Effects of Wastewater and Combined Sewer Overflows on Water Quality in the Blue River Basin, Kansas City, Missouri and Kansas, July 1998–October 2000

By Donald H. Wilkison, Daniel J. Armstrong, *and* Dale W. Blevins

Abstract

Samples were collected from 16 base-flow events and a minimum of 10 stormflow events between July 1998 and October 2000 to characterize the effects of wastewater and combined sewer overflows on water quality in the Blue River Basin, Kansas City, Missouri and Kansas. Water-quality effects were determined by analysis of nutrients, chloride, chemical and biochemical oxygen demand, and suspended sediment samples from three streams (Blue River, Brush Creek, and Indian Creek) in the basin as well as the determination of a suite of compounds known to be indicative of wastewater including antioxidants, caffeine, detergent metabolites, antimicrobials, and selected over-the-counter and prescription pharmaceuticals. Constituent loads were determined for both hydrologic regimes and a measure of the relative water-quality impact of selected stream reaches on the Blue River and Brush Creek was developed. Genetic fingerprint patterns of *Escherichia coli* bacteria from selected stream samples were compared to a data base of known-source patterns to determine possible sources of bacteria.

Water quality in the basin was affected by wastewater during both base flows and stormflows; however, there were two distinct sources that contributed to these effects. In the Blue River and Indian Creek, the nearly continuous discharge of treated wastewater effluent was the primary source of nutrients, wastewater indicator compounds, and pharmaceutical compounds detected in stream samples. Wastewater inputs into Brush Creek were largely the result of intermittent stormflow events that triggered the overflow of combined storm and sanitary sewers, and the subsequent discharge of untreated wastewater into the creek. A portion of the sediment, organic matter, and associated constituents from these events were trapped by a series of impoundments constructed along Brush Creek where they likely continued to affect water quality during base flow.

Concentrations and loads of most wastewater constituents in the Blue River and Indian Creek were significantly greater than in Brush Creek, especially during base flow. However, wastewater indicator compound concentrations were sometimes greater in some Brush Creek stormflow samples. Selected stream reaches along the mid-portion of Brush Creek showed higher effects relative to other sites, primarily because these sites were in impounded reaches with the greatest density of wastewater inputs, or had relatively small drainage areas.

INTRODUCTION

As part of a flood-control, economic development, and beautification program in the Blue River and Brush Creek Basins, the city of Kansas City, Missouri, made channel modifications to the Blue River and Brush Creek. Sections of both streams were deepened and widened to provide increased flood control. A series of lakes, fountains, dams, and waterfalls were created along Brush Creek and the area was landscaped

to provide more than 5 km (kilometers) of urban parkland for recreation. However, the downstream 10 mi (miles) of the Blue River and Brush Creek occasionally receive wastewater from the overflow of combined sanitary and stormwater sewers at 220 locations within the city. Aesthetic and health concerns from these overflows limited the implementation of some recreational activities along the Brush Creek corridor.

The U.S. Geological Survey (USGS) in cooperation with the city of Kansas City, Missouri, began a study in 1998 to better understand the effects of wastewater originating from combined sewer overflows (CSOs) on the water quality of the Blue River and Brush Creek. Compounds indicative of wastewater were targeted for study, and included antioxidants, bisphenol A, cholesterol, coprostanol, 17-β estradiol, nonionic surfactants, disinfectants, fragrances, and selected over-the-counter and prescription drugs. Many wastewater indicator compounds have been broadly characterized as "emerging contaminants" primarily because sampling methodologies and analytical techniques have only recently become available to quantify these constituents in environmental samples (Furlong and others, 2000; Meyer and others, 2000; Lindsey and others, 2001; Zaugg and others, 2001; Kolpin and others, 2002). The environmental effects of many of these compounds currently is poorly understood (Daughton and Jones-Lepp, 2001). A number of them—notably bisphenol A, 17-β estradiol, and the nonionic surfactants—are known, or suspected, agents of endocrine disruption in aquatic environments (Committee on Hormonally Active Agents in the Environment and others, 1999). Some disinfectants, such as the antimicrobial agent triclosan, are suspected of causing bacterial resistance (McMurry and others, 1998a). The presence of human drugs in aquatic environments may be seen as a potential indicator of the adverse effect of humans on the environment (Daughton and Ternes, 1999) because many drugs are administered to humans in high doses, may pass through the body with little or no degradation, and once released into the environment may be readily assimilated by other organisms.

Purpose and Scope

This report presents information to assess the effect of wastewater and combined sewer overflows on the stream water quality in the Blue River Basin in Kansas City, Missouri and Kansas, during June 1998 to October 2000. The report includes concentrations and loads for selected water-quality constituents and wastewater indicator compounds in stream samples from the Blue River, Brush Creek, and Indian Creek during baseflow conditions and from the Blue River and Brush Creek during stormflow conditions. Additionally, estimates of the relative impact of wastewater on selected stream reaches of the Blue River and Brush Creek are provided. Concentrations of wastewater indicator compounds in untreated wastewater also are provided for comparison purposes as are wastewater treatment plant removal efficiencies. Continuous water-quality data for specific conductance, pH, temperature, dissolved oxygen, and turbidity are provided for selected sites. The distribution of *Escherichia coli* (*E. coli*) bacteria in stream samples during base flow is presented along with source ribotypes of *E. coli* for selected samples.

Acknowledgments

The authors express gratitude for the support, technical contributions, and guidance of numerous USGS colleagues in the preparation of this document. S.L. Severn and R.S. Inman were especially instrumental in the preparation of the manuscript. Steven D. Zaugg, D.W. Kolpin, and Don Stoekel provided review and thoughtful criticism of the manuscript. Dr. Ed Furlong and Jeff Cahill guided the collection and analysis of pharmaceutical data. Charles Raab and Brian Schroeder, without whom this work would not have been possible, of the city of Kansas City, Missouri Water Services Department, were especially supportive of this work from its inception. Jim Nanaman, also of the Water Services Department, provided support and access to the Blue River Wastewater Treatment Plant (WWTP) and Jim Mellum provided careful review of the manuscript. Dr. Andy Carson of the University of Missouri provided review and technical advice on bacterial source tracking. Members of the Johnson County Wastewater Department graciously allowed access to the Tomahawk Creek Wastewater Treatment Plant.

Description of Study Area

The study area is located in metropolitan Kansas City, Missouri (fig. 1). The Blue River and its tributaries are located along the Missouri-Kansas border. Blue River and Brush Creek have drainage areas of 700 and 75 km^2 (square kilometers). The drainage area of Indian Creek is approximately 110 km^2. Most of the

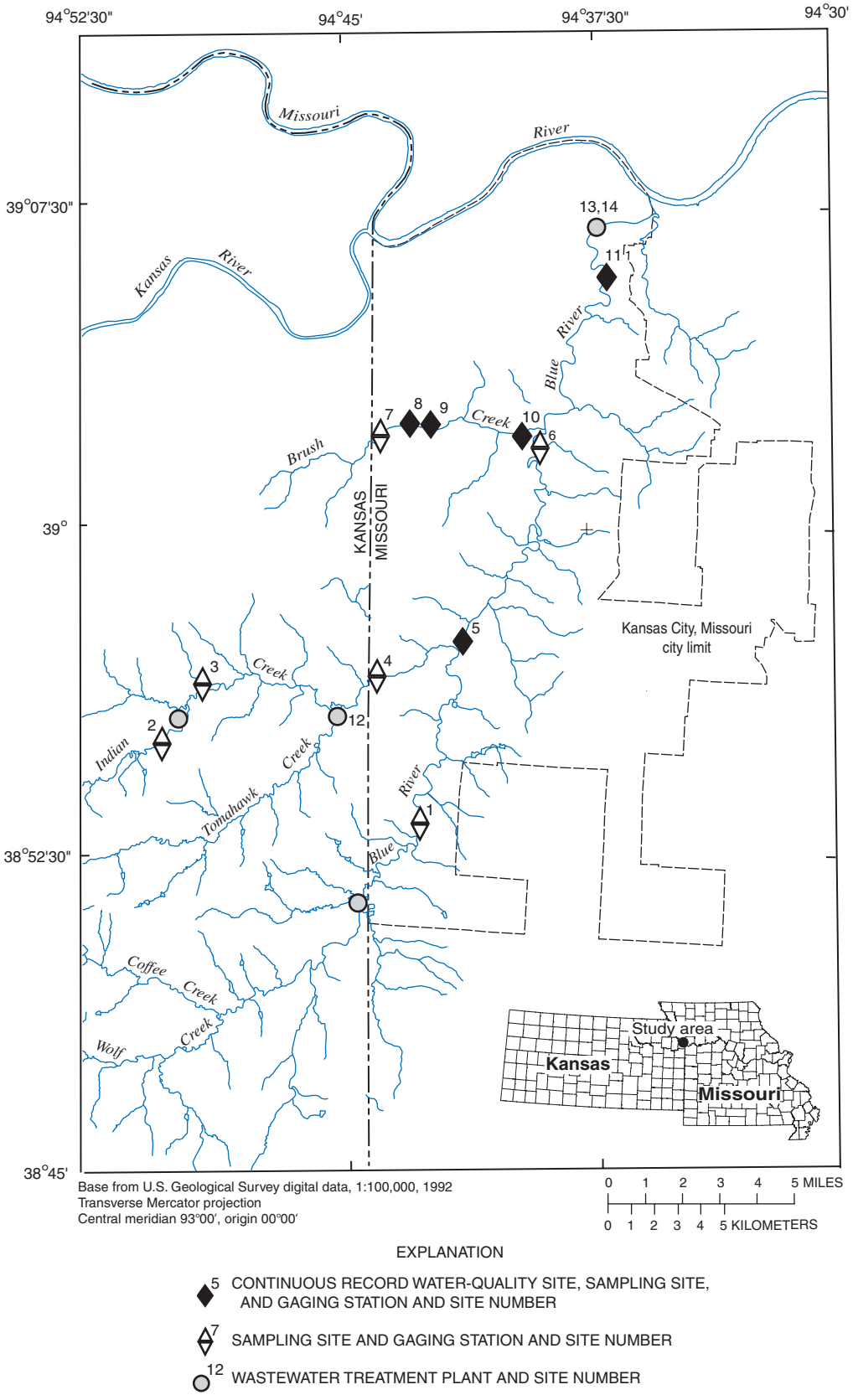


Figure 1. Location of study area and sampling sites.

Kansas City metropolitan area south of the Missouri River lies in the Blue River Basin and the basin continues to become increasingly urbanized. In 1978, one-third was urbanized, with the remaining portion agricultural or undeveloped land (Blevins, 1986). Since 1980, urban land use has increased an estimated 25 percent within the basin (Frank Lenk, Mid-American Regional Council, written commun., 2000) and an equivalent increase has occurred in mean annual runoff for the Blue River near Kansas City (site 5, fig. 1).

Flash flooding is a concern in the area and several floods have resulted in loss of life and extensive property damage (Hauth and Carswell, 1978; Hauth and others, 1981; Becker and others, 1983). In an effort to control flooding, extensive channel modifications were made to the downstream 10 mi of the Blue River and the downstream 4 mi of Brush Creek. A series of three dams were constructed to impound water through the lower reaches of Brush Creek. The upper and lower pools contain large fountains designed to entrain and aerate water to reduce stagnation. Sometimes (especially during late summer) recirculation of stream water intended to maintain the upper pool elevation results in lower water levels in the downstream pools.

Water-quality concerns also are an issue. Combined sewers underlie about 140 km^2 in an area of Kansas City roughly bounded on the north by the Missouri River, on the east by the Blue River, on the south by 85th Street (approximately 1 mi north of site 5), and on the west by the Kansas state line. Previous studies, conducted before the completion of the channel improvements, demonstrated that inflows from CSOs occasionally degraded water quality on the lower Blue River and Brush Creek (Blevins, 1986). Concentrations of nutrients, 5-day biochemical oxygen demand (BOD_5), dissolved solids, suspended sediment, and metals increased in streams following inflows from CSOs (Burns and McDonnell, 1994). The effects were most pronounced in initial stream rises that followed dry antecedent conditions (Blevins, 1986). Three municipal WWTPs discharge treated effluent into either the Blue River or one of its tributaries (Indian and Tomahawk Creeks), and wet-weather wastewater discharges occasionally occur in Brush Creek. The smallest municipal treatment plant (designed for a population of 30,000 people) is on the upper Blue River near the Missouri-Kansas border. Plants designed for populations of 90,000 and 100,000 are on upper Indian Creek and lower Tomahawk Creek, respectively. A large WWTP (serving a population of 250,000) on the lower Blue River discharges its effluent into the Missouri River, but may have occasional wet-weather discharges into the lower Blue River. Large fecal coliform bacteria densities in the Brush Creek pools has limited the implementation of some proposed recreational activities within the basin.

METHODS

Streamflow and water-quality data were collected from July 1998 to October 2001 to characterize selected water-quality parameters and to provide data for estimating constituent loads during base flow and stormflow events. Base flow for this study was defined as streamflow unaffected by storm runoff.

Sampling Protocol

Continuous stream-stage (water-surface elevation) data were collected at seven sampling sites from July 1998 through October 2001. Stage data were measured at 15-minute intervals on the Blue River and at 5-minute intervals on Brush Creek using either a vented submersible pressure transducer, a non-submersible pressure transducer, or by float and stilling well. Streamflow measurements were used to establish and maintain the relation between stage and discharge (Rantz and others, 1982). Mean daily discharge at two sites (5 and 7) for the period October 1997 through September 2000 is shown in figure 2.

Water samples were collected manually at 7 surface-water sites (sites 5 to 11, fig. 1) during 16 base-flow events and analyzed for nutrients, fecal *E. coli* bacteria, physical properties (table 1, at the back of this report), and wastewater indicator compounds (table 2, at the back of this report). The physical properties included specific conductance, pH, temperature, dissolved oxygen concentration, and turbidity. Base-flow events were defined as those occurring at least 72 hours after all rainfall exceeding 0.10 in. (inch) had fallen within the basin, or when flow conditions at sites 5 or 8 had returned to, or below, the long-term median daily discharge. Water samples from wastewater influent streams at three WWTPs (sites 12 to 14, fig. 1) were analyzed for concentrations of wastewater indicator compounds (table 3, at the back of this report) to determine concentrations expected in untreated wastewater during base flow. Beginning in December 1999, samples also were collected on Indian Creek (site 4) to bet-

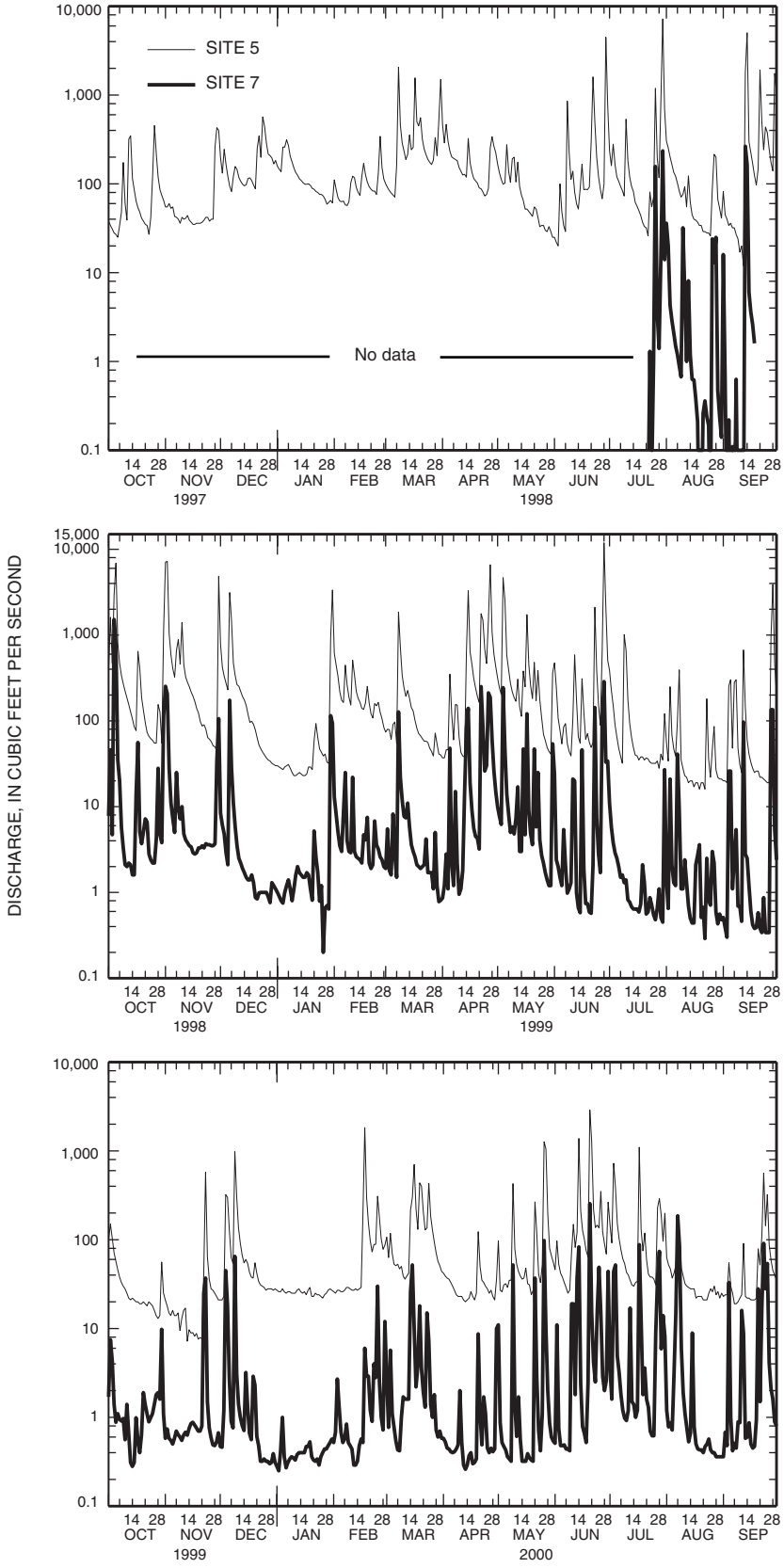


Figure 2. Mean daily discharge for Blue River near Kansas City (site 5) and Brush Creek at Ward Parkway (site 7) from October 1997 through September 2000.

ter evaluate the effects of inflow from Indian Creek and WWTP effluent on the Blue River water quality. Three additional sites (sites 1 to 3, fig. 1) were sampled during two reconnaissance samplings designed to further evaluate the effects of treated wastewater effluent on water quality in the Blue River. Removal rates of wastewater indicator compounds from treatment plants were estimated by comparing the influent loads to the effluent loads. Base-flow samples were depth- and width-integrated across the stream (Wilde and others, 1999a), except on occasions when flow constrictions warranted the collection of grab samples from the centroid of flow.

Stormflow samples were collected using automatic samplers programmed to collect flow-weighed samples after stage thresholds were exceeded. Stormflow water samples were analyzed for nutrients, BOD_5, chemical oxygen demand (COD), chloride, total organic carbon (TOC), and wastewater indicator compounds (tables 4 and 5, at the back of this report). All samples were collected and processed using either glass or fluorocarbon polymer equipment in accordance with established USGS protocols (Wilde and others, 1999a, 1999b). Sampling equipment was cleaned using standard USGS methods for the sampling of organic compounds (Wilde and others, 1998).

At least 10 different storms were sampled at sites 5 to 11, figure 1. Stormflow samples were then composited into segments that corresponded to the rising, peak, and falling phases of the stormflow based on visual inspection of the storm hydrograph for each site. Every attempt was made to sample all three phases of the hydrograph during each storm; however, not all phases were sampled during every storm, and not all sites were sampled during every event. During a few of the storms, phases were combined (for example, rise plus peak) to provide sufficient sample volume for analytical requirements. Stormflow volume was determined for each storm phase from the measured discharge, and loads were calculated by multiplying the measured concentration of each constituent by the stormflow volume. The median percentage of each phase sampled was 98 percent for the rising phase, 100 percent for the peak phase, and 88 percent for the falling phase.

Major nitrogen (N) and phosphorus (P) species were determined on both unfiltered and filtered samples using methods outlined in Fishman and others (1994). Wastewater indicator compounds were determined from unfiltered samples by continuous liquid-liquid extraction with methylene chloride, and determined by capillary-column gas chromatography/mass spectrometry using selected-ion monitoring (Brown and others, 1999; Kolpin and others, 2002). Information in Zaugg and others (2001) provides details about the specific wastewater indicator compounds analyzed and their uses. Human drugs were determined from filtered samples by high-performance liquid chromatography/electrospray ionization-mass spectrometry analysis (Furlong and others, 2000; Kolpin and others, 2002). The wastewater and pharmaceutical analytical methods provide data at extremely low chemical concentrations (micrograms per liter) and are very sensitive to the detection of target analytes. Both methods are termed "information-rich" (Childress and others, 1999) because enhanced analyte identification capabilities provide qualified low-concentration data for interpretation and statistical analysis. Therefore, reported concentrations of some analytes may be marked as estimated (E) if they occur at concentrations outside of instrument calibration ranges or if the compounds exhibit poor analytical method recovery.

Aliquots of base-flow stream samples were cultured and enumerated for *E. coli* bacteria according to most-probable-number methods (Myers and Wilde, 1997). Selected bacteria samples were collected for host-source identification using sterile equipment, packed in ice, and shipped within 6 hours of collection to the University of Missouri Veterinary Pathobiology Department in Columbia, Missouri. Subtle variation in the genetic material of *E. coli* isolates from these samples was determined by ribotyping (Carson and others, 2001) or rep-PCR DNA fingerprinting (Dombek and others, 2000). Association of stream *E. coli* isolates with fecal sources was done with a fingerprint library of fecal *E. coli* from potential animal hosts, including human (Carson and others, 2001).

Continuous water-quality monitors capable of measuring specific conductance, pH, water temperature, dissolved oxygen concentration, and turbidity were used at five sites (5, 8, 9, 10, and 11, fig. 1) to determine physiochemical properties at 15-minute intervals (fig. 3) for a part of each year. Monitors were removed in late November to prevent freezing of water-quality probes and redeployed in April or May of the following year. The monitors were encased in either a polyvinyl chloride (PVC) or 18-in. diameter corrugated pipe with holes drilled into the side to allow for adequate water exchange and anchored to concrete or rock on the bank for protection against floods. Sensors on

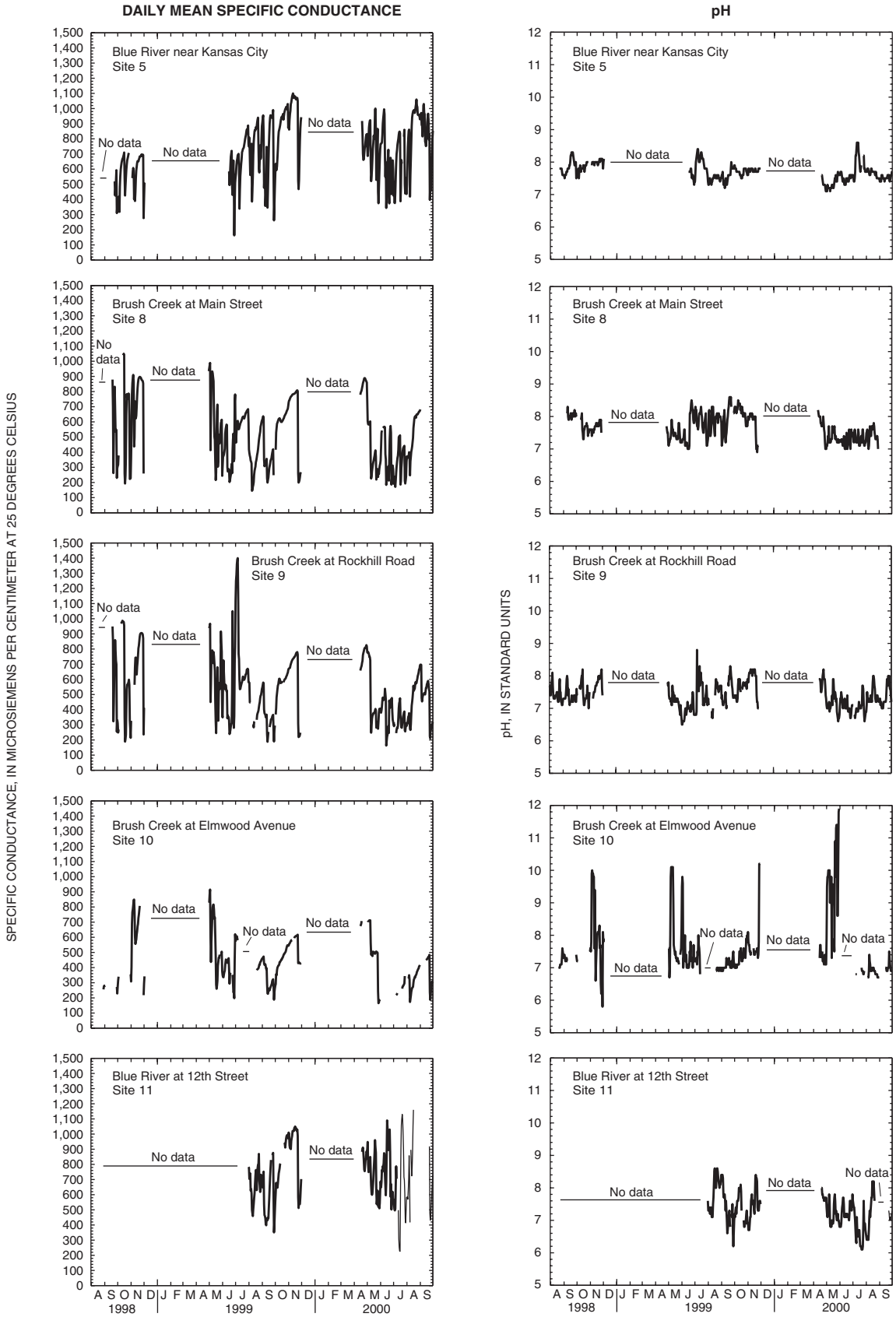


Figure 3. Specific conductance, pH, temperature, dissolved oxygen, and turbidity beginning August 1998 through September 2000.

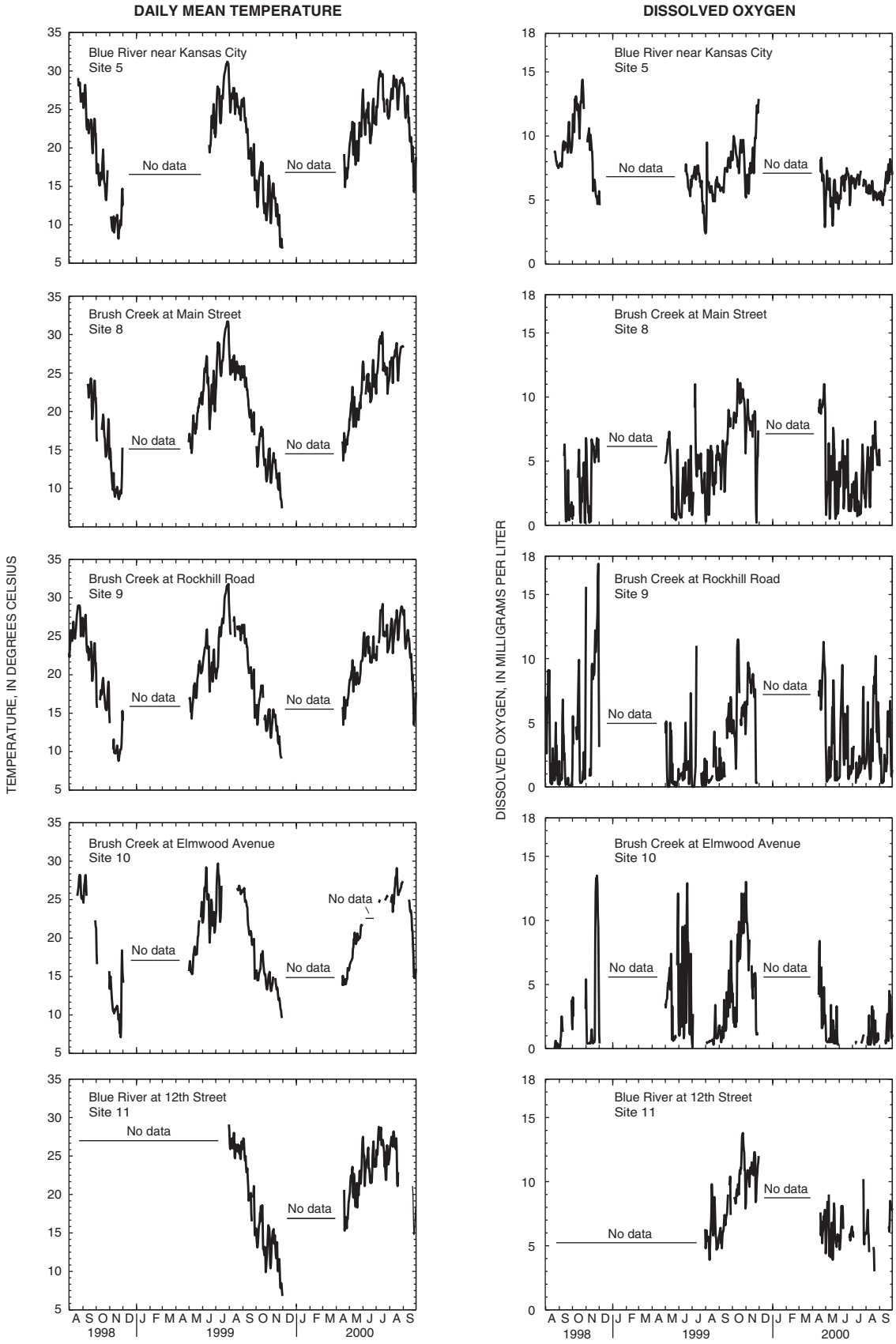


Figure 3. Specific conductance, pH, temperature, dissolved oxygen, and turbidity beginning August 1998 through September 2000—Continued.

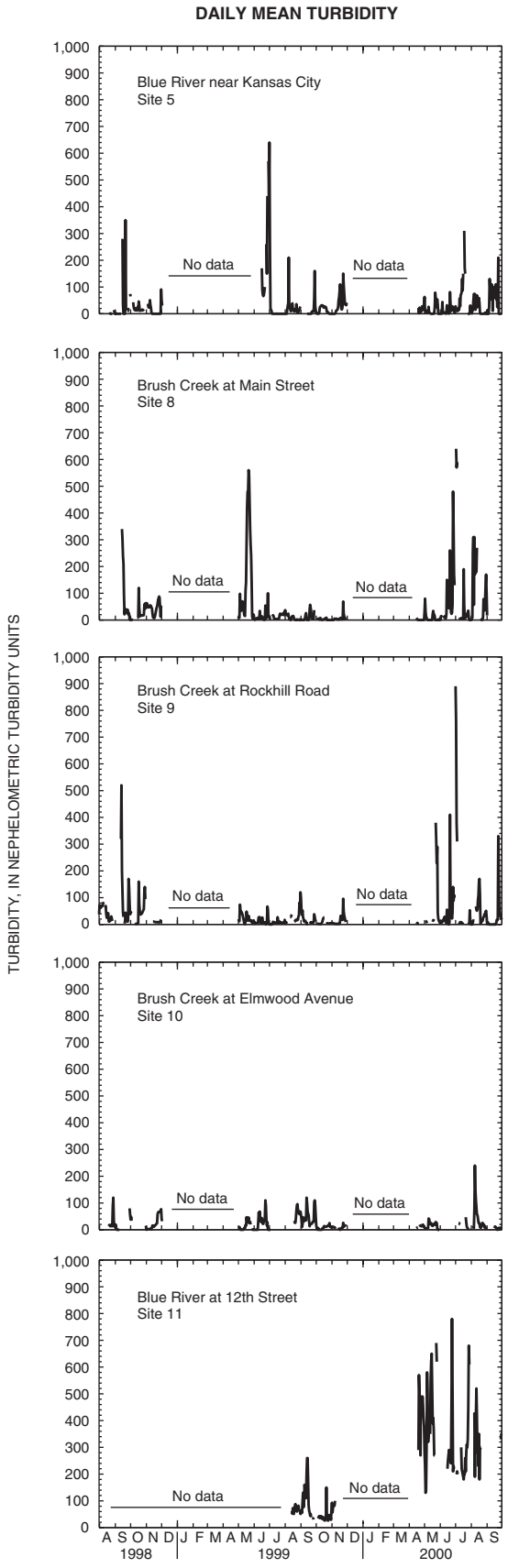


Figure 3. Specific conductance, pH, temperature, dissolved oxygen, and turbidity beginning August 1998 through September 2000—Continued.

the multi-parameter monitors were cleaned and calibrated according to manufacturers specifications at approximately 2-week intervals during the period of use to reduce problems with biofouling and instrument drift (Wagner and others, 2000). Field measurements, using separately calibrated instrumentation, also were taken during calibration visits for comparison purposes and possible adjustment of the continuous data.

Statistical Analyses

Statistical analyses were conducted comparing water-quality characteristics between sites and between base-flow and stormflow samples at individual sampling sites. Nonparametric statistical methods were used to analyze the data when appropriate because water-quality data generally are not normally distributed, and the data often contain values less than the method detection limit (censored data). Nonparametric statistical methods also are used because these methods are not unduly affected by extreme data values (outliers) and because ranks of the data are used instead of the actual concentrations of the water-quality constituents. A significance level (α) of 0.05 was used for all statistical tests in this study. The attained significance level, or probability of error (p-value) from the test, often was much lower and is reported to provide a quantitative indication of the degree of similarity or difference between data sets.

The nonparametric statistical methods included the Kruskal-Wallis test, multiple comparison t-tests on the data ranks, and contingency tables (Helsel and Hirsch, 1992). The Kruskal-Wallis test is an analysis of variance on the ranks of data that test for differences in the central tendency, or medians, of two or more groups. When the Kruskal-Wallis tests indicated a significant difference at the 0.05 level, a t-test on the ranks (Tukey's W) was performed on each paired group to evaluate which groups were statistically different from one another.

QUALITY CONTROL AND ASSURANCE

Quality control and assurance samples were collected and analyzed to insure the integrity of the water-quality data presented in this report. Approximately 10 percent of all samples collected were quality control and assurance samples. Samples for wastewater indicator compounds were collected in replicate in case re-

analysis was needed. The adequacy of the field cleaning and sample processing protocols were evaluated through field and equipment blank samples.

Highly purified water (blank water) was passed through the same equipment used to collect and process water-quality samples and then stored, shipped, and analyzed by the identical methods that were used for environmental samples. Another blank sample was prepared at the laboratory and analyzed alongside environmental samples to insure that laboratory contamination was not a problem during analyses (approximately 100 laboratory blank samples in total; data not shown). Measurable concentrations in blank water can result from trace amounts of constituents in the water, as well as residual material in sample processing or analytical equipment. Results from field and equipment blank samples are listed in table 6, at the back of this report. Most compounds were not detected in any blank samples; if detected, the reported concentrations were near the detection limit for these compounds. Two compounds (tri(2-chloroethyl)phosphate and benzo[a]pyrene) were detected in five blank samples. Tri(2-chloroethyl)phosphate is a common component in many plastics and, although sample collection procedures avoided polyethylene plastics, samples were transported to the laboratory in polyethylene coolers lined with polyethylene bags. Also, samples were processed in vehicles used onsite, and analyzed in laboratories where many plastic parts and components exist. Any of these may have contributed to the detection of tri(2-chloroethyl)phosphate in blank samples and environmental concentrations reported for these compounds may be biased high. Generally, the blank sample data support the conclusion that equipment cleaning, sample collection, and processing procedures provided an inconsequential source of bias to environmental samples.

Replicate samples were collected to determine the variability in sample collection and processing procedures and to examine the affect these variations may have on concentrations determined from environmental samples. Quantile-quantile (Q-Q) plots (fig. 4) show the concentrations of constituents in environmental samples plotted with the concentrations determined from the replicate samples. If no difference exists between these concentrations, then a line extends through the center of all of the data points with a resultant coefficient of determination (r^2) equal to 1. However, concentration differences can, and do, exist in replicate samples. The smaller the difference between the two sets, the higher the level of confidence one can have that this variability is insufficient to significantly bias results. These plots also provide information about how these differences can change as concentration levels vary.

For most constituents, concentration differences in replicate samples were minor, with coefficients of determination generally greater than or equal to 0.95, especially in the concentration ranges observed in environmental samples. These data indicate sample collection and analytical procedures would account for 5 percent or less of any variation in concentrations; however, coefficients of determination were less than 0.90 for some wastewater indicator compounds. These variations are likely related to a number of factors. Replicate samples were collected over a wide spectrum of expected concentrations—from dilute natural waters to raw wastewater. Most Q-Q plots for wastewater compounds show a higher degree of agreement between samples at low concentrations than between samples at higher concentrations. Replicate samples from natural waters constitute most of the lower end data points, whereas the replicate samples collected from wastewater plants represent the bulk of points on the upper end of the plots, where a greater degree of scatter occurs.

Concentrations measured in wastewater samples often were in excess of calibration standards, and reported concentrations routinely were estimated from extrapolations of lower values. Additionally, wastewater samples would be expected to be the most complex and biologically active samples. Therefore, matrix interference, or biological degradation, may have exacerbated variation among some samples. Also, because wastewater influent replicate samples were collected sequentially, some time (usually about 15 minutes) passed between replicate sample collection. Temporal variations can occur within influent streams. Wastewater compounds generally have a high affinity for sediment or suspended organic matter. Thus, slight differences in suspended sediment or organic matter between samples may substantially affect concentrations of other measured constituents.

WATER QUALITY

In highly urbanized basins, a variety of factors determine the concentrations of water-quality constituents measured in surface-water samples. The primary components of streamflow are ground-water discharge and surface runoff. However, treated wastewater efflu-

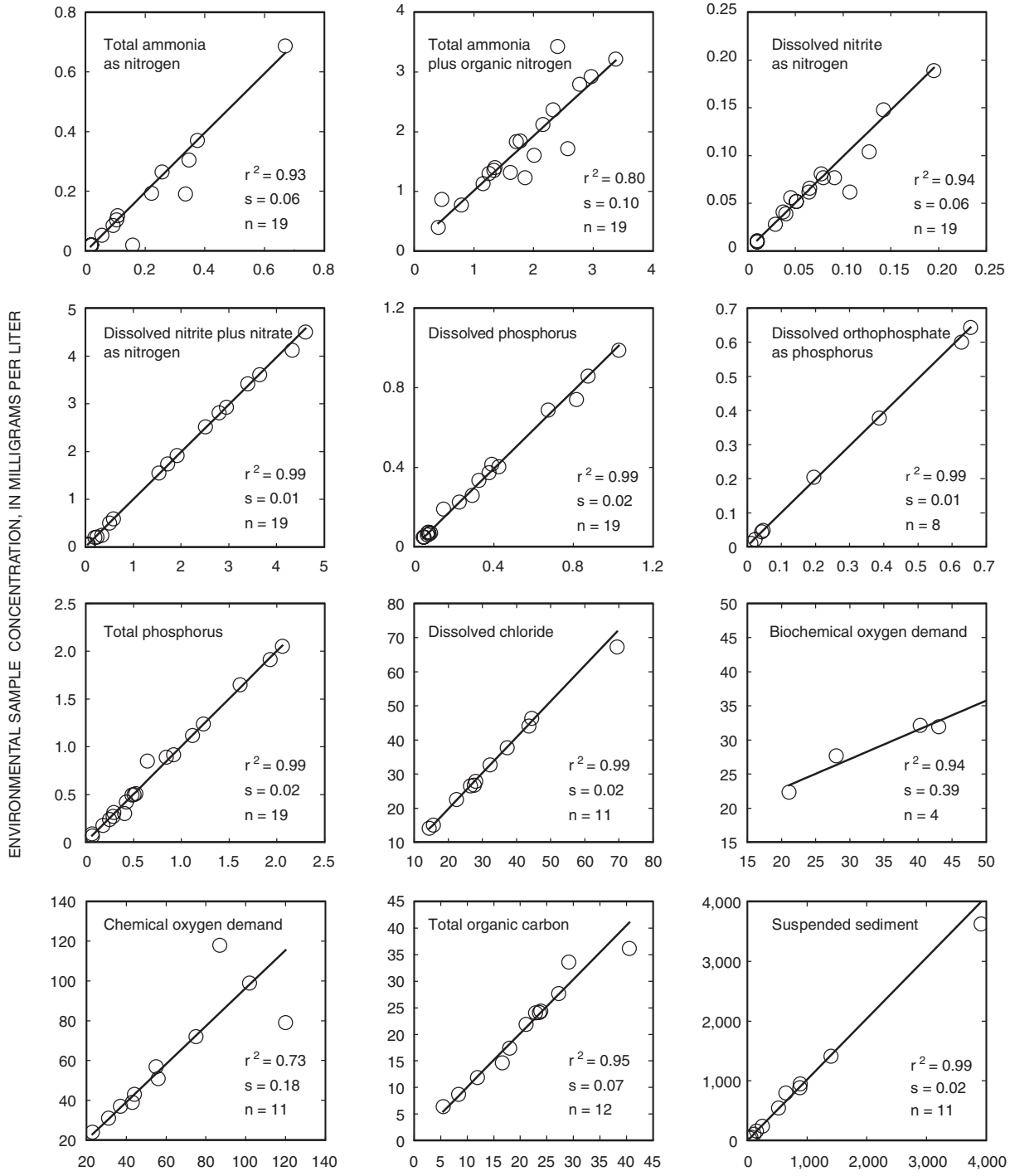


Figure 4. Quality assurance data.

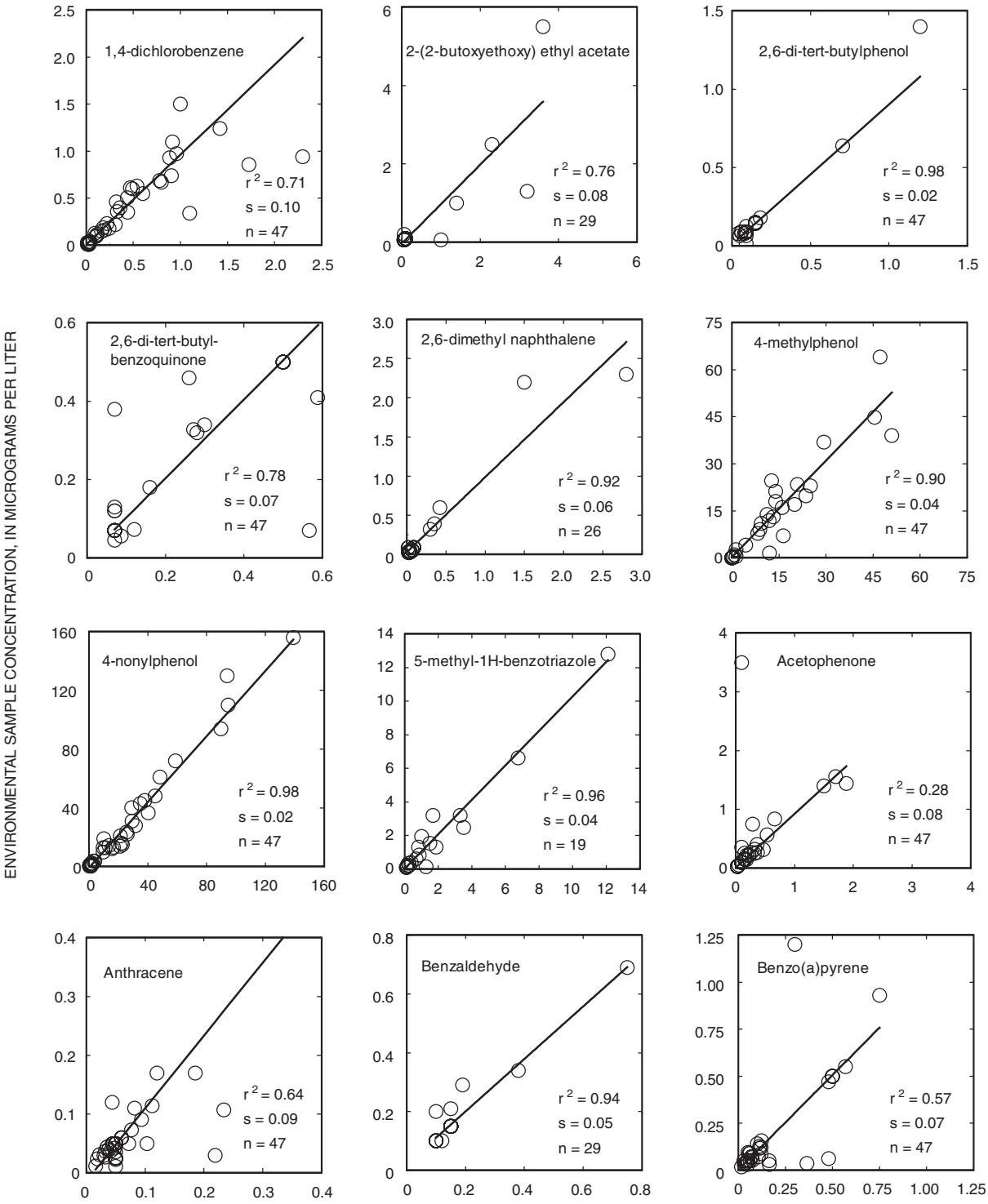


Figure 4. Quality assurance data—Continued.

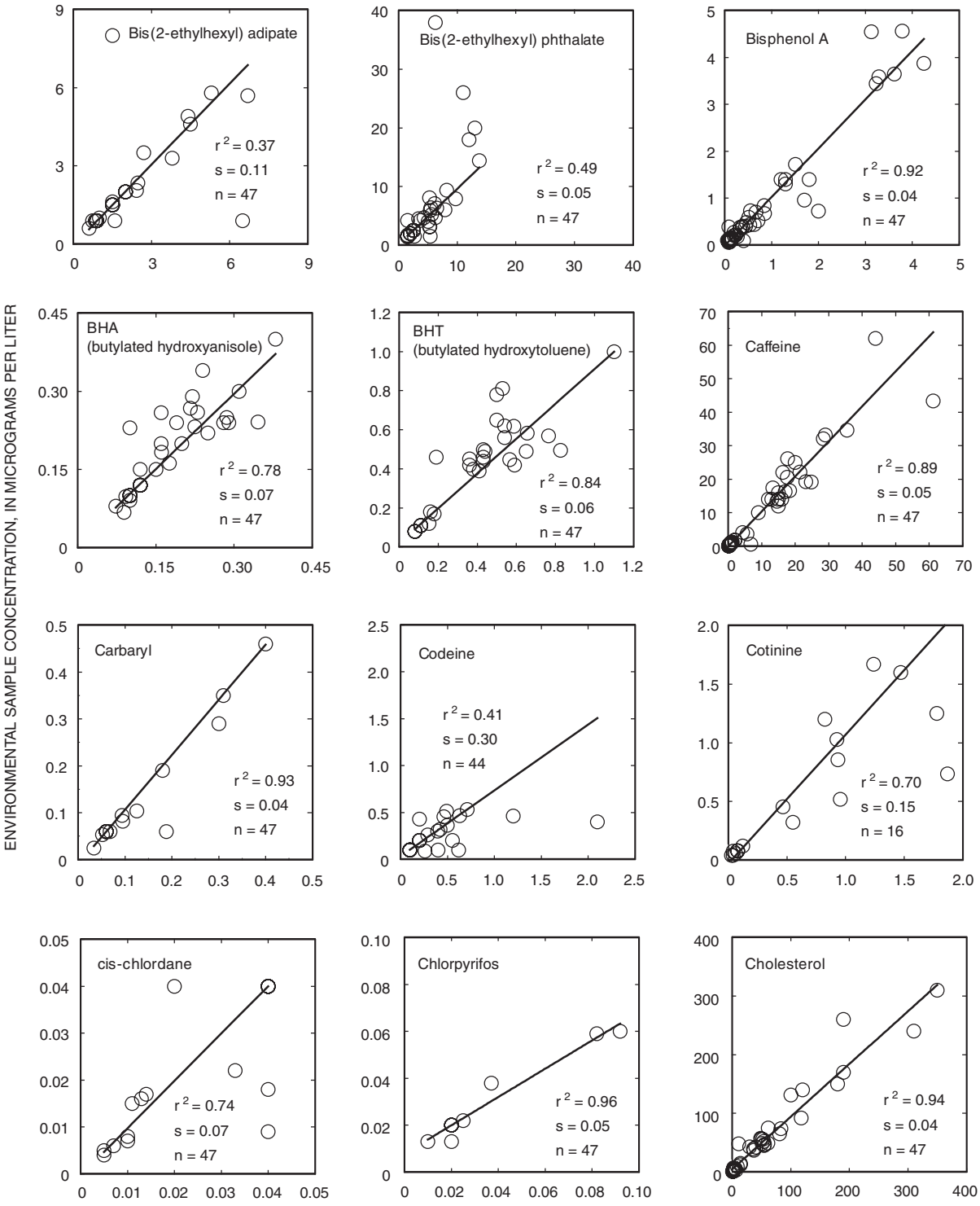


Figure 4. Quality assurance data—Continued.

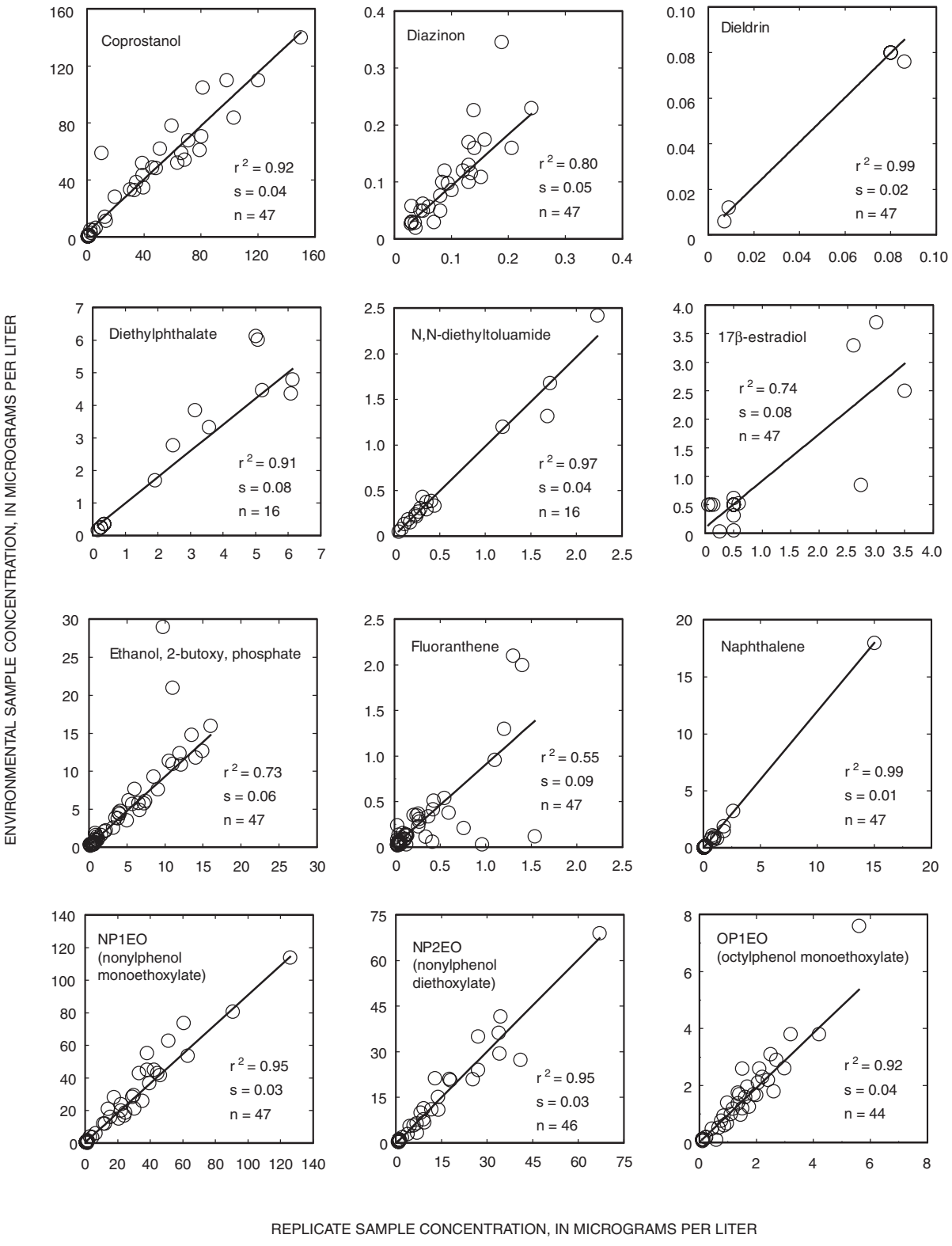


Figure 4. Quality assurance data—Continued.

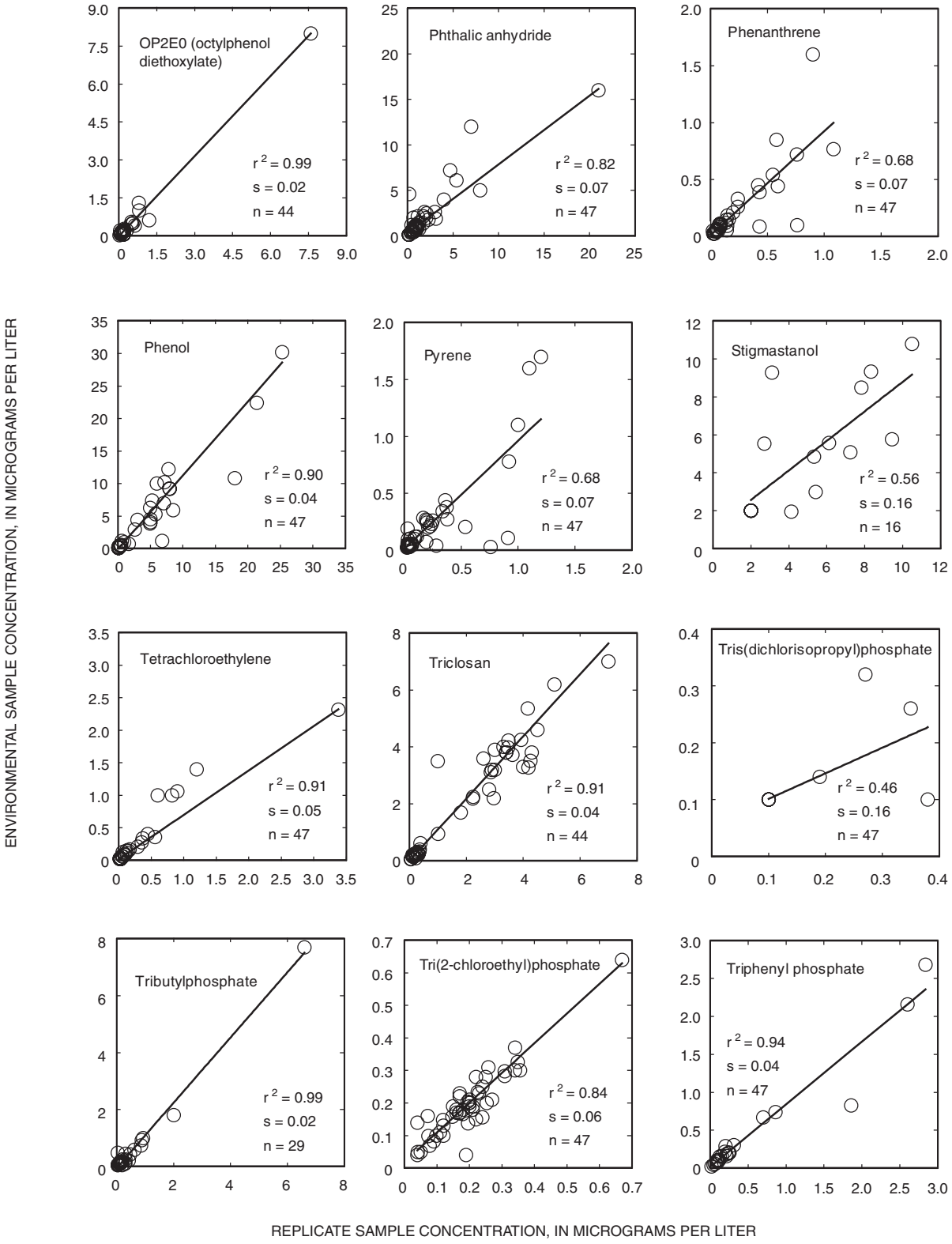


Figure 4. Quality assurance data—Continued.

ent constituted, on average, 15 percent of the flow in the Blue River from 1998 through 2000. During dry periods, the percentage of streamflow derived from wastewater effluent in the Blue River likely approaches 50 percent—with the remaining one-half originating as ground water. Before discharge into the stream, this water migrates through the unsaturated zone. In urban areas, the unsaturated zone is highly dissected by utility trenches, pipes, conduits, and construction activities that provide the infrastructure of telephone, water, sewer, and other utility services to metropolitan residents. The hydrologic result of these perturbations is the creation of a network of flow paths in the unsaturated zone that allows for the preferential movement of water from the surface down into ground water. This process can be important because: (1) the normal filtering and adsorption mechanism of the overlying soil column is short-circuited when contaminants rapidly move through the unsaturated zone, and (2) aging or leaking sewer pipes can provide a continual source of contaminants as water moves along these preferential paths. Although the constituent concentrations detected in base-flow samples should primarily be attributable to ground water, other processes likely are important.

Surface-water runoff is the primary component of streamflow during and immediately after storms. Because a large part of the Blue River Basin includes impervious surfaces, substantial amounts of runoff can quickly be generated during rainfall. As runoff moves across impervious surfaces, constituents deposited during dry periods can be mobilized into streams. Storm sewer capacities often are overwhelmed by runoff volumes during intense storms. Where storm and sanitary sewers are hydraulically connected, excess runoff can combine with untreated wastewater and deliver wastewater directly to receiving streams.

Wastewater Indicator Compounds and Wastewater Treatment Removal Efficiencies

Three untreated wastewater streams (table 3) were sampled 11 times during base-flow conditions to determine the occurrence of these compounds in raw wastewater. All of the wastewater indicator compounds were detected in the raw wastewater samples, confirming their viability as potential indicators of wastewater.

Grab samples collected from treated wastewater effluent (4 samples) and those collected at site 4 (6 samples) immediately downstream from a WWTP discharge point were used to estimate WWTP removal efficiencies of selected wastewater indicator compounds. Removal efficiencies (table 7) represent the ratio of the discharged mass of any given constituent to the influent mass of the same constituent expressed as a percentage. Influent volumes at the Blue River WWTP (sites 13 and 14, fig. 1) were obtained from flow meters at the time of sample collection. An equivalent volume was assumed to exit the plant as effluent, although plant volumes can, and do, fluctuate throughout the day. Volumes entering the Tomahawk Creek WWTP (site 12, fig. 1) were obtained from plant personnel on the day of collection and represent an average daily flow for that day. Samples collected at site 4 may not be representative of effluent concentrations because dilution occurs as effluent mixes with native stream water. Indian Creek also receives effluent from another upstream treatment facility. Many of these compounds have strong affinities for sediments and thus concentrations may quickly decline in-stream. Therefore, samples collected at site 4 probably are more representative of effluent from the Tomahawk Creek facility rather than the upstream treatment facility.

Estimates of removal efficiencies generally were higher for the Tomahawk Creek WWTP than for the Blue River WWTP. Treatment facilities often differ in their ability to remove various constituents, the treatment technology employed, and the amount of waste entering the plant. Some of these factors, along with the different estimation methodologies between facilities, may have affected removal efficiency estimations. Therefore, the estimates may be more accurately viewed as a means of bracketing the removal efficiency endpoints.

The sterols cholesterol (a plant and animal steroid) and coprostanol (a fecal steroid) were detected in all of the WWTP influent samples. Median influent concentration of cholesterol were 35 times that observed in stream samples, and coprostanol concentrations were 70 times those detected in stream samples. Although the calculated removal efficiencies for these compounds ranged from 62 to 99 percent, effluent concentrations often exceeded concentrations detected in stream samples by an order of magnitude. However, improvements in wastewater treatment over the last 30 years has greatly decreased the amount of

Table 7. Average wastewater treatment removal efficiencies, in percent, for selected wastewater indicator compounds

[Numbers below chemical names are CAS numbers (Chemical Abstract Service registry numbers); BHA, butylated hydroxyanisole; BHT, butylated hydroxytoluene; NP1EO, nonylphenol monoethoxylate; NP2EO, nonylphenol diethoxylate; OP1EO, octylphenol monoethoxylate; OP2EO, octylphenol diethoxylate; BR, Blue River Wastewater Treatment Plant; TC, Tomahawk Creek Wastewater Treatment Plant; --, not determined]

Site	1,4-Dichloro-benzene 106-46-7	2,6-Di-*tert*-butyl-benzo-quinone 106-51-4	2,6-Di-*tert*-butyl-phenol 128-39-2	4-Methyl cresol 106-44-5	4-Nonyl-phenol 104-40-5	5-Methyl-1H-benzo-triazole 136-85-6	Aceto-phenone 98-86-2	Anthracene 120-12-7	Benzo[a]-pyrene 50-32-8	Bis(2-ethyl hexyl) adipate 103-23-1	Bis(2-ethyl hexyl) phthalate 117-81-7	Bis-phenol A 80-05-7	BHA 25013-16-5
BR	80	100	--	98	69	-46	73	100	55	--	100	88	100
TC	99	100	100	100	97	92	67	100	99	72	96	94	100

Site	BHT 128-37-0	Caffeine 58-08-2	Cholesterol 57-88-5	Codeine 76-57-3	Cotinine 486-56-6	Coprost-anol 360-68-9	N,N-diethyl-toluamide 134-62-3	Diethyl-phthalate 84-66-2	17-β Estradiol 50-28-2	Ethanol,2-butoxy, phosphate 64-17-5	Fluoran-thene 206-44-0	Naphtha-lene 91-20-3	NP1EO 27986-36-3
BR	90	88	62	-58	71	66	62	100	100	22	92	99	50
TC	100	99	98	85	98	99	91	100	100	94	89	98	97

Site	Phthalic anhydride 85-44-9	NP2EO NA	OP1EO 2315-67-5	OP2EO 2315-61-9	Phenan-threne 85-01-8	Phenol 108-18-4	Pyrene 129-00-0	Tetra-chloro-ethylene 127-18-4	Triclosan 3380-34-5	Tri(2-chloro ethyl) phosphate 115-96-8	Triphenyl phosphate 115-86-6	Tris(dichlor-isopropyl) phosphate 13674-84-5
BR	78	1	28	-473	100	95	79	97	40	-7	53	--
TC	91	94	93	95	99	100	85	100	97	76	90	63

coprostanol discharged to streams. The mean coprostanol concentration measured in effluent at the Blue River WWTP was 381 µg/L (micrograms per liter) in 1970 (Tabak and Bunch, 1970) compared to 21 µg/L measured in this study.

Phenols and detergent metabolites are a major component of waste streams entering and exiting wastewater treatment facilities. Phenolic compounds represent most of the mass of wastewater indicator compounds in both WWTP influent and effluent. Calculated removal efficiencies for phenol and bisphenol A ranged from 88 to 94 percent at the two WWTPs, with the highest removal rates at the Tomahawk Creek WWTP. Removal efficiencies at the Blue River WWTP were less than 50 percent for all detergent metabolites. Effluent concentrations of some metabolites, nonylphenol diethoxalate (NP2EO) and octylphenol diethoxalate (OP2EO), were equivalent to or greater than those measured in the influent. This also may be the result of matrix interferences or poor compound recovery. However, the removal rate is likely affected by the breakdown of nonylphenol and octylphenol polyethoxalate compounds (those that have anywhere from 3 to 20 attached ethoxalate units, which were not analyzed in this study) into the shorter chain compounds: nonylphenol monoethoxalate (NP1EO), NP2EO, alkylphenol monoethoxylate (AP1EO), and alkylphenol diethoxylate (AP2EO) (which were analyzed).

Calculated removal efficiencies for the widely used compounds caffeine, cotinine, triclosan, N,N, diethyl-m-toluamide (DEET), and acetophenone indicate that trace amounts of these compounds survive WWTPs. A few other compounds, notably the antioxidant, 5-methyl-1H-benzotriazole, and the flame retardant, tri(2-choloroethyl)phosphate, were detected at elevated concentrations in effluent at the Blue River WWTP, which discharges to the Missouri River. The reason for this is unclear. These compounds may be bound to organic matter in influent and subsequently liberated into the effluent during the treatment process. Matrix interference also may affect the precise determination of these compounds in wastewater effluent.

Polycyclic aromatic hydrocarbons (PAH's) were common in wastewater influent samples, and the measured concentrations generally were about 4 times greater than concentrations detected in base-flow stream samples. Greater than 90 percent of PAH's are removed during wastewater treatment. WWTP effluent contributes some, but probably not the entire PAH burden seen in base-flow samples.

These data indicate that generally, WWTP processes remove most of the wastewater indicator compounds. However, trace amounts of many compounds survive the treatment process and ultimately are discharged to receiving waters. Although the exact nature and amount of WWTP contributions cannot be determined, these discharges clearly affect the concentration of many wastewater compounds detected in stream samples.

Base-Flow Water Quality

Water-quality assessments were needed during base-flow conditions to characterize the effects of wastewater between storms and to provide a base-line data set for historical comparisons as changes occur within the basin. Sixteen sets of base-flow samples (tables 1 and 2) were collected. Whenever possible, the sample sets were collected synoptically, meaning as close in time as possible, with no intervening rainfall during sample collection. Sample events were dispersed throughout the year. Selected physical properties (specific conductance, pH, water temperature, dissolved oxygen concentration, and turbidity) were measured onsite for each base-flow sampling event. Discharge at each site was either measured or determined from established rating curves and was used to calculate instantaneous loads of selected water-quality constituents and to estimate daily loads.

Physical Properties

No significant difference existed between specific conductance, pH, water temperature, and dissolved oxygen concentration between sites during base-flow sampling events (table 1). Specific conductance varied the most between sites, but the differences were not statistically significant ($p=0.10$). However, specific conductance measurements along Brush Creek were sometimes elevated by as much as 10 times that of the median value of 650 µS/cm (microsiemens per centimeter at 25 degrees Celsius) during winter samplings after the application of de-icing road salts. The median pH value for sites along the Blue River (7.8) was nearly identical to Brush Creek sites (7.7). However, a greater range in values was noted at the Brush Creek sites, and

at two sites (7 and 9), pH values occasionally were below 7.0. This change in pH most likely is related to the effects of algal blooms on water chemistry. Water temperature varied the least between sites, primarily because water temperature was largely affected by air temperature and the synoptic nature of the sampling events. Median dissolved oxygen concentration was 8.9 mg/L (milligrams per liter).

Nutrients

Total N concentrations (calculated by summing the concentrations of ammonia plus organic N plus nitrite plus nitrate) and the percentage of total N as nitrate (NO_3) were significantly higher at Blue River sites compared to Brush Creek sites ($p<0.001$, fig. 5). Median total N concentration in the Blue River was 4.9

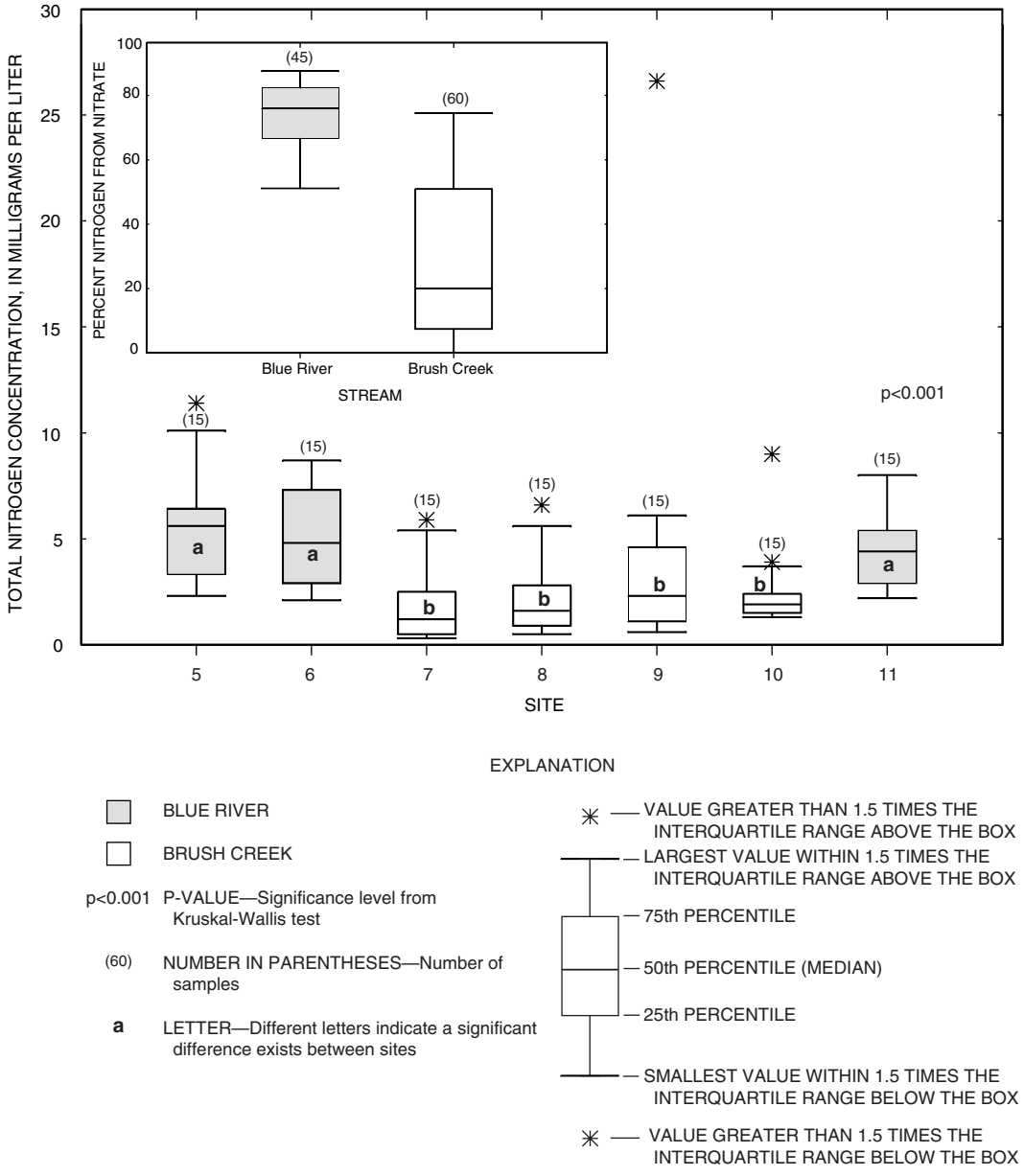


Figure 5. Total nitrogen concentration by site and the percentage of the total nitrogen derived from nitrate by stream (inset) in base-flow samples.

mg/L, compared to 1.8 mg/L in Brush Creek. These differences can be attributed to differences in NO_3 concentrations and N speciation between the two streams. The median NO_3 concentration in the Blue River was 11 times that in Brush Creek (3.78 mg/L compared to 0.33 mg/L). Nitrate accounted for 75 percent of N in the Blue River and 20 percent in Brush Creek. Although the median concentration of organic N was only slightly higher in Brush Creek (0.92 mg/L) than the Blue River (0.82 mg/L), the percentage of total N in organic form is much larger in Brush Creek (58 percent) than in the Blue River (20 percent).

Phosphorus concentrations in the Blue River also were significantly higher than in Brush Creek ($p<0.001$). The majority of P in both streams was dissolved, as orthophosphate, although this percentage was higher in the Blue River (90 percent) than in Brush Creek (55 percent, fig. 6). Aquatic growth is not limited in either stream by the lack of orthophosphate, which often is the case in surface waters.

Nutrients can derive from a number of sources within the basin, including atmospheric deposition, organic matter from soils and algae, fertilizers, and inputs from both treated and untreated wastewater. The Blue River and Brush Creek have an almost continual excess of nutrients; however, the sources of these nutrients differs between the two streams.

Although nonpoint sources cannot entirely be discounted, the primary source of nutrients in the Blue River likely is from the discharge of treated wastewater in the upper part of the basin. Organic N in wastewater is oxidized during the treatment process and subsequently discharged into streams as NO_3. Smaller amounts of ammonia and organic N also may be discharged from these plants into the Blue River, but dissolved oxygen in streams would oxidize these N species into NO_3 where it would remain stable. Nitrate is readily bioavailable and a portion is removed by plants and aquatic organisms; however, the relatively continuous nature of effluent discharges leads to N saturation in the Blue River. The median calculated load of 600 kg/d (kilograms per day) of N moving through the Blue River is almost 40 times the value calculated for Brush Creek (16 kg/d).

Nutrient concentrations in Brush Creek likely result from a myriad of sources, including atmospheric deposition, fertilizers and organic N leached from soils, the decomposition of plants and organic matter, leaks from sewer lines, and inputs from infrequent CSO events or wastewater bypasses. As nutrients are transported downstream they are subject to a variety of biotransformations, especially as they cycle through impoundments. Fountains have been designed in these lakes to entrain and aerate the water, and thus provide an opportunity to oxidize N species (ammonia and organic N) into NO_3. However, a better understanding of the effects of aeration on water quality is needed as the aerated water volume may be small compared to the total volume of lake water. Additional factors also may affect how nutrients are transformed within Brush Creek. Evaporation in these lakes can exceed inflows; to maintain the upper pool elevation, part of the water from the next lowest impoundment is recycled through the upper impoundment. Impoundments often stratify during much of the summer, which results in a layer of decreased dissolved oxygen concentration at depth, and can reduce NO_3 into nitrite (NO_2) and ultimately convert it to nitrogen (N_2) gas, where it can move into the atmosphere. Algal blooms, which convert bioavailable N [mostly ammonia (NH_4) and NO_3] into organic N, also can occur during sunny days. These blooms follow a diurnal periodicity that is marked by increasing dissolved oxygen levels through midday as photosynthesis proceeds. Ultimately, algae growth occurs unabated until light penetration through the water column is attenuated sufficiently to produce algal die-offs, and dissolved oxygen concentrations decline. Algae sinks to the bottom where biogeochemical processes can act to convert the organic N into more soluble forms of N.

Wastewater Indicator Compounds

A number of wastewater indicator compounds were frequently detected (equal to or greater than 50 percent detection frequency) in base-flow samples. The compounds caffeine, triclosan, and DEET—ingredients in coffee, antimicrobial soaps, and insect repellent—were detected in more than 90 percent of samples analyzed and seem to be ubiquitous in this urban environment. Furthermore, the frequent detection of these compounds in a national reconnaissance of 139 streams indicates that their environmental occurrence is widespread (Kolpin and others, 2002).

Wastewater compounds can originate from a variety of sources within the basin. The WWTPs in the upper part of the Blue River Basin serve approximately 235,000 people who discharge an estimated 320 million liters of domestic wastewater daily (Solley and others, 1998). Based on this estimate, WWTP effluent contributed, on average, 40 percent of the

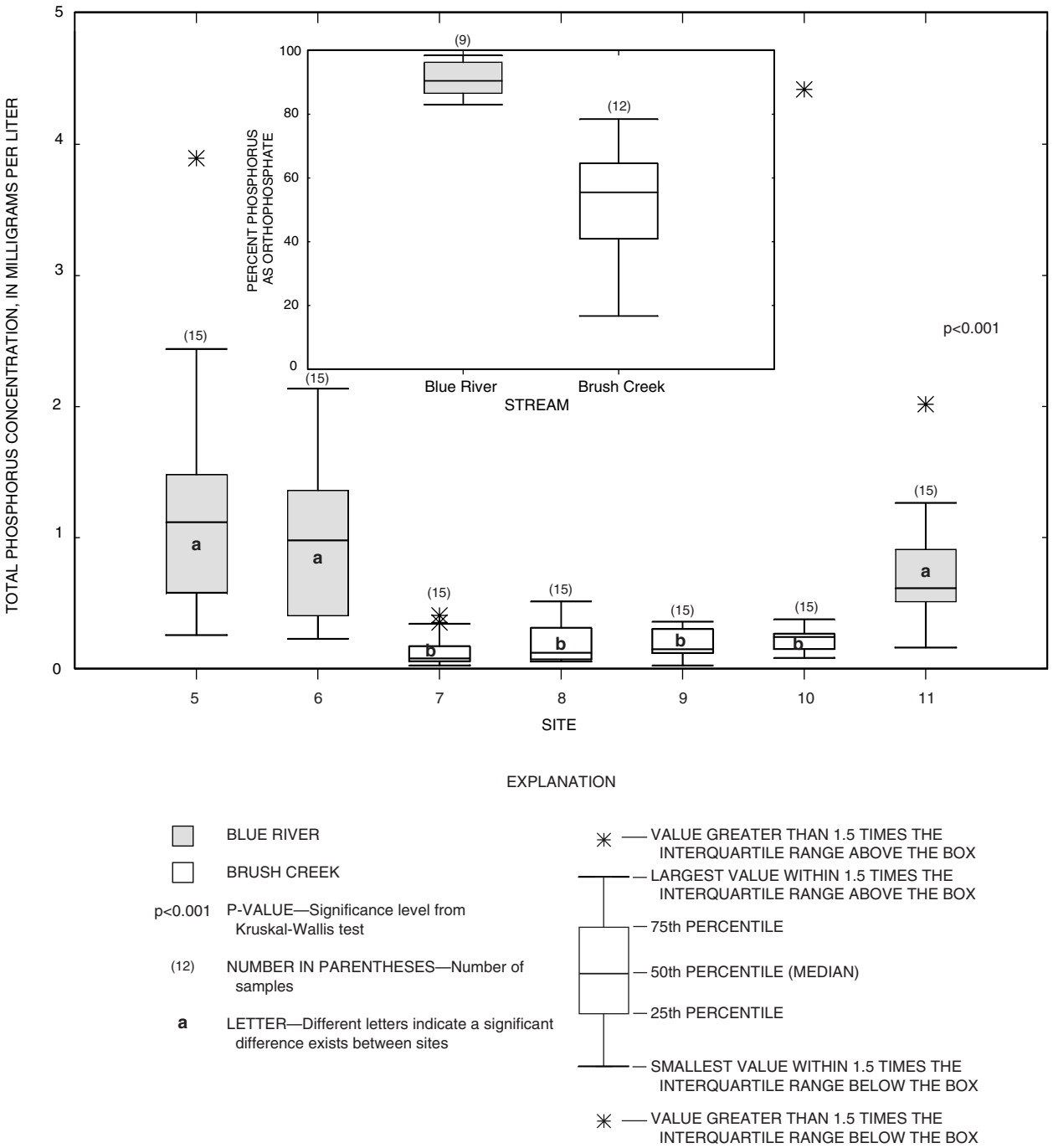


Figure 6. Total phosphorus concentration by site and the percentage of the total phosphorus that is orthophosphate by stream (inset) in base-flow samples.

flow at Blue River site 5 during base-flow sampling events. WWTP effluent is not discharged into Brush Creek.

Comparative analysis of detection frequency, concentrations, and loads between streams and sites provides clues as to the sources and origins of these compounds. Because of the large number of wastewater compounds analyzed, they have been broadly characterized into the following categories: antioxidants, caffeine and cotinine, sterols and stanols, phenols and detergent metabolites, antimicrobials, insect repellents, flame retardants, insecticides, and PAH's.

Antioxidants

Three antioxidants, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and 5-methyl-1H-benzotriazole, as well as the principal metabolites of BHA and BHT—2,6-di-tert-butylphenol and 2,6-di-tert-butyl benzoquinone, respectively—(Lopez-Avila and Hites, 1981) were analyzed. BHA and BHT are added as preservatives to foods and are added to other materials such as food packages and plastics to prevent brittleness. The antioxidant 5-methyl-1H-benzotriazole primarily is used in antifreeze and de-icers as an anti-corrosion agent.

All samples collected from Indian Creek, 94 percent of samples collected from the Blue River, and 67 percent of samples collected from Brush Creek had detectable concentrations of 5-methyl-1H-benzotriazole. The highest concentrations of 5-methyl-1H-benzotriazole were detected in samples downstream from wastewater discharges, and concentrations of this compound were significantly higher ($p=0.002$) on Indian Creek (0.61 µg/L) when compared to the Blue River (0.32 µg/L) or Brush Creek (0.14 µg/L).

The other antioxidants did not follow the distribution pattern of 5-methyl-1H-benzotriazole. BHA and 2,6-di-tert-butyl benzoquinone were detected in 19 percent of samples, but in only one sample from Indian Creek. BHT and 2,6-di-tert-butylphenol were detected in only 5 percent of samples and in no samples from Indian Creek. Previous data on the occurrence of antioxidants in the environment are sparse. Environmental litter, which often accumulates along roadways and in parking lots, is subject to photo degradation and decomposition and can be transported into streams via runoff. Further decomposition may contribute trace amounts of these compounds to streams during base-flow. Although improper stream-side disposal of waste antifreeze cannot be discounted as a source for 5-methyl-1H-benzotriazole during base flow, a substantial portion likely originates from WWTP effluent.

Caffeine and Cotinine

Caffeine was one of the most frequently detected (96 percent of samples) wastewater compounds in base flow. Although the median concentration of caffeine was highest in samples from Indian Creek (1.0 µg/L), the concentrations were not significantly higher ($p= 0.112$) than those detected in samples from the Blue River (0.54 µg/L) or Brush Creek (0.79 µg/L).

The frequent caffeine detections are likely related to several factors. Although ingested caffeine is almost completely metabolized (97 percent) by the body (Tang-Liu and others, 1983), copious amounts of this compound are consumed. Based on a daily per capita use rate of 280 milligrams per consumer (Barone and Roberts, 1996) and the most recent population figures (U.S. Department of the Census, 2000) the average annual consumption of caffeine in the Kansas City metropolitan area is estimated to be 110,000 kg (kilograms) (242,000 pounds). Unconsumed coffee and soft drinks poured down drains or directly disposed into the environment likely contributes to the occurrence of caffeine in water samples. Once released into the environment, caffeine would be expected to easily migrate through soils and the unsaturated zone (Seiler and others, 1999).

Cotinine is the result of the body's rapid assimilation and metabolism of nicotine, the active ingredient in tobacco and smoking-cessation products. Cotinine was detected in 63 percent of base-flow samples. Concentrations in samples from Indian Creek (median value of 0.12 µg/L) and Blue River (median concentration of 0.09 µg/L) were significantly higher than in samples from Brush Creek (median concentration of 0.02 µg/L; $p=0.007$). Cotinine, similar to caffeine, likely has multiple environmental sources, including WWTP effluent discharge, as well as the decomposition of improperly disposed cigarettes.

Sterols and Stanols

The sterols and stanols cholesterol, coprostanol, stigmastanol, and 17-β estradiol were analyzed. Cholesterol is a component of many substances, including plants, but has been shown to occur in wastewater. Within the intestines of humans and other higher animals, cholesterol is microbially reduced into coprostanol (Chan and others, 1998) and related isomers.

Biotransformation in humans favors coprostanol over the isomers, which results in a distinct sterol fingerprint dominated by coprostanol (Leeming and others, 1996). Coprostanol has been shown to account for, on average, 65 percent of the sterols eliminated in human feces (Ferezou and others, 1978). A number of studies have shown sterols and stanols, especially coprostanol, to be efficient tracers of wastewater (Singley and others, 1974; Mudge and others, 1998; Maldonado and others, 1999; O'Leary and others, 1999; Elhmmali and others, 2000). The plant sterol stigmastanol was analyzed in samples beginning in February 2000 with the hope of being able to better determine the portion of the cholesterol that might originate from plants versus animals. However, it also has been shown to be a component of pulp-mill wastes and therefore may be released from the decomposition of paper in the environment (Cook and others, 1997). The natural and endogenous hormone, 17-β estradiol, also was analyzed.

Cholesterol was detected in 81 percent of all samples. Although little difference existed in the detection frequency between streams, the median concentration in Indian Creek (5.2 µg/L) was double that in Brush Creek (2.6 µg/L) and almost 4 times that in the Blue River (1.4 µg/L). Cholesterol concentrations were significantly higher in Indian Creek and Brush Creek samples than in Blue River samples ($p=0.002$). The median concentration generally increased downstream in Indian Creek and Brush Creek, but decreased in the Blue River. This is likely attributable to the fact that both treated and untreated wastewater sources tend to increase downstream in the two tributary streams. The highest concentrations in two samples from Brush Creek (sites 8 and 9) approximated those occasionally seen in wastewater influent and likely indicate recent wastewater inputs. In the Blue River, sediment depositions, dilution, or both may affect the progressive downstream decrease in concentrations.

Coprostanol was detected in 72 percent of all samples and its occurrence in base-flow samples followed a similar trend to that observed for cholesterol. Detections of coprostanol in samples from Indian Creek were higher (92 percent) than those in samples from the Blue River (78 percent) and Brush Creek (64 percent). The median concentration in Indian Creek (2.05 µg/L) was almost 3 times those detected in the samples from the Blue River (0.78 µg/L) and Brush Creek (0.75 µg/L). These differences were significant ($p=0.001$); however, like cholesterol, the highest observed concentrations in any samples were in samples collected from sites 8 and 9 on Brush Creek.

Stigmastanol was detected in about one-fourth of all samples (n=49) but the detection frequency was much greater in samples collected from Brush Creek (43 percent) than for the other sites. The reason for this is unclear. One possibility is that as grass clippings (which are frequently discharged into the sections of the creek during park maintenance) break down, trace amounts of plant sterols, one of which is stigmastanol, are released into the environment. The breakdown of paper in trash also may release stigmastanol into the environment. Longer retention times and lower dissolved oxygen concentrations in Brush Creek also may favor the formation, or stability, of stigmastanol. More than one-half (54 to 96 percent) of stigmastanol generally is removed during wastewater treatment (Cook and others, 1997) so its presence in environmental samples may point to nonpoint and untreated, rather than treated wastewater sources.

The naturally occurring estrogen, 17-β estradiol, was detected in 13 percent of all samples analyzed. Samples collected from Indian Creek had nearly 3 times the frequency (31 percent) of detections than did samples from Brush Creek (11 percent) and the Blue River (12 percent). Additionally, the median detectable concentration was 3 to 4 times higher in samples from Indian Creek (0.58 µg/L) than in samples from Brush Creek (0.16 µg/L) and the Blue River (0.17 µg/L). Although removal efficiencies for estrogens often exceed 85 percent in WWTPs (Baronti and others, 2000) and even though microbial activity is expected to quickly oxidize 17-β estradiol to estrone (Ternes and others, 1999a), estrogens often are detected in wastewater discharges (Ternes and others, 1999b). Although 17-β estradiol was detected only occasionally in base-flow samples in this study (concentrations ranged from 0.10 to 1.9 µg/L), even intermittent exposure to concentrations as low as 0.12 µg/L can induce adverse reproductive changes in fish (Panter and others, 2000; Rogers-Gray and others, 2000).

Sterols have been shown to be important predictors of wastewater contamination (LeBlanc and others, 1992). Sterols analyzed in this study, with the exception of stigmastanol, generally showed a similar distribution pattern. These data indicate that source and fate is similar for each compound. There were higher detection frequencies and concentrations in samples from Indian Creek than samples from Brush Creek or the

Blue River. Indian Creek sites are more directly affected by treated wastewater discharges than are other sites. Sites along Brush Creek occasionally are subjected to large loads of sterols from CSOs and two sites on Brush Creek occasionally have extremely elevated levels of some sterols. The concentrations of coprostanol (r^2=0.82) and stigmastanol (r^2=0.73) correlated well with the concentration of cholesterol at sites.

Once released into the aquatic environment, sterols are subject to a number of biogeochemical transformations (Maldonado and others, 2000). Foremost, they degrade rapidly under aerobic conditions and are strongly sorbed onto sediments. O'Leary and others (1999) reported a 70 percent loss of coprostanol within 1 week in well-mixed waters and suggested, if inputs were sporadic, then coprostanol would be difficult to detect after about 20 days because of decomposition and incorporation into sediments. Once buried in sediments, these compounds have been shown to be stable for many years (LeBlanc and others, 1992); however, sedimentary geochemical processes would likely reduce a portion of the cholesterol into coprostanol (Elhmmali and others, 1997). No significant changes occurred in the ratio of coprostanol/cholesterol between influent and effluent (or adjacent river) samples, indicating that little transformation occurs during wastewater treatment. The median coprostanol/cholesterol ratio for influent at the Blue River WWTP was 0.92, compared to 0.96 for the effluent. The ratio at the Tomahawk Creek WWTP influent was 0.75, compared to 0.78 for river sampling sites immediately downstream from WWTP effluent discharges (sites 3 and 4).

Although coprostanol is stable in anaerobic environments, microbial hydrogenation of the cholesterol double carbon bond (between the 5 and 6 carbons) produces coprostanol (Sherblom and others, 1997). Such biogeochemical transformation also would be expected to occur in anoxic sediments where microbial populations include flora similar to that found in human intestines—for example, sediments derived from CSOs. During summer, the overlying water column at sites 8, 9, and 10 often stratifies, which eventually results in the depletion of dissolved oxygen concentrations at depth. These conditions may favor the stability of some microbial populations, so there may be times when favorable geochemical conditions exist in Brush Creek sediments for the in-situ reduction of cholesterol to coprostanol. This may account for some of the very high levels of coprostanol occasionally found at some Brush Creek sites.

Phenols and Detergent Metabolites

Phenolic compounds analyzed included bisphenol A, phenol, and several metabolites of the alkyl-phenol polyethoxylate (APEO) surfactants. Bisphenol A and phenol primarily are used in plastics manufacturing; however, smaller amounts of phenol are used as a disinfectant and antifungal agent. APEO surfactants are nonanionic surfactants used extensively in laundry detergents and textile manufacturing (Talmage, 1999). They also are a component in many paints, herbicides, pesticides, and cosmetics (Sole and others, 2000). In the United States, most APEO surfactants are nonylphenol exthyloxalates (NPEO). The octylphenol exthyloxalates (OPEO) constitute a much smaller percentage of the total market (Bennett and Metcalfe, 2000). Based on worldwide-use figures, the ratio would be about 80 percent NPEO's to 20 percent OPEO's (White and others, 1994). NPEO and OPEO are commercial mixtures that contain a range (1 to 50) of ethoxylate units (John and White, 2000). As these products break down, ethoxylate units are removed, which results in the formation of compounds with fewer and fewer ethylene oxide groups (Ahel and others, 1994). The degradation products are more persistent, toxic, hydrophobic, and estrogenic than the parent compounds and have been detected frequently in wastewater effluents (Bennie, 1999; Maquire, 1999; Servos, 1999). Samples that contained two, one, and no attached ethoxylate groups, which are identified as NP2EO and OP2EO, NP1EO and octylphenol monoexthoxylate (OP1EO), and nonylphenol (NP), respectively, were analyzed in this study.

No significant difference was determined in either bisphenol A (p=0.82) or phenol (p=0.08) concentrations between streams. Bisphenol A was detected in 71 percent of all stream samples compared to only 24 percent of samples with detectable concentrations of phenol.

The detergent metabolites NP and NP1EO, NP2EO, and OP1EO were detected at a much higher frequency and at significantly higher concentrations in Indian Creek than in Brush Creek or the Blue River. More than 90 percent of samples from Indian Creek had detections of these compounds, and the concentrations were significantly higher ($p \leq 0.01$ for all four compounds) when compared to Brush Creek and the Blue River. Total detergent concentrations (defined as the sum of NP, NP1EO, NP2EO, OP1EO, and OP2EO concentrations) were 5 to 7 times higher on Indian Creek than for Brush Creek or the Blue River (fig. 7).

Concentrations were highest at sites immediately downstream from WWTP discharge points (sites 3 and 4). Consequently, detergent concentrations indicate that a much larger effect occurs at base flow as the result of WWTP effluent than as a result of CSOs.

The nonylphenols (NP1EO, NP2EO, and NP) accounted for, on average, 93 percent of the total measured detergent metabolites, and the octylphenols (OP1EO and OP2EO) only 7 percent. Although the specific use rates of nonylphenols versus octylphenols within the basin were impossible to determine, these detection percentages generally are consistent with use estimates previously discussed.

Two important differences were noted in the distribution of two compounds—NP2EO and NP—between streams. The concentrations of both compounds were significantly higher in samples from Indian Creek than in samples from Brush Creek or the Blue River ($p<0.001$ and $p=0.008$, respectively). Also, the percentage of the total measured detergent metabolites that each compound represented was quite different between streams. For samples collected from Indian Creek, almost one-half (47 percent) of the total detergent metabolites could, on average, be attributed to NP2EO concentrations, compared to 26 percent on Brush Creek and 29 percent on the Blue River. Nonylphenol showed an opposite trend. In samples from Indian Creek, NP concentrations represented only 16 percent of the total measured metabolites, compared to 33 percent in samples from Brush Creek and 34 percent in Blue River samples. Once these compounds are released into the environment, several things act to produce these differences. NP2EO degrades much faster in oxygenated, natural waters than does NP (Ahel and others, 1994). Both compounds have a very strong affinity for sediments (log $K_{ow,}$ [octanol water coefficient]= 4.0 to 4.5; Ahel and Giger, 1993), which results in rapid decreases in concentrations as the distance from the source increases (Bennett and Metcalf, 2000). As decomposition occurs within bottom sediments, NP can be formed from the breakdown of NP1EO and NP2EO. Therefore, as the distance from the source increases, the ratio of NP2EO to NP should decrease. At site 4, located approximately 0.25 km downstream from a WWTP discharge point on Indian Creek, the median ratio was 2.5. At downstream Blue River sampling points, the ratio declined from 1.0 at site 5, to 0.81 at site 6, to 0.65 at site 11. This progressive downstream decrease indicates that site 4 is closer to the source of the detergent metabolites in the stream and that the base-flow effect at Blue River sites is largely related to WWTP effluent.

Antimicrobials

Triclosan has been in use for more than 30 years as an antimicrobial agent in many deodorants and bar soaps (Levy and others, 1999). Triclosan use has risen dramatically in the last few years as it has been added to a wide range of products including body washes, liquid hand soaps, dishwasher powders, toothpastes, fabrics, and plastics (McMurry and others, 1998b). A recent survey determined that three-fourths of liquid soaps contained triclosan (Perencevich and others, 2001). Triclosan was detected in almost every base-flow sample (97 percent of samples), indicating that it is likely an ubiquitous environmental presence in streams that receive wastewater. The presence of triclosan in environmental samples is a concern because of possible development of antiseptic resistant bacteria strains (McMurry and others, 1998a; Suller and Russell, 2000; Meade and others, 2001) and because triclosan has been detected in human breast milk and blood plasma (Adolfsson-Erici and others, 2000; Hovander and others, 2002). Previous work on the presence of triclosan in environmental samples has focused on its occurrence in sediments (Lopez-Avila and Hites, 1980; Hale and others, 2000), aquatic organisms (Miyazaki and others, 1984; Okumura and others, 1996) and possible modes of environmental degradation (Voets and others, 1976).

Concentrations of triclosan in samples from Indian Creek and the Blue River were significantly higher ($p<0.001$) than in samples from Brush Creek. The median concentration of triclosan at site 4 (0.80 µg/L) was 7 times the median concentration for samples from Brush Creek sites (0.11 µg/L). These data indicate that WWTP effluents likely affect the occurrence of triclosan in streams more than CSOs during base flow. This also may be due in part to the fact that a few bacteria—some of which may be present in stream sediments in impounded reaches of Brush Creek—can utilize triclosan as a carbon source, and thus are capable of degrading it (Hundt and others, 2000; Hay and others, 2001; Meade and others, 2001).

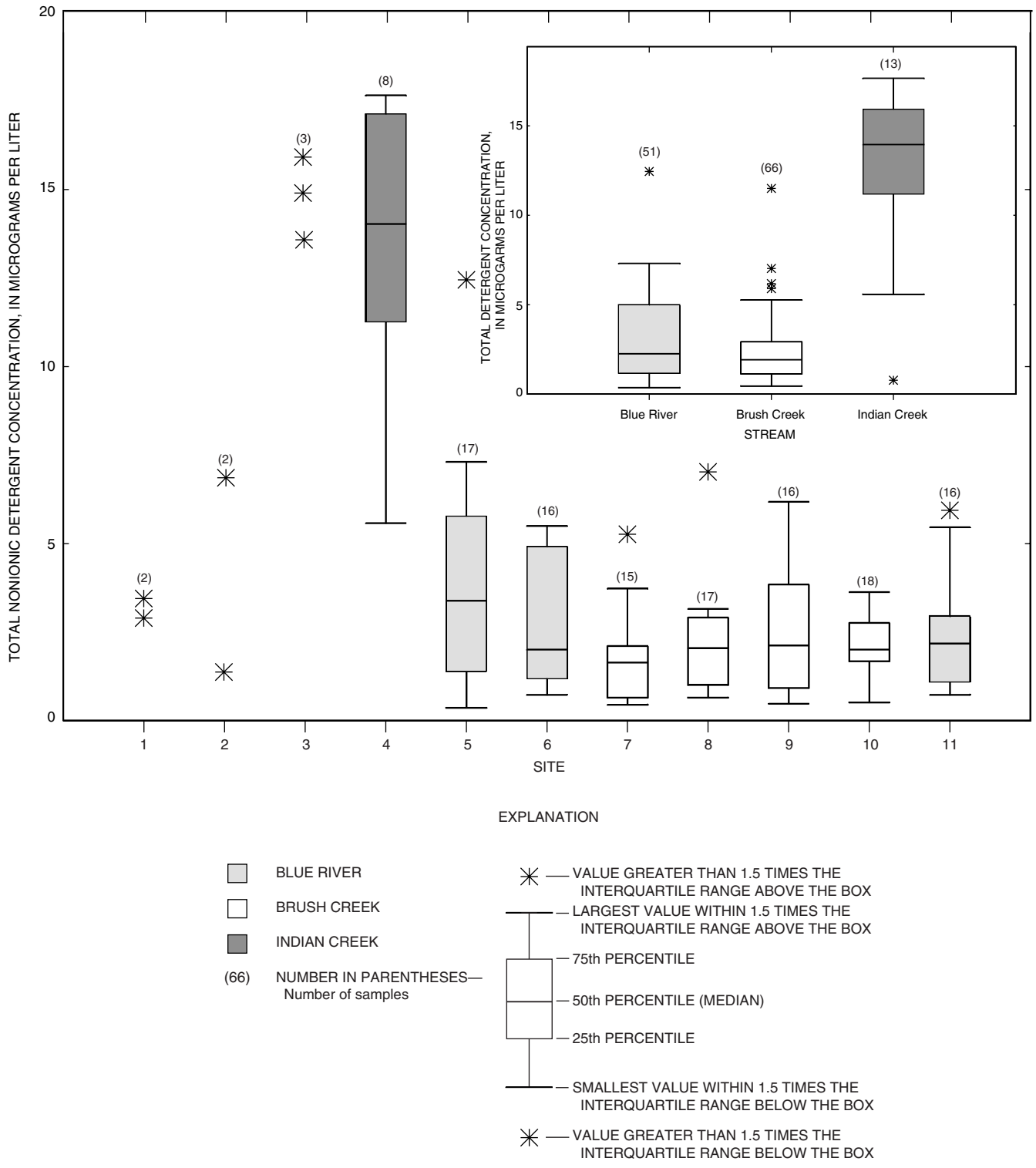


Figure 7. Total nonionic detergent concentration by site and stream (inset) in base-flow samples.

Insect Repellents

DEET is the active ingredient in most commercial insect repellents that are formulated for personal use against mosquitoes, ticks, and other biting insects. Although concentrations were low, DEET was detected in every base-flow sample analyzed. DEET concentrations were significantly higher ($p=0.014$) in samples from Indian Creek (0.20 µg/L) and the Blue River (0.22 µg/L) when compared to Brush Creek (0.13 µg/L). Although DEET commonly is used in recreational areas and many sampling sites were adjacent to, or upstream from parks, stream-side trails, ball fields, and golf courses, these factors would not be expected to be the major effect on the environmental occurrence of DEET. It is more likely that DEET is removed during laundry and bathing, transported to WWTPs where a significant amount survives the treatment process, and is ultimately discharged into receiving streams.

Flame Retardants

Flame-retardant compounds are used in a variety of products including fabrics, carpets, and plastics to break the burning cycle. Three phosphate-based flame retardants—triphenyl phosphate, tri(2-choloroethyl)phosphate, and tris(dichlorisopropyl)phosphate—were analyzed by the wastewater indicator compound method. Most research on the environmental occurrence of flame retardants has focused on the brominated retardants and not on the phosphate-based retardants. Triphenyl phosphate commonly is added to plastics and has been shown to be emitted by the heat of computer video display units (Carlsson and others, 2000).

Tri(2-choloroethyl)phosphate was detected in nearly every sample (92 percent). Concentrations were significantly higher ($p=0.003$) in samples from Indian Creek (median concentration of 0.28 µg/L) when compared to samples from the Blue River (median concentration of 0.15 µg/L) or Brush Creek (median concentration of 0.10 µg/L). Triphenyl phosphate was detected in 38 percent of all samples; however, the detection frequency in samples from Indian Creek was 2 to 2.8 times that compared to the detection frequency in the Blue River and Brush Creek. The concentrations of triphenyl phosphate also were significantly higher in samples from Indian Creek ($p<0.001$) when compared to other streams. Tris(dichlorisopropyl)phosphate was detected in 15 percent of samples analyzed.

Insecticides

The wastewater indicator compound method analyzes for seven insecticides: carbaryl, chlordane (as cis-chlordane), chlorpyrifos, diazinon, dieldrin, lindane, and methyl parathion. With the exception of methyl parathion, these compounds are, or have been, licensed for use on common household pests. Carbaryl, chlorpyrifos, diazinon, and lindane are used to control a variety of lawn and garden pests, but also are registered for home use against termites, fleas, ticks, and lice. Additionally, lindane is registered for human use as a scabicide and pediculcide, and thus is a minor component in some medicinal lotions and creams. Chlordane and dieldrin were registered for use against termites until they were banned by the U.S. Environmental Protection Agency (USEPA) in 1988 and 1987, respectively. Diazinon and chlorpyrifos currently (2002) are being phased out by their manufacturers, a process which is expected to be completed by the end of 2004.

Frequencies of insecticide detections were slightly higher on Brush Creek (24 percent) than on either Indian Creek (16 percent) or the Blue River (15 percent), a difference attributable to the higher detection frequency of chlordane and dieldrin in samples collected from Brush Creek. Neither of these compounds were detected in any samples collected from Indian Creek. Chlordane and dieldrin strongly sorb onto sediments (log K_{ow} = 3 to 5). They are persistent environmental contaminants, with an estimated soil half-life of 7 and 20 years. Insecticides are likely flushed into Brush Creek during runoff and then partition into the overlying water column. Concentrations of chlordane, dieldren, and chlorpyrifos were strongly correlated ($r^2>0.90$) with the occurrence of one another.

Overall, the most frequently detected insecticides were diazinon (61 percent) and chlorpyrifos (23 percent). These compounds are some of the most widely used insecticides in the home and garden. Domestic use of diazinon and chlorpyrifos has been estimated at 4.5 to 5 million pounds per year (U.S. Environmental Protection Agency, Office of Pesticide Programs, written commun., accessed September 2001 at URL http://www.epa.gov/pesticides/op). Analysis of these compounds in 22 urban streams nationwide showed detection frequencies (diazinon, 69 percent; chlorpyrifos, 37 percent) similar to those observed in this study (Larson and others, 1999).

The detection frequency and the median concentration of diazinon was higher in samples collected from Indian Creek than in the Blue River or Brush Creek. Diazinon was detected in 69 percent of samples from Indian Creek and the median concentration for samples with detections was 0.13 µg/L. Diazinon concentrations in Indian Creek were not significantly different (p=0.15) when compared to the Blue River sites (65 percent detections; median concentration of 0.06 µg/L) or to Brush Creek (56 percent detections; median concentration of 0.06 µg/L). Chlorpyrifos detections were more frequent in Indian Creek (46 percent; 0.02 µg/L median concentration) than the Blue River (12 percent; 0.01 µg/L) and Brush Creek (27 percent; 0.02 µg/L) but the concentrations were not significantly different (p=0.50).

Carbaryl was detected in 15 percent of all samples. Most of those samples (15 of 19) were collected from sites along Brush Creek. Estimated United States annual use of carbaryl for home and garden uses ranks just below that of diazinon and chlorpyrifos.

Lindane was detected in three samples. There were no detections of methyl parathion in any samples.

PAH's

PAH's result from the incomplete combustion of organic compounds. Although these compounds can originate from a variety of sources, they are common contaminants in urban environments because of their presence in vehicle exhaust, their tendency to sorb onto road dust, and their subsequent erosion into water bodies (Wakeham and others, 1980; Waker and others, 1999). Although PAH's may be indicators of urban runoff, domestic wastewater has been shown to contribute as much as 60 percent of certain PAH's—pyrene and phenanthrene—to wastewater influent (Paxeus, 1996). The wastewater indicator compound method included six PAH's: anthracene, fluoranthrene, napthalene, phenanthrene, pyrene, and benzo[a]pyrene. Fifty percent of base-flow samples had detectable concentrations of a PAH. Little difference existed between detection frequency on the Blue River (48 percent) and Brush Creek (54 percent), but a smaller number (36 percent) of samples from Indian Creek had detectable concentrations of PAH's.

The lower Brush Creek (site 10) and the lower Blue River (site 11) had the highest observed concentrations of PAH's. This may be related to the proximity of these sites to industrial asphalt facilities. Concentrations of fluoranthene were highly correlated (r^2=0.96) with the concentration of pyrene in samples. Coefficients of determination for anthracene concentrations with phenanthrene and fluoranthrene were 0.65 and 0.62. Coefficients of determination for benzo[a]pyrene with other PAH's ranged from 0.03 to 0.51. This difference in coefficients of determination is likely because the heavier molecular weight PAH's, such as benzo[a]pyrene, are more strongly bound to sediments than are the lighter PAH's (Bruggeman and van der Naald, 1988).

Another possible source of PAH's in base-flow samples is the partitioning of these compounds from bottom sediments into the overlying water column. Bed sediment concentrations were determined at two sites (8 and 9) in January 1999 for the compounds anthracene [904 µg/kg (micrograms per kilogram)], fluoranthrene (8,265 µg/kg), napthalene (57 µg/kg), phenanthrene (5,340 µg/kg), pyrene (6,300 µg/kg), and benzo[a]pyrene (1,945 µg/kg). Although limited, these data indicate that concentrations of some wastewater indicator compounds in bed sediments may be much greater (3 to 4 orders of magnitude greater) than concentrations in the overlying water column and extends the possibility that partitioning may have occurred at the sediment-water interface. This phenomenon warrants additional study.

Additional Wastewater Indicators During Base Flow

Selected base-flow samples also were analyzed for pharmaceutical compounds and for the source of stream *E. coli* using bacterial source tracking methods. Analysis of pharmaceutical compounds in stream samples provided another measure of the relative effect associated with WWTP effluent compared to that from CSOs during base flow. Bacterial source tracking methods were used to assess if some of the measured stream bacteria might originate from human or animal sources.

Pharmaceutical Compounds

Samples selected from base-flow sampling events were analyzed for the occurrence of selected over-the-counter and prescription drugs to help clarify the sources and relative contributions of wastewater inputs, especially those that may result from the discharge of treated effluent in receiving streams. An over-the-counter pain medication, acetaminophen and a metabolite of nicotine (the active ingredient in tobacco products) were the most frequently detected

pharmaceutical compounds in stream samples. Two anti-bacterial drugs, sulfamethoxazole and trimethoprim, prescribed for the treatment of urinary tract infections, were the most frequently detected prescription drugs. These antibiotics are administered in very high doses and about 50 percent of the administered drug typically is not metabolized and, therefore, is discharged in urine within 24 hours. The drugs analyzed and their sample detection frequencies are listed in table 8.

Pharmaceutical compounds in Brush Creek at base flow would be expected to originate from groundwater discharges or from previous CSO events. Although these processes also may contribute pharmaceuticals to the Blue River, an important distinction exists between the two streams—the Blue River receives WWTP effluent and Brush Creek does not. Comparing the concentrations and loads between streams and between sites provides an indication of the relative magnitude of these sources, as well as how these compounds may behave once they enter the aquatic environment.

Concentrations and loads of pharmaceutical compounds for one synoptic sampling event are shown in figure 8. For this event, samples were collected, as nearly as possible, so as to sample the same water as it moved downstream from site to site. Therefore, if stream inputs are additive, then both constituent concentrations and loads should increase downstream. If inputs result from a point source, then downstream constituent concentrations should decline as more water enters the stream, but downstream constituent loads should remain constant unless processes are removing them from the system. Concentrations and loads entering the Tomahawk Creek WWTP are shown for comparison purposes with stream sample concentrations. Treated effluent from this plant is discharged just upstream from site 4. Increases in the concentrations of sulfamethoxazole and trimethoprim between those determined in WWTP influent and those determined in the sample immediately downstream from the effluent discharge may result from upstream inputs of these

Table 8. Detection frequency of selected pharmaceutical compounds in base-flow samples (n=39) and method detection limits

[ND, not determined]

Compound	Detection frequency, percent of samples analyzed	Method detection limit (micrograms per liter)	Compounds with no detections in any samples	Method detection limit (micrograms per liter)
Acetaminophen	77	0.009	Digoxin	0.008
Caffeine	74	.014	Cimitidine	.007
Codeine	18	ND	Enalaprilat	.150
Cotinine	82	.023	Fluoxetine	.018
Diltiazem	33	.012	Furosemide	ND
Gemfibrozil	3	.014	Linsinopril	ND
Ibuprofen	20	.018	Metformin	.003
Sulfamethoxazole	59	.023	Salbutamol	.029
Trimethoprim	49	.014	Ranitidine	.010
			Warfarin	.006

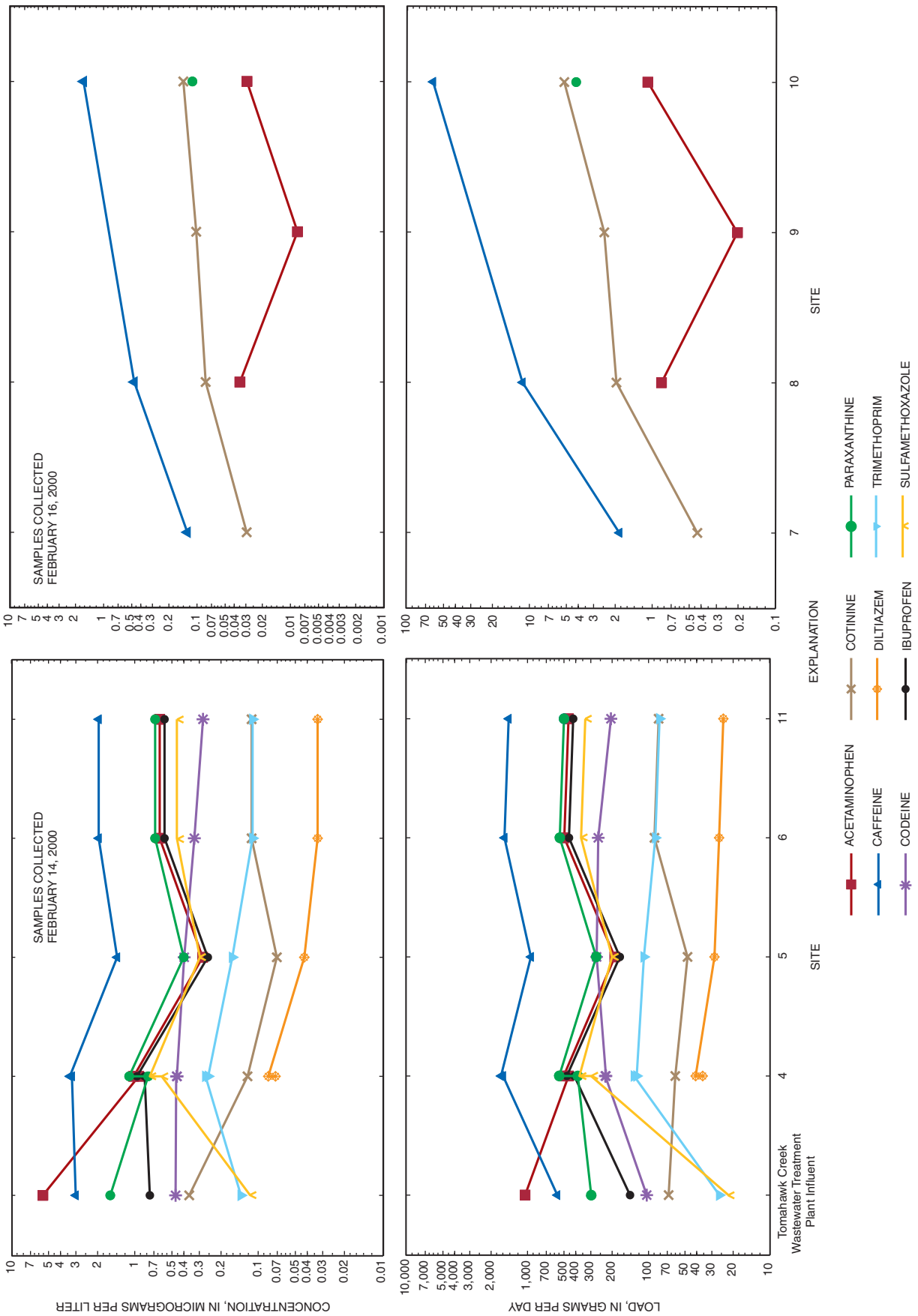


Figure 8. Concentrations and loads of selected pharmaceutical compounds in base-flow samples.

compounds, or may reflect matrix interferences associated with the complex nature of WWTP influent samples.

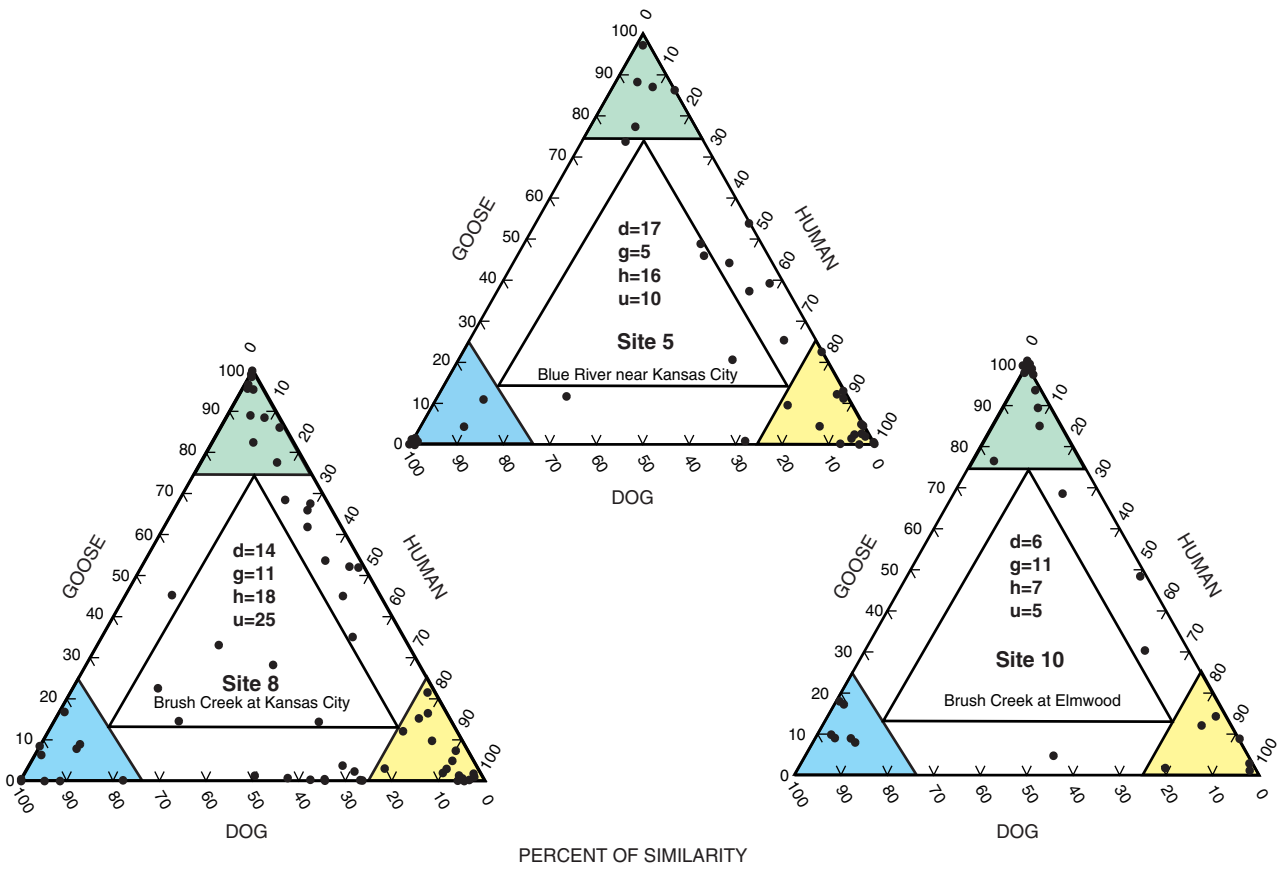
A number of important differences were noted between pharmaceutical compounds in the Blue River and in Brush Creek during the synoptic sampling. First, many more compounds were detected in samples from the Blue River than in Brush Creek. Second, compound concentrations generally were about an order of magnitude greater in samples from the Blue River than in Brush Creek. Also, because the flow in the Blue River generally is an order of magnitude greater than flows in Brush Creek, the mass of pharmaceutical compounds determined in Blue River samples was about 100 times greater than in Brush Creek samples. Therefore, although wastewater treatment removes a significant amount of many pharmaceuticals, a percentage survive the treatment process and are ultimately discharged to surface water. Contributions of pharmaceuticals occur almost continually from WWTPs; however, diurnal and seasonal fluctuations likely occur. Although CSO events may introduce pharmaceuticals into streams, these events are not daily occurrences. Once discharged into streams, the downstream mass of pharmaceuticals did not change much. This indicates that in-stream processes, especially during the winter when water temperatures and biological processes typically are at their lowest levels, may not be available to remove these compounds from streams.

Bacteria and Bacterial Sources

E. coli concentrations were determined from water samples collected during base flow for the Blue River (sites 5, 6, and 11) and Brush Creek (sites 7, 8, 9, and 10). The median concentration of *E. coli* was 800 col/100 mL (colonies per 100 milliliters of water) on the Blue River and 490 col/100 mL on Brush Creek. Bacteria populations in streams often are closely correlated to sediment concentrations (Christensen and others, 2000). The median sediment concentration in the Blue River (72.5 mg/L) was more than double the median concentration in Brush Creek (34.0 mg/L). Single sample *E. coli* concentrations usually were greater than the recommended USEPA full-body contact limit of 235 col/100 mL (Dufour, 1984). The highest concentrations generally were measured from samples collected at the two most downstream stream sites (10 and 11). Median *E. coli* colony concentrations were 1,400 col/100 mL at site 10, and 1,000 col/100 mL at site 11. Bacteria concentrations were not determined on Indian Creek; however, the section of Indian Creek immediately upstream from site 4 in Kansas is listed as an impaired stream because of concerns about elevated fecal coliform bacteria concentrations (Kansas Department of Health and Environment, 2000). Bacteria source-tracking samples were collected at sites 5, 8, and 10. Genetic fingerprint patterns generated from these samples were then compared with a data base of known-source *E. coli* patterns to determine possible sources of *E. coli* contamination in the basin. These data are plotted in figure 9 and show the genetic similarity of *E. coli* isolated from water samples with *E. coli* isolated from three hosts—dogs, geese, and humans—all of which are known to be present in the basin. Genetic fingerprint patterns of water-borne *E. coli* with the closest association to a host plot in the corner of the ternary graph. Assignment to a host group was defined to occur when water sample patterns had a 75 percent or greater similarity to those from a known host. Samples outside of those limits were assumed to be from unknown source(s).

At this time absolute determinations are difficult to make about the source of every water-borne *E. coli* isolate based on the limited sample size (n=900) of the known-source library. Based on the number of observations in stream samples (n=145), *E. coli* originates from a variety of sources. Presumptive sources of *E. coli* were almost equally divided among dogs (28.3 percent), geese (22.1 percent), humans (23.4 percent), and unknown sources (26.2 percent). The most accurate source host determinations (92 percent) are attributable to humans (Carson and others, 2001). *E. coli* from non-human sources, such as turkeys, often present genetic fingerprint patterns similar to those of *E. coli* associated with humans, but in this instance, turkeys would be expected to contribute little, if any, bacteria within the urban basin. The primary source of misclassification with dogs are turkeys or pigs, which also are unlikely sources within the basin. Some of the isolates attributed to geese could originate from dogs, and vice versa, because of the similarities between these two patterns. The pattern recognition method is considered more accurate when limited to three, or fewer, possible host sources, which was how the analyses were constructed. Different combinations of host sources may have provided somewhat different results.

Overflows from CSOs, WWTP bypasses, and leaking sewer lines may be contributing human-derived *E. coli* to Brush Creek. WWTP effluent discharges into the upper Blue River (and it's tributaries) are the likely



NOTE: Points plotting on top of other points are represented by a single point. Sample location shown in center.

EXPLANATION

ISOLATES WITH 75 PERCENT OR GREATER SIMILARITY TO

- Dog
- Goose
- Human

ISOLATES WITH LESS THAN 75 PERCENT SIMILARITY TO ANY GROUP

GROUP AND NUMBER OF ISOLATES ASSIGNED TO THAT GROUP

d=14	Dog
g=11	Goose
h=18	Human
u=25	Unknown

Figure 9. Percentage of similarity between ribosomnal patterns of *Escherichia coli* isolates from water samples at three sites when compared against three possible hosts (dog, goose, or human).

source of human-derived *E. coli* in the Blue River. Given the typical concentrations of *E. coli* generally detected in these streams, bacteria contributed from humans alone would sometimes exceed the maximum level designed for safe whole-body contact recreation. In periods immediately following wastewater discharges into receiving streams, the percentage of stream *E. coli* derived from humans likely increases.

Improved statistical methods may allow for increasing the degree to which sample patterns can be matched to possible sources. One possibility is the method of Dombek and others (2000), which uses dendrogram construction coupled with fuzzy logic and applied-discriminant cluster analysis to determine statistical similarity between patterns. This method claims classification rates of 75 to 100 percent for 7 possible animal sources, including humans, geese, and ducks (not examined in this study). Human patterns, although statistically different, were determined to be most similar to cows and ducks. Samples were not compared against cows or ducks in this study, although cattle may be a source of bacteria in the upper Blue River, and ducks may contribute small sources of bacteria to Brush Creek. Additional bacterial source-tracking data are needed to examine spatial and temporal trends in bacterial sources in receiving streams, to examine the potential of preferential sorption of bacteria from different sources onto bottom sediments, and for further field validation of bacterial source-tracking methods.

Stormflow Water Quality

Samples were collected at sites 5 through 11 during periods of stormflow from May 1999 to October 2000, and analyzed for total and dissolved nutrients, dissolved chloride, chemical and BOD_5, suspended sediment, and wastewater indicator compounds. Generally, water-quality constituent concentrations in stormflow were elevated over those observed in baseflow samples and these increases were higher in Brush Creek than in the Blue River. The highest concentrations of many constituents often were observed at Brush Creek sites that corresponded to areas of the highest population density and near-stream recreational activity. However, constituent loads on the Blue River were much greater than those in Brush Creek because of the greater volume of stormflow in the Blue River.

Nutrients in Stormflow

Nitrogen concentrations, with the exception of ammonia, and loads for all N species, were significantly higher on the Blue River than on Brush Creek during stormflow events. Median total N concentration in stormflow samples from the Blue River was 5.3 mg/L, compared to 2.4 mg/L in samples from Brush Creek. These differences are mostly attributable to higher NO_3 concentrations in the Blue River and to a lesser extent, higher organic N concentrations. The median NO_3 concentration in Blue River stormflow (2.10 mg/L) was 4.5 times that in Brush Creek (0.47 mg/L). NO_3 accounted for slightly less than one-half of the N (47 percent) in the Blue River, compared to 16 percent in Brush Creek. The predominate N species in stormflow in both streams was organic N. Although the median concentration of organic N in stormflow was lower in Brush Creek (1.69 mg/L) than in the Blue River (2.55 mg/L), it constituted a much higher percentage of the total N in Brush Creek (78 percent) than for the Blue River (49 percent).

Median N load in the Blue River during stormflow was more than 20 times the median load calculated for Brush Creek (2,700 and 122 kg). During runoff events, N can be mobilized from a variety of sources. In the Blue River, about one-half of the total N contribution occurs in the dissolved phase—of which more than 90 percent occurs as NO_3—and about one-half as suspended organic matter. Excess fertilizer applied to fields, parks, and lawns likely contributes a part of this N, as do effluents from WWTPs. Row cropping in the upper basin continues to decline, largely replaced by pasture and suburban development. Nutrients also are attached to sediment particles that are easily eroded from the banks of the Blue River. Along Brush Creek, a much higher contribution of the N during stormflow comes from organic matter. Although suspended sediment concentrations in the upper part of the Brush Creek Basin (upstream of, and just downstream of site 5) can be high, most of the middle section of the stream is concrete-lined, which prevents bank erosion. Thus, most of the N in Brush Creek originates from sediments and organic matter flushed from the urban landscape: lawns, golf courses, parks, streets, roofs, gutters, storm sewers, and CSOs. During intense runoff events, increased stream velocities within impounded reaches may scour sediments, releasing N and associated organic matter trapped behind low-water dams.

Total and dissolved P concentrations and loads were significantly higher ($p<0.01$) in Blue River stormflow than in Brush Creek. P in runoff occurred primarily in the particulate phase. Consequently, higher total P concentrations in the Blue River were likely because of higher sediment concentrations.

The median chloride concentration in stormflow samples from the Blue River was slightly higher (43.1 mg/L) than from samples collected from Brush Creek (30.5 mg/L). Chloride loads were significantly higher ($p<0.01$) on the Blue River because of flow differences. On Brush Creek, sites 8 and 10 had the highest median storm loads of chloride.

There was no significant difference between BOD_5 concentrations on the Blue River and Brush Creek ($p=0.26$), or between any of the sites ($p=0.15$). Because of much higher flows in the Blue River, the BOD_5 loads were, however, substantially higher than on Brush Creek. The median BOD_5 storm load was 24,000 kg on the Blue River compared to 2,260 kg on Brush Creek. These values are lower than previously reported BOD_5 storm load values of 41,000 kg for the Blue River, and 3,200 kg for Brush Creek at site 10 (Blevins, 1986), and may reflect changes in stream hydrology that have occurred in these streams in the intervening years but also may be the result of differences in storm intensities between the two studies. Impoundments on Brush Creek now allow part of the sediment and organic matter to settle out before it reaches the Blue River. The stream gradient in the lower Blue River (below its confluence with Brush Creek) also has been lowered. This encourages deposition of sediment and organic matter and can result in reduced stream BOD_5 values.

The median concentration of COD was equivalent in both streams (59 mg/L). The median TOC concentration was slightly higher in stormflow samples from the Blue River (26.6 mg/L) than in samples from Brush Creek (16.8 mg/L). Both COD and TOC loads were significantly higher ($p<0.01$) on the Blue River because of higher flows.

The median suspended sediment concentration during runoff events was 7 times greater on the Blue River (764 mg/L) than on Brush Creek (104 mg/L) primarily because the extensive channel stabilization along Brush Creek limits bank erosion in most stream sections. However, the uppermost Brush Creek site (site 7), often had very high suspended sediment concentrations (median concentration of 523 mg/L) because of sediments mobilized from upstream construction activities and channel-bank erosion. Stream velocities in the upper, unimpounded reaches of the basin are great enough to keep these particles suspended until they encounter lower stream gradients and velocities in the downstream impounded reaches. This results in particle settling and lower suspended sediment concentrations in these reaches.

Brush Creek contributed an average of 10 percent of the flow to the Blue River during storms, but a smaller percentage of the N (6 percent), P (3 percent), chloride (Cl) (6 percent), TOC (7 percent), BOD_5 (8 percent), and sediment (1 percent). Relative loads were determined by dividing the loads measured at the downstream Brush Creek site (site 10) by the loads measured in the next downstream Blue River site (site 11). Additionally, N, P, TOC, COD, and sediment loads measured at the upper Brush Creek site (site 7), exceeded those determined for downstream sites 8 and 10. These data indicate that substantial amounts of nutrients and sediments can originate in the upper part of the basin and eventually accumulate in Brush Creek impoundments. Additional inputs certainly occur downstream on Brush Creek, and part of these loads are likely to be deposited in sediments accumulating in downstream reservoirs. Stormflow contributes substantial nutrients to both streams; however, storm contributions in Brush Creek seem to affect water quality more than they do in the Blue River.

Wastewater Indicator Compounds

A significantly higher number of wastewater indicator compounds were detected in stormflow samples than in base-flow samples ($p<0.01$, fig. 10). Wastewater inputs that occur during storms are in addition to those contributions observed during base-flow conditions. Also, storms activate an increased number of wastewater sources and pathways. Only sites on the Blue River (sites 5, 6, and 11) and on Brush Creek (sites 7 through 10) were sampled during storms (table 4) because of equipment and logistic limitations. Concentrations for many compounds often were greater in stormflow samples, but this was not always the case, and would not always be expected because some storms trigger CSO events and/or wastewater plant bypasses and others do not. A myriad of factors, including rainfall duration and intensity, antecedent moisture conditions, and storm sewer blockages come into play to trigger these events. Ultimately, natural streamflows (which are limited only by runoff volumes) greatly exceed possible wastewater inputs (which have finite

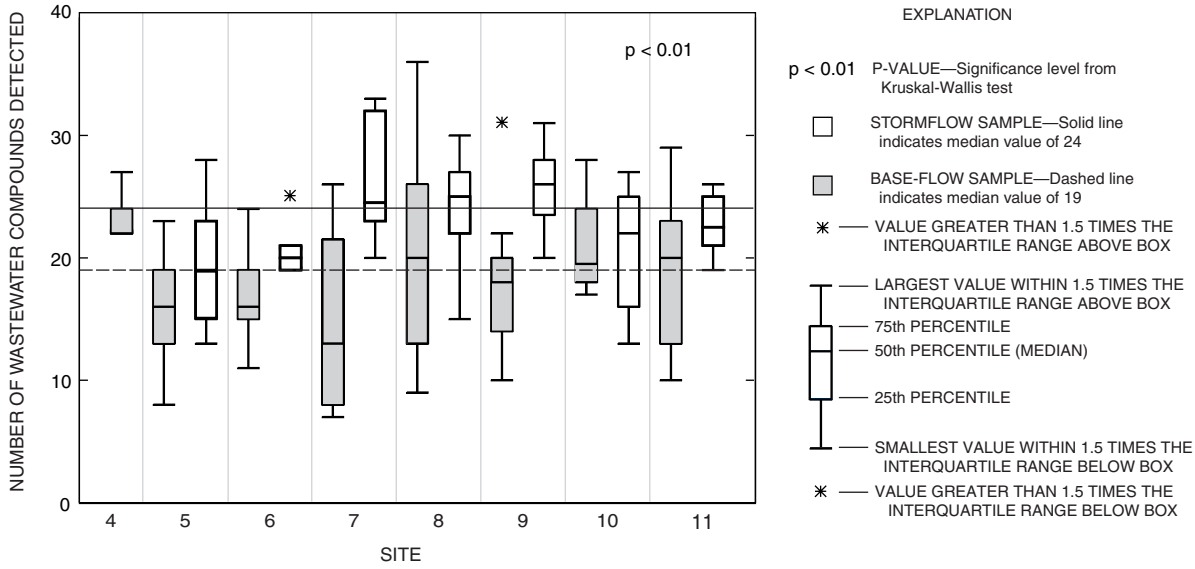


Figure 10. Number of wastewater indicator compounds detected in base-flow and stormflow samples at each site.

limits). This can dilute wastewater indicator concentrations below detection limits. Also, some of the observed concentrations of some compounds are likely flushed into streams from the nonpoint urban landscape of roofs, sidewalks, streets, parks, and storm sewers where they may have accumulated. Additionally, wastewater compounds, many of which have high affinities for sediments, can be resuspended from the disturbance of bottom sediment deposits as stream velocities and carrying capacities increase during stormflows.

Antioxidants

The antioxidant 5-methyl-1H-benzotriazole was detected in 79 percent of stormflow samples and 2,6-di-tert-butyl benzoquinone, a metabolite of BHT, was detected in 35 percent of the samples. There was almost no difference in the detection frequency or the median measured concentration of these compounds between the Blue River and Brush Creek. This differs considerably from base-flow observations, when concentrations in Brush Creek were less than one-half of those in the Blue River, and indicates that runoff has a much greater impact on the concentrations observed in Brush Creek than in the Blue River.

The remaining antioxidants were rarely detected in any of the storm samples. These were BHA, of which there were no detections, 2,6-di-tert-butylphenol, a BHA metabolite, of which there was 1 detection, and BHT which was detected in 2 samples. These compounds often were detected in wastewater effluent samples, generally at concentrations very near the method detection limit, but not in storm or base-flow samples. Dilution, degradation, and analytical sensitivity likely play roles in why these compounds were rarely observed in environmental samples, and these factors limit their use as viable wastewater tracers.

Caffeine and Cotinine

Only one stormflow sample did not have detectable concentrations of caffeine. The median caffeine concentration in Brush Creek (1.0 µg/L) was twice that in the Blue River (0.5 µg/L). This difference was statistically significant ($p<0.001$). These concentrations were near those observed in base-flow samples (0.79 and 0.54 µg/L). Given that increased flows would tend to dilute stream concentrations, these data indicate that runoff provides additional source(s) of caffeine to streams. Some caffeine sources are likely from CSOs, but nonpoint sources also are possible. The highest caf-

feine concentrations in stormflow samples were observed at site 9 on Brush Creek, followed by sites 8 and 10.

Cotinine, the nicotine metabolite, was detected in 70 percent of stormflow samples. Its occurrence and distribution in stormflow was similar to the pattern observed for caffeine. Like caffeine, the median concentration in Brush Creek (0.14 µg/L) was twice that in the Blue River (0.07 µg/L). The highest concentrations were observed at sites 7, 8, and 9. The median cotinine concentration in storm samples from Brush Creek was about 4 times the median concentration in base-flow samples (0.04 µg/L), but the median stormflow sample concentration in the Blue River was slightly less than that observed in base-flow samples (0.09 µg/L). Again, these data indicate that runoff mobilizes additional sources of cotinine, and that these sources play a more important role in the water quality of Brush Creek than in the Blue River.

Sterols and Stanols

Cholesterol was detected in 74 percent of all stormflow samples. The detection frequency in Brush Creek (86 percent) samples was greater than in samples from the Blue River (56 percent) and the median cholesterol concentration in Brush Creek stormflow samples (3.3 µg/L) was twice that in the Blue River (1.6 µg/L). These concentrations represent slight increases over those observed in base-flow samples (2.6 µg/L in Brush Creek and 1.4 µg/L in the Blue River) and indicate that additional inputs of cholesterol occur during storms. Although some cholesterol may derive from nonpoint sources, CSOs likely contribute a portion of the cholesterol observed in runoff.

Coprostanol concentrations in stormflow samples followed a similar trend to that observed for cholesterol. Detections of coprostanol in samples from Brush Creek were higher (80 percent) than those observed in samples from the Blue River (53 percent). The median concentration in Brush Creek (1.1 µg/L) was 1.5 times the concentration in the Blue River (0.71 µg/L). In base-flow samples these concentrations were nearly equivalent (0.75 µg/L compared to 0.79 µg/L), which again indicates the importance of storm wastewater contributions to Brush Creek water quality. The highest concentrations in any samples were collected from sites 8 and 9 on Brush Creek.

Fewer than 10 percent of samples had detectable concentrations of stigmastanol and 17-β estradiol. Stigmastanol was detected in only 7 samples (all on Brush Creek). Increased flow likely acts to dilute concentrations below the relatively high method detection limit for this compound. Also, storms may disturb the optimal geochemical (anoxic) conditions needed for the decomposition of waste paper, which can liberate stigmastanol into the environment.

Site 5 had the greatest detection frequency of 17-β estradiol (25 percent of samples). Other sites had 2 or fewer detections of 17-β estradiol. Dilution, and a relatively high method detection limit, likely plays a role in the relative infrequent detection of this compound in storm samples. Although detections at site 5 may reflect contributions from upstream WWTPs, the relatively small sample size (n=20) warrants caution in this interpretation.

Phenols and Detergent Compounds

Phenolic compounds (phenol, bisphenol A, NP, and the APEO's) were common in stormflow samples. Only two samples did not have a detection of any phenolic compound. NP and APEO are considered especially relevant as wastewater indicators because of their use in detergents.

Phenol was detected in 41 percent of samples from the Blue River (median concentration of 0.34 µg/L) compared to 34 percent of samples from Brush Creek (median concentration of 0.42 µg/L). There was no significant difference in concentrations between the two streams ($p=0.43$).

Bisphenol A was detected in all but one stormflow sample. The median concentration of bisphenol A in samples from Brush Creek (0.34 µg/L) was about double that observed in samples from the Blue River (0.19 µg/L), and this difference was significant ($p<0.001$). The highest concentrations were observed at sites 7, 8, and 9. The environmental occurrence of bisphenol A may be due, in part, to its common use in plastics manufacturing. Plastics are a major component of litter and unless physically removed, tend to accumulate along roadways, in parkland, in storm sewers, and catch basins. Plastics are resistant, but not immune, to degradation. If subjected to ultraviolet radiation, such as that offered by sunlight, plastics slowly break down and may release trace amounts of phenols into the environment, which can then migrate to streams.

Total nonionic detergent concentration (the sum of NP, NP1EO, NP2EO, OP1EO, and OP2EO concentrations) from Brush Creek (median concentration of 3.76 µg/L) was slightly more than double that in sam-

ples from the Blue River (median concentration of 1.69 µg/L). The median total detergent concentrations in stormflow samples was highest at site 9 (5.26 µg/L).

These concentrations represent a 100 percent increase over base-flow concentrations for Brush Creek, and a 25 percent decrease for the Blue River. This phenomenon likely results because the occurrence of these compounds in Brush Creek primarily is dictated by stormflow inputs, whereas in the Blue River the primary source of these compounds is wastewater effluent, which gets increasingly diluted as runoff volume increases.

Antimicrobials

Triclosan was detected in all but four stormflow samples. There was little difference between the median concentration in Blue River samples (0.23 µg/L) and Brush Creek samples (0.20 µg/L) or between individual sites, except for site 7, which had a median concentration slightly more than one-half of those seen at the other sites (0.13 µg/L). The median stormflow concentration in the Blue River was very similar to that seen in base-flow samples (0.27 µg/L), but the median stormflow concentration in Brush Creek was almost twice that observed in base-flow samples (0.11 µg/L). These data underscore the increased importance of wastewater storm contributions to Brush Creek when compared to the Blue River.

Insect Repellents

DEET, the insect repellent, was detected in every stormflow sample. The median concentration was higher on Brush Creek (0.52 µg/L) than in the Blue River (0.32 µg/L); a pattern observed for many other wastewater compounds during storms. The highest concentration was observed at site 9 on Brush Creek (median concentration of 2.06 µg/L); again, this pattern was observed for many other wastewater indicator compounds. These data indicate that CSO inputs into Brush Creek, especially upstream of site 9, play a more substantial water-quality role relative to the Blue River, and that substantial wastewater contributions to Brush Creek occur during storms.

Flame Retardants

The flame retardant, tri(2-choloroethyl)phosphate was detected in every stormflow sample except one. The median concentration in Brush Creek and in Blue River was equivalent (0.15 µg/L). However, between sites, the highest median concentration was observed at site 9. The frequent occurrence of this flame retardant may be related to it being a common component of plastics that tend to accumulate in the environment, especially along roadways and storm sewers. Subsequent degradation and runoff may liberate trace amounts of this compound into receiving streams.

Forty-three percent of stormflow samples had detectable concentrations of triphenyl phosphate. Although detections were more frequent in samples from the Blue River (53 percent) than in Brush Creek, the median concentration in Brush Creek samples (0.10 µg/L) was 2 times that in Blue River samples (0.05 µg/L). Tris(dichlorisopropyl)phosphate was detected in one sample.

Insecticides

Both insecticide detection frequencies and concentrations were greater in stormflow samples from Brush Creek than the Blue River. Stormflow detection frequencies and concentrations also were greater than those seen in base-flow samples. This is likely because of the fact that in addition to any insecticide contributions that may originate from wastewater sources, storm runoff likely mobilizes insecticides from golf courses, lawns, and parks.

Diazinon was the most frequently detected insecticide in stormflow samples (86 percent of all samples) and the median concentration in Brush Creek (0.21 µg/L) was double that in the Blue River (0.10 µg/L). The next most frequently detected insecticide in stormflow samples was carbaryl, detected in two-thirds of all samples, which was a substantial increase over its occurrence in base-flow samples (15 percent of all samples). This increase may be related to its relatively high degree of solubility when compared to the other insecticides examined. Also, as previously reported, carbaryl breaks down rapidly under photolysis, and is not very stable once released in the environment. The median carbaryl concentration in Brush Creek (0.28 µg/L) was significantly higher than that in the Blue River (0.08 µg/L).

The insecticides chlordane and chlorpyrifos were detected in 32 and 22 percent of stormflow samples, respectively. Lindane was detected in four samples, and one sample had detectable concentrations of methyl parathion.

The median total insecticide concentration (the sum of all measured insecticides) was 3 times greater in Brush Creek (0.41 µg/L) than in the Blue River (0.13 µg/L) and greatest at site 7, the uppermost Brush Creek site. Three golf courses in the upper part of the basin may be sources, although contributions from adjacent parkland or lawns also are likely. Also, high in-stream velocities at site 7 may keep sediments (and associated contaminants) suspended in the water column compared to downstream sites below impoundments. The median load of insecticides in stormflow, however, was 3 times greater in the Blue River because of higher flow volumes.

PAH's

PAH's were some of the most frequently detected wastewater indicator compounds in stormflow samples. Fluoranthrene and pyrene were detected in nearly all samples (more than 95 percent), phenanthrene and benzo[a]pyrene were detected in more than 90 percent of samples, and anthracene in 80 percent of samples. Napthalene was detected in 40 percent of samples. Concentrations of PAH's were highly correlated with one another. Total PAH concentrations, defined as the sum of the concentrations of individual PAH's, in Brush Creek (median concentration of 2.0 µg/L) were nearly twice those in the Blue River (median concentration of 1.1 µg/L). These values represent a ten-fold increase in concentrations observed in base-flow samples. PAH concentrations were greatest in samples from site 7, the uppermost Brush Creek site. Consequently, it is likely that nonpoint sources of PAH's are more dominate than wastewater overflows and bypasses as sources in storm runoff.

Relative Hydrograph Contributions of Constituents

Because storm samples were segmented by the rising, peak, or falling stage of the storm hydrograph, the relative contribution of wastewater constituents that were delivered during each phase could be examined. The loads and concentrations for the sum of all wastewater indicator compounds determined in storm samples for the various hydrograph segment samples are shown in figure 11. Loads were significantly higher in peak flow ($p=0.006$) when compared to the rise and recession, primarily because an average of 62 percent of the total stormflow occurred during the hydrograph peak. There was no significant difference in total wastewater concentrations between each phase ($p=0.33$) because of several factors. The highly urbanized nature of the basin results in very rapid hydrologic responses to runoff events. Streams rise and fall quickly during storm events. Concentrations measured in the rise represent those from the initial flush of nonpoint sources superimposed upon base-flow contributions. This tends to increase wastewater indicator concentrations. If rainfall is of sufficient intensity and duration, CSOs are triggered, which contribute wastewater to receiving streams. Relatively high concentrations of wastewater indicator compounds would be expected from CSOs; however, increased flows should suppress concentrations through dilution. Together, these processes would tend to lower concentration levels in peak samples. As flow recedes, the relative importance of any recent inputs becomes more evident since concentrations remain relatively stable. Not all storms trigger CSO events, so peak events also include storms that did not trigger CSOs. Also, and perhaps most importantly, suspended stream sediments, to which most of these indicator compounds are strongly affiliated, are mainly (more than 75 percent) composed of easily transported clay particles (Blevins, 1986). Therefore, very little energy is required to keep these sediments in suspension throughout the course of the hydrograph.

YIELDS AND RELATIVE WATER-QUALITY IMPACT RANKINGS

Contaminant concentrations and fluxes can help better understand sources, the relative magnitude of sources, and information about trends, processes, and transformations. However, loads are biased in favor of streams, or sites, with the largest drainage areas because these areas have higher discharges, which often translates into higher loads. Yields, determined by dividing the load for any given constituent at a particular site by the drainage area for that site, factor out this inherent bias and provide an equivalent measure of comparison for individual stream reaches. The drainage area referred to is the unit area between study sites. The sum of the drainage areas would equal the basin drainage area.

Relative water-quality impact rankings for stream reaches were done according to the following protocol. First, yields were determined for total N and total P, and for wastewater indicator compounds that had a 50 percent or greater detection frequency (figs. 12

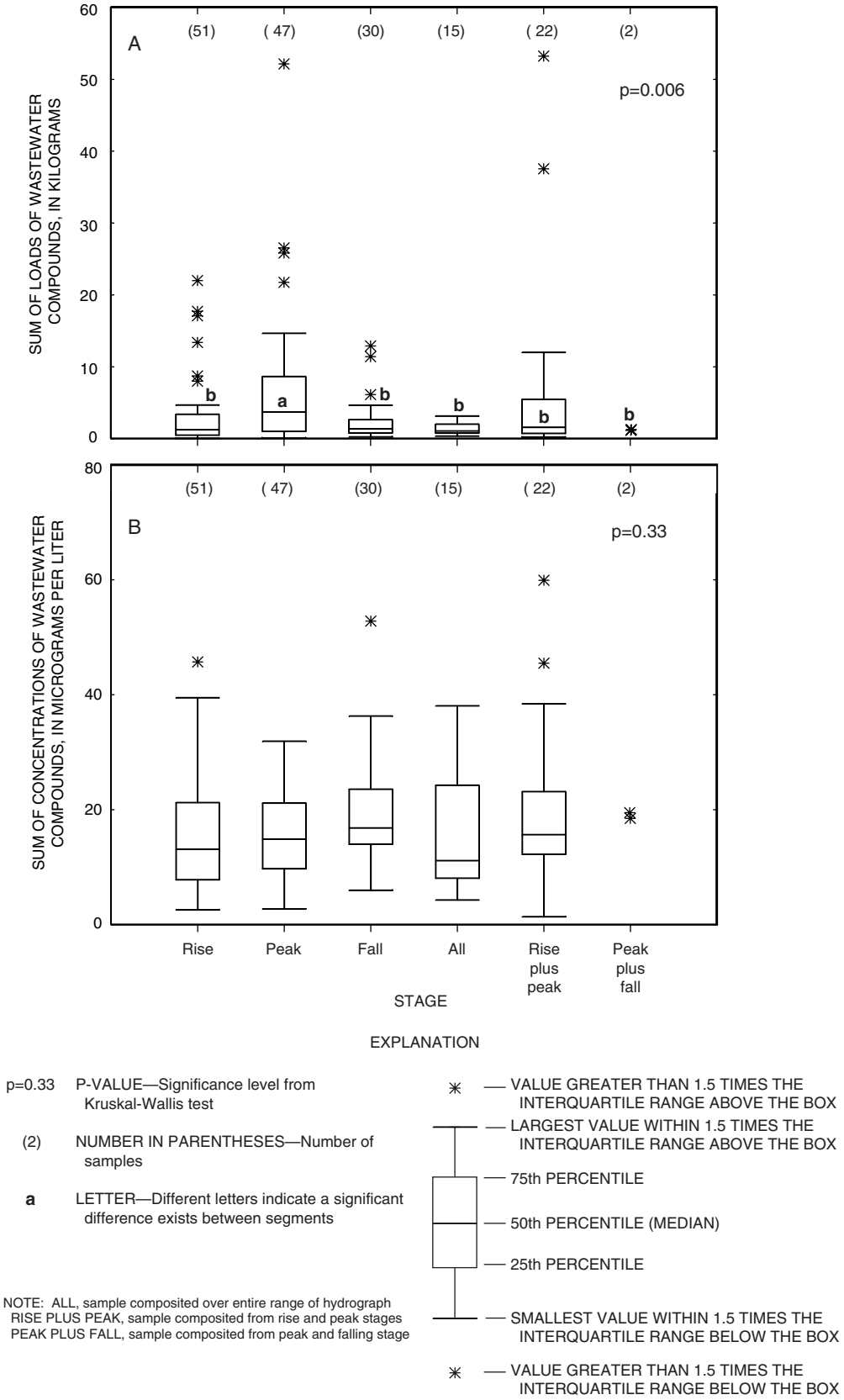


Figure 11. Sum of loads (A) and sum of concentrations (B) for wastewater indicator compounds in storm hydrograph segments.

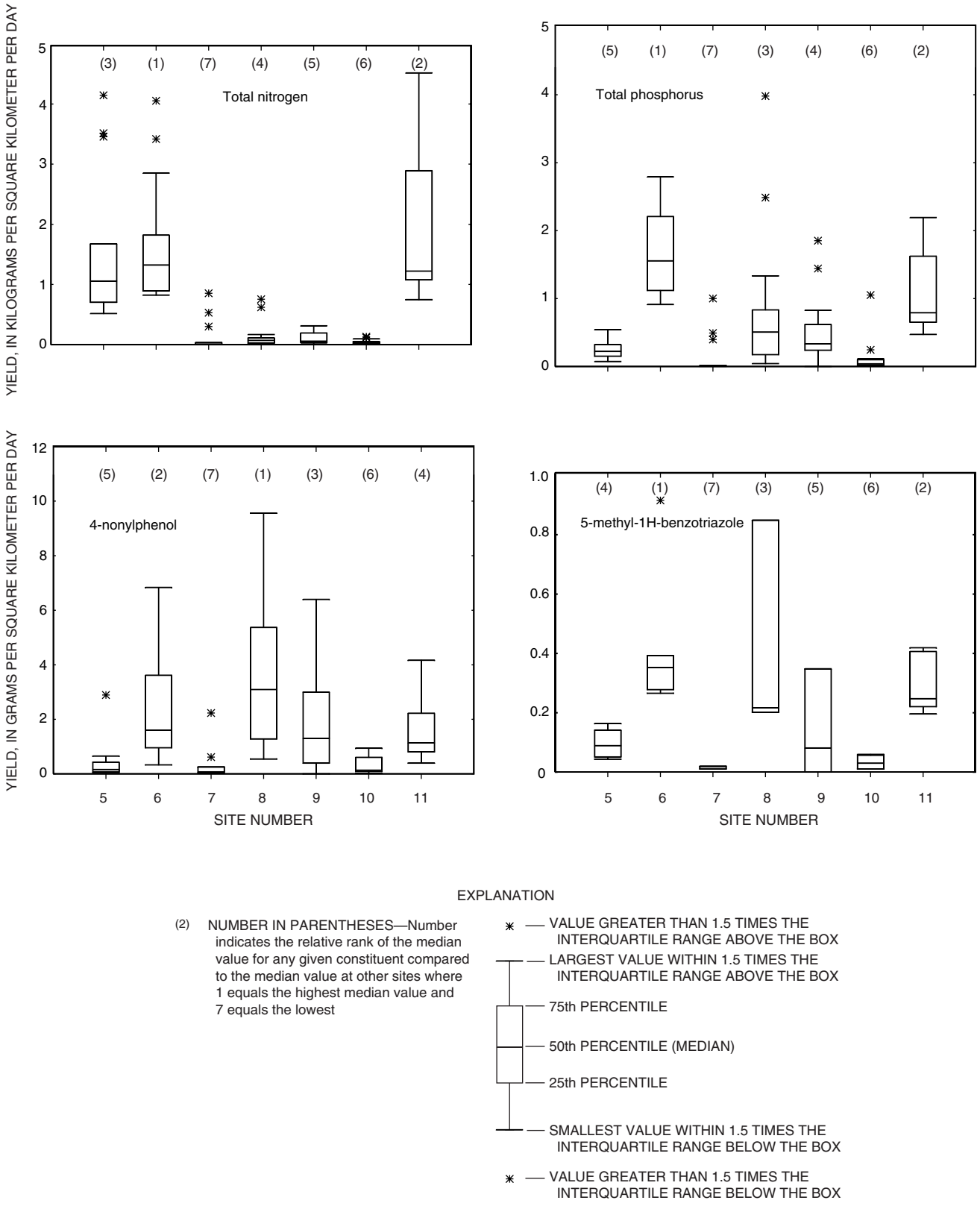


Figure 12. Yield of selected constituents in base-flow samples.

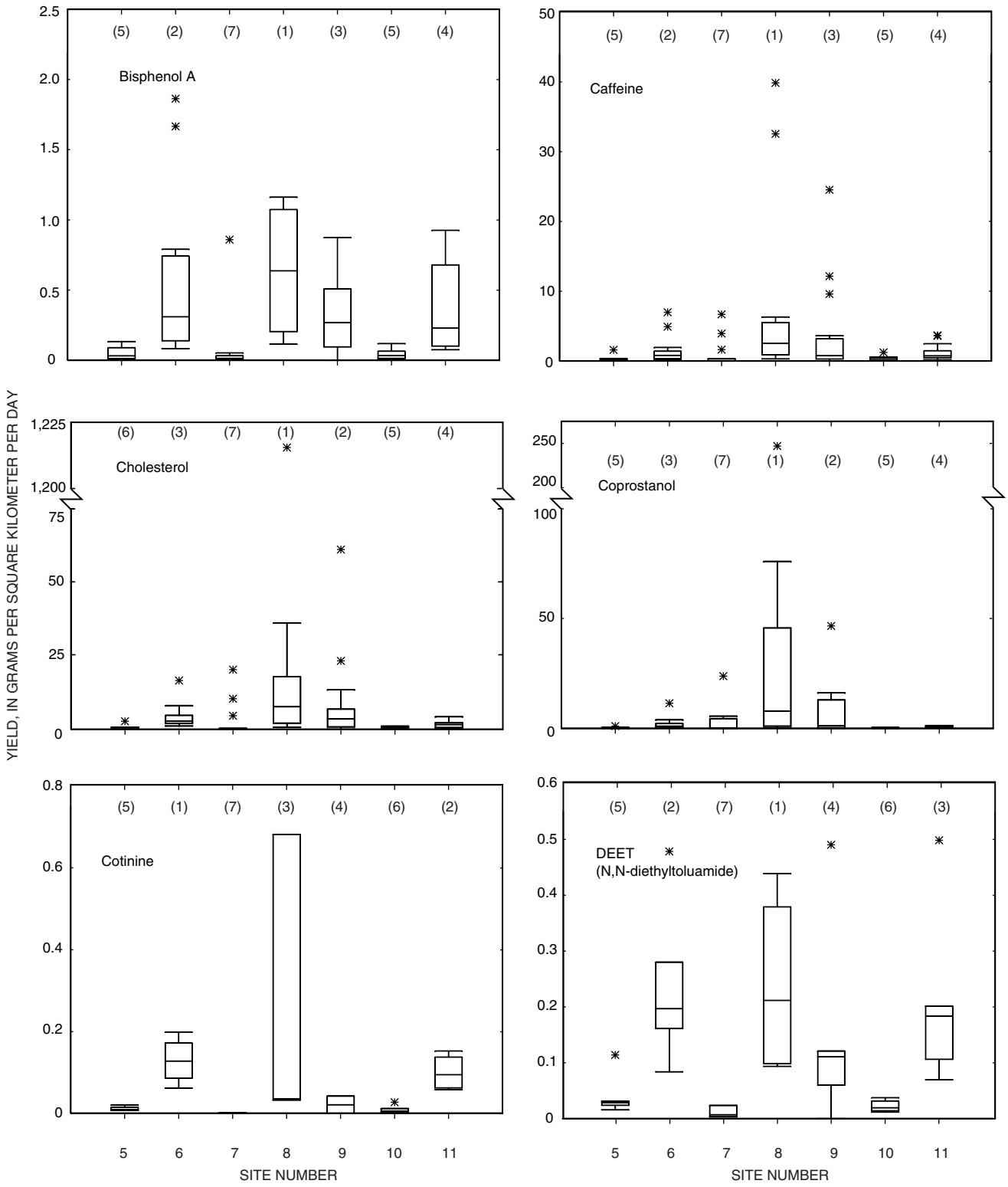


Figure 12. Yield of selected constituents in base-flow samples—Continued.

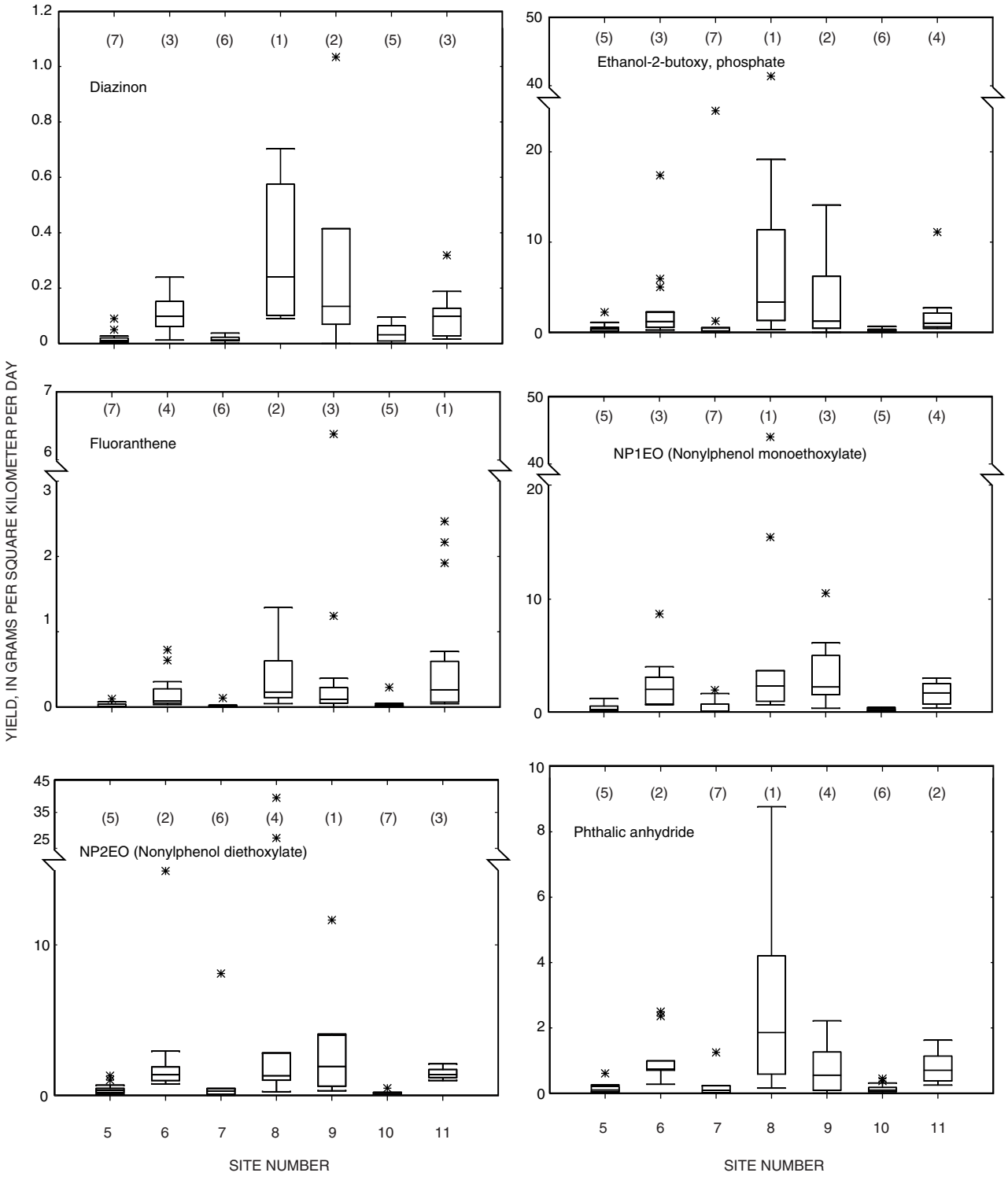


Figure 12. Yield of selected constituents in base-flow samples—Continued.

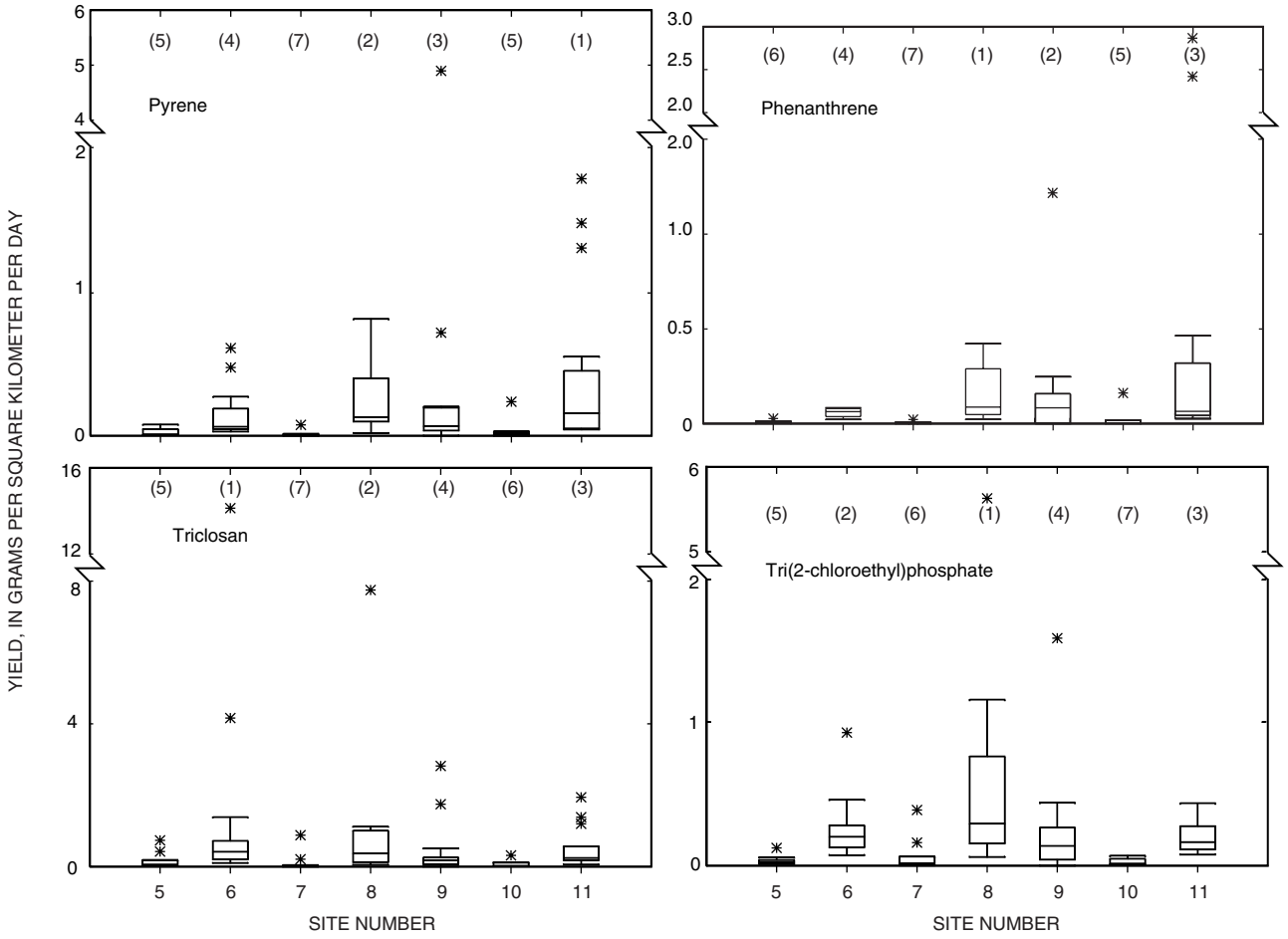


Figure 12. Yield of selected constituents in base-flow samples—Continued.

and 13). There were 18 wastewater indicator compounds in base-flow samples and 22 compounds in storm samples that met this criterion. Stormflow samples also included yields for chloride, TOC, BOD_5, and COD. To prevent outlier bias, the median yield for each constituent was compared against the median yield for all the other sites. The sites were then ranked in order from highest to lowest; the site with the highest median yield was assigned a rank of 1, the site with the lowest median yield was assigned a rank of 7. This was done for each constituent used in the analysis.

Not all compounds behave similarly within the environment, and the fate of many of these compounds is poorly understood; therefore, no special weight was given to any constituent and no consideration was given to potential human, or aquatic, health effects. A myriad of factors and urban processes may further distort the behavior of environmental contaminants. Quantification of all factors and processes is impractical, if not impossible. Therefore, the more measures of impact available, the less likely that any one given measure will skew the results. The relative water-quality impact ranking for each stream reach (table 9) represents the average of the individual yield ranks for that reach. The stream reach with the lowest average rank would have the greatest impact relative to it's drainage area, and to the other stream reaches.

For the Blue River, relative impact during stormflow was directly related to increased downstream constituent loadings. This would be expected as the treated wastewater inputs all occur upstream of site 5 and the number, volume, and opportunity for CSO events increases downstream. Relative impact data for Brush Creek was much different. The highest impact rankings for any stream reach occurred between sites 8 and 9, followed by the reach between sites 7 and 8. Impact rankings at the most upstream Brush Creek reach, upstream of site 7, were higher than those at the most

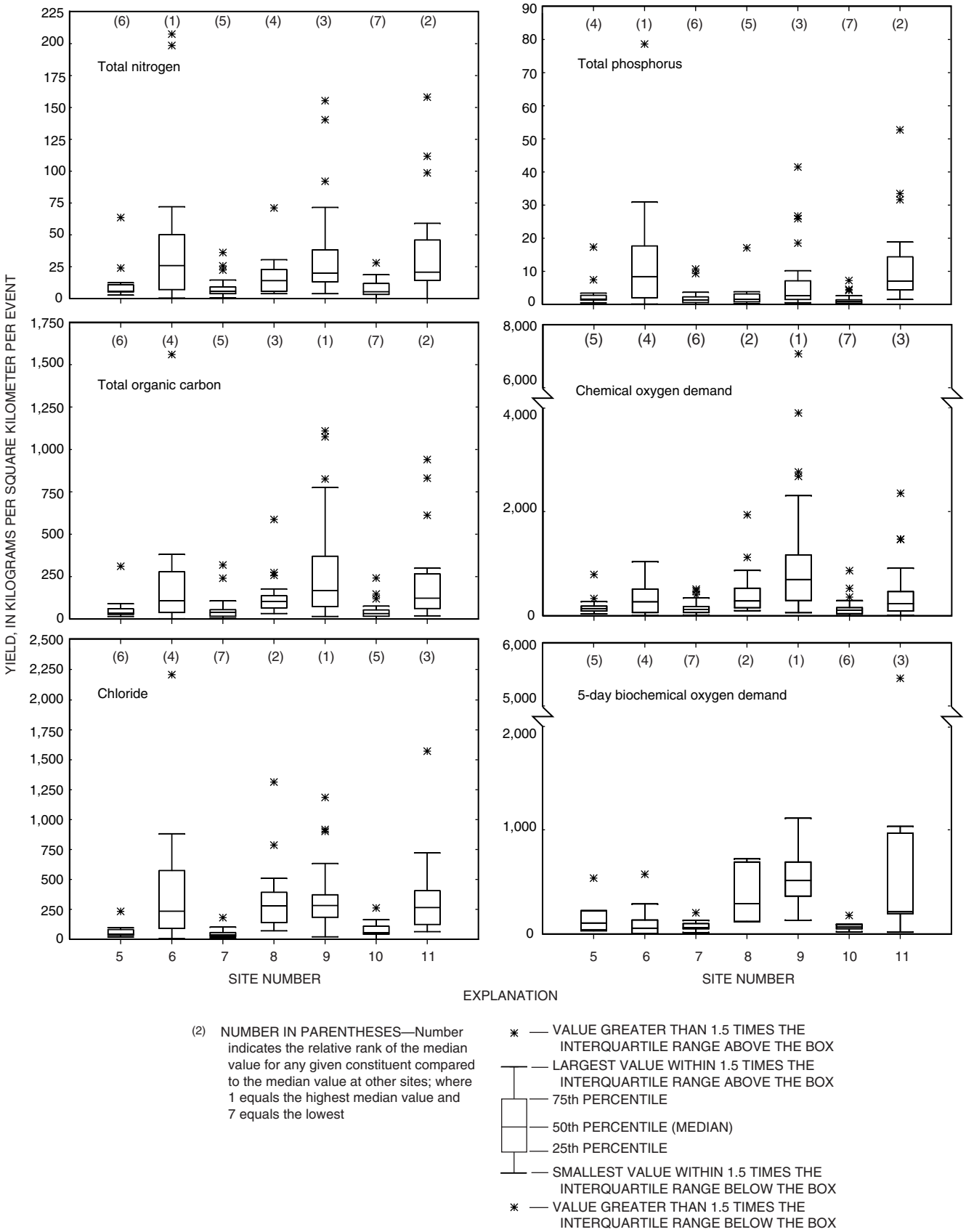


Figure 13. Yield of selected constituents in stormflow samples.

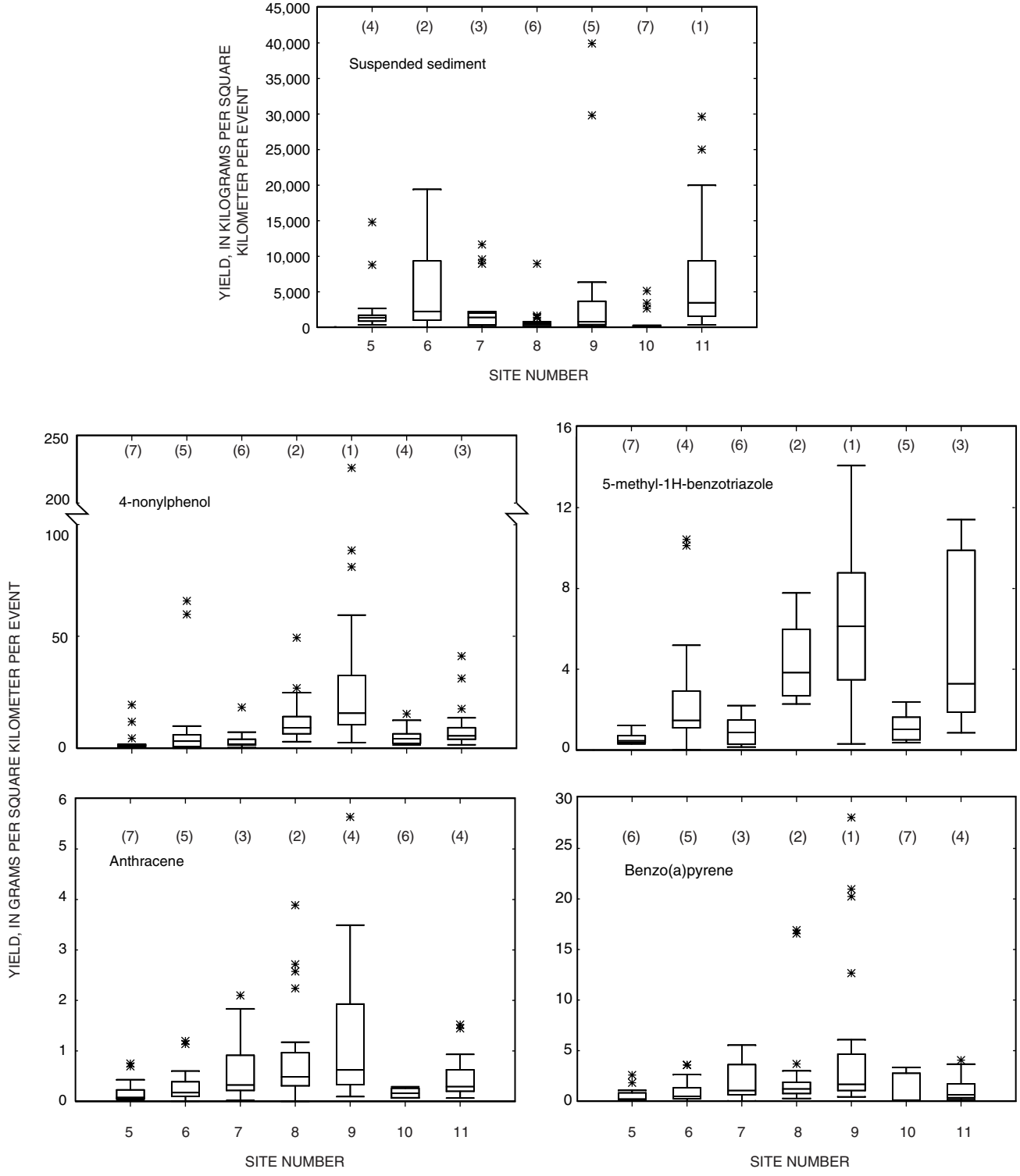


Figure 13. Yield of selected constituents in stormflow samples—Continued.

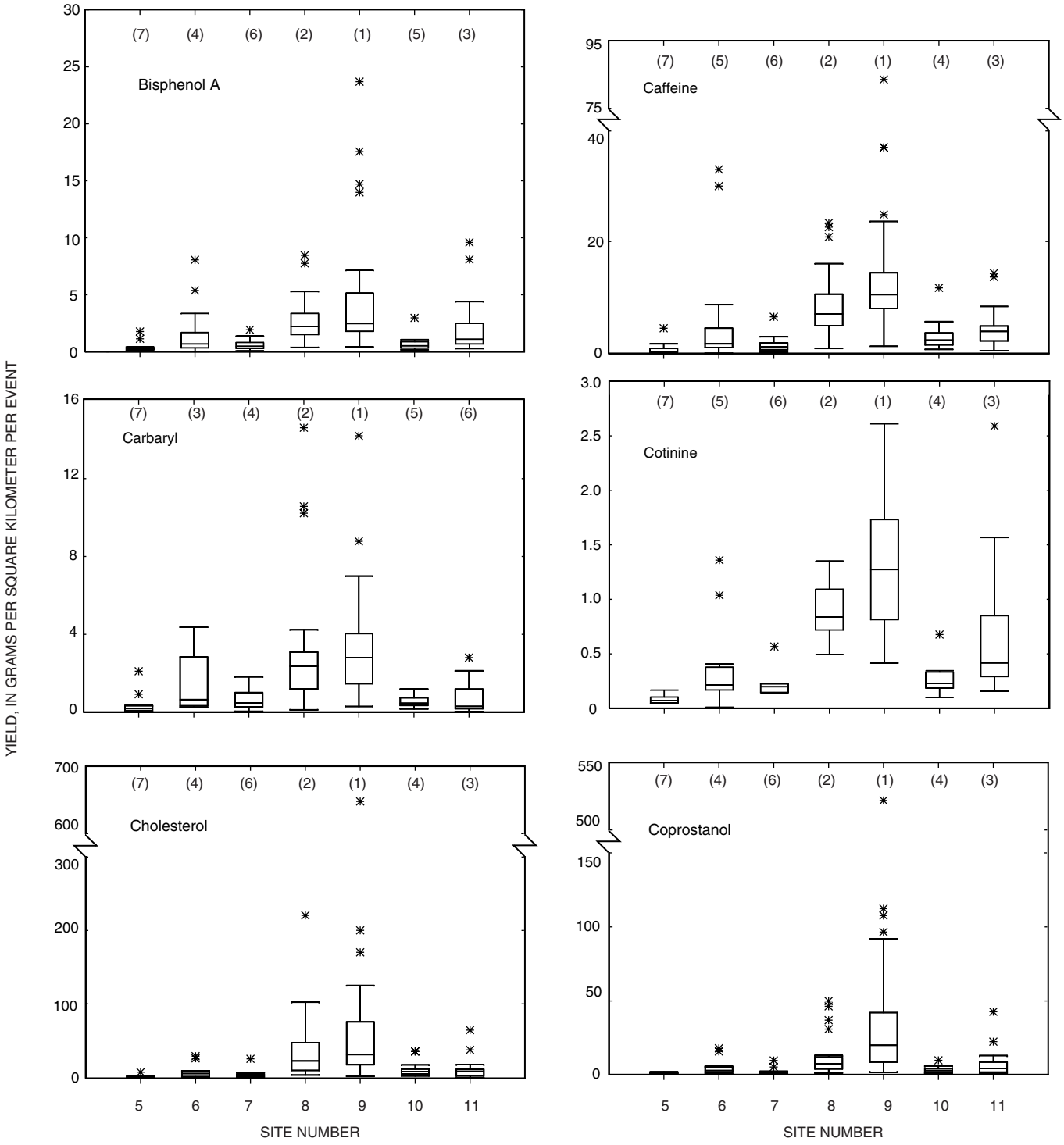


Figure 13. Yield of selected constituents in stormflow samples—Continued.

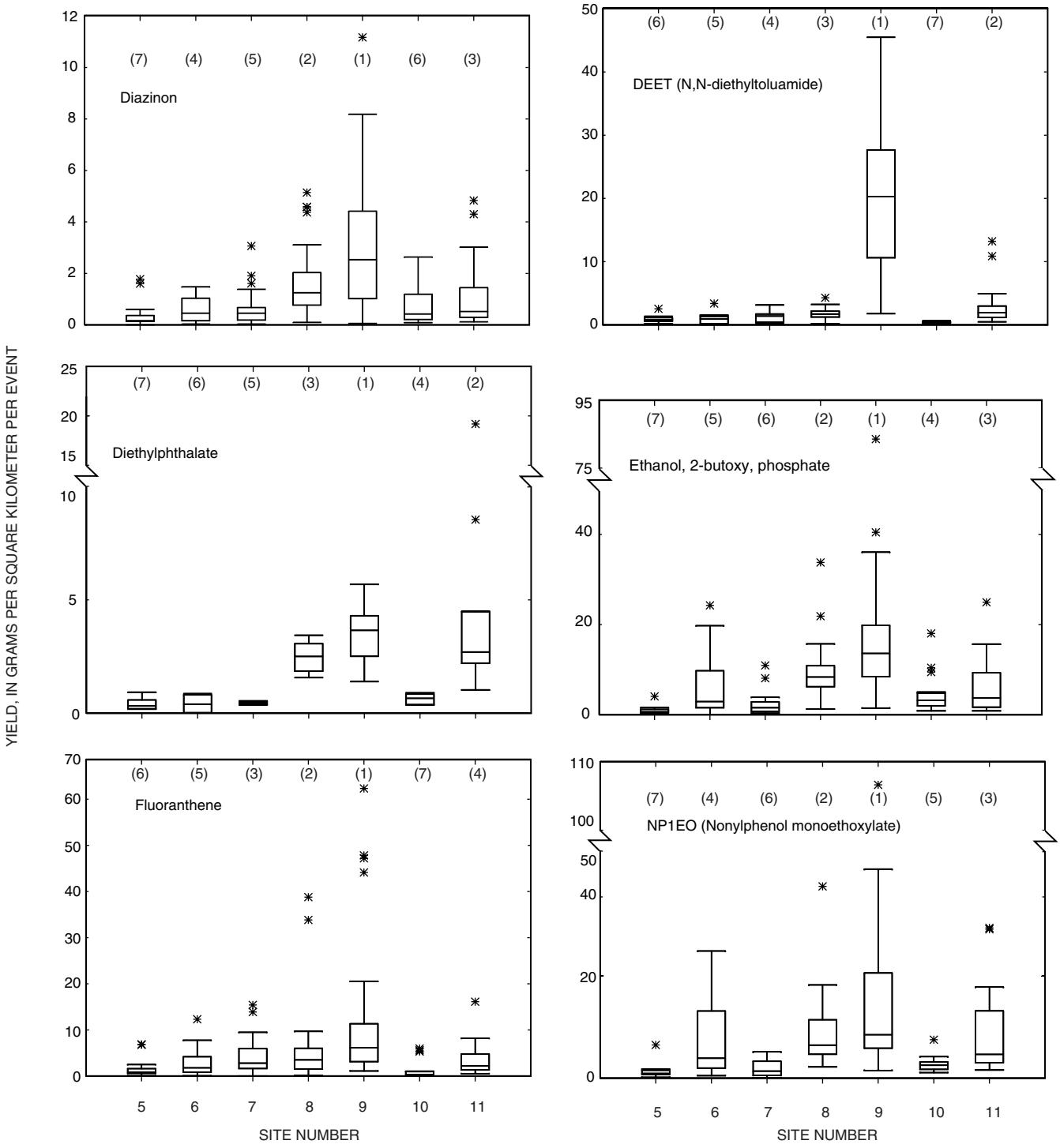


Figure 13. Yield of selected constituents in stormflow samples—Continued.

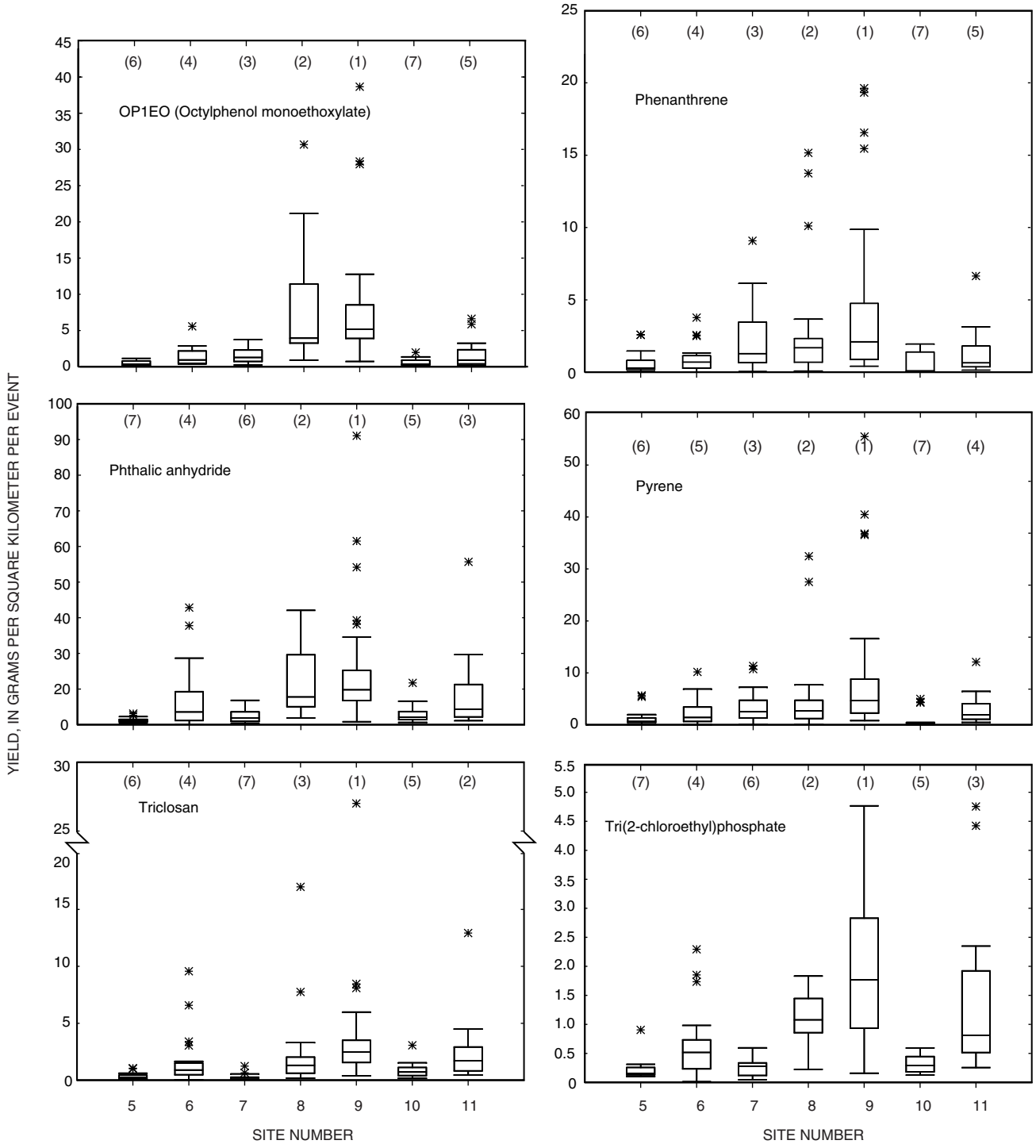


Figure 13. Yield of selected constituents in stormflow samples—Continued.

Table 9. Relative water-quality impact rankings between sites during storm and base-flow conditions

[Lower numbers indicate a higher degree of relative impact]

Stormflow rankings				
Site number (fig. 1)	Site name	Relative drainage area (square kilometers)	Average rank (fig. 11)	Relative water-quality impact rank
5	Blue River near Kansas City, Missouri	490	6.3	7
6	Blue River at Blue Parkway	78	4.1	4
7	Brush Creek at Ward Parkway	32	5.1	5
8	Brush Creek at Kansas City, Missouri	6.9	2.4	2
9	Brush Creek at Rockhill Road	5.4	1.3	1
10	Brush Creek at Elmwood Avenue	30	5.6	6
11	Blue River at 12th Street	120	3.1	3

Base-flow rankings			
Site number (fig. 1)	Site name	Average rank (fig. 11)	Relative water-quality impact rank
5	Blue River near Kansas City, Missouri	5.4	5
6	Blue River at Blue Parkway	2.4	2
7	Brush Creek at Ward Parkway	6.7	7
8	Brush Creek at Kansas City, Missouri	1.5	1
9	Brush Creek at Rockhill Road	3.3	4
10	Brush Creek at Elmwood Avenue	5.7	6
11	Blue River at 12th Street	2.9	3

downstream reach, between sites 9 and 10. The reasons for this order of relative water-quality impact rankings are complex. The middle sections of Brush Creek have the highest population densities and the greatest amount of impervious cover, which may trigger more frequent CSO events. Hydrologic changes related to the stream channel modifications likely plays a role in why the section between sites 8 and 9 showed the highest impact. Consumer complaints related to sewer backups during storms are numerous in this drainage area. Storms deliver sediment, organic matter, and associated pollutants into Brush Creek, which then accumulate in reservoirs upstream of sites 8, 9, and 10. Sediment accumulation is greatest in the reservoirs above sites 8 and 10, where stream velocities during storm events are lowest. Higher stream velocities in the reach between site 8 and 9 result in the transport of higher contaminant loads through this section.

During base flow, the highest relative water-quality impact ranking was determined in the stream reach located between sites 7 and 8 on Brush Creek. The reason for this is not clear. It may be related to the interaction of wastewater sediments with the overlying water column at the downstream end of this reach (near site 8), especially considering that downstream water is recirculated back upstream for a portion of each day in order to maintain the pool elevation at site 8. The interaction of ground and surface water, especially with regard to its interaction with sewer lines, also cannot be ruled out as contributing to the elevated ranking for this stream reach. Base-flow impact rankings for the Blue River were highest in the middle section of the Blue River (between sites 5 and 6). This ranking may be affected by illicit dumping that occurs near site 6, as well as the downstream end of this reach's proximity to several light industrial facilities. However, the procedures used to calculate impact rankings may not sufficiently account for the predominate nature of the Blue River wastewater indicator compound inputs that occur during base flow, which have been shown to be from WWTPs. If the predominate source of wastewater in the Blue River originates as WWTP discharges from Indian Creek, then calculated yields upstream of site 5 (which include the entire basin upstream of site 5) may be biased low. Additional data collected at sites 1 and 4 should help to clarify this possibility.

SUMMARY

The impact of wastewater on water quality in the Blue River Basin was determined during both base-flow and stormflow conditions. Traditional constituent measures coupled with new compounds and analytical tools were used in the evaluation. The study focused primarily on two streams in the basin, the Blue River and Brush Creek. Traditional constituents included total and dissolved nutrients, chloride, total organic carbon (TOC), 5-day biochemical oxygen demand (BOD_5), and chemical oxygen demand (COD). New analyses included a suite of consumer compounds indicative of wastewater, selected over-the-counter and prescription pharmaceuticals, and source-tracking of *Escherichia coli* (*E. coli*) bacteria using genetic fingerprinting. Together, these data were used to identify the predominate sources of wastewater entering these streams during base flows and stormflows, and determine the relative impact of wastewater on the water-quality of selected stream reaches.

Wastewater impacts are governed by many processes; these processes change depending upon the hydrologic regime, or the stream of interest. Wastewater treatment plant discharges into the Blue River or its upper tributaries, are the major source of wastewater in the Blue River. These sources are especially obvious during base-flow conditions.

WWTPs effectively remove most, but not all, constituents. The removal efficiency varies with WWTP and by compound. WWTP removal efficiencies also can be adversely affected by factors such as malfunctioning equipment, insufficient capacity to meet current population demands, or heavy rainfall. Constituents remaining after treatment, although subject to diurnal and seasonal fluctuations, continuously are discharged to receiving streams, and thus have a continued environmental presence. Because a number of WWTPs operate within the Blue River Basin, especially in the upper part of the basin, wastewater inputs are additive.

Wastewater inputs into Brush Creek primarily result from infrequent combined sewer overflow (CSO) events. The sporadic nature of these events generally means that wastewater concentrations and loads in the Blue River during base flow typically exceed those observed in Brush Creek during base flow. However, impounded reaches of Brush Creek trap storm sediments (including those from CSOs) and associated constituents. Once trapped, these sediments may continue to impact Brush Creek water quality as additional processes come into play. During base flow, trace amounts of wastewater contaminants may partition into the overlying water column and affect water quality. Fountains, designed to entrain and aerate water in the impoundments, may facilitate this process. During storms, stream velocities increase in reaches immediately downstream from low-water dams and in areas with constricted flow, and enhance the downstream transport of wastewater constituents. A portion of the wastewater impacts observed in Brush Creek may have resulted from groundwater contributions, especially in areas where the stream channel bisects areas of aging sewer lines.

During storms, the interrelation of additional factors determine wastewater indicator compound detection frequencies and concentrations. In the Blue River, as runoff volume increases in relation to WWTP contributions, wastewater concentrations related to these sources becomes diluted. However, increased stream velocities can also mobilize stream sediments and associated constituents. Minor contributions may have resulted from ground-water discharges to surface water. These contributions, which are small relative to effluent contributions during base flow, decrease during runoff events. Constituents mobilized through surface runoff, storm sewers, leaky sewer pipes, CSOs, and wastewater bypasses play a much greater role in Brush Creek during stormflow. The timing of these events and runoff volume determines in-stream concentrations.

Tributaries, especially those with a large number of CSOs, like Brush Creek, would be expected to contribute substantially to constituent loads in the Blue River. However, low stream gradients in impounded reaches of Brush Creek encourage sediment deposition and allow suspended contaminants to settle from the water column. Some of these sediments also are periodically excavated from upper channel reaches; thus, wastewater stormflow contributions from Brush Creek to the Blue River are less than would be expected.

The smaller drainage area of Brush Creek compared to the Blue River had important implications for the determination of the relative water-quality impact between the two streams. During storms, water-quality impact on the Blue River was largely a function of increased, downstream inputs. For Brush Creek stormflow, the highest relative water-quality impact occurred between the two middle sites (8 and 9), which has a relatively small drainage area but relatively dense, sur-

rounding population. The higher population density likely acts to trigger more frequent CSO events, and to increase the relative water-quality impact associated with ones that do occur. Impact was lowest at the most downstream Brush Creek stream reach because many wastewater compounds which enter Brush Creek during storms are trapped by upstream impoundments.

Relative water-quality impact on Brush Creek during base flow was greatest in the stream reach between sites 7 and 8. Increased relative water-quality impact at this site may result from the repeated contact of recycled water (designed to maintain a stable pool elevation above site 8) with contaminated bottom sediments. The relative impact of Blue River stream segments during base-flow events was highest in the middle reaches of the stream, an area that frequently receives dumping. However, base-flow impact rankings for the Blue River may not sufficiently account for wastewater discharges from WWTPs because of relatively large drainage area upstream of site 5.

This study documents how a variety of analytical approaches can be used together to determine wastewater impacts on stream water quality. Some of these techniques and constituents have been in use for many years while others are just now emerging as tools of hydrologic investigation. These new methods and constituents can be helpful in determining wastewater sources and in characterizing the relation between human activity and stream water quality. Additional research will further characterize the temporal and spatial trends of many of these compounds within the environment as well provide additional data to assess their fate and transport and environmental consequences. Certain compounds, in particular those associated with detergents such as triclosan, alkylphenol polyethoxylates, and sterols seem especially viable as wastewater tracing tools. As populations become increasingly urban and suburban, such methodologies and characterizations should increase in importance.

REFERENCES

Adolfsson-Erici, M., Patterson, M., Parkkonen, J., and Sturve, J., 2000, Triclosan, a commonly used bactericide found in human milk and in the aquatic environment, *in* Abstracts of Dioxin 2000, 20th International Symposium on Halogenated Environmental Organic Pollutants and POP's: Monterey, Calif., p. 39.

Ahel, M., and Giger, W., 1993, Partitioning of alkylphenols and alkylphenol polyethoxylates between water and organic solvents: Chemosphere, v. 26, no. 8, p. 1,471–1,478.

Ahel, M., Giger, W., and Schaffner, C., 1994, Behavior of alkylphenol polyethoxylate surfactants in the aquatic environment—II. Occurrence and transformation in rivers: Water Research, v. 28, no. 5, p. 1,143–1,152.

Barone, J.J., and Roberts, H.R., 1996, Caffeine consumption: Food Chemistry and Toxicology, v. 34, no. 1, p. 119–129.

Baronti, C., Curini, R., D'Ascenzo, G., Di Corcia, A., Gentili, A., and Samperi, R., 2000, Monitoring natural and synthetic estrogens at activated sludge sewage treatment plants and in a receiving river water: Environmental Science and Technology, v. 34, no. 24, p. 5,059–5,066.

Becker, L.D., Alexander, T.W., and Waite, L.A., 1983, Floods in Kansas City, Missouri and Vicinity, August 12–13, 1982: U.S. Geological Survey Water-Resources Investigations Report 83–4141, 35 p.

Bennett, E.R., and Metcalfe, C.D., 2000, Distribution of degradation products of alkylphenol ethoxylates near sewage treatment plants in the lower Great Lakes, North America: Environmental Toxicology and Chemistry, v. 19, no. 4, p. 784–792.

Bennie, D.T., 1999, Review of the environmental occurrence of alkylphenols and alkylphenol ethoxylates: Water Quality Research Journal of Canada, v. 34, no. 1, p. 79–122.

Blevins, D.W., 1986, Quality of stormwater runoff in the Blue River Basin, Missouri and Kansas, July–October 1981 and April–July 1982: U.S. Geological Survey Water-Resources Investigations Report 84–4226, 131 p.

Brown, G.K., Zaugg, S.D., and Barber, L.B., 1999, Wastewater analysis by gas chromatography/mass spectrometry, *in* Morganwalp, D.W., and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program-Proceedings of the Technical Meeting, Charleston, South Carolina, March 8–12, 1999: U.S. Geological Survey Water-Resources Investigations Report 99–4018B, v. 2, p. 431–436.

Bruggeman, W.A., and van der Naald, W.G.H., 1988, Occurrence, distribution, and availability of PAH in surface waters and sediments: Toxicological and Environmental Chemistry, v. 16, no. 4, p. 241–243.

Burns and McDonnell, 1994, Combined sewer overflow water quality impact analysis, system hydraulic modeling and recommendation of corrective action: Kansas City, Mo., variously paged.

Carlsson, H., Nilsson, U., and Ostman, C., 2000, Video display units—An emission source of the contact allergenic flame retardant triphenyl phosphate in the indoor environment: Environmental Science and Technology, v. 34, no. 18, p. 3,885–3,889.

Carson, A.C., Shear, B.L., Ellersieck, M.R., and Asfaw, A., 2001, Identification of fecal *Escherichia Coli* from humans and animals by ribotyping: Applied and Environmental Microbiology, v. 67, no. 4, p. 1,503–1,507.

Chan, K.H., Lam, M.H.W., Poon, K.F., Yeung, H.Y., and Chiu, K.T., 1998, Application of sedimentary fecal stanols and sterols in tracing sewage pollution in coastal waters: Water Research, v. 32, no. 1, p. 225–235.

Childress, C.J.O., Foreman, W.T., Connor, B.F., and Maloney, T.J., 1999, New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U.S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Open-File Report 99–193, 19 p.

Christensen, V.G., Jian, X., and Ziegler, A.C., 2000, Regression analysis and real-time water-quality monitoring to estimate constituent concentrations, loads, and yields in the Little Arkansas River, south-central Kansas, 1995–99: U.S. Geological Survey Water-Resources Investigations Report 00–4126, 36 p.

Committee on Hormonally Active Agents in the Environment, Board on Environmental Studies and Toxicology, Commission on Life Sciences, and National Research Council, 1999, Hormonally active agents in the environment: Washington, D.C., National Academy Press, 430 p.

Cook, D.L., LaFleur, L., Parrish, A., Jones, J., and Hoy, D., 1997, Characterization of plant sterols from 22 U.S. pulp and paper mills: Water Science and Technology, v. 35, no. 2–3, p. 297–303.

Daughton, C.G., and Jones-Lepp, T.L., 2001, Pharmaceuticals and personal care products in the environment—Scientific and regulatory issues: American Chemical Society (ACS) Symposium Series 791, Oxford University Press, 396 p.

Daughton, C.G., and Ternes, T.A., 1999, Pharmaceuticals and personal care products in the environment—Agents of subtle change?: Environmental Health Perspectives, v. 107, suppl. 6, p. 907–938.

Dombek, P.E., Johnson, L.K., Zimmerley, S.T., and Sadowsky, M.J., 2000, Use of repetitive DNA sequences and the PCR to differentiate *Escherichia Coli* isolates from human and animal sources: Applied and Environmental Microbiology, v. 66, no. 6, p. 2,572–2,577.

Dufour, A.P., 1984, Health effects criteria for fresh recreational waters: Cincinnati, Ohio, U.S. Environmental Protection Agency, EPA-600/1-84-004, 33 p.

Elhmmali, M.M., Roberts, D.J., and Evershed, R.P., 1997, Bile acids as a new class of sewage pollution indicator: Environmental Science and Technology, v. 31, no. 12, p. 3,663–3,668.

——— 2000, Combined analysis of bile acids and sterols/stanols from riverine particulates to assess sewage discharges and other fecal sources: Environmental Science and Technology, v. 34, no. 1, p. 39–46.

Ferezou, J., Gouffier, E., Coste, T., and Chevallier, F., 1978, Daily elimination of fecal neutral sterols by humans: Digestion, v. 18, p. 201–212.

Fishman, M.J., Raese, J.W., Gerlitz, C.N., and Husband, R.A., 1994, U.S. Geological Survey approved inorganic and organic methods for the analysis of water and fluvial sediment, 1954–94: U.S. Geological Survey Open-File Report 94–351, 55 p.

Furlong, E.T., Cahill, J.D., Werner, S.L., Burkhardt, M.R., Kolpin, D.W., and Gates, P.M., 2000, High-performance liquid chromatography/electrospray ionization-mass spectrometric analysis of agricultural and human health pharmaceuticals in samples of ground and surface water, *in* Emerging Issues Conference of the National Ground Water Association, June 7–8, 2000, Minneapolis, Minn., p. 6.

Hale, R.C., Smith, C.L., de Fur, P.O., Harvey, E., Bush, E.O., La Guardia, M.J., and Vadas, G.G., 2000, Nonylphenols in sediments and effluents associated with diverse wastewater outfalls: Environmental Toxicology and Chemistry, v. 19, no. 4, p. 946–952.

Hauth, L.D., and Carswell, W.J., Jr., 1978, Floods in Kansas City, Missouri and Kansas, September 12–13, 1977: U.S. Geological Survey Water-Resources Investigations Report 78–63, 36 p.

Hauth, L.D., Carswell, W.J., Jr., and Chin, E.H., 1981, Floods in Kansas City, Missouri and Kansas, September 12–13, 1977: U.S. Geological Survey Professional Paper 1169, 47 p.

Hay, A.G., Dees, P.M., and Sayler, G.S., 2001, Growth of a bacterial consortium on triclosan: FEMS Microbiology Ecology, v. 36, p. 105–112.

Helsel, D.R., and Hirsch, R.M., 1992, Statistical methods in water resources: New York, Elsevier Science Publishing Co., 522 p.

Hovander, L., Malmberg, T., Athanasiadou, M., Athanassiadis, I., Rahm, S., Bergman, A., Klasson Wehler, E., 2002, Identification of hydroxylated PCB metabolites and other phenolic halogenated pollutants in human blood plasma: Archives of Environmental Contamination and Toxicology, v. 42, p. 105–117.

Hundt, K., Martin, D., Hammer, E., Jonas, U., Kindermann, M.K., and Schauer, F., 2000, Transformation of triclosan by *Trametes versicolor* and *Pycnoporus cinnabarinus*: Applied and Environmental Microbiology, v. 66, no. 9, p. 4,157–4,160.

John, D.M., and White, G.F., 2000, Environmental fate of nonylphenol ethoxylates—Differential adsorption of homologs to components of river sediments: Environmental Toxicology and Chemistry, v. 19, no. 2, p. 293–300.

Kansas Department of Health and Environment, 2000, Kansas water quality assessment (305(b) report): Topeka, Kans., 41 p., accessed October 2001 at URL http://www.kdhe.state.ks.us/befs/305b_2000/.

Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., and Buxton, H.T., 2002, Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: A national reconnaissance: Environmental Science and Technology, v. 36, no. 6, p. 1,202–1,211.

Larson, S.J., Gilliom, R.J., and Capel, P.D., 1999, Pesticides in streams of the United States—Initial results from the National Water-Quality Assessment Program: U.S. Geological Survey Water-Resources Investigations Report 98–4222, 99 p.

LeBlanc, L.A., Latimer, J.S., Ellis, J.T., and Quinn, J.G., 1992, The geochemistry of coprostanol in waters and surface sediments from Narragansett Bay: Estuarine, Coastal, and Shelf Science, v. 34, p. 439–458.

Leeming, R., Ball, A., Ashbolt, N., and Nichols, P., 1996, Using faecal sterols from humans and animals to distinguish faecal pollution in receiving waters: Water Research, v. 30, p. 2,893–2,900.

Levy, C.W., Roujeinikova, A., Sedelenikova, S., Baker, P.J., Stuitje, A.R., Slabas, A.R., Rice, D.W., and Rafferty, J.B., 1999, Molecular basis of triclosan activity: Nature, v. 398, p. 383–384.

Lindsey, M.E., Meyer, M.T., and Thurman, E.M., 2001, Analysis of trace levels of sulfonamide and tetracycline antibacterials in groundwater and surface water using solid-phase extraction and liquid chromatography/mass spectrometry: Analytical Chemistry, v. 73, no. 19, p. 4,640–4,646.

Lopez-Avila, V., and Hites, R.A., 1980, Organic compounds in an industrial wastewater—Their transport into sediments: Environmental Science and Technology, v. 14, p. 1,382–1,390.

——— 1981, Oxidation of phenolic antioxidants in a river system: Environmental Science and Technology, v. 15, no. 11, p. 1,388–1,390.

Maldonado, C., Dachs, J., and Bayona, J.M., 1999, Trialkylamines and coprostanol as tracers of urban pollution in waters from enclosed seas—The Mediterranean and Black Sea: Environmental Science and Technology, v. 33, p. 3,290–3,296.

Maquire, R.J., 1999, Review of the persistence of nonylphenol and nonylphenol ethoxylates in aquatic environments: Water Quality Research Journal of Canada, v. 34, no. 1, p. 37–78.

McMurry, L.M., Oethinger, M., and Levy, S.B., 1998a, Over-expression of marA, soxS, or acrAB produces resistance to triclosan in laboratory and clinical strains of *Escherichia coli*: FEMS Microbiology Letters, v. 166, no. 2, p. 305–309.

——— 1998b, Triclosan targets lipid synthesis: Nature v. 394, no. 6, p. 531–532.

Meade, M.J., Waddell, R.L., and Callahan, T.M., 2001, Soil bacteria *Pseudomonas putida* and *Alcaligenes xylosoxidans* subsp. *denitrificans* inactivate triclosan in liquid and solid substrates: FEMS Microbiology Letters, v. 204, p. 45–48.

Meyer, M.T., Bumgarner, J.E., Varns, J.L., Daughtridge, J.V., Thurman, E.M., and Hostltler, K.A., 2000, Use of radioimmunoassay as a screen for antibiotics in con-

fined feeding operations and confirmation by liquid chromatography/mass spectrometry: The Science of the Total Environment, v. 248, p. 181–187.

Miyazaki, T., Yamagishi, T., and Matsumoto, M., 1984, Residues of 4-Chloro-1-(2,4-dichlorphenoxy)-2-methoxybenzene (Triclosan methyl) in aquatic biota: Bulletin of Environmental Contamination and Toxicology, v. 32, no. 2, p. 227–232.

Mudge, S.M., Hooper, L., and Icely, J.D., 1998, Biomarkers associated with sewage in the Arade Estuary, Portugal: Environmental Technology, v. 19, p. 1,055–1,060.

Myers, D.N., and Wilde, F.D., 1997, National field manual for the collection of water-quality data—Biological indicators: U.S. Geological Survey Techniques for Water-Resources Investigations, book 9, chap. A7, variously paged.

Okumura, T., Yamagishi, T., and Matsumoto, M., 1996, Gas chromatography-mass spectrometery determination of triclosans in water, sediment, and fish samples via methylation with diazomethane: Analytica Chimica Acta, v. 325, p. 175–184.

O'Leary, T., Leeming, R., Nichols, P.D., and Volkman, J.K., 1999, Assessment of the sources, transport and fate of sewage-derived organic matter in Port Phillip Bay, Australia, using the signature lipid coprostanol: Marine and Freshwater Research, v. 50, p. 547–556.

Panter, G.H., Thompson, R.S., and Sumpter, J.P., 2000, Intermittent exposure of fish to estradiol: Environmental Science and Technology, v. 34, p. 2,756–2,760.

Paxeus, N., 1996, Organic pollutants in the effluents of large wastewater treatment plants in Sweden: Water Resources, v. 30, no. 5, p. 1,115–1,122.

Perencevich, E.N., Wong, M.T., and Harris, A.D., 2001, National and regional assessment of the antibacterial soap market—A step toward determining the impact of prevalent antibacterial soaps: American Journal of Infection Control, v. 29, no. 5, p. 281–283.

Rantz, S.E., and others, 1982, Measurement and computation of streamflow—Volume 1. Measurement of stage and discharge: U.S. Geological Survey Water-Supply Paper 2175, 284 p.

Rogers-Gray, T.P., Jobling, S., Morris, S., Kelly, C., Kirby, S., Janbakhsh, A., Harries, J.E., Waldock, M.J., Sumpter, J.P., and Tyler, C.R., 2000, Long-term temporal changes in the estrogenic composition of treated sewage effluent and its biological effects on fish: Environmental Science and Technology, v. 34, no. 8, p. 1,521–1,528.

Seiler, R.L., Zaugg, S.D., Thomas, J.M., and Howcroft, D.L., 1999, Caffeine and pharmaceuticals as indicators waste water contamination in wells: Ground Water, v. 37, no. 3, p. 405–410.

Servos, M.R., 1999, Review of the aquatic toxicity, estrogenic responses and the bioaccumulation of alkylphenols and alkylphenol ethoxylates: Water Quality Research Journal of Canada, v. 34, no. 1, p. 123–177.

Sherblom, P.M., Henry, M.S., and Kelly, D., 1997, Questions remain in the use of coprostanol and epicoprostanol as domestic waste markers: examples from coastal Florida, *in* Eganhous, R.P., ed., Molecular Markers in Environmental Geochemistry: American Chemical Society (ACS) Symposium Series, v. 671, p. 320–331.

Singley, J.E., Kirchmer, C.J., Miura, R., 1974, Analysis of coprostanol, an indicator of fecal contamination: Washington, D.C., U.S. Environmental Protection Agency, Environmental Protection Technology Series 660/2-74-021, 114 p.

Sole, M., Lopez de Alda, M.J., Castillo, M., Porte, C., Ladegaard-Pedersen, K., and Barcelo, D., 2000, Estrogenicity determination in sewage treatment plants and surface waters from the Catalonian Area (NE Spain): Environmental Science and Technology, v. 34, no. 24, p. 5,076–5,083.

Solley, W.B., Pierce, R.R., and Perlman, H.A., 1998, Estimated use of water in the United States in 1995: U.S. Geological Survey Circular 1200, 71 p.

Suller, M.T.E., and Russell, A.D., 2000, Triclosan and antibiotic resistance in *Staphylococcus aureus*: Journal of Antimicrobial Chemotherapy, v. 46, p. 11–18.

Tabak, H.H., and Bunch, R.L., 1970, Missouri River Basin sterol assay project report. Coprostanol, a positive marker of domestic and run-off pollution—Sterol assay of wastewater plant effluents and surface waters of the lower main stem Missouri: Cincinnati, Ohio, Federal Water Quality Administration, Advanced Waste Treatment Research Laboratory, 18 p.

Talmage, S.S., 1994, Environmental and human safety of major surfactants—Alcohol ethoxylates and alkylphenol ethoxylates: Boca Raton, Fla., Lewis Publishers, 374 p.

Tang-Liu, D.D., Williams, R.L., and Riegelman, S., 1983, Disposition of caffeine and its metabolites in man: Journal of Pharmacology and Experimental Therapeutics, v. 24, no. 1, p. 180–185.

Ternes, T.A., Kreckel, P., and Mueller, J., 1999a, Behavior and occurrence of estrogens in municipal sewage treatment plants—II. Aerobic batch experiments with activated sludge: The Science of the Total Environment, v. 225, p. 91–99.

Ternes, T.A., Stumpf, M., Mueller, J., Haberer, K., Wilken, R.D., and Servos, M., 1999b, Behavior and occurrence of estrogens in municipal sewage treatment plants—I. Investigations in Germany, Canada, and Brazil: The Science of the Total Environment, v. 225, p. 81–90.

U.S. Department of the Census, 2000, Population estimates program: accessed August 2001, at URL http://www.census.gov/population/estimates.

Voets, J.P., Pipyn, P., van Lancker, P., and Verstraete, W., 1976, Degradation of microbiocides under different environmental conditions: Journal of Applied Bacteriology, v. 40, p. 67–72.

Wagner, R.J., Mattraw, H.C., Ritz, G.F., and Smith, B.A., 2000, Guidelines and standard procedures for continuous water-quality monitors—Site selection, field operation, calibration, record computation, and reporting: U.S. Geological Survey Water-Resources Investigations Report 00–4252, 53 p.

Wakeham, S.G., Schaffner, C., and Giger, W., 1980, Polycyclic aromatic hydrocarbons in recent lake sediments—I. Compounds having anthropogenic origins: Geochimica et Cosmochimica Acta, v. 44, no. 3, p. 403–413.

Waker, W.J., McNutt, R.P., and Maslanka, C.K., 1999, The potential contribution of urban runoff to surface sediments of the Passaic River—Sources and chemical characteristics: Chemosphere, v. 38, no. 2, p. 363–377.

White, R., Jobling, S., Hoarde, S.A., Sumpter, J.P., and Parker, M.G., 1994, Environmentally persistent alkylphenolic compounds are estrogenic: Endocrinology, v. 135, no. 1, p. 175–182.

Wilde, F.D., Radtke, D.B., Gibs, J., and Iwatsubo, R.T., 1998, National field manual for the collection of water-quality data—Cleaning of equipment for water sampling: U.S. Geological Survey Techniques for Water-Resources Investigations, book 9, chap. A3, variously paged.

——— 1999a, National field manual for the collection of water-quality data—Collection of water samples: U.S. Geological Survey Techniques for Water-Resources Investigations, book 9, chap. A4, variously paged.

——— 1999b, National field manual for the collection of water-quality data—Processing of water samples: U.S. Geological Survey Techniques for Water-Resources Investigations, book 9, chap. A5, variously paged.

Zaugg, S.D., Smith, S.G., Schroeder, M.P., Barber, L.B., and Burkhardt, M.R., 2001, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of wastewater compounds by polystyrene divinylbenzene solid-phase extraction and capillary-column gas chromatography/mass spectrometry: U.S. Geological Survey Water-Resources Investigations Report 01–4186, p. 37.