Prong Beaverdam Creek at Raleigh, NC	94.16		1.77	
Raleigh-Durham	N Buffalo Creek at Greensboro, NC	96.91		1.92	
Raleigh-Durham	Bowen Branch near Mouth at Winston-Salem, NC	96.91		1.95	
Raleigh-Durham	Dutchmans Branch at SR 1386 near McCullers Crossroads, NC	39.29	5.05		
Raleigh-Durham	Foundry Branch at Mouth near Oxford, NC	52.98	5.36		
Denver-Fort Collins	Little Dry Creek below Lowell Street near Westminster, CO	90.37	6.88		
Denver-Fort Collins	Lena Gulch at Lewis Meadows Park at Wheat Ridge, CO	68.76			6.94
Portland	North Fork Deep Creek at Barton, OR	27.06		1.50	
Portland	Johnson Creek at Circle Avenue, OR	41.94		1.53	
Milwaukee-Green Bay	Pike River at Cth A near Kenosha, WI	27.32		2.38	
Milwaukee-Green Bay	Honey Creek near Portland Avenue at Wauwatosa, WI	99.06	7.42		
Milwaukee-Green Bay	Root River at Layton Avenue at Greenfield, WI	92.84	7.87		
Milwaukee-Green Bay	Menomonee River at Menomonee Falls, WI	30.39	7.87		
Milwaukee-Green Bay	Little Menomonee River at Milwaukee, WI	44.28	9.97		
AVERAGE		62.9	7.2	1.8	6.9

## Relations with Urban Intensity

A goal of this study was to determine if HOCs and their potential toxicity responded in some way along a gradient of urban land-use intensity. Thirty-nine compounds were detected in 25 percent or more of the streams in at least one metropolitan area (appendix 2). The concentration of these 39 compounds, the total number of compounds detected, and the results of the three bioassays were used as endpoints in correlation analysis to assess relations with the percent of urban land cover (P\_NLCD1\_2). Correlations were analyzed for data from each of the six metropolitan areas and for nationally aggregated data. For the purposes of this report, relations between endpoints and urban intensity were considered “strong” if  $\rho \geq 0.5$  and “very strong” if Spearman’s  $\rho \geq 0.75$ .

Of the 43 endpoints examined, 29 were at least strongly related to increases in urban intensity in one or more metropolitan areas or nationally (appendix 2). These 29 endpoints included 26 individual compounds: 16 PAHs, a wood preservative (pentachloroanisole), 2 insecticides (chlorpyrifos and chlordane), 3 herbicides (benfluralin, trifluralin, and dacthal), a synthetic musk (hexahydrohexamethylcyclopentabenzopyran, HHCB), 2 furans (methyl-dibenzofuran and benzo[*b*]naphtho[2,3-*d*]furan), and a fire retardant (BDE 47). In addition to these individual compounds, the total number of compounds detected and the results of the Fluoroscan and P45ORGS assays were found to be strongly or very strongly related to urban intensity. To facilitate comparisons among metropolitan areas, the Spearman’s  $\rho$  value for each of the 29 endpoints is given in table 5, and scatterplots with LOWESS smoothing lines with P\_NLCD1\_2 are shown in figures 9–16.

## Number of Compounds Detected

The number of compounds detected increased with percent of urban land cover in all six metropolitan areas and was very strongly related (Spearman’s  $\rho \geq 0.75$ ) to P\_NLCD1\_2 in Atlanta, Denver-Fort Collins, and Milwaukee-Green Bay, and strongly related ( $\rho \geq 0.5$ ) in Raleigh-Durham, Dallas-Fort Worth, and at the national scale (table 5). A slightly weaker but significant relation ( $\rho = 0.46$ ,  $p = 0.01$ ) was observed in Portland. More scatter around the LOWESS line is evident in Raleigh-Durham, Portland, and Milwaukee-Green Bay compared to the other metropolitan areas (fig. 9). In streams with between 0 and 10 percent urban land cover, the range in the number of compounds detected was 0–8 in Dallas-Fort Worth, 4–10 in Atlanta, 5–15 in Denver-Fort Collins, 3–15 in Raleigh-Durham, 1–15 in Milwaukee-Green Bay, and 1–18 in Portland.

## Wood Preservatives

Of the two wood preservatives analyzed, pentachloroanisole (PCA) was detected in more than 38 percent of the streams sampled in all six metropolitan areas, whereas *para*-cresol was measured above the reporting level at only one site in Atlanta (appendix 2). The reporting limit for *para*-cresol was 250 ng/SPMD compared to 2 ng/SPMD for pentachloroanisole. Concentrations of PCA increased with increasing urban land cover; strong relations were observed with urban intensity in Atlanta, Raleigh-Durham, Denver-Fort Collins, and Milwaukee-Green Bay. Significant but weaker relations were observed in Portland and where the data were combined nationally (table 5). Pentachloroanisole concentration in one Atlanta stream, (Utoy Creek at Great Southwest Pkwy near Atlanta, Georgia — P\_NLCD1\_2 = 60.56) was much higher (56.6 ng/SPMD) compared to the other streams (fig. 10; appendix 1). The LOWESS smooth lines of PCA concentration with P\_NLCD1\_2 for Atlanta, Raleigh-Durham, and Denver-Fort Collins show no sharp increases in concentration along the gradient (fig. 10, LOWESS line). Compared to Atlanta, Raleigh-Durham, and Denver-Fort Collins, PCA concentrations at the low end of the gradient are higher in Portland and Milwaukee-Green Bay, and a steeper slope is evident at the low end of the gradient (0 to 40 percent urban land cover) followed by a plateau in concentrations as urban land cover increases (fig. 10).

## Insecticides

Two insecticides, chlorpyrifos and chlordane, were detected in greater than 25 percent of the streams in at least one metropolitan area (appendix 2; table 5). Chlorpyrifos was detected in at least one stream in every metropolitan area, but detection frequencies were too low for correlation analysis in Denver-Fort Collins and Milwaukee-Green Bay. One stream in Milwaukee-Green Bay (Black Creek at Curran Road near Denmark, Wisconsin) with a low amount of urban land cover (P\_NLCD1\_2 = 3.23) had a much higher concentration (895 ng/SPMD) of chlorpyrifos than the other streams (fig. 10; appendix 1). A very strong relation was observed between concentrations of chlorpyrifos and urban land cover in Atlanta, and the median concentration for Atlanta (11.4 ng/SPMD) was higher than in the other metropolitan areas (appendix 2). Strong relations between chlorpyrifos concentration and urban intensity were noted in Raleigh-Durham and Dallas-Fort Worth (table 5). In Atlanta, concentrations increased at approximately 10 percent urban land cover compared to 60 percent in Raleigh-Durham (fig. 10, LOWESS lines). In Portland, the relation between chlorpyrifos concentration and percent urban land cover was weak, even though it was detected in 32 percent of the streams. Concentrations at the low end of the urban gradient in Dallas-Fort Worth and Portland were higher compared to streams with comparable urban land cover in the other metropolitan areas.



**Table 5.** Spearman's rank correlations ( $\rho$ ) and significance levels ( $p$ ) for endpoints and percent urban land cover in basin (P\_NLCD1\_2) with  $\rho > 0.5$  in one or more metropolitan areas. (<, compound detected but at less than 25% of the streams in this metropolitan area; nd, compound not detected in this area. Correlation analysis was not performed for compounds detected at < 25% of sites within a metropolitan area or nationally).

Class or Use	Atlanta		Raleigh-Durham		Denver-Fort Collins		Dallas-Fort Worth		Portland		Milwaukee-Green Bay		National	
	$\rho$	$p$	$\rho$	$p$	$\rho$	$p$	$\rho$	$p$	$\rho$	$p$	$\rho$	$p$	$\rho$	$p$
Number of compounds detected	0.85	<0.0001	0.71	<0.0001	0.90	<0.0001	0.61	0.002	0.46	0.015	0.77	<0.0001	0.69	<0.0001
PCA	0.64	0.000	0.65	0.000	0.57	0.007	0.20	0.346	0.45	0.016	0.49	0.007	0.36	<0.0001
chlorpyrifos	0.78	<0.0001	0.63	0.000	<	<	0.69	0.000	0.32	0.101	<	<	0.39	<0.0001
total chlordanes*	<	<	0.67	<0.0001	nd	nd	<	<	nd	nd	nd	nd	<	<
trifluralin	0.58	0.001	0.61	0.000	<	<	<	<	0.43	0.023	0.42	0.023	0.46	<0.0001
benfluralin	0.61	0.000	0.33	0.075	nd	nd	<	<	nd	nd	<	<	<	<
DCPA	nd	nd	<	<	0.74	0.000	<	<	nd	nd	nd	nd	<	<
2,6-dimethylnaphthalene	0.56	0.002	0.40	0.029	<	<	nd	nd	<	<	<	<	0.34	<0.0001
trimethylnaphthalene	0.76	<0.0001	0.50	0.005	0.80	<0.0001	<	<	<	<	<	<	0.46	<0.0001
1,2,3,4-tetramethylnaphthalene	0.67	<0.0001	0.55	0.002	0.89	<0.0001	<	<	nd	nd	nd	nd	0.45	<0.0001
fluorene	0.72	<0.0001	0.41	0.026	0.69	0.001	<	<	<	<	0.40	0.033	0.30	<0.0001
methyl-9H-fluorene	0.67	0.000	0.56	0.001	0.81	<0.0001	<	<	<	<	<	<	0.44	<0.0001
methyl anthracene	0.82	<0.0001	0.64	0.000	0.87	<0.0001	<	<	<	<	0.58	0.001	0.48	<0.0001
phenanthrene	0.83	<0.0001	0.59	0.001	0.74	0.000	0.41	0.045	0.22	0.258	0.84	<0.0001	0.61	<0.0001
4H-cyclopenta[ <i>def</i> ]-phenanthrene	0.75	<0.0001	0.64	0.000	0.73	0.000	<	<	<	<	0.69	<0.0001	0.50	<0.0001
fluoranthene	0.85	<0.0001	0.65	0.000	0.80	<0.0001	0.45	0.027	0.51	0.006	0.84	<0.0001	0.69	<0.0001
pyrene	0.87	<0.0001	0.75	<0.0001	0.84	<0.0001	0.41	0.046	0.41	0.030	0.84	<0.0001	0.66	<0.0001
1-methylpyrene	<	<	0.61	0.000	0.86	<0.0001	<	<	nd	nd	0.60	0.001	<	<
benz[ <i>a</i> ]anthracene	0.92	<0.0001	0.77	<0.0001	0.88	<0.0001	0.48	0.017	0.45	0.017	0.79	<0.0001	0.57	<0.0001
benzo[ <i>a</i> ]pyrene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.80	<0.0001	<	<
dibenzothiophene	0.79	<0.0001	0.67	<0.0001	0.82	<0.0001	<	<	nd	nd	<	<	0.38	<0.0001
benzo[ <i>b</i> ]naphtho[2,1]-thiophene	0.72	<0.0001	0.67	<0.0001	0.84	<0.0001	<	<	nd	nd	0.65	0.000	0.56	<0.0001
benz[ <i>c</i> ]acridine	<	<	0.56	0.001	0.72	0.000	<	<	nd	nd	0.66	0.000	<	<

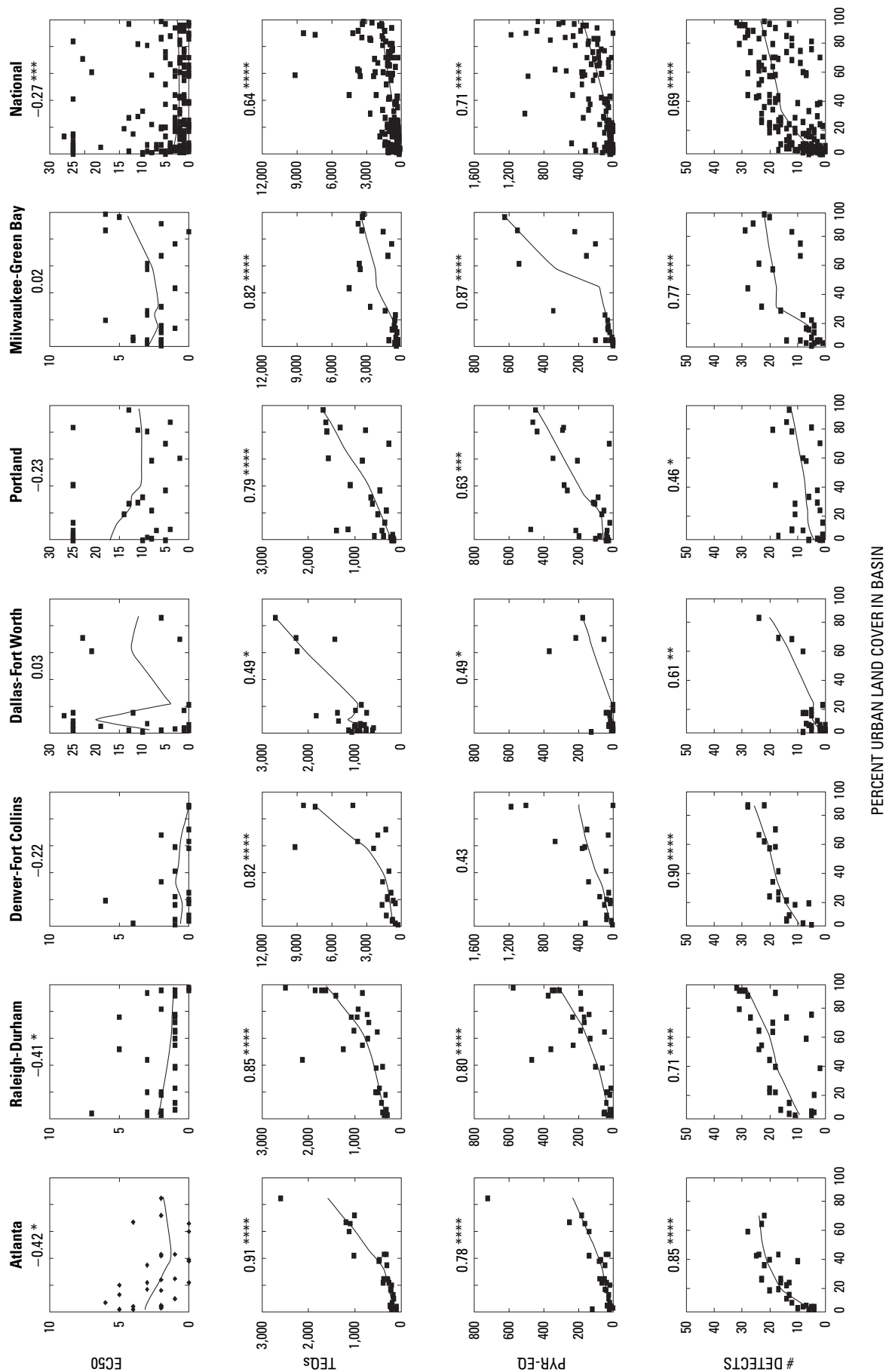
[PCA, pentachloroanisole; DCPA (dacthal), dimethyl tetrachloroterephthalate; PAH, polycyclic aromatic hydrocarbon; HHCb, hexahydrohexamethylcyclopentabenzopyran; >, greater than]

**Table 5.** Spearman's rank correlations (rho) and significance levels (p) for endpoints and percent urban land cover in basin (P\_NLCD1\_2) with rho > 0.5 in one or more metropolitan areas. (<, compound detected but at less than 25% of the streams in this metropolitan area; nd, compound not detected in this area. Correlation analysis was not performed for compounds detected at < 25% of sites within a metropolitan area or nationally). — Continued

[PCA, pentachloroanisole; DCPA (dacthal), dimethyl tetrachloroterephthalate; PAH, polycyclic aromatic hydrocarbon; HHCB, hexahydrohexamethylcyclopentabenzopyran; >, greater than]

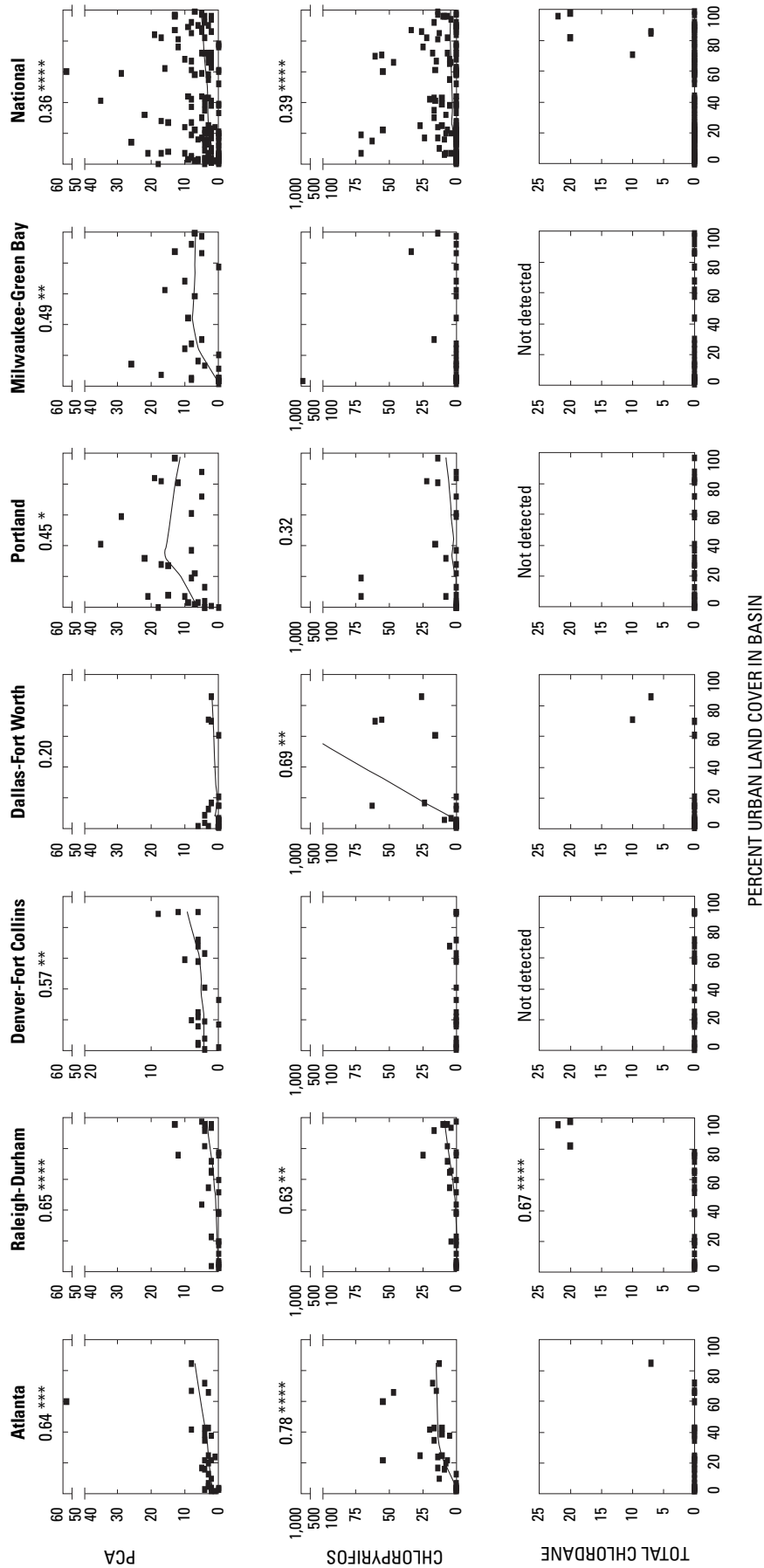
Class or Use	Atlanta		Raleigh-Durham		Denver-Fort Collins		Dallas-Fort Worth		Portland		Milwaukee-Green Bay		National	
	rho	p	rho	p	rho	p	rho	p	rho	p	rho	p	rho	p
methyl dibenzofuran	0.73	<0.0001	0.44	0.014	0.76	<0.0001	<	<	nd	nd	<	<	0.23	0.004
benzo(b)naphtho-[2,3-d] furan	<	<	nd	nd	nd	nd	<	<	nd	nd	0.65	0.000	<	<
HHCB	0.27	0.162	0.66	<0.0001	0.50	0.021	<	<	<	<	<	<	0.39	<0.0001
BDE 47	<	<	<	<	0.38	0.086	0.61	0.002	<	<	<	<	0.28	0.000
Microtox assay	-0.42	0.019	-0.41	0.025	-0.22	0.342	0.03	0.876	-0.23	0.235	0.02	0.917	-0.27	0.000
Fluorescan Assay	0.78	<0.0001	0.80	<0.0001	0.43	0.053	0.49	0.016	0.63	0.000	0.87	<0.0001	0.71	<0.0001
P450RGS Assay	0.91	<0.0001	0.85	<0.0001	0.82	<0.0001	0.49	0.015	0.79	<0.0001	0.82	<0.0001	0.64	<0.0001
Total number of end-points > 0.5	20		21		20		3		3		14		9	

\*Total chlordanes = sum of *cis*-chlordanes and *trans*-chlordanes concentrations, substituting zero for values below the method reporting limit.

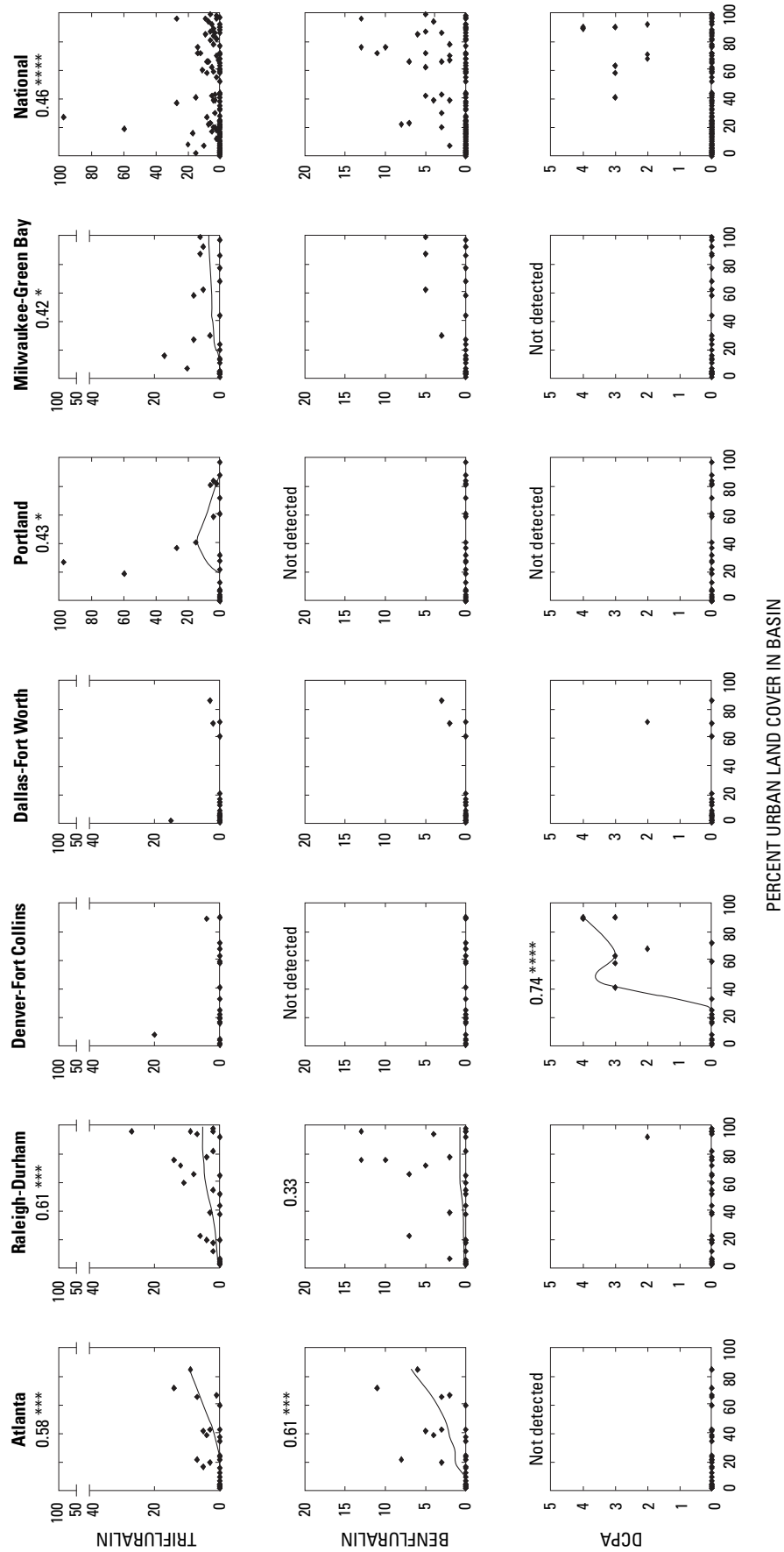


PERCENT URBAN LAND COVER IN BASIN

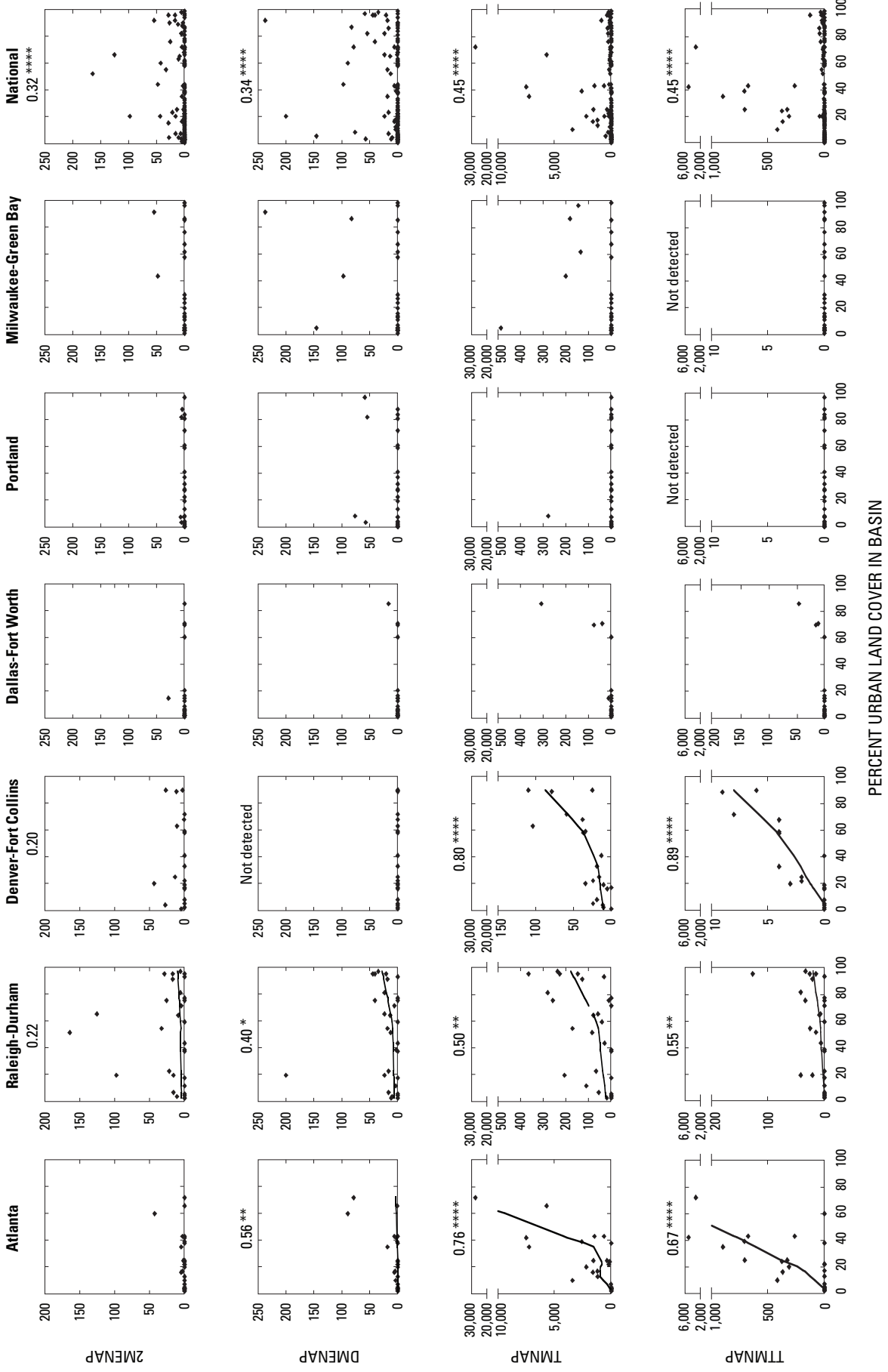
**Figure 9.** Results from Microtox® (EC50), P450RGS (TEQs), and Fluorocan (PYR-EQ) assays, and number of compounds detected (#DETECTS) compared to percent of urban land cover in the basin. LOWESS curves plotted and Spearman's rank correlation coefficients (rho values) shown above graphs for all endpoints with greater than 25-percent detection; asterisks denote significance level (p values are given in appendix 2), \* p<0.05, \*\* p<0.01, \*\*\* p<0.001, \*\*\*\* p<0.0001. PYR-EQ, equivalent micrograms of pyrene per milliliter of SPMD; TEQs, equivalent picograms of 2, 3, 7, 8 TCDD per milliliter of SPMD; EC50, milligram equivalents SPMD that reduces light output by 50 percent. [ $<$ , less than]



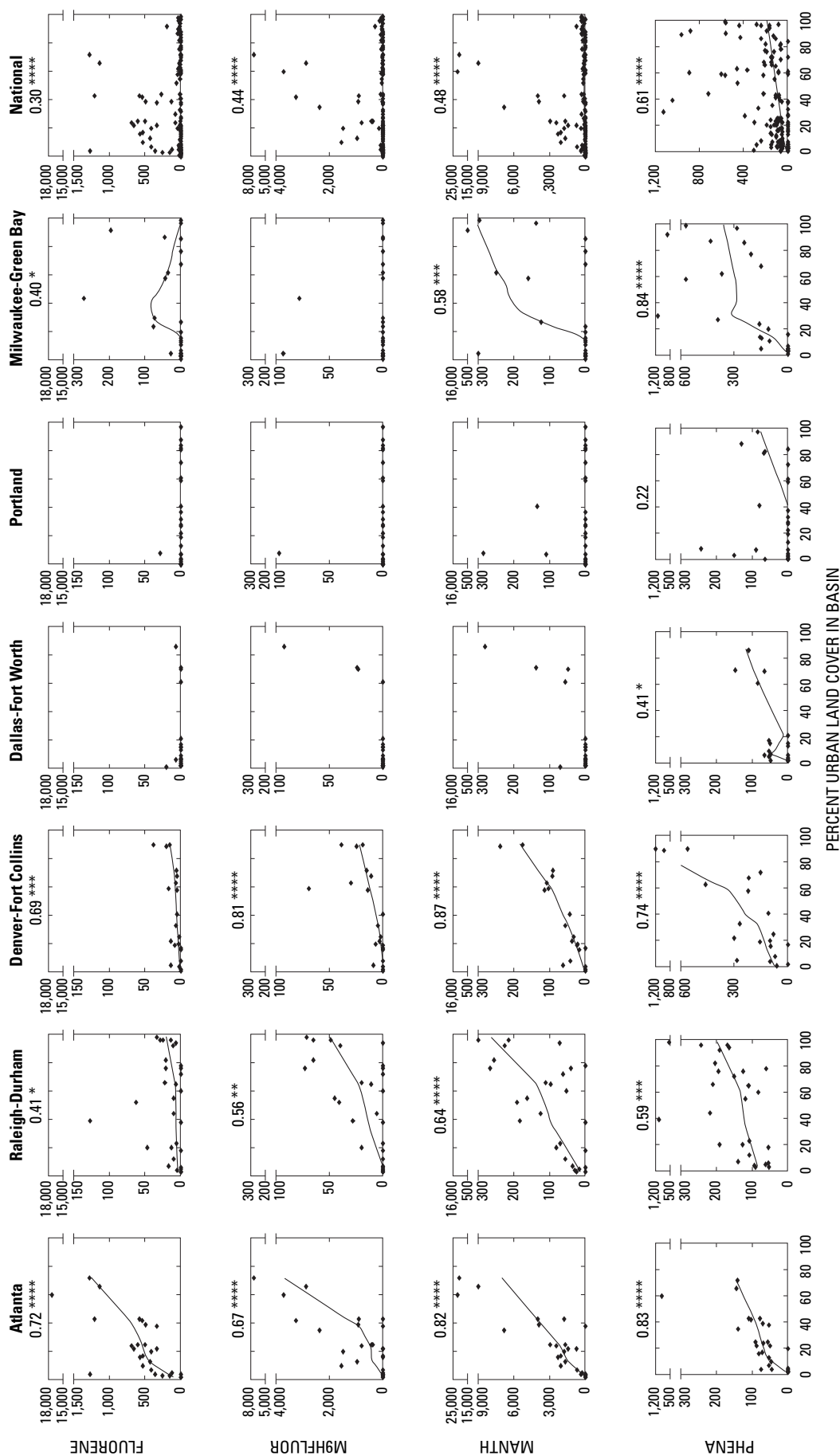
**Figure 10.** Pentachloroisole (PCA), chloryrifos, and total chlordane (organophosphate insecticide) concentrations (nanograms/SPMD) compared to percent urban land cover in the basin. LOWESS curves plotted and Spearman's rank correlation coefficients (rho values) shown above graphs for all endpoints with greater than 25-percent detection; asterisks denote significance level (p values are given in appendix 2), \* p<0.05, \*\* p<0.01, \*\*\* p<0.001, \*\*\*\*\* p<0.0001. [ $<$ , less than]



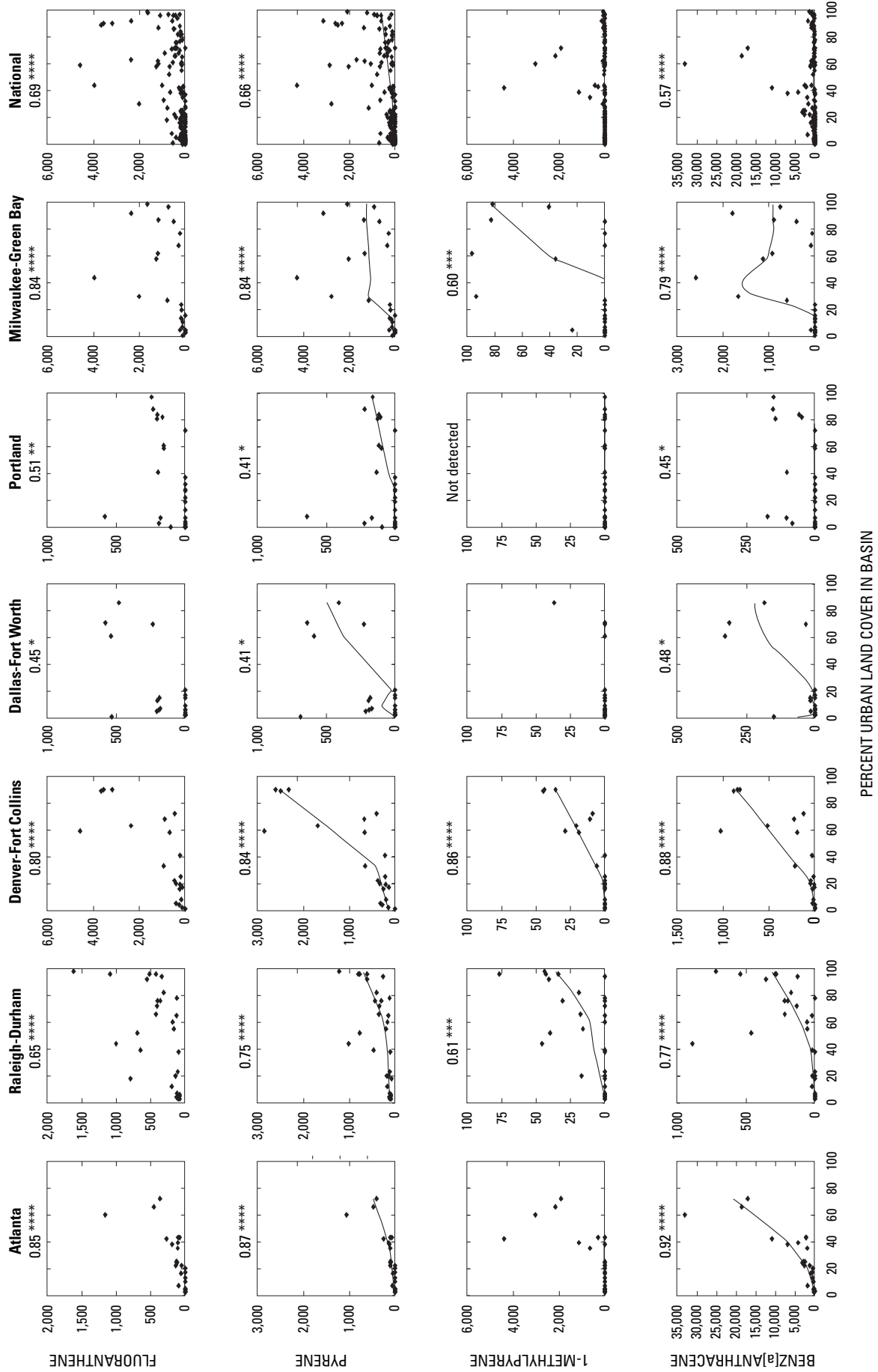
**Figure 11.** Trifluralin, benfluralin, and DCPA (dacthal) (herbicides) concentration (nanograms/SPMD) compared to percent urban land cover in the basin. LOWESS curves plotted and Spearman's rank correlation coefficients (rho values) shown above graphs for all endpoints with greater than 25-percent detection; asterisks denote significance level (p values are given in appendix 2), \* p<0.05, \*\* p<0.01, \*\*\* p<0.001, \*\*\*\* p<0.0001. [ $<$ , less than]



**Figure 12.** Two-ring polycyclic aromatic hydrocarbon concentration (nanograms/SPMD) compared to percent urban land cover in the basin: 2-methylnaphthalene (2MENAP); 2,6-dimethylnaphthalene (DMENAP); trimethylnaphthalene (TMNAP); and 1,2,3,4-tetramethylnaphthalene (TTMNAP). LOWESS curves plotted and Spearman's rank correlation coefficients (rho values) shown above graphs for all endpoints with greater than 25-percent detection; asterisks denote significance level (p values are given in appendix 2), \* p<0.05, \*\* p<0.01, \*\*\* p<0.001, \*\*\*\* p<0.0001. [ $<$ , less than]

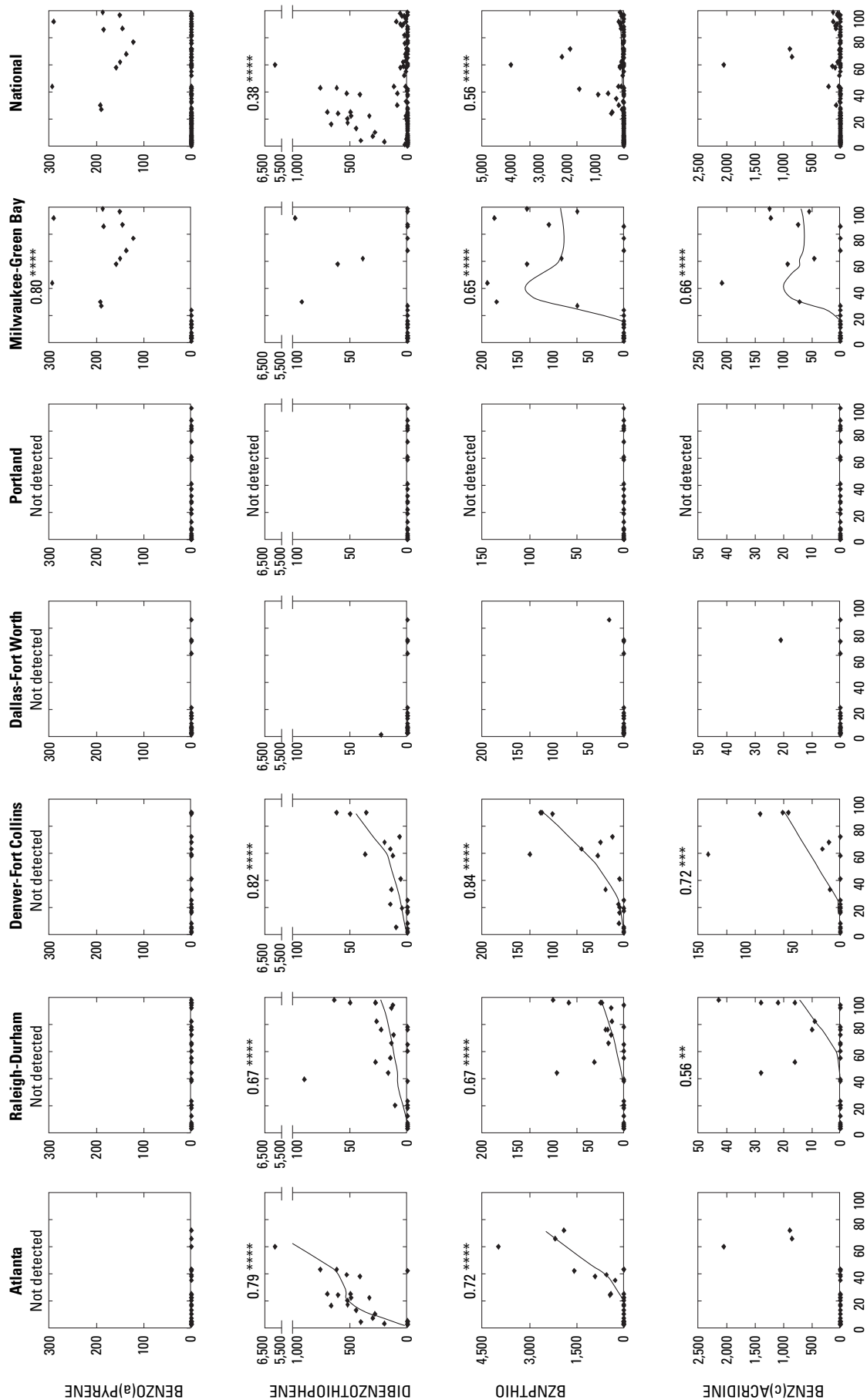


**Figure 13.** Three-ringed polycyclic aromatic hydrocarbon concentration (nanograms/SPMD) compared to percent urban land cover in the basin: fluorene, methyl-9H-fluorene (M9HFLUOR), methylanthracene (MANTH), and phenanthrene (PHENA). LOWESS curves plotted and Spearman's rank correlation coefficients (rho values) shown above graphs for all endpoints with greater than 25-percent detection; asterisks denote significance level (p values are given in appendix 2), \* p<0.05, \*\* p<0.01, \*\*\* p<0.001, \*\*\*\* p<0.0001. [<, less than]



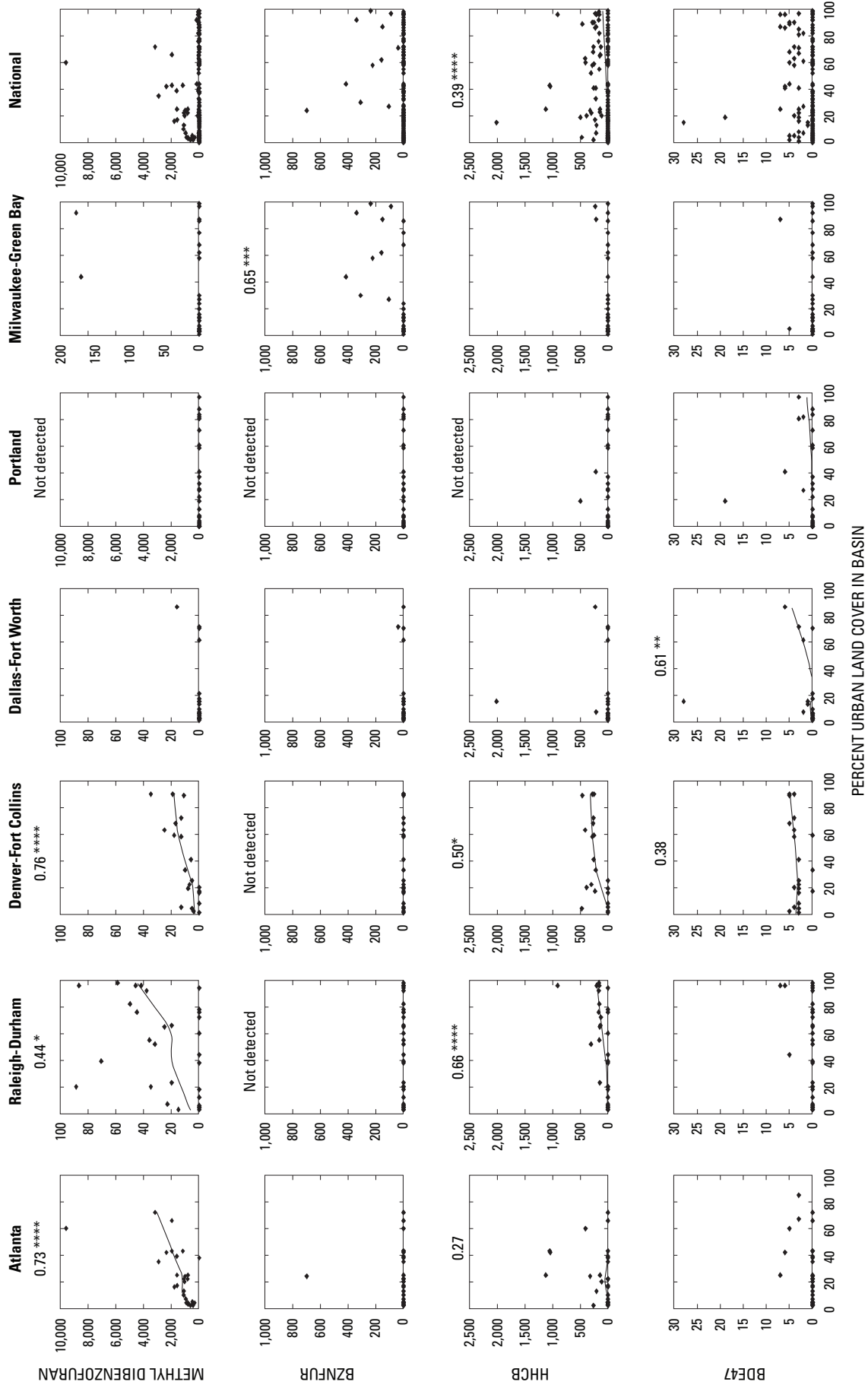
**Figure 14.** Four-ringed polycyclic aromatic hydrocarbon concentration (nanograms/SPMD) compared to percent urban land cover in the basin: fluoranthene, pyrene, 1-methylpyrene, and benzophenanthrene. LOWESS curves plotted and Spearman's rank correlation coefficients (rho values) shown above graphs for all endpoints with greater than 25-percent detection; asterisks denote significance level (p values are given in appendix 2), \* p<0.05, \*\* p<0.01, \*\*\* p<0.001, \*\*\*\* p<0.0001. [ <, less than]





PERCENT URBAN LAND COVER IN BASIN

**Figure 15.** Benz[a]pyrene, dibenzothiophene, benzo[b]naphtho[2,1]-thiophene (BZNPHTIO), and benz[c]acridine concentration (nanograms/SPMD) compared to percent urban land cover in the basin. LOWESS curves plotted and Spearman's rank correlation coefficients (rho values) shown above graphs for all endpoints with greater than 25-percent detection; asterisks denote significance level (p values are given in appendix 2), \* p<0.05, \*\* p<0.01, \*\*\* p<0.001, \*\*\*\* p<0.0001. [<, less than]



**Figure 16.** Methyl dibenzofuran, benzo[*b*]naphtho[2,3-*d*]furan (BzNFUR), HHCb, and BDE47 concentration (nanograms/SPMD) compared to percent urban land cover in the basin. LOWESS curves plotted and Spearman's rank correlation coefficients (rho values) shown above graphs for all endpoints with greater than 25-percent detection; asterisks denote significance level (p values are given in appendix 2), \* p<0.05, \*\* p<0.01, \*\*\* p<0.001, \*\*\*\* p<0.0001. [ $<$ , less than]

Total chlordane (sum of cis and trans isomers) was detected in 27 percent of the streams in Raleigh-Durham and in one stream in Atlanta and two in Dallas-Fort Worth (appendix 2). In Raleigh-Durham, the concentration of total chlordane increased with increasing urban land cover (table 5; fig. 10), and the relation was strong. A sharp break in the LOWESS line is evident in figure 10, highlighting the fact chlordane was not detected in any stream with less than 40 percent urban land cover in Raleigh-Durham (or any other metropolitan area).

## Herbicides

Three herbicides, trifluralin, benfluralin, and dacthal, were detected in greater than 25 percent of the streams sampled in at least one metropolitan area (appendix 2). Trifluralin concentrations were strongly related to percent urban land cover in Atlanta and Raleigh-Durham (table 5). Concentrations increased above the reporting level at between 20 and 40 percent urban land cover in Atlanta and Raleigh-Durham (fig. 11). Although the Spearman's rho for Portland and Milwaukee-Green Bay were just below 0.5, examination of the scatterplots shows a pattern of concentrations below the reporting level in streams with percent urban land cover less than 10–20 percent, followed by streams with 20–40 percent urban land cover in the basin having the highest values measured within the metropolitan area. Trifluralin was detected in Denver-Fort Collins and Dallas-Fort Worth but in less than 25 percent of the streams sampled.

Concentrations of benfluralin increased with increasing urban intensity and were strongly correlated with percent urban land cover in Atlanta (table 5; fig. 11). A positive but weaker relation was noted in Raleigh-Durham. Benfluralin was detected in only 14 percent of the streams in Milwaukee-Green Bay and was not detected in Denver-Fort Collins or Portland (appendix 2). In Atlanta, the response pattern and concentrations measured for benfluralin and trifluralin were similar, with concentrations below the reporting level in streams with percent urban land cover below 20 percent followed by increasing values up to 14.1 ng/SPMD.

Dacthal was detected in 33 percent of the streams in Denver-Fort Collins and in one stream each in Raleigh-Durham and Dallas-Fort Worth (table 5). A very strong relation between concentration of dacthal and urban land cover was observed in Denver-Fort Collins (table 5). Dacthal was not detected in any stream with percent urban land cover below 35 percent (fig. 11; appendix 1).

## Polycyclic Aromatic Hydrocarbons (PAHs)

Twenty-two PAH compounds were detected, and 19 of these were detected in 25 percent or more of the streams in at least one metropolitan area (appendix 2). Of the 19 PAHs, 16 were strongly to very strongly related to percent urban land cover (P\_NLCD1\_2; table 5). Lower molecular weight PAHs

(naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene) showed weak positive and negative relations with urban intensity (appendix 2). A general pattern was observed of increases in frequency of detection and stronger positive relations with urban intensity as the molecular weights of the 2–4 ringed PAHs increased (appendix 2). To illustrate this overall pattern, and to compare the patterns of response with increasing molecular weight, the relations of PAH concentration with urban land cover for several 2-ringed PAHs are shown in figure 12. As the molecular weight increases, the Spearman's rho values increase (fig. 12), and the number of metropolitan areas with rho values greater than 0.5 increases (appendix 2). Also evident is the low number of detections for 2-ringed PAHs in Dallas-Fort Worth, Portland, and Milwaukee-Green Bay (appendix 2). This pattern probably occurs because physical and chemical characteristics of PAHs (for example, vapor pressure,  $K_{ow}$ , decomposition, and photo-oxidation) that influence delivery to streams and uptake by SPMDs vary with molecular weight. PAHs with molecular weights less than that of pyrene exist mostly in the gas phase and have shorter half-lives in the atmosphere, soil, and surficial sediments than higher molecular weight species (Baek and others, 1991).

The lowest molecular weight (MW) PAH that was detected in 25 percent or more of the streams and strongly correlated ( $\rho > 0.5$ ) to urban intensity was 2,6-dimethylnaphthalene (MW = 156.23), and this correlation was strong in Atlanta only (table 5; appendix 2). A weaker relation was observed in Raleigh-Durham and in the national data set.

The responses of trimethylnaphthalene and 1,2,3,4-tetramethylnaphthalene were similar, with detections greater than 25 percent in Atlanta, Raleigh-Durham, and Denver-Fort Collins. Strong to very strong relations with urban intensity were observed in these three metropolitan areas (table 5). These two compounds were measured above the reporting level in just a few streams in Dallas-Fort Worth, Portland, and Milwaukee-Green Bay. The higher concentrations of these two compounds are evident in Atlanta compared to the other metropolitan areas (fig. 12; appendix 2). The 13 highest values recorded for trimethylnaphthalene and the 12 highest values recorded for 1,2,3,4-tetramethylnaphthalene were in Atlanta (appendix 1). Two streams (Sope Creek near Marietta, Georgia—P\_NLCD1\_2 = 72.51 and Utoy Creek at Great Southwest Pkwy near Atlanta, Georgia—P\_NLCD1\_2 = 60.56) had trimethylnaphthalene concentrations greater than 10,000 ng/SPMD. Three streams (Suwanee Creek at Suwanee, Georgia—P\_NLCD1.2=42.56; Sope Creek near Marietta, Georgia—P\_NLCD1\_2 = 72.51; and Nickajack Creek at U.S. 78/278 near Mableton, Georgia—P\_NLCD1\_2 = 66.17) had 1,2,3,4-tetramethylnaphthalene concentrations greater than 1,400 ng/SPMD.

The shapes of the response curves for trimethylnaphthalene and 1,2,3,4-tetramethylnaphthalene were similar in Atlanta with sharp increases in concentration at 20 percent urban land cover in the basin (fig. 12, LOWESS lines). The shapes of the response curves for trimethylnaphthalene and 1,2,3,4-tetramethylnaphthalene in Raleigh-Durham and

Denver-Fort Collins were similar with relatively constant increases in concentration across the gradient.

It should be noted that the concentration of trimethylnaphthalene used to correct for blank contamination in Atlanta was higher than any value recorded for a sample in the other metropolitan areas (table 2) but there was no blank contamination of 1,2,3,4-tetramethylnaphthalene. The trimethylnaphthalene contamination was found in trip blanks exposed to the atmosphere during deployment and retrieval. In other words, more trimethylnaphthalene was sequestered during the brief time the trip blanks were exposed to the atmosphere in Atlanta than was sequestered during the entire 45 days of deployment in all the streams sampled in the other metropolitan areas. This highlights both the ability of SPMDs to sequester contaminants from the atmosphere and the need to implement proper quality-assurance protocols.

Five 3-ringed PAHs—fluorene, methyl-9H-fluorene, methylanthracene, phenanthrene, and 4H-cyclopenta[def]phenanthrene—were detected in greater than 25 percent of the streams in at least one metropolitan area (appendix 2). Scatterplots of the concentration of four of these compounds (4H-cyclopenta[def]phenanthrene not shown) and percent of urban land cover use (P\_NLCD1\_2) in the basin are shown in figure 13.

Fluorene concentrations were strongly related to percent urban land cover in Atlanta and Denver-Fort Collins, and to a lesser extent in Raleigh-Durham and Milwaukee-Green Bay (table 5). Concentrations measured in Atlanta were much higher compared to the other basins (fig. 13), and in one stream (Utoy Creek at Great Southwest Pkwy near Atlanta, Georgia—P\_NLCD1\_2 = 60.56), a value more than 10 times that measured in any other stream was found. The 25th percentile value in Atlanta (332 ng/SPMD) was higher than the maximum value (270 ng/SPMD) recorded in any other stream from the other five metropolitan areas. In Atlanta, sharp increases in fluorene concentrations at the low end of the urban gradient are evident compared to Raleigh-Durham and Denver-Fort Collins where concentrations were much lower and increases more gradual along urban gradients (fig. 13, LOWESS lines). Methyl-9H-fluorene concentrations were very strongly correlated with percent urban land cover in Denver-Fort Collins, and strongly correlated in Atlanta and Raleigh-Durham (table 5). Methyl-9H-fluorene was detected in less than 25 percent of the streams sampled in Milwaukee-Green Bay, Dallas-Fort Worth, and Portland. Again, concentrations were much higher in Atlanta compared to the other basins, and the concentration at Utoy Creek was 50 percent higher than found in any other stream sampled. The patterns of response for methyl-9H-fluorene were similar to those of fluorene.

Correlations between methylanthracene concentrations and percent urban land cover were very strong in Denver-Fort Collins and Atlanta, and strong in Raleigh-Durham and Milwaukee-Green Bay. Methylanthracene concentration was below the reporting level in more than 75 percent of the streams in the other metropolitan areas (appendix 2). Both

methylanthracene (fig. 13) and 4H-cyclopenta[def]phenanthrene (appendix 1) showed the same patterns of response along the urban gradient and had higher concentrations in Atlanta and Utoy Creek, as did the other 3-ringed PAHs.

Phenanthrene was detected in greater than 25 percent of streams in all six basins (table 5). Very strong relations between phenanthrene concentration and percent urban land cover were noted for Atlanta, Denver-Fort Collins, and Milwaukee-Green Bay, and strong relations for Raleigh-Durham and the national data set. A slightly weaker relation was observed in Dallas-Fort Worth, and a much weaker relation was noted in Portland. The major difference between phenanthrene and the other 3-ringed PAHs is that the concentrations of phenanthrene were not higher in Atlanta streams compared to the other metropolitan areas (fig. 13; appendix 2). The lowest median concentration (30.6 ng/SPMD) was in Portland, and the highest median values were in Denver-Fort Collins (157.0 ng/SPMD) and in Milwaukee-Green Bay (150.0 ng/SPMD) (appendix 2). Even with the five-fold difference in median concentrations, the patterns of response across the gradient of urbanization, as illustrated by the LOWESS lines (fig. 13), were relatively consistent across all of the metropolitan areas with strong or very strong relations between phenanthrene concentration and urban intensity. The only noticeable exception was in Denver-Fort Collins where more rapid increases in concentration above 40 percent land uses were observed.

Three of the 4-ringed PAHs analyzed—fluoranthene, pyrene, and benzophenanthrene—were detected in greater than 25 percent of the streams sampled in all six metropolitan areas (table 5; appendix 2). The other 4-ringed PAH analyzed—1-methylpyrene—was detected in greater than 25 percent of the streams in Raleigh-Durham, Denver-Fort Collins, and Milwaukee-Green Bay. The patterns of relations for all of the 4-ringed PAHs are higher rho values in Atlanta, Raleigh-Durham, Denver-Fort Collins, and Milwaukee-Green Bay compared to Dallas-Fort Worth and Portland, even though the Spearman's rho value for fluoranthene in Portland was greater than 0.5 (table 5). Much higher concentrations for both fluoranthene and pyrene were measured in Milwaukee-Green Bay and Denver-Fort Collins compared to the other metropolitan areas (appendix 2; fig. 14). Concentrations of 1-methylpyrene and benzophenanthrene were much higher in Atlanta, but 1-methylpyrene was detected in too few streams to determine relations with urban intensity. A distinct increase in the concentration of most 4-ringed PAHs was observed between 20 and 40 percent urban land cover (fig. 14, LOWESS lines), except in Dallas-Fort Worth and Portland. Streams in a few basins at the low end of the urban gradient in Dallas-Fort Worth and Portland had higher concentrations of fluoroanthene, pyrene, and phenanthrene relative to the more urbanized basins in those metropolitan areas (figs. 12 and 13, see appendix 1 for site names).

Benzo[a]pyrene was detected only in Milwaukee-Green Bay and very strong relations between benzo[a]pyrene concentration and percent urban land cover were observed

(table 5). In the Milwaukee-Green Bay metropolitan area, benzo[*a*]pyrene was not detected in any streams below and at every site above 25 percent urban land cover (fig. 15).

The relation between percent urban land cover and the concentrations of two sulfur-containing PAHs (dibenzothiophene and benzo[*b*]naphtho[2,1]thiophene) and one nitrogen-containing PAH (benz[*c*]acridine) is shown in figure 15. Concentrations of all three compounds increased with increasing urban land use in all basins with sufficient number of detections to consider (table 5). Strong to very strong relations with percent urban land cover were noted in Atlanta, Raleigh-Durham, and Denver-Fort Collins for dibenzothiophene and benzo[*b*]naphtho[2,1]thiophene and for benz[*c*]acridine in Raleigh-Durham, Denver-Fort Collins, and Milwaukee-Green Bay. Much higher concentrations of these three compounds were measured in streams in and around Atlanta, even though benz[*c*]acridine was below reporting levels for most streams in Atlanta. The median value for dibenzothiophene in Atlanta (472.1 ng/SPMD) was higher than the maximum concentration (118.7 ng/SPMD) recorded in the other five metropolitan areas (appendix 2).

High concentrations of dibenzothiophene in streams at the low end of the gradient were measured in Atlanta, and concentrations increased with increasing urban land cover in a steady fashion along the gradient (fig. 15, LOWESS line). In Atlanta, the pattern for benzo[*b*]naphtho[2,1]thiophene was much different than Raleigh-Durham and Denver-Fort Collins, with sharp increases in concentration observed at 20 percent urban land cover in Atlanta. Concentrations of benzo[*b*]naphtho[2,1]thiophene increase dramatically at about 20 percent urban land cover in Atlanta, Denver-Fort Collins, and Milwaukee-Green Bay and at about 40 percent urban land cover in Raleigh-Durham (fig. 15). Benz[*c*]acridine was not detected in any stream with less than 20 percent urban land cover, and sharp increases in concentration are evident at 20 percent urban land cover in Denver-Fort Collins and Milwaukee-Green Bay and at 60 percent urban land cover in Raleigh-Durham (fig. 15).

## Dibenzofurans

In Atlanta and Denver-Fort Collins, methyl dibenzofuran concentrations and percent urban land cover were very strongly related; a weaker relation was observed in Raleigh-Durham (table 5). Detection frequencies were low in Milwaukee-Green Bay and Dallas Fort-Worth, and methyl dibenzofuran was not detected in Portland (appendix 2). Methyl dibenzofuran concentrations were much higher (more than 50 fold) in Atlanta compared with Raleigh-Durham and Denver-Fort Collins (fig. 16; appendix 2). Even with the difference in concentrations, a similar pattern of steady increases in concentrations along the urban gradient was observed (fig. 16, LOWESS line).

Benzo[*b*]naphtho[2,3-*d*]furan was detected in 31 percent of the streams in Milwaukee-Green Bay but in only two other streams in the other metropolitan areas (appendix 2).

In Milwaukee-Green Bay, benzo[*b*]naphtho[2,3-*d*]furan concentrations increased with increasing urban intensity, and a strong relation with percent urban land cover was observed (fig. 16; table 5). It was not detected in any streams with less than 20 percent urban land cover, but also was not detected in some of the more urbanized streams in Milwaukee-Green Bay.

## Fragrances and Personal Care Products

Five of the compounds in this group (HHCb, d-limonene, 3-(4-methoxyphenyl)-2-2 propanoic acid, 2-heptadecanone, and isoquinoline) were detected at greater than 25 percent of the streams in at least one metropolitan area (appendix 2). HHCb, a synthetic musk compound, was detected in 30, 43, and 67 percent of the streams in Atlanta, Raleigh-Durham, and Denver-Fort Collins, respectively. Concentrations of HHCb increased with increasing urban intensity (fig. 16). The relation between HHCb concentrations and percent urban land cover in Raleigh-Durham and Denver-Fort Collins was much stronger than in Atlanta (table 5; fig. 16).

The compound d-limonene is a component of oil extracted from citrus rind and is used to impart an orange fragrance to cleaning products and furniture polish. The compound d-Limonene was measured above the detection limit in 63 percent of the streams sampled in Raleigh-Durham, 47 percent in Atlanta, and 24 percent in Denver-Fort Collins (appendix 2). No strong relations between concentration and urban intensity were observed.

The personal care product 3-(4-methoxyphenyl)-2-2-propanoic acid (MPAA) was detected in streams from four metropolitan areas and in greater than 25 percent of streams sampled in Raleigh-Durham and Portland (appendix 2). Weak negative relations between MPAA concentration and urban land cover were observed in Raleigh, and weak positive relations were noted in Portland. MPAA was detected at high levels in trip blanks (table 2); although concentrations in field samples were corrected to account for blank contamination, measured concentrations and relations with urban intensity should be viewed with caution. This compound was identified based on comparison with a reference mass spectra library. Little information is available relevant to the use and environmental chemistry of MPAA.

The compound 2-heptadecanone was measured above the reporting level in 33 percent of the streams in Dallas-Fort Worth, and isoquinoline was detected in 32 percent of the streams in Portland (appendix 2). No relations with urban intensity were noted for either compound (appendix 2).

## Polybrominated Diphenyl Ethers (PBDEs)

Polybrominated diphenyl ethers (PBDEs) have widespread use as flame retardants. The compound BDE 47 is the most commonly used and was the most frequently detected BDE congener of this group of compounds (appendix 2). Four other BDE congeners also were detected. BDE 47 was

detected in 86 percent of the streams in Denver-Fort Collins and 29 percent of the streams in Dallas-Fort Worth, and concentrations in both metropolitan areas increased with urban intensity (fig. 16). A strong relation between BDE 47 concentration and percent urban land cover was noted in Dallas-Fort Worth (table 5).

## Steroids

Of the four steroid compounds targeted, beta-sitosterol and cholesterol were detected in more than 25 percent of streams sampled in one or more metropolitan areas (appendix 2). Concentrations of beta-sitosterol in Milwaukee-Green Bay increased with increasing urban land cover; the relation was significant but not strong ( $\rho = 0.48$ ,  $p = 0.0079$ ). In Denver-Fort Collins, beta-sitosterol was detected in 43 percent of the streams, but no relation with urban intensity was observed. Cholesterol was measured above the reporting level in 33 percent of the streams in Atlanta and in less than 25 percent of the streams sampled in the other metropolitan areas. In Atlanta, cholesterol concentrations decreased with increasing urban intensity (appendix 2). The cholesterol data are suspect because they were measured in relatively high concentrations compared to environmental samples in both trip and laboratory blanks.

## Plasticizers

Bis(2-ethylhexyl) phthalate and diethyl phthalate were detected in high concentrations in all QC samples (table 2). Summary statistics and Spearman's rho are given in appendix 2 (after blank correction), but these results are suspect due to the levels and percentage of samples affected by contamination of blank samples.

Butyl citrate was detected in 93 percent of Milwaukee-Green Bay streams (appendix 2). A weak negative relation with urban intensity was noted. Butyl citrate was detected in trip blanks but at concentrations below all environmental samples (table 2).

## Fluoroscan Assay

The ultraviolet fluorescence scan provides a semi-quantitative screen for PAHs, which fluoresce under ultraviolet light. Pyrene is used as a reference compound for this assay, but other PAHs contribute to the fluorescence of the samples. Strong to very strong relations between pyrene equivalents and percent urban land cover were found in Atlanta, Raleigh-Durham, Denver-Fort Collins, Milwaukee-Green Bay, and Portland (table 5). Spearman's rho values ranged from 0.49 in Dallas Fort-Worth to 0.87 in Milwaukee (appendix 2). Higher values for pyrene equivalents were measured in Milwaukee-Green Bay and Denver-Fort Collins compared to the other basins (appendix 2; fig. 9). The only values above 1,000  $\mu\text{g}$  pyrene equivalents/mL SPMD were measured in these two

metropolitan areas. The lowest values in basins with greater than 80 percent urban land use were noted in Dallas-Fort Worth (fig. 9). The fluoroscan assay was used to screen samples for levels of PAHs prior to chemical analysis. Given the low cost of the assay compared to chemical analysis, fluoroscan was useful for identifying samples with high levels of PAHs prior to chemical analysis.

## Microtox® Assay

The general pattern in the response of the Microtox® assay was increasing toxicity (lower value for EC50) with increasing urban land cover, but the relations were weak compared to the two other assays (fig. 9; appendix 2). EC50 values below 2.5 mg/SPMD equivalents/mL of solvent were considered acutely toxic (B. Thomas Johnson, U.S. Geological Survey, written commun., 2003), and values below 2.5 were measured in streams across the gradient of urban land use in all six metropolitan areas. The scatterplots of EC50 and percent urban land cover in figure 9 indicate two patterns. In Dallas-Fort Worth and Portland, values from toxic ( $< 2.5$ ) to the blank control (25) were measured in streams at both ends of the urban gradient. This range at both ends of the gradient results in weak and insignificant correlations between EC50 and percent urban land cover. In contrast, streams in Atlanta, Raleigh-Durham, Denver-Fort Collins, and Milwaukee-Green Bay have much lower EC50 values (more toxic, no values above 8) across the entire gradient. Even at lower values across the gradient, EC50 was significantly related ( $p < 0.05$ ) to percent urban land cover in Atlanta and Raleigh-Durham. Further analysis of the relations between EC50 and chemical concentrations indicated the most significant correlations between EC50 and chlorpyrifos concentration in both Atlanta (Pearson's  $r = -0.55$ ,  $p = 0.002$ ) and Raleigh-Durham (Pearson's  $r = -0.35$ ,  $p = 0.06$ ). High concentrations of chlorpyrifos were measured in Dallas-Fort Worth, but no significant relations between EC50 and any of the compounds detected were noted.

## P450RGS Assay

The P450RGS assay provides a tool to measure the potency of complex mixtures of aryl hydrocarbon receptor agonists such as PAHs, planar PCBs, chlorinated dibenzo-p-dioxins, and chlorinated dibenzofurans. A positive correlation between toxic equivalents (TEQs) and urban intensity was observed in all metropolitan areas. Spearman's rho values ranged from 0.49 in Dallas-Fort Worth to 0.91 in Atlanta (table 5). A common pattern was found across the six metropolitan areas, with increases in TEQs between 20 and 40 percent urban land cover as illustrated by changes in the slope of the LOWESS smooth curves (fig. 9).

Two other notable patterns are evident in figure 9. First, higher values were measured in Milwaukee-Green Bay and Denver-Fort Collins (appendix 2, highest 75th percentiles)

compared to the other metropolitan areas. The only streams with values above 3,000 TEQs were in these two metropolitan areas. Four streams in Denver-Fort Collins had values above 4,000 TEQs (see appendix 1 for site names).

The second notable pattern is in the high values at the low end of the urban gradient in Dallas-Fort Worth observed in figure 9 and evident in a comparison of the minimum value (599 TEQs) and 25th percentile (777 TEQs) in Dallas-Fort Worth with the other metropolitan areas (appendix 2). The minimum value in Dallas-Fort Worth was greater than the median values in Atlanta, Portland, and Milwaukee-Green Bay. Examination of the standard curves and QC samples did not reveal any differences in the assay for Dallas-Fort Worth compared to the other metropolitan areas. This pattern is unique to Dallas-Fort Worth, and none of the chemical compounds detected can explain this pattern. This is likely due to a regional source and/or historic use of aryl hydrocarbon agonist(s) in the Dallas-Fort Worth basins that was not identified by chemical analysis. This study targeted several aryl hydrocarbon receptor agonists (PCBs, organochlorine insecticides, PAHs) but did not analyze for chlorinated dibenzo-p-dioxins or chlorinated dibenzofurans, which are potent aryl hydrocarbon receptor agonist(s). Toxaphene, DDT, and its breakdown products, all aryl hydrocarbon receptor agonists, were targeted, but reporting limits were high compared to other compounds.

## Discussion

### Occurrence and Distribution

In addition to traditional sampling methods for environmental contaminants (water, sediment, biota), SPMDs have been used in a variety of settings (Huckins and others, 2006) to assess water quality. This is, however, the first large-scale use of SPMDs to assess the occurrence and distribution of hydrophobic organic compounds (HOCs) in our Nation's streams. Results from the study of 163 streams with varying amounts of urban intensity indicated 73 HOCs occurring in streams in and around six major metropolitan areas of the United States. In only 2 of the 163 streams sampled were no HOCs detected. A number of HOCs have been documented to increase in frequency of occurrence and concentration as a result of urbanization (Makepeace and others, 1995; Pitt and others, 1995; Van Metre and Mahler, 2005). Hydrophobic contaminants of concern in urban streams include pesticides, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls, polychlorinated dioxins and furans, fire retardants (phosphate esters and polydibrominated ethers), detergent metabolites (alkylphenols), plasticizers (phthalates and bisphenol A), and synthetic musks (Makepeace and others, 1995; Pitt and others, 1995; Brabec and others, 2002; Kolpin and others, 2002). Many of these compounds have consumer uses in household and personal care products, such as fire

retardants in blankets or wiring, detergents, plastics, and cosmetics.

Recent studies have documented the occurrence and distribution of many of the pesticide compounds targeted during this study. Culminating a decade of study, the USGS's National Water Quality Assessment (NAWQA) Program has published national statistics for the occurrence and distribution of pesticides in water, bed sediment, and fish tissue (Gilliom and others, 2006). In the six metropolitan areas investigated during this study, the occurrence of the pesticides chlorpyrifos, chlordane, trifluralin, benfluralin, and dacthal in urban streams parallels the findings presented in Gilliom and others (2006).

In this study, PAHs were the most frequently detected group of compounds and have been shown in other studies to be prevalent in urban aquatic systems (Van Metre and others, 2000; Van Metre and Mahler, 2005; Hwang and Foster, 2006). The most frequently detected PAHs in this study were fluoranthene (67 percent), pyrene (66 percent), and phenanthrene (67 percent). This generally agrees with results from sediment in urban lakes where Van Metre and Mahler (2004) found the most dominant PAHs were fluoranthene and pyrene, which was consistent with their strong correlations to urban intensity. More recent research has shown that sealcoats, used to resurface parking lots and roads, are most likely the dominant source of PAHs in many urban streams (Mahler and others, 2005). Especially interesting, with respect to results from this study, are differences in composition and usage patterns in the two types of sealcoats (coal tar and asphalt) used in the United States. Coal tar-derived sealcoats, which have higher PAH concentrations, are used mostly in the eastern United States (east of the Rocky Mountains). Asphalt-derived sealcoats, which have lower PAH concentrations, are used mostly in the western United States (Van Metre and Mahler, 2005). This might provide one reason why PAHs were less frequently detected and at lower concentrations in streams from Portland compared to the five other metropolitan areas studied. Future studies assessing water quality in urban streams should consider documenting the location and area of sealcoated surfaces in the watershed to help determine major sources of PAHs.

Kolpin and others (2002) provided a nationwide assessment (139 streams in 30 states) of pharmaceuticals, hormones, and wastewater products in streams across the Nation and included many of the compounds analyzed in the six metropolitan areas investigated during this study. In the Kolpin study, site selection was biased to increase chances of detection based on knowledge of agriculture or urban activities in the watersheds of the streams sampled. Because streams with known point sources were not sampled during this study, it is not surprising that Kolpin reported higher detections for all of the compounds in common between the two studies (steroids, fragrances, personal care products, detergent metabolites, antimicrobials, and plasticizers).

In high enough concentrations, certain hydrophobic contaminants can result in harmful effects to aquatic biota, such as anomalies in fish, chronic and acute toxicity, and

endocrine disruption (Klein, 1979; Kime, 1998). The use of SPMDs in future water-quality assessments, particularly in urban settings, should be considered for occurrence and distribution of HOCs as well determining potential toxicity to aquatic biota.

## Comparison to Benchmark Values

It is interesting, although not unexpected, that only three hydrophobic compounds have calculated water concentrations above toxicity benchmarks, since hydrophobic compounds with  $\log K_{ow} > 3$  generally partition more into suspended and bed sediment and not into the water column. Thus, assessing the potential toxicity of hydrophobic compounds in urban streams, concentrations in sediment would more likely be the highest and, therefore, the most likely place to find toxicity. However, bioassays conducted on extracts of both sediment and SPMDs at different sites along the Huaihe River in China showed similar patterns of toxicity (Ma and other, 2005). Therefore, urban streams that have high concentrations of hydrophobic compounds or TEQs in SPMD extracts can be expected to have higher potential toxicity in sediments.

Even though only three (anthracene, dieldrin, and diazinon) of the 14 hydrophobic compounds evaluated had calculated average water concentrations over a 45-day period that were above a toxicity threshold, runoff from storm events may result in higher concentrations and subsequent toxicity. Urban stormwater runoff has been identified as having higher numbers and concentrations of contaminants, including PAHs (Richards and Johnson, 2002), and higher toxicity (Pitt and other, 1995). Therefore, during storm events, additional urban streams in this study might have had concentrations of some hydrophobic compounds above toxicity benchmarks.

There are many sources of anthracene, but concentrations in just a few streams in Raleigh-Durham (2), Denver-Fort Collins (1), and Milwaukee-Green Bay (4) were above the threshold value for chronic toxicity. These seven streams with levels of anthracene above the toxic threshold compared to large numbers of streams with high concentrations of the other PAHs suggest a more concentrated source of anthracene within the watershed or airshed. More detailed studies to identify sources and understand transport and fate of anthracene are required to determine why these seven streams are different. Additional in-situ toxicity testing would be required to document if effects to aquatic biota due to anthracene are occurring in these seven streams.

Dieldrin is an organochlorine insecticide that was used to control insects in soil, termites, and other insects that might affect public health (Nowell and others, 1999). By 1972, all uses were banned except for subsurface termite control and a few other limited applications (U.S. Environmental Protection Agency, 1980). Dieldrin use was phased out for all residential use in the late 1980s; therefore, concentrations in urban streams are expected to be in decline. Even so, since the half life of dieldrin is about 10.5 years (U.S. Environmental

Protection Agency, 1992), it was still detected above screening benchmarks in seven streams. The exceedances of benchmarks for human health-based screening levels were found in streams from Milwaukee-Green Bay, Portland, Raleigh-Durham, and Atlanta. This distribution indicates the use of dieldrin in metropolitan areas for control of termites and other urban pests, although it is interesting that no concentrations were above screening benchmarks in streams from the Dallas-Fort Worth area. In a study conducted in Fort Worth, Texas, and Boston, Massachusetts, Van Metre and Mahler (2004) found much higher dieldrin concentrations in stream-suspended sediments than deposited bed sediments and concluded that dieldrin was better preserved in soils than in aquatic sediments. Their study suggests that each time contaminated soils are washed into streams, new dieldrin is introduced to the water column.

Diazinon, an organophosphate insecticide, has been used to control insects on a variety of ornamental plants and food crops as well as nematodes and soil insects in lawns and cropland (Eisler, 1986a). However, an agreement between the U.S. Environmental Protection Agency (USEPA) and diazinon registrants was initiated to phase out and eliminate all residential uses of diazinon, as of December 31, 2004, when it became unlawful to sell diazinon for outdoor and non-agricultural uses in the United States (U.S. Environmental Protection Agency, 2004). Because sampling for this study occurred during the time of the phase out (2003 and 2004) and because diazinon has a very short half life of 14 days (Eisler, 1986a), probably are the reasons it was found in only one stream. In the future, diazinon concentrations in urban streams should be declining over time and not be a concern for ecological or human health in urban streams.

## Patterns in Response to Urbanization

One of the goals of this study was to compare responses to urbanization across metropolitan areas with different environmental characteristics (for example, rainfall, soil permeability). By examining a range of compounds and assays, patterns in the response of individual endpoints and groups of endpoints believed to have common sources or similar environmental chemistries should provide insight into water-quality changes related to urbanization. In addition, results of this study should provide information for the assessing potential effects on the aquatic communities and understanding key driving factors.

Of the 73 compounds detected and three assays used, 29 (including the number of compounds detected) were measured above the detection limit in 25 percent or more of the streams and related to increases in urban intensity—with the latter defined as having concentrations or assay values strongly correlated (Spearman's  $\rho > 0.5$ ) with urban intensity variables—in at least one of the metropolitan areas investigated. PAH compounds and the Fluorocan assay (which estimates the total PAH concentration) accounted for 17 of the 29 endpoints (59 percent) that were strongly related



to urban intensity. Ten endpoints were strongly correlated with urban land-use intensity when analyzed at the national scale, and all 10 were PAHs. This was not unexpected, as numerous studies have documented elevated levels of PAHs in water, sediment, and(or) SPMD extracts in urban streams (Moring and Rose, 1997; Nowell and Capel, 2003; Hwang and Foster, 2006; McCarthy, 2006).

Given the dominance of PAHs in the compounds strongly related with urban intensity and their common sources in urban areas (vehicles, parking lot sealcoats, wood burning, power plant emissions, oil spills) a surprising degree of difference in the numbers of endpoints with strong relations to urban intensity was observed across the six metropolitan areas. The number of endpoints related to urbanization was 21 in Raleigh-Durham and 20 in Atlanta and Denver-Fort Collins, 14 in Milwaukee-Green Bay, 3 in Dallas-Fort Worth, and 3 in Portland. Based on this simple comparison, clear differences exist in one or a combination of factors governing source strength, transport, and fate of hydrophobic compounds.

There were differences in the response of PAHs across the six metropolitan areas. In Portland, fluoranthene and Fluorscan were the only PAH endpoints strongly related with urban intensity and in Dallas-Fort Worth only benzophenanthrene, fluoranthene, and pyrene were strongly related to urban intensity. These results compare to 15 PAH endpoints in Denver-Fort Collins, 14 in Atlanta and Raleigh-Durham, and 11 in Milwaukee-Green Bay. Clearly one or more factors related to source strength and(or) transport of PAHs are different in Portland and Dallas-Fort Worth compared to the other metropolitan areas.

Alkylated PAHs and heterocyclic dibenzothiophenes are used as environmental fate indicators and source-specific markers of oil contaminants (petrogenic), and unsubstituted 4- to 6-ring PAHs are indicative of pyrogenic sources (Almi and others, 2003). The results from the SPMDs (detections and concentrations) are representative of the time of deployment only; therefore, how representative this window of time is to the range of stream conditions is unknown. Taking this limitation into account, one interesting similarity between the six metropolitan areas is apparent with regard to pyrogenic PAHs. The frequency of detections and strong correlations with urban intensity variables for the unsubstituted 4-ring PAHs (fluoranthene, pyrene, and benzophenanthrene) provide evidence that pyrogenic sources, are important across the six metropolitan areas studied as basins urbanize. Van Metre and others (2000) analyzed PAHs in sediment cores in reservoirs and lakes and reported that increases in PAH concentrations in sediments deposited over the past 20–40 years tracked closely with increases in automobile use, even in watersheds that had not undergone substantial urbanization since the 1970s.

Unlike the pyrogenic PAHs, the response of petrogenic PAHs was not consistent across the metropolitan areas studied. Few streams in Dallas-Fort Worth or Portland had detectable levels of petrogenic PAHs (1-methyl pyrene, dibenzothiophene, and benzo[*b*]naphth[2,1]thiophene), indicating low source strength, dilution, or lack of delivery pathways in these

two metropolitan areas. The lack of delivery pathways seems unlikely given the response patterns for pyrogenic PAHs.

Petrogenic PAHs were frequently detected and strongly related to urban intensity in Atlanta, Raleigh-Durham, Milwaukee-Green Bay, and Denver-Fort Collins. This suggests that source strength and transport of petrogenic PAHs increase as basins urbanize in these metropolitan areas. Concentrations of petrogenic PAHs in Atlanta were much higher compared to Raleigh-Durham, Milwaukee-Green Bay, and Denver-Fort Collins, suggesting a difference in source strength. Rastall and others (2004) reported similar results for petrogenic PAHs in Lake Shkodra/Lake Skadar in Albania and Montenegro and suggested spills or discarded oils and hydrocarbon fuels as a significant source of PAHs to the lake.

Recent studies have identified another potential source of petrogenic PAHs to urban streams. Mahler and others (2005) used diagnostic ratios of individual PAHs and extrapolated yields to the watershed scale, and reported that runoff from parking lot sealcoats could account for the majority of PAHs loading in the four urban watersheds studied. Large differences in the concentration of PAHs in parking lot runoff have been documented, and these differences have been linked to the use and type of sealcoat (Van Metre and others, 2005). Mahler and others (2004) reported that the average concentration of total PAHs in runoff from coal-tar sealed lots was about 65 times higher than the average concentration in particles washed off parking lots that had not been sealcoated. In addition, they reported that the average concentration of total PAHs in particles washed off parking lots sealed with asphalt-based sealcoat was about 6 times less than coal-tar based sealcoat, but still 10 times higher than the concentration from unsealed parking lots. Identification of specific sources in 163 streams was beyond the scope of this study, but given the known effects of PAHs on aquatic organisms (Eisler, 1987), the importance of understanding the source and transport of these compounds to streams in urban and urbanizing basins is clear. Information from this study on the differences across metropolitan areas may prove useful in the selection of streams and the design of future investigations.

Taken as a group, the pattern of relations with urban intensity for the dibenzofurans (methyl dibenzofuran and benzo[*b*]naphtho[2,3-*d*]furan) was identical to the patterns observed for petrogenic PAHs. One of the two dibenzofurans analyzed was detected frequently, and relations between concentration and urban intensity were moderate to very strong in Atlanta, Raleigh-Durham, Milwaukee-Green Bay, and Denver-Fort Collins. In addition, concentrations of methyl dibenzofuran were much higher in Atlanta compared to the other metropolitan areas, the same pattern as the petrogenic PAHs. The similarity of the responses between dibenzofurans and petrogenic PAHs was unexpected, as the predominant source of dibenzofurans is believed to be open burning of residential refuse in burn barrels (U.S. Environmental Protection Agency, 2006c).

The response pattern for pentachloroanisole, the most frequently detected compound, was similar to the pattern

noted for the petrogenic PAHs, with strong relations observed in Atlanta, Raleigh-Durham, Milwaukee-Green Bay, and Denver-Fort Collins. A significant but weaker relation was noted in Portland. Although the purchase and use of pentachlorophenol, the parent compound of pentachloroanisole, is restricted and no longer available to the public, it still has industrial uses as a wood preservative for utility poles, railroad ties, and bridge pilings. It makes sense that the number of bridge crossings and utility poles in a basin would increase as basins urbanize. In addition to the number of bridges, the age of and distance to bridges with wood pilings are likely factors influencing the concentration of pentachloroanisole in streams. It follows that the relations between pentachloroanisole and urbanization, while strong, would not be as consistent as pyrogenic PAHs.

Frequency of detections and relations between concentrations and urban intensity for the insecticides and herbicides related to urbanization were not consistent across the six metropolitan areas, but as expected follow patterns of current or historic use. Chlorpyrifos was strongly related to urban intensity in Atlanta, Raleigh-Durham, and Dallas-Fort Worth, and chlordane was strongly related to urban intensity in Raleigh-Durham. These three metropolitan areas are in very heavy (Atlanta) or moderate-heavy (Raleigh-Durham and Dallas-Fort Worth) termite zones (Beal and others, 1994). This pattern corresponds to use of these two compounds for termite control as summarized in Nowell and others (1999) and the detection of chlordane in bed sediment from urban streams in Gilliom and others (2006). In June 2000, the USEPA determined that chlorpyrifos was sufficiently hazardous to human health as to warrant cancellation of nearly all household-use products. Pre-construction use of chlorpyrifos as a termiticide continued until 2005. As of January 2006, chlorpyrifos use is restricted to certified, professional, or agricultural applicators and only for golf courses, road medians, industrial plant sites, nonstructural wood treatments, fire ant mounds, and mosquito control (U.S. Environmental Protection Agency, 2000a). Chlordane was used as a pesticide in the United States during 1948–1988. Before 1978, chlordane was used on agricultural crops, lawns, and gardens. From 1983 to 1988, the only approved use for chlordane was to control termites in homes.

Moderate to strong relations between the concentration of at least one herbicide and urban intensity were observed in all of the metropolitan areas except Dallas-Fort Worth. The similarity in response to percent urban land cover suggests a common-use pattern for benfluralin in Atlanta and Raleigh-Durham and for trifluralin in Atlanta, Raleigh-Durham, Portland, and Milwaukee-Green Bay. The higher trifluralin concentrations in Portland and Milwaukee-Green Bay in streams with 10 to 40 percent urban land cover are likely due to agricultural use. In Denver-Fort Collins, the herbicide of choice appears to be dacthal.

The groups of compounds listed in appendix 2 as fragrances/personal care products, steroids, polybrominated ethers, plasticizers, antimicrobial/disinfectants, and detergent metabolites are used as indicators of wastewater in streams

(Kolpin and others, 2002; Buerge and others, 2003; Burkhardt and others, 2006). The detection frequencies for most of the wastewater compounds were too low to establish relations with urban intensity. Assuming success in avoiding point discharges when selecting sampling sites, sources of “wastewater” compounds to streams in this study would include but not be limited to leaking sewage lines, sewage overflows during storms or due to clogs, septic tanks, overland runoff (for example, animal feces), and atmospheric deposition.

A few moderate to strong relations between individual wastewater indicators and urban intensity were noted (appendix 2), but there were no apparent patterns as observed for PAHs, dibenzofurans, pentachloroanisole, and pesticides. HHCb (a synthetic musk used in soaps and perfumes) in Raleigh-Durham and Denver-Fort Collins, and BDE 47 (flame retardant) in Denver-Fort Collins and Dallas-Fort Worth had the strongest relations with urban intensity of the wastewater compounds analyzed. In addition to being components of wastewater effluents, HHCb and BDE 47 have been found in air collected from urban and rural areas (Standberg and others, 2001; Peck and Hornbuckle, 2004) and along with PDBEs have been shown to be able to move long distances from source regions to nonsource regions (Hoh and Hites, 2005). Research interest in these two compounds is increasing due to their widespread use, lack of regulation, atmospheric transport, presence in wastewater effluents, persistence in the environment, ability to bioaccumulate, and potential to act as endocrine disruptors (Bitsch and others, 2002; Vos and others, 2003; Peck and Hornbuckle, 2004).

As a complement to the chemical analysis, the bioassays Microtox® and P450RGS were used to evaluate the potential and relative toxicity of the complex mixtures sequestered in the SPMDs. The application of bioassays to extracts of SPMDs, coined SPMD-TOX by Johnson and others (2004), is expanding, and a variety of bioassays in addition to Microtox® and P450RGS have been conducted on SPMD extracts. These bioassays include, but are not limited to, the Ames test for mutagenic potential and the yeast estrogen screen (YES assay) for estrogenic potential (Rastall and others, 2004; Vermeirssen and others, 2005; Huckins and others, 2006).

Toxicity ( $EC_{50} < 2.5$ ) was measured in streams all across the designed gradient of urban intensity, and significant relations with urban land cover were found in Atlanta and Raleigh-Durham. In addition to being a relatively low cost and simple assay, much of the utility of the Microtox® assay is based on the fact that it responds to a wide range of chemical compounds (Bulich, 1979; Bulich and others, 1996). Johnson (1998) evaluated the Microtox® assay for more than 50 priority organic pollutants, petroleum products, and industrial compounds and found  $EC_{50}$  values for insecticides, petroleum products, and PCBs to be relatively similar and herbicides to be five-fold less toxic than insecticides.

The P450RGS assay is selective and well suited for large-scale assessments of the presence and relative toxicological significance of complex mixtures due to the greatly increased sensitivity and lower cost relative to chemical analysis (Inouye

and McFarland, 2000; Drastichova, 2004). A large number of studies of streams and lakes have been published using bioassays for AhR-active compounds on SPMD extracts (Huckins and others, 1996; Parrott and Tillett, 1997; Richards and Johnson, 2002; Johnson and others, 2004; Shaw and others, 2004; Ma and others, 2005), but these applications have been restricted to one or a few aquatic systems. A large-scale study (1,309 samples from 19 coastal regions) by the National Oceanic and Atmospheric Administration has been published using the P450RGS assay to evaluate coastal sediments for aryl hydrocarbon receptor (AhR) agonist compounds and to relate relative toxicity to benthic community structure (Anderson and others, 2005). This is the first large-scale study to use SPMD-TOX to assess toxicity in streams.

Results of the P450RGS assay were consistent, as strong to very strong correlations with urban intensity were observed in all six metropolitan areas studied. As previously noted, the highest TEQ values for individual streams were measured in Denver-Fort Collins and Milwaukee-Green Bay, and higher values at the low end of the urban gradient were observed in Dallas-Fort Worth.

The P450RGS assay is used as an analytical chemistry tool to measure the levels of AhR-active compounds but more importantly, it is also used to simulate organism response to these compounds. The effects on aquatic biota of AhR-active compounds, which include PAHs, PCBs, chlorinated dioxins, and chlorinated dibenzofurans, are well documented (Eisler, 1986a,b; Eisler, 1987). Effects of PAHs on aquatic insects include inhibited reproduction, delayed emergence, sediment avoidance, and mortality. Fin erosion, craniofacial and spinal deformities, liver abnormalities, cataracts, immune system impairments, edema of the yolk sac and pericardium, hemorrhaging, disruption of cardiac function, mutations and heritable changes in progeny, neuronal cell death, anemia, and reduced growth have been documented for fish exposed to PAHs (Eisler, 1987; Brinkworth and others, 2003). PCBs and dioxins are mutagenic, carcinogenic, and teratogenic, and documented effects on fish include reduced growth, egg production, and fertilization success (Eisler, 1986a,b).

Of the list of AhR-active compounds, organochlorine insecticides, PAHs, and PCBs were detected in this study, and PAHs were the only group of compounds consistently found to increase in concentration as basins urbanize in the six metropolitan areas investigated. Villeneuve and others (1997) found cytochrome P450 induction in fish hepatoma cells exposed to SPMD extracts from a severely degraded urban stream in Milwaukee, Wisconsin, and presented empirical evidence that AhR-active PAHs could account for 20–50 percent of the potency observed. Barron and others (2004) found 2- and 3-ringed unsubstituted PAHs to be generally inactive AhR-receptor agonists in fish, avian, and mammalian systems, while 4- to 6-ringed PAHs containing fluoranthene or phenanthrene structures with an exposed bay region (refers to arrangement of the rings) were associated with higher potency. It is unknown which compounds in the SPMDs caused the increases in toxic equivalents in the streams sampled in this

study, because the SPMDs undoubtedly contained AhR-active compounds, with varying degrees of potency, not quantified by chemical analysis. What is clear is that the concentrations of bioavailable AhR-active compounds in streams increase with increasing urban intensity in the basin, and AhR-mediated toxicity should be considered in integrated assessments of the response of aquatic systems to urbanization.

## Summary

Numerous studies have documented a wide range of chemical, physical, and biological changes in streams due to urbanization. Urban land is a small component of the landscape in the United States, but these lands have a disproportionate effect on stream condition. With continued increases in population, understanding the complex and interrelated effects of urbanization on streams will be important for water- resource managers. Results from this study further support other research showing that as urban intensity increases in a watershed, the concentration of many hydrophobic organic contaminants also increases, which in turn increases the potential for effects on aquatic biota. PAHs were the major group of hydrophobic organic compounds detected in this study, and the most frequently detected were of pyrogenic origin.

At high enough concentrations, hydrophobic contaminants in urban streams can result in harmful effects to aquatic biota. Therefore, the assessment of hydrophobic contaminants is one important component of understanding stream responses to urbanization. In this study, 140 compounds were measured by GC/MS analysis, and 73 of these compounds were detected. Average water concentrations estimated from SPMDs were compared to screening benchmarks for protection of human health and aquatic life; 3 of 14 compounds with available benchmarks—anthracene, dieldrin, and diazinon—exceeded those levels in one or more streams. As a complement to the chemical analysis, the bioassays Microtox® and P450RGS were used to evaluate the potential and relative toxicity of the complex mixtures sequestered in the SPMDs.

Based on Spearman's rank correlations, 29 endpoints were detected in at least 25 percent of streams and were strongly (positively) related to urban intensity in at least one of the metropolitan areas studied. These 29 endpoints included the concentrations of 16 PAHs, a wood preservative (pentachloroanisole), 2 insecticides (chlorpyrifos and chlordane), 3 herbicides (benfluralin, trifluralin, and dacthal), a synthetic musk (HHCB), 2 furans (methyl dibenzofuran and benzo[*b*]naphtho[2,3-*d*]furan), and a flame retardant (BDE 47). In addition to the concentrations of these individual compounds, the total number of compounds detected and the results of the Fluoroscan and P450RGS assays were strongly correlated with urban intensity.

Evidence of differences in one or a combination of factors governing source strength, transport, and fate of hydrophobic compounds between the six metropolitan areas was observed based on the number and pattern of endpoints correlated with urban intensity variables. The number of endpoints related to urban intensity ranged from 3 in Dallas Fort-Worth and Portland to 21 in Raleigh-Durham. High frequency of detection and strong correlations with urban intensity for pyrogenic PAHs (such as unsubstituted 4-ringed PAHs) in all six metropolitan areas supports the hypothesis that these compounds are an important component of urbanization, regardless of location. Pentachloroanisole, dibenzofurans, and petrogenic PAHs (alkylated PAHs and heterocyclic dibenzothiophenes) frequently were detected and strongly related to urban intensity in Atlanta, Raleigh-Durham, Milwaukee-Green Bay, and Denver-Fort Collins, suggesting a difference in source strength for these compounds.

While not consistent across the six metropolitan areas, the responses of insecticides and herbicides to urbanization generally followed reported patterns of current or historic use. HHCb (a synthetic musk) in Raleigh-Durham and Denver-Fort Collins, and BDE 47 (flame retardant) in Denver-Fort Collins and Dallas-Forth Worth had the strongest relations with urban intensity of the wastewater compounds analyzed. The detection frequencies for most of the wastewater-indicator compounds were too low to establish relations with urban intensity. Assuming success in avoiding point-source discharges during site selection, relatively high levels of wastewater indicators in a few streams suggest the influence of septic tanks or sewage overflows.

In addition to pyrogenic PAHs, levels of aryl hydrocarbon receptor agonists (AhR-agonist) as measured by the P450RGS assay also increased with increasing urban intensity in all six metropolitan areas. Relations were strong in Dallas-Fort Worth and Portland, where few other endpoints were related to urban intensity. Of potential AhR-agonists targeted by chemical analysis, PAHs, organochlorine pesticides, and PCBs were detected. Detection frequencies of PCBs were too low to test relations to urban intensity in any metropolitan area, and organochlorine pesticides were related to urban intensity in only one metropolitan area. On the other hand, PAHs were consistently detected and positively correlated to urban intensity in all six metropolitan areas investigated. It is unknown which compounds in the SPMDs caused the increases in toxicity as measured by P450RGS because the SPMDs undoubtedly contained many AhR-agonists not quantified by chemical analysis. What is clear is that bioavailable, aryl hydrocarbon receptor agonists increase in streams with increasing urban intensity in the basin, and toxicity mediated by this metabolic pathway should be considered in integrated assessments of the response of aquatic systems to urbanization.

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