

Sources of Contamination in an Urban Basin in Marquette, Michigan and an Analysis of Concentrations, Loads, and Data Quality

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U.S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 97-4242

Prepared in cooperation with the
WISCONSIN DEPARTMENT OF NATURAL RESOURCES
and the U.S. ENVIRONMENTAL PROTECTION AGENCY

Middleton, Wisconsin
1997



U.S. DEPARTMENT OF THE INTERIOR
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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
centimeter (cm)	.3937	inch
foot (ft)	0.3048	meter
inch (in.)	25.4	millimeter
mile (mi)	1.609	kilometer
meter (m)	3.281	foot
kilogram (kg)	2.205	pound
gallon (gal)	3.79	liter
liter (L)	.2642	gallon
hectare (ha)	2.471	acre
square mile (mi ²)	2.590	square kilometer
centimeter per hour (cm/hr)	.3937	inch per hour
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second
cubic meter per second (m ³ /s)	35.3107	cubic foot per second
liters per second (L/s)	.0353	cubic feet per second
liter per kilogram (L/kg)	.1198	gallon per pound

Temperature, in degrees Celcius (°C) can be converted to degrees Fahrenheit (°F) by use of the following equation:

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

ABBREVIATED WATER-QUALITY UNITS: Chemical concentrations and water temperature are given in metric units. Chemical concentration is given in milligrams per liter (mg/L) or micrograms per liter (µg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million.

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Abstract

The concentrations of contaminants generated from discrete source areas are critical to urban nonpoint Source Load and Management Model (SLAMM) loading calculations to Lake Superior. This study summarizes data-collection efforts during 12 storms in October 1993 and from May through August 1994, in which stormwater data were collected concurrently at 33 sites representing the eight major source areas in a 117-hectare urban basin in Marquette, Mich. For the 12 storms, commercial rooftops produced the highest geometric mean concentrations of dissolved metals such as lead (20 mg/L), zinc (263 mg/L), cadmium (0.71 mg/L), and copper (17.8 mg/L). Parking lots produced the highest concentration for all of the individual polycyclic aromatic hydrocarbon (PAH) compounds (summation equal to 64 mg/L). Residential lawns generated the highest concentrations of total kjeldahl nitrogen (9.3 mg/L) and total phosphorus (2.3 mg/L). A mass-budget approach, in which summed source area loads are compared to those measured at the basin outlet for individual storms, provided the basis for an error analysis to identify unreliable concentration data. Of the 611 concentration samples used in the mass budgets, 59 were identified as unreliable. Seventy-six percent of the unreliable samples came from collection bottles that were filled prior to the end of runoff. These full bottles may have captured a first-flush effect or acted as a sediment trap. The relative importance of an individual source-area load to the overall basin-outlet load varied according to the individual constituent. Parking lots were a major contributor of total zinc (30 percent), total cadmium (25 percent), total copper (22 percent), and all the PAH compounds (\approx 64 percent);

whereas low-traffic streets were a major producer of total suspended solids (27 percent), nitrate plus nitrite (21 percent), and total cadmium (25 percent). Grass areas were a major producer of total kjeldahl nitrogen (31 percent) and total phosphorus (26 percent), even though the water volume generated from grass areas was low (5.8 percent of the total water volume generated).

INTRODUCTION

The urban nonpoint Source Load and Management Model (SLAMM) (Pitt and Voorhees, 1989) has been used in Wisconsin to integrate local soil and topographic conditions, precipitation, stormwater-runoff contaminant concentrations, land-use practices, and best-management practices (BMP's) to estimate annual contaminant loadings from urban basins to Great Lake water bodies. Most recently, the Wisconsin Department of Natural Resources (WDNR) used SLAMM, updated with the source-area data collected by the U.S. Geological Survey (USGS), to calculate stormwater-contaminant loadings to Lake Superior from 11 cities with populations greater than 5,000 (Prey and others, 1996). Contaminant concentrations generated from discrete source areas such as streets of varied traffic density, commercial and residential rooftops, parking lots, driveways, and residential lawns are critical to the SLAMM loading calculations. Contaminant concentrations for each discrete source area are input into the model, and SLAMM calculates loads as a function of these values.

Previous investigators have described the usefulness of urban contaminant concentration data in loading computations but have noted the scarcity of such data sets (Tsansis and others, 1994; Bannerman and others, 1983; Pitt and Barron, 1989). In addition, Bannerman and others, (1993) described the need to iden-

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tify critical sources—areas that produce large contaminant loads from urban surfaces—as an important component in the development of stormwater BMP's. Contaminant control at critical source areas may be more cost effective than attempts to control pollution with regional structures, such as large wet detention ponds. Comparison of contaminant loads from different source areas can be used to develop BMP's for specific contaminants.

To augment the water-quality data sets for urban source areas and to improve the understanding of the relation between source-area and basinwide constituent loads, the USGS, in cooperation with WDNR and the U.S. Environmental Protection Agency (USEPA), collected stormwater runoff samples from a 117-ha (hectare) basin in Marquette, Mich., in October 1993 and during May-August 1994 and analyzed the samples for selected inorganic and organic contaminants. The Marquette source-area contaminant-concentration data were applied to their respective SLAMM computed water volumes to obtain contaminant loads from each of the source areas on an individual-storm basis. A significant part of the Marquette study was an evaluation of the reliability of the source-data; that is, whether samples from individual source-area collectors were representative of the entire source-area surface during the total period of runoff and whether the aggregate of source-area loads equaled measured loads at the basin outlet. The study examined the feasibility of collecting representative or reliable source-area concentration data.

Purpose and Scope

This report summarizes concentration data for metals (dissolved and total recoverable), nutrients (dissolved and total), and polycyclic aromatic hydrocarbons (PAH's) collected from eight source areas and a basin-outlet storm sewer in the study basin in Marquette, Mich. In addition, the overall quality and reliability of the source-area data are described in terms of a mass-budget comparison of summed source-area contaminant loads with contaminant loads measured at the basin outlet. Finally, the Marquette data are compared with data from similar basins in Madison, Wis., to examine similarities and differences in contaminant concentrations from similar source areas.

Acknowledgments

The authors acknowledge the field assistance and technical advice of John Thomas of the Minnesota Pollution Control Agency and Roger Bannerman (WDNR). The field assistance of Wallace Larson, John Knudson, and Tom Gambucci of the USGS and the statistical insight of John Walker (USGS) were extremely valuable. The authors are grateful for the geographic information system and field verification assistance of David Hart of the University of Wisconsin - Madison. The more than 3,700 analyses done by personnel of the Wisconsin State Laboratory of Hygiene were crucial to the success of the study. Lastly, the authors are grateful to Karen Barr, Heather Whitman, Jan Fuller, and Karen Lonsdorf of the USGS for the manuscript preparation.

Study Approach

The study approach was to (1) measure mean contaminant concentrations during storms from eight different types of urban surfaces (source areas) within one storm-sewer basin in Marquette, Mich., (2) multiply these concentrations by their respective simulated water volumes to calculate loads, and (3) compare the summed source area loads to the total load measured at the basin-outlet storm sewer.

To represent the eight types of source areas, stormwater was collected concurrently at 33 sites during a storm, with multiple sites in each source area. At the same time, flow-weighted composite samples were collected at the basin-outlet flume site (fig. 1). Source-area sample-collection sites were selected to isolate stormwater runoff from the specific source area and to adequately represent the overall source area. Additionally, an attempt was made to use sample-collection methods and equipment that minimized the possibility of obtaining a first-flush sample—a situation in which the collection bottle filled prior to the end of the runoff and thus functioned as a sediment trap.

The total volume of stormwater runoff generated in the basin was measured using a Palmer-Bowlus flume in the basin-outlet storm sewer. Associated basin-outlet water quality samples were collected by use of a flow-weighted composite approach based on discharge measured at the flume. Rainfall was monitored at two basin locations in October 1993 and from May through August 1994.

A geographic information system (ARC/INFO) was used to determine land-use and source-area dimen-

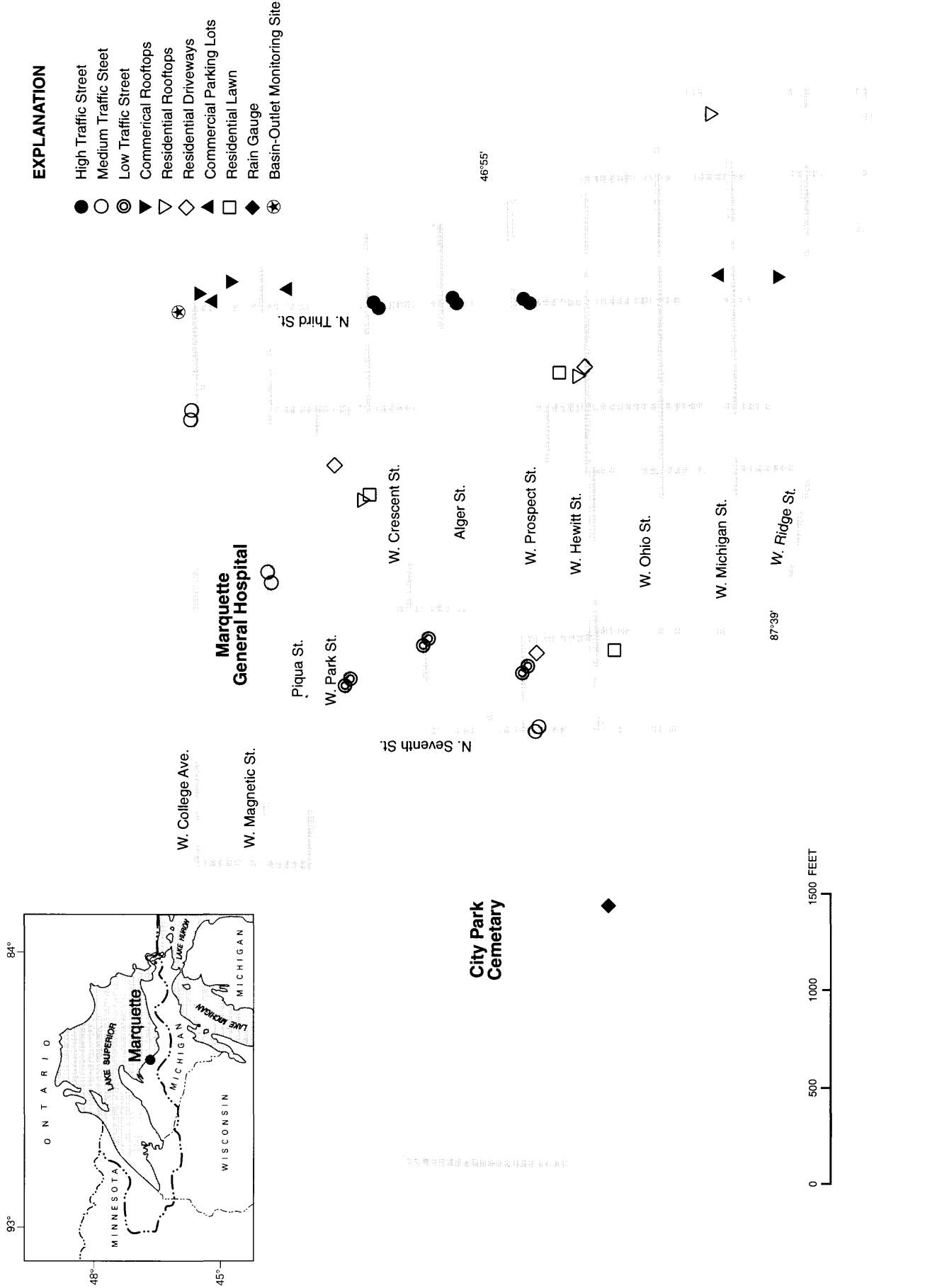


Figure 1. Locations of source area data-collection sites in the Marquette, Michigan study basin.

sions from digitized USGS topographic maps, digitized aerial photographs, and other digital base maps. Source-area and land-use information and hydraulic connectivity from source areas to the basin-outlet system were verified by field study (Hart, 1996).

A mass-budget analysis was made to compare the summed source-area loads to those measured at the basin-outlet sewer to identify unrepresentative sites or inadequate sample-collection methods. A balanced mass budget, on an individual storm and constituent basis, would support the position that sampler sites were sufficient to represent the significant source areas and that sample-collection techniques adequately sampled sheet flow over the runoff duration.

DESCRIPTION OF STUDY AREA

Marquette, Mich. has a population of 21,977 (based on 1990 census). Climate is moderate and annual precipitation is 81 cm. The monitored basin has a mixed land use (table 1) with residential and open areas making up 55 percent and 29 percent of the basin, respectively. The commercial area (8 percent) primarily consists of small shops and businesses; there was not a commercial strip setting in the monitored basin. The institutional area (7 percent) included a major hospital and two schools.

The source area water-quality sample collection sites are identified in figure 1. Residential rooftops are the predominant impervious source area (9.8 percent), and the high-traffic-street source area is the smallest impervious surface (1.4 percent). Open space and residential lawns (grass areas) make up 62 percent of the basin area (table 2).

METHODS OF DATA COLLECTION

Source-Area Sampling Sites

Selection of a sample-collection site that isolated storm-water runoff from the specific source-area while adequately representing the overall source-area classification was inherent in obtaining a reliable source-area sample. For example, samples from source-area collectors located in each of three small parking lots were composited to represent the 5.4 ha of parking lots in the monitored basin. Street samplers were positioned to avoid gutter flow that may have originated from driveways, parking lots, or rooftops. On streets of high- and medium-volume traffic, collectors were positioned near the center of the street to eliminate interference from parked vehicles. For a given source area, runoff was

Table 1. Characteristics of the study basin, Marquette, Michigan

[Numbers in parenthesis indicate percent of basin area. Basin is depicted in fig. 1.]

Drainage area	117 hectares
Land-use types:	
Residential	64.8 hectares (55%)
Open	33.6 hectares (29%)
Commercial	9.5 hectares (8%)
Institutional	8.6 hectares (7%)
Industrial	0 hectares
Pervious area	73.1 hectares (63%)
Impervious area	43.9 hectares (37%)
Age of development, years	Mixed; 50 to 100 years
Soil type ¹	Sand
Hydrologic soil type ²	A
Average slope	3.7
Mean summer temperature	57° Fahrenheit
Mean winter temperature	26° Fahrenheit
Mean annual precipitation	81 centimeters

¹Marquette County soil survey maps prepared by the U.S. Soil Conservation Service.

²U.S. Soil Conservation Service classification.

collected at three sites, then composited to represent the overall source area. Streets were an exception in that water was collected at six locations for each street type (high-, medium-, and low-traffic density) and was then composited into one sample to represent the overall source area. This resulted in stormwater being collected concurrently at 33 sites during a storm in addition to a flow-weighted composite sample being collected at the basin outlet flume site. Additionally, it was important to use collection methods that did not obtain solely a first-flush sample or fill the sample-collection bottle before the end of runoff and function as a sediment trap. The residential lawn samplers (three) were assumed to represent not only residential lawns but also open-grass areas, such as parks and cemeteries.

Source-Area Sample-Collection Methods and Stormwater-Runoff Volumes

Samplers were designed to coincide with daily activities within their respective source areas and were subsequently left in place between storms. Clean sample-collection bottles were installed before each storm,

Table 2. Monitored source-area characteristics, Marquette study basin

Monitored source area	Area abbreviation	Description	Area in hectares	Percentage of basin area
High-traffic street (3d St.) ¹	HST	Asphalt; 10,600 vehicles per day; commercial on-street parking	1.6	1.4
Medium-traffic street (College Ave, Magnetic St, 7th St.) ¹	MST	Asphalt; 3,100 to 5,100 vehicles per day; limited commercial on-street parking	2.1	1.8
Low-traffic street (Park, Crescent, Harrison St.) ¹	LST	Asphalt; less than 3,100 vehicles per day; residential area	10.4	8.9
Commercial parking lots	CP	Two asphalt lots with tar-sealed cracks; one weathered concrete lot with fractures	5.4	4.6
Residential driveways	RD	One eroded asphalt driveway with oil patches; one eroded cement driveway with oil patches; one concrete driveway, good condition	4.9	4.2
Residential rooftops	RR	Pitched, shingled; no gutters; runoff from painted upper sides of houses to lower rooftops, galvanized flashing, aluminum trim	11.4	9.8
Commercial rooftops	CR	Flat, rubber, or tar sealed; galvanized or aluminum trim	4.1	3.5
Grass area	RL	Residential lawns; degree of grass area maintenance not considered	72.8	62.4
TOTAL			² 113	² 97

¹ Streets were swept in the spring to remove accumulated sand and thereafter on an as-needed basis.

² No water was collected from sidewalks (3.9 hectares.)

monitored periodically during the storm to regulate runoff-volume collection, then removed shortly after runoff ceased. Before installation, the glass sample-collection bottles were washed with non-phosphate soap; the wash was followed by a tapwater rinse, a 5 percent hydrochloric acid (HCl) rinse, three rinses of Nanopure water, a methanol rinse, and three final rinses of Nanopure water. In most instances, collection bottles were installed less than 24 hours before a storm. Individual storms were defined as rainfall separated by 6 or more hours of no precipitation.

Basic construction of source-area sample collectors has been previously detailed by Bannerman and others (1993) and will not be described here. The following sampler modifications, however, were made to accommodate PAH collection and to improve time-composite sample-collection:

- Runoff inflow into the street, rooftop, driveway, and parking-lot samplers was controlled by modifying the collector cap described in Bannerman and others

(1993). A threaded polycarbonate set screw that intersected the center drain hole was installed to control the aperture size and resulting inflow rate. The 2.54-cm-thick concave collection cap was constructed from polycarbonate material to prevent adsorption of PAH compounds.

- Commercial and residential rooftop and parking-lot samplers were not fitted with collection tubing as described in Bannerman and others (1993) except for the October 1993 storm. Rooftop runoff drained directly onto the polycarbonate cap, which was suspended from a polycarbonate trough at the rooftop edge. Parking-lot collectors were suspended from the drain grating, and runoff fell directly onto the collector cap.

- Driveway samplers were buried adjacent to the pavement; a Teflon tube directed driveway storm water runoff to the collector cap.

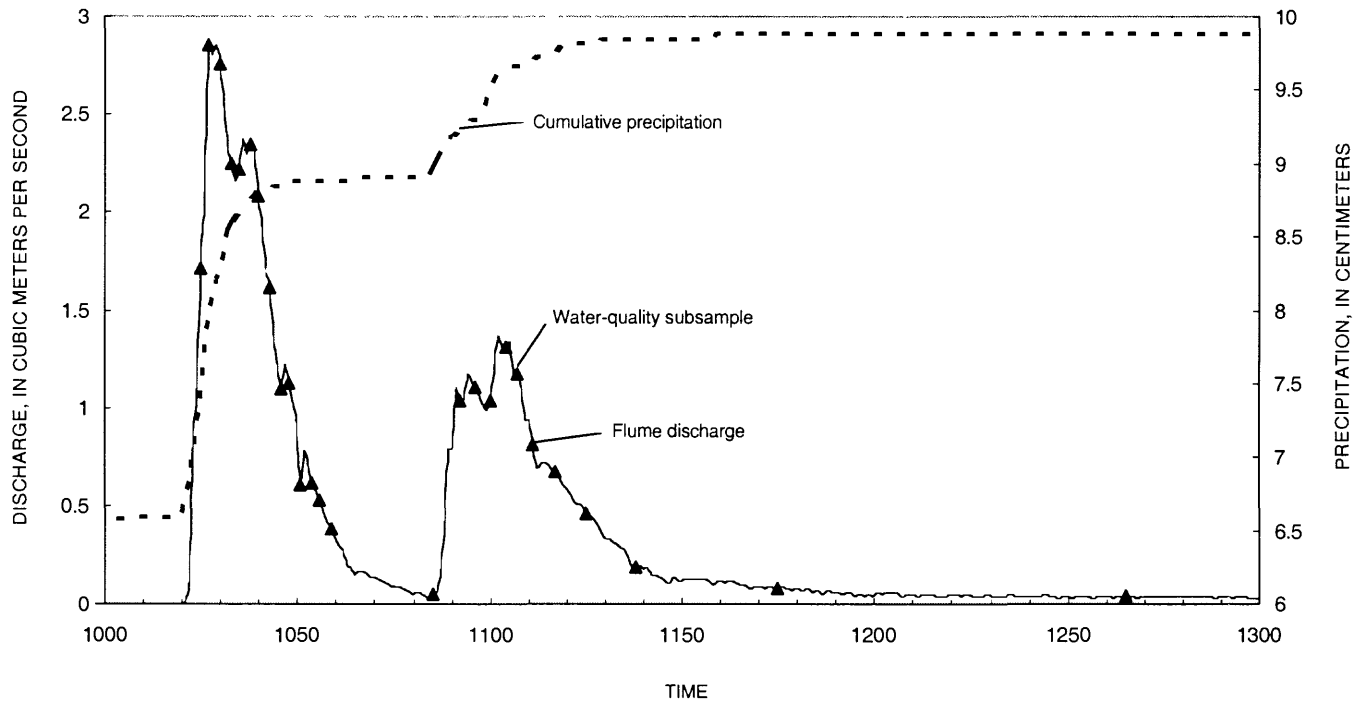


Figure 2. Precipitation, basin-outlet discharge, and volume-weighted water-quality samples collected in the Marquette, Mich. study basin on June 11, 1994.

Runoff volumes calculated by SLAMM for specific source areas were based on individual rainfall and source-area characteristics such as surface area, hydrologic soil type, street length, connected imperviousness, building density, and roof pitch. Documentation for the model, along with parameter files, is available from WDNR.

Basin-Outlet Sample-Collection Methods and Stormwater-Runoff Volumes

An automated sampling station monitored flow and collected water samples from the 1.37 -m-diameter (4.5-foot-diameter) storm-sewer pipe at the basin outlet. Equipment at the site consisted of a refrigerated automatic sampler with four 9.4-L glass jars, a 9.5-mm (3/8-inch) Teflon-lined suction line, a datalogger programmed to activate the automatic sampler and store data, a modem for remote data retrieval, and a tipping-bucket rain gage. The storm sewer contained an aluminum Palmer-Bowlus flume and continuous stage-sensing equipment for discharge computation. Instantaneous discharge was computed and flow-weighted water-quality subsamples were collected at a

predetermined runoff volume in the storm sewer. These subsamples were composited into a single sample by use of a Teflon churn splitter. The Teflon suction line was purged before and immediately after obtaining a subsample. The open collection bottles were retrieved from the refrigerated sampler within 24 hours after runoff ceased.

Instantaneous flume discharge, Q , was calculated as follows:

$$Q = 9.53H_a^{1.868}, \quad (1)$$

where H_a is the flume approach head (in feet). Stormwater-runoff volume was calculated by summing the 1-minute-interval instantaneous discharge over the runoff duration. During the study, 38 stormwater-runoff hydrographs were generated, and source-area water-quality samples were collected during 12 of these storms. An example of flow-weighted sampling for a storm on June 11, 1994, is illustrated in figure 2.

Discharge at this site was predominantly stormwater runoff. There was, however, some dry weather flow—approximately 1.1 (L/s) (0.04 cubic foot per second) originating from ponds in the southern part of

the basin, as well as periodic discharge from an unidentified point source. None of the monitored storms produced pipeful flow.

Basin precipitation was monitored by use of two tipping-bucket rain gages at opposite ends of the basin (fig. 1). Basin precipitation volume was calculated by use of Thiessen polygons to area-weight the precipitation.

METHODS OF SAMPLE PROCESSING AND ANALYSIS

Sample-Processing Procedures

A Teflon-coated, stainless steel churn splitter was used to composite samples in collection bottles from the multiple sites representing a source area. The churn splitter was washed with non-phosphate soap; the wash was followed by a tapwater rinse, a 5 percent HCl rinse, three rinses of Nanopure water, a methanol rinse, and three final rinses of Nanopure water after each sample processing. Gelman 0.45 μm capsule filters, pretreated with 500 mL of 5 percent HCl and 1 L of analyte-free Nanopure water, were used to filter sample water for dissolved constituents. Selected samples were preserved, metals samples with nitric acid and nutrient samples with sulfuric acid. All samples were put on ice and sent to the Wisconsin State Laboratory of Hygiene (WSLOH) in Madison for analysis.

To ensure sample integrity, two field and sample-processing equipment blanks were collected by drawing analyte-free Nanopure water through the suction line and basin-outlet automatic sampler into a collection bottle. As was in the case in collecting a storm sample, the suction line was purged before obtaining the blank sample. The suction line and automated sampler were not cleaned before obtaining the blank samples.

Biological oxygen demand (BOD) and copper concentration determined from the blank samples were greater than some field data (fig. 4). The median BOD concentration from the blank samples was 5.8 mg/L; the reason for this high value is unknown. In addition, sample-process and laboratory-analysis BOD replicates had a coefficient of variation of 30 percent. A second notable blank concentration was total recoverable copper, at 18 $\mu\text{g/L}$. A follow-up analysis of the locally procured Nanopure blank water, with no exposure to

sample or processing equipment, resulted in a total copper concentration of 15 $\mu\text{g/L}$. A field sample-processing equipment blank using the same procedure but with different blank water was collected at a different site. That blank sample had a total recoverable copper concentration of less than detection (3.0 $\mu\text{g/L}$). Thus, it appears the high copper concentrations may have been from the locally procured Nanopure water. At the 15- to 18- $\mu\text{g/L}$ concentration range, any possible copper residue remaining from the Nanopure water used in the cleaning procedure should have been minor when compared to the mass of water in the field samples. It is possible that copper in the rinse water may have contaminated the capsule filter during pretreatment and that this contamination would be reflected in the dissolved copper concentrations. In the field samples, however, concentration of total recoverable copper in water that did not pass through a pretreated filter was generally found to be 2 to 3 times that of the dissolved phase (table 4).

Laboratory Analysis

The laboratory (WSLOH) analyzed samples for the constituents listed in table 4 using procedures approved by the U.S. Environmental Protection Agency (USEPA). The organic determinations by the WSLOH included the 16 PAH compounds listed in table 3. The five PAH compounds with organic carbon coefficients (Koc) less than 14,000 L/kg (U.S. Environmental Protection Agency, (EPA), 1986) were not detected, whereas phenanthrene, with a Koc of 14,000 L/kg, was detected intermittently (limit of detection (LOD)=0.17 $\mu\text{g/L}$). The 10 PAH compounds with Koc's above 38,000 were commonly detected. Most figures and tables in this report include a summation of the PAH compounds, along with two specific PAH compounds that provide a range of hydrophobicity: pyrene (Koc=38,000 L/kg) and benzo[ghi]perylene (Koc=1,600,000 L/kg). Method documentation and laboratory quality-assurance data are available from WSLOH. Contaminant concentration data have been stored in the USGS QWDATA and the USEPA STORET data bases.

Table 3. Limits of detection, organic carbon partition coefficients, and detection frequencies of polycyclic aromatic hydrocarbon

[Intermittent detection frequency denotes between 10 and 15 analysis at less than the limit of detection. Common detection frequency denotes fewer than 10 analyses at less than the limit of detection]

Polycyclic aromatic hydrocarbon	Limit of detection (µg/L)	Organic carbon partition coefficient	Detection frequency
Naphthalene	10.	2,000	None
Acenaphthylene	8.2	2,500	None
Acenaphthene	3.4	4,600	None
Fluorene	0.6	7,300	None
Anthracene	0.12	14,000	None
Phenanthrene	0.17	14,000	Intermittent
Fluoranthene	0.0087	38,000	Common
Pyrene	0.0065	38,000	Common
Chrysene	0.023	200,000	Common
Benzo[a]anthracene	0.003	436,500	Common
Benzo[b]fluoranthene	0.0045	550,000	Common
Benzo[k]fluoranthene	0.0034	550,000	Common
Benzo [a]pyrene	0.0023	890,000	Common
Benzo[ghi]perylene	0.0047	1,600,000	Common
Indeno[1,2,3-cd]pyrene	0.02	1,600,000	Common
Dibenzo[a,h]anthracene	0.0054	3,300,000	None

EXAMINATION OF CONCENTRATIONS, LOADS, AND DATA QUALITY

Runoff Volumes

From May 11 through September 25, 1994, the rain-gage sites recorded a total of 33.5 cm (13.2 inches) of rainfall with a mean rainfall amount and intensity of 1.0 cm (0.40 inch) and 0.36 cm/hr (0.14 inch per hour) respectively. Average basin stormwater runoff was 14 percent of rainfall, consistent with the basin's sandy soil and 37 percent impervious area. The range of rainfall intensity, total rainfall, and percentage of runoff for the 1994 study period is detailed in figure 3. The small runoff coefficients generated from storms on June 5, July 1, and August 14, 1994, appear to be a result of either dry antecedent conditions or low precipitation intensity.

Although precautions were taken to prevent source-area collection bottles from completely filling

during a storm, these efforts were not entirely successful. Of the 264 collection bottles used for analyses, 23 percent, primarily those collecting water from commercial and residential rooftops, were filled before the storm runoff had ended. In some instances, the premature filling of the bottles affected the quality of the sample. This problem is discussed in a later section. At the basin-outlet site, overfilling did not occur because of the automated flow-monitoring and volumetric-sampler control, combined with larger bottle capacity.

Source-Area Concentrations

The variability in source-area and basin-outlet sample constituent concentrations for 12 storms [in the Marquette study basin] is illustrated in figure 4. Even with the variability observed in the source-area concentration data due to environmental and loading conditions, there are, for certain constituents, discernible differences between source areas. Commercial rooftops produced the most acidic runoff, possibly because

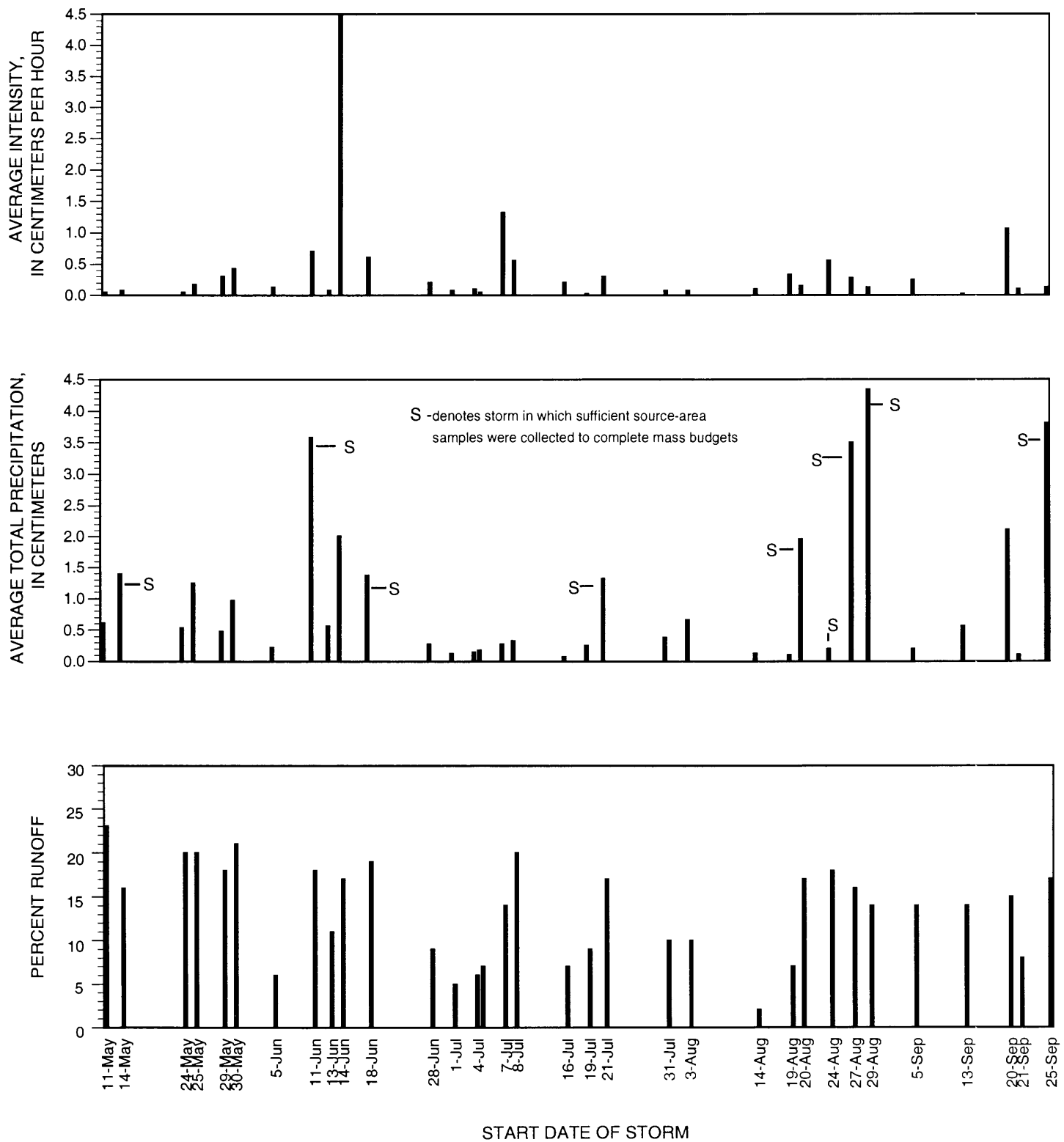


Figure 3. Average precipitation and runoff statistics for the Marquette study basin, May 11 through September 25, 1994.

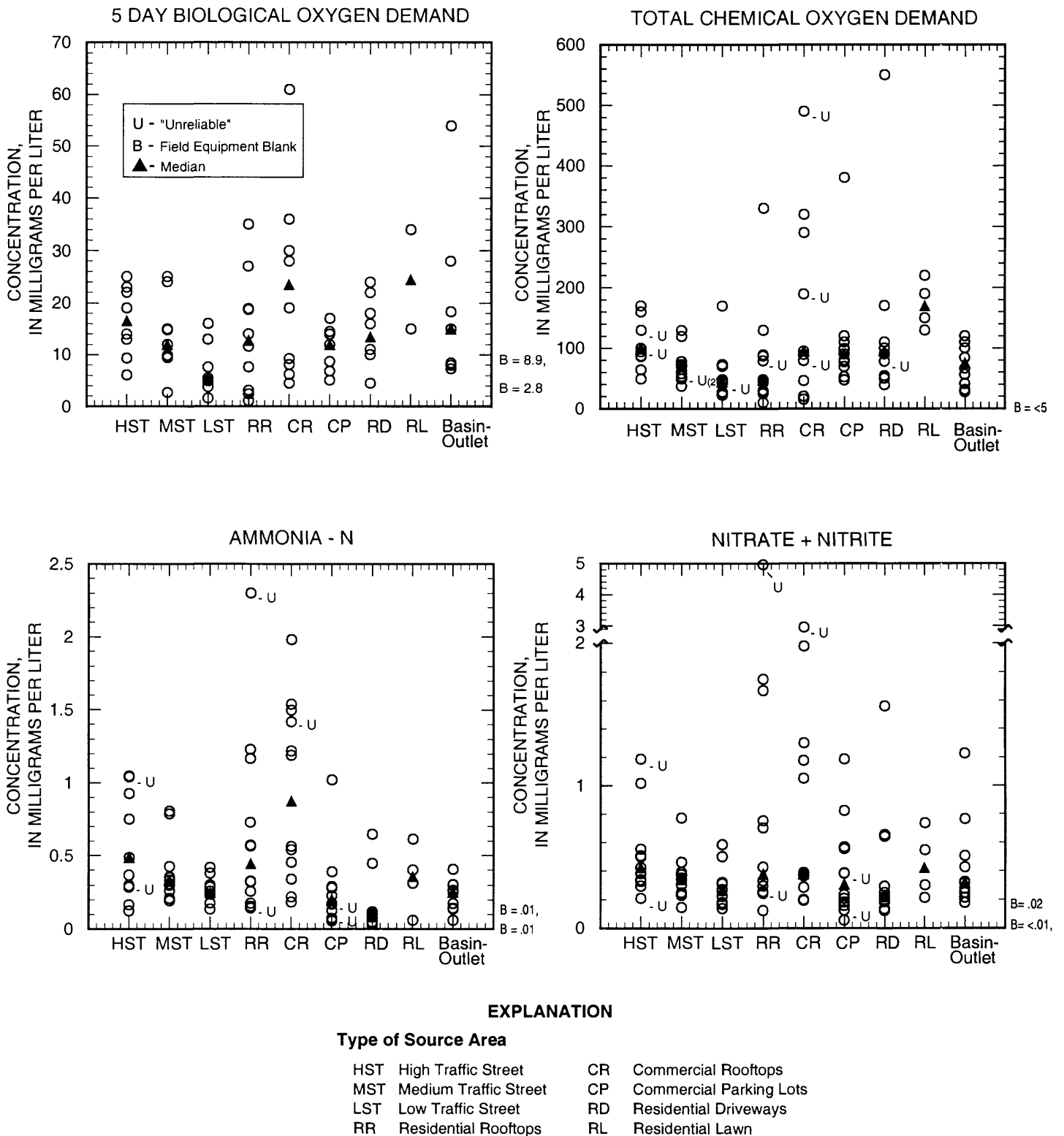


Figure 4. Source-area, basin-outlet, and field-equipment blank concentrations from the Marquette study basin.

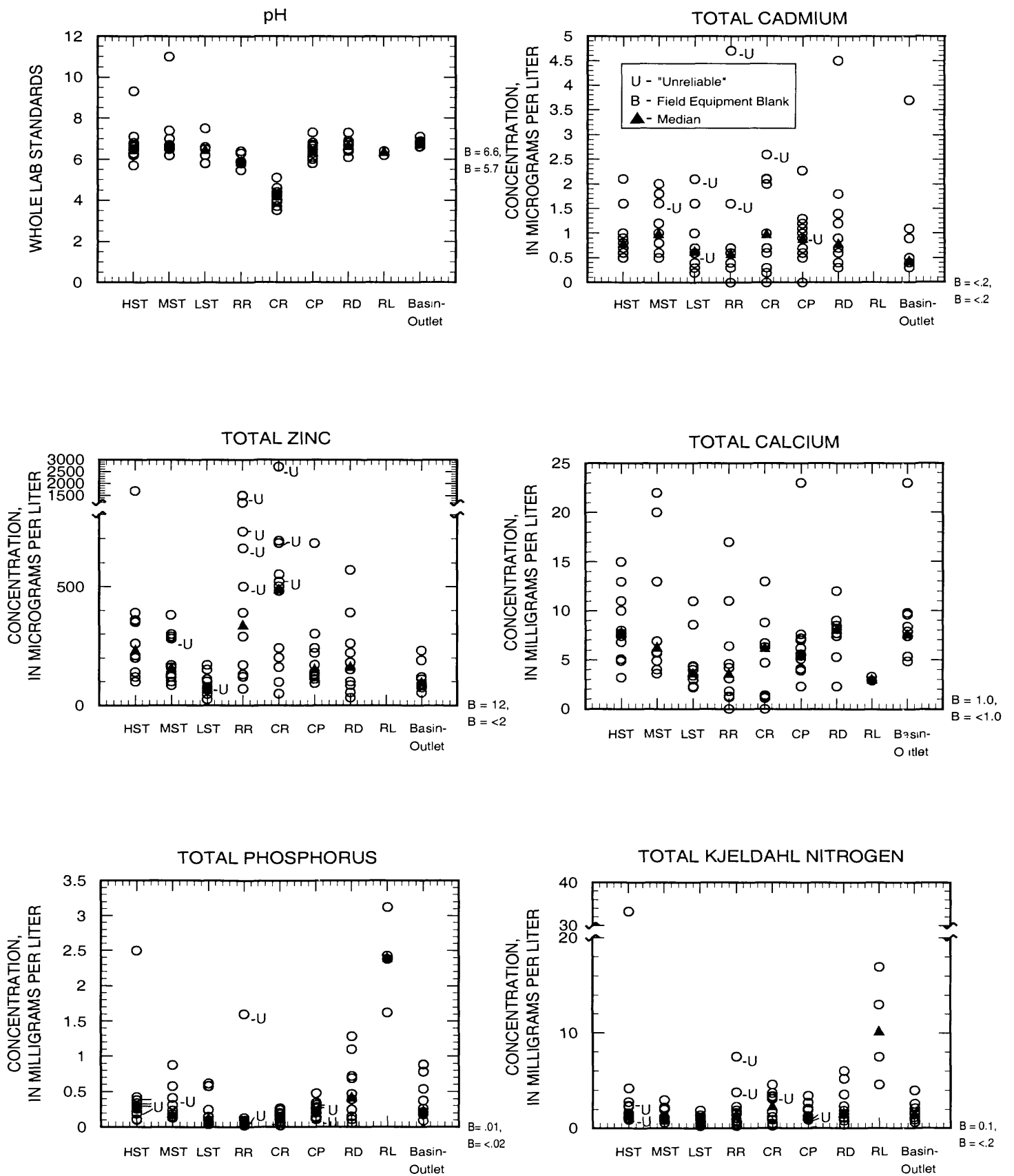


Figure 4. Source-area, basin-outlet, and field-equipment blank concentrations from the Marquette study basin—Continued.

U - "Unreliable"

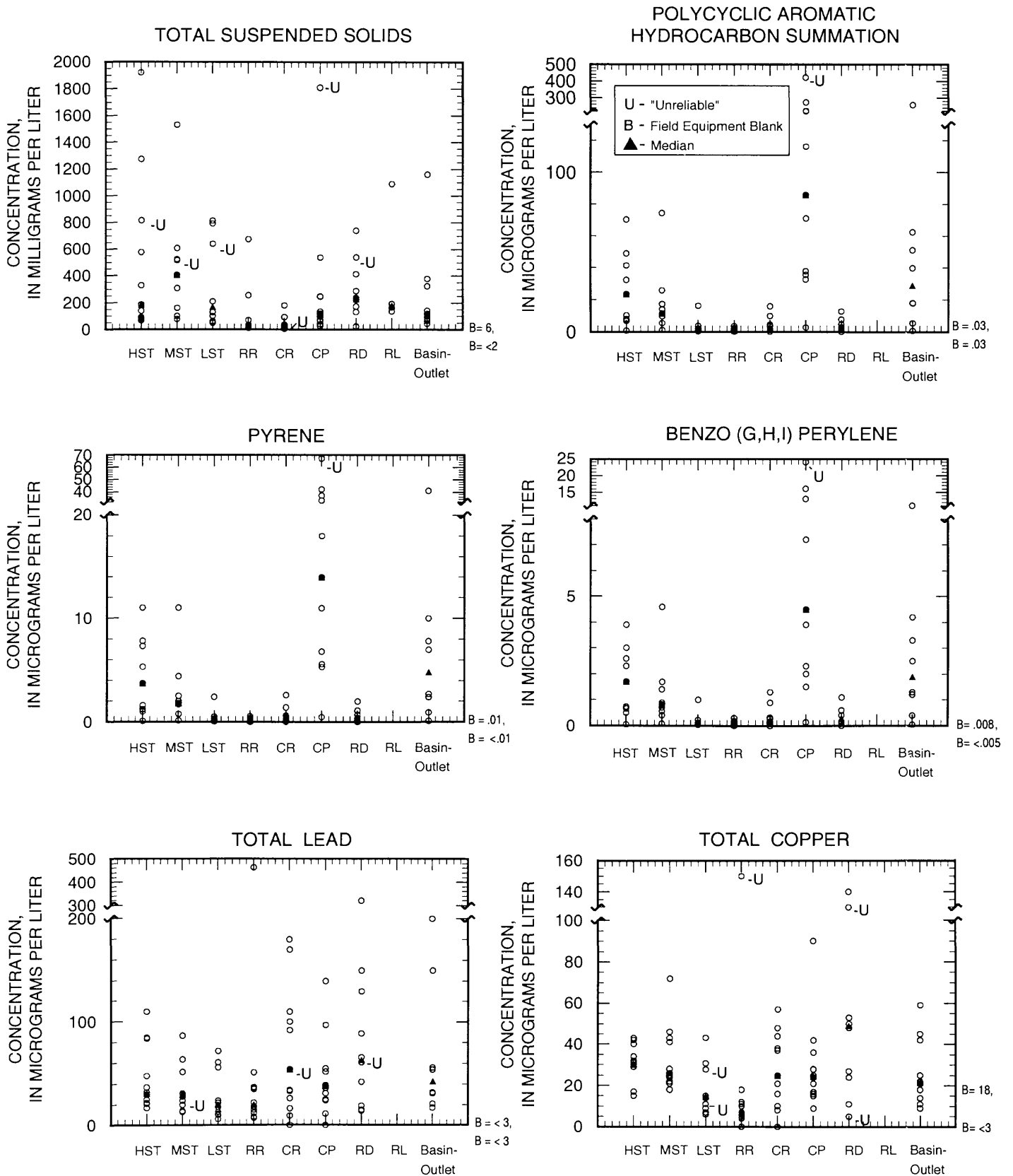
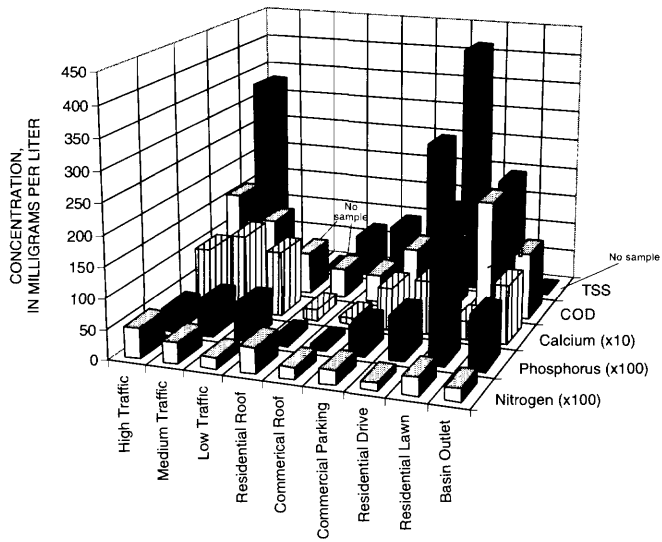
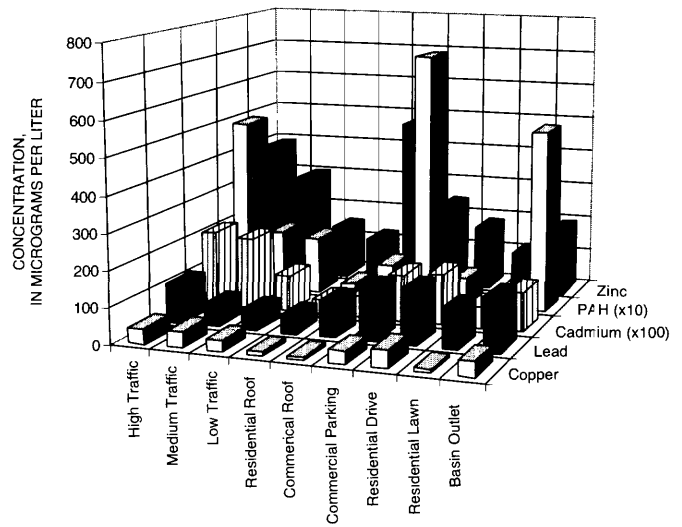


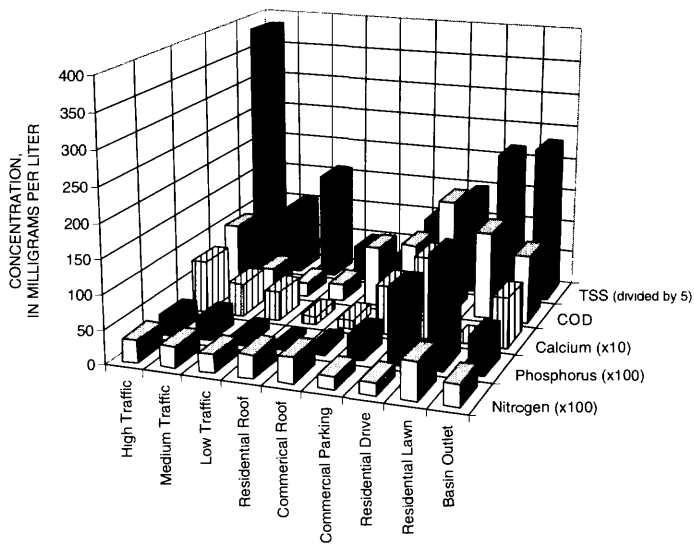
Figure 4. Source-area, basin-outlet, and field-equipment blank concentrations from the Marquette study basin—Continued.



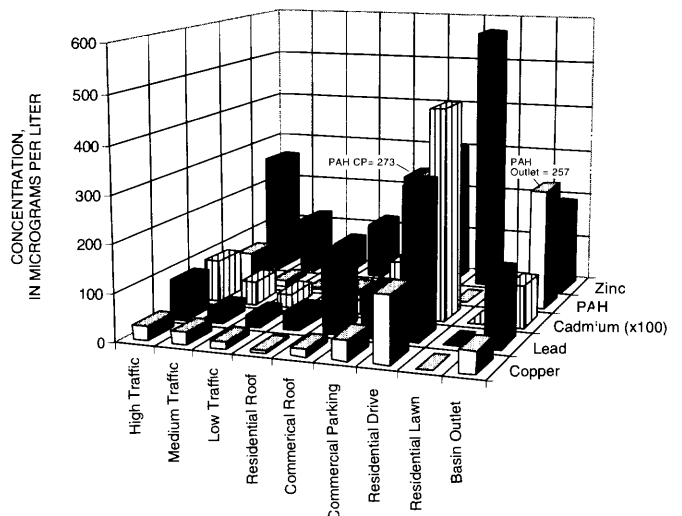
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JUNE 11, 1994



AUGUST 27, 1994



AUGUST 27, 1994

Figure 5. Source-area and basin-outlet concentrations for selected constituents, Marquette study basin, June 11, 1994 and August 27, 1995.

of decomposition in stagnant water retained on the flat roofs and the subsequent production of humic and fulvic acids. Commercial and residential rooftops produced the lowest concentration of suspended solids. Commercial rooftops produced the highest concentration of dissolved metals, such as lead, zinc, cadmium, and copper. Residential lawns generated the highest total kjeldahl nitrogen and total phosphorus concentrations, whereas parking lots produced the highest concentration for all PAH compounds.

Bracketing of the basin-outlet concentrations by the individual source-area concentrations (fig. 5) indicates that the basin outlet was generally an integration of the monitored source areas. If the basin-outlet concentration for a certain constituent had been greater than that for all source areas, the question would arise as to what source area contributed to the high basin outlet concentration. A similar argument would arise if the basin-outlet concentration had been lower than all the source-area concentrations. For 199 of the 207 constituent/storm combinations, at least one source-area concentration was higher and at least one source-area concentration was lower than the basin-outlet concentration. Total suspended solids on August 27, 1994, is an example of when only one source-area (high-traffic streets—HST) produced a higher concentration than was found at the basin outlet. This bracketing of basin-outlet concentrations by source-area concentrations provides confidence that the significant critical source areas were identified and monitored. As is discussed in the following section, if source-area water volumes can be calculated, then a more robust mass budget analysis is possible. Only total concentrations were considered in the above analysis; partitioning between the dissolved and particulate phases was not considered, nor were volatilization losses accounted for.

For a given constituent, the source area producing the highest concentration may change for any given storm (fig. 5). For example, on June 11, 1994, the source area producing the highest zinc concentration (480 $\mu\text{g/L}$) was the commercial rooftops. On August 27, 1994, residential driveways produced the highest zinc concentration (570 $\mu\text{g/L}$). This variability in source-area concentrations indicates that antecedent conditions, including various constituent loading mechanisms, may be important for water-quality modeling on an individual-storm basis.

Error Analysis and Mass Budget Results

A mass-budget approach was used to compare loads computed from source-area data to loads measured at the basin outlet. This mass-budget approach provides insight into the reliability of the source-area data. Reliable mass budgets provide confidence that adequate collector-site selection and collection methods have been developed, resulting in representative source-area concentration data.

The water volume generated by SLAMM for each source area was multiplied by the corresponding constituent concentration to obtain an estimate of the source-area load on an individual-storm basis. Assumed in this approach is that the concentration measured by the source-area sampler represented the mean concentration for the storm. The SLAMM-generated water volume for the entire basin (source-area summation) was forced to match the volume measured at the basin-outlet flume by adjusting the overall basin precipitation used by SLAMM. No water-volume calibration, however, was done between individual source areas. The eight individual source-area loads were summed to derive an estimate of the total generated basin load. For comparison, the basin-outlet load was estimated by multiplying the volume measured at the basin-outlet flume by the flow-weighted composite sample concentration at the basin outlet. The basin-outlet load was assumed to be the “true” load for each storm.

Water volumes and constituent loads for the eight monitored source areas, expressed as a percentage of the “true” basin-outlet load for selected storms, are shown in figures 6a through 6c. For the small rainfalls, grass areas (RL) and the flat commercial rooftops (CR) generated a decreased proportion of basin runoff because of their storage or infiltration capacities. For example, on the August 24, 1994, storm (0.23 cm, fig. 3), no runoff was computed for the grass areas, a reflection of the infiltration and storage capacity of this source area.

In a qualitative sense, all of the June 11 budget's match acceptably well with the “true” load except lead and the PAH's. In contrast, the August 20 chemical oxygen demand (COD) and zinc budgets and the September 25 suspended-solids budget deviate substantially from the “true” load. The following uncertainty analysis is a quantitative approach used to identify unreliable budgets. These budgets were then used to

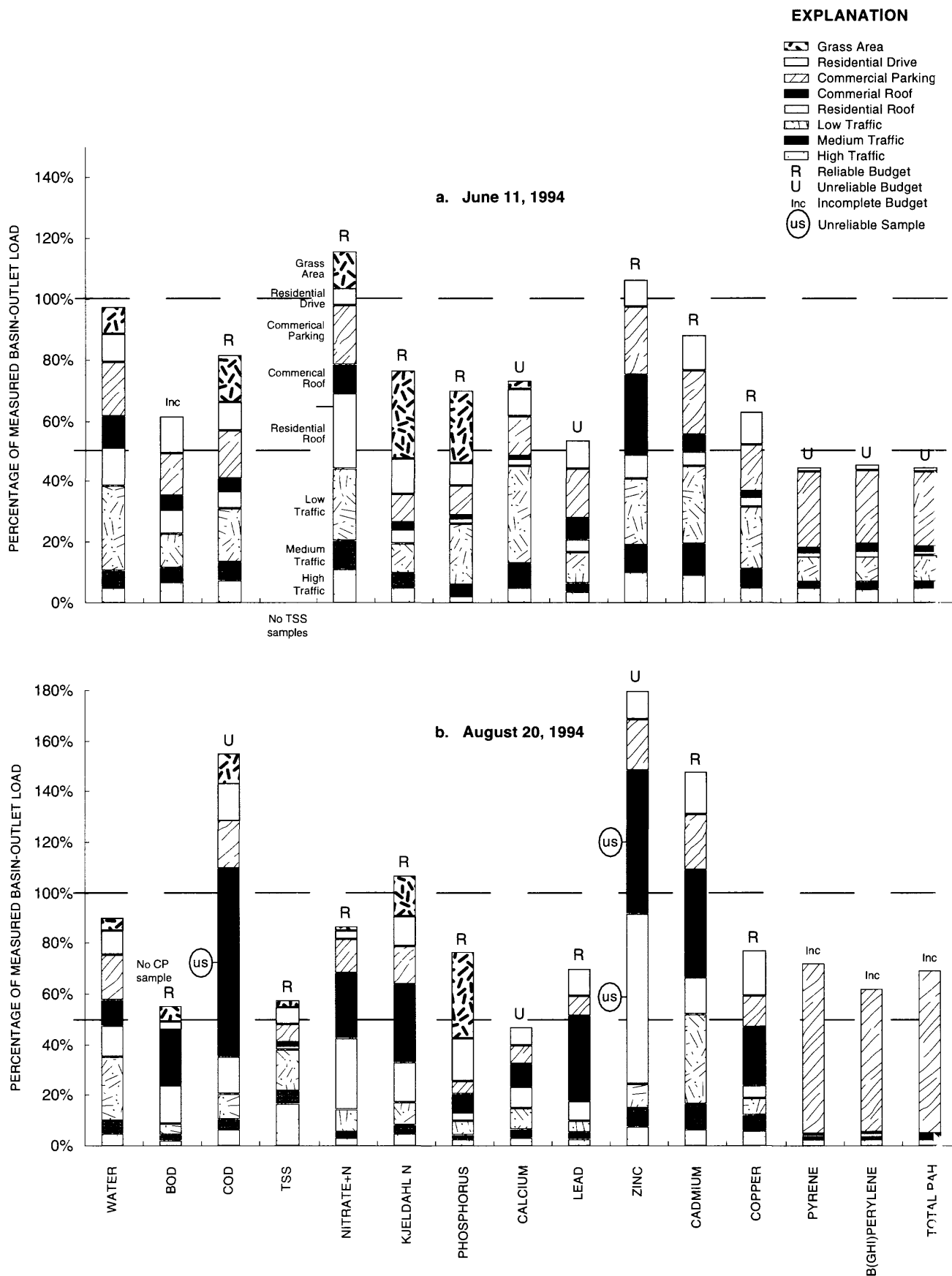


Figure 6. Source-area contributions as percentage of the basin-outlet loads for selected storms at the Marquette study basin.

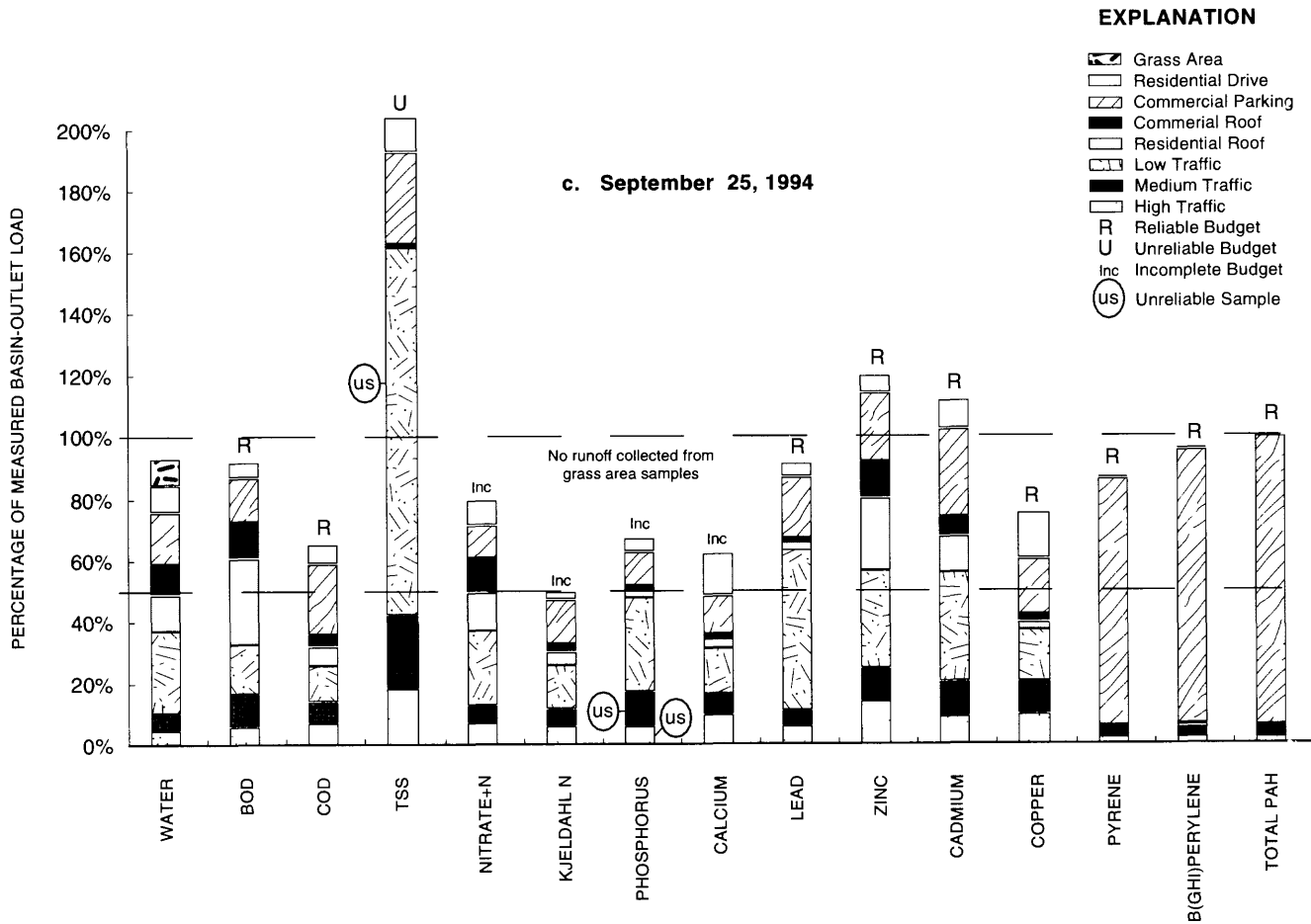


Figure 6. Source-area contributions as percentage of the basin-outlet loads for selected storms at the Marquette study basin—Continued.

single out specific unreliable source-area concentration data points responsible for the unbalanced budget.

For a given constituent, the summed source-area loads of a reliable mass budget should be approximately equal to the “true” basin-outlet load. Quantitatively, the load budget can be expressed as

$$B = \sum_{i=1}^8 S_i + R \quad (2)$$

where B is the “true” basin-outlet load, S_i is a specific source-area load for source i , and R is a residual term. For a reliable mass budget, R should be approximately equal to zero.

For any particular storm, the residual term is obtained by rearranging equation 2 to give

$$R = B - \sum_{i=1}^8 S_i \quad (3)$$

The residual should be a random variable because of uncertainty in the estimate of the random variables B and S_i . The variance in the budget residual (R) error can be determined from equation 3 as

$$\sigma_R^2 = \sigma_B^2 + \sum_{i=1}^8 \sigma_{S_i}^2 \quad (4)$$

where σ_R^2 is the variance in the budget residual error, σ_B^2 is the variance in the basin-outlet load error, and $\sigma_{S_i}^2$ is the variance in the error for source-area load S_i . Given estimates of the mean and variance of the residual term (R) for a particular storm, a hypothesis test can be done to determine whether R is different from zero. A budget, by definition, is considered unreliable if R is determined to be different from zero. If R cannot be distinguished from zero, that budget, by definition, is considered reliable. In the following uncertainty analysis, the mean of a particular

random variable (X), such as basin-outlet and source-area constituent concentration or water volume, is denoted by X , and the variance is denoted by σ_X^2 .

One component in the uncertainty in R is the inherent error in the individual source-area loads. The source-area load was estimated from the water volume computed by SLAMM (V_i) multiplied by the sampled source-area concentration (C_i). Individual source-area loads (S_i) are calculated on an individual-storm basis for a given constituent as

$$S_i = V_i \cdot C_i \quad (5)$$

The variance of the error in an individual source-area load can be determined as the product of two independent random variables (Benjamin and Cornell, 1970)

$$\sigma_{S_i}^2 = \sigma_{C_i}^2 \cdot V_i^2 + \sigma_{V_i}^2 \cdot C_i^2 \quad (6)$$

where $\sigma_{S_i}^2$ is the variance of the error in source-area load (S_i), $\sigma_{C_i}^2$ is the variance of the error in the source-area concentration (C_i), and $\sigma_{V_i}^2$ is the variance of the error in the source-area water volume (V_i). Because the runoff volumes and concentrations were determined independently, the assumption of independence should be valid. Dividing equation 6 by the squared expected value of an individual source-area load, $(V_i C_i)^2$, yields an expression for the variance of the error in source-area load as a function of coefficients of variation, namely

$$\sigma_{S_i}^2 = \left[\left(\frac{\sigma_{C_i}}{C_i} \right)^2 + \left(\frac{\sigma_{V_i}}{V_i} \right)^2 \right] \cdot S_i^2 \quad (7)$$

where σ_{C_i}/C_i is the coefficient of variation of the error in C_i and σ_{V_i}/V_i is the coefficient of variation of the error in V_i .

Similarly, the basin-outlet load (B) was estimated from the basin-outlet water volume (V_B) and flow-weighted basin-outlet storm mean concentration (C_B) as

$$B = V_B \cdot C_B \quad (8)$$

The variance of the error in basin-outlet load was determined for a product of independent random variables (Benjamin and Cornell, 1970) as

$$\sigma_B^2 = \sigma_{C_B}^2 \cdot V_B^2 + \sigma_{V_B}^2 \cdot C_B^2 \quad (9)$$

where $\sigma_{C_B}^2$ is the variance of the error in basin-outlet concentration and $\sigma_{V_B}^2$ is the variance of the error in basin-outlet water volume. Dividing equation 9 by the squared expected value of B (eq. 8 squared) and simplifying, one obtains the variance of the error in outlet load expressed as a function of coefficients of variation, namely

$$\sigma_B^2 = \left[\left(\frac{\sigma_{C_B}}{C_B} \right)^2 + \left(\frac{\sigma_{V_B}}{V_B} \right)^2 \right] \cdot B^2 \quad (10)$$

The error associated with an individual source-area concentration value $\sigma_{C_i}^2$ varied according to the constituent and was established from sample-processing replicates and laboratory-analysis replicates. The standard deviation, expressed as a percentage of the mean value, ranged from 1.5 percent for calcium to 51 percent for the nitrogen series (kjeldahl plus nitrite plus nitrate); heavy metal and suspended solids concentration variations were 15 percent. On the basis of historical SLAMM calculations, the uncertainty in the source-area water volume was estimated to be 20 percent. Using a 99-percent confidence interval results in the following coefficient of variation

$$2.58 \cdot \frac{\sigma_{V_i}}{V_i} = 0.20 \quad \text{or} \quad \frac{\sigma_{V_i}}{V_i} = 0.078$$

The coefficient of variation for the basin-outlet water volume also was estimated to be 20 percent. The error associated with the basin-outlet concentration value (σ_{C_B}) did not include, by definition, sample-collection error; thus, it is the same as σ_{C_i} . The concentration error is solely a function of the specific constituent and includes sample processing and laboratory analysis error.

By definition, the estimates of uncertainty for a source-area collector do not include sample-collection error, that which is either associated with selecting a representative collection site or involved in sampling representative sheet flow over the entire storm. Should the ensuing analysis produce a large number of mass budgets that have a significant difference between the summed source-area loads and the basin-outlet load (budgets with R different from zero), one may conclude that the source-area sampling procedures were not appropriate.

For each sampled storm and constituent, an error variance was estimated for individual source areas (eq. 7, $i=1,8$) and for the basin outlet (eq. 10). These vari-

ances were then used to estimate the error variance for the budget residual (eq. 4). A 99-percent confidence interval was used in the hypothesis tests; thus, the residual-error standard deviation was multiplied by 2.58 to establish the acceptable range in residual for a reliable budget. The following is an example calculation for the June 11, 1994, phosphorus budget.

Using equations 5 and 7, the low-traffic-street load variance was

$$\sigma_{LST}^2 = [(0.26)^2 + (0.078)^2] \cdot (1.3\text{kg})^2, \text{ where}$$

$$\frac{\sigma_{C_{LST}}}{C_{LST}} = 0.26 \text{ and } \frac{\sigma_{V_{LST}}}{V_{LST}} = 0.078.$$

$$\sigma_{LST}^2 = 0.12\text{kg}^2.$$

The other seven source-area variances were calculated in a similar manner.

Using equations 8 and 10, the basin-outlet phosphorus load and variance were estimated as

$$B = 6.5\text{kg}.$$

$$\sigma_B^2 = [(0.26)^2 + (0.078)^2] \cdot (6.5\text{kg})^2 = 3.1\text{kg}^2.$$

The difference between the outlet and summed source loads (eq. 3) was

$$R = (S_{HST} + S_{MST} + S_{LST} + S_{RR} + S_{CR} + S_{CP} + S_{RD} + S_{RL}) - B = 4.5 - 6.5 = 2.0\text{kg}$$

and the residual variance was

$$\sigma_R^2 = \sigma_{HST}^2 + \sigma_{MST}^2 + \sigma_{LST}^2 + \sigma_{RR}^2 + \sigma_{CR}^2 + \sigma_{CP}^2 + \sigma_{RD}^2 + \sigma_{RL}^2 + \sigma_B^2 = 3.5\text{kg}^2$$

Applying a 99-percent confidence interval to σ_R produced the following residual error (E_R)

$$E_R = 2.58 \cdot \sigma_R = 2.58\sqrt{3.5} = (4.8)\text{kg}.$$

Because the residual error (4.8 kg) is greater than the residual (2.0 kg), it cannot be stated with 99-percent certainty that the summed source phosphorus load is different from the basin-outlet phosphorus load; thus, this budget was considered reliable.

This error analysis was done on 83 budgets (146 budgets if the 9 individual PAH compounds are consid-

ered), resulting in 65 percent of the budgets being classified as reliable. For some budgets, an important source-area constituent concentration was missing and a budget was not possible. Figure 6c is an example in which insufficient residential lawn water was collected for the laboratory analysis. Figures 6a through 6c illustrate the budget-analysis results for three storms; budgets are labeled reliable (R), unreliable (U), or not possible because of incomplete source-area data (inc).

The next step after the error analysis was to identify the specific source-area concentration sample(s) that contributed to the unreliable budgets. From the reliable budgets, a mean relative load contribution was determined for each source area, along with a 99-percent confidence interval based on sample size and the variance around the mean. Source-area contributions from the unreliable budgets were then examined to determine whether they were outside of the 99-percent confidence interval. Concentrations used in computing a source-area load that were outside the 99-percent confidence interval were identified as unreliable.

For example, on August 20 (fig. 6b), individual source-area load contributions from the unreliable zinc budget were compared against means derived from the reliable budgets. The mean residential rooftop contribution derived from the reliable budgets was 15 percent \pm 11 percent. This 11-percent range was a function of sample size (six reliable budgets), the standard deviation (7 percent; table 5), and the 99-percent confidence interval. The August 20, 1994, residential rooftop contribution was 67 percent of the basin-outlet load and was outside the reliable range (4–26 percent). Consequently the associated residential rooftop concentration was identified as unreliable. Similarly, the commercial-rooftop zinc and COD samples from August 20 and the low-traffic-street suspended-solids sample from September 25 were identified as unreliable. As is evident in figure 4, the unreliable samples were not necessarily those with the highest concentrations.

Of the 611 concentration samples used in the mass budgets, 59 were identified as unreliable, and 76 percent of these unreliable samples were obtained from collection bottles that filled before the end of the storm. These full bottles may have captured a first-flush effect or acted as a sediment trap. The unreliable concentration data were removed from the source-area concentration data set, and the geometric means were recomputed. These recomputed geometric means are included in table 4 for constituents for which mass budgets were computed. The most significant differences (\approx 38-percent reduction) were found for the residential

Table 4. Source-area and basin-outlet geometric mean concentrations of selected properties and constituents for urban basins in Marquette, Michigan, and Madison, Wisconsin

[The Marquette concentrations are bolded and include two storms in addition to the mass-budget storms. *, indicates mass budgets computed. Coefficients in parentheses identify geometric mean with unreliable concentration data removed. --, indicates no analyses done. ND, indicates no detection.

a. From Bannerman and others, 1993 (High-traffic street 19,800–20,000 vehicles per day; Medium-traffic street 500–7,300 vehicles per day; Low-traffic street 100–400 vehicles per day)

b. From Madison 1994, 1995 street study, R.J. Waschbusch written (USGS) communication. High traffic—Monroe Street (18,600 cars per day; commercial on-street parking); medium traffic—Glenway Avenue (6,157 cars per day; limited on-street parking); low traffic—Monroe Street (378 cars per day; residential).

Constituent	High-traffic street	Medium-traffic street	Low-traffic street	Residential rooftops	Commercial rooftops	Commercial parking lots	Residential driveways	Residential lawns	Basin outlet
Inorganic									
Total solids (milligrams per liter)	300	498	244	81	115	240	255	395	224
a	373	493	796	91	112	127	306	600	369
b	186	130	188						
Suspended solids (milligrams per liter)*	251 (226)	323 (305)	206 (175)	36	24	138 (110)	178 (157)	262	159
a	232	326	662	27	15	58	173	397	262
b	117	79	104						
Ammonia-N (milligrams per liter)*	0.44 (0.42)	0.35	0.26	0.46 (0.44)	0.72 (0.67)	0.19 (0.22)	0.12	0.26	0.20
Nitrate plus nitrite (milligrams per liter)*	0.46 (0.45)	0.32	0.27	0.54 (0.46)	0.57 (0.49)	0.30 (0.34)	0.30	0.40	0.37
Total kjeldahl nitrogen (milligrams per liter)*	2.3 (2.5)	1.3	0.9	1.3 (1.0)	1.7 (1.6)	1.5 (1.6)	1.8	9.3	1.5
Dissolved kjeldahl nitrogen (milligrams per liter)	0.9	0.6	0.4	0.8	1.3	0.7	0.5	1.8	0.6
Total phosphorus (milligrams per liter)*	0.29 (0.31)	0.24 (0.23)	0.14	0.08 (0.06)	0.09	0.21 (0.20)	0.35	2.33	0.29
a	0.47	1.07	1.31	0.15	0.20	0.19	1.16	2.67	0.66
b	0.19	0.19	0.41						
Dissolved phosphorus (milligrams per liter)	0.015	0.013	0.008	0.016	0.033	0.022	0.037	0.092	0.043
a	0.1	0.31	0.37	0.06	0.08	0.05	0.49	1.45	.27
b	0.03	0.05	0.18						
pH	6.69	7.09	6.39	5.97	4.21	6.43	6.65	6.33	6.80
Total recoverable hardness (milligrams per liter)	28	31	14	21	22	20	24	11	26
b	68	46	84						
Dissolved hardness (milligrams per liter)	16	11	9	18	24	13	14	9	15
Total recoverable calcium (milligrams per liter)*	7.9	8.5	3.9	3.5	4.0	5.9	7.4	3.1	7.7
b	16.0	10.8	18.4						
Dissolved calcium (milligrams per liter)									

Table 4. Source-area and basin-outlet geometric mean concentrations of selected properties and constituents for urban basins in Marquette, Michigan, and Madison, Wisconsin—Continued

Constituent	High-traffic street	Medium-traffic street	Low-traffic street	Residential rooftops	Commercial rooftops	Commercial parking lots	Residential driveways	Residential lawns	Basin outlet
Dissolved calcium (milligrams per liter)									
	5.0	3.6	1.8	3.5	3.7	4.1	4.7	1.9	5.1
Total recoverable magnesium (milligrams per liter)									
	2.1	2.5	1.8	2.5	2.3	1.5	1.7	--	1.7
b	6.7	4.6	9.0						
Dissolved magnesium (milligrams per liter)									
	1.3	--	--	1.9	2.0	1.7	2.0	--	3.0
Total recoverable lead (micrograms per liter)*									
	37	30 (29)	21	25	52 (48)	40	57 (52)	--	4^a
a	50	55	33	21	9	22	17		32
b	25	46	10						
Dissolved lead (micrograms per liter)									
	2.1	1.5	1.5	4.4	20	2.2	2.3	--	2.4
b	1.7	1.9	0.5						
Total recoverable zinc (micrograms per liter)*									
	256	174 (166)	78 (75)	318 (201)	348 (215)	178	148	--	111
a	508	339	220	149	330	178	107		203
b	202	118	66						
Dissolved zinc (micrograms per liter)									
	73	44	24	188	263	64	27	--	23
b	51	42	22						
Total recoverable cadmium (micrograms per liter)*									
	0.9	1.0 (0.9)	0.6 (0.5)	0.7 (0.5)	0.9 (0.8)	0.9	0.8	--	0.6
a	1.8	1.4	0.8			0.6	0.5		0.4
b	0.8	0.4	0.3						
Dissolved cadmium (micrograms per liter)									
	0.33	0.30	0.27	0.31	0.71	0.32	0.21	--	0.13
a	0.9	0.30	0.5			0.4	0.5		0.3
b	0.25	0.16	0.14						
Total recoverable copper (micrograms per liter)*									
	30 (28)	31 (30)	15 (14)	10 (7)	23 (20)	25 (22)	36 (34)	--	22
a	46	56	24	15	9	15	17		16
b	26	24	9						
Dissolved copper (micrograms per liter)									
	11.2	7.3	7.5	6.6	17.8	10.7	11.8	--	7.0
a	18	24	9	10	6	9	9		5
b	6.8	9.6	3.3						
Fecal coliform (colonies per 100 milliliter)									
	1,900	2,400	280	2,200	30	4,200	1,900	4,700	10,200
a	9,627	56,554	92,061	294	1,117	1,758	34,294	42,093	175,106
Total 5-day biological oxygen demand (milligrams per liter)*									
	14.9	11.6	5.8	9.0	17.5	10.5	13.0	22.6	15.4

Table 4. Source-area and basin-outlet geometric mean concentrations of selected properties and constituents for urban basins in Marquette, Michigan, and Madison, Wisconsin—Continued

Constituent	High-traffic street	Medium-traffic street	Low-traffic street	Residential rooftops	Commercial rooftops	Commercial parking lots	Residential driveways	Residential lawns	Basin outlet
Dissolved 5-day biological oxygen demand (milligrams per liter)									
	9.8	8.3	4.9	5.8	12.3	6.3	4.7	1.6	8.2
Chemical oxygen demand (milligrams per liter)*									
	98 (94)	69 (73)	44	53 (51)	104 (82)	93	98 (99)	169	66
Dissolved chemical oxygen demand (milligrams per liter)									
	40	34	16	32	96	42	44	82	33
Organic									
Anthracene (micrograms per liter)									
	0.48	0.33	0.18	ND	ND	0.70	ND	--	0.60
b	0.21								
Benzo[b]fluoranthene (micrograms per liter)									
	1.29	1.00	0.17	0.06	0.21	6.71	0.21	--	1.83
b	1.19	0.44	0.44						
Benzo[k]fluoranthene (micrograms per liter)									
	0.74	0.59	0.09	0.04	0.18	3.67	0.22	--	1.00
b	0.66	0.23	0.25						
Benzo[a]pyrene (micrograms per liter)									
	1.15	0.90	0.14	0.05	0.25	4.45	0.28	--	1.63
b	0.99	0.31	0.35						
Chrysene (micrograms per liter)									
	1.17	0.86	0.19	0.12	0.27	6.75	0.36	--	1.83
b	1.21	0.44	0.42						
Fluoranthene (micrograms per liter)									
	3.43	2.51	0.39	0.15	0.48	21.04	0.50	--	5.03
b	3.00	0.99	0.97						
Ideno [1,2,3- <i>cd</i>] pyrene (micrograms per liter)									
	0.99	0.80	0.20	0.09	0.28	4.82	0.31	--	1.38
b	1.04	0.38	0.38						
Phenanthrene (micrograms per liter)									
	1.9	1.37	0.60	0.24	0.35	7.14	0.47	--	3.8
b	1.2	0.49	0.50						
Pyrene (micrograms per liter)*									
	2.37	1.75	0.27	0.10	0.33	12.24 (10.33)	0.34	--	3.36
b	2.10	0.70	0.48						
Benzo[ghi]perylene (micrograms per liter)*									
	1.03	0.77	0.14	0.05	0.24	4.24 (3.56)	0.29	--	1.35
b	0.99	0.41	0.34						
Benzo[a]anthracene (micrograms per liter)									
	0.78	0.64	0.09	0.03	0.15	2.99	0.18	--	1.09
b	0.70	0.18	0.24						
PAH summation (micrograms per liter)*									
	15.18	11.43	1.72	0.61	2.06	75.58 (63.64)	1.79	--	21.03
b	13.40	4.66	4.55						

and commercial rooftop zinc samples, which had the highest frequency of full bottles (47 percent) and which included 8 of the 10 unreliable zinc samples (fig. 4).

There were numerous budgets in which full bottles were used in the composite sample, but the resulting concentrations were still identified as reliable. This may indicate that the collector bottles filled near the end of the storm and, as a result, collected water during most of the runoff duration. In some cases, the sampled storm occurred soon after previous precipitation (fig. 3); thus, there may have been insufficient material accumulation on the surface so that a first flush effect would not be significant. For example, after the storm of July 21, 1994, collection bottles for the commercial roof, residential roof, and residential lawns were full. Yet, none of the concentrations from these source-area samples were determined to be unreliable.

On several occasions, a source-area sample was determined to be unreliable, yet the collector bottle was not overfilled; the September 25, 1994, low-traffic-street (LST) suspended-solids sample is an example (fig. 6c). In this case, street construction in the vicinity of the LST collectors could have generated a disproportionate amount of suspended solids, an amount not generated basinwide on the low-traffic streets. Thus, the sample obtained from the LST collectors was not representative of the basinwide low-traffic street source area. As one might expect, the suspended-solids budget did not balance; however, other nutrient, metal, and PAH budgets did balance. Possibly, the local construction produced suspended solids, but did not increase the nutrient, metal, or PAH loading.

A second example of the variable effects of using full bottles was observed for two parking-lot samples. For the storm of August 29, 1994, bottles from two parking-lot sites were composited (the third site was not usable), and both bottles had filled before runoff had ceased. The parking-lot sample concentration yielded a load that was 1,200 percent of the PAH load as measured at the basin outlet. Conversely, during the storm on September 25, 1994, bottles at the two parking-lot sites (the third site was again not usable) were found to be filled and were replaced with two fresh bottles, both of which ultimately filled to capacity. Yet, these four full bottles yielded a concentration that produced a reliable mass budget (fig. 6c). Possibly, the initial bottles sampled the first flush, but these samples were tempered by the second set of bottles, which filled later in the storm runoff. Based upon those results, the four bottles did not appear to have acted as a significant sediment trap.

Source-Area Concentration Comparisons

In table 4, the geometric mean concentrations from the eight monitored source areas and the basin outlet in the Marquette study area are listed along with data from Madison, Wis. source-area studies (Bannerman and others, 1993; R.J. Waschbusch, U.S. Geological Survey, written commun., 1996). Land use in the Madison study basins differed from that in the Marquette study basin; thus, one would expect to see differences in the basin-outlet constituent concentrations. If, however, specific source-area concentrations are applicable across a range of urban basins, one should see a similarity in source-area contaminant concentration data collected for Madison and Marquette studies.

For many of the source-area constituents, concentrations were similar between the Madison and Marquette studies. For total and suspended solids, the comparison was favorable across most of the source areas. In contrast, total and dissolved phosphorus concentrations were consistently higher in Madison than in Marquette, not only for source areas but also for the basin outlet. For most source areas, the metal and PAH concentrations were similar between the cities. The 1995 Madison data, obtained with collectors that could control inflow, are especially comparable to the Marquette data.

An initial assessment based on data in table 4 indicates that source-area data collected in one basin may be applicable to another basin. A rigorous analysis on a greater number of basins would be needed to provide definitive conclusions. In the final assessment, the applicability of source-area data to a variety of basins may depend on the source-area type and the contaminant of interest. Variability in source-area concentration between the study areas may be attributed to factors ranging from differences in basin geology, source-area construction materials, conditions prior to the monitored storm, sample-collection methods, atmospheric-deposition rates, or loading of unique contaminants due to vehicular traffic. Pitt and Bozeman (1982), Bannerman and others, (1993), and Pitt and others (1995) provide further details as to the causes of variability in source-area contaminants.

Source-Area Load Contributions

Source-area load contributions compiled from the 10 storm budgets with the unreliable samples removed are listed in table 5. The summed source-area loads are somewhat lower than those measured at the basin outlet. This may be attributed in part to the

unsampled source area (sidewalks), which generated about 5 percent of the basin runoff. Nevertheless, given the uncertainty of the SLAMM source-area water volumes, there is reasonable agreement in the summed source-area contaminant loads and those measured at the basin outlet. Source-area loads that constitute more than 20 percent of the basin outlet load are in bold type.

The relative importance of individual source areas to the basin-outlet load varied by constituent. Parking lots were a major contributor of total zinc (30 percent), total cadmium (25 percent), total copper (22 percent), and all the PAH compounds (≈ 64 percent). Low-traffic streets were a major producer of total suspended solids (27 percent), nitrate plus nitrite (21 percent), and total cadmium (25 percent). Grass areas were a major producer of total kjeldahl nitrogen (31 percent) and total phosphorus (26 percent), even though the water volume generated from these areas was low (5.8 percent).

Basin-outlet contaminant loads for the 10 storm budgets are listed in table 6. These summed storm loads represent only part of the load that would be produced from an urban basin in an entire year. Prey and others (1996) provide SLAMM-calculated source-area loads based on 81 cm of annual precipitation in the Marquette study basin.

SUMMARY AND CONCLUSIONS

To represent the eight types of contaminant source areas in the Marquette, Mich., study basin, stormwater was collected concurrently at 33 sites during 12 storms. At the same time, flow-weighted composite samples were collected from a flume at the basin outlet. The resulting geometric mean concentrations for many of the source-area constituents in the Marquette, Mich. basin compared favorably to results from source-area studies in Madison, Wis., an indication that source-area data may be applicable to a range of basins.

Even with the temporal variability observed in the source-area concentration data, discernible differences between source areas were noted for certain constituents.

- Commercial rooftops produced the most acidic runoff.
- Commercial and residential rooftops produced the lowest concentration of suspended solids, whereas commercial rooftops produced the highest concentration of dissolved metals such as lead, zinc, cadmium, and copper.

- Grass areas generated the highest total kjeldahl nitrogen and phosphorus concentrations, whereas parking lots produced the highest concentration for all the PAH compounds.

For 199 of the 207 constituent/storm combinations, at least one source-area concentration was higher and at least one source-area concentration was lower than the basin-outlet concentration. This bracketing of basin-outlet concentrations by source-area concentrations provided an initial indication that the significant critical source-areas were identified and monitored.

Summed source-area contaminant loads, which were a result of Source Load and Management Model (SLAMM) simulated source-area water volumes and source-area concentration data, generally compared favorably with basin-outlet loads. This mass budget approach, coupled with an error analysis, provided a tool to identify unreliable samples, such as first-flush samples or collected stormwater runoff that was not representative of the entire source-area classification. Seventy-six percent of the unreliable samples came from full collection bottles, emphasizing the importance of collecting source-area runoff for the entire duration of the storm. Removal of the unreliable source-area concentration data did affect the computed geometric means; specifically, residential and commercial rooftop zinc concentrations were reduced by ≈ 38 percent after removal of the unreliable sample data. These two source areas also had the highest frequency of full bottles.

The preponderance of reliable mass budgets indicates that it is possible to collect source-area samples that represent runoff from the eight source areas and provides confidence that site-selection and sample collection methods resulted in representative source-area concentration data.

The relative importance of individual source-areas loads to the overall basin-outlet load varied according to the individual constituent. Parking lots were a major contributor of total zinc (30 percent), total cadmium (25 percent), total copper (22 percent) and all the PAH compounds (≈ 64 percent); whereas low-traffic streets were a major producer of total suspended solids (27 percent), nitrate plus nitrite (21 percent), and total cadmium (25 percent). Grass areas were a major producer of total kjeldahl nitrogen (31 percent) and total phosphorus (26 percent), even though the water volume generated from grass areas was low (5.8 percent of the total water volume generated.)

Table 5. Source-area contributions expressed as a percentage of the basin load as monitored at the Marquette Study basin-outlet, October 1993 and May through August 1994
 [Contributions greater than 20 percent are bold. Number following \pm , indicates one standard deviation. --, indicates no data]

5-day Biological Oxygen Demand	Chem- ical Oxygen Demand	Suspended solids	Nitrate & nitrite	Total kjeldahl nitrogen	Total phosphorus	Total calcium	Total lead	Total zinc	Total cadmium	Total copper	Total benzo [gh] perylene	Total pyrene	Summary of Polycy- clic Aro- matic Hydrocar- bon	Water volume
5±3	5±2	8±6	6±2	5±2	2±0	5±2	5±3	10±5	7±4	6±4	6±9	7±11	7±11	4.5±0.2
Traffic street (HST)with 10,600 or more vehicles per day														
6±5	6±3	13±10	5±2	5±2	5±2	7±5	3±2	8±2	9±5	8±3	6±6	6±8	6±8	5.5±0.2
Medium traffic street (MST)														
17±14	19±11	27±16	21±7	17±7	15±7	16±9	15±14	19±7	25±11	17±6	6±8	5±5	5±5	26.9±1.0
Low traffic street (LST)														
10±8	10±10	11±24	15±8	8±5	3±1	8±13	18±33	15±7	8±4	5±4	1±1	1±1	1±1	12.8±0.8
Residential roof (RR)														
13±7	11±9	2±1	14±8	12±10	5±4	5±6	10±10	16±10	15±16	11±9	4±6	3±5	3±5	10.2±0.7
Commercial roof (CR)														
18±9	23±11	16±12	16±8	14±6	8±3	14±6	19±14	30±15	25±13	22±15	57±34	52±28	64±41	19.1±1.8
Commercial parking lot (CP)														
11±7	11±6	14±17	7±4	12±7	14±10	10±5	14±12	18±12	21±17	18±10	3±4	3±3	3±3	9.8±0.8
Residential drive (RD)														
11±7	12±2	4±3	10±6	31±21	26±6	2±0	--	--	--	--	--	--	--	5.8±2.7
Grass areas (RL)														
90	97	95	94	104	77	68	83	116	111	87	--	77	89	--
Summation of monitored source areas														

Table 6. Selected constituent loads and precipitation as measured at the Marquette study basin outlet.

[g, grams; kg, kilograms; m³, cubic meters; cm, centimeters]

	Maximum	Median	Minimum
5-day BOD (kg)	162	59	>9
COD (kg)	813	275	38
Suspended solids (kg)	7,581	354	37
Nitrate & nitrite (kg)	3.1	1.3	0.5
Total kjeldahl nitrogen (kg)	30	5.3	0.8
Total phosphorus (kg)	6.5	1.1	0.1
Total calcium (kg)	71	29	9
Total lead (g)	1,109	192	9
Total zinc (g)	1,404	437	41
Total cadmium (g)	8	2	0.2
Total copper (g)	310	83	10
Total benzo[ghi]perylene (g)	72	17	3
Total pyrene (g)	268	40	6
Polycyclic aromatic hydrocarbon (PAH) (g)	1,681	250	39
Water volume (m ³)	7,477	3,492	550
Precipitation (cm)	3.18	1.47	.10

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