

Prepared in collaboration with the North Carolina Department of Transportation

Characterization of Stormwater Runoff from Bridges in North Carolina and the Effects of Bridge Deck Runoff on Receiving Streams



Scientific Investigations Report 2011–5180

Cover. *Front*—Traffic on I-40 Business bridge crossing Salem Creek in Forsyth County, North Carolina, during a precipitation event, January 6, 2009. Photograph taken by NCDOT contractor. Used with permission.

Back—Stormwater collection system on U.S. 64 bridge over the Hiwassee River in Cherokee County, North Carolina, July 15, 2008. Photograph taken by NCDOT staff during routine inspections. Used with permission.

Characterization of Stormwater Runoff from Bridges in North Carolina and the Effects of Bridge Deck Runoff on Receiving Streams

By Chad R. Wagner, Sharon A. Fitzgerald, Roy D. Sherrell, Douglas A. Harned, Erik L. Staub, Brian H. Pointer, and Loren L. Wehmeyer

Prepared in collaboration with the North Carolina Department of Transportation

Scientific Investigations Report 2011–5180

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

U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2011

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment, visit <http://www.usgs.gov> or call 1–888–ASK–USGS.

For an overview of USGS information products, including maps, imagery, and publications, visit <http://www.usgs.gov/pubprod>

To order this and other USGS information products, visit <http://store.usgs.gov>

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

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

Suggested citation:

Wagner, C.R., Fitzgerald, S.A., Sherrell, R.D., Harned, D.A., Staub, E.L., Pointer, B.H., and Wehmeyer, L.L., 2011, Characterization of stormwater runoff from bridges in North Carolina and the effects of bridge deck runoff on receiving streams: U.S. Geological Survey Scientific Investigations Report 2011–5180, 95 p. + 8 appendix tables.

Available online at <http://pubs.usgs.gov/sir/2011/5180/>.

Acknowledgments

The authors appreciate the efforts of the North Carolina Department of Transportation (NCDOT) Division Staff for their support and work in modifying the monitoring sites to facilitate flow measurement and water-quality sampling and the NCDOT Highway Stormwater Program and the URS Corporation for their support and insights in defining parameters of concern, calculating hardness and biotic ligand corrections, and other tasks.

The authors express sincere gratitude to Sean Egen, John Mazurek, Brad Huffman, Jason Jarvis, Keith Ryan, and Corey Petersohn in the U.S. Geological Survey (USGS) North Carolina Water Science Center for their tireless efforts in sample collection, delivery, and processing support. The authors also want to thank Kirk Smith, USGS, for his advice and guidance in establishing the runoff monitoring network; Mary Giorgino, USGS, for numerous contributions to the proposal and advice throughout the course of the study; Jeanne Robbins, USGS, for her assistance in developing efficient techniques and tools to process 1-minute stage, velocity, and precipitation data; Wendi Young, USGS, for her efforts in developing scripts to incorporate data transmitted via cell modem into the USGS database; Duane Wydoski and Steve Zaugg, USGS National Water Quality Laboratory, for advice on a huge array of analytical issues; and Art Horowitz and Kent Elrick, USGS Georgia Water Science Center, for the analysis of bed sediments and advice on many analytical and operational issues.

Contents

Acknowledgments	iii
Abstract	1
Introduction.....	2
Study Approach.....	3
Purpose and Scope	4
Methods of Evaluation and Characterization of Bridge Deck Runoff	4
Study Design and Site Descriptions	4
Bridge Deck Runoff and Precipitation Sites.....	4
Stream Sites.....	8
Bed Sediment Sites	8
Measurement of Precipitation and Discharge	11
Precipitation.....	11
Discharge	11
Bridge Deck	11
Stream (Routine and Storm).....	12
Field Sampling and Preliminary Laboratory Processing	12
Bridge Deck Runoff	12
Stream (Routine and Storm).....	13
Bed Sediments	13
Laboratory Analyses.....	14
Water Quality (Bridge Deck Runoff and Stream).....	14
Bed Sediment Chemistry	14
Quality Assurance and Quality Control Design.....	14
Precipitation.....	15
Discharge	15
Bridge Deck	15
Stream (Routine and Storm).....	15
Water Quality (Bridge Deck and Stream)	15
Field	16
Laboratory	22
Bed Sediment	24
Field	24
Laboratory	24
Bridge Deck Runoff Event Load and Annual Stream Load Computations.....	27
Water Quality and Effect of Stormwater Bridge Runoff on Receiving Streams.....	27
Parameters of Concern.....	27
Precipitation Data for Sampled Events	28
Bridge Deck Runoff.....	28
Discharge	30
Water Quality.....	32
Constituent Concentrations Associated with the Dissolved and Particulate Phases	34
Summary and Statistical Analysis of Constituent Concentrations.....	36

Summary of Bridge Deck Event Loads and Development of Predictive Equations for Runoff Loads	43
Stream (Routine and Storms).....	47
Discharge	47
Water Quality.....	50
Comparisons of Bridge Deck Stormwater Runoff and Stream Water Quality.....	56
Distribution of Concentrations from Bridge Deck Runoff	56
Annual Loads and Yields of Bridge Deck Runoff	58
Mixing Calculations of Bridge Deck Stormwater and Stream Constituents.....	62
Bed Sediment Characteristics Upstream and Downstream from Bridges	75
Summary and Conclusions.....	83
References Cited.....	85

Figures

1. Map showing locations where bridge deck and streamwater samples were collected in North Carolina	5
2. Photograph showing discharge pipe sampling configuration at the Black River site.....	5
3. Map showing locations where bed sediment samples were collected in North Carolina	11
4. Graph showing average relative percent difference of parameters of concern in water replicates and in autosampler/equal-width interval method comparison water samples.....	21
5. Graph showing average relative percent differences of the percent absolute differ- ence between pairs of inorganic analytes, total organic carbon, and the percent less than the 63-micron fraction in field replicates, field splits, and analytical replicates in bed sediment samples	25
6. Graph showing average relative percent differences of the percent absolute differ- ence between pairs of inorganic analytes and total organic carbon in bed sediment standard reference materials with “known” concentrations.....	25
7. Box plots showing summary of bridge deck runoff measured during water-quality sampling events	30
8. Box plots showing percent runoff sampled at the bridge deck sites	31
9. Seasonal Piper diagrams showing general water types of runoff from bridge decks ...	33
10. Graphs showing percent dissolved fraction of total recoverable aluminum, lead, iron, and total phosphorus in bridge deck samples for each season.....	34
11. Graphs showing percent dissolved fraction of total nitrogen and total recoverable manganese, nickel, arsenic, cadmium, copper, zinc, and mercury in bridge deck samples for each season	35
12. Box plots showing concentrations of metals in rural and urban bridge deck runoff samples	38
13. Box plots showing concentrations of nutrients and total suspended solids in rural and urban bridge deck runoff samples	39
14. Box plots showing concentrations of total nitrogen, total phosphorus, total suspended solids, pH, dissolved zinc, total recoverable nickel, dissolved copper, dissolved lead, dissolved cadmium, total recoverable arsenic, total recoverable mercury, total recov- erable manganese, total recoverable iron, total recoverable aluminum, and polycyclic aromatic hydrocarbons in bridge deck runoff samples arranged in order of increasing annual average daily traffic	40

15. Box plots showing summary of average measured stream discharge during routine and storm water-quality sampling at the four stream study sites with both routine and storm sampling	49
16. Piper diagrams showing general water types during routine (non-storm) and storm sampling events at stream sampling sites	50
17. Box plots showing concentrations of total nitrogen, total phosphorus, total suspended solids, pH, dissolved zinc, total recoverable nickel, dissolved copper, dissolved lead, dissolved cadmium, total recoverable arsenic, total recoverable mercury, total recoverable manganese, total recoverable iron, and total recoverable aluminum for stream routine, bridge deck runoff, and stream storm samples for the four stream sampling sites.....	53
18. Stream sites discharge hydrographs with stream sampling periods used to generate dilution curves.....	62
19. Plan view of Black River channel configuration and location of streamflow-gaging and sampling site near Tomahawk, North Carolina.....	66
20. Plan view of Little River channel configuration and location of streamflow-gaging and sampling site at Secondary Road 1461 near Orange Factory, North Carolina	67
21. Plan view of Mountain Creek channel configuration and location of streamflow-gaging and sampling sites near Bahama, North Carolina	68
22. Plan view of Swannanoa River channel configuration and location of streamflow-gaging and sampling site at Interstate 40 at Black Mountain, North Carolina	69
23. Graph showing an example of a computed bridge deck runoff plume migration from a right-bank injection point at U.S. Geological Survey streamflow-gaging station 03448800 Swannanoa River at Interstate 40 at Black Mountain, North Carolina	70
24. Graphs showing dilution curves for bridge deck runoff plumes at Black River near Tomahawk, North Carolina, for total recoverable arsenic, dissolved copper, total recoverable nickel, dissolved zinc, total nitrogen, and total phosphorus.....	71
25. Graphs showing dilution curves for bridge deck runoff plumes at Little River at Secondary Road 1461 near Orange Factory, North Carolina, for total recoverable arsenic, dissolved copper, total recoverable nickel, dissolved zinc, total nitrogen, and total phosphorus	72
26. Graphs showing dilution curves for bridge deck runoff plumes at Mountain Creek at Secondary Road 1617 near Bahama, North Carolina, for total recoverable arsenic, dissolved copper, total recoverable nickel, dissolved zinc, total nitrogen, and total phosphorus	73
27. Graphs showing dilution curves for bridge deck runoff plumes at Swannanoa River at Interstate 40 near Black Mountain, North Carolina, for total recoverable arsenic, dissolved copper, total recoverable nickel, dissolved zinc, total nitrogen, and total phosphorus	74
28. Graphs showing downstream minus upstream concentration differences for all data, and data focusing near the zero line for all inorganic analytes and total organic carbon in bed sediment at scuppered bridge sites, bridge sites with best management practices, and scuppered sites with reverse flow.....	76
29. Graphs showing downstream minus upstream concentration differences for all data, and data focusing near the zero line for semivolatile organic compounds in bed sediment at scuppered bridge sites, bridge sites with best management practices, and scuppered sites with reverse flow.....	80

Tables

1. Common highway runoff pollutants and their primary sources.....	3
2. Characteristics of bridge deck runoff study sites	6
3. Watershed characteristics of stream monitoring sites	8
4. Summary of sample types at each study site	9
5. Analytes measured in water and bed sediment samples.....	90
6. Comparison of bridge deck runoff measured volumetrically with discharge reported from velocity/stage meters.....	16
7. Selected quality-assurance programs for water chemistry analyses operated by the U.S. Geological Survey Branch of Quality Systems and the National Water Quality Laboratory	17
8. Bridge deck and stream field quality-assurance and quality-control samples.....	18
9. Detections of parameters of concern among total recoverable analytes in blanks.....	19
10. Detections of parameters of concern among dissolved analytes in blanks.....	20
11. Concentrations of selected dissolved and total recoverable analytes in the field blank from July 15, 2009.....	20
12. Analytes that were potentially omitted from the parameters of concern list and the reasons why	21
13. Spike recoveries for semivolatile organic compounds in water matrix samples and reagent	22
14. Spike recoveries for semivolatile organic compounds in bed sediment samples	26
15. Identification of parameters of concern by comparison of maximum concentration in bridge deck runoff to selected water-quality thresholds	29
16. Detections of semivolatile organic compounds as parameters of concern and relative abundances in bridge deck samples	32
17. Median concentrations for bridge deck runoff samples grouped by ecoregion and season.....	37
18. Summary of statistical comparisons of bridge deck runoff concentrations from concrete and asphalt bridges.....	39
19. Summary of minimum and maximum storm event bridge deck runoff loads of parameters of concern measured at the bridge deck sites	44
20. Summary of significant variables and regression coefficients used to develop the predictive equations of loads for parameters of concern at bridges with runoff discharge data	45
21. Summary of significant variables and regression coefficients used to develop the predictive equations of loads for parameters of concern at bridges without runoff discharge data	48
22. Correlation of total nutrient and total recoverable metal parameters of concern to suspended-sediment concentrations in stream samples.....	50
23. Detections of semivolatile organic compounds as parameters of concern in stream samples	51
24. Median concentrations for stream samples grouped by season.....	52
25. Summary of p-values derived from statistical comparisons between bridge deck runoff concentrations and stream routine and storm samples at the stream monitoring sites.....	57
26. Comparison of stream and bridge deck runoff parameters of concern concentrations	59

27. Comparison of stream and bridge deck runoff parameters of concern annual loads and yields	60
28. Summary of the bridge deck runoff sample dates, corresponding stream conditions, and the adjusted mixing lengths computed for each mixing scenario.....	64
29. Relative abundances of upstream-downstream pairs of semivolatile organic compounds in bed sediment.....	79

Appendix Tables

- A1. Individual event loads of pollutants of concern for each sampled storm at all bridge deck sites
- A2. Detailed summary of the date, duration, mean temperature, and selected pertinent measured precipitation properties for all sampled events at the bridge deck sites
- A3. Detailed summary of the measured precipitation, runoff volume and start and end times for runoff samples collected at the bridge deck sites
- A4. Daily runoff discharge data for the bridge deck sites over the entire study period
- A5. Concentrations of all analytes in samples collected at the bridge deck sites
- A6. Average measured discharge and start and end times for each stream water-quality sample collected at each stream site
- A7. Concentrations of all analytes in routine and storm water-quality samples collected at the stream sites
- A8. Concentrations of all analytes in bed sediment samples

Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
Length		
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square foot (ft ²)	0.09290	square meter (m ²)
square mile (mi ²)	2.590	square kilometer (km ²)
Volume		
gallon (gal)	3.785	liter (L)
Flow		
foot per second (ft/s)	0.3048	meter per second (m/s)
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
Pressure		
pound per acre (lb/acre)	1.14	kilogram per hectare (kg/ha)

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

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) / 1.8$$

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 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). Concentrations of chemical constituents in sediments are given either in milligrams per kilogram (mg/kg) or weight percent (Wt%).

Other units used in this report in this report include liter (L), mL (milliliter), µm (micron), milligram per kilogram (mg/kg), microgram per kilogram (µg/kg), and feet per foot (ft/ft). Use of hectare (ha) as an alternative name for square hectometer (hm²) is restricted to the measurement of small land or water areas. Use of liter (L) as a special name for cubic decimeter (dm³) is restricted to the measurement of liquids and gases. No prefix other than milli should be used with liter. Metric ton (t) as a name for megagram (Mg) should be restricted to commercial usage, and no prefixes should be used with it.

Acronyms

AADT	Annual average daily traffic
AAS	Atomic absorption spectrometry
ADT	Average daily traffic
CNS	Carbon-nitrogen-sulfur analyzer
CS	Carbon-sulfur analyzer
DCP	Data-collection platform
EWI	Equal-width interval
HIF	Hydrologic Instrumentation Facility
ICP–AES	Inductively coupled plasma–atomic emission spectroscopy
LT-MDL	long-term method detection limit
NAWQA	National Water Quality Assessment Program
NCDOT	North Carolina Department of Transportation
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
PAH	Polycyclic aromatic hydrocarbon
PbCO ₃	Cerussite
POC	Parameter of concern
QA/QC	Quality assurance and quality control
R ²	Coefficient of determination
RPD	Relative percent difference
SCM	Stormwater control measure
SELDM	Stochastic Empirical Loading and Dilution Model
SVOC	Semivolatile organic compound
TMDL	Total maximum daily load
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

Characterization of Stormwater Runoff from Bridges in North Carolina and the Effects of Bridge Deck Runoff on Receiving Streams

By Chad R. Wagner, Sharon A. Fitzgerald, Roy D. Sherrell, Douglas A. Harned, Erik L. Staub, Brian H. Pointer, and Loren L. Wehmeyer

Abstract

In 2008, the North Carolina General Assembly passed House Bill 2436 that required the North Carolina Department of Transportation (NCDOT) to study the water-quality effects of bridges on receiving streams. In response, the NCDOT and the U.S. Geological Survey (USGS) collaborated on a study to provide information necessary to address the requirements of the Bill. To better understand the effects of stormwater runoff from bridges on receiving streams, the following tasks were performed: (1) characterize stormwater runoff quality and quantity from a representative selection of bridges in North Carolina; (2) measure stream water quality upstream from selected bridges to compare bridge deck stormwater concentrations and loads to stream constituent concentrations and loads; and (3) determine if the chemistry of bed sediments upstream and downstream from selected bridges differs substantially based on presence or absence of a best management practice for bridge runoff.

The USGS measured bridge deck runoff from 15 bridges, stream water-quality data at 4 bridge deck runoff sites, and streambed sediment chemistry at 30 bridges across North Carolina. The bridges selected for study had differing sizes, differing ecoregions and land-use characteristics, and a range of annual average daily traffic (AADT). Runoff from both concrete and asphalt deck bridges was sampled. Composite samples of bridge deck runoff were collected for 12 to 15 storms at each bridge. Additionally, routine (monthly) samples of base-flow streamwater and at least seven samples of streamwater during storms were collected over a 12-month period at four sites. Samples were analyzed for a wide range of constituents, including dissolved and total recoverable metals and nutrients, major ions, total suspended solids, suspended-sediment concentration, oil and grease, petroleum hydrocarbons, and semivolatile organic compounds (SVOCs). Parameters of concern (POCs) were defined as analytes with at least one exceedance of a water-quality threshold or were otherwise known to have potentially deleterious effects on receiving streams. The 28 POCs included metals, nutrients,

pH, suspended solids concentration, polycyclic aromatic hydrocarbons, and other organic compounds. Results and discussion were limited to these POCs for water samples.

Bridge deck runoff concentrations were generally shown to be statistically higher for bridges located in urban areas than those in rural areas. There was no strong relation between concentrations and AADT, which could be explained by the relatively low traffic volumes at the study sites. When sites with larger ranges of AADT have been studied, especially sites with volumes substantially above and below about 30,000 vehicles, runoff concentrations tended to roughly scale with AADT. The selection process for monitoring sites included an analysis of the AADT frequency distributions in North Carolina; only about 1 percent of bridges in North Carolina have AADT volumes in excess of 30,000 vehicles. Because of the small percentage of bridges in North Carolina with AADT volumes in excess of 30,000 and the extremely limited number of those bridges with runoff collection systems, only two bridge sites with an AADT volume greater than 30,000 (Mallard Creek and Mango Creek) were included in the study. Concentrations of most constituents in bridge deck runoff samples were generally statistically higher in winter compared to all other seasons, pointing to reduced volatilization at lower temperatures and higher total suspended solids concentrations in the winter (likely from deicing treatments) as potential explanations. The runoff samples from the Coastal Plain bridges generally had statistically lower concentrations than samples from the bridges in the Blue Ridge and Piedmont ecoregions.

Results of the statistical testing and comparisons of the bridge deck runoff and stream concentrations indicate that the bridge deck runoff concentrations were only statistically higher than the corresponding stream (routine and storm) concentrations for 36 percent of the comparisons. Thus, with the exception of concentrations of dissolved copper and zinc, total recoverable nickel, and polycyclic aromatic hydrocarbons, which were consistently higher in bridge deck runoff, the bridge deck runoff concentrations at all sites were similar to those measured in the receiving streams at the four stream sampling sites. Comparisons of bridge deck and stream

loads indicate that all the bridge deck runoff loads were lower (and generally orders of magnitude lower) than the stream loads for all POCs. The inverse was true for total yields (load per unit drainage area) of the POCs. The bridge deck runoff yields were generally higher than the yields from the four stream sites for all of the POCs. The bridge deck runoff yields can be used to estimate loads at other bridges with similar characteristics and to provide planning-level estimates of the contributing total load from all highways in a watershed. The effect of bridge deck runoff loads on receiving waters should also be evaluated in light of the bioassays, which only showed potential ecological effects for one bridge deck runoff sample (collected in the winter), and benthic macroinvertebrate survey results, which revealed no significant difference upstream and downstream from the study bridge sites.

The rate at which bridge deck runoff mixes with, and is diluted by, the receiving stream was determined by using empirical relations and measured flow conditions at the four gaged stream sites for various steady-state hydraulic conditions. The dilution curves indicated that although in a few cases the maximum concentrations of some constituents in the bridge deck runoff plume exceeded water-quality thresholds by up to 4 times the threshold, levels were reduced to the ambient stream concentration rapidly (generally within 50 feet downstream from the injection point), and in some cases, were actually lower than the stream concentration.

The analysis of the bed sediment quality revealed no obvious patterns in downstream increases in inorganic analytes and total organic carbon at the sampled bridge sites. There was no consistent downstream enrichment of bed sediment with SVOCs, even at the bituminous (asphalt) bridges nor were there any obvious patterns related to urban versus rural bridges or with traffic volume. Possible explanations of these bed sediment results are as follows: (1) bridge decks are not contributing measurable quantities of these analytes to bed sediments; (2) these analytes were efficiently transported downstream, or contaminated bed sediments were scoured from the immediate bridge vicinity during high-flow events; (3) the contributing watershed effects on the bed sediment overwhelm any signature that the relatively small bridge deck area contributes; or most likely (4) a combination of all three of the possible explanations.

Although this study did not show bridge deck runoff to consistently be a primary source of pollutants to receiving streams, there is an indication that under certain conditions (that is, runoff following deicing treatments into stream base-flow conditions) bridge deck runoff can be a significant environmental stressor. The data, analysis, and relations associated with this study can be used by the NCDOT to (1) predict the constituent load from a bridge; (2) provide general information regarding the potential effects a bridge may have on its receiving stream or that all highways may have within a watershed; and (3) provide information needed to select the most efficient best management practice at a bridge construction, replacement, or other highway project site.

Introduction

Roadway runoff generated from within transportation rights-of-way is one of several pollutant source categories that may contribute to surface-water impairment (U.S. Environmental Protection Agency, 2009). The proximity and direct connection between bridge runoff and streams have facilitated most regulatory agencies throughout the United States to implement stormwater management criteria for bridges. It is commonly recommended that instead of directly discharging bridge deck runoff to receiving streams, the runoff should be directed to the vegetated right-of-way prior to discharge, with the assumption that such a configuration is better for surface-water quality (Dupuis, 2002). While extensive information exists on roadway runoff as a whole, few studies have focused on bridge deck runoff. Roadway runoff water-quality data are generally used as an approximation for the pollutant profile of bridge deck runoff (Dupuis, 2002).

On July 1, 2008, the North Carolina General Assembly passed House Bill 2436, Session Law 2008-107, Stormwater Runoff from Bridges Section 25.18 (North Carolina General Assembly, 2008). This Bill requires that the North Carolina Department of Transportation (NCDOT) select 50 bridges to study the effects of stormwater runoff from bridges over waterways and report the results to the Joint Legislative Transportation Oversight Committee. The following overarching goals were established to meet the requirements of the law:

- Characterize bridge deck runoff quality and quantity using scientifically accepted methods and identify stormwater constituents that are present at levels that may raise concern about receiving stream impairment.
- Estimate the effects of bridge deck runoff on surface-water bodies by evaluating water-quality chemistry and effects on aquatic life.
- Conduct a pilot study of at least 50 sites to evaluate stormwater treatment controls for their ability to provide necessary hydrologic control and stormwater treatment for target parameters in bridge deck runoff.
- Determine the cost of implementing effective treatments for existing and new bridges over waterways in North Carolina.

The U.S. Geological Survey (USGS), in collaboration with the NCDOT, conducted a study to characterize bridge deck runoff quality and quantity using scientifically accepted methods and identify parameters of concern (POCs; goal 1). The primary focus of the study was to examine bridge deck runoff on receiving streams in North Carolina.

Study Approach

In the development of the study approach, the USGS conducted a literature search to identify previous studies of bridge deck and highway stormwater runoff and of investigations of highway runoff treatment practices. Several studies relevant to the requirements of North Carolina House Bill 2436 were identified, including those by Irwin and Losey (1978), Van Hassel and others (1980), Wanielista and others (1980), McKenzie and Irwin (1983), Yousef and others (1984), Harned (1987), Zellhoefer (1989), Driscoll and others (1990), Stoker (1996), Marsalek and others (1997), Jongedyk (1999), Dupuis (2002), Smith (2002), Granato (2003), Kayhanian and others (2003; 2007), and Malina and others (2005). Additionally, the North Carolina Division of Water Quality conducted stormwater sampling at Bonner Bridge on the Outer Banks of North Carolina in 2007. These studies described various strategies for sampling highway and bridge deck runoff, provided information on the types of constituents that might be detected in highway runoff, and helped guide the approach used for this study. Common constituents found in roadway stormwater runoff include metals, inorganic salts,

polycyclic aromatic hydrocarbons (PAHs), suspended solids, and materials that are a result of wear and tear on a vehicle, such as oil and grease, rust, and rubber particles (Jongedyk, 1999; Dupuis, 2002). Each of these constituents is generally linked to automotive sources, roadway materials, and roadway maintenance activities. Table 1 provides a list of common highway runoff pollutants and their primary sources.

Data from the study are planned to be integrated into the Highway-Runoff Database (Granato and Czenas, 2009), which serves as a preprocessor for the recently developed Stochastic Empirical Loading and Dilution Model—SELDM (Granato, 2007). The integration of these data with a technically sound highway-runoff model can be used to guide, substantiate, and support highway planning, design, and maintenance decisions on a local, State, and national level. The findings of this study will also provide information that can be used by Departments of Transportation when developing strategies to meet total maximum daily load (TMDL) requirements and aid in determining the potential effects of bridge deck and highway runoff on receiving streams and the potential effectiveness of various best management practices.

Table 1. Common highway runoff pollutants and their primary sources.

[Modified from Dupuis (2002) and URS Corporation (2010)]

Constituent	Sources
Aluminum	Tire wear, leachate from recycled asphalt surfaces and patches
Bromide	Exhaust
Cadmium	Tire wear, insecticides
Chloride	Deicing salts
Chromium	Metal plating, moving engine parts, brake lining wear
Copper	Metal plating, bearing and bushing wear, moving engine parts, brake lining wear, fungicides and insecticides
Cyanide	Anti-cake compound used to keep deicing salt granular
Iron	Rust (automobile body and bridge structure), moving engine parts
Lead	Bearing and tire wear, oil and grease
Manganese	Moving engine parts
Nickel	Diesel fuel and gasoline (exhaust), lubricating oil, metal plating, bushing wear, brake lining wear, asphalt paving
Nitrogen	Atmosphere, fertilizer application, diesel fuel and gasoline (exhaust)
Particulates	Pavement wear, vehicles, atmosphere, maintenance
Petroleum	Spills, motor lubricants, antifreeze and hydraulic fluids, leachate from asphalt surfaces
Phosphorus	Atmosphere, fertilizer application
Polychlorinated biphenyls (PCBs)	Background atmospheric deposition, PCB catalyst in synthetic tires
Sodium, calcium	Deicing salts, grease
Sulfate	Roadway beds, fuel, deicing salts
Zinc	Tire wear, motor oil, grease, metal plating

Purpose and Scope

The purposes of this report are to characterize stormwater runoff from selected bridges across North Carolina and assess the water quality and effects of runoff on the receiving streams at the bridge sites. Concentrations and loadings of numerous water-quality constituents were determined in flow-weighted composite samples of stormwater collected from typical highway-drainage conveyance structures at 15 bridges across North Carolina. Specifically, this report (1) documents differences in chemistry of bed sediments upstream and downstream from selected bridges; (2) presents a comparison of bridge deck stormwater concentrations and loads to stream constituent concentrations and loads; and (3) estimates the distance required for the bridge deck runoff to become uniformly mixed across the receiving stream, and thus estimates the zone in which effects of bridge runoff are most pronounced.

Stormwater characterization was done at 15 bridges that represented the Blue Ridge, Piedmont, and Coastal Plain ecoregions of North Carolina. The bridges had runoff collection systems and varied in size and average daily traffic (ADT) volume. The surface types of the bridge decks were concrete and asphalt (bituminous). At least 12 runoff events were sampled at each bridge for a wide range of constituents, including dissolved and total recoverable metals and nutrients, oil and grease, and semivolatile organic compounds (SVOCs). Both dissolved and total recoverable concentrations of metals and nutrients were measured. Bottom sediment quality was measured at 30 sites—about one-half of which were the bridge deck runoff monitoring sites and about one-half were at bridges in which runoff discharged from scuppers directly into the stream. Bed sediment samples, collected from both the upstream and downstream reaches from each bridge, were analyzed for total nutrients and metals and total recoverable SVOCs. Streams at four bridge deck runoff sites were sampled intensively to estimate annual loadings of suspended sediment, nutrients, metals, and SVOCs. Stream concentrations and loads were compared to bridge deck runoff concentrations and loadings at these sites to understand the relative contribution of bridge deck runoff to total stream quality.

Methods of Evaluation and Characterization of Bridge Deck Runoff

The following sections outline how the study was designed and what factors guided the selection of the study sites. In addition, a brief overview of the methods used to collect, analyze, and quality assure the hydraulic and water-quality data is presented.

Study Design and Site Descriptions

All monitoring sites selected for the study were instrumented to measure bridge deck runoff quantity and quality and precipitation. A subset of these monitoring sites was colocated with USGS streamflow-gaging stations, which were instrumented and operated to provide water-quality data and continuous discharge records for the receiving streams. Streambed sediment was also sampled for chemical analysis at the monitoring sites.

Bridge Deck Runoff and Precipitation Sites

Bridge deck runoff sampling was conducted at 15 bridge sites (fig. 1; table 2) across North Carolina. The 15 sites were carefully selected to represent the ecological and topographic variability of the State. For the purpose of the study, the four U.S. Environmental Protection Agency (USEPA) level III ecoregions (Griffith and others, 2002) in North Carolina were collapsed into three major ecoregions (Blue Ridge, Piedmont, and Coastal Plain) by combining the Middle Atlantic Coastal Plain and Southeastern Plains into the Coastal Plain ecoregion. The study sites were also carefully selected to represent a range of bridge characteristics, such as drainage area and land use of the contributing watershed upstream from the bridge, annual average daily traffic (AADT), bridge type, bridge deck area, and bridge deck material. All the bridge sites selected for bridge deck runoff monitoring had an existing collection system so that all bridge runoff flows through a single pipe, thereby facilitating sampling (fig. 2). Discharge from the collection system flows across a grass swale, through a pond or riprap-lined bank before entering the stream.

The bridge deck runoff was sampled from the collection system discharge pipe using ISCO 6712 series automatic samplers (autosamplers) with a single 20-liter (L) Teflon-lined bottle to collect a flow-weighted composite sample for each storm runoff event. Although rare, samples sometimes remained in the autosamplers for up to 36 hours prior to filtration and preservation, and thus, partitioning between the dissolved and particulate phases may have changed. While the total recoverable concentrations likely were representative of ambient conditions, the dissolved concentrations of nutrients and metals may not reflect ambient conditions at the time of collection. Thus the study results were discussed with this issue in mind. An integrated acoustic Doppler velocity meter and pressure sensor was used to continuously measure water depth and discharge (calculated from velocity and depth) in the collection system pipe. The autosamplers were equipped with two-way cell phone telemetry, which allowed (1) data to be downloaded to the USGS National Water Information System (NWIS) nightly and (2) samplers to be queried and controlled remotely. A tipping bucket rain gage was also installed at each bridge deck site. A 1- to 2-inch (in.) plate with small weep holes was installed at the outlet of the collection pipes to increase flow depth (the velocity meters required

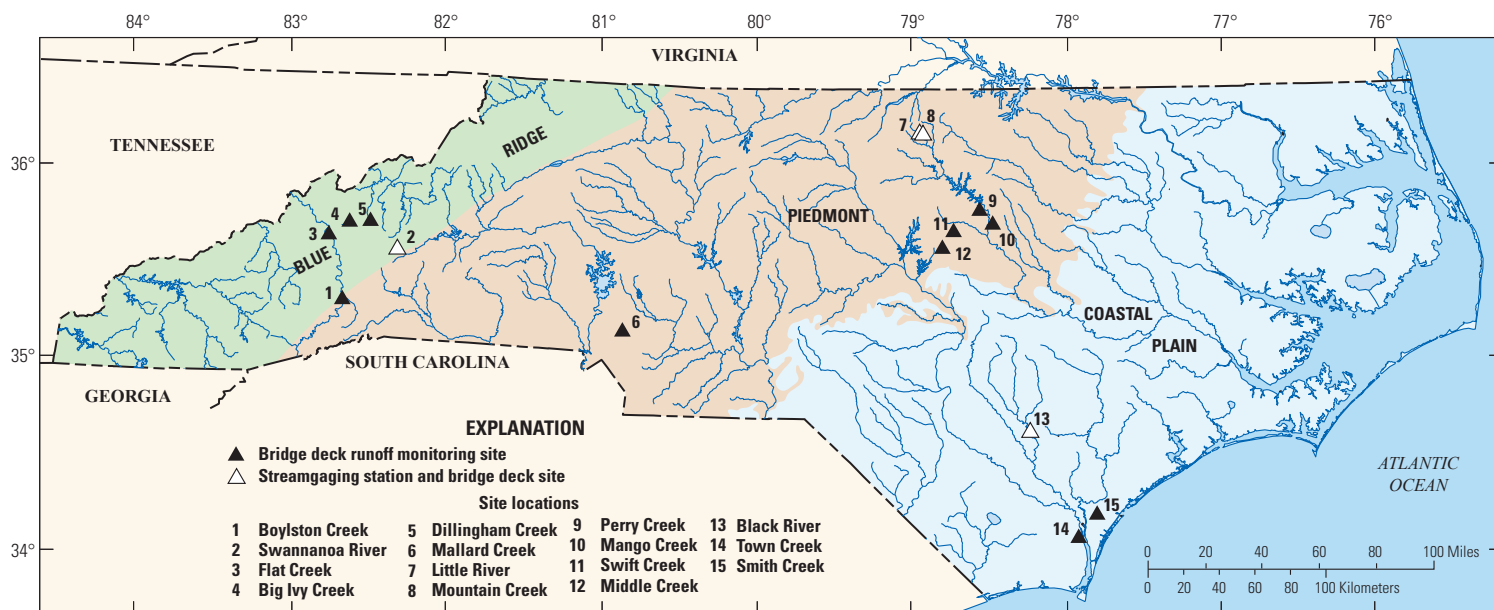


Figure 1. Locations where bridge deck and streamwater samples were collected in North Carolina



Figure 2. Discharge pipe sampling configuration at the Black River site.

a depth of at least 1 in. to measure flow) and agitate the flow. This approach has been shown (Smith, 2002) to result in more representative samples than sampling in an unmodified pipe. Three factors controlled the bridge deck runoff sample collection and analysis. First, a minimum of about 5 L of water was required to run all the chemical analyses. Second, a water depth of about 1 in. is required in the collection system discharge pipe in order to collect a representative sample and measure velocity. Third, samples were collected over a range of antecedent rainfall (time since last storm) conditions because this affected runoff

quality. These factors were used to determine whether runoff from any given event could be collected and (or) submitted for chemical analysis.

The NCDOT conducted a traffic survey study during the study to obtain up-to-date traffic volumes for the 15 bridge deck sites that were studied (table 2). Traffic volumes are a useful characteristic in analyzing the sources of chemical contaminants. As indicated in previous studies, high traffic routes have greater incidence of pollutants in runoff than low traffic routes (Van Hassel and others, 1980; Driscoll and others, 1990; Kayhanian and others, 2003). The NCDOT traffic survey study was conducted from May 2009 through March 2010 by the NCDOT Traffic Survey Group. Traffic surveys were generally conducted on a quarterly basis to capture seasonal differences in traffic patterns; however, due to site-specific constraints, this schedule was not met at all of the sites. In order to collect traffic volume data for the project, each bridge site was equipped with portable (short-term), automated traffic counting devices, using one of two data-collection methods—radar devices or pneumatic road tubes. Traffic volumes at each site were collected on a continuous basis in hourly increments over a 7-day survey period. At all sites, the available quarterly traffic volumes were averaged over the 7-day survey period to yield quarterly ADT volumes. These quarterly ADT volumes were used to compute an AADT volume, which was used in the study because quarterly counts at all 15 sites indicate consistent traffic volumes over the monitoring period. Additional details related to the traffic volume survey can be found in a publication by the URS Corporation (2010).

Table 2. Characteristics of bridge deck runoff study sites.

[NCDWQ stream classification: WS-IV, water supply-highly developed; C, aquatic life, secondary recreation, freshwater; WS-I, water supply-undeveloped; HQW, high quality waters; Tr, trout waters; NSW, nutrient sensitive waters; CA, water supply critical area; Sw, swamp waters; ORW, outstanding resource waters; SC, saltwater; aquatic life, secondary recreation. Route name: SR, secondary road; I, interstate; NC, North Carolina route; US, U.S. Highway. Other acronyms: USGS, U.S. Geological Survey; NCDWQ, North Carolina Division of Water Quality; PA, principal artery]

Map no. (fig. 1)	Station name	USGS station no.	Ecoregion	NCDWQ stream classification ¹	County	Latitude	Longitude	Route name	Roadway classification	Surface type	Measured annual average daily traffic volume ²	Stream crossing drainage area (square miles)	Runoff collection pipe drainage area (square feet)	Bridge deck area (square feet)	Bridge length (feet)	Bridge width (feet)
1	Boylston Creek at Mills River, Bridge 440008	352231082325601	Blue Ridge	WS-IV	Henderson	35.375	-82.549	SR 1314	Rural - Local	Bituminous	1,400	15.4	10,454	4,050	90	45
2	Swannanoa River near Black Mtn, Bridge 100494	353708082182101	Blue Ridge	C	Buncombe	35.619	-82.308	I-40	Urban - PA - Interstate	Concrete	25,500	4.2	61,420	56,470	558	101.2
3	Flat Creek near Weaverville, Bridge 100250	354306082372601	Blue Ridge	C	Buncombe	35.719	-82.624	SR 1742	Rural - Minor collector	Bituminous	400	24.6	2,178	824	41	20.1
4	Big Ivy Creek near Mars Hill, Bridge 100734	354728082321901	Blue Ridge	WS-II; HQW	Buncombe	35.791	-82.539	SR 2207	Rural - Major collector	Concrete	1,500	60.6	3,485	3,780	126	30
5	Dillingham Creek at Barnhardsville, Bridge 100145	354607082260901	Blue Ridge	WS-II; Tr; HQW	Buncombe	35.769	-82.436	SR 2173	Rural - Minor collector	Concrete	1,800	24.6	13,939	5,362	140	38.3
6	Mallard Creek near Charlotte, Bridge 590296	351911080450501	Piedmont	C	Mecklenburg	35.320	-80.752	I-85	Urban - PA - Interstate	Concrete	112,000	19.6	16,988	34,298	197	174.1
7	Little River at Orange Factory, Bridge 310064	360829078550901	Piedmont	WS-II; HQW, NSW, CA	Durham	36.142	-78.919	SR 1461	Rural - Local	Concrete	500	78.2	5,663	5,299	184	28.8
8	Mountain Creek near Bahama, Bridge 310005	360908078540701	Piedmont	WS-II; HQW, NSW, CA	Durham	36.152	-78.902	SR 1616	Rural - Minor collector	Bituminous	2,800	7.4	9,148	5,880	150	39
9	Perry Creek near Raleigh, Bridge 910124	35524708325001	Piedmont	C, NSW	Wake	35.880	-78.548	SR 2006	Urban - Local	Concrete	13,000	11.2	13,068	7,330	114	64.3

Table 2. Characteristics of bridge deck runoff study sites.—Continued

[NCDWQ stream classification: WS-IV, water supply-highly developed; C, aquatic life, secondary recreation, freshwater; WS-II, water supply-undeveloped; HQW, high quality waters; Tr, trout waters; NSW, nutrient sensitive waters; CA, water supply critical area; Sw, swamp waters; ORW, outstanding resource waters; SC, saltwater, aquatic life, secondary recreation. Route name: SR, secondary road; I, interstate; NC, North Carolina route; US, U.S. Highway. Other acronyms: USGS, U.S. Geological Survey; NCDWQ, North Carolina Division of Water Quality; PA, principal artery]

Map no. (fig. 1)	Station name	USGS station no.	Ecoregion	NCDWQ stream classification ¹	County	Latitude	Longitude	Route name	Roadway classification	Surface type	Measured annual average daily traffic volume ²	Stream crossing drainage area (square feet)	Runoff collection pipe drainage area (square feet)	Bridge deck area (square feet)	Bridge length (feet)	Bridge width (feet)
10	Mango Creek near Raleigh, Bridge 911102	354703078304801	Piedmont	C; NSW	Wake	35.784	-78.514	I-540	Urban - PA - Interstate	Concrete	34,000	2.4	56,192	78,619	1,266	62.1
11	Swift Creek at Garner, Bridge 910255	354217078392201	Piedmont	WS-II; NSW	Wake	35.705	-78.656	SR 1006	Urban - Minor arterial	Concrete	11,500	1.7	7,841	1,802	53	34
12	Middle Creek near Fuquay-Varina, Bridge 910273	353633078411001	Piedmont	C; NSW	Wake	35.609	-78.686	SR 1006	Rural - Minor collector	Bituminous	5,000	57.5	6,534	5,652	157	36
13	Black River near Tomahawk, Bridge 810014	344516078172101	Coastal	C; Sw, ORW	Sampson	34.755	-78.289	NC 411	Rural - Major collector	Bituminous	750	676	4,792	7,897	203	38.9
14	Town Creek near Wilmington, Bridge 90061	340813077591601	Coastal	SC	Brunswick	34.137	-77.987	NC 133	Rural - Major collector	Bituminous	5,600	115.1	7,840	10,872	302	36
15	Smith Creek near Wilmington, Bridge 640131	341528077550701	Coastal	C; Sw, ORW	New Hanover	34.258	-77.919	US 74	Urban - Local	Concrete	26,000	21.8	21,344	112,804	2,161	52.2

¹ North Carolina Department of Environment and Natural Resources (2007).

² Numbers were rounded off as per guidelines established by the American Association of State Highway and Transportation Officials (2009).

Stream Sites

Stream water-quality sampling was conducted at four of the 15 bridge deck sites (table 3) that are colocated with USGS streamflow gages. These four stream sites were sampled monthly for 1 year to characterize stream concentrations and flux upstream from the bridges. About eight additional stream samples were collected during high-flow conditions using automated samplers. The four stream sites represent a gradient of watershed size ranging from 4.2 square miles (mi²) for Swannanoa River in the Blue Ridge to 676 mi² for Black River in the Coastal Plain.

Bed Sediment Sites

Bed sediment was sampled upstream and downstream from 30 bridges in the Blue Ridge, Piedmont, and Coastal Plain ecoregions during summer 2009 to yield 60 environmental samples (table 4; fig. 3). For each upstream and downstream section (generally 5 to 10 stream widths), a composite sample of surficial bed sediment (0–0.8 in. or 2 centimeters (cm)) consisting of approximately equal masses from 5 to 10 depositional zones within each section was collected. Samples were first collected from the downstream section before the upstream section was sampled. For the coastal streams (Smith Creek and Town Creek) when flow was reversed, the upstream sample was collected prior to the downstream sample. Because flow direction is tidally affected, samples at these streams were not expected to show any upstream-downstream difference.

Table 3. Watershed characteristics of stream monitoring sites.

[NCDWQ stream classification: C, aquatic Life, secondary recreation, freshwater; WS-II, water supply-undeveloped; HQW, high quality waters; NSW, nutrient sensitive waters; CA, water supply critical area; Sw, swamp waters; ORW, outstanding resource waters. Route name: SR, secondary road; I, Interstate; NC, North Carolina route; US, U.S. Highway. Other acronym: USGS, U.S. Geological Survey; NCDWQ, North Carolina Division of Water Quality]

Map no. (fig. 1)	Station name	USGS station no.	Ecoregion	NCDWQ stream classification ¹	County	Latitude	Longitude	Drainage area (square mile)	Percent of watershed in forest	Percent of watershed impervious
2	Swannanoa River near Black Mountain, NC	03448800	Blue Ridge	C	Buncombe	35.619	-82.308	4.2	75	3.1
7	Little River at SR 1461 near Orange Factory, NC	0208521324	Piedmont	WS-II; HQW, NSW, CA	Durham	36.142	-78.919	78.2	59.2	0.6
8	Mountain Creek at SR 1616 near Bahama, NC	0208524088	Piedmont	WS-II; HQW, NSW, CA	Durham	36.152	-78.902	7.4	53.1	1.3
13	Black River near Tomahawk, NC	02106500	Coastal Plain	C; Sw, ORW	Sampson	34.755	-78.289	676	26.1	1.4

¹ North Carolina Department of Environment and Natural Resources (2007).

Table 4. Summary of sample types at each study site.

NCDWQ stream classification: WS-IV, water supply-highly developed; C, aquatic life, secondary recreation, freshwater; WS-II, water supply-undeveloped; HQW, high quality waters; Tr, trout waters; NSW, nutrient sensitive waters; CA, water supply critical area; Sw, swamp waters; ORW, outstanding resource waters; SC, saltwater, aquatic life, secondary recreation. Other acronyms: U.S. Geological Survey; NCDWQ, North Carolina Division of Water Quality]

Map no. (figs. 1 and 3)	Station name	USGS station no.	Ecoregion	NCDWQ stream classification ¹	Samples collected and types of analyses				
					Bridge deck runoff (quality and quantity)	In-stream (quality and quantity)	Streambed sediment	Bioassay	Traffic survey
1	Boylston Creek at Mills River, Bridge 440008	352231082325601-3	Blue Ridge	WS-IV	X		X	X	X
2	Swannanoa River near Black Mtn, Bridge 100494	353708082182101-3	Blue Ridge	C	X	X	X	X	X
3	Flat Creek near Weaverville, Bridge 100250	354306082372601-3	Blue Ridge	C	X		X		X
4	Big Ivy Creek near Mars Hill, Bridge 100734	354728082321901-3	Blue Ridge	WS-II; HQW	X		X	X	X
5	Dillingham Creek at Barnardsville, Bridge 100145	354607082260901-3	Blue Ridge	WS-II; Tr; HQW	X		X	X	X
6	Mallard Creek near Charlotte, Bridge 590296	351911080450501-3	Piedmont	C	X		X	X	X
7	Little River at Orange Factory, Bridge 310064	360829078550901-3	Piedmont	WS-II; HQW; NSW,CA	X	X	X	X	X
8	Mountain Creek near Bahama, Bridge 310005	360908078540701-3	Piedmont	WS-II; HQW, NSW, CA	X	X	X	X	X
9	Perry Creek near Raleigh, Bridge 910124	355247078325001-3	Piedmont	C; NSW	X		X	X	X
10	Mango Creek near Raleigh, Bridge 911102	354703078304801-3	Piedmont	C; NSW	X		X	X	X
11	Swift Creek at Garner, Bridge 910255	354217078392201-3	Piedmont	WS-II; NSW	X		X	X	X
12	Middle Creek nr Fuquay-Varina, Bridge 910273	353633078411001-3	Piedmont	C; NSW	X		X	X	X
13	Black River near Tomahawk, Bridge 810014	344516078172101	Coastal Plain	C; Sw; ORW	X	X	X	X	X
14	Town Creek near Wilmington, Bridge 90061	340813077591601-3	Coastal Plain	SC	X		X	X	X
15	Smith Creek near Wilmington, Bridge 640131	341528077550701-3	Coastal Plain	C; Sw; ORW	X		X	X	X
16	Cataloochee Creek at Highway 284 Bridge	354003083042202-3	Blue Ridge	C; Tr; ORW			X		
17	Boylston Creek near Blantyre, Bridge 870106	351836082394702-3	Blue Ridge	WS-IV			X		
18	Boylston Creek at Mills River, Bridge 440007	352213082335002-3	Blue Ridge	WS-IV			X		
19	Little Ivy Creek near Forks of Ivy, Bridge 560522	354746082320702-3	Blue Ridge	WS-II; HQW			X		
20	Flat Creek near Weaverville, Bridge 100124	354445082311402-3	Blue Ridge	C			X		
21	Swannanoa River near Asheville, Bridge 100498	353442082310802-3	Blue Ridge	C			X		
22	Dillingham Creek at Dillingham, Bridge 100147	354518082241502-3	Blue Ridge	WS-II; Tr; HQW			X		
23	Mallard Creek near Harrisburg, Bridge 590083	351934080462402-3	Piedmont	C			X		

Table 4. Summary of sample types at each study site.—Continued

NCDWQ stream classification: WS-IV, water supply-highly developed; C, aquatic life, secondary recreation, freshwater; WS-II, water supply-undeveloped; HQW, high quality waters; Tr, trout waters; NSW, nutrient sensitive waters; CA, water supply critical area; Sw, swamp waters; ORW, outstanding resource waters; SC, saltwater, aquatic life, secondary recreation. Other acronyms: U.S. Geological Survey; NCDWQ, North Carolina Division of Water Quality]

Map no. (figs. 1 and 3)	Station name	USGS station no.	Ecoregion	NCDWQ stream classification ¹	Samples collected and types of analyses				
					Bridge deck runoff (quality and quantity)	In-stream (quality and quantity)	Streambed sediment	Bioassay	Traffic survey
24	Clarke Creek nr Wallace Crossroads, Bridge 120008	352451080450802-3	Piedmont	WS-IV			X		
25	Mountain Creek near Bahama, Bridge 310061	361037078545402-3	Piedmont	WS-II; HQW, NSW, CA			X		
26	Little River near Durham, Bridge 310025	360456078511602-3	Piedmont	WS-II; HQW, NSW, CA			X		
27	Middle Creek near Smithfield, Bridge 500050	353029078240402-3	Piedmont	C; NSW			X		
28	Black River near Kerr, Bridge 810058	344030078135702-3	Coastal Plain	C; Sw, ORW			X		
29	Black River near Ivanhoe, Bridge 080085	343312078151602-3	Coastal Plain	C; Sw, ORW			X		
30	Town Creek at Wilmington, Bridge 090074	340933078052202-3	Coastal Plain	SC			X		
31	Smith Creek at Wilmington, Bridge 640002	341554077530602-3	Coastal Plain	C; Sw, ORW			X		

¹ North Carolina Department of Environment and Natural Resources (2007).

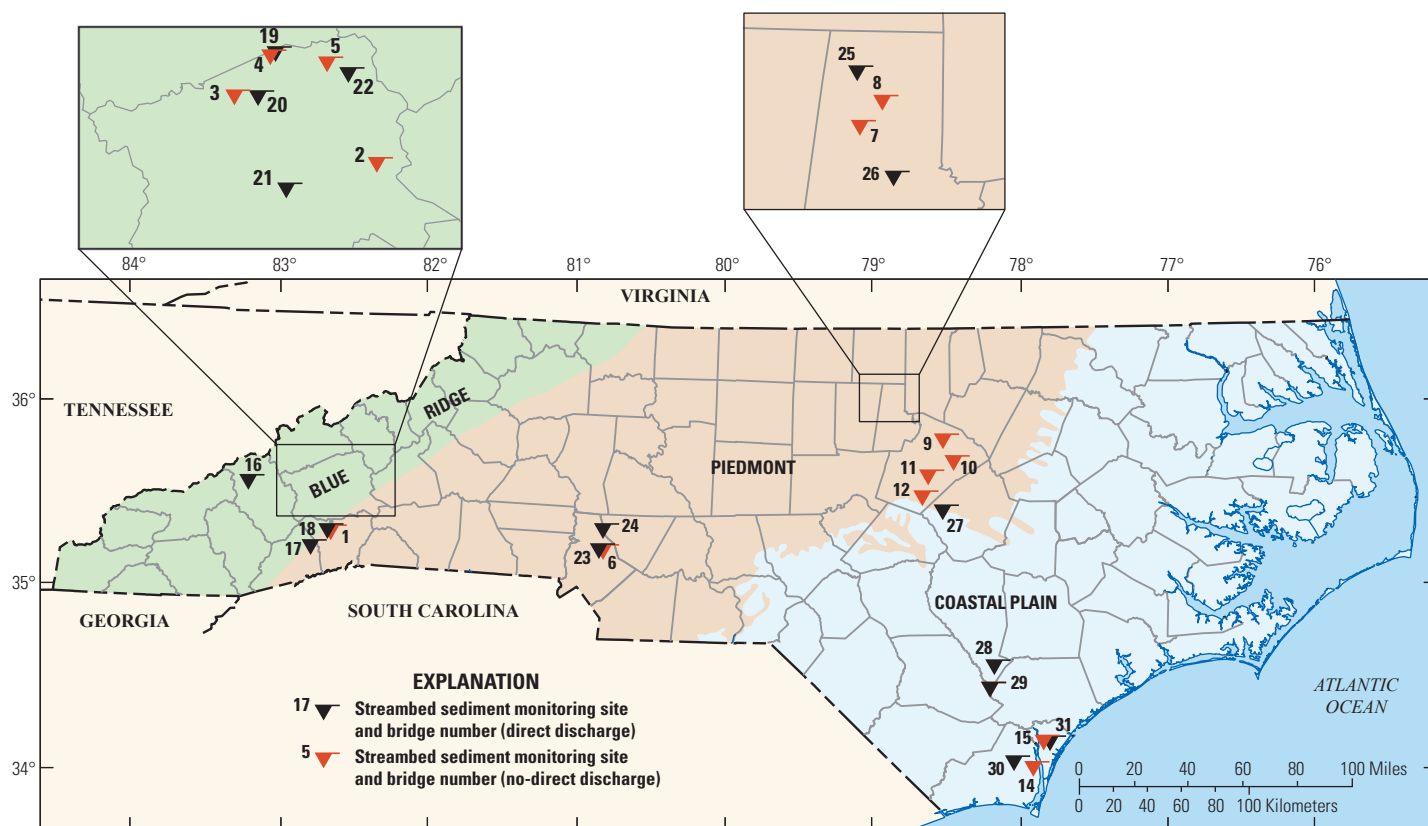


Figure 3. Locations where bed sediment samples were collected in North Carolina.

Measurement of Precipitation and Discharge

Precipitation

Rainfall data were measured using an ISCO 674 tipping bucket rain gage at a resolution of 0.01 in. per tip. Typically, the rain gages were attached directly to the autosampler, which recorded the rainfall data at 1-minute intervals. The data were transmitted on a daily basis via cell phone modem into the USGS NWIS database.

Installation of the rain gages followed the guidance in USGS Office of Surface Water Technical Memorandum No. 2006.01, Collection, Quality Assurance, and Presentation of Precipitation Data (U.S. Geological Survey, 2006a). At 2 of the 15 bridge deck sites (Town Creek and Smith Creek), a site with proper exposure to the sky could not be located adjacent to the autosampler location. In these instances the tipping bucket rain gages were installed close to the site, within 600 feet (ft), and attached to a Sutron 8200 data-collection platform (DCP). The DCP collected and stored rainfall data at 15-minute intervals. These data were transmitted via satellite telemetry to the USGS NWIS database. Precipitation data were also processed in accordance with USGS Office of Surface Water Technical Memorandum No. 2006.01 (U.S. Geological Survey, 2006a).

Discharge

The techniques and instrumentation used to measure and process the continuous discharge record in the collection system discharge pipes and at the stream monitoring sites are presented in subsequent sections. Discharge was required to (1) trigger the autosamplers to collect flow-weighted bridge deck runoff samples and (2) compute constituent loads in both the bridge deck runoff and the receiving streams from analyzed chemical concentrations.

Bridge Deck

Bridge deck runoff samples were collected during storms using automated samplers. Stage and velocity were measured at 1-minute intervals in the collection system discharge pipe by using a pressure transducer and an area velocity sensor. The area velocity sensor contains a pair of ultrasonic transducers; one transmits ultrasonic sound waves as the second receives reflected waves. These data were used for computation of flow within the collection system. Data were collected at 1-minute intervals for each of the following five characteristics: (1) precipitation, (2) stage in pipe, (3) velocity in pipe, (4) discharge from pipe, and (5) sample event.

Discharge was computed using the index-velocity method (U.S. Geological Survey, 2008). In the index-velocity method, two ratings (or relations) were used—a stage-area rating and an index-velocity rating. In this case, the stage-area rating was based on the cross-sectional area of the circular pipe in which the water-level measurements were taken. The velocity meters require at least 1 in. of depth to measure velocity; therefore, small sharp-crested weirs, about 2 in. tall, were installed at the outlet of each pipe to back water up and facilitate measurement of velocity. The stage-area ratings were adjusted to account for the backwater or ineffective flow behind the weirs in the pipes by subtracting the pipe area corresponding to the height of the weirs for each pipe. The index-velocity rating for these sites assumes that the velocity within the pipe is a direct measure of the average cross-sectional area velocity within the pipe and includes a conversion factor, so that when the velocity (feet per second) is multiplied by the associated area for a given gage height (in feet), the resulting discharge is recorded in gallons per minute rather than cubic feet per second. Recorded bridge deck runoff discharge data were entered into the USGS NWIS database and processed and reviewed using standard USGS methods (Rantz and others, 1982; Turnipseed and Sauer, 2010a and 2010b).

Stream (Routine and Storm)

Stream discharge was measured and recorded and a stage-discharge rating curve was developed for each stream site during this investigation according to standard USGS methods (Rantz and others, 1982; Mueller and Wagner, 2009; Turnipseed and Sauer, 2010a,b). All four sites were equipped with DCPs that record river stage at 15-minute intervals. Instantaneous streamflow was calculated from the established rating curve at the time that stream-stage records were transmitted to the USGS NWIS. Gage height and discharge have been collected by the USGS at Black River near Tomahawk (02106500) since 1996, Little River near Orange Factory (0208521324) since 1987, and Mountain Creek near Bahama (0208524090) since 1994. The streamflow-gaging station at Swannanoa at Black Mountain (03448800) was established on March 19, 2009, specifically for this project.

Field Sampling and Preliminary Laboratory Processing

Water and suspended-sediment samples were collected from both bridge deck runoff and receiving streams during the study. The subsequent sections provide details on field sampling and processing protocols that were used to collect the samples.

Bridge Deck Runoff

Bridge deck runoff was sampled using autosamplers with either a single 20-L Teflon-lined bottle or four 5-L glass bottles

to collect a flow-weighted composite sample for every storm event. Each autosampler was housed inside an aluminum box anchored to a concrete pad near the outlet of each monitored collection system discharge pipe. Teflon tubing was run from the autosampler to the collection system discharge pipe with one end attached to the peristaltic pump of the autosampler, and the other end fixed to the lowest point of the drainage pipe downstream from the flow sensor, upstream from the weir (fig. 2). Before a storm event, the autosamplers were programmed to composite a number of aliquots of a certain volume on a flow-weighted basis. For example, 100 aliquots of 120 milliliters (mL) would be collected from every 50 gallons (gal) that flowed through the drainage pipe, assuming that the expected event would produce about 5,000 gal of runoff. These three factors were determined from forecasts of amount and duration of rainfall to occur during each event.

Ideally, runoff samples were retrieved from the autosampler within 24 hours of the last automated water sample for the runoff event. In rare situations, runoff samples remained in the autosampler for up to 36 hours before being retrieved. The sample bottles were removed from the autosampler using gloves, sealed in plastic bags, and placed on ice. The sampling tubing was cleaned onsite by back flushing at least 0.5 gal of a 0.1- to 0.2-percent solution of a non-phosphate detergent (Liquinox) through the system, followed by at least 2 gal of deionized water or until no bubbles were seen coming from the intake tubing. After the tubing had been cleaned, a new bottle would be installed in the autosampler for the next sampling event.

After each field sampling event, samples were placed on ice and transported to a laboratory for processing. Established protocols for processing samples for chemical analyses were followed (U.S. Geological Survey, variously dated; 2010b). First, total organic carbon and dissolved organic carbon (more correctly, filterable organic carbon at 0.45 micron (μm)) samples were collected from the Teflon bottle before transfer to the Teflon churn to prevent contamination from the methanol rinse. Samples were then collected in the following order: total (raw, unfiltered) nutrients, dissolved (filtered) nutrients, SVOCs, suspended-sediment concentration, total suspended solids, major ions and other inorganic constituents, total recoverable (unfiltered) metals including metalloids, and dissolved (filtered) metals including metalloids. Hereafter, filterable analytes will be referred to as dissolved to follow convention and to facilitate comparison with the literature. Additionally, the term metals will be used to include metalloids for brevity. Total suspended solids and suspended-sediment concentration samples were then collected. The final samples collected were for analysis of oil and grease and total petroleum hydrocarbons. For these samples, the bottle was placed at the water surface so as to preferentially collect water at the air-water interface—an area where hydrophilic compounds were expected to concentrate. Water temperature, specific conductance, and pH were determined at the USGS North Carolina Water Science Center laboratory during sample processing by instruments calibrated that morning.

The samples were preserved in the laboratory and shipped on ice overnight to the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado. Concentrations of oil and grease and total petroleum hydrocarbons were analyzed in the Test America Denver Laboratory in Arvada, Colorado. Total suspended solids, suspended-sediment concentration, and particle-size information were determined in water samples at the USGS Kentucky Water Science Center sediment laboratory in Louisville.

Samples were also collected at four bridge deck runoff sites (Smith Creek, Mango Creek, Mallard Creek, and Swannanoa River) between September 2009 and April 2010 (inclusive) and analyzed at the NWQL for platinum, palladium, and rubidium (both total recoverable and dissolved phases). These three platinum-series metals are present in catalytic converters.

A contractor for the NCDOT conducted bioassays using stormwater samples collected from 14 of the 15 bridge deck monitoring sites (table 4) and three of the stream sites (Swannanoa, Little, and Black Rivers). In this study, time-variable chronic bioassays were conducted to measure the effects of bridge deck runoff and streamwater samples on living organisms relative to a control water sample. The test procedures are adapted from the State of North Carolina freshwater time-variable bioassays using *Ceriodaphnia dubia* described by Dupuis (2002). Separate 1-L aliquots were extracted from the samples collected by the USGS and delivered to the NCDOT contractor laboratory for bioassay analysis. A combined total of 25 bridge deck runoff samples at all sites, except Flat Creek, were submitted for bioassay analysis. Bioassay subsamples were collected from the churn after the sediment sample was collected. A combined total of 22 bioassay samples were also collected at the Swannanoa River, Little River, and Black River stream sites. Both base-flow and storm stream samples were collected for each of the three river sites. All bioassay samples were processed and analyzed by a contract laboratory for the North Carolina Department of Environment and Natural Resources Division of Water Quality located in Asheville, North Carolina. Results of the bioassay tests were reported directly to the NCDOT and are discussed in a publication by URS Corporation (2010).

Stream (Routine and Storm)

Streamwater samples were collected from receiving streams at four bridge sites, a subset of the bridge deck runoff monitoring sites. Samples were collected upstream from each bridge during storm and base-flow conditions to be analyzed for chemical constituents and concentrations. Stream storm samples were collected by an autosampler located at the site over the entire duration of the storm hydrograph and processed in the same manner as composite samplers of bridge deck runoff.

When flow was sufficient, routine stream samples were collected upstream from the bridge using the integrated equal-width interval (EWI) sampling technique from a

bridge or by wading the stream, which involves collecting an isokinetic width- and depth-integrated sample composited in a splitter and processed and preserved according to USGS standard operating procedures (Edwards and Glysson, 1999; U.S. Geological Survey, 2006b). When flow conditions did not permit EWI sampling, grab samples were collected at equal-width intervals. EWI samples were collected using a DH-81 (Federal Interagency Sedimentation Project, 2001) or other suitable water-quality sampler with a Teflon nozzle and bottle. Sediment samples were collected using a DH-48 (Federal Interagency Sedimentation Project 1965a) when wading and a DH-59 (Federal Interagency Sedimentation Project, 1965b) from a bridge at each of the quarter points of the stream.

When wading, samples to be analyzed for total organic carbon and SVOCs were collected at the midpoint of the stream by opening the bottle underwater at the midpoint of the water column and resealing the bottle before breaking the surface. The samples to be analyzed for oil and grease and total petroleum hydrocarbons were collected by filling the bottle at the surface of the stream at the midpoint of the stream. When sampling from a bridge, samples of total organic carbon, SVOC, oil and grease, and total petroleum hydrocarbon were collected out of the Teflon churn in the same manner as for the composite samples of streamwater and bridge deck runoff.

Water temperature, specific conductance, pH, dissolved oxygen, and barometric pressure were determined in the field at the time of sample collection. Field instruments were calibrated before each sampling period, and the results were documented along with the sample date and time. Alkalinity was measured as soon as possible after sample processing for routine stream samples via incremental equivalence titration (U.S. Geological Survey, variously dated).

Bed Sediments

The sampling protocol was based on the USGS National Water Quality Assessment (NAWQA) Program guidelines (Shelton and Capel, 1994). One notable difference, though, was that the samples for SVOCs were determined on the less than 63- μm (maximum particle diameter) fraction of bed sediment in the present study as opposed to the less than 2-millimeter (maximum particle diameter) fraction used for the NAWQA Program. The likely effect was to lower the detection limit for the NCDOT sampling because of the larger total surface area normalized to mass associated with smaller particles. Teflon tubes were used to scoop off the upper 2 cm of bed sediment, which was then transferred directly to cleaned, baked 1-L wide mouth glass jars with Teflon-lined lids for environmental samples and replicate samples. For the field split and matrix spike samples, two jars were collected in the field and then combined and thoroughly mixed in the laboratory prior to splitting and then sieving (see next section). Samples were kept on ice or refrigerated during temporary storage and shipment to the USGS Sediment Partitioning Research Laboratory in Atlanta, Georgia.

Laboratory Analyses

A summary of the broad range of constituent groups that were measured in the bridge deck runoff, receiving streams, and bed sediment is presented in subsequent sections. These constituents were measured in at least 20 percent of the 218 highway runoff studies summarized in the National Highway Runoff Data and Methodology Synthesis (Granato, 2003) and include physical properties, solids, nutrients, major ions, metals, polynuclear aromatic hydrocarbons, and plasticizers.

Water Quality (Bridge Deck Runoff and Stream)

Analytes were measured in water and bed sediment samples during the study. A list of the measured analytes and associated analytical information is given in table 5 (p. 90). Stormwater constituents that were determined in the study to be “parameters of concern” by URS (2010) are highlighted in **bold**. Analytes determined in the blanks as well as SVOC surrogates added at the laboratory for quality assurance and control purposes also are presented in table 5. All analytes were determined throughout the duration of the study except for the three platinum series metals (platinum, palladium, and rubidium), which were only determined at four sites (Smith Creek, Mango Creek, Mallard Creek, and Swannanoa River) between September 2009 and April 2010 (inclusive) as mentioned above.

Bed Sediment Chemistry

In the USGS Sediment Partitioning Research Laboratory, sediment samples were homogenized, rough-split into two subsamples, and then wet-sieved (63 micron) under pressure using either a stainless steel sieve for SVOCs or a nylon/polyethylene mesh for metals (includes metalloids), nutrients, total carbon, and total organic carbon. The weight percent of material less than 63 μm in maximum diameter was calculated for all samples. For split and matrix spike subsamples, a final splitting of the two sieved subsamples was done. A few grams of this wet-sieved sediment were retained at the USGS Georgia Water Science Center for metal, nutrient, and carbon analyses. About 50 to 100 grams of wet-sieved sediment was shipped on ice in 500-mL baked jars with Teflon-lined lids to the NWQL for SVOC analysis.

Sediment samples analyzed at the USGS Sediment Partitioning Research Laboratory were dried at 105 degrees Celsius ($^{\circ}\text{C}$) to constant weight and analyzed for silver, copper, lead, zinc, cadmium, chromium, cobalt, nickel, barium, vanadium, lithium, beryllium, molybdenum, strontium, arsenic, antimony, selenium, mercury, iron, manganese, aluminum, sodium, potassium, calcium, magnesium, and titanium as well as phosphorus, total carbon, total organic carbon, nitrogen, and sulfur (table 5). All analyses yielded total concentrations (that is, greater than 95 percent of the element present in the sample). For all analytes other than antimony, selenium,

and mercury, 500-milligram (mg) aliquots, if possible, were digested with a combination of hydrofluoric acid/perchloric acid/*aqua regia* (nitric acid and hydrochloric acid in a 1:3 volume ratio) in Teflon beakers at 200 $^{\circ}\text{C}$; the resulting salts were solubilized using 50 mL of 2-percent hydrochloric acid. Silver, cadmium, and lead were determined by flame atomic absorption spectrometry (AAS) using mixed salt standards and background correction. All the other constituents were determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES) using a lutetium internal standard and inter-element correction factors. Aliquots from the same digestion were used for antimony and selenium; selenium was determined on the digestate by hydride generation AES, whereas arsenic and antimony were determined by hydride generation ICP–AES. Mercury was analyzed using separate 500-mg aliquots, if possible, digested with LeFort *aqua regia* at 140 $^{\circ}\text{C}$; quantification was by cold vapor, employing an AAS as the detector. Total carbon and nitrogen were determined by passing the combustion products of separate 250-mg to 500-mg sample aliquots through a gas chromatograph, with a thermal conductivity detector in a carbon-nitrogen-sulfur (CNS) analyzer. Total organic carbon also was determined by combustion, but in a carbon-sulfur (CS) analyzer that quantifies the evolved carbon dioxide with an infrared detector after pretreatment with 10-percent hydrochloric acid (volume/volume) to remove carbonates.

Sediment samples sent to the NWQL were analyzed for 38 SVOCs (table 5). Solvent extraction was done under pressure using water/isopropyl alcohol mixtures, and target analytes were isolated on disposable solid-phase extraction cartridges containing divinylbenzene-vinylpyrrolidone copolymer resin. The cartridges were dried using nitrogen gas, and sorbed compounds were eluted with dichloromethane/diethyl ether (80:20 volume ratio). Extracts were dewatered and cleaned up by passing through a solid-phase extraction cartridge containing sodium sulfate/Florisol and then exchanged into ethyl acetate and reduced in volume to 0.5 mL. After addition of internal standards, samples were analyzed by capillary-column gas chromatography with mass spectrometry detection.

Quality Assurance and Quality Control Design

As the Nation’s principal earth-science information agency, the USGS has developed a worldwide reputation for collecting accurate data and producing factual and impartial interpretive reports. To ensure continued confidence in its products, all scientific work is conducted in accordance with documented quality assurance and quality control (QA/QC) policies and procedures.

The USGS Quality Assurance Plan for Water-Resources Activities in North Carolina (U.S. Geological Survey, 2010a) provides a framework for defining the precision and accuracy of collected data. The plan is supported by a series of quality-assurance policy statements that describe responsibilities for specific functional elements including project planning and

implementation, equipment calibration and maintenance, data collection, data processing and storage, data analysis and interpretation, synthesis, reports preparation and processing, and training. Activities of the USGS North Carolina Water Science Center are systematically conducted under a hierarchy of supervision and management that is designed to ensure conformance with Agency goals of quality assurance.

Each component of data collection included QA/QC procedures, as described in subsequent sections. All methods used by the USGS to collect and review scientific data are fully documented, and project data and records are archived in accordance with guidelines jointly approved by the USGS and the National Archives and Records Administration.

Precipitation

The rain gages were checked for calibration twice during the data-collection period (March 2009 to April 2010). These calibration checks were done in accordance with USGS Office of Surface Water Technical Memorandum No. 2006.01. On average there were 10 visits to each site to check for obstructions and general cleanliness of the rain gage. The tipping mechanism was checked after inspection and cleaned, if required, to ensure accurate measurements. If obstructions to the bucket funnel or impedance to the tipping mechanisms were found, the data were closely scrutinized and removed, as needed, from the USGS NWIS database. Periods of frozen precipitation and subsequent days of associated melt were removed from the dataset. All data were worked, checked, and reviewed in accordance with USGS Office of Surface Water Technical Memorandum No. 2006.01 to ensure proper QA/QC guidelines were followed for each site.

Discharge

The QA/QC procedures used to measure continuous discharge for computation of constituent loads and control automated sample collection from bridge deck runoff are summarized in subsequent sections. Protocols used to QA/QC discharge measurements in both the collection system discharge pipes and the receiving streams are presented.

Bridge Deck

Gage heights measured by the ISCO pressure transducer/velocity meters were checked in the field by physically measuring the depth of flowing water in the pipe at the downstream end of the pressure transducer/velocity meters, which corresponds to the location of the pressure transducer on the meter. These measurements were taken when site visits corresponded with stormwater runoff. If a difference between the physical and meter measurement of gage height was found, the pressure transducer was reset to match the physical measurement. All gage height verification measurements during runoff events showed that the pressure transducer was within 0.01 ft of the physical measurement.

Bridge deck runoff data were combined with measured chemical concentrations to compute loads from the bridge decks. Each ISCO velocity/stage meter was calibrated by the manufacturer in accordance with their standards to the following accuracies:

- Velocity: -5 to 5 feet per second (ft/s; ± 0.1 ft/s)
- Velocity: 5 to 20 ft/s (± 2 percent of reading)
- Stage: 0.033 to 5 ft (± 0.008 ft/ft)
- Stage: 5 to 10 ft (± 0.012 ft/ft)

The stage/velocity meters were also tested at the USGS Hydrological Instrumentation Facility (HIF) for accuracy in measuring velocity and stage. HIF testing confirmed the stated accuracies for velocity and stage, yet noted some temperature dependent variations in stage measurements.

Volumetric measurements of bridge deck runoff were taken at selected sites, when possible, and compared with discharge reported from the velocity/stage meters (table 6). For the sites that had more than 30-percent variance between computed and measured runoff, a theoretical storm runoff volume calculated using the bridge deck drainage area, total precipitation, and a 0.95 runoff coefficient was used in the load computations.

Stream (Routine and Storm)

The USGS operated and maintained continuous record streamflow-gaging stations at the four stream monitoring sites during this study (table 3). Stage and streamflow data were collected, processed, and analyzed in accordance with the quality-assurance plan for surface-water activities of the USGS North Carolina Water Science Center (Rantz and others, 1982; Mueller and Wagner, 2009; U.S. Geological Survey, 2010b). Final results were entered into the USGS NWIS database. Data for project streamflow-gaging sites are available online at <http://waterdata.usgs.gov/nc/nwis/>.

Water Quality (Bridge Deck and Stream)

The bias, precision, and representativeness of sampling water from the bridge decks and streams entailed several field- and laboratory-based procedures, which are discussed in detail here. Beyond these, various blind sample programs are conducted by non-NWQL programs within the USGS to monitor the accuracy of reported analyte (organic, inorganic, and sediment) concentrations as well as for analytes typically determined in the field (pH, specific conductance, and alkalinity). In addition, formal procedures are used to evaluate non-NWQL laboratories wherein the accuracy of reported results for standard reference materials is examined. Finally, the NWQL maintains long-term records of analytical performance that are useful for evaluating project data analyzed in a given time period. All these programs are briefly described in table 7.

Table 6. Comparison of bridge deck runoff measured volumetrically with discharge reported from velocity/stage meters.

[gal, gallon; gal/min, gallon per minute]

Site name and measurement no.	Date	Time	Volume collected (gal)	Collection time (minutes)	Volumetric discharge (gal/min)	Autosampler reported discharge (gal/min)
Boylston - 1	4/8/2010	16:27	3.83	0.15	25.5	28.4
Boylston - 2	4/8/2010	16:28	2.38	0.08	28.5	28.6
Big Ivy - 1	4/8/2010	14:17	4.29	0.50	8.6	19.2
Big Ivy - 2	4/8/2010	14:23	6.67	0.50	13.3	29.4
Big Ivy - 3	4/8/2010	14:31	3.83	0.25	15.3	25.4
Dillingham - 2	4/8/2010	14:57	2.77	0.17	16.6	74.0
Flat Creek - 1	4/8/2010	15:29	1.45	0.25	5.8	7.4
Flat Creek - 3	4/8/2010	15:35	1.72	0.33	5.2	6.9
Little River - 1	2/22/2010	12:00	3.06	0.20	15.3	28.6
Little River - 2	2/22/2010	12:05	3.01	0.20	15.1	22.8
Swift Creek - 1	2/5/2010	13:58	2.14	0.17	12.8	12.8
Swift Creek - 2	2/5/2010	15:00	2.51	0.11	23.2	46.2
Middle Creek - 1	2/5/2010	14:23	2.25	0.15	15.0	16.0
Middle Creek - 2	2/5/2010	14:28	2.18	0.15	14.1	16.4

Field

Bias, precision, and representativeness of measured analyte concentrations affected by field sampling and handling of bridge deck and streamwaters were assessed through various types of sample blanks and replicates, respectively (table 8). Forty-eight blanks of three different types were used to assess potential analyte contamination from the ambient environment including during transport in vehicles (vehicle blanks) and exposure to ambient air (ambient blanks), processing through supplies and equipment (equipment blanks), and contact with samplers (field blanks). Uncensored detections in all blank samples occurred in 1.4 percent of analyses of all analytes and 2.0 percent of analyses for POCs. Sixteen of the 48 blanks had at least one detection among the total recoverable POCs although three of these had only estimated (E-coded) detections (table 9). There were 23 detections and 28 qualified detections for 15 total recoverable POCs, but there were no detections for the remaining 7 total recoverable POCs (arsenic, hexachlorobenzene, pentachlorophenol, benzo[*a*]anthracene, bis(2-chloroethyl)ether, n-nitrosodimethylamine, and n-nitroso-di-n-propylamine). Last, only two detections for metals (aluminum and mercury) exceeded the water-quality threshold, whereas detections for several SVOCs exceeded the thresholds (table 9) for those compounds.

Among the uncensored detections of total recoverable metal and nutrient values, manganese was found most frequently, occurring in seven blanks. Aluminum and iron were next most frequently detected, each in five blanks. Both aluminum and iron had sporadically high detections in a few autosampler field blanks associated with bridge decks. Often these three metals, or two of the three, occurred in the same blank suggesting a common source. Among the environmental bridge deck runoff samples (discussed later), about 5 percent of the aluminum values, about 91 percent of the iron values, and about 87 percent of the manganese values were greater than the largest concentrations measured in any blank. Thus, the potential contamination was probably sporadic and likely did not bias the environmental data to any great extent. Staying within the uncensored detections, three POCs (total nitrogen, total phosphorus, and nickel) were detected only once each. Mercury was detected twice, and there were no detections of any SVOCs. That said, there was a relatively high censored value of bis(2-ethylhexyl)phthalate (E4.2 micrograms per liter ($\mu\text{g/L}$) in an autosampler blank from a bridge deck. This plasticizer has been detected a few times in blind blanks submitted by others during the NCDOT study period at levels similar to that in the field blank (data not shown). Thus, the single censored detection may not reflect anything specific

Table 7. Selected quality-assurance programs for water chemistry analyses operated by the U.S. Geological Survey Branch of Quality Systems and the National Water Quality Laboratory (NWQL).

Program	Description	Matrix
Blind Blank Program (BBP)	The BBP submits double-blind blank samples to the NWQL to help determine method detection limits and monitor analytical performance. Samples are prepared weekly for every possible analytical line. The same bottles and preservatives are used by U.S. Geological Survey field personnel. Data are collected and analyzed for trends, cycles, and biases. Online charts are posted once a week so analysts and supervisors can assure quality data.	Water
Inorganic Blind Sample Program (IBSP)	The purpose of the IBSP is to monitor and evaluate the quality of laboratory analytical results through the use of double-blind quality-control samples.	Water
Organic Blind Sample Program (OBSP)	The OBSP assesses the operational performance of organic analytical methods used for determining water-quality constituents for the NWQL by means of blind submissions of quality-assurance samples.	Water
Sediment Laboratory Quality Assurance (SLQA)	Two single-blind SLQA studies are conducted annually. Participating laboratories are asked to determine suspended-sediment concentration, sediment mass, separation of fine- and sand-size material, and particle-size distribution using the standard techniques with which they analyze environmental samples. Results are used to assess variability in environmental data and to improve laboratory performance.	Water, sediment
National Field Quality Assurance Program (NFQA)	The NFQA was created in 1979 to provide quality-assurance reference samples to field personnel, who make water-quality field measurements. The program monitors the proficiency of alkalinity, pH, and specific conductance measurements determined by water-quality field analysts.	Water
Laboratory Evaluation Program (LEP)	Analytical laboratories that provide chemical, radiochemical, and biological analyses to the U.S. Geological Survey, Water Resources Discipline, must be evaluated relative to the objectives of a project requiring analyses and approved for use for that specific project.	Water, sediment
NWQL quality-control data	Charts, tables, histograms, and tests for normal distributions (analytes and surrogates); program for creating quality-control charts, with extra options to assist in troubleshooting; box plots and tables of statistics for all compounds in schedules; retrieve quality-control set data associated with specified environmental samples.	Blank, environmental water, and sediment

Table 8. Bridge deck and stream field quality-assurance and quality-control (QA/QC) samples.

[Blanks analyzed for a subset of all analytes. EWI, equal-width increment; SVOCs, semivolatile organic compounds]

QA/QC sample type	Number	Description and purpose
Blanks		
Ambient:		
• Vehicle	2	Blank water exposed to collection and processing equipment in the vehicle and processed as an environmental sample to assess contamination from the ambient atmosphere.
• Autosampler	5	Blank water exposed in uncapped bottles in the autosampler for 7 to 10 days to assess contamination from the ambient atmosphere.
Equipment	3	Blank water exposed to collection and processing equipment in the laboratory and processed as an environmental sample to assess contamination and to verify cleaning procedures.
Field:		
• Decks (autosampler)	32	Blank water passed through the autosampler line and bottle in the field and processed as an environmental sample to assess contamination from sampling, processing, and analysis.
• Streams (autosampler)	5	Same as above.
• Streams (EWI)	1	Blank water exposed to the sampler and processed in the field as an environmental sample to assess contamination from sampling, processing, and analysis.
Replicate sets		
Field:		
• Decks (autosampler)	5	Split replicates – two samples taken sequentially from the churn to assess processing and analytical precision combined.
• Streams (EWI)	4	Sequential replicates – two samples collected sequentially from the stream to assess sampling, processing, and analytical precision combined.
• Streams – autosampler (point sampler) versus EWI (cross-sectional composite sample)	5	Two stream samples taken during normal flow (non-storm) periods to assess the representativeness (accuracy) of the point sampler of the entire stream width.
Spike sets (SVOCs only)		
Matrix spike (stream)	6	Known concentrations of target SVOCs added to paired environmental replicates to assess the analytical recovery efficiency within the sample matrices.

to the equipment cleaning procedure in the present study. More importantly, this compound was detected in only 2 of the 48 blanks. This sporadic pattern supported the suggestion that the environmental dataset was largely unbiased.

The four dissolved metal POCs (cadmium, copper, lead, and zinc) were detected in only 1 of 10 blanks—a field blank collected July 15, 2009 (table 10). The cadmium and zinc values were E-coded because they were below the reporting level. The lead value was about five times above the reporting level and the copper value was extremely high (26 µg/L), well above most of the study data both for dissolved and total recoverable copper (results discussed later). This high copper value was well above the water-quality threshold, and the lead value was about one-half of that threshold. Additionally,

the dissolved concentration of five metals exceeded the total recoverable concentration in that particular blank sample (table 11). This sample was probably compromised in some way, and there remains no evidence for any systematic bias in the measured concentrations of these dissolved metals.

While positive bias in the form of contamination has been discussed, negative bias was also a potential issue. That is, was there a failure to identify POCs for some reason? In the case of five analytes, the reporting level was greater than the threshold level (table 12.) Additionally, three analytes were permanently E-coded due to low and (or) variable recoveries. Thus, for these few analytes, it is not possible in principle to rule them out as POCs.

Table 9. Detections of parameters of concern among total recoverable analytes in blanks.

[Values in red indicate frank detections. Concentrations shown in micrograms per liter, except for total nitrogen and total phosphorus, which are in milligrams per liter. NA, not applicable; E, estimated; EW1, equal-width increment]

Blank type and date	No. of blanks with detections	Total nitrogen	Total phosphorus	Aluminum	Iron	Manganese	Mercury	Nickel	Benzo [a]pyrene	Benzo [b]fluoranthene	Benzo [k]fluoranthene	Bis(2-ethylhexyl)phthalate	Chrysene	Dibenzo [a,h]anthracene	Indeno [1,2,3-cd]pyrene	Phenanthrene
Reporting limit	(#)	0.10	0.01	3.4	9.2	0.8	0.010	0.36	0.33	0.30	0.30	2	0.33	0.42	0.38	0.32
Water-quality threshold		NA	NA	87 ^a	300 ^b	50 ^b	0.012 ^c	25 ^d	0.0038 ^b	0.0038 ^b	0.0038 ^b	1,2 ^b	0.0038 ^b	0.0038 ^b	0.0038 ^b	4.6 ^e
Vehicle	1 2															
03/12/10		E.052		E5.9	39.7	E0.22	0.0274			E0.005			E0.005	E0.005	E0.005	
Equipment	1 3															
07/14/09																
Ambient	2 5															
07/14/09				E4.6												
12/09/09								0.683								
Field – decks (autosampler)	7 32															
07/15/09			E.004			0.41				E0.0095			E0.0077	E0.0104	E0.0086	
04/01/10				E3.06	E5.11											
04/20/10				124	229	6.15										
04/21/10		0.981	0.11	E4.81												
04/28/10				9.38	27.4											
05/12/10				82.8	110	2.95			E0.025	E0.040		E4.2	E0.025		E0.022	E0.022
Field – decks (EWI)																
04/29/10				6.09	E5.02											
Field – streams (autosampler)	5 6															
09/15/09						1.6										
09/25/09				E4.0	E10.1	5.06	0.01									E0.0119
04/02/10		E.057				1.11						E0.6				
04/21/10				12.9	32.9	15.1										
05/11/10																
Detections	16 48	1 1	1 1	5 5	5 5	7 7	2 2	1 1	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0
E-coded detections	NA NA	2 1	1 5	3 3	1 1	0 0	1 1	2 2	3 3	2 2	3 3	2 2	3 3	2 2	3 3	2 2

^a U.S. Environmental Protection Agency freshwater criteria continuous concentration (U.S. Environmental Protection Agency, 2009).

^b Human health water + organism (U.S. Environmental Protection Agency, 2009).

^c Freshwater aquatic life (North Carolina Department of Environment and Natural Resources, 2010).

^d North Carolina Surface Water Quality Standard water supply (North Carolina Department of Environment and Natural Resources, 2010).

^e Texas Commission on Environmental Quality Saltwater Chronic (Texas Commission on Environmental Quality, 2000).

Table 10. Detections of parameters of concern among dissolved analytes in blanks.

[Concentrations shown in micrograms per liter. <, less than; E, estimated]

	Cadmium	Copper	Lead	Zinc
Reporting limit	0.02	1	0.03	2
Water-quality threshold ¹	0.07	1.6	0.33	25
Vehicle				
05/05/09	<0.02	<1	<0.06	<2
Equipment				
07/01/09	<0.02	<1	<0.06	<2
07/01/09	<0.02	<1	<0.06	<2
07/14/09	<0.02	<1	<0.06	<2
Ambient				
07/14/09	<0.02	<1	<0.06	<2
12/09/09	<0.02	<1	<0.030	<2.8
Field – ISCO (Bridge decks)				
03/17/09	<0.02	<1	<0.06	<2
07/15/09	E0.012	26	0.152	E1.2
09/02/09	<0.02	<1	<0.06	<2
Field – ISCO (In-stream)				
09/15/09	<0.02	<1	<0.06	<2

¹ U.S. Environmental Protection Agency freshwater criteria continuous concentration (U.S. Environmental Protection Agency, 2009).

Table 11. Concentrations of selected dissolved and total recoverable analytes in the field blank from July 15, 2009.

[Concentrations shown in micrograms per liter. E, estimated; <, less than]

Analyte	Dissolved concentration	Total recoverable concentration	Dissolved greater than total recoverable?
Aluminum	E3.6	<6	-
Cadmium	E0.01	<0.06	-
Chromium	0.47	<0.40	Yes
Copper	26	<4.0	Yes
Iron	24	<14	Yes
Lead	0.15	<0.10	Yes
Manganese	0.3	0.4	No
Mercury	<0.010	<0.010	-
Nickel	1.2	<0.20	Yes
Zinc	E1.2	<2.0	-
Arsenic	<0.06	<0.20	-
Selenium	<0.06	<0.12	-

Table 12. Analytes that were potentially omitted from the parameters of concern list and the reasons why.

[Concentrations shown in micrograms per liter. >, greater than]

Analyte	Reporting level	Threshold level ¹	Reason(s)
Water, Dissolved			
Arsenic	0.04	0.018	Reporting level > threshold level
Water, Recoverable			
1,2-Diphenylhydrazine	0.3	0.036	Reporting level > threshold level
2,4-Dinitrotoluene	0.56	0.11	Reporting level > threshold level
3,3'-Dichlorobenzidine	0.42	0.021	Reporting level > threshold level; Permanent E-coding
Benzidine	10	0.000086	Reporting level > threshold level; Permanent E-coding
2,4-Dinitrophenol	1.4	69	Permanent E-coding

¹ U.S. Environmental Protection Agency, human health water + organism (U.S. Environmental Protection Agency, 2009).

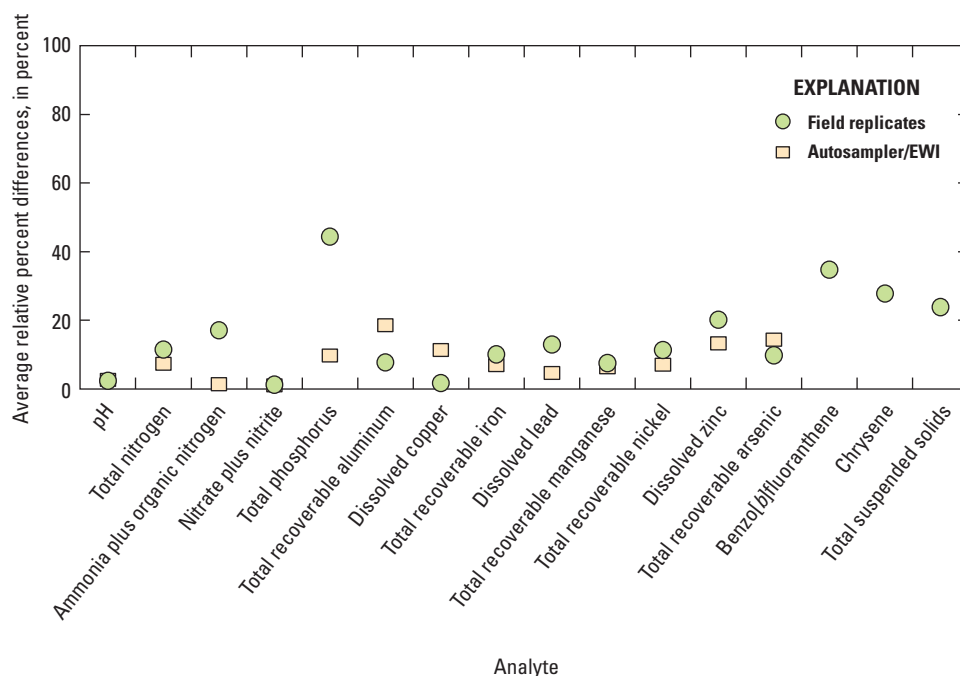


Figure 4. Average relative percent difference of parameters of concern in water replicates and in autosampler/equal-width interval method comparison water samples.

Precision and representativeness of sampling and analysis taken together for the POCs were assessed with 14 sets of field replicates (fig. 4) of two types. First, nine field replicate pairs (five stream and four bridge deck) were collected to assess the overall precision of the entire collection, handling, and analysis approach. The average relative percent difference (RPD, in percent) of the percent absolute differences for these field replicates was usually below about 20 percent with only phosphorus, two SVOCs (benzo[b]fluoranthene and chrysene), and total suspended solids having more variability. Generally, this precision was quite good considering all the steps involved from collection to analysis.

Second, five sets of stream autosampler/EWI (a cross section) pairs were used to assess the representativeness of the point sampling done by the autosamplers when compared to concurrent samples collected using the EWI technique. These autosampler/EWI comparisons were done during non-storm conditions and thus may have been the worst case. As was the case for the field replicates, the autosampler collected a fairly representative sample of the entire stream during base flow.

Finally, bias of SVOC concentrations was assessed by spiking a pair of replicate samples from three of the stream sites (Mountain Creek, Little River, and Town Creek) and calculating analytical recoveries against an unspiked sample

with comparison to 77 reagent spikes analyzed at the NWQL during the relevant period from March 3, 2009, to May 27, 2010 (table 13). Of the SVOCs included as POCs, median recoveries in sample matrices ranged from 26 to 66 percent although this could not be determined for five compounds. Compared to the recoveries in sample matrices, median recoveries in reagent spikes for the POCs were higher as expected due to the absence of interferences. Still, the range of recoveries generally encompassed the median recoveries in the sample matrix spikes. Of the five compounds that were permanently E-coded, dibenzo[*a,h*]anthracene and indeno[1,2,3-*cd*]pyrene partially co-elute with each other. These two compounds were included as POCs because the maximum concentration still exceeded the threshold considering the co-elution factor (about 20 percent as a maximum). Of the non-POC compounds where the matrix spike recovery could be determined, the median recoveries ranged from 22 to 89 percent (table 13). As for the POCs, the median recoveries in reagent spikes were somewhat higher compared to those in the sample matrix spikes. Finally, recoveries of several compounds in sample matrix spikes could not be determined though the median recoveries in reagent spikes ranged from 33 to 93 percent. This directly demonstrated the difficulty of being able to quantify analyte recoveries in complex matrices compared to pure reagent.

Relatively low sample matrix spike recoveries might indicate a negative bias in measured concentrations in environmental samples, but that is not necessarily the case and measured concentrations should not be corrected based on such.

Laboratory

In general, for the metals, nutrients, and carbons among the POCs, analytical bias and precision were assessed with analytical blanks, standard solutions, and analytical replicates (see references in table 5). For SVOCs, quality-control samples in a typical analytical run included internal standards and surrogate standards added to all samples, target compound calibration standards, target compound reagent spikes, and a detector performance evaluation solution (Fishman, 1993). Some of these results are maintained and made available by the NWQL for use in assessing long-term method performance. Finally, recovery of several surrogate compounds added to all samples was used to monitor overall performance of the method. These compounds are similar to the target analytes, but should not be used to correct the recovery of target analytes.

Table 13. Spike recoveries for semivolatile organic compounds in water matrix samples and reagent.

[A total of 77 reagent spikes from March 3, 2009, to May 27, 2010. ---, no data]

Compound	Recovery, in percent					
	Matrix spikes			Reagent spikes		
	Median	Minimum	Maximum	Median	Minimum	Maximum
Parameters of concern						
Benzo[<i>a</i>]anthracene	34	33	35	76	37	104
Benzo[<i>a</i>]pyrene	34	26	48	68	34	102
Benzo[<i>b</i>]fluoranthene	33	29	52	74	41	104
Benzo[<i>k</i>]fluoranthene	39	25	51	73	38	102
Bis(2-chloroethyl)ether	---	---	---	84	40	123
Bis(2-ethylhexyl)phthalate	36	-7	40	55	25	139
Chrysene	44	35	63	80	41	106
Dibenzo[<i>a,h</i>]anthracene	---	---	---	51	19	86
Hexachlorobenzene	46	42	49	74	36	119
Indeno[1,2,3- <i>cd</i>]pyrene	26	20	40	57	24	90
n-Nitrosodimethylamine	---	---	---	57	23	146
n-Nitrosodi-n-propylamine	---	---	---	84	35	127
Pentachlorophenol	---	---	---	80	22	141
Phenanthrene	66	60	80	82	39	106
Permanent E-coding						
Dibenzo[<i>a,h</i>]anthracene	---	---	---	51	19	86
Indeno[1,2,3- <i>cd</i>]pyrene	26	20	40	57	24	90
2,4-Dinitrophenol	---	---	---	52	0	132
Benzidine	---	---	---	0	0	0
3,3'-Dichlorobenzidine	---	---	---	23	0	93

Table 13. Spike recoveries for semivolatile organic compounds in water matrix samples and reagent.—Continued

[A total of 77 reagent spikes from March 3, 2009, to May 27, 2010. ---, no data]

Compound	Recovery, in percent					
	Matrix spikes			Reagent spikes		
	Median	Minimum	Maximum	Median	Minimum	Maximum
All other (sorted on median matrix)						
Benzo[ghi]perylene	22	18	37	56	18	92
n-Nitrosodiphenylamine	28	23	33	75	18	109
Phenol	35	3	49	55	27	93
Pyrene	55	50	75	86	41	111
4Bromophenyl phenyl ether	56	53	59	78	38	116
Anthracene	57	54	60	77	34	104
4-Nitrophenol	57	17	93	54	17	112
Fluoranthene	57	53	76	87	42	110
Acenaphthene	61	57	65	75	34	103
Diethyl phthalate	62	62	62	89	33	127
2,4,6-Trichlorophenol	62	61	63	79	31	115
9H-Fluorene	67	64	71	83	39	110
Naphthalene	70	61	84	77	36	101
2-Nitrophenol	81	13	85	76	28	109
Di-n-butyl phthalate	89	64	90	101	43	171
Other (sorted on median reagent)						
Hexachlorocyclopentadiene	---	---	---	33	6	90
Di-n-octyl phthalate	---	---	---	47	21	130
Hexachlorobutadiene	---	---	---	48	21	87
Hexachloroethane	---	---	---	51	22	96
1,3-Dichlorobenzene	---	---	---	63	26	94
4,6-Dinitro-2-methylphenol (DNOC)	---	---	---	63	10	118
1,4-Dichlorobenzene	---	---	---	65	27	93
1,2,4-Trichlorobenzene	---	---	---	66	30	91
2,4-Dimethylphenol	---	---	---	66	5	119
1,2-Dichlorobenzene	---	---	---	68	29	96
Acenaphthylene	---	---	---	74	34	100
2,4-Dichlorophenol	---	---	---	77	28	112
2-Chlorophenol	---	---	---	78	31	111
2-Chloronaphthalene	---	---	---	79	36	99
4-Chloro-3-methylphenol	---	---	---	79	27	118
4Chlorophenyl phenyl ether	---	---	---	80	39	107
1,2-Diphenylhydrazine	---	---	---	80	36	127
2,6-Dinitrotoluene	---	---	---	83	35	118
Bis(2-chloroisopropyl)ether	---	---	---	83	35	115
Dimethyl phthalate	---	---	---	83	31	117
Bis(2-chloroethoxy)methane	---	---	---	84	40	111
Isophorone	---	---	---	85	37	114
Nitrobenzene	---	---	---	86	37	107
2,4-Dinitrotoluene	---	---	---	86	34	119
Butyl benzyl phthalate	---	---	---	93	41	168

Bed Sediment

Field

Nine field QA/QC samples representing 15 percent of the total samples collected were used to assess overall sampling precision and bias. All QA/QC samples were collected from three sites, one in each ecoregion. These sites were Boylston Creek (bridge 440008, downstream reach), Middle Creek (bridge 910273, upstream reach), and Smith Creek (bridge 640131, downstream reach). Sites were chosen on the basis of abundant fine-grained sediment and likelihood of SVOC presence. At each of the three QA/QC sites, in addition to the environmental sample, a replicate sample and a bulk sample to be split were collected. These field QA/QC samples were defined and interpreted as follows:

- *Replicate sample* – A second sample collected sequentially in the vicinity of the environmental sample used to assess representativeness and repeatability of the sediment sampling, handling, and analysis procedures for all target analytes. Replicates reflected the overall maximum variability of the sampling.
- *Split sample* – Two subsamples taken from one homogenized bulk sample (after sieving) used to assess representativeness and repeatability of the sediment handling and analysis procedures apart from variability of the field sampling proper. Therefore splits, in conjunction with replicates, were used to assess the spatial variability of target analyte concentrations at the sampling site. For SVOCs only, one split was analyzed directly and one was spiked with target compounds (see next item).
- *Matrix spike* – For SVOCs only, consisted of one of the two split samples and was used to assess recovery efficiency and analytical interferences within the specific sample matrices.

Laboratory

Analytical blanks, duplicates, and “known” concentration materials including standard reference materials accounted for about 30 to 40 percent of each analytical run for metals, nutrients, and carbons. Overall precision was determined from the average relative percent difference of the percent absolute differences between pairs for the following:

- Environmental and field replicates
- Field splits
- Analytical replicates

These data pairs are nested within each other in that the analytical precision is reflected completely within the precision of the field splits, which in turn, is reflected completely within the precision of the environmental and field replicates. Average absolute differences for each set of data pairs were

less than about 15 percent for almost all analytes (fig. 5). Therefore the overall variability was largely determined by the analytical variability. Thus the sampling approach and methods yielded representative samples of each reach and the sampling handling did not add measurable variability. Aside from the less than 63-micron fraction, the few large average relative percent differences were associated with analytes present in relatively small concentrations (molybdenum, mercury, cadmium, and antimony) and thus were not likely to be significant. The differences in absolute concentration were relatively small.

Bias was determined from 19 analyses of 10 unique standard reference materials and other “knowns” selected from a collection of more than 60 materials for best match to expected target analyte concentrations in the samples. The average relative standard deviations of the percent absolute difference for each pair between the observed and “known” concentrations were less than about 15 percent for all but five analytes, including cadmium, molybdenum, tin, mercury, and total carbon (fig. 6). As was the case for precision, these five analytes were present in relatively small concentrations and were associated with relatively small absolute concentrations differences.

For SVOCs, quality-control samples in a typical analytical run included a detector calibration solution, an instrument blanking solution (pure solvent), two instrument detection level solutions, three continuing calibration verification solutions, a reagent set spike, a set blank solution, and a set quality-control reference material sample (Zaugg and others, 2006). Together, these accounted for about 43 percent of the typical analytical run. Some of these results are maintained and made available by the NWQL for use in assessing long-term method performance. Finally, recovery of several surrogate compounds added to all samples was calculated to monitor overall performance of the method. These compounds are similar to the target analytes, but should not be used to correct the recovery of target analytes.

Precision and bias of SVOC analysis in bed sediments were determined from field replicates and laboratory spikes, respectively. The average relative standard deviation of the percent absolute difference in pairs of SVOCs between the environmental and field replicates was about 20 percent. This precision was calculated from only 16 concentration pairs (including E-coded values) for only 14 SVOCs because many of the target analytes were below their respective reporting limits. The median recoveries for SVOCs that were present in at least one set of upstream-downstream sample pairs (results discussed later) ranged from 43 to 70 percent (table 14). Other SVOCs not present in pairs had generally similar recoveries to those present in pairs. Finally, three compounds were permanently E-coded including the two previously mentioned compounds (dibenzo[*a,h*]anthracene and indeno[1,2,3-*cd*]pyrene) for partial co-elution with each other and the compound 1,2,4-trichlorobenzene for relatively high variability coupled with relatively low recoveries.

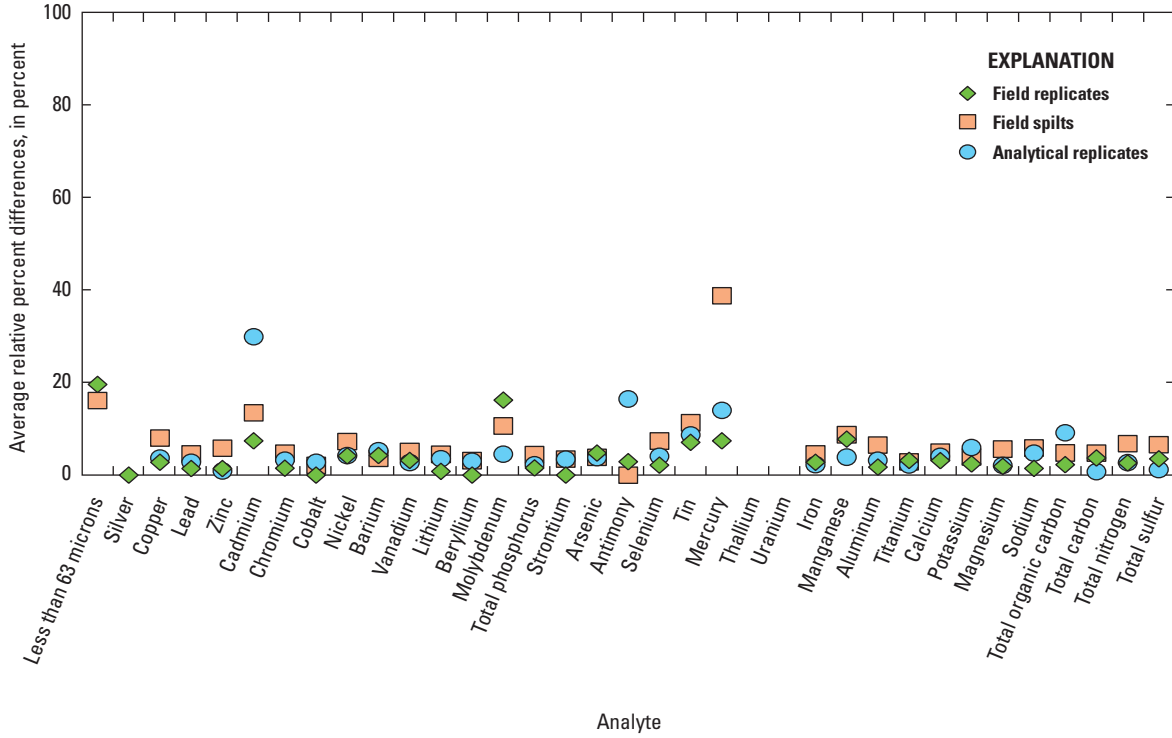


Figure 5. Average relative percent differences of the percent absolute difference between pairs of inorganic analytes, total organic carbon, and the percent less than the 63-micron fraction in field replicates, field splits, and analytical replicates in bed sediment samples.

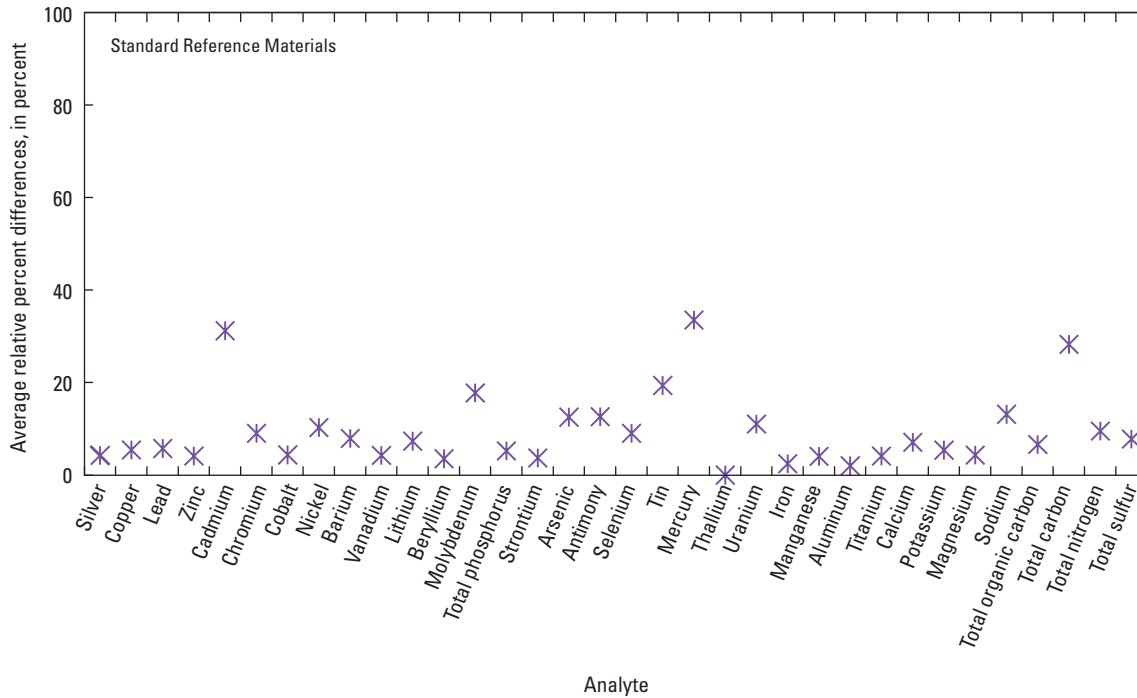


Figure 6. Average relative percent differences of the percent absolute difference between pairs of inorganic analytes and total organic carbon in bed sediment standard reference materials with “known” concentrations.

Table 14. Spike recoveries for semivolatile organic compounds in bed sediment samples.

Compound (sorted)	Recovery, in percent			
	Spike 1	Spike 2	Spike 3	Median
Presence in upstream-downstream pairs (sorted by prevalence)				
Perylene	46	42	54	46
Fluoranthene	59	62	63	62
Pyrene	58	65	61	61
2,6-Dimethylnaphthalene	57	61	55	57
Benzo(<i>b</i>)fluoranthene	50	44	58	50
Bis(2-ethylhexyl)phthalate	54	33	129	54
Anthraquinone ¹	69	70	72	70
Phenanthrene	58	61	57	58
Benzo(<i>a</i>)pyrene	49	41	57	49
Benzo(<i>e</i>)pyrene	49	42	56	49
Chrysene	56	52	60	56
Carbazole ²	61	69	63	63
Benz(<i>a</i>)anthracene	57	49	61	57
Benzo(<i>k</i>)fluoranthene	50	39	58	50
Anthracene	57	60	58	58
Benzo(<i>g,h,i</i>)perylene	43	23	43	43
4H-Cyclo[<i>def</i>]phenanthrene ³	58	58	59	58
Indeno(1,2,3- <i>cd</i>)pyrene	44	23	47	44
1,6-Dimethylnaphthalene	59	60	57	59
Acenaphthylene	48	50	49	49
1-Methylphenanthrene	58	60	58	58
9H-Fluorene	56	60	57	57
Naphthalene	47	50	44	47
Other (sorted on median)				
Diethylphthalate	38	39	36	38
Pentachloronitrobenzene	50	38	51	50
Hexachlorobenzene	53	39	56	53
Pentachloroanisol	53	44	57	53
Acenaphthene	53	55	54	54
1-Methyl-9H-fluorene	56	54	59	56
Dibenzothiophene	58	57	59	58
1,2-Dimethylnaphthalene	58	59	58	58
2-Ethyl-naphthalene	58	59	56	58
Phenanthridine	55	61	59	59
2,3,6-Trimethylnaphthalene	60	58	59	59
1-Methylpyrene	60	58	63	60
2-Methylantracene	66	64	65	65
Permanent E-coding				
1,2,4-Trichlorobenzene	39	43	36	39
Indeno(1,2,3- <i>cd</i>)pyrene	44	23	47	44
Dibenzo(<i>a,h</i>)anthracene	46	28	50	46

¹ Occasionally shown as 9,10-Anthraquinone.² Occasionally shown as 9H-Carbazol.³ Occasionally shown as 4,5-Methylenephenanthrene.

Bridge Deck Runoff Event Load and Annual Stream Load Computations

Bridge deck runoff loads of the POCs for each sampled storm event were computed by multiplying the concentrations and total measured discharges from the bridges. The bridge deck runoff event loads for all bridge deck runoff sites are presented in table A1 of the appendix.

Stream loads of the POCs at the four gaged stream sites were computed using continuous records of streamflow and measured (routine and storm) stream concentrations and represent loads upstream from the bridges. Annual stream POC loads were not computed for total recoverable mercury, total suspended solids, and SVOCs (with the exception of PAHs at the Swannanoa River site) because there were less than eight noncensored data points for these constituents at each site. Annual stream load estimates were calculated using the statistical program LOADEST (Runkel and others, 2004). The specific software used was S-LOADEST, which is a "USGS plug-in" version of LOADEST in S-PLUS (version 6.1), a PC-based statistical software package. Documentation is contained in the publicly available USGS library for S-PLUS for Windows, release 2.1 (Slack and others, 2003). S-LOADEST software can be downloaded from the USGS Web page at <http://water.usgs.gov/software/loadest.html>. The load estimates were obtained using the best combination of seven variables in a log-linear regression model selected with ranking by the Akaike information criterion (Akaike, 1974; Cohn and others, 1989; Gilroy and others, 1990; Cohn and others, 1992). The full seven-variable model is:

$$\ln L = a_0 + a_1 \ln Q + a_2 (\ln Q)^2 + a_3 t + a_4 t^2 + a_5 \sin(2\pi t) + a_6 \cos(2\pi t) + e \quad (1)$$

where

- \ln is natural logarithm function;
- L is load, in tons;
- $a_0, a_1, a_2, a_3, a_4, a_5, a_6$ are coefficients of the regression model;
- Q is instantaneous discharge at time of sampling, in cubic feet per second;
- t is time, in decimal years;
- \sin is sine function;
- $\pi = 3.14169$;
- \cos is cosine function; and
- e is model error term.

The discharge terms ($a_1 \ln Q$ and $a_2 (\ln Q)^2$) in the model address variability in concentration resulting from discharge variability. The time terms ($a_3 t$ and $a_4 t^2$) adjust for variability resulting from a linear time trend in concentration, and the sine and cosine terms adjust for seasonal variability in concentration. Bias generated in the estimated load when the load is transformed from log to linear units was corrected using the minimum variance unbiased estimator correction (Bradu and Mundlak, 1970). Censored data were statistically adjusted using the adjusted maximum likelihood estimator (Cohn and others, 1989).

Water Quality and Effect of Stormwater Bridge Runoff on Receiving Streams

Section 25.18 of Session Law 2008-107, House Bill 2436 enacted by the North Carolina General Assembly (2008), requires that a study be conducted to examine effective and implementable stormwater control measures (SCMs) for bridge deck runoff in North Carolina. Before the NCDOT can develop a statewide selection plan for implementing SCMs to address water-quality concerns, the relative impact of bridge deck runoff on receiving streams in North Carolina must be first understood. While water chemistry evaluations provide important context relative to established water-quality thresholds and some indication of important constituents to consider for further investigation, the impact of bridge deck runoff on receiving streams cannot be fully addressed without evaluating water chemistry and bioassessment results (bioassays and macroinvertebrate surveys) in tandem. The subsequent sections focus on water chemistry collected and analyzed by the USGS and bioassay and macroinvertebrate survey results are documented by the URS Corporation (2010).

Parameters of Concern

Despite substantial roadway stormwater characterization data available in the literature, a standard method does not exist for evaluating roadway stormwater concentrations in the context of impairment to receiving streams. The North Carolina Department of Environment and Natural Resources (2003) previously used USEPA's National Ambient Water Quality Criteria for freshwaters to evaluate stream data during storm flows, but no standards or regulatory guidance exist for stormwater concentrations. In the current absence of guidance, the NCDOT and the URS Corporation developed a methodology for focusing stormwater data analysis on constituents present at levels that could be related to adverse environmental effects (URS Corporation, 2010). The methodology used in this study involves consideration of available surface-water-quality data from North Carolina, USEPA, and other resources to select thresholds for environmental significance for stormwater runoff. This approach allows the analysis to be limited to constituents present at levels that may raise concern about receiving stream impairment, rather than attempting to analyze data obtained from the entire suite of 112 water-quality constituents (URS Corporation, 2010).

The use of surface-water-quality standards to assess the effects of runoff from highways on receiving streams was originally proposed by Dupuis (2002). However, using surface-water-quality data in this context has the following limitations as outlined by Burton and Pitt (2002):

- Surface-water standards and criteria based on biological effects may not be applicable to conditions at every site.

- Thresholds often do not account for antagonistic or synergistic effects that alter pollutant bioavailability.
- Abundant surface-water-quality criteria are designed for single acute and chronic average exposures that do not consider pulsed exposures for short time periods.
- Previous studies have shown stream degradation identified through biosurveys when measured water-quality constituents have met criteria.

Therefore, while exceedance of these thresholds may indicate a stormwater effect, it does not definitively do so, nor does the lack of an exceedance definitively exonerate bridge deck runoff of contributing to receiving stream impairment. These thresholds are instead intended to be used in concert with each other to support a weight-of-evidence analysis (URS Corporation, 2010).

For the purpose of consistency with URS (2010), which documents the methodology used to focus the data analysis on stormwater constituents that could be related to adverse environmental effects, the use of the POC terminology is used in this report. POCs were defined as any monitored analyte whose maximum measured concentration exceeded the most stringent threshold from available local and nationally recognized surface-water-quality criteria or environmental datasets. If the maximum measured concentration in either the bridge deck runoff or stream was lower than the most stringent threshold, regardless of stream classification or target receptor, that particular constituent was not identified as a POC in a site-specific comparison of stormwater runoff and thresholds (URS Corporation, 2010).

Given that chemical analysis for more than 100 analytes was conducted for the study, the benefit of the POC determination was to eliminate analytes that did not pose a substantial risk of receiving stream impairment and focus the data analysis and interpretation and load computations on those analytes that were most likely to have an adverse effect. It should be noted that a single occurrence of a concentration above the most stringent water-quality threshold at any site would trigger that analyte to be considered a POC. Some POCs were barely over the threshold, including dissolved lead, total recoverable nickel, and phenanthrene, whereas other POCs far exceeded the threshold (herein defined as at least three orders of magnitude, including total recoverable aluminum, several PAHs, and total suspended solids (table 15). Additional details regarding (1) the various resources used to compile surface-water-quality thresholds, (2) the thresholds used to establish the POCs, and (3) how the USEPA hardness-dependant equations for dissolved metals and biotic ligand model for dissolved copper were used are provided by the URS Corporation (2010).

Precipitation Data for Sampled Events

At least 12 storm events with total precipitation depths greater than 0.10 in. were sampled at each of the 15 bridge deck sites. A summary of the date, duration, mean temperature, and selected pertinent precipitation properties for all sampled events at each site is presented in table A2 in the appendix. Samples were collected during storms where precipitation ranged from 0.10 to 5.3 in., with an average of 0.70 in. and a standard deviation of 0.70 in. Any differences between the precipitation during sampling and total precipitation for an event represent situations where a maximum sample volume had been reached prior to the conclusion of precipitation. This was a common situation because the sampling program in each autosampler had to be configured to sample over an estimated runoff volume prior to the arrival of the storm based on precipitation forecasts, which at times were not accurate. If more precipitation or runoff occurred than the general range of amounts forecasted or estimated based on bridge deck drainage area, respectively, the autosampler bottle would fill to the maximum volume allowable for processing in the churn splitter (14 L) prior to the end of the storm. The maximum precipitation intensity was calculated by averaging the precipitation intensity over the maximum 10-minute period during each storm. Antecedent dry days represent the time prior to each storm event since at least 0.10 in. of precipitation was measured, which is an indication of the amount of time for constituents to accumulate on the bridge deck. The duration of precipitation is a quantification of the actual time over the sampled storm that precipitation was actually measured, whereas the entire wet-weather period represents the duration of the entire sampled storm, including the periods where no precipitation was measured. A discrete wet-weather period for this study was considered finished once no precipitation occurred over 6 consecutive hours.

Bridge Deck Runoff

Subsequent sections summarize measured bridge deck runoff quantity and quality at all 15 sites. The information will provide the framework for comparing bridge deck runoff concentrations and loads between bridge sites and to the measured stream water-quality data and developing predictive equations for parameter loadings from bridges in North Carolina.

Table 15. Identification of parameters of concern (POCs) by comparison of maximum concentration in bridge deck runoff to selected water-quality thresholds.

[Source is URS Corporation (2010). Concentrations shown in milligrams per liter, except where noted. EMC, event mean concentration; USEPA, U.S. Environmental Protection Agency; NCDENR, North Carolina Department of Environment and Natural Resources; TCEQ, Texas Commission on Environmental Quality; NCSWQS, North Carolina Surface Water Quality Standard; NA, not applicable]

Parameter of concern (POC)	Maximum EMC	Site of maximum EMC	Date of maximum EMC	Threshold	Reference
Metals					
Aluminum, total recoverable	22,400	Big Ivy Creek	03/11/10 and 04/08/10	87	USEPA (2009) ^e
Arsenic, total recoverable	5.1	Mallard Creek	02/13/10	0.018	USEPA (2009) ^e
Cadmium, dissolved	2.33	Mallard Creek	02/13/10	0.07 ^a	USEPA (2009) ^e
Copper, dissolved	46.1	Mallard Creek	02/13/10	1.6 ^b	USEPA (2009) ^e
Iron, total recoverable	46,900	Swannanoa River	03/27/09	300	USEPA (2009) ^e
Lead, dissolved	0.66	Black River	04/11/09	0.33 ^a	USEPA (2009) ^e
		Swift Creek	07/13/09		
Manganese, total recoverable	786	Big Ivy Creek	04/08/10	50	USEPA (2009) ^e
Mercury, total recoverable	0.039	Mallard Creek	09/16/09	0.012	NCDENR (2010) ^f
Nickel, total recoverable	76.4	Smith Creek	03/29/10	25	NCDENR (2010) ^f
Zinc, dissolved	411	Mallard Creek	02/13/10	25 ^a	USEPA (2009) ^e
Semivolatile organic compounds					
Benzo[<i>a</i>]anthracene	5.3	Perry Creek	02/05/10	0.0038	USEPA (2009) ^e
Benzo[<i>a</i>]pyrene	6.83	Perry Creek	02/05/10	0.0038	USEPA (2009) ^e
Benzo[<i>b</i>]fluoranthene	13.1	Perry Creek	02/05/10	0.0038	USEPA (2009) ^e
Benzo[<i>k</i>]fluoranthene	6.81	Perry Creek	02/05/10	0.0038	USEPA (2009) ^e
Bis(2-chloroethyl)ether	0.23	Middle Creek	05/17/09	0.03	USEPA (2009) ^e
Bis(2-ethylhexyl)phthalate	26.2	Smith Creek	05/26/09	1.2	USEPA (2009) ^e
Chrysene	11	Perry Creek	02/05/10	0.0038	USEPA (2009) ^e
Dibenzo[<i>a,h</i>]anthracene	0.328	Perry Creek	05/04/09	0.0038	USEPA (2009) ^e
Hexachlorobenzene	0.019	Black River	03/28/10	0.00028	USEPA (2009) ^e
Indeno[1,2,3- <i>cd</i>]pyrene	4.32	Perry Creek	02/05/10	0.0038	USEPA (2009) ^e
n-Nitrosodimethylamine	0.062	Mango Creek	04/21/10	0.00069	USEPA (2009) ^e
n-Nitrosodi-n-propylamine	0.384	Perry Creek	05/24/09	0.005	USEPA (2009) ^e
Pentachlorophenol	0.957	Smith Creek	07/16/09	0.27	USEPA (2009) ^e
Phenanthrene	6.03	Perry Creek	02/05/10	4.6	TCEQ (2000) ^g
Other analytes					
pH (acidic), standard units	3.5	Black River	04/11/09	5	USEPA (2009) ^e
pH (basic), standard units	9.5	Mango Creek	03/27/09	9	USEPA (2009), ^e NCDENR (2010) ^f
Nitrogen, total, mg/L	4.3	Flat Creek	07/27/09	NA ^c	None
Phosphorus, total, mg/L	8.28	Big Ivy Creek	09/16/09	NA ^c	None
Suspended solids, total, mg/L	1,210	Big Ivy Creek	04/08/10	10 ^d	NCDENR (2010) ^f

^a Thresholds for dissolved cadmium, lead, and zinc were calculated using hardness-dependent equation after USEPA (2009) by the URS Corporation (project consultant). The 25th percentile hardness value from the pooled data from all the bridge deck monitoring sites was used for the calculations.

^b The threshold for dissolved copper was calculated using a biotic ligand model (USEPA, 2007a; 2007b) by the URS Corporation.

^c Thresholds for total nitrogen and total phosphorus do not exist beyond those for specific watersheds. Nutrients were included because of their known potential contribution to eutrophication and depressed dissolved oxygen levels in water bodies.

^d The total suspended solids threshold is the “worst case” of a National Pollutant Discharge Elimination System discharge into a trout stream (NCDENR, 2007).

^e USEPA Freshwater Criteria Continuous Concentration for aluminum, cadmium, copper, lead, zinc, and pH (basic). USEPA Human Health Water + Organism for arsenic, iron, manganese, pH (acidic and basic), and all semivolatile organic compounds (except for phenanthrene). USEPA Freshwater Criteria Maximum Concentration for zinc.

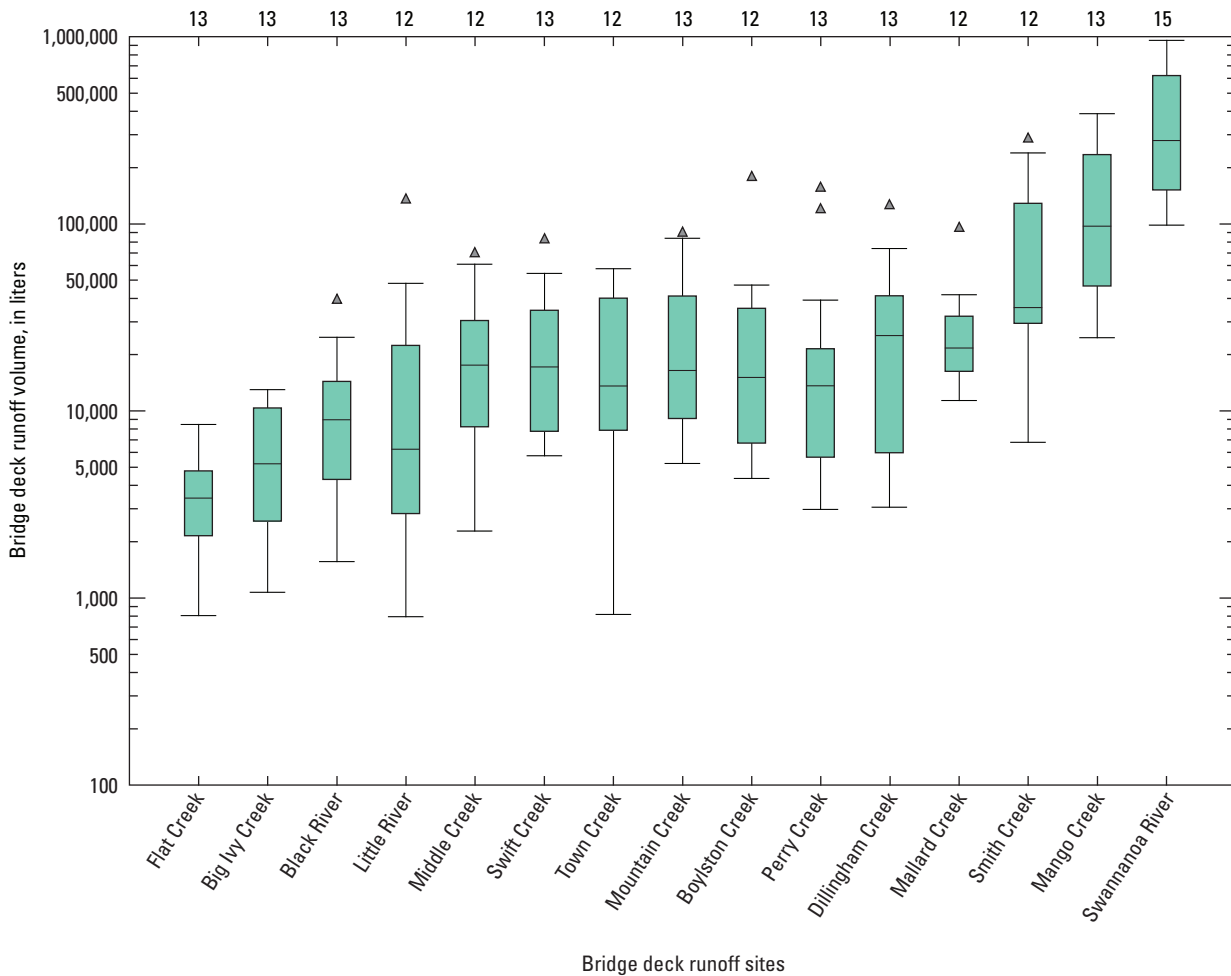
^f NCSWQS Freshwater Aquatic Life for mercury and pH (basic). NCSWQS Water Supply for nickel. NCSWQS High Quality Waters/Trout Waters for total suspended solids.

^g TCEQ Saltwater Chronic for phenanthrene.

Discharge

Bridge deck runoff was measured at the 15 sites for each of the sampled events as shown in figure 7. The sites are ordered on the horizontal axis by increasing size of the drainage area contributing to bridge deck runoff. The contributing deck drainage area for each site was provided by the NCDOT. In general, the median runoff volume for the sampled storms increases with increasing bridge deck drainage area.

As previously mentioned, there were situations where actual precipitation for a storm exceeded the upper range of forecasted amounts. Prior to the onset of a storm, the sampling program in each autosampler had to be configured to sample over an estimated runoff volume based on precipitation forecasts. When precipitation exceeded the upper range of forecasts or if the bridge deck drainage pipe received water from an area larger than the contributing drainage areas indicated by NCDOT, the autosampler bottle would fill to the



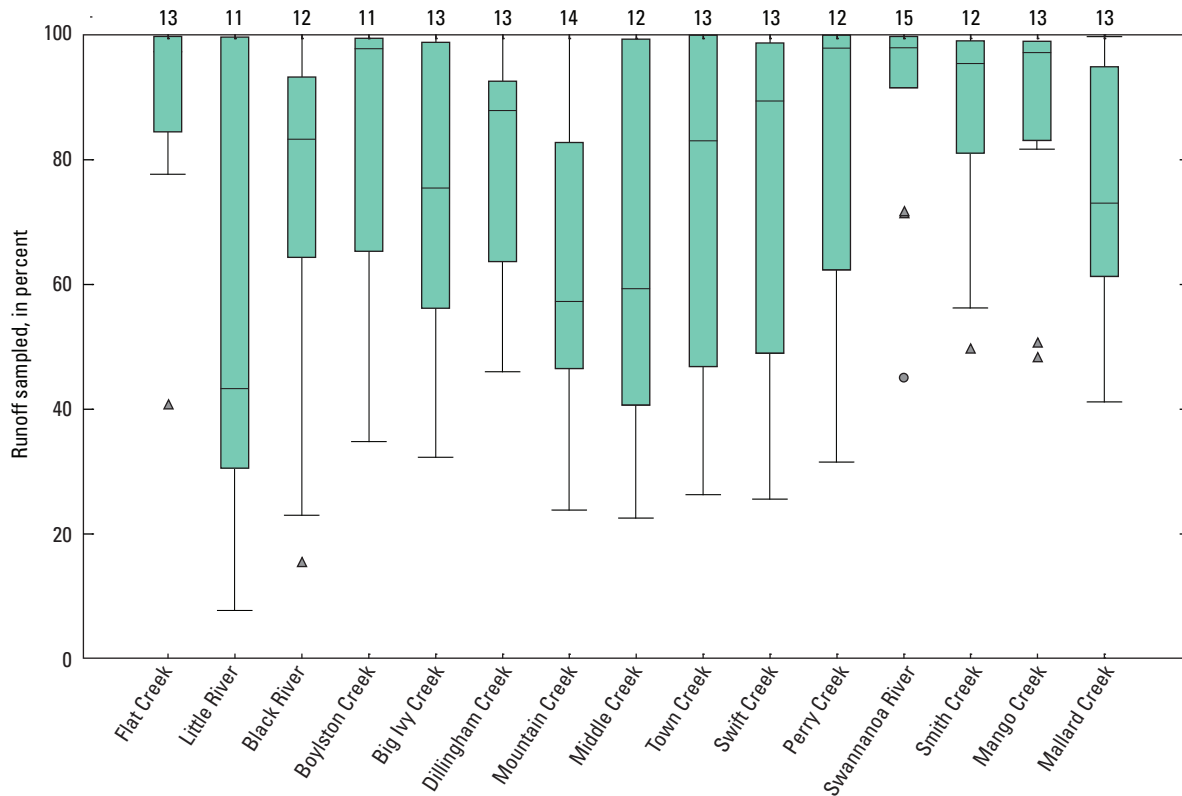
EXPLANATION

- 11 Number of samples
 - ▲ Upper outside
 - 95th percentile
 - 75th percentile
 - 50th percentile
 - 25th percentile
 - 5th percentile
- } Interquartile range

Figure 7. Summary of bridge deck runoff measured during water-quality sampling events. Sites are listed in order of increasing deck drainage area.

maximum volume allowable for processing in the churn splitter prior to the end of the storm. In these situations, the first flush from the bridge decks would be sampled, but the tail end of the runoff hydrograph would not be sampled. The resulting concentrations for these situations tend to be higher than for those storms with runoff that was fully sampled because they were less diluted with the relatively cleaner runoff that occurs toward the end of the hydrograph. The relative portion of the total runoff volume over which samples were collected for each sampled event is illustrated for all sites (fig. 8). The median portion of total measured runoff volume over which samples were collected is greater than 80 percent for 10 of the 15 sites. The median portion of total measured runoff volume

over which samples were collected at the Little River runoff site is substantially lower than all other sites, which can be attributed to an apparent error in the contributing drainage area used for programming the autosampler. Near the conclusion of the study, visual inspections conducted at the site during a precipitation event revealed that runoff from areas outside the specified contributing drainage area was actually draining into the discharge pipe. A detailed summary of the measured precipitation, runoff volume, and start and end times for runoff samples collected at the bridge deck sites is presented in table A3 of the appendix. The daily discharge data for the entire study period at the bridge deck runoff sites are presented in table A4 of the appendix.



EXPLANATION

- 13 Number of values
 - 95th percentile
 - 75th percentile
 - 50th percentile
 - 25th percentile
 - 5th percentile
 - ▲ Lower outside
 - Lower detached
- } Interquartile range

Figure 8. Percent runoff sampled at the bridge deck sites. Sites are listed in order of increasing annual average daily traffic volume.

Water Quality

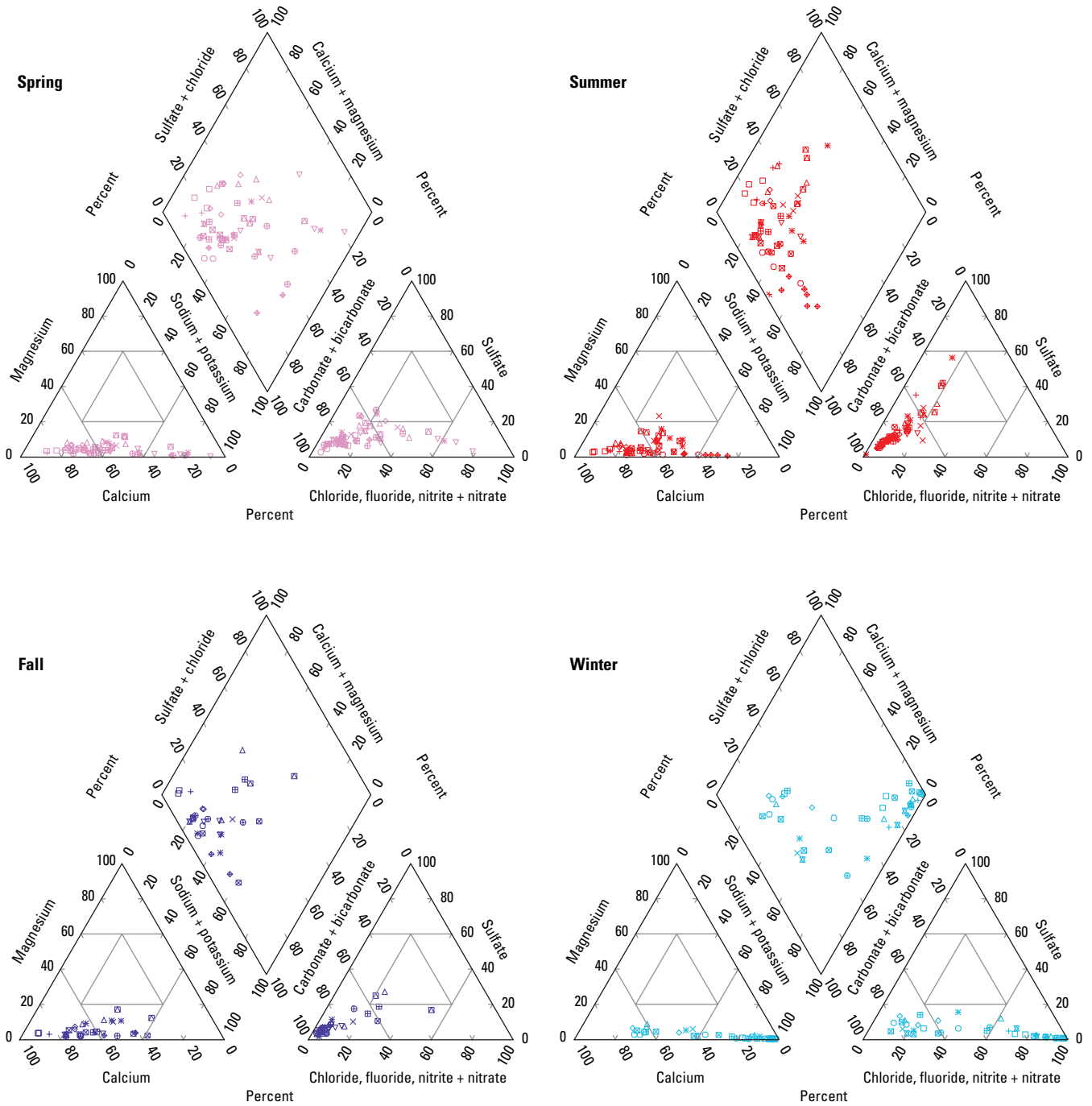
A detailed summary of the analytical results for the inorganic POCs in all runoff samples collected at the bridge deck sites is presented in table A5 of the appendix. Bridge deck runoff from the 15 sites can be characterized on the basis of the major cations and anions as quite variable among the sites and between seasons (fig. 9). First, considering all the sites and seasons together, there was a large range in calcium and sodium + potassium though all samples were low in magnesium. Carbonate + bicarbonate dominated the anions, and some samples had high relative concentrations of chloride/fluoride/nitrite + nitrate. Most samples were low in sulfate. As a general statement, these waters were largely of the calcium carbonate + bicarbonate type with some waters high in sodium chloride that likely were associated with road salting. Second, considering the seasonal patterns, the winter samples as a group appeared somewhat different as might be expected. These samples tended to have relatively high percentages of sodium + potassium and chloride/fluoride/nitrite + nitrate and relatively low percentages of calcium. The sodium chloride type water was very evident in the winter samples and was absent in samples from the other seasons.

The 14 SVOCs identified as POCs in bridge deck runoff were detected in 42 percent of the analyses for SVOCs (table 16). This SVOC suite was dominated by pyrogenic PAHs both in terms of number of compounds and number of detections. Six PAHs including phenanthrene, indeno[1,2,3-*cd*]pyrene, benzo[*b*]fluoranthene, benzo[*a*]pyrene, chrysene, and benzo[*k*]fluoranthene were most frequently detected and together accounted for 74 percent of all SVOC detections. About another 11 percent of the detections were associated with benzo[*a*]anthracene and dibenzo[*a,h*]anthracene. Thus, about 85 percent of the detections were pyrogenic PAHs. A total of 10 percent of the detections were associated with bis(2-ethylhexyl) phthalate (a plasticizer), and 4 percent of the detections were associated with pentachlorophenol (a wood preservative). The remaining four SVOCs were only rarely detected. The frequency of detection (number of detections divided by the number of analyses times 100) ranged from 6.1 percent for the most commonly detected compound (phenanthrene) to 0.04 percent for the two less commonly detected compounds (the two nitrosoamines). A detailed summary of the analytical results for organic POCs in all runoff samples collected at the bridge deck sites is presented in table A5 of the appendix.

Table 16. Detections of semivolatile organic compounds (SVOCs) as parameters of concern (POCs) and relative abundances in bridge deck samples.

[PAH, polycyclic aromatic hydrocarbon]

Analyte	Chemical class	Number of detections	Percentage of total detections	Frequency of detection
Phenanthrene	PAH (pyrogenic)	167	14	6.1
Indeno[1,2,3- <i>cd</i>]pyrene	PAH (pyrogenic)	154	13	5.6
Benzo[<i>b</i>]fluoranthene	PAH (pyrogenic)	149	13	5.4
Benzo[<i>a</i>]pyrene	PAH (pyrogenic)	143	12	5.2
Chrysene	PAH (pyrogenic)	135	12	4.9
Benzo[<i>k</i>]fluoranthene	PAH (pyrogenic)	116	10	4.2
Bis(2-ethylhexyl)phthalate	Phthalate	110	10	4.0
Benzo[<i>a</i>]anthracene	PAH (pyrogenic)	89	7.7	3.2
Pentachlorophenol	Phenol	46	4.0	1.7
Dibenzo[<i>a,h</i>]anthracene	PAH (pyrogenic)	37	3.2	1.3
Hexachlorobenzene	Chloroaromatic	4	0.3	0.1
Bis(2-chloroethyl)ether	Chloro ether	2	0.2	0.1
n-Nitrosodimethylamine	Nitrosoamine	1	0.1	0.04
n-Nitrosodi-n-propylamine	Nitrosoamine	1	0.1	0.04
Total detections of SVOCs as POCs		1,154		
Total analyses of SVOCs as POCs		2,744		
Percent detections of total analyses of SVOCs as POCs		42		



EXPLANATION

Seasonal data collections

- Spring
- Summer
- Fall
- Winter

Bridge deck sample sites

- Town Creek
- Smith Creek
- Black River
- Mallard Creek
- Boylston Creek
- Middle Creek
- Swannanoa River
- Swift Creek
- Dillingham Creek
- Mayo Creek
- Big Ivy Creek
- Perry Creek
- Flat Creek
- Little River
- Mountain Creek

Figure 9. Seasonal Piper diagrams of general water types of runoff from bridge decks.

Constituent Concentrations Associated with the Dissolved and Particulate Phases

Knowing the distribution of a POC between the dissolved and particulate fractions in runoff from bridge decks can suggest efficient mitigation strategies to avoid input to surface-water bodies. Bridge sweepings might be expected to remove most of a POC that was associated largely with particles. In this case, determining only the total recoverable concentrations might be sufficient if it is known to be dominated by the particulate phase and where the dissolved phase is thought to be minor. For POCs largely associated with the dissolved phase, intercepting and diverting runoff might suffice to protect surface-water bodies. In this case, the total recoverable concentration would approximate the “dissolved” concentration and the added time and expense of filtering samples could be obviated. In both examples, knowing the dominant phase can determine both the type of analysis required and the best, most economical remediation practice.

Among the metal and nutrient POCs, aluminum, iron, lead, and possibly total phosphorus were present largely associated with the particulate phase (fig. 10). The first two POCs are major components of common minerals, and lead is relatively insoluble in oxic waters due to formation of cerussite ($PbCO_3$) and (or) any of the $PbSO_4$ minerals (Hem, 1970). Total phosphorus might be largely adsorbed on iron

oxides. The remainder of the metal and nutrient POCs either exhibited large ranges in dissolved particulate partitioning (total nitrogen, manganese, cadmium, copper, zinc, nickel, and arsenic), or there were too few data points (such as for mercury) to make much of a conclusion (fig. 11). If these phase distributions were accurate and representative of the bridge deck runoff, then solid-phase removal approaches, including sweeping, might only be able to minimize aluminum, iron, lead, and possibly total phosphorus inputs. The remainder of the POCs, because the dissolved fraction can be high and variable, would have to be addressed in some other way. It should be noted, however, that these observed phase distributions might not reflect actual distributions in the sample prior to storage, filtering, and preservation.

As previously mentioned, post-collection changes in partitioning between the dissolved and particulate phases prior to filtration and preservation needed to be considered, especially for the dissolved POCs (cadmium, copper, lead, and zinc). For cadmium, the maximum exceedance concentration was 2.33 $\mu\text{g/L}$, which was three orders of magnitude above the water-quality threshold concentration of 0.07 $\mu\text{g/L}$ (see table 15). The maximum exceedance concentrations for copper and zinc (46.1 and 411 $\mu\text{g/L}$, respectively) were one order of magnitude above their threshold concentrations (1.6 and 25 $\mu\text{g/L}$, respectively). Finally, the maximum exceedance

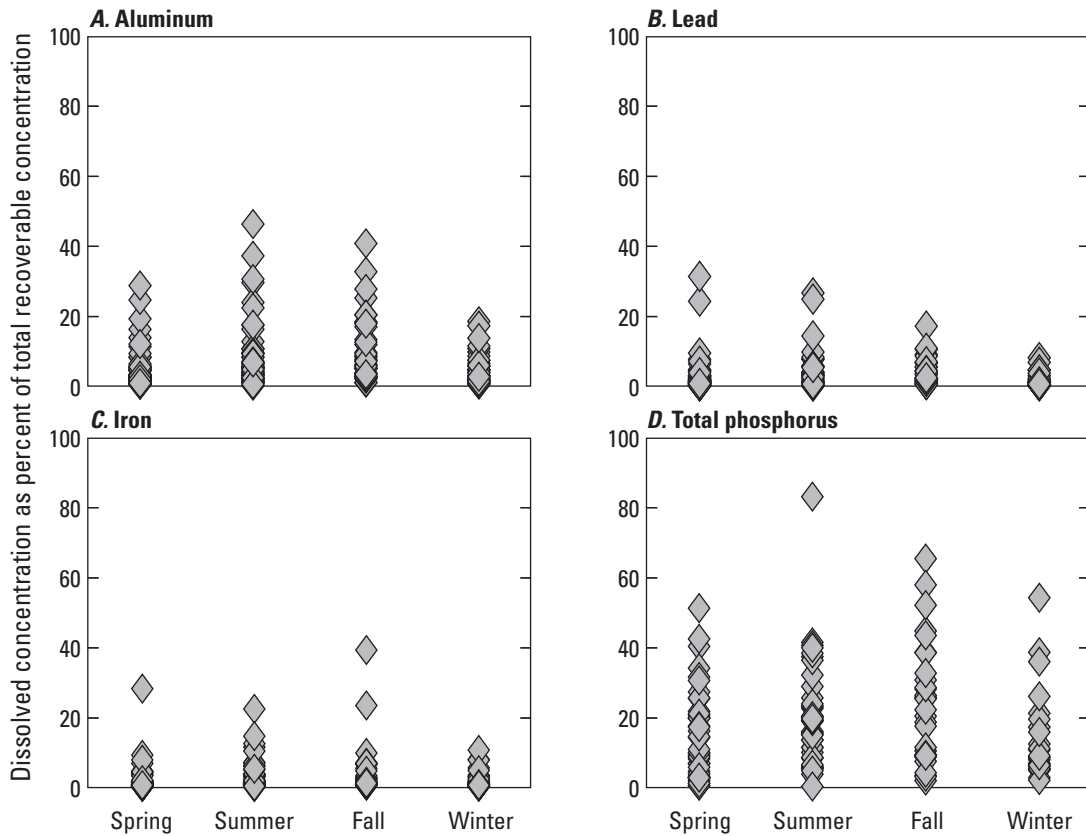


Figure 10. Percent dissolved fraction of total recoverable (A) aluminum, (B) lead, (C) iron, and (D) total phosphorus in bridge deck samples for each season.

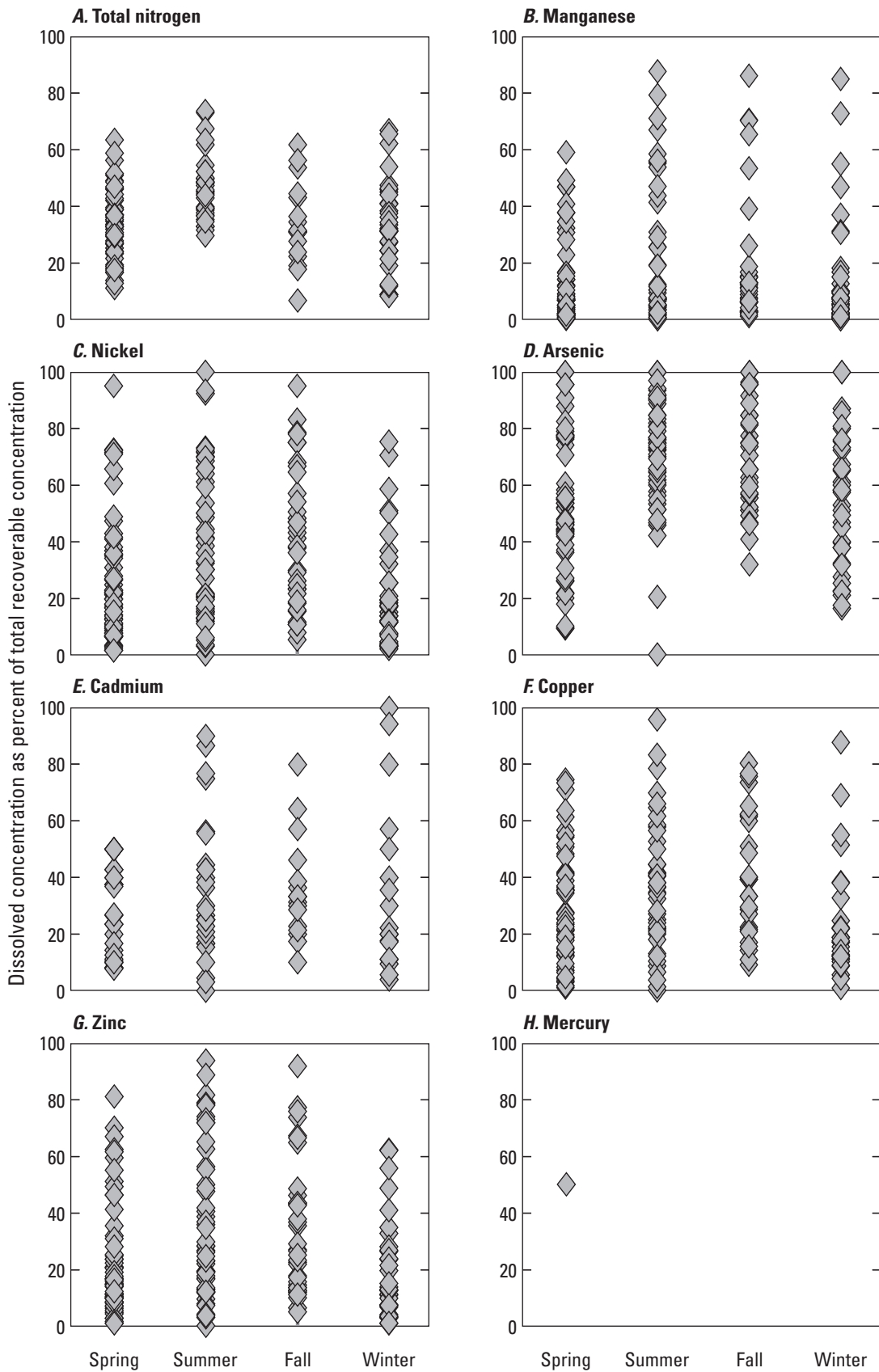


Figure 11. Percent dissolved fraction of (A) total nitrogen and total recoverable (B) manganese, (C) nickel, (D) arsenic, (E) cadmium, (F) copper, (G) zinc, and (H) mercury in bridge deck samples for each season.

concentration for lead (0.66 µg/L) was double that of the threshold concentration (0.33 µg/L). The concentrations for cadmium, copper, and zinc all occurred in one winter sample (February 13, 2009) from the Mallard Creek bridge deck. In contrast, the lead exceedance occurred at two bridge decks, Black River in spring (April 11, 2009) and Swift Creek in summer (July 13, 2009), respectively. At the relatively low ambient winter temperature in February, biotic and abiotic reactions that alter phase partitioning might be minimal. Thus, the inclusion of dissolved cadmium, copper, and zinc as POCs might be less concerning than inclusion of lead. Additional studies are needed to quantify any such sampling artifacts.

Summary and Statistical Analysis of Constituent Concentrations

To evaluate if any statistically significant relation among concentrations of POCs in bridge deck runoff samples and areal sources exist, incidence over the year, and roadway setting or surface type, the concentration data for the metal and nutrient POCs were grouped by ecoregion, season, official NCDOT roadway classification (rural or urban), and wearing surface (concrete or asphalt) for statistical comparison testing. The nonparametric Mann-Whitney test (Mann and Whitney, 1947) was used to determine whether the independent populations were statistically different at the 95-percent confidence level (p-value less than 0.05) for POCs with less than 5 percent of the data that were censored (estimated to be less than the long-term method detection limit or LT-MDL). For POCs with greater than 5 percent of the data being censored (mercury, cadmium, lead, and total suspended solids), the nonparametric Gehan test (Gehan, 1965) was used to determine whether the independent populations were statistically different at the 95-percent confidence level (p-value less than 0.05). For concentrations of POCs that were not detected or were estimated to be less than the LT-MDL (censored data), concentrations were set equal to one-half of the respective LT-MDL. This approach is appropriate for rank-based nonparametric methods for singly censored data (Helsel, 2005). The Kruskal-Wallis statistical test (Kruskal and Wallis, 1952) was used to determine whether data groups with three or more independent populations (seasons and ecoregions) were statistically different. If the Kruskal-Wallis test indicated that the populations were statistically different, a subsequent Tukey-Kramer multiple comparison test (Tukey, 1977) was used to determine which populations were different. Statistical analyses for the PAH and phthalate compounds determined to be POCs were not performed because these compounds either were detected in less than eight samples at a site or all of the concentrations were estimated to be less than the LT-MDL.

With the exception of arsenic, the Coastal Plain samples had statistically lower concentrations than samples from the Blue Ridge and there were no statistical differences in concentrations for cadmium, copper, lead, total nitrogen, total phosphorus, pH, and zinc. The Coastal Plain sites had statistically lower concentrations than samples from the Piedmont

ecoregion except for arsenic and there were no statistical differences in concentrations for aluminum, manganese, iron, nickel, total nitrogen, total phosphorus, pH, and zinc. The Blue Ridge samples had statistically higher concentrations than the Piedmont samples except for copper and there were no statistical differences in concentrations for arsenic, cadmium, manganese, mercury, nickel, total phosphorus, pH, total suspended solids, and zinc. In the case of the metals, this may have reflected differences in soil mineralogy between these ecoregions. A summary of the median concentrations for bridge deck runoff grouped by ecoregion is presented in table 17.

In terms of seasons, POC concentrations were statistically higher in winter compared to summer and fall, except for dissolved cadmium, copper, lead, zinc, and total recoverable mercury (which were not statistically different), pointing to reduced volatilization at lower temperatures and higher total suspended solids concentrations in the winter (likely from deicing treatments) as potential explanations. With the exception of pH and total suspended solids (both higher in the winter), the winter and spring POC concentrations were not statistically different. Similar results have been found by Smith and Granato (2010). A summary of the median concentrations for samples collected in each season is presented in table 17.

Statistical testing revealed no significant difference between rural and urban populations of concentrations for total nitrogen (p-value = 0.849), total phosphorus (p-value = 0.233), arsenic (p-value = 0.613), zinc (p-value = 0.964), and mercury (p-value = 0.519). The urban concentrations were statistically higher than the rural concentrations for aluminum (p-value = 0.003), lead (p-value = 0.049), manganese (p-value = 0.007), total suspended solids (p-value = 0.01), and cadmium, copper, iron, and nickel (all with p-values less than 0.001; figs. 12 and 13). Although the statistical testing did not indicate that the urban sites contributed statistically significant higher concentrations for all metals, they were detected more often in samples collected from urban sites than rural sites. Visual inspection of the box plots in figure 14 indicates that substantially higher levels of the PAHs were measured at the urban sites compared to the rural sites.

The analysis of POCs and bridge surface type (concrete and asphalt) revealed that runoff concentrations of constituents, except for lead and zinc, were statistically higher in samples from concrete bridges than asphalt bridges; there were no statistical differences in concentrations for arsenic, cadmium, mercury, and total nitrogen (table 18). When interpreting these results of the surface-type analysis, it should be noted that all six of the asphalt bridges were classified as rural, and the nine concrete bridges were classified as rural (three bridges) and urban (six bridges). Therefore, results may be more reflective of the bridge classification, as presented in the analysis above, than the bridge-surface type. The analysis of surface type would be greatly enhanced if urban bridges with an asphalt surface type would have been included in the study.

Table 17. Median concentrations for bridge deck runoff samples grouped by ecoregion and season.

[Concentrations shown in micrograms per liter, except for total phosphorus and total nitrogen, which are in milligrams per liter, and pH, which are in standard units]

Parameter of concern	Bridge deck runoff samples ¹						
	Ecoregion			Season			
	Blue Ridge	Piedmont	Coastal Plain	Spring	Summer	Fall	Winter
pH	6.9	6.8	6.9	6.8	6.6	6.8	7.2
Total phosphorus	0.22	0.17	0.16	0.25	0.16	0.15	0.25
Total nitrogen	0.89	1.1	0.68	0.99	0.97	0.67	1.10
Total recoverable aluminum	1,580	1,090	321	1,580	885	414	2,220
Total recoverable arsenic	0.95	0.97	1.45	1.2	0.89	0.87	1.4
Dissolved cadmium	0.02	0.03	0.02	0.02	0.03	0.02	0.02
Dissolved copper	2.11	3.69	1.84	3.16	2.61	2.41	2.02
Total recoverable iron	2,730	1,620	442	2,600	1,230	643	3,420
Dissolved lead	0.06	0.11	0.05	0.11	0.07	0.07	0.08
Total recoverable manganese	63.7	68.6	20.4	75	47	27	107
Total recoverable mercury	0.007	0.007	0.004	0.007	0.007	0.005	0.007
Total recoverable nickel	3.19	2.93	1.42	3.61	2.13	1.67	4.53
Dissolved zinc	14.3	17.35	12	17.0	20.7	13.6	11.5
Total suspended solids	57	50.5	8	51	37	22	74

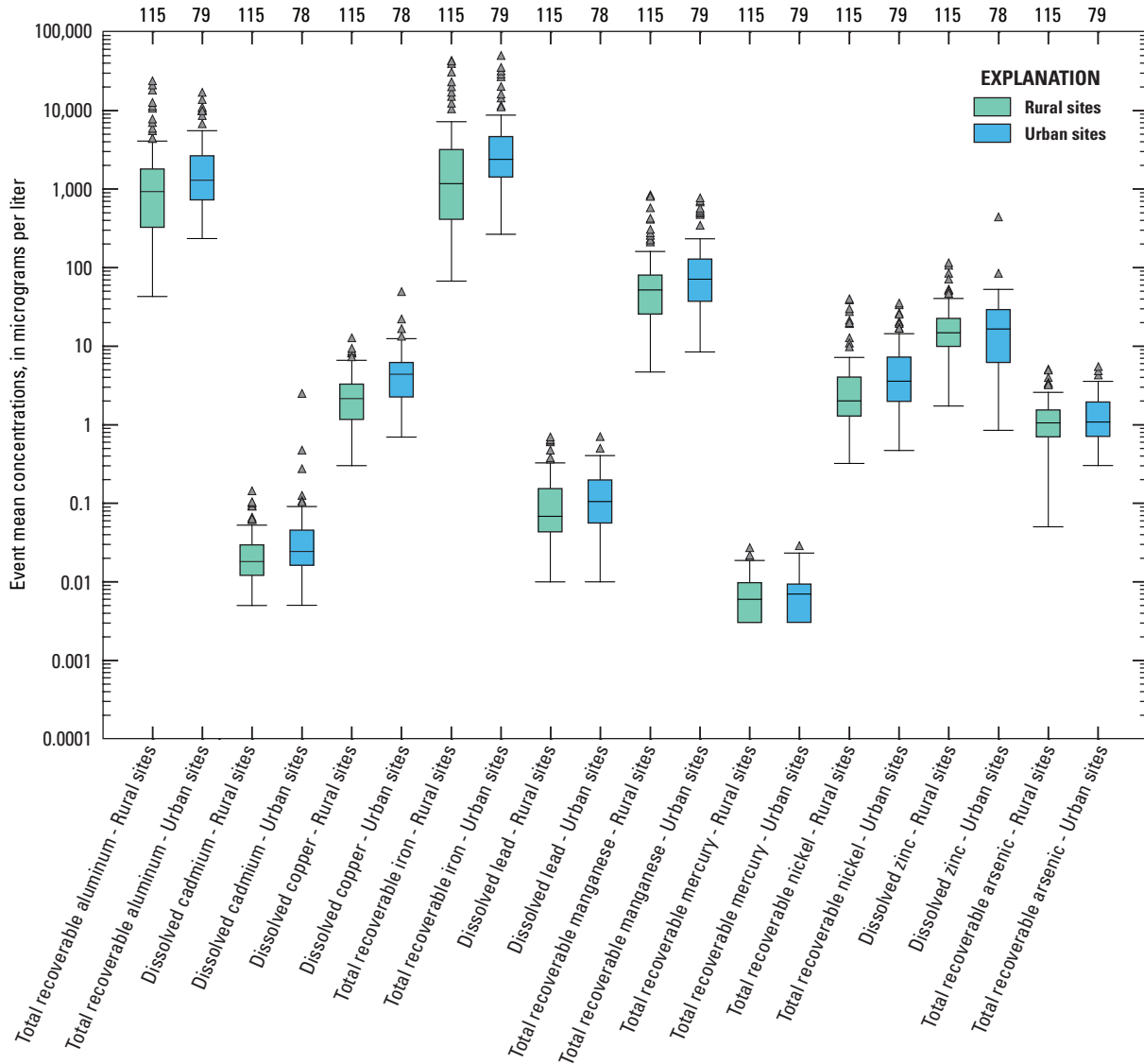
¹ Concentrations less than the reporting limit were replaced with the long-term method detection limit for the purpose of median calculations. For parameters with greater than 5-percent censored data, medians were computed using the rank method as described by Bonn (2008).

Among the concentrations of metals, there was no strong relation to AADT, except for cadmium, copper, and nickel (fig. 14). Additionally, there was no overarching pattern difference between total recoverable and dissolved metals in this group. Finally, there was no obvious relation to AADT for total nitrogen, total phosphorus, pH, and total suspended solids. A potential explanation for the lack of a strong relation between AADT and POC concentrations is that the range was too small to overcome the inherent variability of the measurements. Malina and others (2005) also found that a strong relation between concentration and AADT did not exist. When larger ranges of AADT were studied, especially those sites substantially above and below about 30,000, concentrations tended to roughly scale with AADT (Driscoll and others, 1990; Smith and Granato, 2010). The selection process for monitoring sites included an analysis of the AADT frequency distributions in North Carolina, and only about 1 percent of bridges in North Carolina have AADT volumes in excess of 30,000 vehicles. The small percentage of bridges in North Carolina with AADT volumes in excess of 30,000 and extremely limited number of those bridges with runoff collection systems only allowed for two bridge sites with an AADT volume greater than 30,000 vehicles (Mallard Creek and Mango Creek; table 2) to be included in the current study.

The remaining 13 sites had lower AADT values that ranged from 400 to 26,000 vehicles.

As might be expected, the median concentrations of the summed PAHs were generally higher at the urban sites (larger AADT volumes) than at the rural sites (fig. 14). The highest concentrations for most PAHs occurred at the urban Perry Creek bridge site, and the lowest concentrations generally occurred at the urban Mango Creek site. The concentrations at the Mango Creek bridge site were more typical of the rural sites, which could be due to dilution related to the large sampled runoff volumes associated with the bridge. The urban Smith Creek bridge site had the highest observed phthalate concentrations. The laboratory results for all analytes are presented for all runoff samples at each bridge deck site in table A5 of the appendix.

Beyond those generalities, the Big Ivy Creek site had somewhat elevated concentrations of many POCs where concentrations of aluminum, iron, manganese, nickel, total suspended solids, total phosphorus, and all SVOCs were higher compared to all of the other rural sites. The area around the Big Ivy Creek site experienced multiple disturbances before and during the period of this study. A building completely burned within 100 ft of the bridge deck surface some time before the beginning of the study. Paint chips and charred debris from this building were often noticed in the



Site classification and constituent

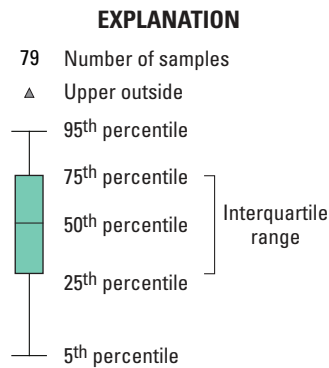


Figure 12. Concentrations of metals in rural and urban bridge deck runoff samples.

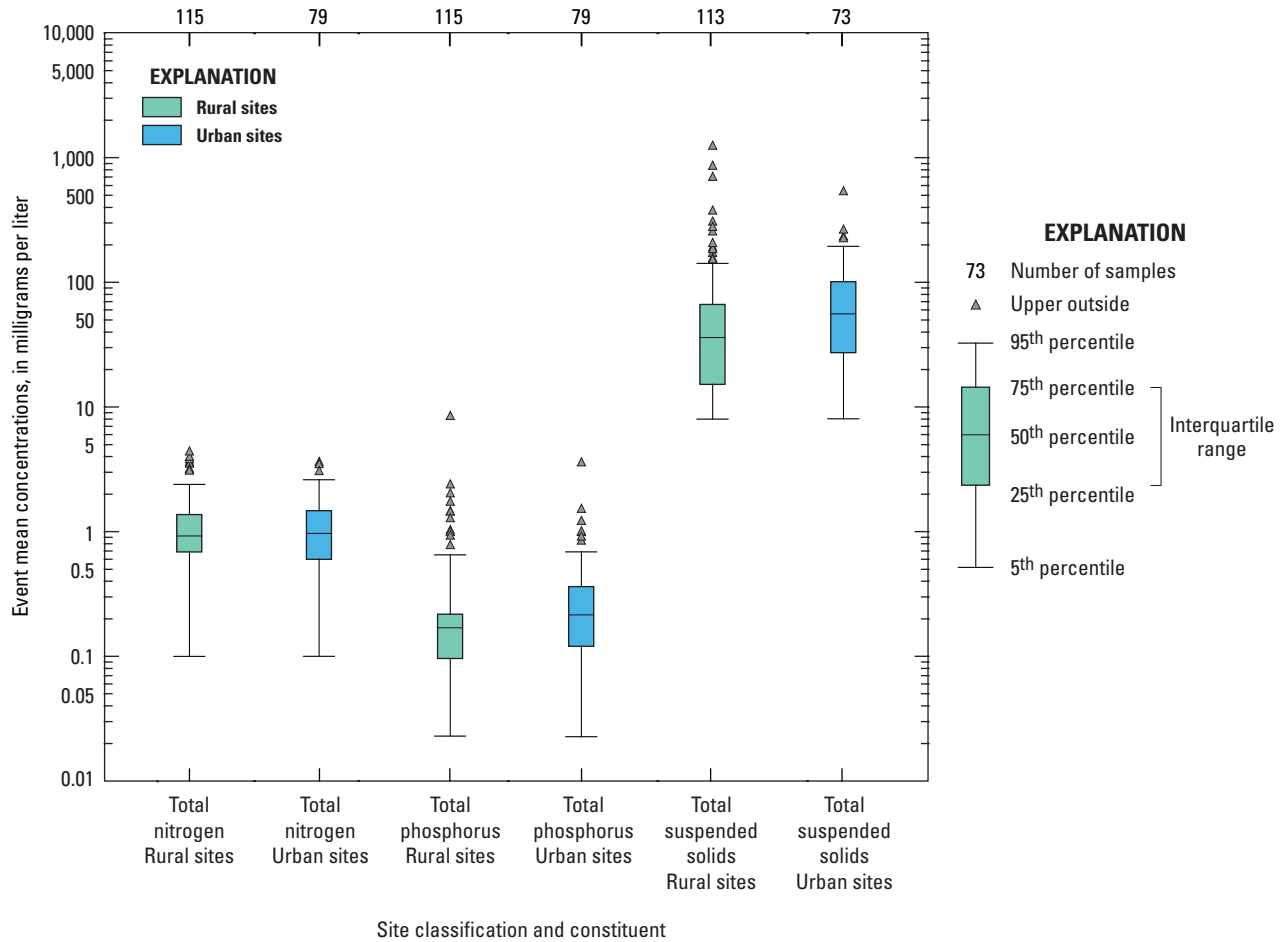


Figure 13. Concentrations of nutrients and total suspended solids in rural and urban bridge deck runoff samples.

Table 18. Summary of statistical comparisons of bridge deck runoff concentrations from concrete and asphalt bridges.

[The null hypothesis was that medians of each distribution were the same. Concentrations are shown in micrograms per liter, except for total phosphorus, total nitrogen, and total suspended solids, which are in milligrams per liter. <, less than]

Parameter of concern	Median concentration		p-value
	Concrete	Asphalt	
Total recoverable aluminum	1,385	557	<0.001
Total recoverable arsenic	1.09	1.04	0.322
Dissolved cadmium	0.026	0.023	0.571
Dissolved copper	2.84	2.23	0.003
Total recoverable iron	2,395	824.5	<0.001
Dissolved lead	0.081	0.11	0.021
Total recoverable manganese	70.1	37.95	<0.001
Total recoverable mercury	0.008	0.009	0.151
Total recoverable nickel	3.39	1.895	<0.001
Dissolved zinc	13.5	16.95	<0.001
Total phosphorus	0.198	0.168	0.048
Total nitrogen	0.92	1.05	0.236
Total suspended solids	65.5	46	<0.001

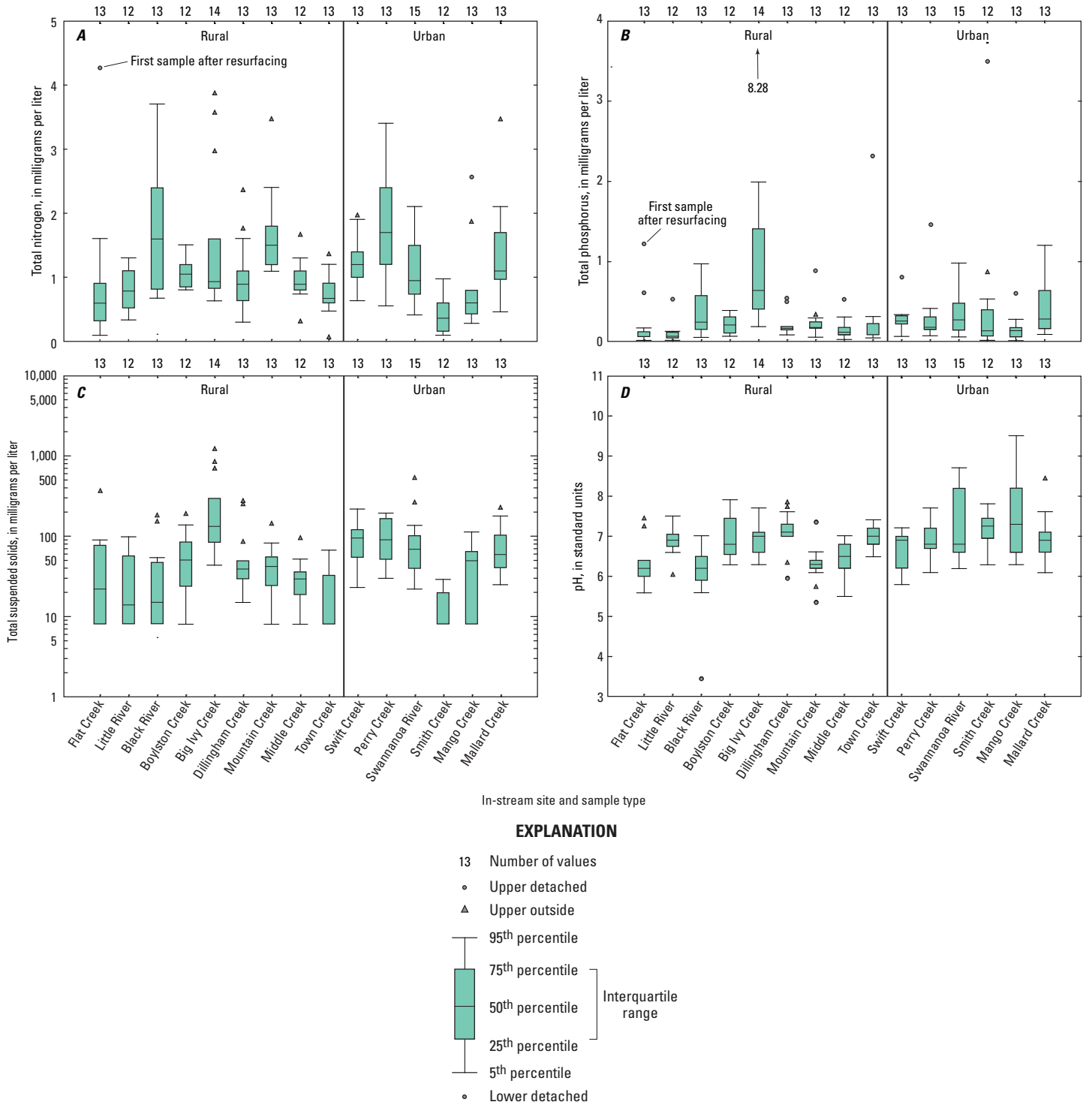
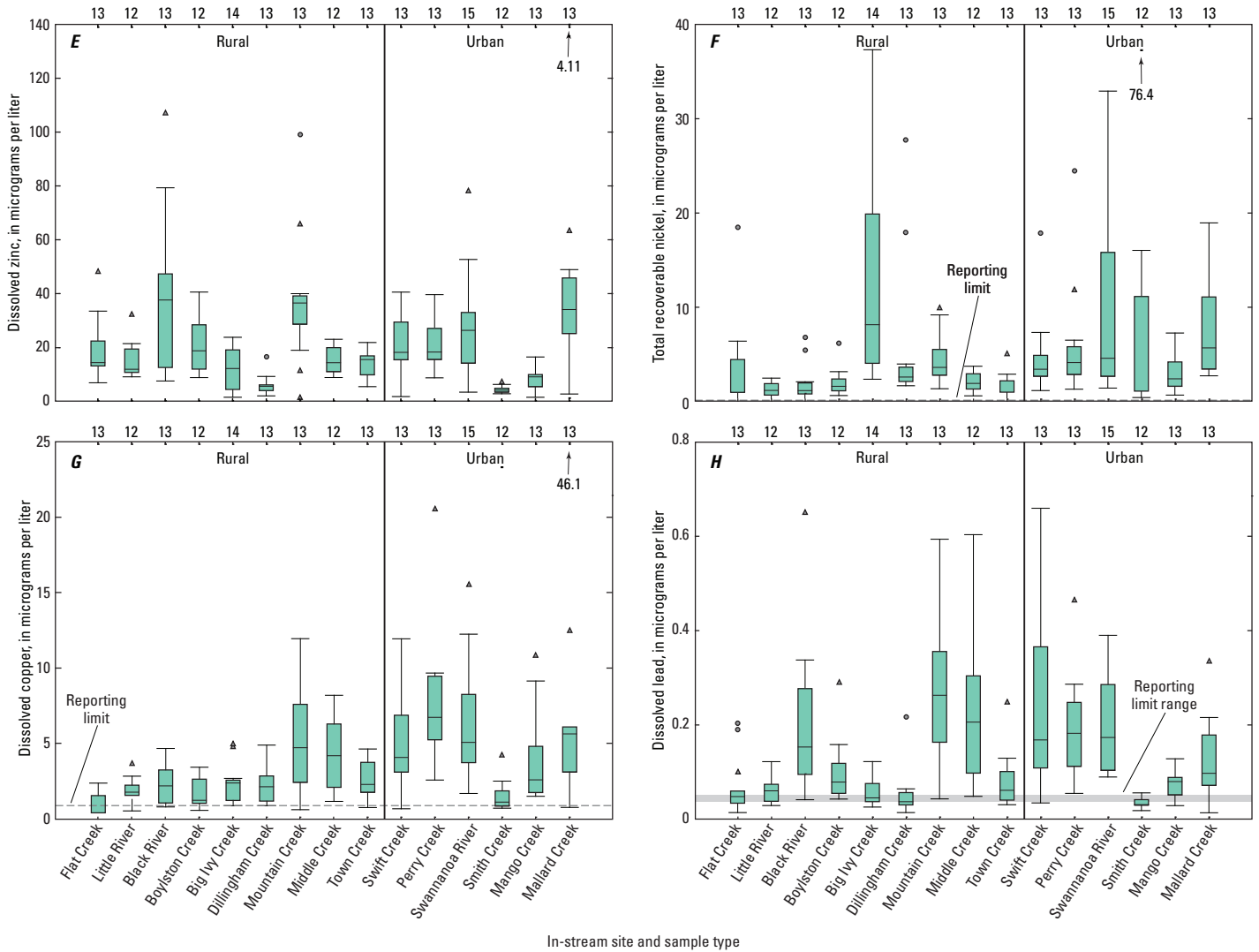


Figure 14A–D. Concentrations of (A) total nitrogen, (B) total phosphorus, (C) total suspended solids, and (D) pH in bridge deck runoff samples arranged in order of increasing annual average daily traffic. Censored data were plotted using a value of one-half of the respective long-term method detection limit.



In-stream site and sample type

EXPLANATION

- 13 Number of values
 - Upper detached
 - ▲ Upper outside
 - 95th percentile
 - 75th percentile
 - 50th percentile
 - 25th percentile
 - 5th percentile
 - ▲ Lower outside
- } Interquartile range

Figure 14E–H. Concentrations of (E) dissolved zinc, (F) total recoverable nickel, (G) dissolved copper, and (H) dissolved lead in bridge deck runoff samples arranged in order of increasing annual average daily traffic. Censored data were plotted using a value of one-half of the respective long-term method detection limit.

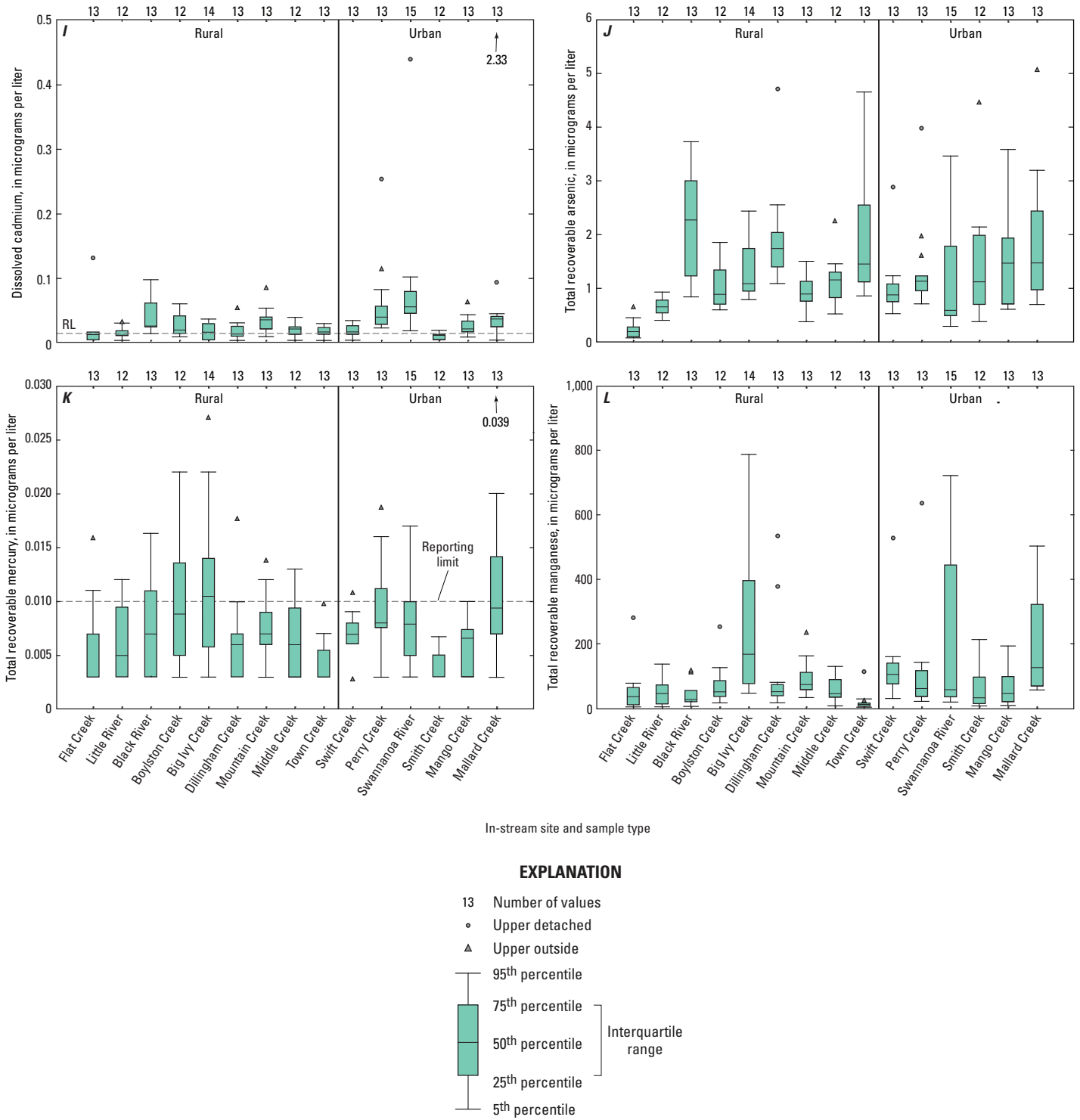


Figure 14I–L. Concentrations of (I) dissolved cadmium, (J) total recoverable arsenic, (K) total recoverable mercury, and (L) total recoverable manganese in bridge deck runoff samples arranged in order of increasing annual average daily traffic. Censored data were plotted using a value of one-half of the respective long-term method detection limit.

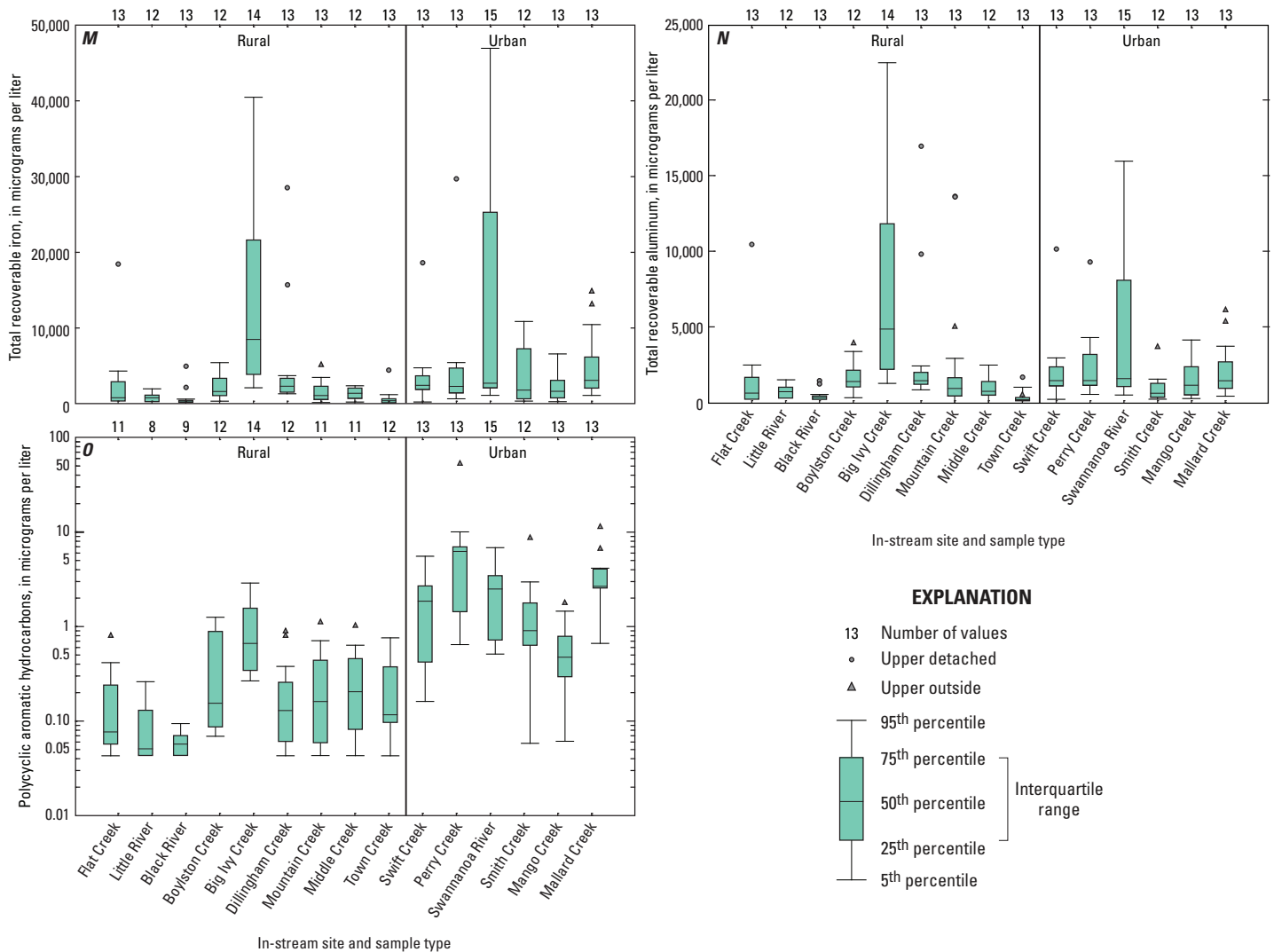


Figure 14M–O. Concentrations of (M) total recoverable iron, (N) total recoverable aluminum, and (O) polycyclic aromatic hydrocarbons in bridge deck runoff samples arranged in order of increasing annual average daily traffic. Censored data were plotted using a value of one-half of the respective long-term method detection limit.

storm drainage pipe where the autosampler was collecting runoff. Additionally, pipes were installed uphill from the bridge deck at the Big Ivy Creek site over the course of the study. Critically, sediment from this operation washed onto the bridge deck and was found in the storm drainage pipe. Thus, these types of relatively short-term site disturbances seem to have a measurable effect on measured analyte concentration in bridge deck runoff.

The AADT for the bridge deck sites was also normalized to the relative amount of pavement exposed to the vehicles by dividing the AADT by bridge width to determine if the number of lanes on a bridge had an effect on runoff concentrations for a given traffic volume. This analysis did not produce results that were any different than grouping the bridge deck sites by AADT alone or by roadway classification (rural and urban).

Summary of Bridge Deck Event Loads and Development of Predictive Equations for Runoff Loads

Bridge deck runoff loads of the POCs for sampled storm events were computed by multiplying the concentrations and total measured discharges from the bridges. A summary of the minimum and maximum event loads at the bridge deck sites is presented in table 19. Results indicate that the loads were generally highest for total nitrogen, total suspended solids, and metals, whereas loads of SVOCs were orders of magnitude lower. The bridge deck runoff loads varied considerably among events and study sites depending on rainfall and bridge characteristics.

Table 19. Summary of minimum and maximum storm event bridge deck runoff loads of parameters of concern measured at the bridge deck sites.[Loads shown in pounds. Σ , summation]

Parameters of concern	Minimum event load	Maximum event load
Total phosphorus	1.0E-4	7.0E-1
Total nitrogen	8.1E-4	5.9E-1
Total recoverable aluminum	2.3E-4	5.5E+0
Total recoverable arsenic	0	1.4E-3
Dissolved cadmium	0	7.2E-5
Dissolved copper	0	3.1E-3
Total recoverable iron	2.3E-4	2.6E+1
Dissolved lead	0	1.6E-4
Total recoverable manganese	1.2E-5	4.0E-1
Total recoverable mercury	0	5.2E-6
Total recoverable nickel	1.6E-6	1.7E-2
Dissolved zinc	0	2.5E-2
Benzo[<i>a</i>]anthracene	0	1.8E-3
Benzo[<i>a</i>]pyrene	0	2.4E-3
Benzo[<i>b</i>]fluoranthene	0	4.5E-3
Benzo[<i>k</i>]fluoranthene	0	2.4E-3
Bis(2-ethylhexyl)phthalate	0	7.4E-3
Chrysene	0	3.8E-3
Indeno[1,2,3- <i>cd</i>]pyrene	0	1.5E-3
Phenanthrene	0	2.1E-3
Bis(2-chloroethyl)ether	0	1.1E-5
Dibenzo[<i>a,h</i>]anthracene	0	5.4E-5
Hexachlorobenzene	0	6.5E-7
n-Nitrosodimethylamine	0	4.8E-6
n-Nitrosodi-n-propylamine	0	1.6E-5
Pentachlorophenol	0	9.4E-5
Phenanthrene	0	2.1E-3
Σ Polycyclic aromatic hydrocarbons	0	1.9E-2
Total suspended solids	0	9.5E+1

The bridge deck runoff event loads were used as the dependent variables in a multiple linear regression analysis to develop predictive equations for bridge deck loads. The multiple linear regression analysis included the development of a calibration dataset with independent variables (rainfall characteristics, antecedent dry days, AADT, bridge drainage area, bridge deck area, mean air temperature, and bridge deck runoff) and the dependent variable of bridge deck constituent load. The calibration dataset was used to develop a bridge deck runoff load prediction equation for the POCs (table 20). The MAXR (SAS Institute, 1999) procedure was used in the selection of the constituent regression equations. The MAXR

procedure selects the one-variable regression with the highest R^2 (coefficient of determination), the two-variable equation with the highest R^2 , the three-variable equation with the highest R^2 , and so forth. The Mallows Cp statistic (Mallows, 1973) was used to determine how many variables to include in the regression along with judgment about the physical sense of the equation, review of the relative statistical significance of each variable, regression-residuals plots, and predicted versus observed constituent-load plots. The independent variables included in the predictive multiple-regression equations selected though this review varied (table 20); however, the bridge drainage area, bridge deck area, mean temperature,

Table 20. Summary of significant variables and regression coefficients used to develop the predictive equations of loads for the parameters of concern at bridges with runoff discharge data.

[AADT, annual average daily traffic volume; °F, degrees Fahrenheit; log, logarithm function; R², regression correlation coefficient]

Parameter of concern ¹	Intercept	Number of parameters in equation	Maximum pre-cipitation intensity (inches/hour)	Total precipitation (inches)	Antecedent dry days	AADT	Traffic volume during antecedent dry days	Runoff discharge pipe contributing drainage area (acres)	Bridge deck area (square feet)	Precipitation duration (hours)	Mean air temperature during sampling (°F)	Log of average precipitation intensity (inches/hour)	Log of maximum pre-cipitation intensity (inches/hour)
Total nitrogen	-2.81	7					0.13	-0.000005		-0.009			-0.13
Total phosphorus	-2.70	5		0.014						-0.007	-0.006		
Total recoverable aluminum	-1.40	4								-0.009	-0.017		
Dissolved cadmium	-7.80	5				0.000004	0.38	-0.000005					
Dissolved copper	-6.24	6					0.23	-0.000006					
Total recoverable iron	-1.16	5		-0.20							-0.018		0.76
Dissolved lead	-6.82	4					0.31	-0.000007					
Total recoverable manganese	-3.13	6		-0.15				-0.000004			-0.013		0.60
Total recoverable mercury	-7.09	5				0.000002	-2.35E-7					0.17	
Total recoverable nickel	-4.98	4								-0.011	-0.007		
Dissolved zinc	-4.28	5				0.000005		-0.000007			0.006		
Total recoverable arsenic	-5.90	2					0.24						
Bis(2-ethylhexyl) phthalate	-5.94	4					0.23	-0.000004					
Dibenzo[a,h]anthracene	-7.76	3						-0.000005					
Pentachlorophenol	-5.40	4											
Total polycyclic aromatic hydrocarbons	-6.42	4									-0.016		
Total suspended solids	-2.20	5	0.39					0.15					-0.015

Table 20. Summary of significant variables and regression coefficients used to develop the predictive equations of loads for the parameters of concern at bridges with runoff discharge data. —Continued

[AADT, annual average daily traffic volume; °F, degrees Fahrenheit; log, logarithm function; R², regression correlation coefficient]

Parameter of concern ¹	Intercept	Number of parameters in equation	Log of total precipitation (inches)	Log of AADT	Log of traffic volume during antecedent dry days	Log of runoff charge pipe drainage area (acres)	Log of bridge deck area (square feet)	Log of wet-weather period (hours)	Log of precipitation duration (hours)	Log of total runoff (gallons)	Log of maximum runoff discharge (gallons/minute)	R ²
Total nitrogen	-2.81	7			0.12			0.10		0.95		0.85
Total phosphorus	-2.70	5								0.89	0.21	0.69
Total recoverable aluminum	-1.40	4								0.85	0.39	0.68
Dissolved cadmium	-7.80	5	-0.32							1.02		0.83
Dissolved copper	-6.24	6	-0.43	0.31				0.16		0.98		0.86
Total recoverable iron	-1.16	5		0.22						0.96		0.68
Dissolved lead	-6.82	4		0.22						0.90		0.79
Total recoverable manganese	-3.13	6		0.23						1.00		0.72
Total recoverable mercury	-7.09	5						0.11		0.91		0.92
Total recoverable nickel	-4.98	4		0.22						0.94		0.72
Dissolved zinc	-4.28	5								0.90		0.75
Total recoverable arsenic	-5.90	2		0.14		0.14				0.99		0.83
Bis(2-ethylhexyl) phthalate	-5.94	4		0.32						0.88		0.79
Dibenzo[<i>a,h</i>]anthracene	-7.76	3		0.30						1.02		0.70
Pentachlorophenol	-5.40	4		-0.18				0.36	-0.52	1.02		0.70
Total polycyclic aromatic hydrocarbons	-6.42	4		1.00			-0.40			0.84		0.72
Total suspended solids	-2.20	5			0.08					0.70		0.75

¹ All individual constituent loads were log-transformed to develop the presented variables and regression coefficients.

and log AADT were frequently included, and log total runoff was always included in the selected models. The individual constituent loads were log-transformed to develop the equations presented in table 20. These models explained at least 68 percent of the variance in constituent loads, with R^2 values ranging from 0.68 to 0.92.

Regression equations were also developed from the calibration dataset with the total runoff variables excluded to provide models that could be used to predict bridge deck loads from only ancillary variables and rainfall characteristics (useful for sites that do not have measured runoff volume). The independent variables used in these non-flow predictive multiple-regression equations also varied (table 21); however, mean temperature, log total precipitation, and log bridge drainage area were frequently included. The individual constituent loads were also log-transformed to develop the equations presented in table 21. The R^2 values for these equations were lower than those for the regression equations incorporating total runoff volume, ranging from 0.12 to 0.70. However, all but one model (pentachlorophenol) explained at least 50 percent of the variance in the constituent loads.

The total study period load was derived for each POC using the associated multiple linear regression equations presented in tables 20 and 21. A period of record prediction dataset was developed for the study sites that included ancillary variables and the most complete set of bridge deck discharge data available for each site. The prediction dataset included storm events with at least 0.10 in. of rainfall. The equations, including bridge deck discharge, were used to predict constituent loads for the storm periods with flow data, and the non-flow equations were used to predict constituent loads for storm periods when flow was not measured. These loads were then summed for the entire period of record to predict the total period loads (discussed in the next section that compares bridge deck runoff and stream routine and storm constituent concentrations and loads). Because the regression equations produce a log-transformed load prediction, the final reported loads need to be transformed into linear units. The bias generated in the estimated load when the load is transformed from log to linear units was corrected using the minimum variance Duan's Smearing unbiased estimator correction (Duan, 1983; Gilroy and others, 1990).

Stream (Routine and Storms)

The subsequent sections summarize streamflow and water-quality analyses at the four stream monitoring sites, which were monitored during both routine (base-flow) and storm conditions. The information will complete the framework necessary to put the bridge deck runoff concentrations and loads in context of the water-quality potential effects on receiving streams in North Carolina.

Discharge

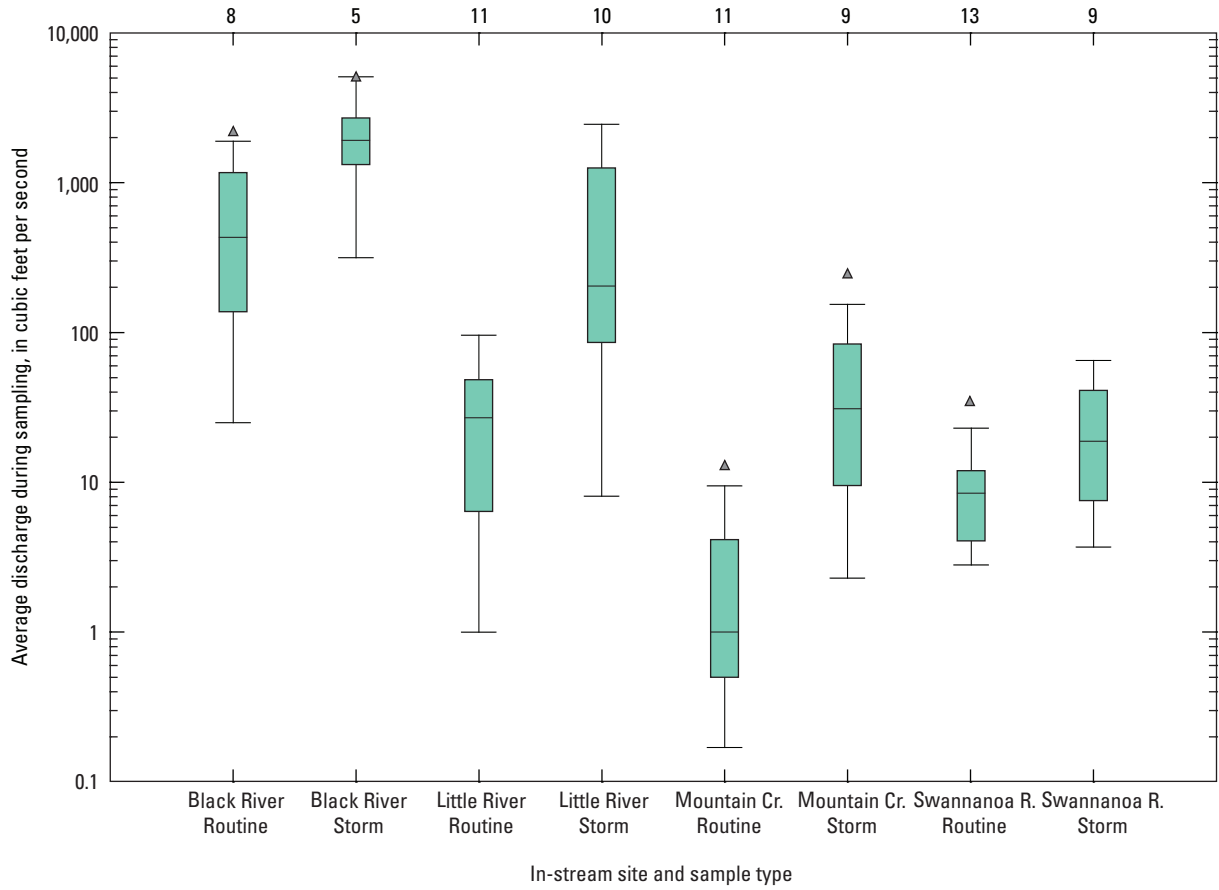
As previously mentioned, discharge was recorded at the four in-stream sites at 15-minute intervals throughout the study period. A summary of the recorded streamflow for the water-quality samples collected at the stream sites is shown in figure 15. Streamflows were generally an order of magnitude higher during storm sampling than during routine sampling events at three of the four sites. The magnitude of the difference was not as pronounced at the Swannanoa River site, which had the smallest drainage area. The sites are arranged on the x-axis by order of decreasing drainage area. Streamflow and start and end times for all stream water-quality samples are presented in table A6 of the appendix. The discharge value associated with the stream samples is the average of the 15-minute values corresponding to the period when the samples were collected either manually or by the autosampler.

Table 21. Summary of significant variables and regression coefficients used to develop the predictive equations of loads for the parameters of concern at bridges without runoff discharge data.

[°F, degrees Fahrenheit; AADT, annual average daily traffic volume; log, logarithm function; R², regression correlation coefficient]

Parameter of concern ¹	Intercept	Number of parameters in equation	Traffic volume during antecedent dry days	Bridge deck area (square feet)	Wet weather period (hours)	Mean air temperature during sampling (°F)	Log of average precipitation intensity (inches/hour)	Log of maximum precipitation intensity (inches/hour)	Log of total precipitation (inches)	Log of AADT	Log of traffic volume during antecedent dry days	Log of runoff discharge pipe drainage area (acres)	Log of precipitation duration (hours)	Log of mean air temperature during sampling (°F)	R ²
Total nitrogen	1.85	5	-0.000004			-0.008			0.66	0.14	0.87				0.65
Total phosphorus	0.76	4				-0.008			0.82	0.18	0.60				0.50
Total recoverable aluminum	4.24	3				-0.026	1.09				1.11				0.58
Total recoverable arsenic	-0.97	2						0.87			1.03				0.62
Dissolved cadmium	-2.68	5		0.005		-0.009		0.51		0.11	0.89				0.65
Dissolved copper	-1.56	3						0.49		0.10	0.92				0.63
Total recoverable iron	4.58	3				-0.027	1.21				1.22				0.57
Dissolved lead	-2.39	4	-0.000007					0.76		0.17	1.17				0.62
Total recoverable manganese	2.74	3				-0.023	1.14				1.02				0.55
Total recoverable mercury	-2.58	4				-0.007	0.90				0.86	0.72			0.70
Total recoverable nickel	-0.06	4				-0.019	0.87			0.26	0.75				0.58
Dissolved zinc	0.19	4	4.60E-07	-0.000005				0.72			1.00				0.54
Bis(2-ethylhexyl) phthalate	-1.49	4				-0.010		0.72		0.32	0.78				0.68
Dibenzo[a,h]anthracene	5.97	3					0.54				0.72			-4.48	0.56
Pentachlorophenol	-2.27	1						0.63							0.12
Total polycyclic aromatic hydrocarbons	-4.56	3				-0.023		0.71	1.06						0.66
Total suspended solids	1.15	4				-0.017		0.78		0.10	0.68				0.66

¹ All individual constituent loads were log-transformed to develop the presented variables and regression coefficients.



EXPLANATION

- 11 Number of samples
 - ▲ Upper outside
 - 95th percentile
 - 75th percentile
 - 50th percentile
 - 25th percentile
 - 5th percentile
- } Interquartile range

Figure 15. Summary of average measured stream discharge during routine and storm water-quality sampling at the four stream study sites with both routine and storm sampling.

Water Quality

As might be expected, the routine (base-flow) water type in terms of major cations and anions at the four stream sites was balanced and less variable than that for the bridge deck runoff (fig. 16). Cations plotted near the center of the triangular diagram were present in roughly equal concentrations. Anions had a wide range in carbonate + bicarbonate and chloride/fluoride/nitrite + nitrate and a smaller range in sulfate. The water type thus could be described generally as mixed with somewhat lower sodium + potassium. The storm sample water types were more tightly grouped and extensively overlapped by the routine sample types. The main difference was the presence of two outliers (both at the Swannanoa site), which were enriched in sodium + potassium and chloride/fluoride/nitrite + nitrate that likely represented road salting in winter as for the deck runoff. Additionally, though the cation suites were generally similar among the three ecoregions, the anion suites changed from chloride/fluoride/nitrite + nitrate dominated to carbonate + bicarbonate moving eastward from the Blue Ridge Mountains to the Coastal Plain.

In contrast to deck runoff, total recoverable nutrient and metal POCs were relatively well correlated with suspended-sediment concentration (table 22). This result was consistent with dominance of a mineral source for recoverable aluminum, iron, and manganese. Additionally, the relatively high correlation between suspended-sediment concentration and nickel and arsenic was consistent with these POCs being predominantly sorbed to particles once in the stream. Concentrations of inorganic POCs in all water-quality samples collected at stream sites is presented in table A7 of the appendix.

Table 22. Correlation of total nutrient and total recoverable metal parameters of concern to suspended-sediment concentrations in stream samples.

[R² is regressional correlation coefficient]

Parameter of concern	R ²
Total phosphorus	0.860
Ammonia plus organic nitrogen	0.723
Aluminum	0.817
Iron	0.797
Manganese	0.790
Nickel	0.665
Arsenic	0.593

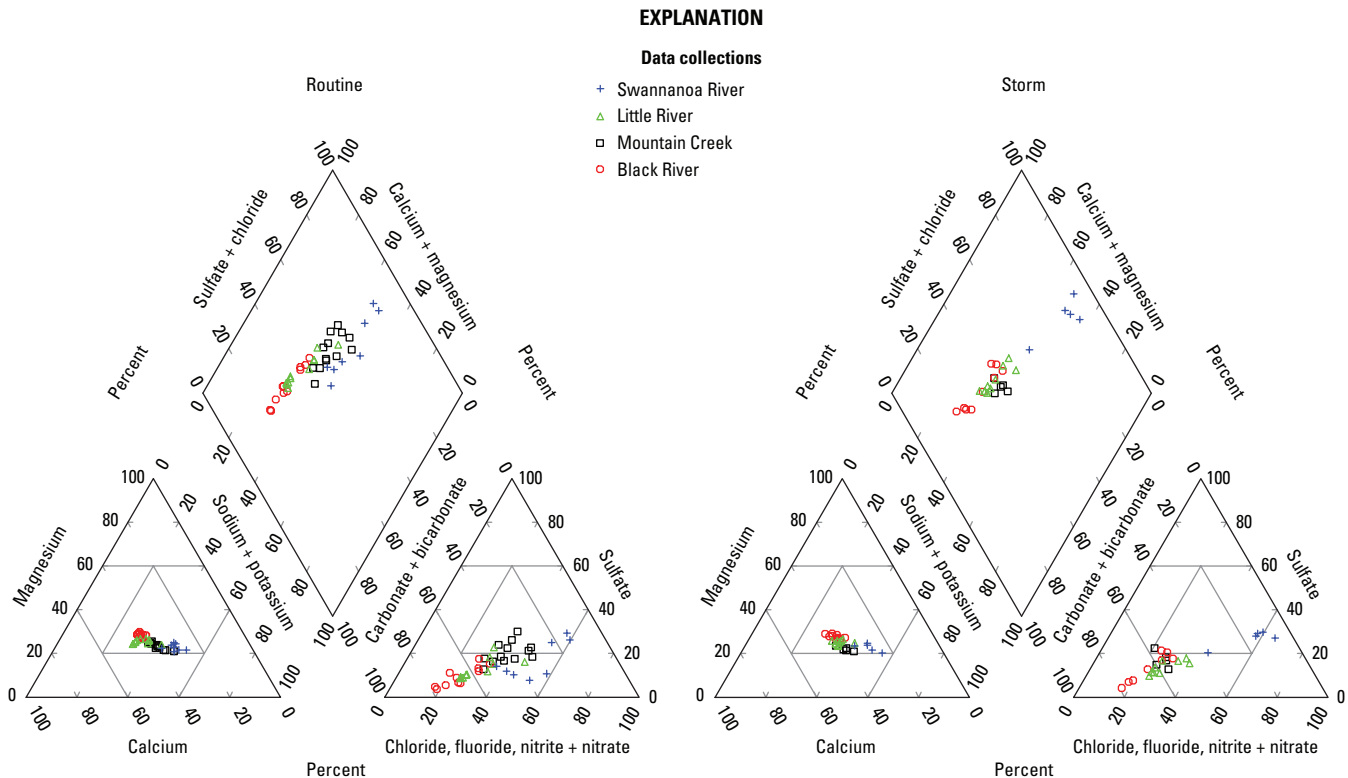


Figure 16. Piper diagrams of general water types during routine (non-storm) and storm sampling events at stream sampling sites.

Only 9 of the 14 SVOCs identified as parameters of concern in bridge deck runoff samples (table 16), were detected in streamwater samples (table 23). Similar to the bridge deck runoff results, stream detections were dominated by pyrogenic PAHs. Overall, there were considerably less detections of SVOCs identified as POCs in the streams during both routine and storm conditions than in bridge deck runoff. The SVOCs were detected in only 2 percent of the routine stream samples and were dominated by pyrogenic PAHs as was the case for deck runoff. The SVOCs were detected more frequently in storm samples than in routine samples though

the suite of compounds was similar. Concentrations of SVOCs identified as POCs in all water-quality samples collected at the stream sites are presented in table A7 of the appendix.

The POC concentrations for all samples collected at the stream sites were grouped by season to determine if a significant relation between concentrations and season existed (table 24). Unlike the results for the bridge decks, values did not vary much between seasons nor was there a season(s) with consistently higher or lower concentrations than other seasons. Therefore, the source of these POCs to the streams did not appear to have a strong seasonal component.

Table 23. Detections of semivolatile organic compounds (SVOCs) as parameters of concern (POCs) in stream samples.

[PAH, polycyclic aromatic hydrocarbon]

Parameter of concern	Chemical class	Routine samples			Storm samples		
		Number of detections	Percent of total detections	Frequency of detection	Number of detections	Percent of total detections	Frequency of detection
Phenanthrene	PAH (pyrogenic)	2	20	0.3	12	19	2.6
Benzo[<i>b</i>]fluoranthene	PAH (pyrogenic)	1	10	0.2	9	15	1.9
Chrysene	PAH (pyrogenic)	1	10	0.2	9	15	1.9
Benzo[<i>a</i>]pyrene	PAH (pyrogenic)	1	10	0.2	8	13	1.7
Benzo[<i>k</i>]fluoranthene	PAH (pyrogenic)	1	10	0.2	8	13	1.7
Indeno[1,2,3- <i>cd</i>]pyrene	PAH (pyrogenic)	1	10	0.2	7	11	1.5
Benzo[<i>a</i>]anthracene	PAH (pyrogenic)	1	10	0.2	4	6.5	0.9
Pentachlorophenol	Phenol	1	10	0.2	3	4.8	0.6
Bis(2-ethylhexyl)phthalate	Phthalate	1	10	0.2	2	3.2	0.4
Hexachlorobenzene	Chloroaromatic	0	0	0	0	0	0
Bis(2-chloroethyl)ether	Chloro ether	0	0	0	0	0	0
Dibenzo[<i>a,h</i>]anthracene	PAH (pyrogenic)	0	0	0	0	0	0
n-Nitrosodimethylamine	Nitrosoamine	0	0	0	0	0	0
n-Nitrosodi-n-propylamine	Nitrosoamine	0	0	0	0	0	0
Total detections of POCs for SVOCs		10			62		
Total analyses of POCs for SVOCs		602			462		
Percent detections of POC analyses for SVOCs		2			13		

Table 24. Median concentrations for stream samples grouped by season.

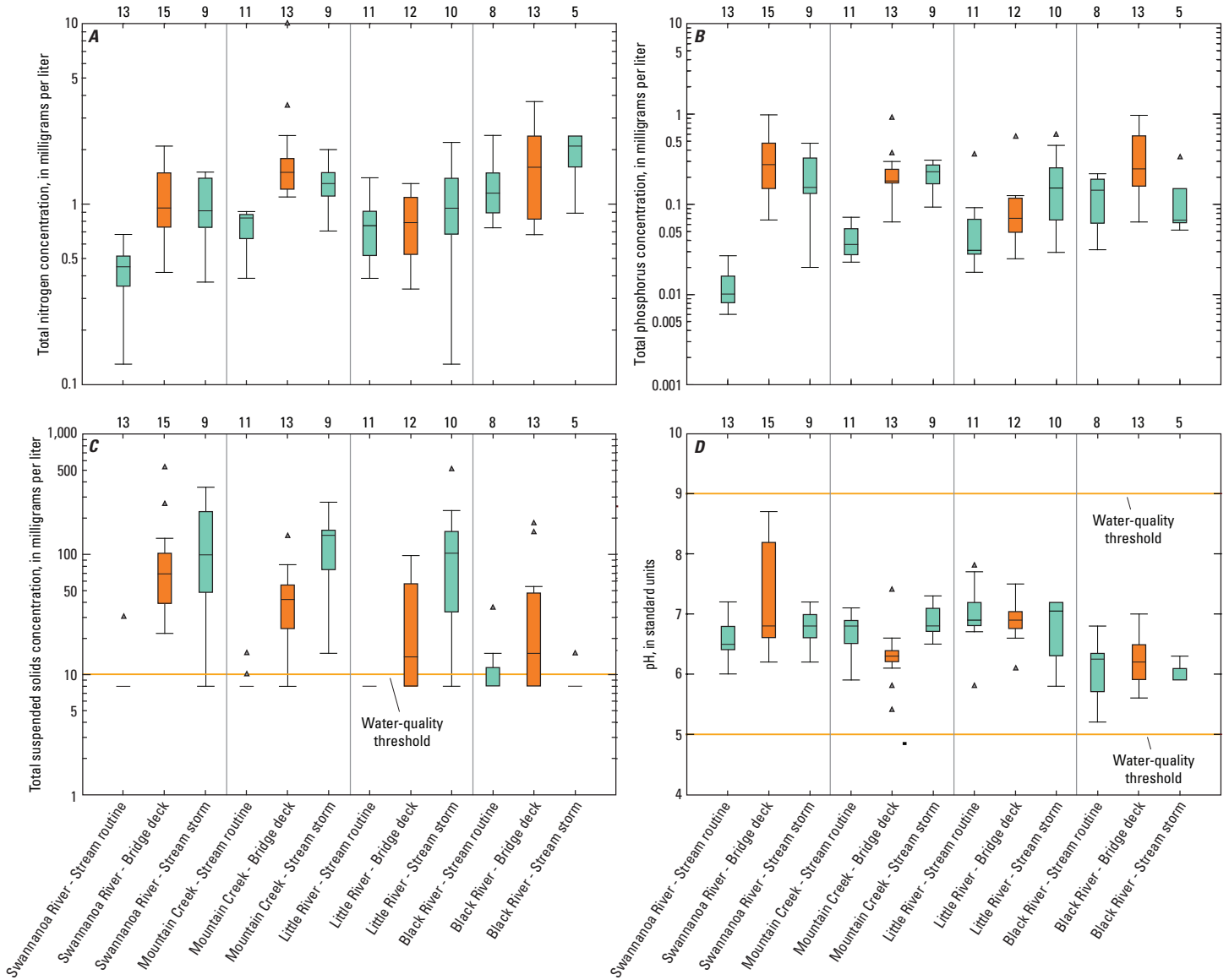
[Concentrations shown in micrograms per liter, except for total phosphorus and total nitrogen which are in milligrams per liter. ---, no statistics computed—less than eight laboratory detections]

Parameter of concern	Stream samples ¹			
	Spring	Summer	Fall	Winter
pH (units)	6.8	6.8	6.6	6.3
Total phosphorus	0.07	0.07	0.07	0.05
Total nitrogen	0.85	0.84	0.78	0.92
Total recoverable aluminum	352	222	251	236
Total recoverable arsenic	0.53	0.75	0.51	0.41
Dissolved cadmium	0.02	0.01	0.01	0.01
Dissolved copper	0.58	0.84	0.65	0.85
Total recoverable iron	1,510	1,370	870	620
Dissolved lead	0.14	0.16	0.15	0.12
Total recoverable manganese	182	103	114	81
Total recoverable mercury	---	---	---	---
Total recoverable nickel	0.51	0.54	0.59	0.56
Dissolved zinc	2.61	1.90	2.12	3.28
Total suspended solids	---	---	---	---

¹ Concentrations less than the reporting limit were replaced with the long-term method detection limit for the purpose of median calculations. For parameters with greater than 5-percent censored data, medians were computed using the rank method as described in Bonn (2008).

Concentrations of total nitrogen were generally higher in storm samples at all four sites, and total phosphorus concentrations were higher in storm samples at three of the four sites (fig. 17A,B), likely reflecting increased input of particle-associated nitrogen and phosphorus during storms. This result was consistent with stormwater input having had a lower dissolved inorganic nitrogen content. Other POCs, including total suspended solids and pH, showed no obvious pattern between base-flow and storm conditions (fig. 17C,D).

Many stream metal concentrations (zinc, nickel, copper, lead, cadmium, arsenic, mercury, manganese, iron, and aluminum) were elevated during storms at most sites (fig. 17E–N). This group included most of the dissolved and some of the total recoverable analytes. Finally, no box plots were shown for SVOCs as POCs because detections were extremely infrequent in the stream samples. Laboratory results for all analytes are presented for water-quality samples collected at the stream sites in table A7 of the appendix.



EXPLANATION

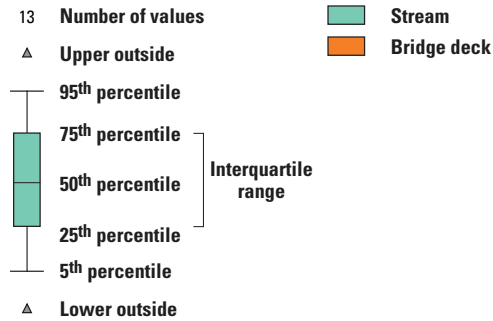


Figure 17A–D. Concentrations of (A) total nitrogen, (B) total phosphorus, (C) total suspended solids, and (D) pH for stream routine, bridge deck runoff, and stream storm samples for the four stream sampling sites.

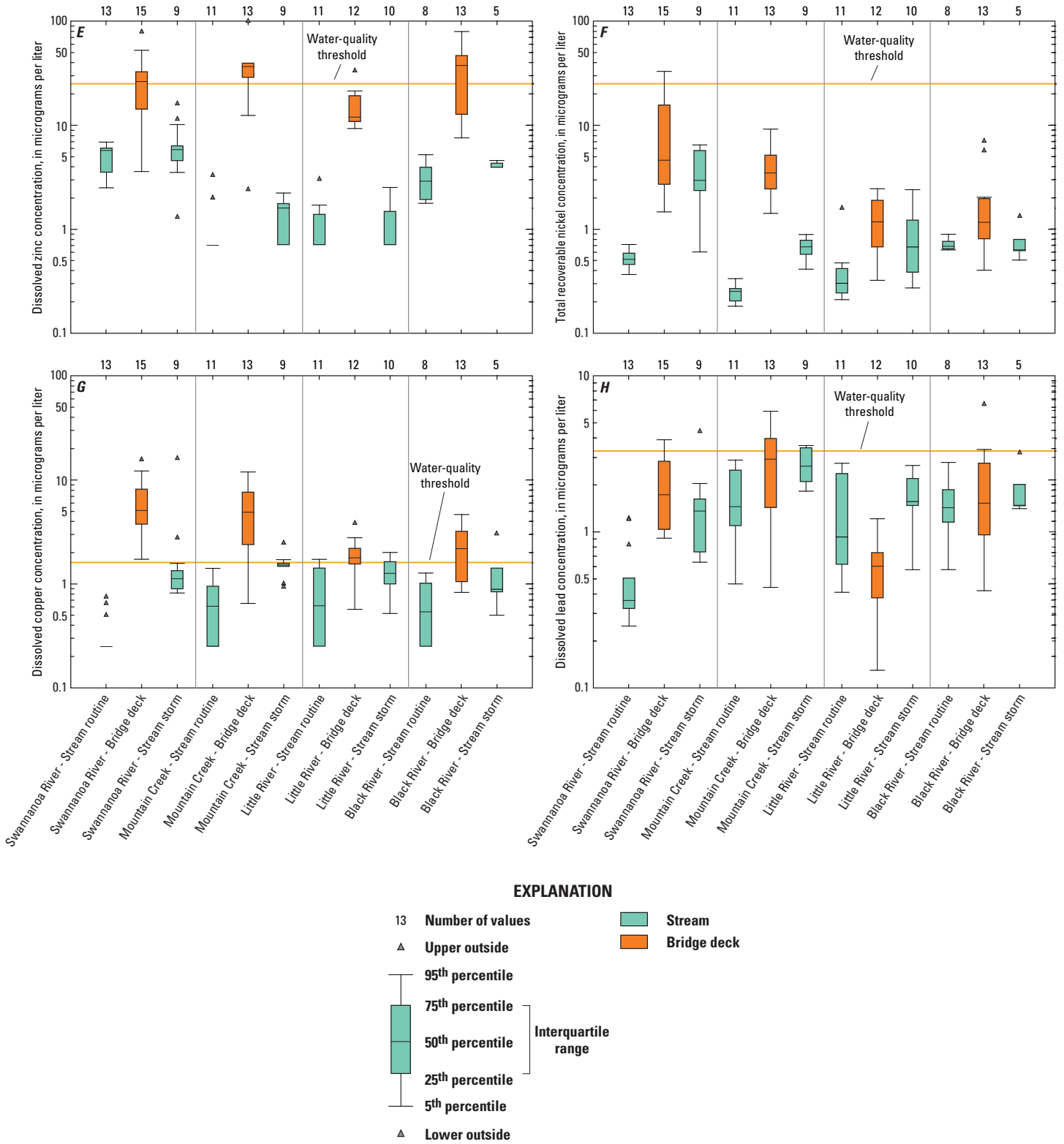


Figure 17E–H. Concentrations of (E) dissolved zinc, (F) total recoverable nickel, (G) dissolved copper, and (H) dissolved lead for stream routine, bridge deck runoff, and stream storm samples for the four stream sampling sites.

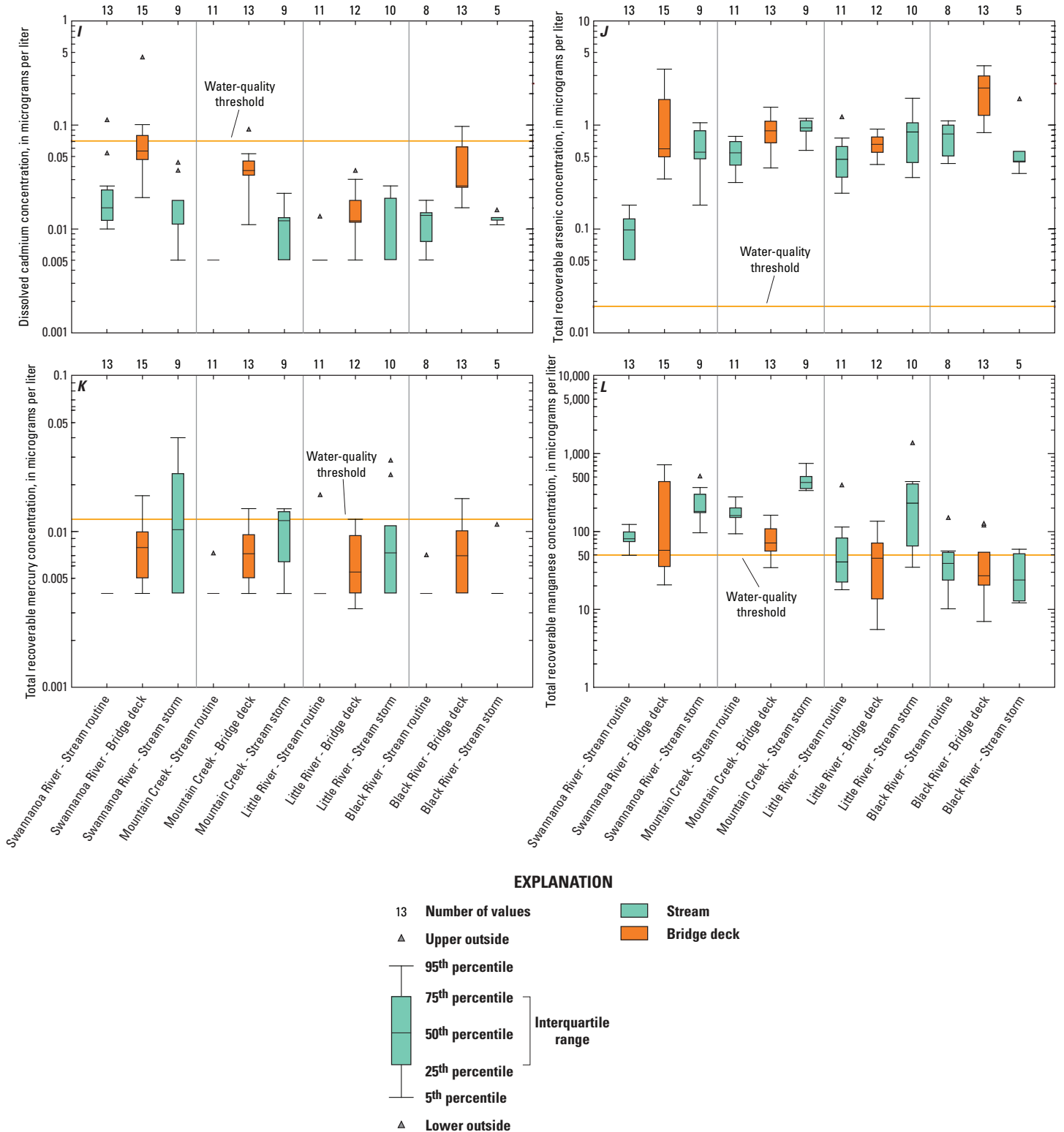


Figure 17I–L. Concentrations of (I) dissolved cadmium, (J) total recoverable arsenic, (K) total recoverable mercury, and (L) total recoverable manganese for stream routine, bridge deck runoff, and stream storm samples for the four stream sampling sites.

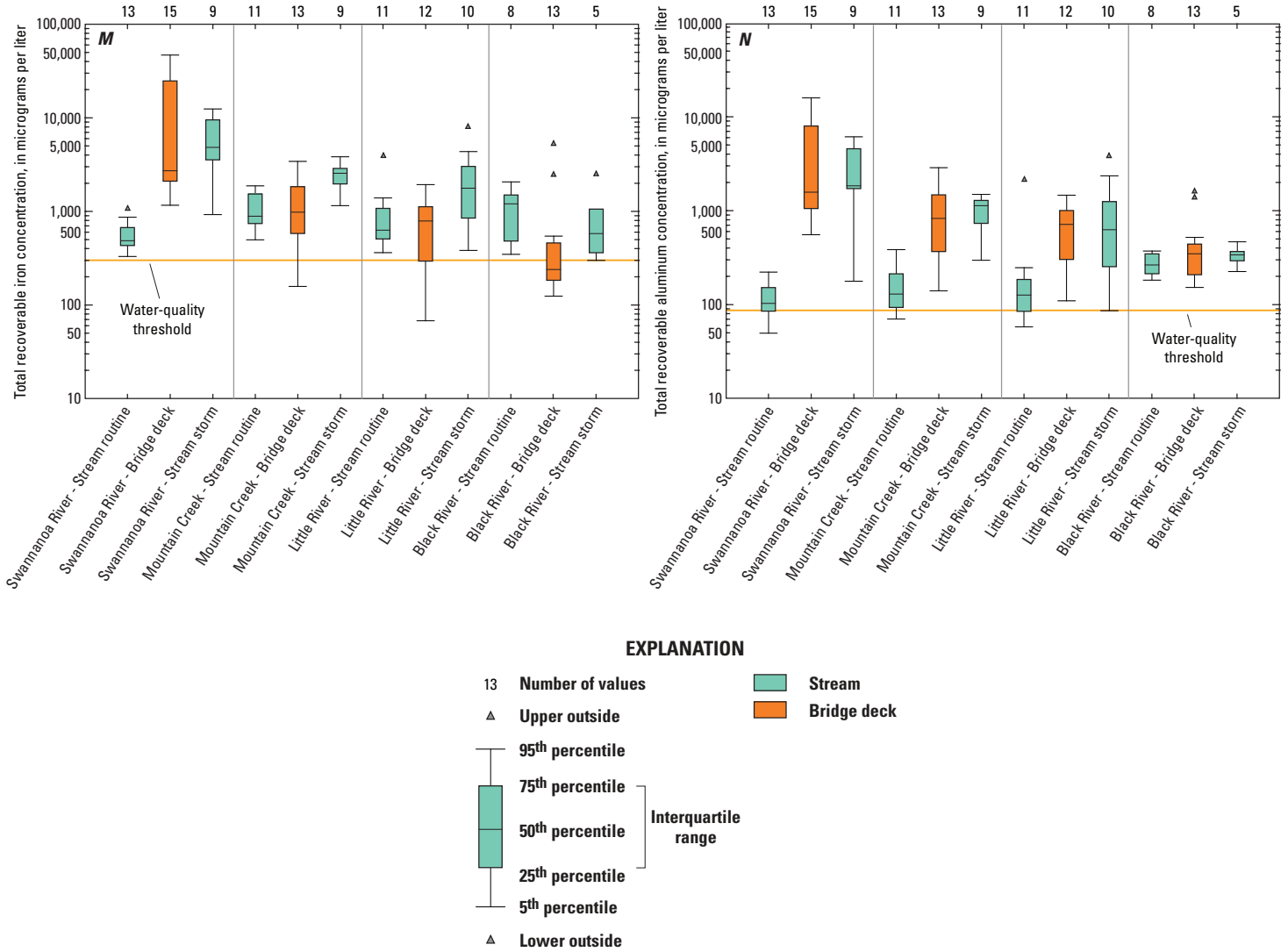


Figure 17M–N. Concentrations of (M) total recoverable iron and (N) total recoverable aluminum for stream routine, bridge deck runoff, and stream storm samples for the four stream sampling sites.

Comparisons of Bridge Deck Stormwater Runoff and Stream Water Quality

The effects of bridge deck runoff are evaluated herein by (1) comparing constituent concentrations, loads, and yields (load per acre of drainage area) in the bridge deck stormwater from the 15 monitored bridges and receiving streams at the four stream monitoring sites and (2) estimating the rate of dilution of bridge deck runoff downstream from the discharge point for the four stream monitoring sites to identify the zone of maximum effect and the relative reduction of concentration due to dilution. The four stream sites cannot represent all the stream (or bridge) settings in North Carolina. However, the sites do represent unimpaired freshwater streams in relatively non-urbanized watersheds in the three major ecoregions, which

provide reasonable potential for bridge effects to be observed, and therefore, conservative comparisons can be made.

Distribution of Concentrations from Bridge Deck Runoff

The distribution of concentrations from the bridge deck runoff at the four stream monitoring sites was compared to the corresponding distributions of stream routine and storm sample concentrations using the nonparametric Mann-Whitney test (Mann and Whitney, 1947) and a 95-percent confidence level. Results of the statistical testing (table 25) and comparisons of the bridge deck runoff and stream concentrations (fig. 17) indicate that the bridge deck runoff concentrations were only statistically higher than the corresponding stream

Table 25. Summary of p-values derived from statistical comparisons between bridge deck runoff concentrations and stream routine and storm samples at the stream monitoring sites.

[The null hypothesis was that medians of each distribution were the same. Only five storm samples were collected from Black River (statistical analyses still made for reference if all values are detections). <, less than; TR, total recoverable; ---, no statistics—less than eight laboratory detections]

Parameter of concern	Stream sample type	p-values for comparison with bridge deck runoff samples ^{1,2}			
		Stream monitoring sites			
		Swannanoa River	Mountain Creek	Little River	Black River
Total nitrogen	Routine	<0.001	<0.001	0.667	0.293
	Storm	0.928	0.364	0.254	0.656
Total phosphorus	Routine	<0.001	<0.001	0.049	0.021
	Storm	0.27	0.664	0.129	0.043
TR aluminum	Routine	<0.001	<0.001	0.003	0.365
	Storm	0.81	0.72	0.58	0.961
TR arsenic	Routine	---	<0.001	0.07	0.001
	Storm	0.42	0.62	0.42	0.007
Dissolved cadmium	Routine	<0.001	---	---	---
	Storm	<0.001	---	---	---
Dissolved copper	Routine	---	---	0.002	---
	Storm	<0.001	0.004	0.075	0.115
TR iron	Routine	<0.001	0.950	0.580	0.030
	Storm	0.53	0.014	0.020	0.127
Dissolved lead	Routine	<0.001	<0.001	0.009	1.0
	Storm	0.128	1.0	<0.001	0.657
TR manganese	Routine	0.189	<0.001	0.356	0.491
	Storm	0.056	<0.001	0.006	0.657
TR mercury	Routine	---	---	---	---
	Storm	---	0.174	---	---
TR nickel	Routine	<0.001	<0.001	0.001	0.06
	Storm	0.222	<0.001	0.242	0.218
Dissolved zinc	Routine	<0.001	---	---	<0.001
	Storm	0.002	---	---	0.001
Total suspended solids	Routine	---	---	---	---
	Storm	0.550	0.012	---	---

¹ Red shaded cell indicates bridge deck runoff median concentration is statistically higher than the corresponding median stream concentration at the 95% confidence level.

² Blue shaded cell indicates median stream concentration is statistically higher than the corresponding bridge deck runoff median concentration at the 95% confidence level.

(routine and storm) concentrations for 36 percent of the comparisons. PAHs were not included in the analyses because of an insufficient number of detections in the stream samples. The bridge deck runoff concentrations of the POCs, except for three metals, were similar to those measured in the receiving streams at the four stream sampling sites. Dissolved copper and zinc and total recoverable nickel concentrations were consistently higher in bridge deck runoff.

To further evaluate the potential effects of bridge deck runoff on receiving streams, median concentrations of POCs in the bridge deck runoff at the 15 sites were compared to the median stream concentrations in table 26. The median bridge deck runoff concentrations of the POCs at the 15 bridge deck runoff sites were similar to those measured in the receiving streams at the 4 stream sampling sites. The exceptions were dissolved copper and zinc, total recoverable nickel, and PAHs (which were not plotted because of an insufficient number of detections in the stream samples). However, even for copper, zinc, and nickel, there are instances where the maximum median stream concentration exceeded the median concentration at some of the bridge deck runoff sites.

Annual Loads and Yields of Bridge Deck Runoff

The computed sampling period loads and yields from the 15 bridge deck runoff sites were compared to the computed stream loads and yields at the 4 stream sampling sites. The periods for comparison of bridge deck runoff and stream loads is April 1, 2009, to March 31, 2010, for the Swannanoa River and Black River sites and May 1, 2009, through March 31, 2010, for the Mountain Creek and Little River sites. The period over which the bridge deck runoff total loads are computed for all other sites is given in table 27. With few exceptions, median bridge deck runoff loads of all POCs were lower (and generally orders of magnitude lower) than the stream loads at the monitoring sites (table 27). These results are not surprising, given the similarity between the concentrations (fig. 17; tables 25 and 26) coupled with large differences in contributing drainage areas. The inverse was true for total yields of the POCs in pounds per acre of drainage area. The bridge deck runoff yields were generally higher than the yields from the four stream sites for most of the POCs (table 27). The bridge deck runoff yields data can be used to estimate loads at other bridges with similar characteristics and to estimate the contributing total load from all highways in a watershed. The effect of bridge deck runoff loads on receiving waters should also be evaluated in light of the bioassays, which only showed potential ecological effects for one bridge deck runoff sample (collected in the winter), and benthic macroinvertebrate survey results, which revealed no significant difference upstream and downstream from the study bridge sites. The full bioassay and benthic macroinvertebrate survey results are presented in URS Corporation, 2010.

Table 26. Comparison of stream and bridge deck runoff parameters of concern concentrations.

[Concentrations shown in micrograms per liter, except for total phosphorus, total nitrogen, and total suspended solids, which are in milligrams per liter. Only five samples were collected for Black River (median concentrations are still reported for reference if all values are detections). TR, total recoverable; PAHs, polycyclic aromatic hydrocarbons; ---, less than eight laboratory detections]

Site name	pH	Total phosphorus	Total nitrogen	TR aluminum	TR arsenic	Dis-solved cadmium	Dis-solved copper	TR iron	Dis-solved lead	TR manganese	TR mercury	TR nickel	Dis-solved zinc	Total suspended solids	Total PAHs
Median concentration for bridge deck runoff samples															
Big Ivy Creek	7.0	0.64	0.9	4,880	1.1	0.02	2.4	8,485	0.04	168	---	8.1	12.2	133	0.65
Black River	6.2	0.25	1.6	348	2.3	0.03	2.2	239	0.15	27	---	1.2	37.6	15.0	0.02
Boylston Creek	6.8	0.21	1.1	1,390	0.9	0.02	1.2	1,640	0.08	51	0.009	1.6	18.8	51.0	0.13
Dillingham Creek	7.1	0.17	0.9	1,450	1.7	0.01	2.1	2,340	0.04	52	0.007	2.6	5.5	39.0	0.11
Flat Creek	6.2	0.11	0.6	630	0.2	0.02	0.3	1,080	0.05	36	0.005	1.6	14.4	22.0	0.05
Little River	6.9	0.07	0.8	713	0.7	0.01	1.8	790	0.06	45	0.005	1.2	12.0	---	0.01
Mallard Creek	6.9	0.33	1.3	1,970	1.8	0.04	5.7	3,805	0.09	162	0.010	7.1	35.0	66.5	2.66
Middle Creek	6.5	0.12	0.9	744	1.2	0.02	4.2	1,410	0.21	46	0.006	1.9	14.3	29.5	0.18
Mingo Creek	7.3	0.14	0.6	1,140	1.5	0.02	2.6	1,620	0.08	47	---	2.4	9.1	---	0.47
Mountain Creek	6.3	0.18	1.5	931	0.9	0.04	4.7	1,100	0.26	74	0.007	3.6	36.5	42.0	0.04
Perry Creek	6.8	0.18	1.7	1,460	1.1	0.04	6.7	2,280	0.18	61	0.008	4.1	18.3	118	6.24
Smith Creek	7.3	0.14	0.4	618	1.1	0.01	1.1	1,830	0.04	33	0.005	1.8	4.2	---	0.90
Swannanoa River	6.8	0.28	1.0	1,570	0.6	0.06	5.1	2,720	0.17	57	---	4.6	26.3	69.0	2.49
Swift Creek	6.9	0.26	1.2	1,450	0.9	0.02	4.1	2,440	0.17	105	0.007	3.4	18.3	95.0	1.85
Town Creek	7.0	0.12	0.7	171	1.5	0.02	2.3	406	0.06	12	0.005	1.7	15.5	---	0.09
Median concentration for in-stream samples															
Swannanoa River – Routine	6.5	0.01	0.5	103	---	0.01	---	488	0.04	80.7	---	0.5	5.7	---	---
Swannanoa River – Storm	6.8	0.15	0.9	1,840	0.55	0.02	1.1	4,840	0.14	182	---	3.0	5.8	99.0	0.397
Mountain Creek – Routine	6.8	0.04	0.8	130	0.54	---	---	888	0.15	160	---	0.2	---	---	---
Mountain Creek – Storm	6.8	0.23	1.3	1,130	0.94	---	1.5	2,560	0.26	427	0.010	0.7	---	144	---
Little River – Routine	7.0	0.03	0.8	138	0.47	---	1.4	683	0.09	37.8	---	0.3	---	---	---
Little River – Storm	6.8	0.23	1.1	1,130	0.91	---	1.4	2,315	0.18	370	---	0.9	---	103	---
Black River – Routine	6.3	0.14	1.2	263	0.82	---	---	1,200	0.14	39.0	---	0.7	2.9	---	---
Black River – Storm	6.1	0.07	2.1	339	0.45	0.01	0.9	582	0.15	23.9	---	0.6	3.9	---	---

Table 27. Comparison of stream and bridge deck runoff parameters of concern annual loads and yields.

[---, insufficient number of laboratory detections to compute a load; Σ, summation; PAHs, polycyclic aromatic hydrocarbons]

Site name	Total bridge deck runoff loads (in pounds) and yields (in pounds per acre) ¹														Total in-stream loads and yields at in-stream monitoring sites ²				
	Flat Creek	Little River	Black River	Boylston Creek	Big Ivy Creek	Dillingham Creek	Mountain Creek	Middle Creek	Town Creek	Swift Creek	Perry Creek	Swannanoa River	Smith Creek	Mango Creek	Mallard Creek	Swannanoa River	Mountain Creek	Little River	Black River
Total load reporting period	7/27/09 to 4/27/10	5/9/09 to 03/31/10	4/14/09 to 03/31/10	5/26/09 to 4/8/10	6/3/09 to 4/8/10	5/24/09 to 4/8/10	5/4/09 to 03/31/10	5/17/09 to 3/13/10	5/7/09 to 4/25/10	5/14/09 to 3/31/10	4/20/09 to 4/9/10	3/25/09 to 3/31/10	5/11/09 to 4/25/10	3/13/09 to 7/17/09; 11/3/09 to 4/24/10	5/2/09 to 4/27/10	4/1/09 to 3/31/10	5/1/09 to 3/31/10	5/1/09 to 3/31/10	4/1/09 to 3/31/10
Total nitrogen load	3.2E-01	1.9E+00	9.3E-01	2.4E+00	7.0E-01	3.3E+00	3.9E+00	1.2E+00	3.3E+00	2.0E+00	4.7E+00	1.1E+01	2.7E+00	7.3E+00	4.2E+00	1.5E+04	2.3E+04	2.0E+05	2.8E+06
Total nitrogen yield	6.4E+00	1.4E+01	8.5E+00	9.8E+00	8.7E+00	1.0E+01	1.8E+01	8.2E+00	1.8E+01	1.1E+01	1.6E+01	7.9E+00	5.6E+00	5.7E+00	1.1E+01	5.5E+00	4.9E+00	4.0E+00	7.1E+00
Total phosphorus load	1.2E-01	1.0E+00	4.0E-01	8.5E-01	2.5E-01	1.2E+00	1.6E+00	3.8E-01	1.2E+00	5.7E-01	1.5E+00	4.1E+00	2.6E+00	3.6E+00	1.3E+00	4.3E+03	3.8E+03	3.9E+04	1.6E+05
Total phosphorus yield	2.4E+00	7.9E+00	3.6E+00	3.5E+00	3.1E+00	3.9E+00	7.5E+00	2.5E+00	6.9E+00	3.2E+00	4.9E+00	2.9E+00	5.3E+00	2.8E+00	3.5E+00	1.6E+00	8.2E-01	7.7E-01	4.1E-01
Total recoverable aluminum load	6.9E-01	9.9E+00	2.5E+00	6.7E+00	1.5E+00	1.0E+01	1.3E+01	2.6E+00	9.5E+00	3.9E+00	1.3E+01	3.7E+01	2.1E+01	3.2E+01	9.4E+00	5.8E+04	2.2E+04	2.4E+05	5.1E+05
Total recoverable aluminum yield	1.4E+01	7.6E+01	2.3E+01	2.8E+01	1.9E+01	3.3E+01	6.3E+01	1.7E+01	5.3E+01	2.2E+01	4.3E+01	2.6E+01	4.3E+01	2.4E+01	2.4E+01	2.1E+01	4.6E+00	4.8E+00	1.3E+00
Total recoverable arsenic load	3.0E-04	2.9E-03	1.3E-03	2.9E-03	7.5E-04	3.7E-03	4.6E-03	1.2E-03	4.2E-03	1.6E-03	4.8E-03	2.1E-02	1.3E-02	1.6E-02	5.4E-03	8.1E+00	1.5E+01	1.3E+02	9.0E+02
Total recoverable arsenic yield	6.0E-03	2.2E-02	1.2E-02	1.2E-02	9.4E-03	1.1E-02	2.2E-02	8.2E-03	2.3E-02	8.6E-03	1.6E-02	1.5E-02	2.6E-02	1.2E-02	1.4E-02	3.0E-03	3.2E-03	2.6E-03	2.3E-03
Dissolved cadmium load	4.6E-06	1.7E-05	9.3E-06	3.5E-05	8.4E-06	3.6E-05	3.1E-05	8.0E-06	2.7E-05	1.5E-05	3.8E-05	2.3E-04	3.5E-05	1.6E-04	7.3E-05	4.6E-01	---	---	3.9E+01
Dissolved cadmium yield	9.1E-05	1.3E-04	8.5E-05	1.5E-04	1.0E-04	1.1E-04	1.5E-04	5.3E-05	1.5E-04	8.4E-05	1.3E-04	1.7E-04	7.1E-05	1.2E-04	1.9E-04	1.7E-04	---	---	9.7E-05
Dissolved copper load	4.6E-04	3.1E-03	1.7E-03	4.2E-03	1.4E-03	9.1E-03	9.6E-03	3.3E-03	8.6E-03	5.8E-03	1.8E-02	5.2E-02	9.1E-03	3.0E-02	2.2E-02	1.9E+01	2.4E+01	2.5E+02	1.7E+03
Dissolved copper yield	9.1E-03	2.4E-02	1.5E-02	1.7E-02	1.7E-02	2.8E-02	4.6E-02	2.2E-02	4.8E-02	3.2E-02	6.0E-02	3.7E-02	1.9E-02	2.3E-02	5.5E-02	7.1E-03	5.0E-03	4.9E-03	4.3E-03
Total recoverable iron load	1.0E+00	1.0E+01	3.8E+00	1.0E+01	2.5E+00	1.1E+01	2.1E+01	4.7E+00	1.7E+01	8.9E+00	2.5E+01	7.9E+01	5.6E+01	6.6E+01	2.9E+01	8.0E+04	3.9E+04	4.0E+05	1.2E+06
Total recoverable iron yield	2.1E+01	7.9E+01	3.5E+01	4.2E+01	3.2E+01	3.6E+01	1.0E+02	3.1E+01	9.7E+01	4.9E+01	8.3E+01	5.6E+01	1.1E+02	5.1E+01	7.6E+01	3.0E+01	8.2E+00	7.9E+00	2.9E+00

Table 27. Comparison of stream and bridge deck runoff parameters of concern annual loads and yields.—Continued

[---, insufficient number of laboratory detections to compute a load; Σ, summation; PAHs, polycyclic aromatic hydrocarbons]

Site name	Total bridge deck runoff loads (in pounds) and yields (in pounds per acre) ¹												Total in-stream loads and yields at in-stream monitoring sites ²						
	Flat Creek	Little River	Black River	Boylston Creek	Big Ivy Creek	Dillingham Creek	Mountain Creek	Middle Creek	Town Creek	Swift Creek	Perry Creek	Swannanoa River	Smith Creek	Mango Creek	Mallard Creek	Swannanoa River	Mountain Creek	Little River	Black River
Total load reporting period	7/27/09 to 4/27/10	5/9/09 to 03/31/10	4/14/09 to 03/31/10	5/26/09 to 4/8/10	6/3/09 to 4/8/10	5/24/09 to 4/8/10	5/4/09 to 03/31/10	5/17/09 to 3/13/10	5/7/09 to 4/25/10	5/14/09 to 3/31/10	4/20/09 to 4/9/10	3/25/09 to 3/31/10	5/11/09 to 4/25/10	3/13/09 to 7/17/09; 11/3/09 to 4/27/10	5/2/09 to 4/27/10	4/1/09 to 3/31/10	5/1/09 to 3/31/10	5/1/09 to 3/31/10	4/1/09 to 3/31/10
Dissolved lead load	2.7E-05	1.6E-04	8.6E-05	2.2E-04	6.8E-05	2.4E-04	3.5E-04	1.2E-04	3.4E-04	2.2E-04	4.5E-04	6.3E-04	1.4E-04	3.5E-04	4.2E-04	2.2E+00	4.2E+00	3.2E+01	2.8E+02
Dissolved lead yield	5.4E-04	1.2E-03	7.8E-04	9.2E-04	8.4E-04	7.5E-04	1.7E-03	8.0E-04	1.9E-03	1.2E-03	1.5E-03	4.5E-04	2.8E-04	2.7E-04	1.1E-03	8.0E-04	9.0E-04	6.4E-04	7.0E-04
Total recoverable manganese load	2.8E-02	2.6E-01	1.0E-01	2.6E-01	6.8E-02	3.2E-01	5.5E-01	1.3E-01	4.6E-01	2.5E-01	6.8E-01	1.5E+00	6.1E-01	1.0E+00	6.6E-01	3.0E+03	6.9E+03	5.3E+04	5.8E+04
Total recoverable manganese yield	5.7E-01	2.0E+00	9.1E-01	1.1E+00	8.5E-01	9.9E-01	2.6E+00	8.4E-01	2.6E+00	1.4E+00	2.3E+00	1.0E+00	1.2E+00	8.0E-01	1.7E+00	1.1E+00	1.5E+00	1.0E+00	1.5E-01
Total recoverable mercury load	7.1E-06	2.9E-05	1.7E-05	5.3E-05	1.2E-05	3.2E-05	4.1E-05	1.1E-05	4.5E-05	1.9E-05	4.0E-05	2.2E-04	8.3E-05	1.5E-04	5.9E-05	---	---	---	---
Total recoverable mercury yield	1.4E-04	2.2E-04	1.5E-04	2.2E-04	1.6E-04	1.0E-04	2.0E-04	7.3E-05	2.5E-04	1.1E-04	1.3E-04	1.6E-04	1.7E-04	1.2E-04	1.5E-04	---	---	---	---
Total recoverable nickel load	1.2E-03	7.3E-03	3.8E-03	8.9E-03	2.8E-03	1.2E-02	1.7E-02	5.2E-03	1.7E-02	9.1E-03	2.4E-02	7.6E-02	4.8E-02	6.6E-02	3.4E-02	4.5E+01	1.1E+01	1.9E+02	1.2E+03
Total recoverable nickel yield	2.4E-02	5.6E-02	3.5E-02	3.7E-02	3.6E-02	3.9E-02	8.2E-02	3.5E-02	9.4E-02	5.0E-02	7.9E-02	5.4E-02	9.8E-02	5.1E-02	8.7E-02	1.6E-02	2.4E-03	3.7E-03	2.9E-03
Dissolved zinc load	6.4E-03	3.7E-02	2.0E-02	4.4E-02	1.2E-02	5.4E-02	6.4E-02	1.8E-02	5.6E-02	3.2E-02	7.2E-02	2.2E-01	3.4E-02	1.2E-01	1.5E-01	1.3E+02	---	---	7.3E+03
Dissolved zinc yield	1.3E-01	2.8E-01	1.8E-01	1.8E-01	1.5E-01	1.7E-01	3.0E-01	1.2E-01	3.1E-01	1.8E-01	2.4E-01	1.5E-01	7.0E-01	9.2E-02	3.9E-01	4.6E-02	---	---	1.8E-02
Total suspended solids load	8.9E+00	3.2E+00	1.1E+01	6.3E+01	2.3E+01	6.8E+00	1.6E+00	9.4E-02	2.0E+01	3.5E+00	3.2E-01	1.6E+02	5.6E+01	1.8E+02	9.1E+01	---	---	---	---
Total suspended solids yield	1.8E-02	2.5E+01	9.6E+01	2.6E+02	2.9E+02	2.1E+01	7.6E+00	6.3E-01	1.1E+02	1.9E+01	1.1E+00	1.1E+02	1.1E+02	1.4E+02	2.3E+02	---	---	---	---
ΣPAHs load	1.0E-04	3.0E-04	1.5E-04	1.1E-03	3.8E-04	1.2E-03	2.4E-03	1.3E-03	2.7E-03	6.3E-03	1.0E-02	2.1E-02	9.6E-03	2.0E-02	4.2E-02	5.8E+00	---	---	---
ΣPAHs yield	2.1E-03	2.3E-03	1.4E-03	4.6E-03	4.7E-03	3.9E-03	1.2E-02	8.4E-03	1.5E-02	3.5E-02	3.5E-02	1.5E-02	2.0E-02	1.5E-02	1.1E-01	2.1E-03	---	---	---
Pentachlorophenol load	2.0E-04	8.2E-04	4.1E-04	7.0E-04	2.7E-04	8.5E-04	9.7E-04	2.2E-04	8.0E-04	3.1E-04	7.3E-04	1.8E-03	1.2E-03	1.4E-03	4.9E-04	---	---	---	---
Pentachlorophenol yield	3.9E-03	6.3E-03	3.8E-03	2.9E-03	3.3E-03	2.7E-03	4.6E-03	1.5E-03	4.4E-03	1.7E-03	2.4E-03	1.3E-03	2.5E-03	1.1E-03	1.3E-03	---	---	---	---
Bis(2-ethylhexyl) phthalate load	4.7E-04	2.8E-03	1.5E-03	4.7E-03	1.3E-03	5.8E-03	7.9E-03	2.7E-03	8.0E-03	5.4E-03	1.3E-02	5.3E-02	1.3E-02	3.4E-02	2.1E-02	---	---	---	---
Bis(2-ethylhexyl) phthalate yield	9.4E-03	2.1E-02	1.4E-02	1.9E-02	1.6E-02	1.8E-02	3.8E-02	1.8E-02	4.4E-02	3.0E-02	4.5E-02	3.8E-02	2.6E-02	2.6E-02	5.3E-02	---	---	---	---

¹ Blue shaded cell with outline indicates bridge deck yield is smaller than maximum in-stream yield for that parameter of concern.

² Red shaded cell indicates stream load is larger than maximum bridge deck load for that parameter of concern.

Mixing Calculations of Bridge Deck Stormwater and Stream Constituents

The rate at which bridge deck runoff mixes with and is diluted by the receiving stream was determined by using empirical relations and measured flow conditions at the four stream sites for eight steady-state hydraulic conditions. The eight stream samples were selected to include at least one sample each season, if possible, and across a range of stream discharges and water levels (fig. 18). The empirical mixing calculations (Fischer and others, 1979) provide an estimate of the distance required for the runoff to become uniformly mixed across the stream, and thus, an estimate of the zone in which effects of bridge runoff are most pronounced. From these calculations, plots of dilution as a function of distance downstream from the bridge and stream concentration and discharge were developed. These plots provide the basis to quantify the differences between maximum constituent

concentrations in the bridge deck runoff and concentrations at the point of uniform mixing in the receiving stream, which help to illustrate the magnitude and spatial extent of the stormwater effects.

Mixing of bridge deck runoff with the stream occurs through the additive process of diffusion (random movement of particles in the stream) and advection (transport by the mean motion of the stream). At some distance, L , downstream from the hypothetical bridge deck runoff injection point, vertical and transverse diffusion and turbulence mix the bridge deck runoff with the streamflow below a threshold criteria and it is assumed to be completely mixed. The computation of dilution curves involves estimating the shape of the bridge deck runoff plume downstream to L . In this study, the threshold was set at 5 percent, meaning the concentration at any point in the river cross section was within 5 percent of its mean value at L downstream from the injection point.

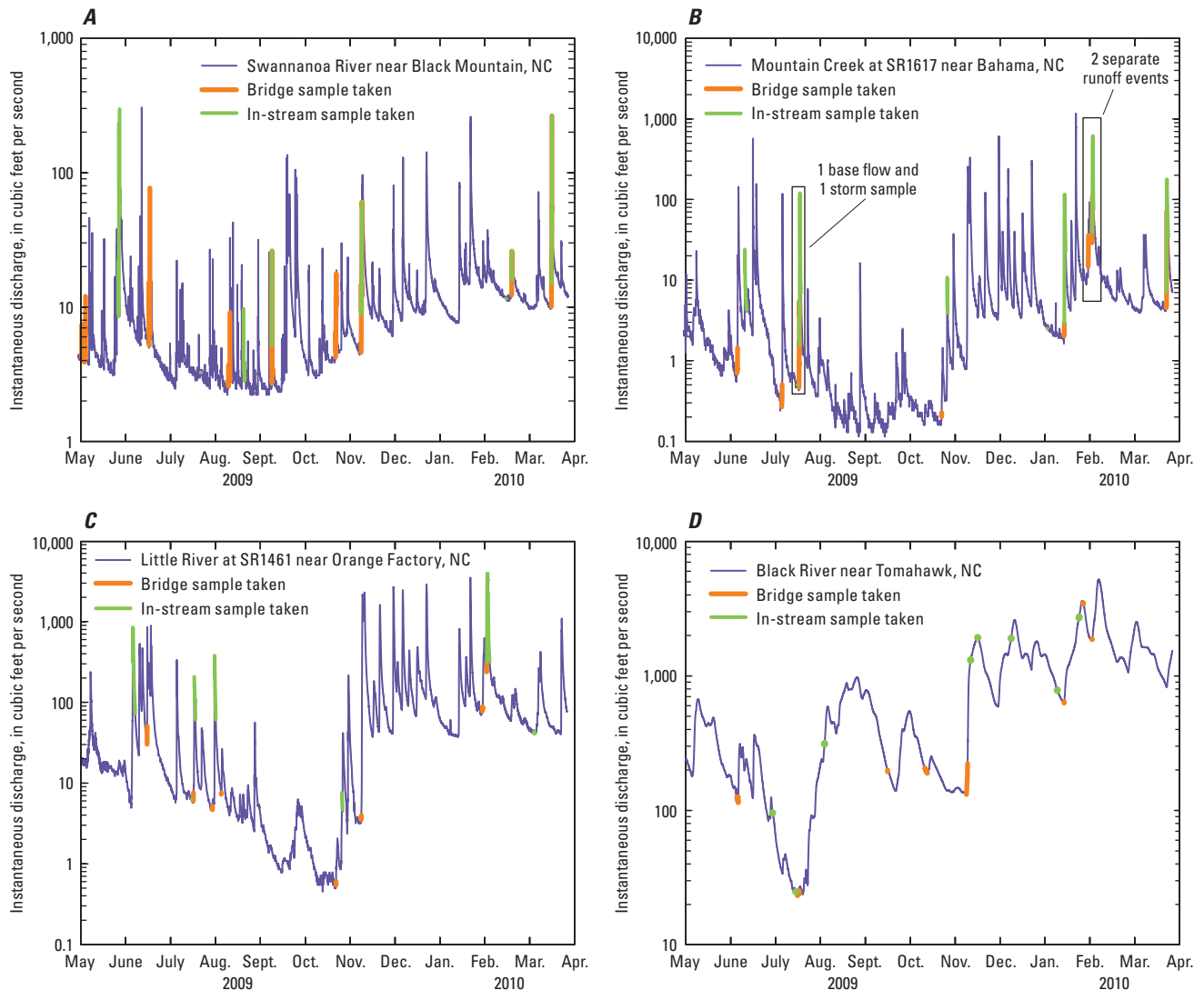


Figure 18. Stream sites discharge hydrographs with stream sampling periods used to generate dilution curves.

The approximation of L for turbulent mixing in the transverse direction of a natural stream when the bridge deck runoff is injected from the side of the channel is given by equation 2:

$$L = 0.4 \cdot \bar{u} \cdot w^2 / \epsilon_y, \tag{2}$$

where

- \bar{u} is the average velocity, in feet per second, approximated by the stream discharge, Q , divided by the cross-sectional area of the stream (A);
- w is the channel width, in feet; and
- ϵ_y is the transverse mixing coefficient, approximated as $0.6 \cdot h \cdot u^*$ (coefficient is 0.6 for a wide slow meandering stream with a range from 0.4 to 0.8 for nearly straight or slowly meandering rivers and higher for sharply curving channels), where h is the average flow depth, in feet, and u^* is the shear friction, in feet per second, and is approximated by $\sqrt{(g \cdot h \cdot S)}$, where g is the gravitational constant (31.174 feet per second squared (ft/s²)), and S is the dimensionless channel bottom slope (Fischer and others, 1979).

Therefore, L can be computed with measurements of stream width (w), discharge (Q), cross-sectional area (A), average flow depth (h), channel bottom slope (S), and the gravitational constant (g). Stream discharge and stage are reported at each site by a USGS streamflow gage, and as part of maintaining the streamflow gages, river cross sections are periodically surveyed. The gravitational constant does not change. Therefore, to determine L for each site, w , A , h , and S must be computed and incorporated with adjustments made due to local conditions that enhance or retard dilution. The mixing lengths presented here are conservative and do not fully consider the stream conditions and characteristics (for example, local bathymetry variations, debris, and so forth) that would enhance mixing. A summary of the L values and corresponding stream conditions at all sites for each of the eight analyzed steady-state hydraulic conditions is presented in table 28.

At the stream sampling sites, stream width was estimated from recent cross-sectional surveys (September 12, 2008, for 02106500 Black River near Tomahawk, NC; January 25, 2009, for 0208524090 Mountain Creek at SR 1617 near Bahama, NC; January 28, 2010, for 0208521324 Little River at SR 1461 near Orange Factory, NC; November 10, 2009, for 03448800 Swannanoa River near Black Mountain, NC) and the stage and gage datum provided at the streamflow gages. Mean channel depth was computed by approximating the interval of the cross-sectional area based on the channel shape and water level. The channel bottom slope was computed uniquely for each site based on available topographic data (North Carolina Division of Emergency Management,

Floodplain Mapping Program, 2002), surveyed channel bottom elevations at the streamflow-gaging stations, and channel lengths determined from the 1:24,000-scale National Hydrography Dataset.

The Black River downstream from the Black River near Tomahawk, NC (USGS streamflow-gaging station 02106500) includes several features (tributaries and sharp bends) that likely increase lateral mixing faster than predicted by the equations (fig. 19). Three tributaries enter the Black River at 5,000 ft downstream from the bridge. A large bend with an embayment feature at a distance of 10,500 ft downstream from the streamflow gage likely would complete the mixing of any remaining unmixed plume; therefore, L was capped at 10,500 ft for this analysis.

The USGS streamflow-gaging station (0208521324) Little River at SR 1461 near Orange Factory, NC, is about 3,300 ft upstream from the Durham County water-supply reservoir on the Little River (fig. 20). The mixing downstream of the Little River streamflow-gaging station can be approximated as being complete as soon as it enters the reservoir because the stream velocity decreases to nearly zero in the reservoir, which induces strong lateral mixing forces. Therefore, L for the site was capped at 3,300 ft.

The computation of L on Mountain Creek was made using USGS streamflow-gaging station 0208524090, Mountain Creek at SR 1617 near Bahama, NC, because discharge measurements and all associated channel characteristics are available at the site; however, water-quality samples were collected upstream at USGS streamflow-gaging station 0208524088, Mountain Creek at SR 1616 near Bahama, NC (fig. 21). The channel characteristics are similar between the two sites, which are located within 3,500 ft of each other and have a drainage area difference of only 0.5 mi². Therefore, the L computed using the available hydraulic data from streamflow-gaging station 0208524090 was applied to gaging station 0208524088 where all water-quality data were collected. For sampled events, the mixing length does not include any tributaries or sharp bends, so no local adjustments were applied to L .

For the Swannanoa River at I-40 near Black Mountain, NC (USGS streamflow-gaging station 03448800), the channel is straight for 1 mi upstream from the streamflow gage, so the transverse mixing coefficient was defined as $0.4 \cdot h \cdot u^*$, whereas the transverse mixing coefficient for all other sites was defined as $0.6 \cdot h \cdot u^*$ (Fischer and others, 1979). Because the channel is straight and no tributaries join the channel within the distance L downstream from the bridge for any of the events sampled (fig. 22), no local adjustments to L were made for this site.

If the concentration of a constituent in the bridge deck runoff exceeds a water-quality threshold, it is useful to estimate if the constituent level is above this threshold once discharged into the stream and, if so, the distance downstream from the bridge that the threshold is exceeded. To make this determination, the width of the plume from a side injection is estimated as $b = 2n \cdot \sqrt{(2 \cdot \epsilon_y \cdot [x/\bar{u}])}$, where b

Table 28. Summary of the bridge deck runoff sample dates, corresponding stream conditions, and the adjusted mixing lengths computed for each mixing scenario.

[USGS, U.S. Geological Survey; As, total recoverable arsenic; Cu, dissolved copper; Ni, total recoverable nickel; Zn, dissolved zinc; N, total nitrogen; P, total phosphorus; ---, inadequate length of flow record to compute percentiles]

In-stream USGS station no.	Station name and data description	Mixing scenario 1	Mixing scenario 2	Mixing scenario 3	Mixing scenario 4	Mixing scenario 5	Mixing scenario 6	Mixing scenario 7	Mixing scenario 8
02106500	Black River near Tomahawk, NC								
	Bridge deck runoff sample date	6/29/2009	7/15/2009	8/4/2009	11/13/2009	11/18/2009	12/11/2009	1/12/2010	1/27/2010
	In-stream conditions	Base-flow	Base-flow	Storm	Storm	Storm	Storm	Base-flow	Storm
	In-stream discharge in cubic feet per second	96.0	24.9	313	1,310	1,920	1,888	780	2,710
	Streamflow percentile	9.2	1.0	34.0	81.8	91.4	91.1	65.4	97.0
	Adjusted mixing length (L) in feet ¹	6,027	2,383	10,500	8,741	9,419	8,623	9,739	10,119
	In-stream ambient concentrations for As, Cu, Ni, Zn, N, P in micro-grams per liter	1.0, 0.54, 0.73, 2.5, 1200, 179	1.0, 1.3, 0.72, 1.9, 740, 196	1.8, 1.4, 1.33, 3.9, 1600, 332	0.56, 0.89, 0.80, 4.4, 2400, 150	0.44, 0.50, 0.63, 3.9, 890, 60	0.45, 1.2, 0.63, 5.2, 1600, 80	0.55, 0.25, 0.80, 3.8, 2400, 30	0.45, 3.0, 0.61, 4.6, 2100, 70
0208524090	Mountain Creek at SR 1617 near Bahama, NC								
	Bridge deck runoff sample date	6/10/2009	7/16/2009	7/17/2009	10/28/2009	1/5/2010	1/17/2010	2/5/2010	3/29/2010
	In-stream conditions	Storm	Base-flow	Storm	Storm	Base-flow	Storm	Storm	Storm
	In-stream discharge in cubic feet per second	7.95	0.50	27.6	6.44	0.70	33.7	277	77.2
	Streamflow percentile	82.3	28.0	96.0	78.0	32.6	97.0	99.8	99.0
	Adjusted mixing length (L) in feet	214	40	626	178	44	573	1,231	728
	In-stream ambient concentrations for As, Cu, Ni, Zn, N, P in micro-grams per liter	0.71, 1.6, 0.46, 1.6, 1000, 120	0.70, 1.4, 0.18, 1.0, 860, 35	1.2, 1.6, 0.65, 1.0, 1300, 240	0.57, 0.93, 0.57, 1.4, 710, 94	0.28, 0.25, 0.21, 1.4, 880, 27	0.87, 1.5, 0.67, 2.1, 1500, 215	0.87, 1.0, 0.67, 1.7, 1100, 222	1.1, 2.5, 0.89, 1.8, 1700, 300

Table 28. Summary of the bridge deck runoff sample dates, corresponding stream conditions, and the adjusted mixing lengths computed for each mixing scenario.—Continued

[USGS, U.S. Geological Survey; As, total recoverable arsenic; Cu, dissolved copper; Ni, total recoverable nickel; Zn, dissolved zinc; N, total nitrogen; P, total phosphorus; ---, inadequate length of flow record to compute percentiles]

In-stream USGS station no.	Station name and data description	Mixing scenario 1	Mixing scenario 2	Mixing scenario 3	Mixing scenario 4	Mixing scenario 5	Mixing scenario 6	Mixing scenario 7	Mixing scenario 8
0208521324	Little River at SR 1461 near Orange Factory, NC								
	Bridge deck runoff sample date	6/5/2009	7/16/2009	7/18/2009	8/1/2009	10/28/2009	2/5/2010	11/11/2009	3/10/2010
	In-stream conditions	Storm	Base-flow	Storm	Storm	Storm	Storm	Storm	Base-flow
	In-stream discharge in cubic feet per second	285	6.30	120	165	5.85	2,814	1,260	41.8
	Streamflow percentile	94.0	25.6	87.4	91.0	24.6	99.8	99.4	64.6
	Adjusted mixing length (L) in feet ²	3,300	644	3,300	3,300	699	3,300	3,300	1,931
03448800	Swannanoa River near Black Mountain, NC								
	Bridge deck runoff sample date	5/26/2009	7/22/2009	8/21/2009	9/9/2009	11/10/2009	2/18/2010	2/22/2010	3/21/2010
	In-stream conditions	Base-flow	Storm	Storm	Storm	Base-flow	Storm	Storm	Storm
	In-stream discharge in cubic feet per second	50.6	3.26	3.39	12.9	21.7	11.3	19.5	54.7
	Streamflow percentile	---	---	---	---	---	---	---	---
	Adjusted mixing length (L) in feet	546	201	203	293	427	240	295	469
03448800	In-stream ambient concentrations for As, Cu, Ni, Zn, N, P in micro-grams per liter	0.89, 1.6, 4.5, 4.8, 1400, 294	0.15, 0.25, 0.62, 3.2, 350, 22	0.17, 0.84, 0.60, 3.5, 370, 20	1.1, 0.97, 6.1, 1.3, 1500, 407	0.39, 1.4, 1.4, 5.9, 740, 91	0.13, 0.25, 0.40, 5.8, 430, 10	0.55, 0.89, 2.9, 16.1, 920, 130	1.0, 1.3, 6.4, 6.4, 1500, 480

¹ Mixing lengths were capped at 10,500 feet because of location in-stream conditions.

² Mixing lengths were capped at 3,300 feet because of the influence of the Litte River reservoir.

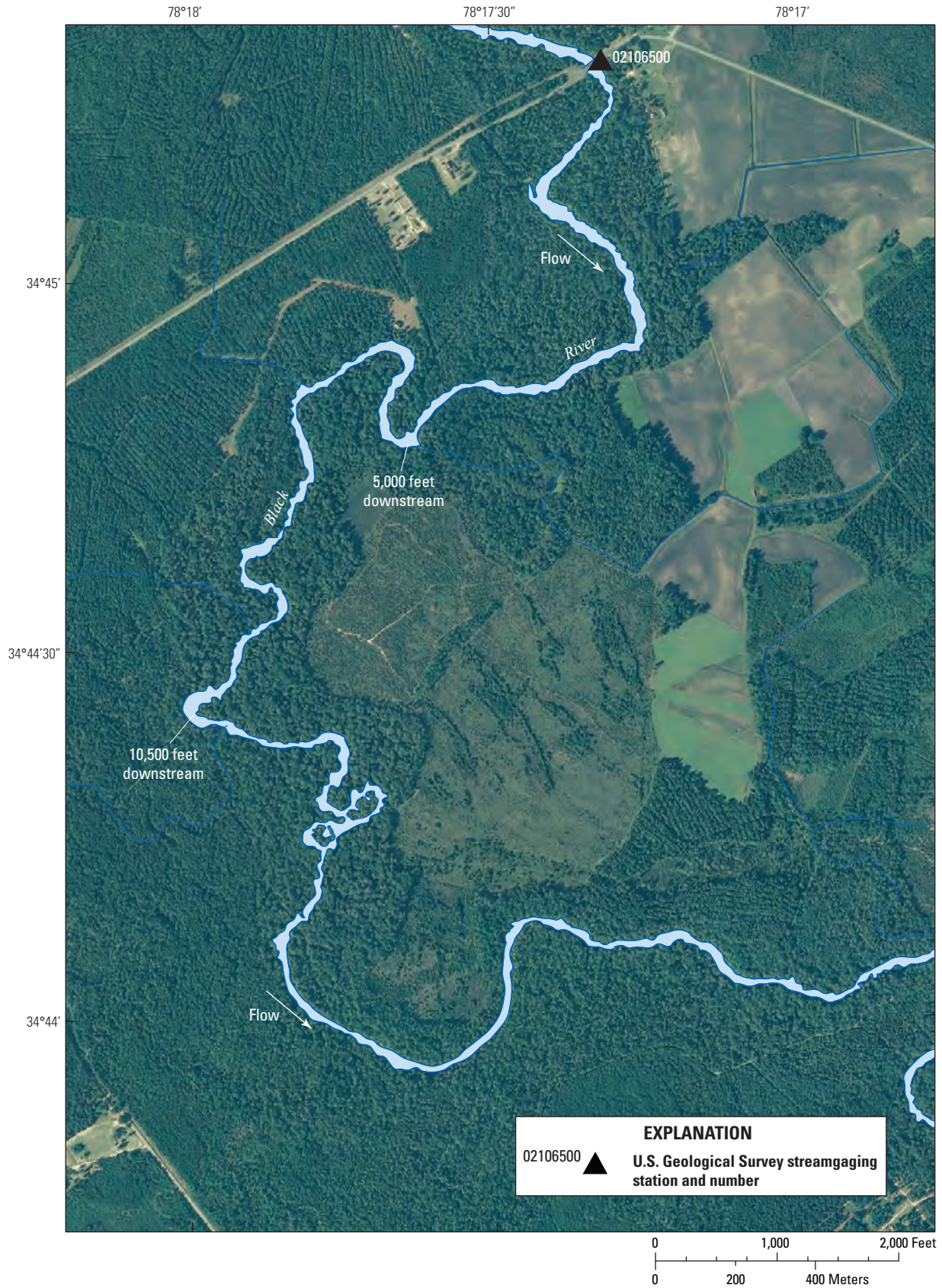


Figure 19. Plan view of Black River channel configuration and location of streamflow-gaging and sampling site near Tomahawk, North Carolina.



Figure 20. Plan view of Little River channel configuration and location of streamflow-gaging and sampling site at Secondary Road 1461 near Orange Factory, North Carolina.



Figure 21. Plan view of Mountain Creek channel configuration and location of streamflow-gaging and sampling sites near Bahama, North Carolina.



Figure 22. Plan view of Swannanoa River channel configuration and location of streamflow-gaging and sampling site at Interstate 40 at Black Mountain, North Carolina.

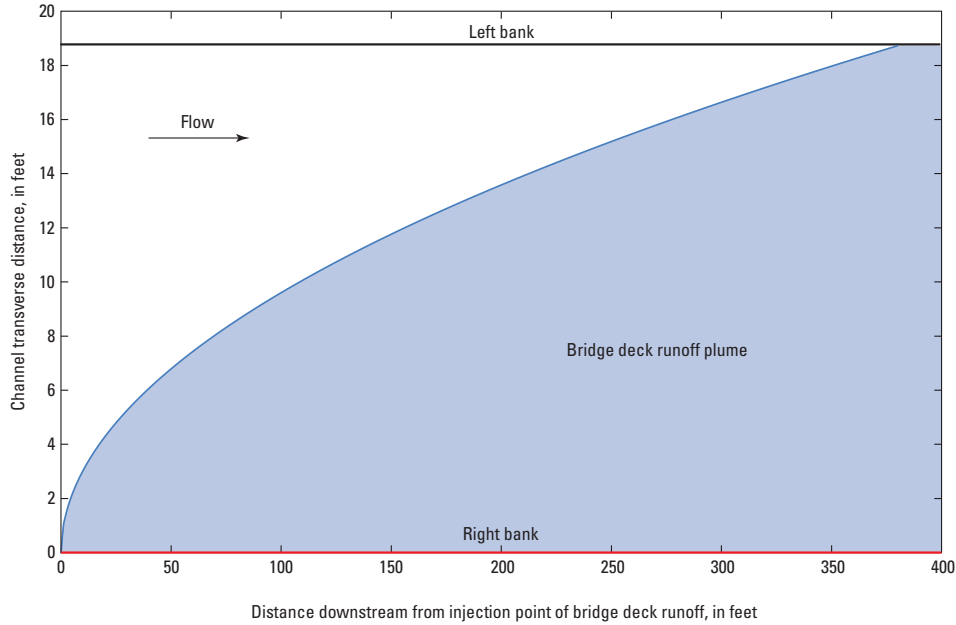


Figure 23. An example of a computed bridge deck runoff plume migration from a right-bank injection point at U.S. Geological Survey streamflow-gaging station 03448800 Swannanoa River at Interstate 40 at Black Mountain, North Carolina.

is the stream width, n is a scaling factor that calibrates the equation for b such that b equals the measured stream width at L downstream, and x is the distance downstream from the injection. With no local turbulence, such as sharp bends or tributaries, the spread of the plume is idealized to be parabolic as illustrated in figure 23.

The maximum concentration of the bridge deck runoff plume, C_{max} , downstream from the bridge deck runoff injection point is defined as $(Q_{BD} * C_{BD} + Q * C) / (Q_{BD} + Q)$, where Q_{BD} is the maximum 10-minute average discharge of bridge deck runoff, Q is the mean stream discharge over the storm hydrograph or base-flow discharge within the plume width, C_{BD} is the constituent concentration of the bridge deck runoff for the associated storm, and C is the residual constituent concentration in the stream for the associated storm. If $Q \gg Q_{BD}$, the bridge deck runoff plume is quickly diluted. However, high concentrations of constituents from bridge deck runoff during low streamflow will not dilute as quickly. Dilution curves, based on the previously defined empirical mixing equations from Fischer and others (1979), were developed for selected POCs by injecting sampled bridge deck runoff concentrations into the receiving streams from one of the stream banks under both base-flow and storm conditions and computing C_{max} values at downstream distance intervals of 10 ft. The

dilution curves for selected POCs (total recoverable arsenic, dissolved copper, total recoverable nickel, dissolved zinc, total nitrogen, and total phosphorus) at each site for eight different streamflow conditions are illustrated in figures 24 to 27. The dilution curves are truncated at the L distance for each stream condition or the point at which the maximum concentration asymptotically approaches the ambient stream concentration, whichever comes first. The dilution curves, based on the previously defined empirical mixing equations from Fischer and others (1979), were developed by injecting sampled bridge deck runoff concentrations into the receiving streams from one of the stream banks under both base-flow and storm conditions.

The dilution curves indicate that the maximum concentration of the runoff plume from the bridge deck, although in many cases appreciably exceed some water-quality thresholds, is reduced rapidly (generally within 50 ft downstream of the injection point) to the ambient stream concentration and in some cases is actually lower than the stream concentration. For many of the mixing scenarios, the maximum stream concentration does not drop below the associated POC water-quality threshold. This occurred when the ambient stream concentrations exceeded the POC water-quality thresholds before bridge deck runoff was injected.

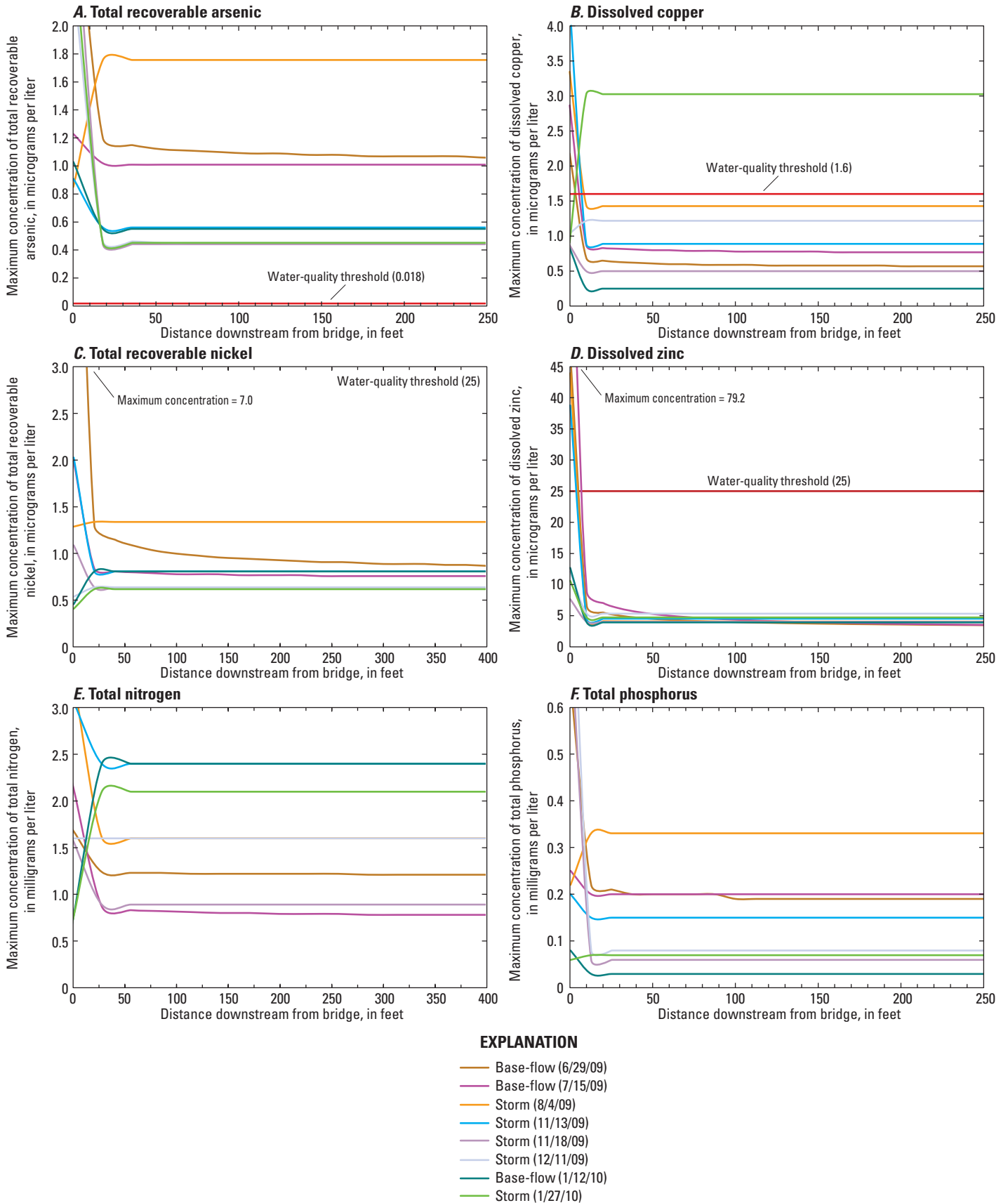


Figure 24. Dilution curves for bridge deck runoff plumes at Black River near Tomahawk, North Carolina, for (A) total recoverable arsenic, (B) dissolved copper, (C) total recoverable nickel, (D) dissolved zinc, (E) total nitrogen, and (F) total phosphorus.

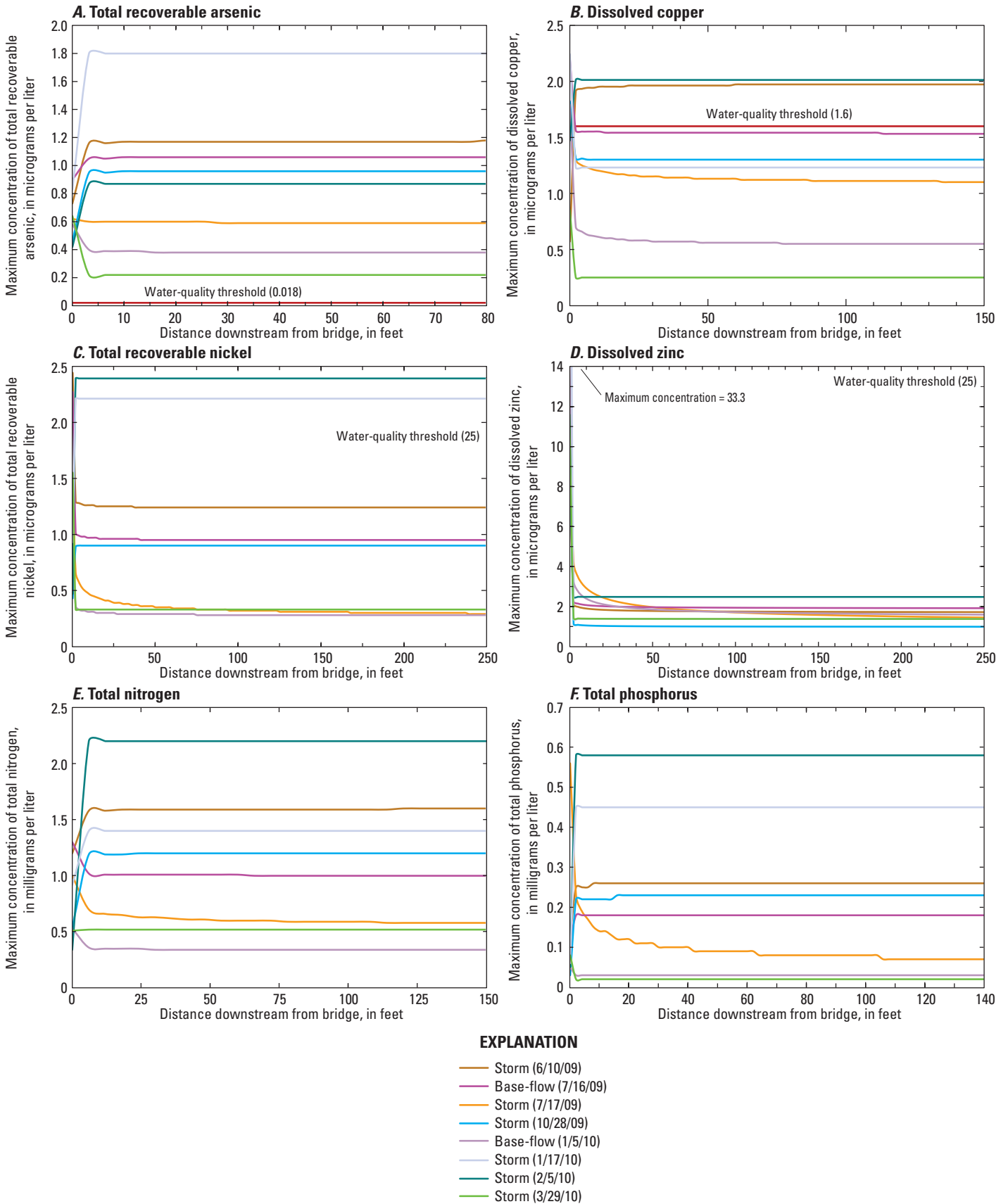


Figure 25. Dilution curves for bridge deck runoff plumes at Little River at Secondary Road 1461 near Orange Factory, North Carolina, for (A) total recoverable arsenic, (B) dissolved copper, (C) total recoverable nickel, (D) dissolved zinc, (E) total nitrogen, and (F) total phosphorus.

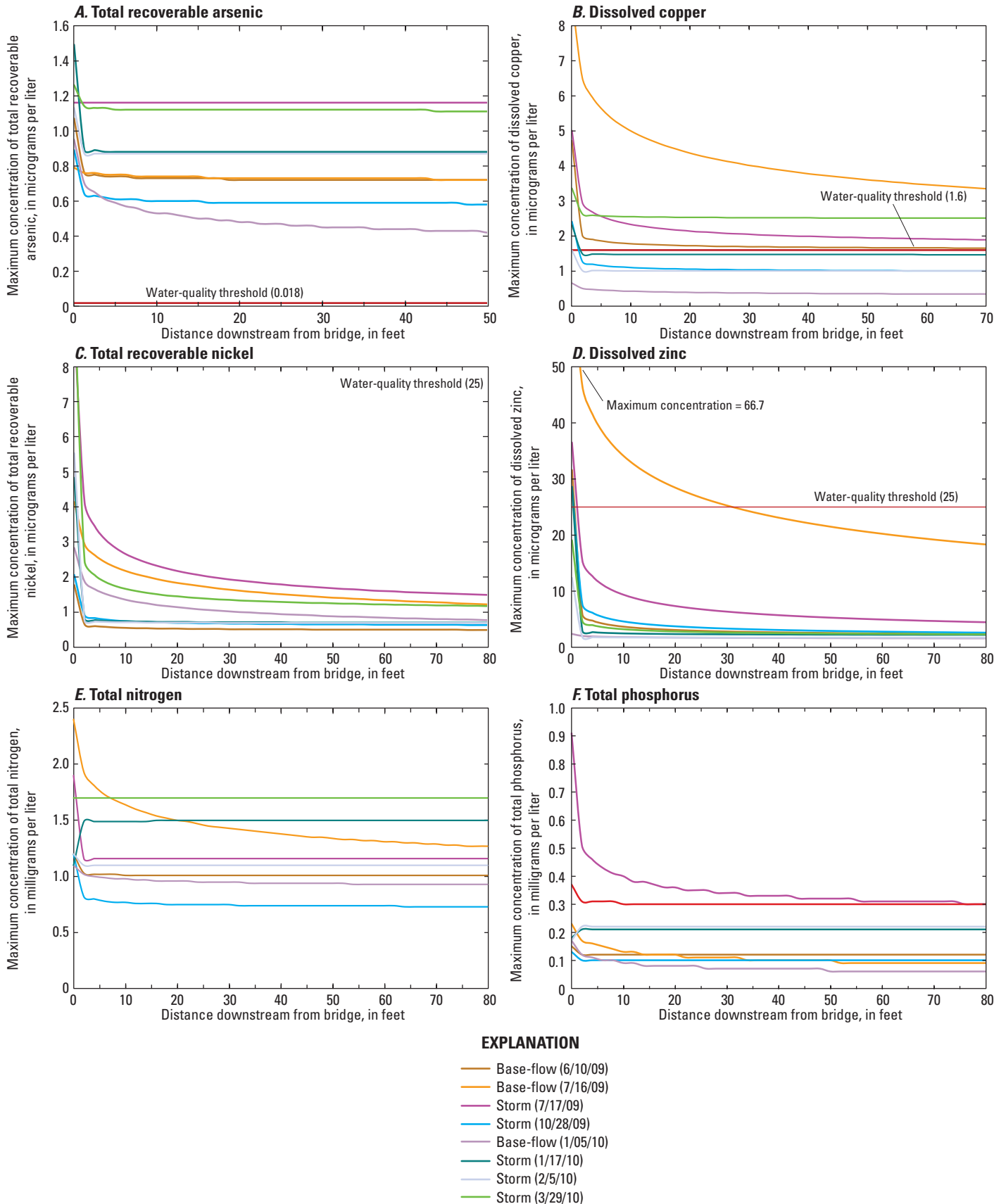


Figure 26. Dilution curves for bridge deck runoff plumes at Mountain Creek at Secondary Road 1617 near Bahama, North Carolina, for (A) total recoverable arsenic, (B) dissolved copper, (C) total recoverable nickel, (D) dissolved zinc, (E) total nitrogen, and (F) total phosphorus.

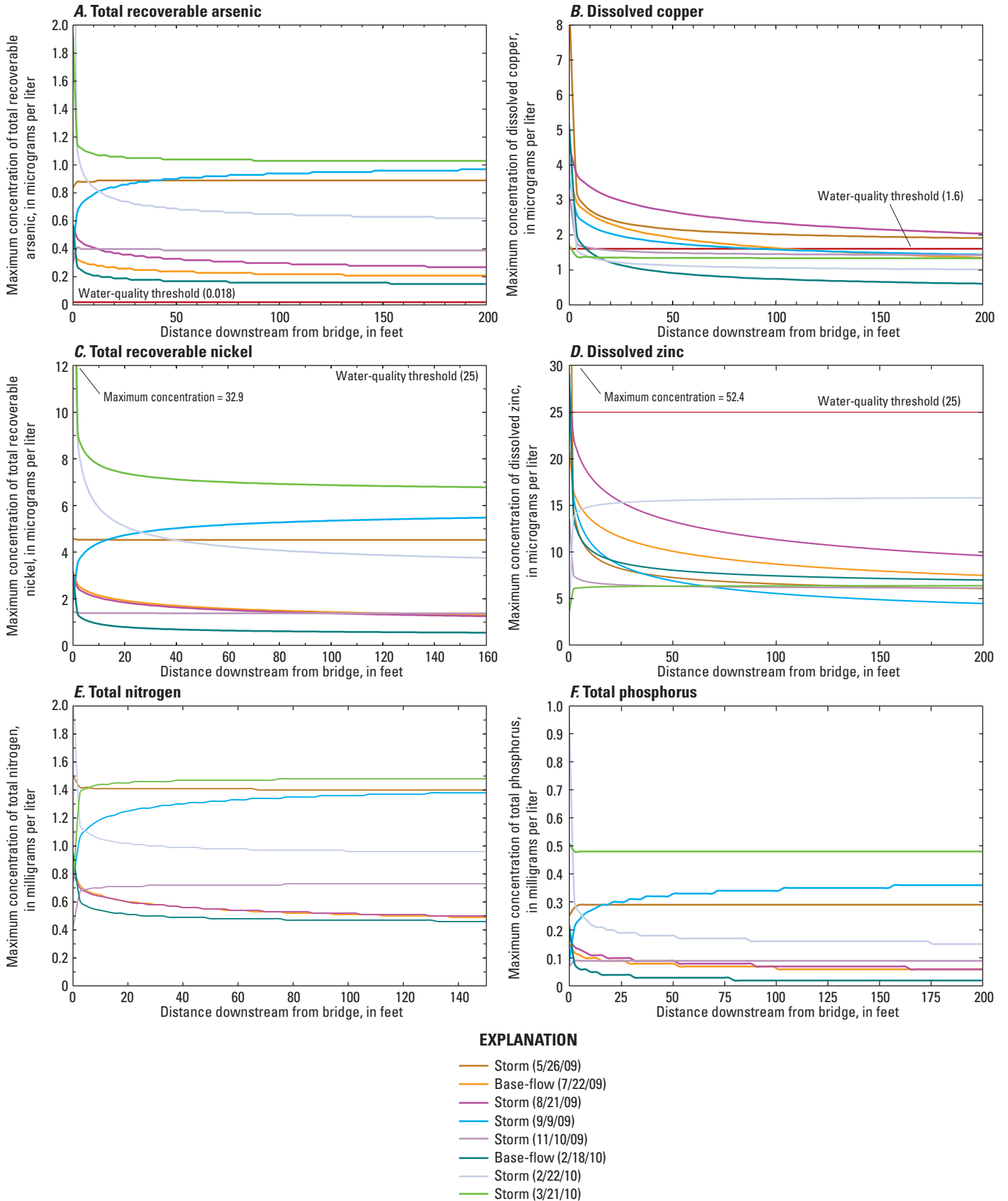


Figure 27. Dilution curves for bridge deck runoff plumes at Swannanoa River at Interstate 40 near Black Mountain, North Carolina, for (A) total recoverable arsenic, (B) dissolved copper, (C) total recoverable nickel, (D) dissolved zinc, (E) total nitrogen, and (F) total phosphorus.

Bed Sediment Characteristics Upstream and Downstream from Bridges

Bed sediment was analyzed for 31 major ions and trace metals and 38 SVOCs (table 5) at 30 bridges (fig. 3; table 4). The overall hypothesis of the bed sediment sampling was that analyte concentrations in downstream reaches would exceed those in upstream reaches at the 16 bridges where deck runoff entered the stream by means of scuppers (orifices in the decks allowing deck drainage) or simply off the edges (Cataloochee bridge). Because bed sediment quality criteria are somewhat less defined compared to those for water, all analytes were considered, not just those previously identified as POCs. A control group consisted of the 14 bridges mentioned earlier with collection systems (best management practices) designed to divert deck runoff from entering the stream. At these sites, downstream concentrations would not be expected to be greater than those upstream. A second much smaller control group consisted of two bridges with direct deck runoff into tidally influenced streams at the location of the bridge crossing (Smith Creek, bridge 640002 and Town Creek, bridge 90074). The flow direction at these sites reverses with tides, and upstream and downstream concentration differences were not expected despite the direct input of bridge deck runoff to the streams. Within that overarching comparison between sites with scuppers versus collection systems, it was postulated that any relative downstream increases might show a relation between deck surface material (bitumen versus concrete) and certain analytes, specifically some PAHs of the SVOC suite, which are known to be present in bituminous materials. Additionally, any downstream increases present at the scuppered sites might be expected to scale with traffic volume. Finally, the Cataloochee bridge is wooden, has no runoff collection system and no scuppers, and is located in a remote, relatively pristine area.

While sampling of the deck runoff captured the near instantaneous analyte masses entering the stream during storms, streambed sediments integrated the inputs over weeks to months by their nature and as a general rule. Additionally, bed sediments retain only the hydrophobic and (or) lipophilic analytes and those that tend to sorb at sediment surfaces. Analytes were determined on the fraction of sediment particles smaller than 63 microns in maximum diameter (silt or smaller). This minimized grain-size artifacts on measured concentrations of analytes that were largely sorbed to sediment surfaces including SVOCs and metals associated with surficial oxyhydroxide and organic sediment coatings (copper, lead, zinc, cadmium, nickel, selenium, and mercury). Last, total concentrations were determined for all analytes. As such, this included the mineral matrices of the sediment. Thus aluminum, and to a lesser extent iron and manganese, had a high "background" signal that might mask any signal from the deck runoff.

Bridge decks can accumulate both organic and inorganic analytes from several sources including atmospheric deposition, vehicles (wear of tire, engine, bushing, brake lining,

paint; leakage of fuel, oil, antifreeze, hydraulic fluids; and exhaust particles), deck pavement wear, and random losses of transported materials (Sansalone and Buchberger, 1997; Lopes and Dionne, 1998; Dupuis, 2002). Differences in downstream and upstream sediment concentrations were calculated for the entire analytical suite (previously indicated), although focus was placed on the subset that was known to be both associated with bridges or highways and to have demonstrated toxicity to aquatic life.

Downstream minus upstream concentration differences for inorganic analytes and total organic carbon for bridges with scuppers appeared as scattered as these differences for the bridges with best management practices and those with scuppers and reverse flow (fig. 28). The overall picture from the 30 sites is that there is no clear, consistent, predictable downstream increase in the concentration of these or any of the analytes in bed sediment. Additionally, the precision of the individual measurements (about 15 percent) and the precision associated with calculating the concentration difference (about 21 percent, square root of the sum of the squares) made any connection even more tenuous. A summary of all inorganic analyte concentrations, total organic carbon, and the less than 63-micron fraction in all bed sediment samples collected is presented in table A8 of the appendix.

For SVOCs, 28 of the 30 bridge sites (excluding Dillingham Creek, bridge 100145 and Cataloochee) had at least one upstream-downstream analyte pair wherein the compound was detected in both the upstream and downstream samples from the site. There were 183 upstream-downstream pairs, which was 16 percent of all possible pairs (38 analytes times 30 sites) (table 29). About one-third of all pairs were accounted for by just three compounds (perylene, fluoranthene, and pyrene). Perylene is considered a diagenetic PAH whereas fluoranthene and pyrene are both largely pyrogenic (Page and others, 1999). Other relatively abundant concentration pairs included 2,6-dimethylnaphthalene, benzo[*b*]fluoranthene, bis(2-ethylhexyl)phthalate, 9,10-anthraquinone, phenanthrene, benzo[*a*]pyrene, benzo[*e*]pyrene, chrysene, carbazole, benzo[*a*]anthracene, and benzo[*a*]fluoranthene. These are a mixed bag of compound classes dominated by pyrogenic PAHs.

The hypothesis for SVOCs in bed sediments was that the scuppered bridges with bituminous decks would have the best chance of having a downstream enrichment both with respect to the upstream reach at those sites and also with respect to the concentrations (both upstream and downstream) at the bridges with collection systems. Overall, there were no obvious patterns in downstream concentration increases at the scuppered sites (fig. 29). This was especially true considering the precision of both the chemical analyses and that for calculating the concentration differences mentioned above. Furthermore, there was no obvious difference between bitumen and concrete bridge decks when considering the precision. Additionally, while acenaphthene, 9H-fluorene, and 9,10-anthraquinone concentrations were somewhat increased downstream from bituminous scuppered bridges, those three points represented a total of two bridges (Black River, bridge 810058 and

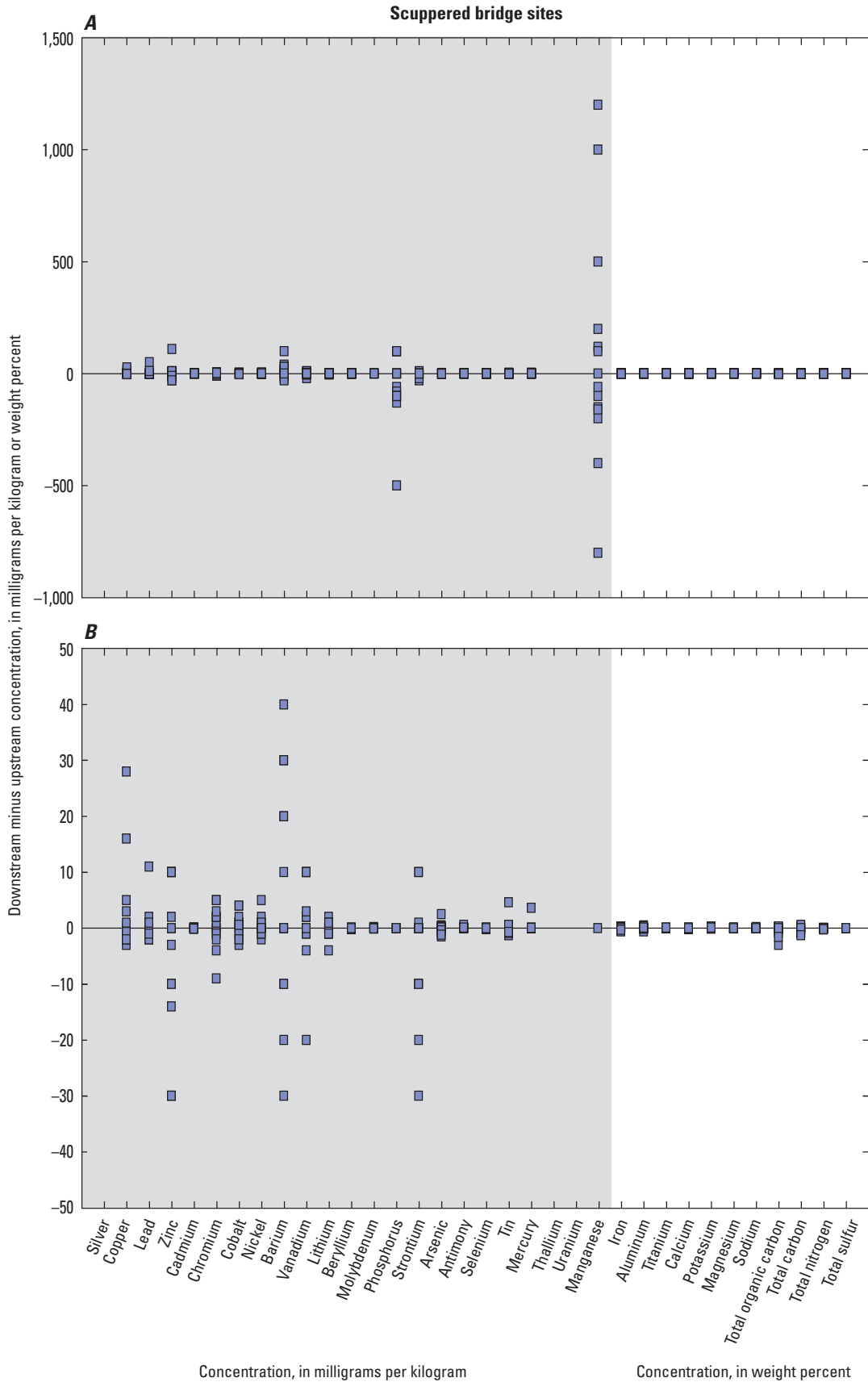


Figure 28. Downstream minus upstream concentration differences for (A) all data, and (B) data focusing near the zero line for all inorganic analytes and total organic carbon in bed sediment at scuppered bridge sites, bridge sites with best management practices, and scuppered sites with reverse flow.

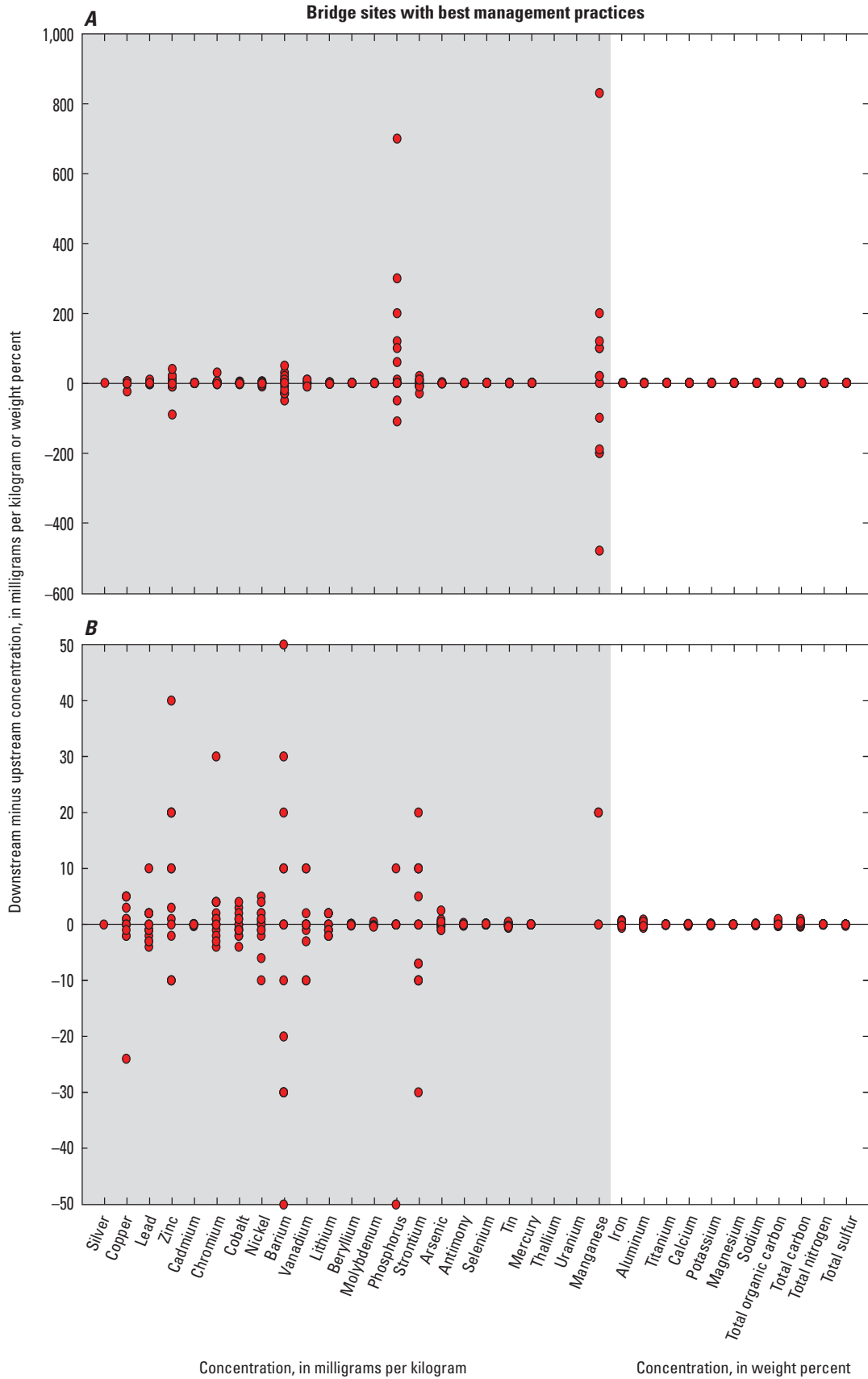


Figure 28 (Continued). Downstream minus upstream concentration differences for (A) all data, and (B) data focusing near the zero line for all inorganic analytes and total organic carbon in bed sediment at scuppered bridge sites, bridge sites with best management practices, and scuppered sites with reverse flow.

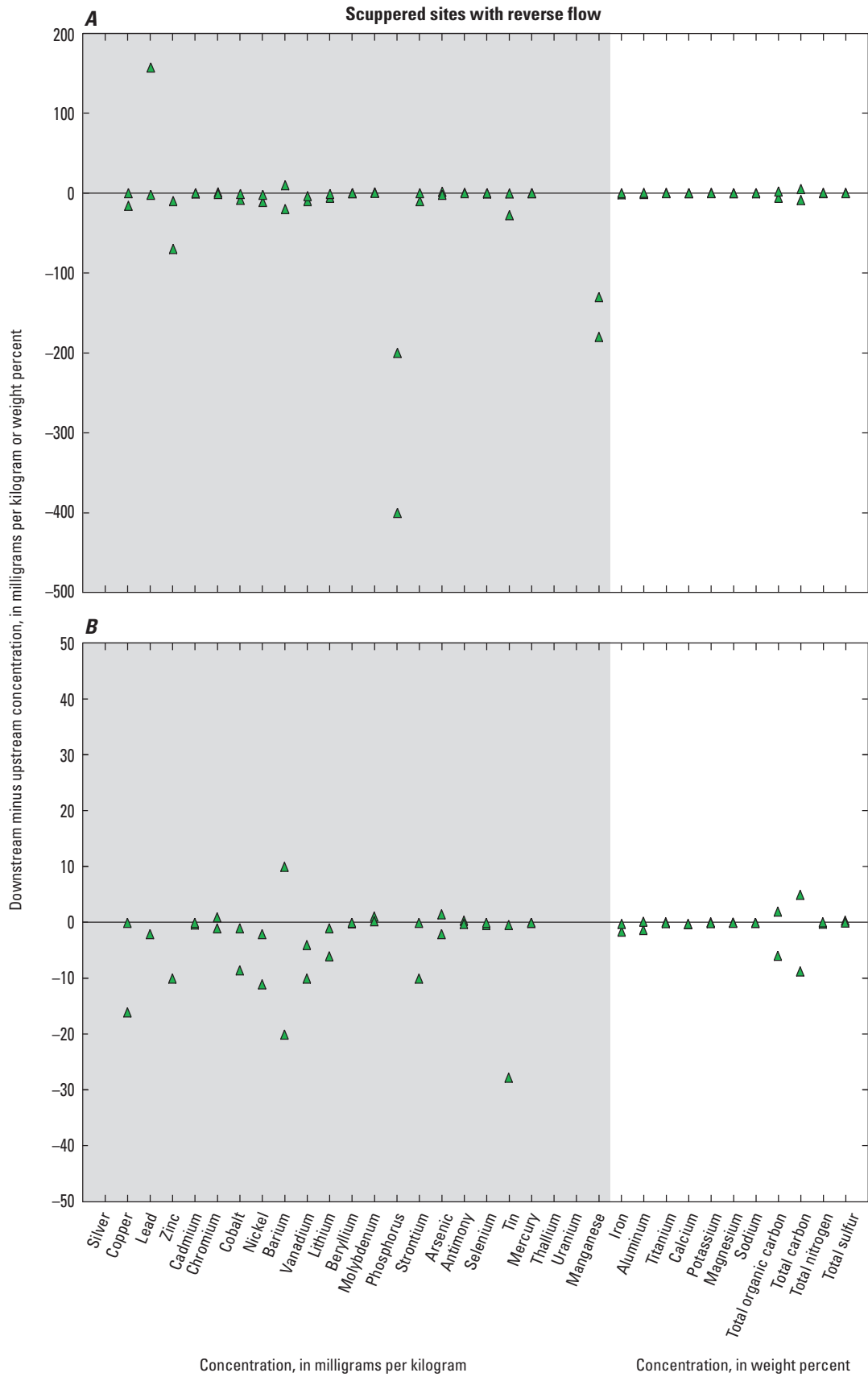


Figure 28 (Continued). Downstream minus upstream concentration differences for (A) all data, and (B) data focusing near the zero line for all inorganic analytes and total organic carbon in bed sediment at scuppered bridge sites, bridge sites with best management practices, and scuppered sites with reverse flow.

Table 29. Relative abundances of upstream-downstream pairs of semivolatile organic compounds in bed sediment.

[PAH, polycyclic aromatic hydrocarbon]

Analyte	Class	No. of pairs	Relative abundance of pairs (percent)
Perylene	PAH (diagenetic)	22	12.0
Fluoranthene	PAH (pyrogenic)	21	11.5
Pyrene	PAH (pyrogenic)	19	10.4
2,6-Dimethylnaphthalene	Alkyl-PAH	11	6.0
Benzo[<i>b</i>]fluoranthene	PAH (pyrogenic)	11	6.0
Bis(2-ethylhexyl)phthalate	Phthalate	11	6.0
Anthraquinone	Quinone	10	5.5
Phenanthrene	PAH (pyrogenic)	10	5.5
Benzo[<i>a</i>]pyrene	PAH (pyrogenic)	9	4.9
Benzo[<i>e</i>]pyrene	PAH (pyrogenic)	9	4.9
Chrysene	PAH (pyrogenic)	9	4.9
Carbazole	Azaarene	7	3.8
Benzo[<i>a</i>]anthracene	PAH (pyrogenic)	7	3.8
Benzo[<i>k</i>]fluoranthene	PAH (pyrogenic)	6	3.3
Anthracene	PAH (pyrogenic)	4	2.2
Benzo[<i>ghi</i>]perylene	PAH (pyrogenic)	4	2.2
4H-Cyclopenta[<i>def</i>]phenanthrene	PAH (petrogenic)	3	1.6
Indeno[1,2,3- <i>cd</i>]pyrene	PAH (pyrogenic)	3	1.6
1,6-Dimethylnaphthalene	Alkyl-PAH	2	1.1
Acenaphthene	PAH (pyrogenic)	2	1.1
1-Methylphenanthrene	Alkyl-PAH	1	0.5
9H-Fluorene	PAH (petrogenic)	1	0.5
Naphthalene	PAH (petrogenic)	1	0.5
TOTAL		183	
Pair of detections (percent)		16	

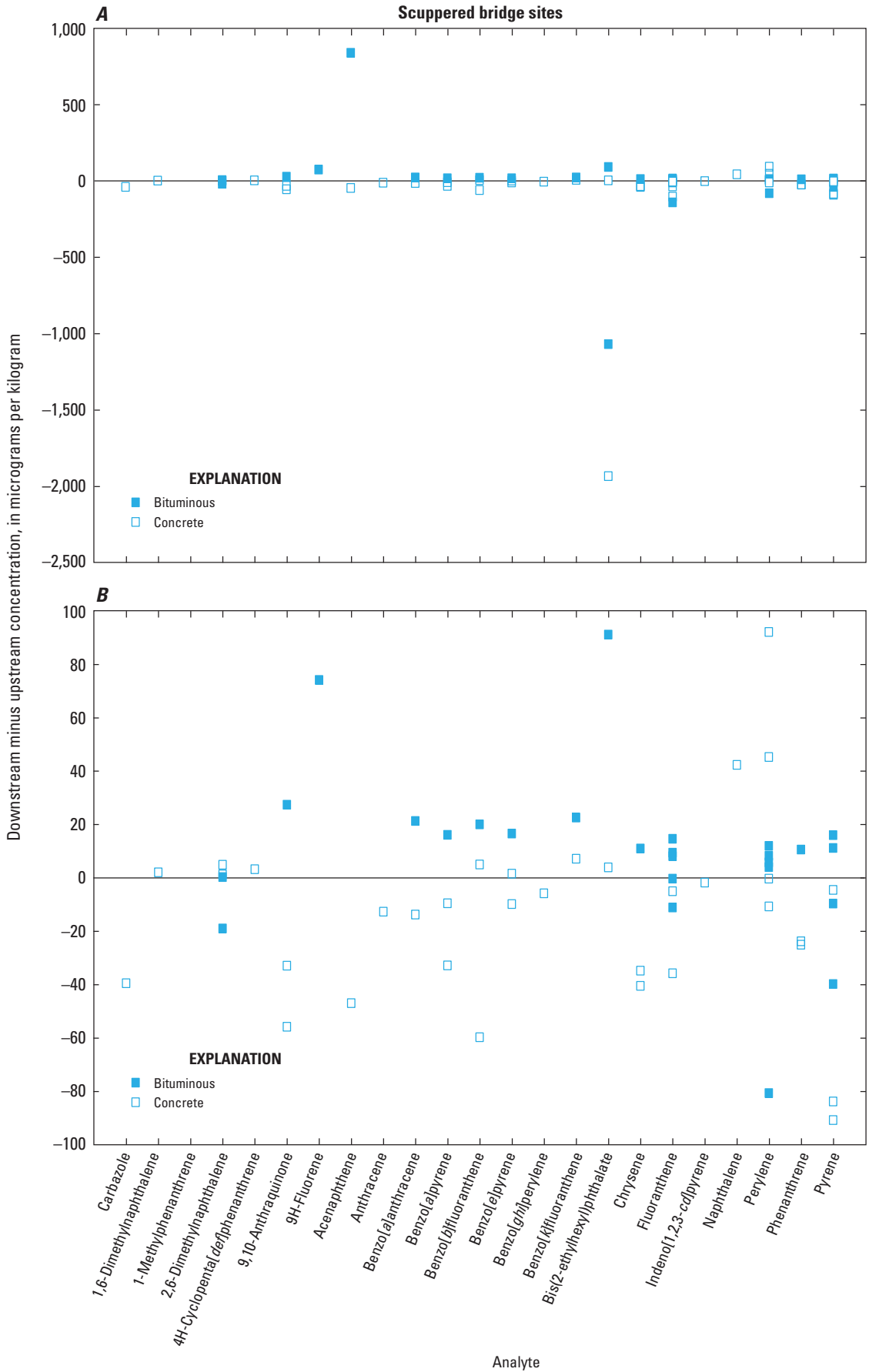


Figure 29. Downstream minus upstream concentration differences for (A) all data, and (B) data focusing near the zero line for semivolatile organic compounds in bed sediment at scuppered bridge sites, bridge sites with best management practices, and scuppered sites with reverse flow.

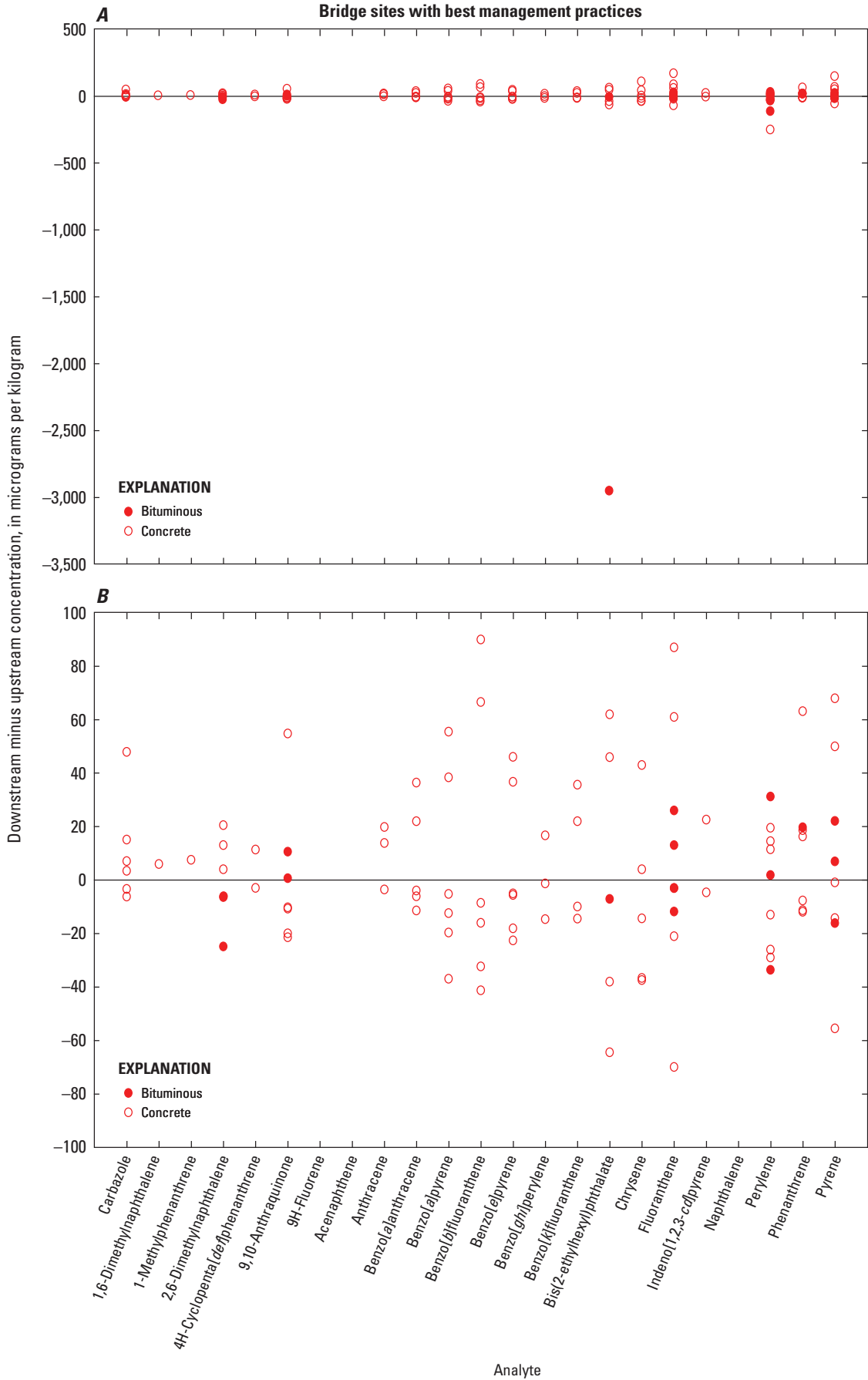


Figure 29 (Continued). Downstream minus upstream concentration differences for (A) all data, and (B) data focusing near the zero line for semivolatile organic compounds in bed sediment at scuppered bridge sites, bridge sites with best management practices, and scuppered sites with reverse flow.

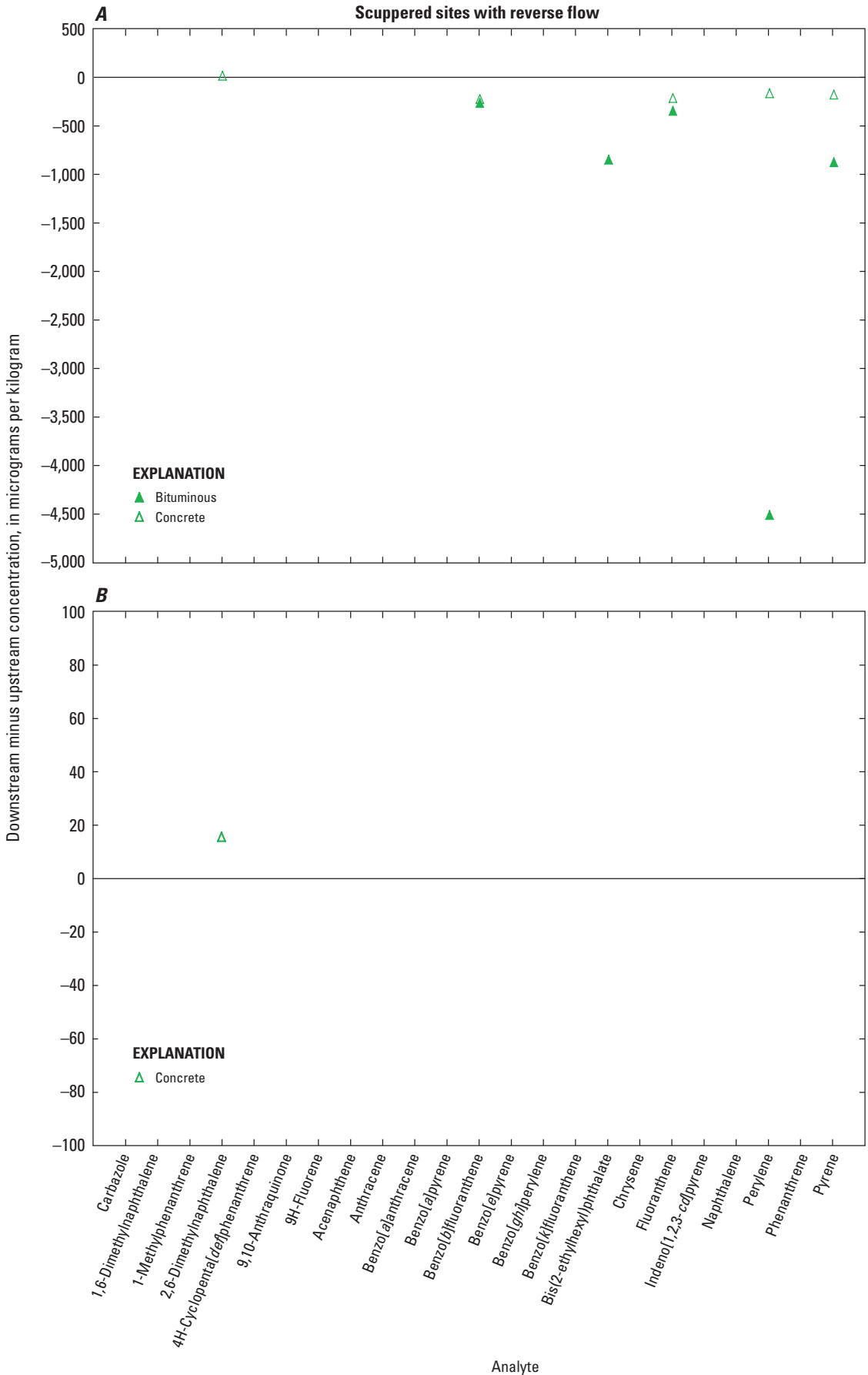


Figure 29 (Continued). Downstream minus upstream concentration differences for (A) all data, and (B) data focusing near the zero line for semivolatile organic compounds in bed sediment at scuppered bridge sites, bridge sites with best management practices, and scuppered sites with reverse flow.

Boylston Creek, bridge 870106) out of nine in the category (scuppered, bitumen). Thus, any conclusion about the bridge decks being a major source of those compounds in those bed sediments was tenuous at best. Finally, there were no obvious patterns related to urban versus rural bridges nor were there relations with AADT (data not shown). A summary of all SVOC concentrations in all bed sediment samples collected is presented in table A8 of the appendix.

Summary and Conclusions

Roadway runoff, defined as any runoff that is generated from within transportation rights-of-way, has been identified as one of several pollutant source categories that may contribute to surface-water impairment. The proximity and direct connection between bridge runoff and streams have facilitated most regulatory agencies throughout the United States to implement stormwater management criteria for bridges. On July 1, 2008, the North Carolina General Assembly passed House Bill 2436, Session Law 2008-107, Stormwater Runoff from Bridges Section 25.18.(a,b,c). This bill requires the NCDOT to select 50 bridges for study of the effects of stormwater runoff from bridges over waterways and report the results to the Joint Legislative Transportation Oversight Committee. The NCDOT collaborated with the USGS to address one of the main goals of the bill, which was to characterize bridge deck runoff quality and quantity using scientifically accepted methods.

The investigation measured bridge deck runoff from 15 bridges across North Carolina, which represented a range of ecoregion, land-use, and climatic conditions, a range of AADT, and a range in size. Runoff from both concrete deck and asphalt (bituminous) deck bridges was sampled. At least 12 runoff events were sampled at each bridge during the study. Streams at four bridge deck runoff sites were sampled intensively to estimate annual loadings and yields. Samples were analyzed for a wide range of constituents, including metals, nutrients, major ions, oil and grease, total phosphorus, total suspended solids, suspended solids concentration, and SVOCs. Both dissolved and total recoverable concentrations of metals and nutrients were measured. Streambed sediment quality was measured from both the upstream and downstream reaches of 30 bridges, 14 of which were the bridge deck runoff monitoring sites and 16 were at bridges in which runoff discharged from scuppers directly into the stream. Bed sediment was analyzed for total nutrients and metals and total recoverable SVOCs.

For the purposes of this study to evaluate water quality associated with bridge deck runoff, POCs were first defined by the URS Corporation as any monitored analyte whose maximum measured concentration exceeds the most stringent threshold from available local and nationally recognized surface-water-quality criteria or environmental datasets. Additionally, a few analytes were designated as POCs despite

the lack of published thresholds because they are known to negatively affect aquatic habitats. Given that chemical analysis for 112 analytes was conducted for the study, the benefit of the POC determination was to eliminate analytes that do not pose a substantial risk of receiving stream impairment and focus the data analysis and interpretation and load computations on those analytes that were most likely to have an adverse effect. A total of 29 POCs were identified in the study using the criteria established by the URS Corporation to be consistent with their approach, which the USGS neither endorses nor refutes. There were 10 metals, 14 SVOCs, pH, total nitrogen, total phosphorus, and total suspended solids.

Bias, precision, and representativeness were assessed for all sample types in the field with replicates, splits, and blanks and in the laboratory with replicates, blanks, standards, performance solutions, and comparisons to known material concentrations. For water samples from bridge decks and stream samples, POCs were found in only 2 percent of all the analyses of the 48 blanks and generally at low levels that likely did not compromise data analysis. Replicate analyses of POCs generally had average relative percent difference values of less than about 20 percent, and spikes revealed reasonable recoveries for most SVOCs. For bed sediment samples, analyses of inorganic analytes in field replicates, splits, and analytical replicates all had average relative percent difference values less than about 15 percent, and the precision was largely associated with the analytical step. Thus, sampling and handling generally did not introduce variability. Analyte concentrations measured in known concentration materials were generally within about 15 percent of the target value. Replicate analyses of SVOC concentrations generally were less than about 20 percent (average relative percent difference), and there was a reasonable recovery of most SVOCs given this type of analysis.

To evaluate if any statistically significant relation (at the 95-percent confidence interval) exists between concentrations of POCs in bridge deck runoff samples and areal sources, incidence over the year, roadway setting, or surface type, the concentration data for the metal and nutrient POCs were grouped by ecoregion, season, official NCDOT roadway classification (rural or urban), and wearing surface (concrete or asphalt) for statistical comparison testing. Statistical analyses for the PAH and phthalate compounds determined to be POCs were not performed because they either were detected in less than eight of the samples or all of the concentrations were estimated to be less than the long-term method detection limit.

With the exception of arsenic, the Coastal Plain samples had statistically lower concentrations than samples from the Blue Ridge and there were no statistical differences in concentrations for cadmium, copper, lead, total nitrogen, total phosphorus, pH, and zinc. The Coastal Plain sites had statistically lower concentrations than samples from the Piedmont ecoregion except for arsenic and there were no statistical differences in concentrations for aluminum, manganese, iron, nickel, total nitrogen, total phosphorus, pH, and zinc. The Blue Ridge samples had statistically higher concentrations than

the Piedmont samples except for copper and there were no statistical differences in concentrations for arsenic, cadmium, manganese, mercury, nickel, total phosphorus, pH, total suspended solids, and zinc. In the case of the metals, this may have reflected differences in soil mineralogy between these ecoregions.

In terms of seasons, POC concentrations were statistically higher in winter compared to summer and fall, except for dissolved cadmium, copper, lead, zinc, and total recoverable mercury (which were not statistically different), pointing to reduced volatilization at lower temperatures and higher total suspended solids concentrations in the winter (likely from deicing treatments) as potential explanations. With the exception of pH and total suspended solids (both higher in the winter), the winter and spring POC concentrations were not statistically different.

Statistical testing revealed statistically higher concentrations in runoff from urban bridges than rural bridges for aluminum, cadmium, copper, iron, lead, manganese, nickel, and total suspended solids. There were no significant differences between rural and urban bridges for total nitrogen, total phosphorus, arsenic, zinc, and mercury. Although the statistical testing did not indicate that the urban sites contributed statistically significant higher concentrations for all metals, they were detected more often in samples collected from urban sites than rural sites. Visual inspection of the rural and urban data indicates that appreciably higher levels of all SVOCs were measured at the urban sites compared to the rural sites.

The analysis of POCs and bridge surface type (concrete and asphalt) revealed that the runoff concentrations, except for lead and zinc, were statistically higher from concrete bridges than asphalt bridges, and there were no statistical differences in concentrations for arsenic, cadmium, mercury, and total nitrogen. When interpreting these results of the surface type analysis, it should be noted that all six of the asphalt bridges were classified as rural, and the concrete bridges consisted of three rural and six urban classified bridges. Therefore, results may be more reflective of the bridge classification than the bridge surface type. The analysis of surface type would have been greatly enhanced if urban bridges with an asphalt surface type had been included in the study.

There was no strong relation between POC concentrations and AADT or AADT normalized by bridge width. A potential explanation for the lack of a strong relation between AADT and POC concentrations is that few, if any, of the AADTs in the study were high enough to see a relation with POC concentrations. An AADT of about 30,000 vehicles tends to separate sites with relatively low and high concentrations of many analytes. The selection process for monitoring sites included an analysis of the AADT frequency distributions in North Carolina and only about 1 percent of bridges in North Carolina have AADT volumes in excess of 30,000 vehicles. Because of the small percentage of bridges in North Carolina with AADT volumes in excess of 30,000 vehicles and the extremely limited number of those bridges with runoff collection systems, only two bridge sites with an AADT volume

greater than 30,000 (Mallard Creek and Mango Creek) were included in the study. The remaining sites had lower AADT values that ranged from 400 to 26,000 vehicles.

The POC concentrations for all samples collected at the stream sites were grouped by season to determine if a significant relation between concentrations and season existed. Unlike results for the bridge decks, the values did not vary much between seasons. Thus, the source of these POCs to the streams did not appear to have a strong seasonal component. Many of the metal and nutrient (both total nitrogen and total phosphorus) concentrations were elevated during storms at most stream sites. There were considerably less detections of SVOCs as POCs in the streams during both routine and storm conditions compared to the bridge deck runoff samples. The SVOCs were detected in only 2 percent of the routine stream samples and were dominated by pyrogenic PAHs as was the case for deck runoff. There was a sixfold increase in the number of SVOC detections during storm conditions compared to that for base-flow conditions though the compound suites were similar.

The effects of bridge deck runoff were evaluated by (1) comparing constituent concentrations, loads, and yields in the bridge deck stormwater from the 15 monitoring bridges and receiving streams at the four stream monitoring sites and (2) estimating rate of dilution of bridge deck runoff downstream from the discharge point for the four stream monitoring sites to identify the zone of maximum effect and the relative reduction of concentration due to dilution. Results of the statistical testing and comparisons of the bridge deck runoff and stream concentrations indicate that the bridge deck runoff concentrations were only statistically higher than the corresponding stream (routine and storm) concentrations for 36 percent of the comparisons. The PAHs were not included in the statistical analysis because of an insufficient number of detections in the stream samples. Thus, with the exceptions of dissolved copper and zinc and total recoverable nickel concentrations, which were consistently higher in bridge deck runoff, the bridge deck runoff concentrations of the POCs at all sites were similar to those measured in the receiving streams at the four stream sampling sites. However, even for dissolved copper and zinc and total recoverable nickel, there are instances where the maximum median stream concentration exceeded the median concentration for some of the bridge deck runoff sites.

The comparisons of the bridge deck and stream loads indicate that all the bridge deck runoff loads were lower (and generally orders of magnitude lower) than the stream loads for all POCs. Given the similarity between the concentrations, it is not surprising that the comparison of the bridge deck and stream sampling period loads indicates that the bridge deck runoff loads are typically orders of magnitude lower than the stream loads at all sites. The inverse was true for total yields for each of the POCs in pounds per acre of drainage area. The bridge deck runoff yields were generally higher than the yields from the four stream sites for all the POCs. The bridge deck runoff yields data can be used to estimate loads at other

bridges with similar characteristics and provide planning-level estimates of the contributing total load from all highways in a watershed. The effect of bridge deck runoff loads on receiving waters should also be evaluated in light of the bioassays, which only showed potential ecological effects for one bridge deck runoff sample (collected in the winter), and benthic macroinvertebrate survey results, which revealed no significant difference upstream and downstream from the study bridge sites. The full bioassay and benthic macroinvertebrate survey results are presented in URS Corporation, 2010.

The rate at which bridge deck runoff mixes with and is diluted by the receiving streams was determined by using empirical relations and measured flow conditions at the four gaged stream sites for eight different steady-state hydraulic conditions. The eight samples were selected to include at least one sample per season, if possible, and across a range of stream discharges. Empirical mixing calculations provide an estimate of the distance required for the runoff to become uniformly mixed across the stream, and thus, an estimate of the zone in which effects of bridge runoff are most pronounced. From these calculations, plots of dilution as a function of distance downstream from the bridge and stream concentration and discharge were developed. These plots provide the basis to quantify the differences between maximum constituent concentrations in the bridge deck runoff and concentrations at the point of direct runoff into the stream and of uniform mixing in the receiving stream, which help to illustrate the magnitude and spatial extent of the stormwater effects. The dilution curves were computed by injecting bridge deck runoff concentrations for a subsample of the POCs (total recoverable arsenic, nickel, total nitrogen, total phosphorus and dissolved copper and zinc) into the receiving streams at each stream site for eight different streamflow conditions (base-flow and storm conditions). The dilution curves indicate that the maximum concentration of the runoff plume from the bridge deck, although in many cases appreciably exceeds some water-quality thresholds, is reduced rapidly (generally within 50 ft downstream from the injection point) to the ambient stream concentration and in some cases is actually lower than the stream concentration.

The analysis of the bed sediment quality revealed no obvious downstream increases in inorganic analytes and total organic carbon at the sampled upstream and downstream bridge reaches. Analytes determined in bed sediments were not limited to the POCs, which were identified by exceedance of thresholds for water samples. For SVOCs, downstream minus upstream differences could only be calculated for 16 percent of the possible pairs. Just three compounds (perylene, fluoranthene, and pyrene) accounted for one-third of all the upstream-downstream pairs. Perylene is considered largely diagenetic and the other two are pyrogenic. There was no overall pattern of downstream enrichment of bed sediment with any SVOCs even at the bituminous bridges. Lastly, there were no obvious patterns related to urban versus rural bridges nor was there any relation with AADT. Possible explanations of these results include (1) bridge decks are not contributing

measurable quantities of these analytes to bed sediments, (2) these analytes were efficiently transported downstream or contaminated bed sediment were scoured from the immediate bridge vicinity during high-flow events, (3) the contributing watershed effects on the bed sediment overwhelm any signature that the relatively small bridge deck area contributes or most likely, (4) a combination of all three of the previous possible explanations.

Although this study did not show bridge deck runoff to consistently be a primary source of pollutants to receiving streams, there is an indication that under certain conditions (that is, runoff following deicing treatments into stream base-flow conditions) bridge deck runoff can be a substantial environmental stressor. The data, analysis, and relations associated with this study can be used by the NCDOT to (1) predict the constituent load from a bridge, (2) provide general information regarding the potential effects a bridge may have on its receiving stream or that all highways may have within a watershed, and (3) provide information needed to select the most efficient best management practices at a bridge construction, replacement, or other highway project site.

References Cited

- Akaike, H., 1974, A new look at the statistical model identification: *IEEE Transactions on Automatic Control*, v. 19, no. 6, p. 716–723.
- American Association of State Highway and Transportation Officials (AASHTO), 2009, *AASHTO guidelines for traffic data programs* (2d ed.): Washington, D.C., American Association of State Highway and Transportation Officials.
- Bonn, B.A., 2008, Using the U.S. Geological Survey National Water Quality Laboratory LT-MDL to evaluate and analyze data: U.S. Geological Survey Open-File Report 2008–1227, 73 p.
- Bradu, D., and Mundlak, Y., 1970, Estimation in lognormal linear models: *Journal of the American Statistical Association*, v. 65, p. 198–211.
- Brenton, R.W., and Arnett, T.L., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of dissolved organic carbon by UV-promoted persulfate oxidation and infrared spectrometry: U.S. Geological Survey Open-File Report 92–480, 12 p.
- Burton, G.A., and Pitt, R.E., 2002, *Stormwater effects handbook—A toolbox for watershed managers, scientists, and engineers*: Boca Raton, Florida, Lewis Publishers, CRC Press.

- Clesceri, L.S., Greenberg, A.E., and Eaton, A.D., 1998, High-temperature combustion method 5310 B, Standard methods for the examination of water and wastewater (20th ed.): Washington, D.C., American Public Health Association, American Water Works Association, and Water Environment Federation.
- Cohn, T.A., Caulder, D.L., Gilroy, E.J., Zynjul, L.D., and Summers, R.M., 1992, The validity of a simple statistical model for estimating fluvial constituent loads—An empirical study involving nutrient loads entering Chesapeake Bay: *Water Resources Research*, v. 28, no. 9, p. 2353–2363.
- Cohn, T.A., DeLong, L.L., Gilroy, E.J., Hirsch, R.M., and Wells, D.K., 1989, Estimating constituent loads: *Water Resources Research*, v. 25, no. 5, p. 937–942.
- Driscoll, E.D., Shelley, P.E., and Strecker, E.W., 1990, Pollutant loadings and impacts from highway stormwater runoff, volume III—Analytical investigations and research report: Washington, D.C., Federal Highway Administration Final Report FHWA RD–88–008.
- Duan, N., 1983, Smearing estimate—A nonparametric retransformation method: *Journal of the American Statistical Association*, v. 78, no. 383, p. 605–610.
- Dupuis, T.V., 2002, Assessing the impacts of bridge deck runoff contaminants in receiving waters, volume 1—Final report: Washington, D.C., Transportation Research Board, NCHRP Report 474.
- Edwards, T.K., and Glysson, G.D., 1999, Field methods for measurement of fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. C2, 89 p.
- Federal Interagency Sedimentation Project, 1965a, Sampling with the US DH-48 depth-integrating suspended-sediment sampler, 12 p., accessed May 3, 2011, at <http://fisp.wes.army.mil/Instructions%20US%20DH-48%20001010.PDF>.
- Federal Interagency Sedimentation Project, 1965b, Instructions for sampling with depth-integrating suspended-sediment samplers US D-49 and US DH-59, 6 p., accessed May 3, 2011, at <http://fisp.wes.army.mil/Report%20%20US%20D-49%20and%20US%20DH-59%20Instructions.pdf>.
- Federal Interagency Sedimentation Project, 2001, Operator's manual of the US DH-81 depth-integrating suspended-sediment sampler, 23 p., accessed May 3, 2011, at http://fisp.wes.army.mil/Instructions%20US_DH-81_010612.pdf.
- Fischer, H.B., List, E.J., Koh, R.C.Y., Imberger, J., and Brooks, N.H., 1979, Mixing in inland and coastal waters: San Diego, California, Academic Press, Inc., 483 p.
- Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125, 217 p.
- Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.
- Garbarino, J.R., and Damrau, D.L., 2001, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of organic plus inorganic mercury in filtered and unfiltered natural water with cold vapor-atomic fluorescence spectrometry: U.S. Geological Survey Water-Resources Investigations Report 01–4132, 16 p.
- Garbarino, J.R., Kanagy, L.K., and Cree, M.E., 2006, Determination of elements in natural-water, biota, sediment, and soil samples using collision/reaction cell inductively coupled plasma–mass spectrometry: U.S. Geological Survey Techniques and Methods 5–B1, 88 p.
- Garbarino, J.R., and Struzeski, T.M., 1998, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of elements in whole-water digests using inductively coupled plasma–optical emission spectrometry and inductively coupled plasma–mass spectrometry: U.S. Geological Survey Open-File Report 98–165, 101 p.
- Gehan, E.A., 1965, A generalized Wilcoxon test for comparing arbitrarily singly censored samples: *Biometrika*, v. 52, p. 203–213.
- Gilroy, E.J., Hirsch, R.M., and Cohn, T.A., 1990, Mean square error of regression-based constituent transport estimates: *Water Resources Research*, v. 26, p. 2069.
- Granato, G.E., 2003, National highway runoff water-quality data and methodology synthesis, volume III—Availability and documentation of published information of synthesis of regional or national highway-runoff quality data: Federal Highway Administration Publication (FHWA–EP–03–056), 71 p.
- Granato, G.E., 2007, Stochastic Empirical Loading and Dilution Model (SELDM): U.S. Geological Survey and the Federal Highway Administration, National highway runoff water-quality data and methodology synthesis, accessed February 16, 2011, at <http://ma.water.usgs.gov/FHWA/SELDM.htm>.
- Granato, G.E., and Cazenias, P.A., 2009, Highway-runoff database (HRDB version 1.0)—A data warehouse and pre-processor for the stochastic empirical loading and dilution model: U.S. Department of Transportation, Federal Highway Administration FHWA–HEP–09–004, 57 p.

- Griffith, G.E., Omernik, J.M., Comstock, J.A., Schafale, M.P., McNab, W.H., Lenat, D.R., MacPherson, T.F., Glover, J.B., and Shelburne, V.B., 2002, Ecoregions of North Carolina and South Carolina (color poster with map, descriptive text, summary tables, and photographs): U.S. Geological Survey, map scale 1:1,500,000.
- Guy, H.P., 1969, Laboratory theory and methods for sediment analysis: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. C1, 58 p.
- Harned, D.A., 1987, Effects of highway runoff on streamflow and water quality in the Sevenmile Creek basin, a rural area in the Piedmont Province of North Carolina, July 1981 to July 1982: U.S. Geological Survey Water-Supply Paper 2329, 33 p.
- Helsel, D.R., 2005, Nondetects and data analysis—Statistics for censored environmental data: New York, John Wiley and Sons, 250 p.
- Hem, J.D., 1970, Study and interpretation of the chemical characteristics of natural water (2d ed.): U.S. Geological Survey Water-Supply Paper 1473, 363 p.
- Horowitz, A.J., Elrick, K.A., and Smith, J.J., 2001, Estimating suspended sediment and trace element fluxes in large river basins, Methodological considerations as applied to the NASQAN Program: Hydrological Processes, v. 15, p. 1107–1132.
- Irwin, G.A., and Losey, G.T., 1978, Water-quality assessment of runoff from a rural highway bridge near Tallahassee, Florida: U.S. Geological Survey Water-Resources Investigations Report 79–1, 27 p.
- Jongedyk, H., 1999, FHWA environmental technology brief—Is highway runoff a serious problem?: Washington D.C., Federal Highway Administration, FHWA–RD–98–079, accessed November 23, 2010, at <http://www.fhwa.dot.gov/publications/research/infrastructure/structures/98079/runoff.cfm>.
- Kayhanian, M., Singh, A., Suverkropp, C., and Borroum, S., 2003, Impact of annual average daily traffic on highway runoff pollutant concentrations: Journal of Environmental Engineering, v. 129, no. 11, p. 975–990.
- Kayhanian, M., Suverkropp, C., Ruby, A., and Tsay, K., 2007, Characterization and prediction of highway runoff constituent event mean concentration: Journal of Environmental Management, v. 85, no. 1, p. 279–295.
- Kruskal, W.H., and Wallis, W.A., 1952, Use of ranks in one-criterion variance analysis: Journal of the American Statistical Association, v. 47, no. 260, p. 583–621.
- Lopes, T.J., and Dionne, S.G., 1998, A review of semivolatile and volatile organic compounds in highway runoff and urban stormwater: U.S. Geological Survey Open-File Report 98–409, 19 p.
- Malina, J.F., Barrett, M.E., Jackson, A., and Kramer, T., 2005, Characterization of stormwater runoff from a bridge deck and approach highway, effects on receiving water quality: Center for Transportation Research, University of Texas at Austin, Federal Highway Administration Publication (FHWA/TX–06/0–4543–1), 88 p.
- Mallows, C.L., 1973, Data analysis in a regression context, in Thompson, W.O., and Cady, F.B., eds., Proceedings of University of Kentucky Conference on Regression with a Large Number of Predictor Variables: Department of Statistics, University of Kentucky.
- Mann, H.B., and Whitney, D.R., 1947, On a test of whether one of two random variables is stochastically larger than the other: Annals of Mathematical Statistics, v. 18, no. 1, p. 50–60, accessed October 13, 2011, at http://projecteuclid.org/DPubS/Repository/1.0/Disseminate?view=body&id=pdf_1&handle=euclid.aoms/1177730491.
- Marsalek, J., Brownlee, B., Mayer, T., Lawal, S., and Larkin, G.A., 1997, Heavy metals and PAHs in stormwater runoff from the Skyway Bridge, Burlington, Ontario: Water Quality Research Journal of Canada, v. 32, no. 4, p. 815–827.
- McKenzie, D.J., and Irwin, G.A., 1983, Water-quality assessment of stormwater runoff from a heavily used urban highway bridge in Miami, Florida: U.S. Geological Survey Water-Resources Investigations Report 83–4153, 45 p.
- Mueller, D.S., and Wagner, C.R., 2009, Measuring discharge with acoustic Doppler current profilers from a moving boat: U.S. Geological Survey Techniques and Methods 3A–22, 71 p. (also available at <http://pubs.usgs.gov/tm/3a22/>).
- North Carolina Department of Environment and Natural Resources, 2003, Assessment report—Biological impairment in the Upper Swift Creek Watershed: Raleigh, North Carolina Department of Environment and Natural Resources, Division of Water Quality, Planning Branch.
- North Carolina Department of Environment and Natural Resources, 2007, Surface water and wetlands standards: Raleigh, North Carolina Office of Administrative Hearings, accessed April 12, 2010, at http://portal.ncdenr.org/c/document_library/get_file?p_l_id=38446&folderId=285750&name=DLFE-8513.pdf.
- North Carolina Department of Environment and Natural Resources, 2010, NC and EPA criteria table: Raleigh, North Carolina Division of Water Quality, accessed October 13, 2011, at http://portal.ncdenr.org/c/document_library/get_file?p_l_id=38446&folderId=521751&name=DLFE-14919.pdf.

- North Carolina Division of Emergency Management, Floodplain Mapping Program, 2002, NC Floodplain Mapping—Durham County, 20 ft Digital Elevation Model, May 2002, v. 1, no. 1: Cary, North Carolina, Watershed Concepts.
- North Carolina General Assembly, 2008, The Current Operations and Capital Improvements Appropriations Act of 2007, Session Law 2008-107, House Bill 2436, Session 2007, approved July 16, 2008, 220 p., accessed October 13, 2011, at <http://www.ncga.state.nc.us/sessions/2007/bills/house/pdf/h2436v9.pdf>.
- O'Dell, J.W., ed., 1993, Method 365.1, Determination of phosphorus by semi-automated colorimetry: U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, 17 p.
- Page, D.S., Boehm, P.D., Douglas, G.S., Bence, A.E., Burns, W.A., and Mankiewicz, P.J., 1999, Pyrogenic polycyclic aromatic hydrocarbons in sediment record past human activity—A case study in prince William Sound, Alaska: *Marine Pollution Bulletin*, v. 38, no. 4, p. 247–260.
- Patton, C.J., and Truitt, E.P., 2000, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of ammonium plus organic nitrogen by a Kjeldahl digestion method and an automated photometric finish that includes digest cleanup by gas diffusion: U.S. Geological Survey Open-File Report 00–170, 31 p.
- Rantz, S.E., and others, 1982, Measurement and computation of streamflow, volumes 1 and 2: U.S. Geological Survey Water-Supply Paper 2175, 631 p.
- Runkel, R.L., Crawford, C.G., and Cohn, T.A., 2004, Load Estimator (LOADEST)—A FORTRAN program for estimating constituent loads in streams and rivers: U.S. Geological Survey Techniques and Methods, book 4, chap. A5, 69 p.
- Sansalone, J.J., and Buchberger, S.G., 1997, Partitioning and first flush of metals in urban roadway storm water: *Journal of Environmental Engineering*, v. 123, no. 2, p. 134–143.
- SAS Institute Inc., 1999, SAS procedures guide, version 8, volumes 1 and 2: Cary, North Carolina, SAS Institute Inc., 1563 p.
- Shelton, L.R., and Capel, P.D., 1994, Guideline for collecting and processing samples of stream bed sediment for analysis of trace elements and organic contaminants for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94–458, 20 p.
- Slack, J.R., Lorenz, D.L., and others, 2003, USGS library for S-PLUS for Windows, release 2: U.S. Geological Survey Open-File Report 2003–357, accessed in December 2007 at <http://pubs.er.usgs.gov/usgspubs/ofr/ofr03357> [release 2.1 was available in January 2008 at <http://water.usgs.gov/software/S-PLUS/>].
- Smith, K.P., 2002, Effectiveness of three best management practices for highway-runoff quality along the southeast expressway, Boston, Massachusetts: U.S. Geological Survey Water-Resources Investigations Report 02–4059, 62 p.
- Smith, K.P., and Granato, G.E., 2010, Quality of stormwater runoff discharged from Massachusetts highways, 2005–07: U.S. Geological Survey Scientific Investigations Report 2009–5269, 198 p., with CD-R (also available at <http://pubs.usgs.gov/sir/2009/5269/>).
- Stoker, Y.E., 1996, Effectiveness of a stormwater collection and detention system for reducing constituent loads from bridge runoff in Pinellas County, Florida: U.S. Geological Survey Open-File Report 96–484, 38 p.
- Texas Commission on Environmental Quality (TCEQ), 2000, Texas surface water quality standards, 30 TAC 307, Austin, Texas: Texas Secretary of State, accessed April 13, 2010, at [http://info.sos.state.tx.us/pls/pub/readtac\\$ext.TacPage?sl=R&app=9&p_dir=&p_rloc=&p_tloc=&p_ploc=&pg=1&p_tac=&ti=30&pt=1&ch=307&rl=6](http://info.sos.state.tx.us/pls/pub/readtac$ext.TacPage?sl=R&app=9&p_dir=&p_rloc=&p_tloc=&p_ploc=&pg=1&p_tac=&ti=30&pt=1&ch=307&rl=6).
- Tukey, J.W., 1977, *Exploratory data analysis*: Reading, Massachusetts, Addison-Wesley Publishing, 506 p.
- Turnipseed, D.P., and Sauer, V.B., 2010a, Discharge measurements at gaging stations: U.S. Geological Survey Techniques and Methods, book 3, chap. A8, 87 p. (also available at <http://pubs.usgs.gov/tm/tm3-a8/>).
- Turnipseed, D.P., and Sauer, V.B., 2010b, Stage measurements at gaging stations: U.S. Geological Survey Techniques and Methods, book 3, chap. A7, 45 p. (also available at <http://pubs.usgs.gov/tm/tm3a7/>).
- URS Corporation, 2010, Stormwater runoff from bridges, Final report to North Carolina Joint Legislation Transportation Committee, prepared for the North Carolina Department of Transportation, Raleigh, North Carolina, 262 p., accessed October 13, 2011, at <http://www.ncdot.org/doh/preconstruct/highway/hydro/pdf/StormwaterRunofffromBridgesFinalReport.pdf>.
- U.S. Environmental Protection Agency, 1999, Method 1664, Revision A, n-hexane extractable material (HEM; oil and grease) and silica gel treated n-hexane extractable material (SGT-HEM; non-polar material) by extraction and gravimetry: U.S. Environmental Protection Agency, EPA–821–R–98–002.

- U.S. Environmental Protection Agency, 2007a, Biotic Ligand Model Windows Interface, version 2.2.1, User's guide and reference manual: Mahwah, New Jersey, HydroQual, Inc., prepared for the U.S. Environmental Protection Agency.
- U.S. Environmental Protection Agency, 2007b, Copper aquatic life criteria supplementary training materials: U.S. Environmental Protection Agency, Office of Science and Technology, Standards and Health Protection Division, accessed December 10, 2009, at <http://www.epa.gov/waterscience/criteria/copper/faq/data-requirements.pdf>.
- U.S. Environmental Protection Agency, 2009, National recommended water quality criteria: U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology, accessed October 13, 2011, at <http://www.epa.gov/waterscience/criteria/wqctable/>.
- U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9, available online at <http://pubs.water.usgs.gov/twri9A>.
- U.S. Geological Survey, 2006a, Collection, quality assurance, and presentation of precipitation data: U.S. Geological Survey, Office of Surface Water Technical Memorandum No. 2006.01 (revised December 2009), 29 p., accessed October 20, 2011, at: http://water.usgs.gov/admin/memo/SW/sw06.012_Revised_122009.pdf.
- U.S. Geological Survey, 2006b, Collection of water samples, version 2.0: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, accessed October 20, 2011, at <http://pubs.water.usgs.gov/twri9A4/>.
- U.S. Geological Survey, 2008, Acoustic Doppler current profiler applications used in rivers and estuaries by the U.S. Geological Survey: U.S. Geological Survey Fact Sheet 2008–3096, 4 p., available online at <http://pubs.usgs.gov/fs/2008/3096/pdf/fs2008-3096.pdf>.
- U.S. Geological Survey, 2010a, North Carolina District operating procedures and guidelines, Chapter A—Quality-assurance plan for water-resources activities of the North Carolina Water Science Center, accessed November 1, 2010, at <http://nc.water.usgs.gov/usgs/info/qaplan/>.
- U.S. Geological Survey, 2010b, North Carolina District operating procedures and guidelines, Chapter B—Quality-assurance plan for water-quality activities of the North Carolina Water Science Center, accessed November 1, 2010, at <http://nc.water.usgs.gov/usgs/info/qaplan/quality.html>.
- Van Hassel, J.H., Ney, J.J., and Garling, D.L., Jr., 1980, Heavy metals in a stream ecosystem at sites near highways: Transactions of the American Fisheries Society, v. 109, no. 6, p. 636–643.
- Wanielista, M.P., Yousef, Y.A., and Christopher, J.E., 1980, Management of runoff from highway bridges: Florida Department of Transportation Final Report, FL–ER–10–80, 140 p.
- Yousef, Y.A., Wanielista, M.P., Hvitved-Jacobsen, T., and Harper, H.H., 1984, Fate of heavy metals in stormwater runoff from highway bridges: Science of the Total Environment, v. 33, p. 233–244.
- Zaugg, S.D., Burkhardt, M.R., Burbank, T.L., Olsen, M.C., Iverson, J.L., and Schroeder, M.P., 2006, Determination of semivolatile organic compounds and polycyclic aromatic hydrocarbons in solids by gas chromatography/mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, chap. B3, 44 p.
- Zellhoefer, W.F., 1989, Investigation of water quality impacts of stormwater runoff from Robert E. Lee bridge, Richmond, Virginia: Virginia Department of Transportation, 40 p.

Table 5. Analytes measured in water and bed sediment samples.

[Parameters of concern are highlighted in **bold**. Method of instrumentation: ICP–MS, inductively coupled plasma–mass spectrometry; cICP–MS, collision/reaction cell inductively coupled plasma–mass spectrometry; ICP–AES, inductively coupled plasma–atomic emission spectrometry; CV–AFS, cold vapor–atomic fluorescence spectrometry; HEM, n-hexane extractable material; SGT–HEM, silica gel treated–n-hexane extractable material (non-polar fraction); GC–MS, gas chromatography–mass spectrometry; AAS, atomic absorption spectrometry; CV–AAS, cold vapor–atomic absorption spectrometry; CNS/TCD, carbon-nitrogen-sulfur analyzer with thermal conductivity detection; CS, carbon-sulfur analyzer. Report level unit: mg/L, milligram per liter; µg/L, microgram per liter; µS/cm, microsiemens per centimeter; Wt %, weight percent; mg/kg, milligram per kilogram; µg/kg, microgram per kilogram. Reporting level type: lrl, laboratory reporting limit; irl, interim reporting level; mrl, minimum reporting limit. Other abbreviations: Σ, summation; N, nitrogen, NH₃, ammonia; NO₂, nitrite; NO₃, nitrate; <, less than; µm, micron. Dashes indicate no data or not detected]

Analyte	Method instrumentation	CAS number ¹	Reporting level			Reference
			Value	Unit	Type	
Water – dissolved						
Alkalinity	Fixed endpoint titration	471-34-1	8	mg/L	lrl	Fishman and Friedman (1989)
Aluminum	ICP–MS	7429-90-5	5.6	µg/L	lrl	Garbarino and Struzeski (1998)
Arsenic	cICP–MS	7440-38-2	0.04	µg/L	lrl	Garbarino and others (2006)
Bromide ²	Ion Chromatography	24959-67-9	0.02	mg/L	irl	Fishman and Friedman (1989)
Cadmium	ICP–MS	7440-43-9	0.04	µg/L	lrl	Garbarino and Struzeski (1998)
Calcium ²	ICP–AES	7440-70-2	0.04	mg/L	lrl	Fishman (1993)
Carbon, organic	Infrared Spectrometry	---	0.4(0.66) ³	mg/L	lrl	Brenton and Arnett (1993)
Chloride ²	Ion Chromatography	16887-00-6	0.12	mg/L	lrl	Fishman and Friedman (1989)
Chromium	cICP–MS	7440-47-3	0.42	µg/L	lrl	Garbarino and others (2006)
Copper	cICP–MS	7440-50-8	1.4	µg/L	lrl	Garbarino and others (2006)
Dissolved solids, total ²	Gravimetry	---	10	mg/L	mrl	Fishman and Friedman (1989)
Iron	ICP–AES	7439-89-6	9.2	µg/L	lrl	Fishman (1993)
Lead	ICP–MS	7439-92-1	0.03	µg/L	lrl	Garbarino and Struzeski (1998)
Magnesium ²	ICP–AES	7439-95-4	0.02	mg/L	lrl	Fishman (1993)
Manganese	ICP–MS	7439-96-5	0.26	µg/L	lrl	Garbarino and Struzeski (1998)
Mercury	CV–AFS	7439-97-6	0.01	µg/L	lrl	Garbarino and Damrau (2001)
Nickel	cICP–MS	7440-02-0	0.36	µg/L	lrl	Garbarino and others (2006)
Nitrogen, NH ₃ as N	Spectrophotometry	7664-41-7	0.02	mg/L	lrl	Fishman (1993)
Nitrogen, NO ₂ + NO ₃ as N ²	Spectrophotometry	---	0.04	mg/L	lrl	Fishman (1993)
Oxygen	Clark cell	7782-44-7	0.0	mg/L	---	U.S. Geological Survey (variously dated)
Palladium	ICP–MS	7440-05-3	1.0	µg/L	mrl	Garbarino and Struzeski (1998)
Phosphorus, o-PO ₄	Spectrophotometry	14265-44-2	0.01	mg/L	lrl	Fishman (1993)
Platinum	ICP–MS	7440-06-3	1.0	µg/L	mrl	Garbarino and Struzeski (1998)
Potassium ²	ICP–AES	7440-09-7	0.06	mg/L	lrl	Fishman and Friedman (1989)
Rhodium	ICP–MS	7440-17-1	1.0	µg/L	mrl	Garbarino and Struzeski (1998)
Selenium	cICP–MS	7782-49-2	0.04	µg/L	lrl	Garbarino and others (2006)
Sodium ²	ICP–AES	7440-23-5	0.1	mg/L	lrl	Fishman (1993)
Sulfate	Ion Chromatography	14808-79-8	0.18	mg/L	lrl	Fishman and Friedman (1989)
Zinc	cICP–MS	7440-66-6	2.8	µg/L	lrl	Garbarino and others (2006)
Water – total recoverable and other						
Aluminum²	ICP–MS	7429-90-5	3.4	µg/L	lrl	Garbarino and Struzeski (1998)
Arsenic²	cICP–MS	7440-38-2	0.18	µg/L	lrl	Garbarino and others (2006)
Cadmium ²	ICP–MS	7440-43-9	0.02	µg/L	lrl	Garbarino and Struzeski (1998)

Table 5. Analytes measured in water and bed sediment samples.—Continued

[Parameters of concern are highlighted in **bold**. Method of instrumentation: ICP–MS, inductively coupled plasma–mass spectrometry; cICP–MS, collision/reaction cell inductively coupled plasma–mass spectrometry; ICP–AES, inductively coupled plasma–atomic emission spectrometry; CV–AFS, cold vapor–atomic fluorescence spectrometry; HEM, n-hexane extractable material; SGT–HEM, silica gel treated–n-hexane extractable material (non-polar fraction); GC–MS, gas chromatography–mass spectrometry; AAS, atomic absorption spectrometry; CV–AAS, cold vapor–atomic absorption spectrometry; CNS/TCD, carbon–nitrogen–sulfur analyzer with thermal conductivity detection; CS, carbon–sulfur analyzer. Report level unit: mg/L, milligram per liter; µg/L, microgram per liter; µS/cm, microsiemens per centimeter; Wt %, weight percent; mg/kg, milligram per kilogram; µg/kg, microgram per kilogram. Reporting level type: lrl, laboratory reporting limit; irl, interim reporting level; mrl, minimum reporting limit. Other abbreviations: Σ, summation; N, nitrogen, NH₃, ammonia; NO₂, nitrite; NO₃, nitrate; <, less than; µm, micron. Dashes indicate no data or not detected]

Analyte	Method instrumentation	CAS number ¹	Reporting level			Reference
			Value	Unit	Type	
Water – total recoverable and other (Continued)						
Carbon, organic ²	Infrared Spectrometry	---	0.6	mg/L	irl	Clesceri and others (1998)
Chromium ²	cICP–MS	7440-47-3	0.12	µg/L	lrl	Garbarino and others (2006)
Copper ²	cICP–MS	7440-50-8	1	µg/L	lrl	Garbarino and others (2006)
Iron²	ICP–AES	7439-89-6	6	µg/L	lrl	Fishman (1993)
Lead ²	ICP–MS	7439-92-1	0.06	µg/L	lrl	Garbarino and Struzeski (1998)
Manganese²	ICP–MS	7439-96-5	0.8	µg/L	lrl	Garbarino and Struzeski (1998)
Mercury²	CV–AFS	7439-97-6	0.01	µg/L	lrl	Garbarino and Damrau, 2001
Nickel²	cICP–MS	7440-02-0	0.12	µg/L	lrl	Garbarino and others (2006)
Nitrogen, NH ₃ + Organic N ²	Spectrophotometry	17778-88-0	0.1	mg/L	lrl	Patton and Truitt, 2000
Nitrogen, total	Σ(Organic N, NH₃, NO₂, NO₃)	---	0.14	mg/L	lrl	---
Oil+grease	Gravimetry (HEM)	---	5	mg/L	mrl	U.S. Environmental Protection (1999)
Palladium	ICP–MS	7440-05-3	1.0	µg/L	mrl	Garbarino and Struzeski (1998)
Petroleum hydrocarbons	Gravimetry (SGT–HEM)	---	5	mg/L	mrl	U.S. Environmental Protection (1999)
pH	Glass electrode	---	---	---	---	U.S. Geological Survey (variously dated)
Phosphorus, total²	Spectrophotometry	7723-14-0	0.01	mg/L	lrl	O'Dell (1993)
Platinum	ICP–MS	7440-06-3	1.0	µg/L	mrl	Garbarino and Struzeski (1998)
Suspended solids, total	Gravimetry	---	15	mg/L	mrl	Fishman and Friedman (1989)
Rhodium	ICP–MS	7440-17-1	1.0	µg/L	mrl	Garbarino and Struzeski (1998)
Selenium ²	cICP–MS	7782-49-2	0.1	µg/L	lrl	Garbarino and others (2006)
Specific conductance ²	Wheatstone bridge	---	5	µS/cm	mrl	Fishman and Friedman (1989)
Suspended sediment	Gravimetry	---	1	mg/L	mrl	Guy (1969)
Suspended sediment (percent <62.5 µm)	Gravimetry	---	1	Percent	mrl	Guy (1969)
Zinc ²	cICP–MS	7440-66-6	2	µg/L	irl	Garbarino and others (2006)
Water – total recoverable semivolatile organic compounds ²						
1,2,4-Trichlorobenzene	GC–MS	120-82-1	0.26	µg/L	lrl	Fishman (1993)
1,2-Dichlorobenzene	GC–MS	95-50-1	0.2	µg/L	lrl	Fishman (1993)
1,2-Diphenylhydrazine	GC–MS	122-66-7	0.3	µg/L	lrl	Fishman (1993)
1,3-Dichlorobenzene	GC–MS	541-73-1	0.22	µg/L	lrl	Fishman (1993)
1,4-Dichlorobenzene	GC–MS	106-46-7	0.22	µg/L	lrl	Fishman (1993)
2,4,6-Trichlorophenol	GC–MS	88-06-2	0.34	µg/L	lrl	Fishman (1993)
2,4-Dichlorophenol	GC–MS	120-83-2	0.36	µg/L	lrl	Fishman (1993)

Table 5. Analytes measured in water and bed sediment samples.—Continued

[Parameters of concern are highlighted in **bold**. Method of instrumentation: ICP–MS, inductively coupled plasma–mass spectrometry; cICP–MS, collision/reaction cell inductively coupled plasma–mass spectrometry; ICP–AES, inductively coupled plasma–atomic emission spectrometry; CV–AFS, cold vapor–atomic fluorescence spectrometry; HEM, n-hexane extractable material; SGT–HEM, silica gel treated–n-hexane extractable material (non-polar fraction); GC–MS, gas chromatography–mass spectrometry; AAS, atomic absorption spectrometry; CV–AAS, cold vapor–atomic absorption spectrometry; CNS/TCD, carbon-nitrogen-sulfur analyzer with thermal conductivity detection; CS, carbon-sulfur analyzer. Report level unit: mg/L, milligram per liter; µg/L, microgram per liter; µS/cm, microsiemens per centimeter; Wt %, weight percent; mg/kg, milligram per kilogram; µg/kg, microgram per kilogram. Reporting level type: lrl, laboratory reporting limit; irl, interim reporting level; mrl, minimum reporting limit. Other abbreviations: Σ, summation; N, nitrogen, NH₃, ammonia; NO₂, nitrite; NO₃, nitrate; <, less than; µm, micron. Dashes indicate no data or not detected]

Analyte	Method instrumentation	CAS number ¹	Reporting level			Reference
			Value	Unit	Type	
Water – total recoverable semivolatile organic compounds ² (Continued)						
2,4-Dimethylphenol	GC–MS	105-67-9	0.8	µg/L	lrl	Fishman (1993)
2,4-Dinitrophenol	GC–MS	51-28-5	1.4	µg/L	lrl	Fishman (1993)
2,4-Dinitrotoluene	GC–MS	121-14-2	0.56	µg/L	lrl	Fishman (1993)
2,6-Dinitrotoluene	GC–MS	606-20-2	0.4	µg/L	lrl	Fishman (1993)
2-Chloronaphthalene	GC–MS	91-58-7	0.16	µg/L	lrl	Fishman (1993)
2-Chlorophenol	GC–MS	95-57-8	0.26	µg/L	lrl	Fishman (1993)
2-Nitrophenol	GC–MS	88-75-5	0.4	µg/L	lrl	Fishman (1993)
3,3'-Dichlorobenzidine	GC–MS	91-94-1	0.42	µg/L	lrl	Fishman (1993)
4,6-Dinitro-2-methylphenol	GC–MS	534-52-1	0.76	µg/L	lrl	Fishman (1993)
4-Bromophenylphenylether	GC–MS	101-55-3	0.24	µg/L	lrl	Fishman (1993)
4-Chloro-3-methylphenol	GC–MS	59-50-7	0.55	µg/L	lrl	Fishman (1993)
4-Chlorophenyl phenyl ether	GC–MS	7005-72-3	0.34	µg/L	lrl	Fishman (1993)
4-Nitrophenol	GC–MS	100-02-7	0.51	µg/L	lrl	Fishman (1993)
Acenaphthene	GC–MS	83-32-9	0.28	µg/L	lrl	Fishman (1993)
Acenaphthylene	GC–MS	208-96-8	0.3	µg/L	lrl	Fishman (1993)
Anthracene	GC–MS	120-12-7	0.39	µg/L	lrl	Fishman (1993)
Benz[a]anthracene	GC–MS	56-55-3	0.26	µg/L	lrl	Fishman (1993)
Benzidine	GC–MS	92-87-5	10	µg/L	irl	Fishman (1993)
Benzo[a]pyrene	GC–MS	50-32-8	0.33	µg/L	lrl	Fishman (1993)
Benzo[b]fluoranthene	GC–MS	205-99-2	0.3	µg/L	lrl	Fishman (1993)
Benzo[ghi]perylene	GC–MS	191-24-2	0.38	µg/L	lrl	Fishman (1993)
Benzo[k]fluoranthene	GC–MS	207-08-9	0.3	µg/L	lrl	Fishman (1993)
Bis(2-Chloroethoxy)methane	GC–MS	111-91-1	0.24	µg/L	lrl	Fishman (1993)
Bis(2-Chloroethyl)ether	GC–MS	111-44-4	0.3	µg/L	lrl	Fishman (1993)
Bis(2-chloroisopropyl)ether	GC–MS	108-60-1	0.14	µg/L	lrl	Fishman (1993)
Bis(2-Ethylhexyl)phthalate	GC–MS	117-81-7	2	µg/L	irl	Fishman (1993)
Butylbenzyl phthalate	GC–MS	85-68-7	1.8	µg/L	irl	Fishman (1993)
Chrysene	GC–MS	218-01-9	0.33	µg/L	lrl	Fishman (1993)
Di-n-butyl phthalate	GC–MS	84-74-2	2	µg/L	irl	Fishman (1993)
Di-n-octyl phthalate	GC–MS	117-84-0	0.6	µg/L	lrl	Fishman (1993)
Dibenz[a,h]anthracene	GC–MS	53-70-3	0.42	µg/L	lrl	Fishman (1993)
Diethyl phthalate	GC–MS	84-66-2	0.61	µg/L	lrl	Fishman (1993)
Dimethyl phthalate	GC–MS	131-11-3	0.36	µg/L	lrl	Fishman (1993)
Fluoranthene	GC–MS	206-44-0	0.3	µg/L	lrl	Fishman (1993)
Fluorene	GC–MS	86-73-7	0.33	µg/L	lrl	Fishman (1993)
Hexachlorobenzene	GC–MS	118-74-1	0.3	µg/L	lrl	Fishman (1993)
Hexachlorobutadiene	GC–MS	87-68-3	0.24	µg/L	lrl	Fishman (1993)

Table 5. Analytes measured in water and bed sediment samples.—Continued

[Parameters of concern are highlighted in **bold**. Method of instrumentation: ICP–MS, inductively coupled plasma–mass spectrometry; cICP–MS, collision/reaction cell inductively coupled plasma–mass spectrometry; ICP–AES, inductively coupled plasma–atomic emission spectrometry; CV–AFS, cold vapor–atomic fluorescence spectrometry; HEM, n-hexane extractable material; SGT–HEM, silica gel treated–n-hexane extractable material (non-polar fraction); GC–MS, gas chromatography–mass spectrometry; AAS, atomic absorption spectrometry; CV–AAS, cold vapor–atomic absorption spectrometry; CNS/TCD, carbon–nitrogen–sulfur analyzer with thermal conductivity detection; CS, carbon–sulfur analyzer. Report level unit: mg/L, milligram per liter; µg/L, microgram per liter; µS/cm, microsiemens per centimeter; Wt %, weight percent; mg/kg, milligram per kilogram; µg/kg, microgram per kilogram. Reporting level type: lrl, laboratory reporting limit; irl, interim reporting level; mrl, minimum reporting limit. Other abbreviations: Σ, summation; N, nitrogen, NH₃, ammonia; NO₂, nitrite; NO₃, nitrate; <, less than; µm, micron. Dashes indicate no data or not detected]

Analyte	Method instrumentation	CAS number ¹	Reporting level			Reference
			Value	Unit	Type	
Water – total recoverable semivolatile organic compounds² (Continued)						
Hexachlorocyclopentadiene	GC–MS	77-47-4	0.5	µg/L	lrl	Fishman (1993)
Hexachloroethane	GC–MS	67-72-1	0.24	µg/L	lrl	Fishman (1993)
Indeno[1,2,3-<i>cd</i>]pyrene	GC–MS	193-39-5	0.38	µg/L	lrl	Fishman (1993)
Isophorone	GC–MS	78-59-1	0.26	µg/L	lrl	Fishman (1993)
n-Nitrosodi-n-propylamine	GC–MS	621-64-7	0.4	µg/L	lrl	Fishman (1993)
n-Nitrosodimethylamine	GC–MS	62-75-9	0.24	µg/L	lrl	Fishman (1993)
n-Nitrosodiphenylamine	GC–MS	86-30-6	0.28	µg/L	lrl	Fishman (1993)
Naphthalene	GC–MS	91-20-3	0.22	µg/L	lrl	Fishman (1993)
Nitrobenzene	GC–MS	98-95-3	0.26	µg/L	lrl	Fishman (1993)
Pentachlorophenol	GC–MS	87-86-5	0.6	µg/L	lrl	Fishman (1993)
Phenanthrene	GC–MS	85-01-8	0.32	µg/L	lrl	Fishman (1993)
Phenol	GC–MS	108-95-2	0.28	µg/L	lrl	Fishman (1993)
Pyrene	GC–MS	129-00-0	0.35	µg/L	lrl	Fishman (1993)
2,4,6-Tribromophenol (surrogate) ⁴	GC–MS	118-79-6	---	Percent	---	Fishman (1993)
2-Fluorobiphenyl (surrogate) ⁴	GC–MS	321-60-8	---	Percent	---	Fishman (1993)
Nitrobenzene-d5 (surrogate) ⁴	GC–MS	4165-60-0	---	Percent	---	Fishman (1993)
Phenol-d5 (surrogate) ⁴	GC–MS	4165-62-2	---	Percent	---	Fishman (1993)
Terphenyl-d14 (surrogate) ⁴	GC–MS	1718-51-0	---	Percent	---	Fishman (1993)
Bed sediment – total						
Aluminum	ICP–AES	7429-90-5	0.1	Wt %	lrl	Horowitz and others (2001)
Antimony	Hydride generation/ICP–AES	7440-36-0	0.1	mg/kg	lrl	Horowitz and others (2001)
Arsenic	Hydride generation/ICP–AES	7440-38-2	0.1	mg/kg	lrl	Horowitz and others (2001)
Barium	ICP–AES	7440-39-3	1	mg/kg	lrl	Horowitz and others (2001)
Beryllium	ICP–AES	7440-41-7	0.1	mg/kg	lrl	Horowitz and others (2001)
Cadmium	Flame AAS	7440-43-9	0.1	mg/kg	lrl	Horowitz and others (2001)
Calcium	ICP–AES	7440-70-2	0.1	Wt %	lrl	Horowitz and others (2001)
Carbon, total	CNS analyzer/TCD	7440-44-0	0.1	Wt %	lrl	Horowitz and others (2001)
Carbon, total organic	CS analyzer/Infrared Detection	---	0.1	Wt %	lrl	Horowitz and others (2001)
Chromium	ICP–AES	7440-47-3	1	mg/kg	lrl	Horowitz and others (2001)
Cobalt	ICP–AES	7440-48-4	1	mg/kg	lrl	Horowitz and others (2001)
Copper	ICP–AES	7440-50-8	1	mg/kg	lrl	Horowitz and others (2001)
Iron	ICP–AES	7439-89-6	0.1	Wt %	lrl	Horowitz and others (2001)
Lead	Flame AAS	7439-92-1	1	mg/kg	lrl	Horowitz and others (2001)
Lithium	ICP–AES	7439-93-2	1	mg/kg	lrl	Horowitz and others (2001)
Magnesium	ICP–AES	7439-95-4	0.1	Wt %	lrl	Horowitz and others (2001)
Manganese	ICP–AES	7439-96-5	10	mg/kg	lrl	Horowitz and others (2001)

Table 5. Analytes measured in water and bed sediment samples.—Continued

[Parameters of concern are highlighted in **bold**. Method of instrumentation: ICP–MS, inductively coupled plasma–mass spectrometry; cICP–MS, collision/reaction cell inductively coupled plasma–mass spectrometry; ICP–AES, inductively coupled plasma–atomic emission spectrometry; CV–AFS, cold vapor–atomic fluorescence spectrometry; HEM, n-hexane extractable material; SGT–HEM, silica gel treated–n-hexane extractable material (non-polar fraction); GC–MS, gas chromatography–mass spectrometry; AAS, atomic absorption spectrometry; CV–AAS, cold vapor–atomic absorption spectrometry; CNS/TCD, carbon-nitrogen-sulfur analyzer with thermal conductivity detection; CS, carbon-sulfur analyzer. Report level unit: mg/L, milligram per liter; µg/L, microgram per liter; µS/cm, microsiemens per centimeter; Wt %, weight percent; mg/kg, milligram per kilogram; µg/kg, microgram per kilogram. Reporting level type: lrl, laboratory reporting limit; irl, interim reporting level; mrl, minimum reporting limit. Other abbreviations: Σ, summation; N, nitrogen, NH₃, ammonia; NO₂, nitrite; NO₃, nitrate; <, less than; µm, micron. Dashes indicate no data or not detected]

Analyte	Method instrumentation	CAS number ¹	Reporting level			Reference
			Value	Unit	Type	
Bed sediment – total (Continued)						
Mercury	CV–AAS	7439-97-6	0.01	mg/kg	lrl	Horowitz and others (2001)
Molybdenum	ICP–AES	7439-98-7	1	mg/kg	lrl	Horowitz and others (2001)
Nickel	ICP–AES	7440-02-0	1	mg/kg	lrl	Horowitz and others (2001)
Nitrogen	CNS analyzer/TCD	7727-37-9	0.01	Wt %	lrl	Horowitz and others (2001)
Phosphorus	ICP–AES	7723-14-0	1	mg/kg	lrl	Horowitz and others (2001)
Potassium	ICP–AES	7440-09-7	0.1	Wt %	lrl	Horowitz and others (2001)
Selenium	Hydride generation/AAS	7782-49-2	0.1	mg/kg	lrl	Horowitz and others (2001)
Silver	Flame AAS	7440-22-4	0.05	mg/kg	lrl	Horowitz and others (2001)
Sodium	ICP–AES	7440-23-5	0.1	Wt %	lrl	Horowitz and others (2001)
Strontium	ICP–AES	7440-24-6	1	mg/kg	lrl	Horowitz and others (2001)
Sulfur	ICP–AES	7704-34-9	0.1	Wt %	lrl	Horowitz and others (2001)
Thallium	ICP–AES	7440-28-0	50	mg/kg	lrl	Horowitz and others (2001)
Tin	ICP–AES	7440-31-5	0.1	mg/kg	lrl	Horowitz and others (2001)
Titanium	ICP–AES	7440-32-6	0.01	Wt %	lrl	Horowitz and others (2001)
Uranium	ICP–AES	7440-61-1	50	mg/kg	lrl	Horowitz and others (2001)
Vanadium	ICP–AES	7440-62-2	1	mg/kg	lrl	Horowitz and others (2001)
Zinc	ICP–AES	7440-66-6	1	mg/kg	lrl	Horowitz and others (2001)
Bed sediments – semivolative organic compounds						
1,2,4-Trichlorobenzene	GC–MS	120-82-1	50	µg/kg	irl	Zaugg and others (2006)
1,2-Dimethylnaphthalene	GC–MS	573-98-8	50	µg/kg	irl	Zaugg and others (2006)
1,6-Dimethylnaphthalene	GC–MS	575-43-9	50	µg/kg	irl	Zaugg and others (2006)
1-Methyl-9H-fluorene	GC–MS	1730-37-6	50	µg/kg	irl	Zaugg and others (2006)
1-Methylphenanthrene	GC–MS	832-69-9	50	µg/kg	irl	Zaugg and others (2006)
1-Methylpyrene	GC–MS	2381-21-7	50	µg/kg	irl	Zaugg and others (2006)
2,3,6-Trimethylnaphthalene	GC–MS	829-26-5	50	µg/kg	irl	Zaugg and others (2006)
2,6-Dimethylnaphthalene	GC–MS	581-42-0	50	µg/kg	irl	Zaugg and others (2006)
2-Ethyl-naphthalene	GC–MS	939-27-5	50	µg/kg	irl	Zaugg and others (2006)
2-Methylantracene	GC–MS	613-12-7	50	µg/kg	irl	Zaugg and others (2006)
4H-Cyclopenta[<i>def</i>]phenanthrene	GC–MS	203-64-5	50	µg/kg	irl	Zaugg and others (2006)
Acenaphthene	GC–MS	83-32-9	50	µg/kg	irl	Zaugg and others (2006)
Acenaphthylene	GC–MS	208-96-8	50	µg/kg	irl	Zaugg and others (2006)
Anthracene	GC–MS	120-12-7	50	µg/kg	irl	Zaugg and others (2006)
Anthraquinone	GC–MS	84-65-1	50	µg/kg	irl	Zaugg and others (2006)
Benz[<i>a</i>]anthracene	GC–MS	56-55-3	50	µg/kg	irl	Zaugg and others (2006)
Benzo[<i>a</i>]pyrene	GC–MS	50-32-8	50	µg/kg	irl	Zaugg and others (2006)
Benzo[<i>b</i>]fluoranthene	GC–MS	205-99-2	50	µg/kg	irl	Zaugg and others (2006)
Benzo[<i>e</i>]pyrene	GC–MS	192-97-2	50	µg/kg	irl	Zaugg and others (2006)

Table 5. Analytes measured in water and bed sediment samples.—Continued

[Parameters of concern are highlighted in **bold**. Method of instrumentation: ICP–MS, inductively coupled plasma–mass spectrometry; cICP–MS, collision/reaction cell inductively coupled plasma–mass spectrometry; ICP–AES, inductively coupled plasma–atomic emission spectrometry; CV–AFS, cold vapor–atomic fluorescence spectrometry; HEM, n-hexane extractable material; SGT–HEM, silica gel treated–n-hexane extractable material (non-polar fraction); GC–MS, gas chromatography–mass spectrometry; AAS, atomic absorption spectrometry; CV–AAS, cold vapor–atomic absorption spectrometry; CNS/TCD, carbon-nitrogen-sulfur analyzer with thermal conductivity detection; CS, carbon-sulfur analyzer. Report level unit: mg/L, milligram per liter; µg/L, microgram per liter; µS/cm, microsiemens per centimeter; Wt %, weight percent; mg/kg, milligram per kilogram; µg/kg, microgram per kilogram. Reporting level type: lrl, laboratory reporting limit; irl, interim reporting level; mrl, minimum reporting limit. Other abbreviations: Σ, summation; N, nitrogen, NH₃, ammonia; NO₂, nitrite; NO₃, nitrate; <, less than; µm, micron. Dashes indicate no data or not detected]

Analyte	Method instrumentation	CAS number ¹	Reporting level			Reference
			Value	Unit	Type	
Bed sediments – semivolatile organic compounds (Continued)						
Benzo[<i>ghi</i>]perylene	GC–MS	191-24-2	50	µg/kg	irl	Zaugg and others (2006)
Benzo[<i>k</i>]fluoranthene	GC–MS	207-08-9	50	µg/kg	irl	Zaugg and others (2006)
Bis(2-Ethylhexyl)phthalate	GC–MS	117-81-7	50	µg/kg	irl	Zaugg and others (2006)
Carbazole	GC–MS	86-74-8	50	µg/kg	irl	Zaugg and others (2006)
Chrysene	GC–MS	218-01-9	50	µg/kg	irl	Zaugg and others (2006)
Dibenz[<i>a,h</i>]anthracene	GC–MS	53-70-3	50	µg/kg	irl	Zaugg and others (2006)
Dibenzothiophene	GC–MS	132-65-0	50	µg/kg	irl	Zaugg and others (2006)
Diethyl phthalate	GC–MS	84-66-2	50	µg/kg	irl	Zaugg and others (2006)
Fluoranthene	GC–MS	206-44-0	50	µg/kg	irl	Zaugg and others (2006)
Fluorene	GC–MS	86-73-7	50	µg/kg	irl	Zaugg and others (2006)
Hexachlorobenzene	GC–MS	118-74-1	50	µg/kg	irl	Zaugg and others (2006)
Indeno[1,2,3- <i>cd</i>]pyrene	GC–MS	193-39-5	50	µg/kg	irl	Zaugg and others (2006)
Naphthalene	GC–MS	91-20-3	50	µg/kg	irl	Zaugg and others (2006)
Pentachloroanisole	GC–MS	1825-21-4	50	µg/kg	irl	Zaugg and others (2006)
Pentachloronitrobenzene	GC–MS	82-68-8	50	µg/kg	irl	Zaugg and others (2006)
Perylene	GC–MS	198-55-0	50	µg/kg	irl	Zaugg and others (2006)
Phenanthrene	GC–MS	85-01-8	50	µg/kg	irl	Zaugg and others (2006)
Phenanthridine	GC–MS	229-87-8	50	µg/kg	irl	Zaugg and others (2006)
Pyrene	GC–MS	129-00-0	50	µg/kg	irl	Zaugg and others (2006)
2-Fluorobiphenyl (surrogate) ⁴	GC–MS	321-60-8	---	Percent	---	Zaugg and others (2006)
Nitrobenzene-d5 (surrogate) ⁴	GC–MS	4165-60-0	---	Percent	---	Zaugg and others (2006)
Terphenyl-d14 (surrogate) ⁴	GC–MS	1718-51-0	---	Percent	---	Zaugg and others (2006)

¹ The Chemical Abstract Service (CAS) Registry Number is a unique identifier assigned to each chemical and to some mixtures of chemicals by the CAS, a division of the American Chemical Society.

² Analyzed in the blanks.

³ The reporting limit changed approximately half way through the project.

⁴ Used for quality control only.

Manuscript approved on September 30, 2011.

Prepared by:

USGS Science Publishing Network
Raleigh Publishing Service Center
3916 Sunset Ridge Road
Raleigh, NC 27607

For additional information regarding this publication, contact:

Chad R. Wagner, Hydrologist
USGS North Carolina Water Science Center
3916 Sunset Ridge Road
Raleigh, NC 27607
phone: 919-571-4000
e-mail: cwagner@usgs.gov

Or visit the North Carolina Water Science Center Web site at:

<http://nc.water.usgs.gov>

A PDF version of this publication is available online at
<http://pubs.usgs.gov/sir/2011/5180/>

