

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

Prepared in cooperation with the
FEDERAL HIGHWAY ADMINISTRATION

A Synopsis of Technical Issues of Concern for Monitoring Trace Elements in Highway and Urban Runoff

Open-File Report 00-422

A Contribution to the
NATIONAL HIGHWAY RUNOFF DATA AND METHODOLOGY SYNTHESIS



U.S. Department
of Transportation



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By ROBERT F. BREault and GREGORY E. GRANATO

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Northborough, Massachusetts
2000

U.S. DEPARTMENT OF THE INTERIOR
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PREFACE

Knowledge of the characteristics of highway runoff (concentrations and loads of constituents and the physical and chemical processes which produce this runoff) is important for decision makers, planners, and highway engineers to assess and mitigate possible adverse impacts of highway runoff on the Nation's receiving waters. In October 1996, the Federal Highway Administration and the U.S. Geological Survey began the National Highway Runoff Data and Methodology Synthesis to provide a catalog of the pertinent information available; to define the necessary documentation to determine if data are valid (useful for intended purposes), current, and technically supportable; and to evaluate available sources in terms of current and foreseeable information needs. This paper is one contribution to the National Highway Runoff Data and Methodology Synthesis and is being made available as a U.S. Geological Survey Open-File Report pending its inclusion in a volume or series to be published by the Federal Highway Administration. More information about this project is available on the World Wide Web at <http://ma.water.usgs.gov/fhwa/runwater.htm>

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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS FROM SI UNITS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol	When You Know	Multiply By	To Find	Symbol
LENGTH								
in	inches	25.4	millimeters	mm	millimeters	0.039	inches	in
ft	feet	0.305	meters	m	meters	3.28	feet	ft
yd	yards	0.914	meters	m	meters	1.09	yards	yd
mi	miles	1.61	kilometers	km	kilometers	0.621	miles	mi
AREA								
in ²	square inches	645.2	square millimeters	mm ²	square millimeters	0.0016	square inches	in ²
ft ²	square feet	0.093	square meters	m ²	square meters	10.764	square feet	ft ²
yd ²	square yards	0.836	square meters	m ²	square meters	1.195	square yards	yd ²
ac	acres	0.405	hectares	ha	hectares	2.47	acres	ac
mi ²	square miles	2.59	square kilometers	km ²	square kilometers	0.386	square miles	mi ²
VOLUME								
fl oz	fluid ounces	29.57	milliliters	mL	milliliters	0.034	fluid ounces	fl oz
gal	gallons	3.785	liters	L	liters	0.264	gallons	gal
ft ³	cubic feet	0.028	cubic meters	m ³	cubic meters	35.71	cubic feet	ft ³
yd ³	cubic yards	0.765	cubic meters	m ³	cubic meters	1.307	cubic yards	yd ³
NOTE: Volumes greater than 1000 l shall be shown in m ³ .								
MASS								
oz	ounces	28.35	grams	g	grams	0.035	ounces	oz
lb	pounds	0.454	kilograms	kg	kilograms	2.202	pounds	lb
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
TEMPERATURE (exact)								
°F	Fahrenheit temperature	5(F-32)/9 or (F-32)/1.8	Celsius temperature	°C	Celsius temperature	1.8C + 32	Fahrenheit temperature	°F
ILLUMINATION								
fc	foot-candles	10.76	lux	lx	lux	0.0929	foot-candles	fc
fl	foot-Lamberts	3.426	candela/m ²	cd/m ²	candela/m ²	0.2919	foot-Lamberts	fl
FORCE and PRESSURE or STRESS								
lbf	poundforce	4.45	newtons	N	newtons	0.225	poundforce	lbf
lbf/in ²	poundforce per square inch	6.89	kilopascals	kPa	kilopascals	0.145	poundforce per square inch	lbf/in ²

* SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.

(Revised September 1993)

A Synopsis of Technical Issues of Concern for Monitoring Trace Elements in Highway and Urban Runoff

By Robert F. Breault and Gregory E. Granato

Abstract

Trace elements, which are regulated for aquatic life protection, are a primary concern in highway- and urban-runoff studies because stormwater runoff may transport these constituents from the land surface to receiving waters. Many of these trace elements are essential for biological activity and become detrimental only when geologic or anthropogenic sources exceed concentrations beyond ranges typical of the natural environment. The Federal Highway Administration and State Transportation Agencies are concerned about the potential effects of highway runoff on the watershed scale and for the management and protection of watersheds. Transportation agencies need information that is documented as valid, current, and scientifically defensible to support planning and management decisions. There are many technical issues of concern for monitoring trace elements; therefore, trace-element data commonly are considered suspect, and the responsibility to provide data-quality information to support the validity of reported results rests with the data-collection agency.

Paved surfaces are fundamentally different physically, hydraulically, and chemically from the natural surfaces typical of most freshwater systems that have been the focus of many trace-element-monitoring studies. Existing scientific conceptions of the behavior of trace elements in the environment are based largely upon research

on natural systems, rather than on systems typical of pavement runoff. Additionally, the logistics of stormwater sampling are difficult because of the great uncertainty in the occurrence and magnitude of storm events. Therefore, trace-element monitoring programs may be enhanced if monitoring and sampling programs are automated. Automation would standardize the process and provide a continuous record of the variations in flow and water-quality characteristics.

Great care is required to collect and process samples in a manner that will minimize potential contamination or attenuation of trace elements and other sources of bias and variability in the sampling process. Trace elements have both natural and anthropogenic sources that may affect the sampling process, including the sample-collection and handling materials used in many trace-element monitoring studies. Trace elements also react with these materials within the timescales typical for collection, processing and analysis of runoff samples. To study the characteristics and potential effects of trace elements in highway and urban runoff, investigators typically sample one or more operationally defined matrixes including: whole water, dissolved (filtered water), suspended sediment, bottom sediment, biological tissue, and contaminant sources. The sampling and analysis of each of these sample matrixes can provide specific information about the occurrence and distribution of trace elements in runoff and receiving waters.

There are, however, technical concerns specific to each matrix that must be understood and addressed through use of proper collection and processing protocols. Valid protocols are designed to minimize inherent problems and to maximize the accuracy, precision, comparability, and representativeness of data collected. Documentation, including information about monitoring protocols, quality assurance and quality control efforts, and ancillary data also is necessary to establish data quality. This documentation is especially important for evaluation of historical trace-element monitoring data, because trace-element monitoring protocols and analysis methods have been constantly changing over the past 30 years.

INTRODUCTION

Trace elements that are considered contaminants have been a focus of highway- and urban-runoff studies because stormwater runoff may be a source of trace elements that are regulated for the protection of aquatic life (Gupta and others, 1981; Driscoll and others, 1990; Makepeace and others 1995; Young and others, 1996). In highway- and urban-stormwater literature, the term metal is usually used to describe a trace element that has adverse effects on aquatic biota at relatively low concentrations. The trace elements included in these studies, however, commonly were measured at concentrations that were above the detection limits for laboratory analysis-techniques used in runoff studies during the 1960's, 1970's, and early 1980's (Gupta and others, 1981; Athayde and others, 1983).

Trace element concentration, transport and fate are difficult to quantify, especially in stormwater-runoff studies. Determination of accurate trace element data in runoff studies is made difficult by the complexity of the physical and chemical processes involved and the difficult monitoring environment. Storms occur at random, and when they do occur the intensity of precipitation and the resultant volume and quality of runoff can vary by orders of magnitude within a storm and between storms (Spangberg and Niemczynowicz, 1992; Granato and Smith, 1999). Highway runoff is a complex mixture. It can include constituents from

atmospheric deposition, vehicles, the highway, and many other sources. The physicochemical processes that influence the quality of highway runoff also are complex (Bricker, 1999). Large variations in values of explanatory variables (such as traffic volume, antecedent conditions, and precipitation characteristics) that characterize runoff quality and quantity within a storm, between storms, from season-to-season, and from year-to-year may preclude quantitative interpretation of cause and effect relations (Driscoll and others, 1990). Furthermore, the logistics of stormwater sampling are demanding (U.S. Environmental Protection Agency, 1992a).

Highway-runoff contaminants of concern include trace elements, inorganic salts, solids, organic compounds, and pathogens that accumulate on the road surface as a result of local and regional atmospheric deposition and regular highway operation and maintenance activities (Smith and Lord, 1990; Lopes and Dionne, 1998; Buckler and Granato, 1999). Historically, trace elements have been the prime focus of most state- and federal-highway runoff studies and include, but are not limited to, the elements cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), and zinc (Zn). Trace elements washed off the highway during rain storms, snow storms, or periods of snow-melt may have adverse effects on ecosystems and receiving waters if effective measures are not taken for attenuation of potential contaminants (Buckler and Granato, 1999).

The Federal Highway Administration (FHWA) and State Transportation Agencies (SDOT) have conducted an extensive program of water-quality monitoring and research since the early 1970's. SDOTs and the FHWA are increasingly concerned about potential effects of highway runoff at the watershed scale and responsibilities for management and protection of watersheds (Driscoll and others, 1990; Bank, 1996). The increasing environmental emphasis on non-point sources of contamination such as highway runoff as a component of total maximum daily loads (TMDLs) for watersheds will further increase the need for reliable information with which to make planning and management decisions (Rossman, 1991; Shoemaker and others, 1997). Historically, data from State and Federal studies have been combined to:

- characterize the quality of highway runoff;
- determine contaminant loads for highway-runoff constituents;
- assess the effects of highway stormwater discharges on ecosystems and receiving waters;
- identify the sources and mechanisms that determine the quantity of contaminants in highway runoff;
- develop information for the design and operation of best management practices (BMPs); and
- develop models and monitoring data to meet regulatory needs (Granato and others, 1998).

Information that is documented as valid, current, and scientifically defensible is needed by transportation agencies to support necessary planning and management decisions for these diverse objectives.

Problem

Since the 1970's, requirements for documentation of study-site characteristics, methods and materials used, quality assurance and quality control (QA/QC) information, and other ancillary information for runoff quality studies have been increasing (Granato and others, 1998). During the same period, the accuracy, precision, and detection limits of analytical techniques and instrumentation commonly employed to measure trace elements have improved (van Loon, 1985; Thompson and Walsh, 1989; Garbarino and Struzeski, 1998). In addition, field and laboratory studies have demonstrated that sample collection and processing methods can have a substantial effect on measured concentrations of trace constituents (Kennedy and others, 1974; Patterson and Settle, 1976; Shiller and Boyle, 1987; Horowitz and others, 1992; Benoit, 1994; Taylor and Shiller, 1995; Bloom, 1995; Benoit and others, 1997; Dupuis and others, 1999). These factors have led to substantial disagreements within the scientific and regulatory communities about the validity of existing data, have contributed to the current lack of standardization for trace-element monitoring methods, and have made it difficult to interpret and assess historical and current trace-element data. Therefore, trace-element data are considered suspect, and the responsibility to provide published data-quality information to support the validity of reported results rests with the data-collection agency.

Purpose and Scope

The purposes of this report are to examine the technical issues associated with the monitoring of the trace-element chemistry of highway and urban runoff, to discuss trace element monitoring artifacts, and to discuss matrixes of potential use for monitoring trace elements. These issues are discussed in terms of the information requirements for a regional or national synthesis of trace-element-monitoring data. The primary focus of the report will be the sampling of trace elements in stormwater flow—specifically, runoff on the pavement, in drainage structures, in structural BMPs, and at discharges to receiving waters—and in other matrixes potentially affecting trace elements measured in runoff and receiving waters. Ground-water trace-element-monitoring programs are not discussed because these programs are complicated further by the unique physical and chemical characteristics of the subsurface at each individual sampling well (Puls and Barcelona, 1989; Miller, 1993; Lapham and others, 1997).

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BACKGROUND

The terms trace element, trace metal, toxic metal, or heavy metal are commonly used to describe the largest class of inorganic elements (Elder, 1988; Hem, 1992). Historically, the term "trace" is an operational definition that denotes an inorganic constituent that could not be precisely measured with the techniques available at the time when trace elements were classified (Hem, 1992). For example, trace elements are constituents that are found in the structure of minerals or adsorbed to a solid's surface at concentrations less than 0.1 percent and(or) found in natural waters at concentrations less than about 1.0 mg/L (Hem, 1992; table 1.). These definitions, however, are not absolute; for example, despite the fact that aluminum (Al) is the third most abundant element in the earth's outer crust, it is present at very low concentrations in most fresh waters because of the chemical properties of the element (table 1). The term toxic metal is also an operational definition. Many metals are actually essential for biological activity and become "toxic" only when geologic or anthropogenic sources exceed concentrations typical of the natural environment (Elder, 1988). For example, the U.S. Environmental Protection Agency (USEPA) issued a policy establishing site-specific aquatic life criteria that are equal to natural background (non-anthropogenic) concentrations at sites where these concentrations exceed national water-quality criteria (Davies, 1997).

Trace elements have a variety of both natural sources (such as weathering of rock and soil) and anthropogenic sources (such as ore processing and combustion of fossil fuels) (Forstner and Wittmann, 1981; Salomons and Forstner, 1984; van Loon, 1985; Horowitz, 1991). Although the crustal abundance, average soil abundance, and natural fresh-water concentrations listed in table 1 are only qualitative order-of-magnitude estimates, these values indicate that many of the trace elements measured in highway runoff have natural as well as anthropogenic sources within the local environment. Therefore, the constituents of interest must be measured in a complex matrix of major elements, trace elements, and organic chemicals. The presence of, and the large spatial and temporal variability

of these geological, biological, and anthropogenic sources make the interpretation of trace-element data more difficult than the interpretation of data for anthropogenic organic compounds (Forstner and Wittmann, 1981; Salomons and Forstner, 1984; van Loon, 1985; Horowitz, 1991). For example, natural concentrations of Zn range from less than 5 to about 2,900 parts per million in soils of the conterminous United States (Shacklette and Boerngen, 1984). Particulates in road runoff are derived in part from these natural materials. The relative abundance of major and trace elements in local rocks and soils is expected to affect the geochemistry of highway runoff and receiving waters and, therefore, the potential effect of contaminants on the local aquatic environment (Gupta and others, 1981; Bricker, 1999; Buckler and Granato, 1999). Construction materials, vehicles, and roadway-maintenance activities also are substantial sources of trace-element contamination to surface water and ground water near highways and urban areas (Gupta and others, 1981; Makepeace and others, 1995; Barrett and others, 1993). For example, sanding, salting, traffic activities, vehicular wear, pavement degradation, and littering result in the release of exhaust, oil, grease, rust, hydrocarbons, rubber particles, and other materials that contain trace elements (Gupta and others, 1981; Sansalone and Buchberger, 1997).

The chemistry of natural waters is the product of many sources of constituents including atmospheric deposition, weathering and erosion of soil and rocks, and geochemical processes that determine the solubility and form of constituents in the solid, colloidal and dissolved phases entrained in flowing waters (Hem, 1992, Bricker, 1999). Many factors determine the partitioning of trace elements that are mobilized and transported from the highway, through drainage systems, into structural BMPs, and potentially into receiving waters and aquatic biota. Partitioning of trace elements is defined as the processes by which trace elements are transferred among the different physical, chemical, and biological phases of an aquatic environment. Transfer among these phases is usually multi-directional; that is, trace elements rarely remain in one phase permanently (Elder, 1988). The important characteristics of the mixture that effect the partitioning of trace elements include pH, ionic strength, temperature, hardness (base cations), anions, suspended sediment, oxidation-reduction potential (redox), and in some cases, the presence of other trace elements (Bricker, 1999).

Table 1. Characteristics of selected major and trace elements of potential interest to studies of urban and highway runoff

[**Elemental Groups:** Sources: Chang (1984); Hem (1992). M, Major element; T, Trace element; m, metal; n, nutrient; o, other. **Essential Element:** Sources: Chang (1984); Forstner and Whittmann (1981); van Loon (1985); Chapman (1992). Y, yes; U, unidentified. **Natural Abundance:** Sources: **Crust:** Lide and Frederikse (1997). **Soils:** Shacklette Boergen (1984). **Fresh waters:** Brownlow (1979); Drever (1988); Appelo and Postma (1993). Crustal Abundance is the estimated abundance in the continental earth crust; Soil Abundance is the average from analysis of about 1300 soil samples taken throughout the conterminous United States; Fresh Water Abundance is an order of magnitude estimate of the elemental abundance in unpolluted fresh waters of the United States based on older literature values. ppm, parts per million; mg/kg, milligrams per kilograms; mg/L, milligrams per liter; ~, about; --, not available. **USEPA water quality criteria:** Source: U.S. Environmental Protection Agency (1999). USEPA, U.S. Environmental Protection Agency. P, Priority Toxic Pollutants; F, Fresh water; S, Salt water; H, Human Health for consumption of water. **Potential highway source(s):** source: Bourcier, Hinden, and Cook (1980); Falahi-Ardakani (1984); Kobriger and Geinopolos (1984); Hodge and Stallard (1986); Smith and Lord (1990); Hildemann, Markowski, and Cass (1991); Armstrong (1994); Hee (1994); Granato (1996); Helmers (1996); Farago, Thornton, Kazantzis, and Simpson (1997); Pearce, Brothwood, Fuge, and Perkins (1997)

Element name (abbreviation)	Elemental groups	Essential element	Natural abundance (ppm)			USEPA water-quality criteria	Potential highway source(s)
			Crust (mg/kg)	Soils (mg/kg)	Fresh waters		
Aluminum (Al)	Mm	Y	8.23x10 ⁴	7.2x10 ⁴	~10 ⁻²	F	Auto exhaust, brakes
Antimony (Sb)	To	Y	2x10 ⁻¹	6.6x10 ⁻¹	~10 ⁻³	PH	Auto exhaust, brakes
Arsenic (As)	To	Y	1.8x10 ⁰	7.2x10 ⁰	~10 ⁻³	PFSH	
Barium (Ba)	Tm	Y	4.25x10 ²	5.8x10 ²	~10 ⁻³	H	Auto exhaust, brakes, fuel
Beryllium (Be)	Tm	Y	2.8x10 ⁰	9.2x10 ⁻¹	--	PH	
Bismuth (Bi)	Tm	Y	8.5x10 ⁻³	--	--	FSH	
Boron (B)	Mo	Y	1.0x10 ¹	3.3x10 ¹	~10 ⁻¹		Auto exhaust, deicers
Bromide (Br)	Mo	Y	2.4x10 ⁰	8.5x10 ⁻¹	~10 ⁻²		Auto exhaust, deicers, fuel
Cadmium (Cd)	Tm	Y	1.5x10 ⁻¹	--	--	PFSH	Auto wear, insecticide application, lubricants, tire wear
Calcium (Ca)	Mm	Y	4.15x10 ⁴	2.4x10 ⁴	~10 ¹		Auto exhaust, brakes, deicers
Carbon (C)	Mo	Y	2.00x10 ²	2.5x10 ⁴	~10 ²		Auto exhaust, fuel
Cerium (Ce)	Tm	U	6.65x10 ¹	7.5x10 ¹	~10 ⁻⁵		Catalytic converters
Chloride (Cl)	Mo	Y	1.45x10 ²	--	~10 ¹	F	Brakes, deicers
Chromium (Cr)	Tm	Y	1.02x10 ²	5.4x10 ¹	~10 ⁻³	PFSH	Auto exhaust, auto wear, brakes
Cobalt (Co)	Tm	Y	2.5x10 ¹	9.1x10 ⁰	~10 ⁻⁴		Auto exhaust
Copper (Cu)	Tm	Y	6.0x10 ¹	2.5x10 ¹	~10 ⁻³	PFSH	Auto exhaust, auto wear, brakes, deicers
Fluoride (F)	Mo	Y	5.85x10 ²	4.3x10 ²	~10 ⁻¹		Deicers
Gold (Au)	Tm	Y	4x10 ⁻³	--	~10 ⁻⁶		
Iodine (I)	To	Y	4.5x10 ⁻¹	1.2x10 ⁰	~10 ⁻³		
Iron (Fe)	Mm	Y	5.63x10 ⁴	2.6x10 ⁴	~10 ⁻²	FH	Auto exhaust, auto rust and wear, brakes, deicers
Lead (Pb)	Tm	Y	1.4x10 ¹	1.9x10 ¹	~10 ⁻³	PFSH	Auto exhaust, bearing wear, deicers, lubricants, tire wear
Lithium (Li)	Tm	Y	2.0x10 ¹	2.4x10 ¹	~10 ⁻²		Auto exhaust
Magnesium (Mg)	Mm	Y	2.33x10 ⁴	9.0x10 ³	~10 ⁰		Auto exhaust, brakes, deicers
Manganese (Mn)	Mm	Y	9.5x10 ²	5.5x10 ²	~10 ⁻²	F	Engine wear, fuel additive
Mercury (Hg)	Tm	Y	8.5x10 ⁻²	9.0x10 ⁻²	~10 ⁻⁵	PFSH	

Table 1. Characteristics of selected major and trace elements of potential interest to studies of urban and highway runoff—*Continued*

Element name (abbreviation)	Elemental groups	Essential element	Natural abundance (ppm)			USEPA water-quality criteria	Potential highway source(s)
			Crust (mg/kg)	Soils (mg/kg)	Fresh waters		
Molybdenum (Mo)	Tm	Y	1.2x10 ⁰	9.7x10 ⁻¹	~10 ⁻⁴		Brakes
Nitrogen	Mn	Y	1.9x10 ¹	--	~10 ⁰	FH	Auto exhaust, deicers, roadside fertilizer
Nickel (Ni)	Tm	Y	8.4x10 ¹	1.9x10 ¹	~10 ⁻³	PFSH	Auto exhaust, wear, asphalt, deicers, fuel, lubricants
Palladium (Pd)	Tm	Y	1.5x10 ⁻²	--	--		Catalytic converters
Phosphorus (P)	Mn	Y	1.05x10 ³	4.3x10 ²	~10 ⁻¹		Auto exhaust, fuel, lubricants
Platinum (Pt)	Tm	Y	5x10 ⁻³	--	--		Auto exhaust, catalytic converters
Potassium (K)	Mm	Y	2.09x10 ⁴	1.5x10 ⁴	~10 ⁰		Auto exhaust, deicers
Rhodium (Rh)	Tm	U	1x10 ⁻³	--	--		Catalytic converters
Selenium (Se)	To	Y	5x10 ⁻²	3.9x10 ⁻¹	~10 ⁻⁴	PFSH	Auto exhaust
Silicon (Si)	Mo	Y	2.82x10 ⁵	3.1x10 ⁵	~10 ¹		Auto exhaust, brakes, deicers
Silver (Ag)	Tm	Y	7.5x10 ⁻²	--	~10 ⁻⁴	PFSH	
Sodium (Na)	Mm	Y	2.36x10 ⁴	1.2x10 ⁴	~10 ¹		Auto exhaust, deicers
Strontium (Sr)	Tm	Y	3.70x10 ²	2.4x10 ²	~10 ⁻²		Auto exhaust, deicers
Sulfur (S)	Mo	Y	3.5x10 ²	1.6x10 ³	~10 ⁻⁴	FS	Auto exhaust, deicers, fuel, roadway beds
Tellurium (Te)	Tm	Y	1x10 ⁻³	--	--		
Titanium (Ti)	Tm	Y	5.65x10 ³	2.9x10 ³	~10 ⁻²		Studded tires
Tin (Sn)	Tm	Y	2.3x10 ⁰	1.3x10 ⁰	--		Brakes
Tungsten (W)	Tm	U	1.25x10 ⁰	--	~10 ⁻⁵		Studded tires
Vanadium (V)	Tm	Y	1.20x10 ²	8.0x10 ¹	~10 ⁻³		Auto exhaust, deicers
Zinc (Zn)	Tm	Y	7.0x10 ¹	6.0x10 ¹	~10 ⁻³	PFSH	Auto exhaust, brakes, tire wear, lubricants

For simplicity, the aquatic environment can be viewed as a four-phase system (fig. 1) consisting of water, suspended material, bottom material, and biota (Chapman and others, 1982; Elder, 1988; Chapman, 1992). The phase to which a particular trace element will partition depends upon the chemical and physical environmental conditions and the chemistry of the trace element of interest. For example, trace elements tend to partition toward the water phase (dissolved) when conditions of low pH, low Eh (a measure of the redox condition), low particulate loads, and high concentrations of organic matter are prevalent (Elder, 1988). In contrast, high pH and Eh, increased particulate loads, and high hydraulic energies are conditions that favor partitioning of trace elements to the particulate phase

(suspended). Low hydraulic energies and high concentrations of organic matter (>0.5 percent), moderate to high sedimentation rates, and the presence of sulfide favor the partitioning of trace elements to bottom sediment (Morse, 1995). Many complex chemical and physical conditions control partitioning of trace elements to organic matter, plants, and animals (Elder, 1988).

The mobilization, transport, and fate of trace elements from highway surfaces are affected by the abundance and chemical and physical properties of solids carried by runoff. Concentrations of suspended solids and grain size distributions in runoff vary at individual sites and between different sites (Gupta and others, 1981; Athayde and others, 1983; Driscoll and others,

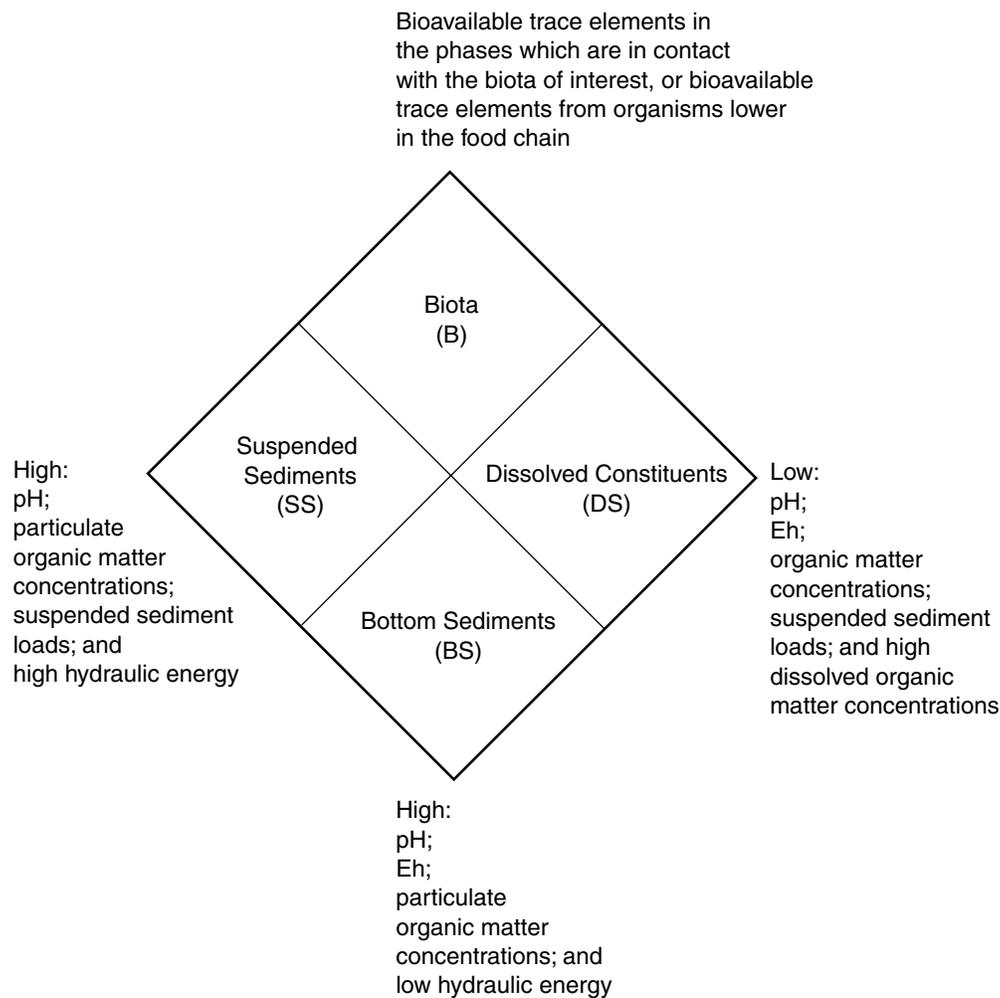


Figure 1. The four phases of aquatic ecosystems that may receive trace elements from nonpoint runoff and the environmental conditions that favor partitioning into each phase (modified from Elder, 1988).

1990; Smith and Lord, 1990). Trace-element transport can be enhanced by sorption onto Fe- and Mn-hydrous oxide coatings on silt and clay particles, and by sorption onto colloidal material including humic substances, viruses, oxides, bacteria, algae, and fecal pellets (Thibodeaux, 1996). These colloids range in size from less than 0.001 micrometer (μm) to about 1000 μm (Hem, 1992). Surface complexation of trace elements onto particulate matter (silts and clays) and colloidal surfaces has little effect on the colloid surface chemistry (because trace elements are present in low concentrations) but significantly enhances trace-element transport (Thibodeaux, 1996). Sorbed trace elements tend to accumulate in bottom sediment. Accumulation in bottom sediment, however, is not necessarily equivalent to permanent removal or to complete export from an aqueous ecosystem. Trace elements accumulated in bottom sediment may repartition into one of the other phases by way of physical, chemical, or biological processes.

The effects of trace-element chemistry on trace-element partitioning—in terms of the ratio of dissolved to total trace-element concentrations in natural fresh water systems—was studied by Martin and Meybeck (1979) and Meybeck and Helmer (1989). They found that the partitioning of many trace elements between the dissolved (water) and particulate matter phases (suspended and bottom) was highly dependent on the solubility of the trace element of interest (table 2). For

example, about 50 percent of antimony (Sb) was associated with particulate matter, indicating that Sb is relatively soluble compared to other trace elements. On the other hand, mercury (Hg) appears to be the least soluble because more than 99.9 percent of Hg is associated with particulate matter (table 2). In receiving waters that approach geochemical equilibrium, many trace elements are expected to be associated with particulate matter (Drever, 1988). Although generally true for large rivers with sufficient contact time and favorable geochemical conditions, this generalization must be used with caution when applied to the study of the chemistry of highway- and urban-runoff.

Paved surfaces are fundamentally different physically, chemically, and hydraulically from the receiving waters that have been the focus of most trace-element-monitoring studies. Existing scientific conceptions of the behavior of trace elements in the environment are based largely upon research on natural systems approaching geochemical equilibrium, not on systems typical of pavement runoff. For example, in contrast to the behavior of trace elements in natural systems (table 2), more than 90 percent of some trace elements have been found in the dissolved phase (water) of freshly weathered pavement runoff from highways and urban areas (Yousef and others 1985a; 1985b; Morrison and others, 1990; Revitt and others, 1990; Legret and others, 1995; Sansalone and Buchberger, 1997). Physical mobilization, pulverization, and

Table 2. Ratio between natural dissolved and total elemental concentrations in rivers

[Modified from Meybeck and Helmer, 1989. The higher the percentage, the greater the partitioning into the dissolved phase. Arranged vertically in order of decreasing solubility. >, greater than]

>99 percent	>90–99 percent	>50–90 percent	>10–50 percent	>5–10 percent	>1–5 percent	>0.5–1 percent	>0.1–0.5 percent	>0.05–0.1 percent
Chloride	Bromide	Sodium	Antimony	Copper	Nickel	Gallium	Titanium	Scandium
	Sulfur	Strontium	Magnesium	Phosphorus	Silicon	Lead	Gadolinium	Mercury
		Carbon	Nitrogen		Rubidium	Lutetium	Lanthanium	
		Calcium	Boron		Uranium		Holmium	
		Lithium	Molybdenum		Cobalt		Ytterbium	
			Arsenic		Cadmium		Terbium	
			Fluoride		Manganese		Erbium	
			Barium		Thorium		Samarium	
			Potassium		Vanadium		Chromium	
					Cesium		Iron	
							Europium	
							Cerium	
							Zinc	
							Aluminum	

transport of roadway dirt and dust, lubricants, hydraulic fluids, and other materials on paved surfaces and vehicles is enhanced by the erosive power of precipitation and the kinetic energy of moving vehicles (Irish and others, 1996). Hydraulically, the impervious nature of the pavement and drainage-system designs (which favor rapid turbulent flow to quickly remove water and to keep sediment in suspension) are also responsible for the relatively high mobilization and transport of dissolved and solid phases in highway runoff in comparison to flows in natural systems. Vehicles are composed of trace-element-laden components exposed to high temperatures, pressures, and kinetic energy during combustion of fuel, lubrication of moving parts, and braking. Also, tires and pavement contribute trace elements and organic ligands through road wear. These materials, temperatures, and pressures are generally not found in natural aquatic environments. For example, the combustion of fuel produces carbon dioxide and water in an engine at high temperatures and pressures as well as unburned organic residues and trace elements (from gasoline, lubricants and the engine itself). These trace elements are entrained with the water vapor, carbon dioxide and residues from the engine and the exhaust system. As the water of combustion condenses, it forms a hot acidic solution that contains hundreds of hydrocarbon compounds (Hoekman, 1992) as well as anions, including bromide (Br), chloride (Cl), sulfate (SO₄), and nitrate (NO₃) (Hildemann and others, 1991; Laxen and Harrison, 1977). These organic and inorganic compounds in exhaust particulates and aerosols washed out from the atmosphere, vehicles, the road surface, dust, and dirt can complex trace elements in pavement runoff.

Complexation of trace elements increases their mobility and transport into the natural environment. For example, Breault and others (1996) demonstrated that Cu was 84-99 percent dissolved (as organometallic complexes) in whole-water samples from an urban river spiked with Cu to a total concentration of about 12.6 µg/L, which is a concentration comparable to that in pavement runoff (Driscoll and others, 1990; Makepeace and others, 1995). Conversely, existing scientific conceptions of the behavior of trace elements in the natural environment would predict that less than 10 percent of the Cu would be measured in the dissolved phase (table 2). Furthermore, the concentration and type of complexing agent and geochemical conditions will control the phase of the aquatic ecosystem to which the trace element will partition. For example,

adsorption of trace elements to sediment may be either increased or reduced, depending on whether complexing agents are available in solution or adsorbed to the sediment surfaces (Elder, 1988).

Another important factor that distinguishes the chemistry of highway runoff from that of natural fresh waters is the magnitude of variation in the ionic strength of pavement runoff caused by seasonal use of deicing chemicals. The range of specific conductance (a measure of ionic strength) in fresh water is from about 1 to about 1,500 microsiemens per centimeter (Granato and Smith, 1999). In comparison, the specific conductance of highway runoff varies from about 3 to more than 60,000 µS/cm. These values represent a Cl concentration range from about 1 to 20,000 mg/L (these measurements approximate the range between distilled water and a dilute brine solution; Granato and Smith, 1999). Similarly, the range of Cl concentrations measured in urban-runoff studies was reported to be 0.30–25,000 mg/L (Makepeace and others, 1995). At high conductance, the associated salinity can shift pH, saturate available ion-exchange sites on sediment with major ions, and form trace-element Cl complexes that increase trace-element mobilization measured in the dissolved phase (Granato and others, 1995). Conversely, high salinities also may cause flocculation of fine particulates and organometallic complexes (Burton, 1976), which may in turn cause these trace elements to be deposited with the flocculated particulates in highway sediment near discharge points. Conductance, and therefore salinity, varies by orders of magnitude within storms, between storms, and from season to season; this variation further complicates measurement and interpretation of trace-element highway-runoff data.

TRACE-ELEMENT MONITORING

Currently, any trace-element data that is not supported by quality-assurance and quality-control (QA/QC) documentation that demonstrates the validity of those data is viewed as suspect. Data may be suspect because artifacts of the monitoring process can substantially affect the measured concentrations of trace elements and(or) the representativeness of samples collected. In several studies, the problem of sample contamination is identified as an issue that may overshadow all other potential problems that result from the use of different sampling, processing, preservation, and

analytical procedures, as well as problems that are associated with spatial and temporal variability of trace elements (Brewer and Spencer, 1970; Bruland, 1983; Shiller and Boyle, 1987; Horowitz and others, 1994; Taylor and Shiller, 1995; Benoit and others, 1997). Dupuis and others (1999) raised the issue for evaluation of available highway-bridge-runoff data, but determined that no highway-runoff studies to date have addressed the issue of sampling artifacts (errors in the actual concentration of trace elements present). Sample collection, handling, and processing materials can contribute and/or sorb trace elements within the time scales typical for collection, processing and analysis of runoff samples. The relative effect of potential contamination and/or attenuation of trace elements in runoff samples is a function of the concentration of major and trace elements, organic chemicals, and sediment in solution. Sampling artifacts are especially important when measured concentrations are at or near analytical detection limits. Historically, measured concentrations of trace elements in highway and urban runoff have ranged from less than detection limits to several orders of magnitude greater than detection limits within and between studies (Athayde and others, 1983; Driscoll and others, 1990; Barrett and others, 1993; Makepeace and others, 1995). Without sufficient supporting documentation, however, it is impossible to determine how sampling artifacts affect data in these ranges. For example, contamination introduced during sampling can mask temporal differences at the same location as well as spatial differences among different sampling locations. Trace elements such as uranium (U), and thallium (Tl) that are not commonly used in sampling materials and/or are not generally prevalent in the environment may not be affected, or may be minimally affected by contamination; however, common highway-runoff constituents such as Al, Cr, Fe, Ni, Pb, and Zn may be substantially affected (Shiller and Boyle, 1987; Windom and others, 1991; Benoit, 1994; Benoit and others 1997). Therefore, great care is required to

collect and process samples in a manner that will minimize potential contamination and variability in the sampling process.

Clean Monitoring Methods

Historically, anthropogenic sources in developed areas were thought to produce trace-element concentrations high enough to obscure the effects of contamination from most sample collection and processing procedures. Benoit and others (1997), however, compared sampling artifacts of silver (Ag), Cd, Cu, and Pb from a rural stream and an urban stream in an industrial area in Connecticut. That study showed that even for the urban-stream samples, skipping even one step of the clean collection and processing protocol introduced substantial contamination (fig. 2). Lack of process control increased contamination by up to three times for each of several steps. Some steps reduced potential contamination by only about 20 percent, whereas others led to reductions of two to three orders of magnitude. In particular, when sample bottles were not cleaned properly, measured Cd concentrations were 15 times greater than when ultraclean bottles were used (Benoit and others, 1997).

The so-called "clean/ultra-clean" sampling, processing, preservation, and analytical techniques were developed during the 1970s, 1980s, and 1990s to address concerns about the validity of existing data and to produce reliable trace-element data (Patterson and Settle, 1976; Trefrey and others, 1986; Shiller and Boyle, 1987; Flegal and Coale, 1989; Windom and others, 1991; Nriagu and others, 1993; Benoit, 1994; Horowitz and others, 1994; Taylor and Shiller, 1995; Benoit and others, 1997). These techniques have led to marked reductions in sample contamination and to an associated decrease in the reported concentrations of ambient trace elements in marine and freshwater systems. In fact, during the past

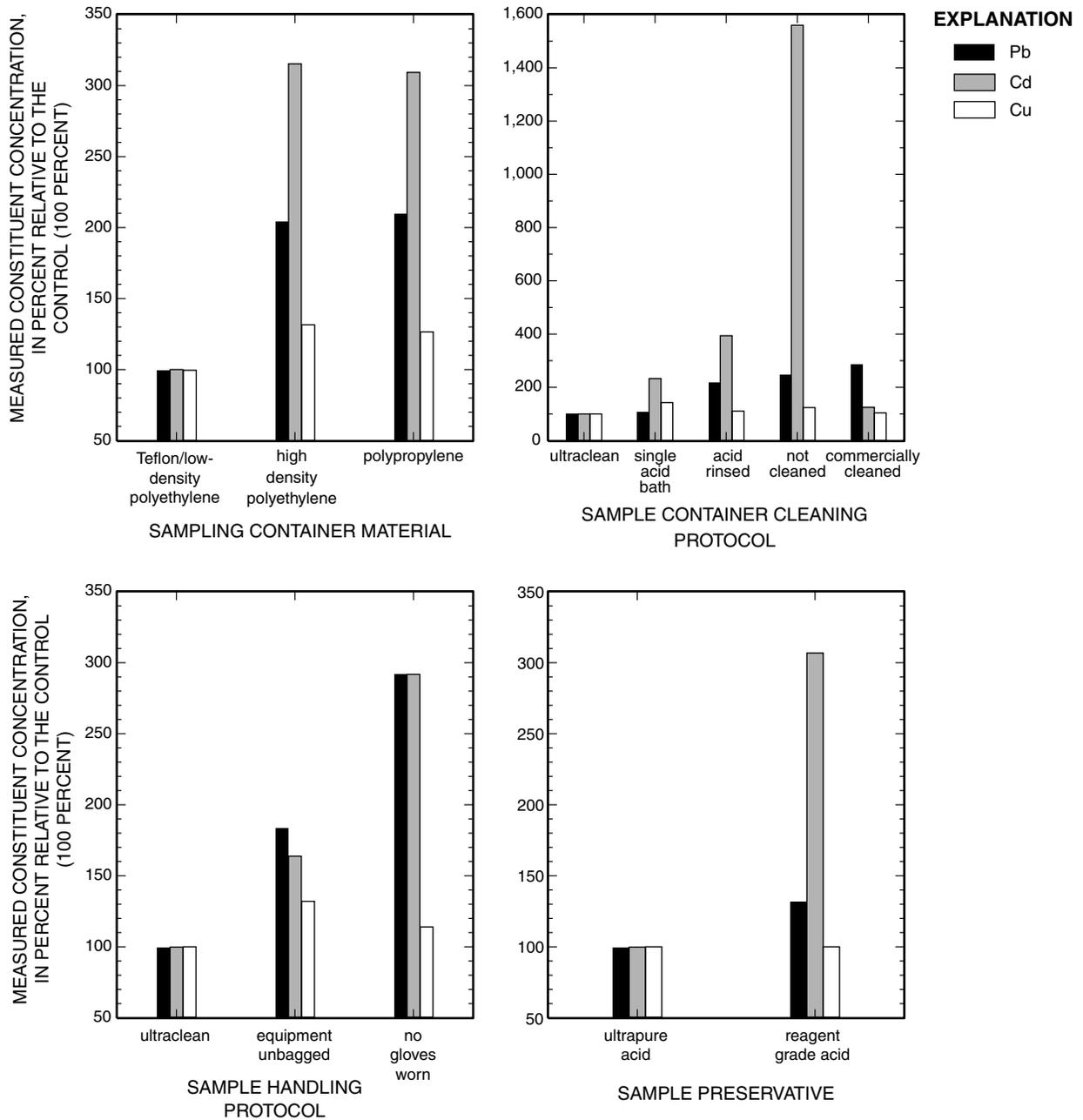


Figure 2. Potential contamination introduced in different components of the sample-handling process (data from Benoit and others, 1997).

10 years, reported concentrations in samples collected by clean methods have declined from tens of parts-per-billion ($\mu\text{g/L}$) to parts-per-billion to the parts-per-trillion (ng/L) range for many trace elements in natural systems (Shiller and Boyle, 1987; Windom and others, 1991; Benoit, 1994; Nriagu and others, 1996).

These rigorous sample collection and processing methods, also known as "clean hands-dirty hands" techniques, are used to minimize the contamination introduced during the collection of samples for analysis of trace elements (Wilde and Radtke, 1999). The basic strategy is to handle all containers while wearing non-contaminating gloves and to change gloves whenever they have touched something that is not "clean." To perform the clean hands-dirty hands procedure correctly, a field crew should consist of at least two persons, each with rigorously defined roles. "Clean-hands" is the person who collects and processes the water sample using sampling and processing equipment that has been cleaned in a controlled environment and transported to the field inside two or more airtight bags. "Dirty-hands" is the person who handles all sampling equipment that could be in contact with any potential source of contaminants. These methods were developed and tested by a number of researchers (Fitzgerald and Watras, 1989; Bloom, 1995; Benoit and others, 1997) and have been accepted as protocols for regional and national water-quality-monitoring programs (Horowitz and others, 1994; Wilde and Radtke, 1999). For example, Benoit and others (1997) demonstrated that the use of gloves and prebagged equipment was critical for the success of these protocols (fig 2). Strict adherence to the clean hands-dirty hands protocols, however, is sometimes considered excessive for some trace-element-monitoring programs; departures from these protocols are accepted if sufficient quality-control data is collected to establish that the modified (relaxed) protocols meet data-quality objectives. Details of these protocols and related QA/QC measures are described by Wilde and Radtke (1999).

Samples collected for the analysis of trace elements must be preserved in order to mitigate the effect of chemical reactions in sample storage containers as well as sorptive losses to the sample container (Batley, 1989; Radtke, 1999). Samples are typically preserved by chilling and/or adding chemicals. For example, sample pH is adjusted to about 2 standard units by the addition of nitric acid, which is expected to fix the sample chemistry during storage (Radtke, 1999). Chemicals used as preservatives for trace-element

samples must be analyzed and certified as being free of the constituents of interest to ensure a minimum of contamination (Benoit and others, 1997; fig 2). Ideally, the procedures for preservation and storage should be started the moment the sample has been collected. Once treated, samples can be stored for extended time periods (sometimes weeks to months), but in some cases, data quality was improved by analysis sooner rather than later during the holding period (Batley, 1989; Kramer, 1994).

Clean Monitoring Materials

Monitoring of trace elements in environmental studies also is complicated by several factors related to the materials used for collection, processing and storage of trace-element samples (Radtke and Wilde, 1998). Substantial gains or losses of trace elements can occur by means of adsorption or desorption from the surfaces of collection, processing and storage containers. For example, the chemical composition, surface roughness, cleanliness, permeability, wall thickness, and closure integrity of the container can affect the quality of stored samples (Moody and Lindstrom, 1977; Sansalone and Buchberger, 1996). Other factors that affect interactions of trace elements with sample collection, processing, and storage materials include the characteristics of the constituent of interest, characteristics of the monitoring matrix, and external factors such as temperature, contact time, access of light, and the degree of agitation (Masse and others, 1981, Sansalone and Buchberger, 1997).

Numerous articles and reports have been published about the use of plastic as the ideal material for sampling equipment and sample containers. The suitability of any individual plastic, however, depends on the type of material and on the cleaning procedure (Moody and Lindstrom, 1977). Different types of plastics have been evaluated for desorption (Moody and Lindstrom, 1977) and adsorption of trace elements onto container surfaces (Good and Schroder, 1984). Good and Schroder (1984) found that polypropylene, polyethylene and polyester/polyolefin would not be suitable as collection or storage vessels for water samples to be analyzed for Cu, Fe, molybdenum (Mo), Pb, and vanadium (V), all of which showed adsorption losses. Consequently, these plastics should not be used in the collection, processing, and analysis of samples for the determination of these trace elements at low

levels. Materials such as rubber and Viton also should be avoided, as they may contain leachable trace elements (Bloom, 1995). The plastic Teflon is commonly considered the most suitable material for trace-element sampling (Moody and Lindstrom, 1977; Benoit and others 1997) in terms of its non-reactive chemical properties (fig. 2)

Regardless of the material selected for use in trace-element sampling, procedures for cleaning are necessary to reduce trace-element contamination to concentrations below analytical detection limits. Cleaning instructions suitable for materials used in the collection, processing and storage of trace-element-monitoring samples have been published (Moody and Lindstrom, 1977; Bloom, 1995; Benoit and others 1997; Horowitz and Sandstrom, 1998). Briefly, protocols include a wash and rinse to remove gross contaminants and a subsequent cleaning with a suitable acid and(or) deionized water to remove the remaining trace elements (fig. 3). The protocols used for cleaning will determine the potential for contamination from equipment and materials (Benoit and others, 1997; fig. 2). Data-quality objectives dictate the cleaning protocols and QA/QC that are necessary (Granato and others, 1998; Jones, 1999).

Spatial and Temporal Variability

Spatial variability between highway monitoring sites including the environmental setting, local land use, traffic characteristics, highway and drainage design characteristics, and many other features are also recognized as potential explanatory factors for variations in measured concentrations (Gupta and others, 1981; Driscoll and others, 1990; Young and others, 1996). For example, runoff from curbed highways tends to have higher constituent concentrations and loads than that from flush-shouldered highways, because the curbed highway-drainage design structures tend to trap sediment on the paved surface (Gupta and others, 1981; Driscoll and others, 1990; Young and others, 1996). Spatial variability among potential sites along a single highway also is a concern. For example, one would expect the acceleration, deceleration, and braking of vehicles to cause increased constituent loadings at a site near an interchange than at a comparable

site within a long straight section where vehicles are traveling at constant speed (Gupta and others, 1981; Driscoll and others, 1990; Legret and Pagotto, 1999).

The distribution of sediment, as well as major and trace elements, can be highly variable within a cross-section of the water column in natural waters. Therefore, methods for depth and width integration of samples are commonly recommended (Edwards and Glysson, 1999; Hem, 1992; Shelton, 1994; Averett and Schroder, 1994; Webb and others, 1999). Automatic point samplers generally do not provide depth or width integration (Horowitz, Rinella, and others, 1989). The small cross-sectional areas of drainage pipes, rapid mixing, and turbulent flows characteristic of many runoff drainage systems, however, may preclude the need for depth and width integration. Flow and concentrations of water-quality constituents change rapidly in storm flows. Therefore, depth and width integration methods may not be suitable for runoff studies because the concentration is changing while the sample is being collected within the cross section. It is, however, important to recognize the potential for this spatial variability within the water column, to choose sites where the potential for stratification is minimized, where possible, to promote vertical and horizontal mixing upstream of the sampling point, and (if possible) to test the hypothesis that the point sample is representative of the cross section.

Temporal variability also is an important consideration for trace-element monitoring studies. Long-term trends (such as the effects of the ban on leaded gasoline) can affect the comparability of data from different studies (Young and others, 1996; U.S. Environmental Protection Agency, 1999). Seasonality also is a major issue for runoff studies. For example, Driscoll and others (1990) analyzed data from more than 990 storm events at 31 sites in 11 states and concluded that winter "snow" storms were significantly different from nonwinter storms. Long-term nationwide experience with both hydrologic and water-quality studies indicates that, if possible, studies should span several years to quantify seasonal and interannual variations in weather (Averett and Schroder, 1994).

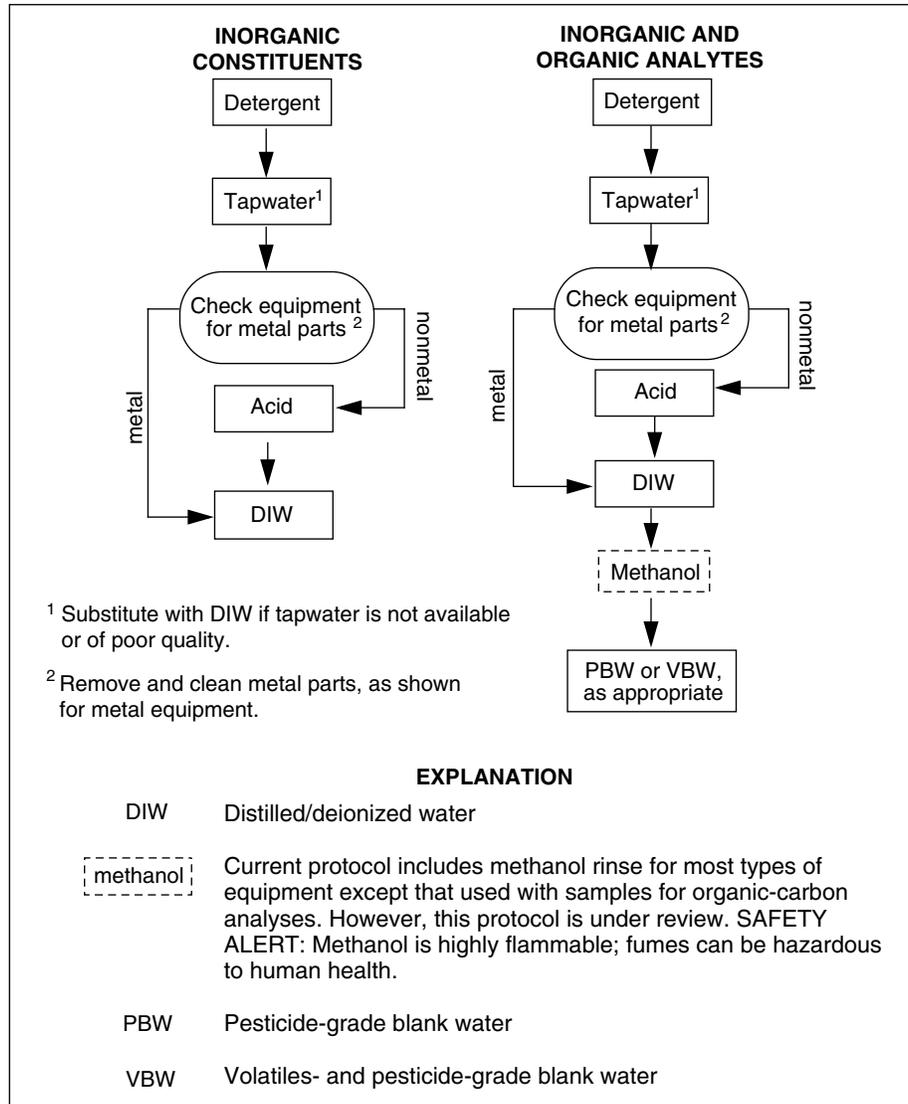


Figure 3. General sequence for cleaning equipment before sampling for inorganic and organic analytes (modified from Horowitz and Sandstrom, 1998).

Stormwater Monitoring Logistics

Trace-element data collection and interpretation efforts are further compounded by the logistics of sampling stormwater in the highway environment. Storms can occur any day of the week at all hours, and the arrival and magnitude of each storm is a source of great uncertainty. For example, Thiem and others (1998) employed a meteorologist to predict the occurrence of design storms for a highway study in Rhode Island but still mobilized the sampling crew when storms did not materialize, and missed storms that were not predicted

accurately. To sample a complete event on very small, impervious catchments, it often is necessary to initiate sample collection within minutes of the onset of precipitation and to collect a relatively large number of subsamples. This is necessary because concentrations of dissolved and suspended solids change rapidly in response to changes in rainfall intensity and other factors. To generate meaningful event mean concentrations (EMCs), it is necessary to record the runoff flow (Church and others, 1999) and either to calculate an EMC from the analysis of a number of discrete samples (Driscoll and others 1990), or to composite one EMC sample using an accepted compositing protocol (U.S.

Environmental Protection Agency, 1992a). Therefore, storm sampling should be conducted within the framework of an automated monitoring and automatic sampling program to standardize the process and to provide a record of the variations in flow and water-quality characteristics (Driscoll and others 1990; U.S. Environmental Protection Agency, 1992a; Spangberg and Niemczynowicz, 1992; Church and others, 1999; Granato and Smith, 1999).

Quality Assurance and Quality Control

A QA/QC program that includes steps to minimize contamination as well as measures of gains and losses of each constituent of interest throughout the sampling and analysis process is necessary to document the accuracy, precision, and comparability of data collected. Quality assurance is designed to prevent systematic error (Jones, 1999). If the monitoring project is extensive (multiple sites or long study periods), the QA program should be documented and published (for example, Mueller and others, 1997). The QA program should be documented in the same report as the study results for less extensive monitoring projects. The QA program also should include a schedule of intraoffice quality reviews and documentation for all methods, field personnel, and analytical laboratories used in the data collection process (Federal Highway Administration, 1986). Documentation allows others to interpret the data and to verify that appropriate practices were followed in the design and execution of the study.

Quality control (QC) includes the steps used to check that QA is effective and to evaluate bias and variability. QC techniques include preparation and analysis of equipment blank samples to ensure that equipment is clean, replicate samples to assess sample variance and analytical precision, and samples spiked with analytes to evaluate analyte degradation and recovery (Jones, 1999). The field and ambient-atmosphere blank samples described by Jones (1999) also are important for highway and urban runoff studies because samples are collected in environments exposed to airborne particulates suspended by local winds and vehicular turbulence along the roadway (Smith, K.P., U.S. Geological Survey, written commun., 2000).

The fundamental trace-element-monitoring concepts covered herein are generally considered applicable for most trace-element monitoring matrixes. It is necessary to use methods and materials that will minimize sampling artifacts, to characterize real sources of variability, and to document these efforts within the context of a defined QA/QC program. These and many other factors, however, need to be addressed and documented in detailed sampling plans that define the data-quality objectives that are developed for each matrix of interest (Granato and others, 1998; Jones, 1999).

SAMPLING MATRIX

The objective(s) of an individual study often determine which matrixes and therefore, which materials and methods are used for trace-element monitoring at a given site. If data are to be used in a regional or national synthesis, the matrixes, materials, and methods used also must be considered in this broader context. For example, a need for information about the speciation of trace elements among the dissolved, suspended-sediment, bottom-sediment, and tissue matrixes will dictate that each matrix be sampled, processed, and analyzed using appropriate materials and methods. Historically, study objectives have affected the suitability of a given data set for regional or national synthesis (Driscoll and others, 1990; Granato and others, 1998).

For simplicity, the aquatic environment may be divided into four phases including biota, dissolved constituents, suspended sediment, and bottom sediment (fig. 1). In practice, however, the boundaries between these phases are not easy to define and the wide spectrum of geochemical conditions encountered often precludes the definitive physical and chemical characterization of aqueous systems. For example, trace elements in bacteria or algae in highway runoff may be measured as a component of biota, dissolved, suspended sediment, or bottom sediment, depending upon the methods used and the site selected. Operational definitions to describe these four phases are therefore used to establish sampling matrixes without reference to the character of individual aquatic environments being studied. The techniques that are established for collecting, processing, and analyzing each matrix should not be considered absolute, but rather as common methods and guidelines chosen by investigators to provide relatively comparable and scientifically

defensible data. Therefore, an understanding of operational definitions and careful selection of the appropriate sample matrix is necessary to meet the objectives of the monitoring program.

Whole Water

Whole-water samples are unfiltered samples from the water column, which include suspended materials and the water matrix. Three recognized methods—"total", "total recoverable," and "acid soluble"—are used for analysis of dissolved and sediment-associated trace elements in whole water samples. These methods differ in the amount of sediment-associated trace elements that may be solubilized prior to analysis (U.S. Environmental Protection Agency, 1992c). The total technique is designed to dissolve 95 percent of the constituent of interest in the whole water sample, so that the analysis measures most of the target constituents in the sample, including sediment-grain matrix constituents (Fishman and Friedman, 1989). The total-recoverable technique is designed to dissolve constituents associated with sediment surfaces, but less than 95 percent of the constituents present (Fishman and Friedman, 1989). The acid soluble method is a less rigorous digestion technique than the total-recoverable method, but research shows that it commonly yields similar results (U.S. Environmental Protection Agency, 1992c). In practice digestion techniques are defined by standard methods that prescribe reagents, concentrations of reagents, temperature, and contact time rather than an exact percent recovery (for example American Public Health Association-American Water Works Association-Water Pollution Control Federation, 1989; Hoffman and others, 1996). Furthermore, these standard methods may solubilize different percentages of the constituent of interest in samples with differing water chemistry, sediment chemistry, and sediment concentrations.

Benefits

If the information gained from analysis of constituent concentrations in whole-water matrix samples will meet the data-quality objectives of a given study, use of this matrix precludes many of the problems that are of concern when sampling trace element concentrations in individual matrixes (dissolved (filtered) water and(or) suspended sediment). In a national synthesis of

highway or urban runoff, it is important to be able to predict the total concentration and load of trace elements generated by a given highway or land use on the basis of local climate, site characteristics, and other explanatory variables such as average daily traffic (Granato and others, 1998). For highway- and urban-runoff water-quality studies, therefore, the whole-water matrix may be the most robust sampling matrix because speciation among the dissolved (water) and solid (sediment) matrixes is not a factor. This is an important consideration in stormwater studies, because the chemistry and kinetics that control speciation of trace elements depend on

- concentration and geochemistry of the solids suspended in solution;
- geochemistry of the solution (pH, ionic strength, redox, and major ions);
- biological activity in the sample;
- chemistry of, concentration of, and competition between trace elements; and
- sample temperature;

all of which are variable within and between storms and are a function of the time between collection and processing of each sample. Avoiding these contact-time issues by use of the whole-water sampling matrix allows for fully automatic sample collection so that sampling crews can be dispatched to gather the samples that have been collected (usually during normal business hours when visibility and safety are maximized).

Whole-water sampling also has logistical benefits in comparison to sampling other matrixes. Once whole-water samples are collected, composited and(or) split (if necessary), and preserved, there are no additional field-processing steps to introduce bias. Whole-water samples are relatively uncomplicated and inexpensive to collect, process, and analyze, because there is no physical separation (or associated labor, equipment, and material costs) of water from sediment. Use of whole-water samples requires less contact between the sample and processing equipment than does phase separation (the dissolved- or suspended-sediment matrix), which minimizes the potential pathways for contamination or attenuation of measured constituents. Analysis of whole-water samples also is cost effective because one analysis defines the total contribution of all matrixes in the sample. Solids control using structural BMPs is currently the most practicable method to address non-point runoff contamination (Young and

others, 1996). Therefore, at present, whole water samples also are necessary to provide information for the design of structural BMPs, because concentrations of sediment and associated trace elements in samples collected at the inflow and outflow are directly comparable (based upon sedimentation and the contact time issues to be discussed).

By law (40 CFR 122.45), analysis of whole-water samples is required for monitoring effluents and for monitoring within the Non-Point Discharge Elimination System (NPDES) permit process because it is recognized that the partitioning of trace elements in effluents may be different than in receiving waters (U.S. Environmental Protection Agency, 1992c). Whole-water samples, therefore, are most comparable to the bulk of historical highway- and urban-runoff data and are specified for use in nonpoint source monitoring studies (Gupta and others 1981; Athayde and others, 1983; Driscoll and others, 1990; U.S. Environmental Protection Agency, 1992a). Driscoll and others (1990) compiled precipitation, flow, and water-quality data from more than 990 individual storm events from 31 highway sites in 11 states during the 1970s and early 1980s. They determined that median event mean concentrations (EMCs) in whole-water samples of total suspended solids (TSS), Cu, Pb, and Zn were about 93,000; 39; 234; and 217 $\mu\text{g/L}$, respectively. The coefficients of variation (COVs) for these sample populations are about 1.2, 0.9, 2.0, and 1.4 for suspended solids, Cu, Pb, and Zn, respectively. These COVs indicate that measured concentrations may vary by more than plus or minus two orders of magnitude. The National Urban Runoff Program (NURP) data base of urban loading sites (sites without upstream BMPs), which includes total recoverable whole-water EMCs from 2,300 separate storm events from 81 sites in 22 different cities, also was conducted in the late 1970s and early 1980s (Athayde and others, 1983). The NURP was advanced for its time in that it included a substantial QA/QC component and that detection-limit issues were addressed. The median EMCs for all the urban NURP sites are about 70,000, 30, 110, and 150 $\mu\text{g/L}$ for TSS and total recoverable Cu, Pb, and Zn in whole-water samples, respectively. The coefficients of variation for these populations are about 1.0, 1.0, 0.8, and 0.8 for suspended solids, Cu, Pb, and Zn, respectively, indicating that measured concentrations in urban runoff also may vary by more than plus or minus two orders of magnitude. In more recent studies,

investigators find that concentrations of Cu may be higher than historical values (possibly a consequence of the use of metallic brake pads on vehicles), concentrations of Pb are substantially lower than historical values (possibly from the reduction of Pb in gasoline; Callendar and Van Metre, 1997), and Zn concentrations are generally equivalent to the historical values (Marsalek and others, 1997; Sansalone and Buchberger, 1997; Dupuis and others, 1999; Legret and Pagotto, 1999).

Technical Concerns

Although the whole-water sampling matrix would seem to be a simple and universal solution for runoff-monitoring studies, some technical concerns must be understood and evaluated. Suspended sediment is an integral part of the whole-water matrix. When the suspended-sediment distribution in the water column is highly heterogeneous, therefore, proper techniques for suspended-sediment sampling are critical for the collection of representative whole-water samples (Webb and others, 1999).

Many of the constituents reported as "total" are actually "total recoverable." Because differences in measured constituents between methods may be substantial (especially in mineral-rich areas of the country), it is important to establish the digestion method with appropriate documentation, especially in the context of a regional or national monitoring program. The total recoverable method may yield results comparable to the total method if the digestion proceeds to the point at which the natural mineral substrate is being dissolved. Measured concentrations of trace element are dependent on the geochemical composition of the particulate matter in whole-water samples for all total recoverable digestion procedures (Hoffman and others, 1996; Garbarino and Hoffman, 1999). Differences in measured concentrations, therefore, may be accentuated by regional differences in the amount of natural minerals that are solubilized during digestion, because solubilization is a function of the mineralogy of the solids.

Potential differences in performance among water-quality laboratories are an issue with whole-water samples because the digestion, separation of residuals, and analysis is not always a trivial matter. The results of an interlaboratory comparison (fig. 4) involving about 40 professional water-quality laboratories indicates that laboratory performance can be

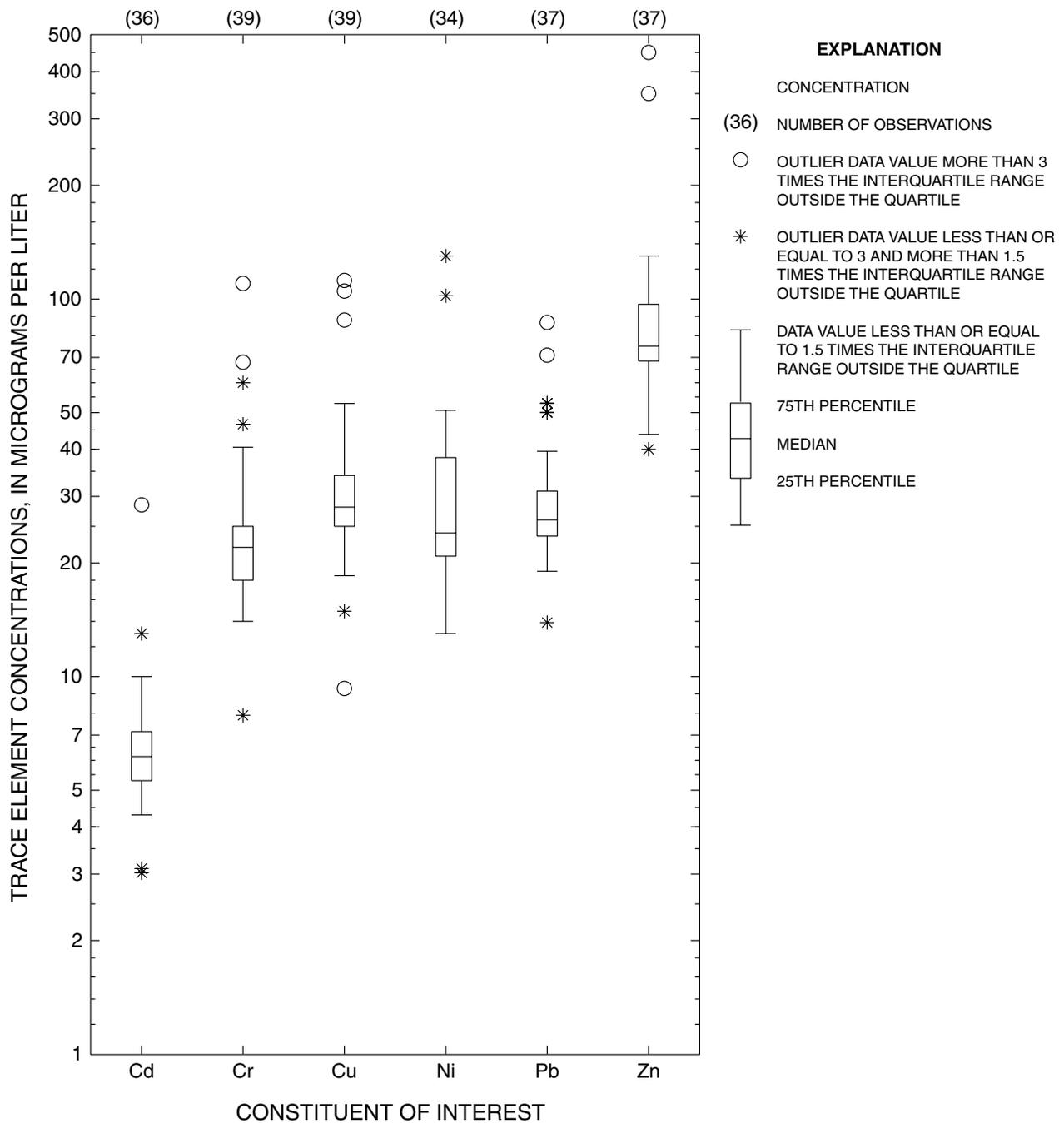


Figure 4. The distribution of total-recoverable trace-element concentrations measured in a natural-water matrix standard reference solution of a whole-water sample (excluding far outliers of 0.5 micrograms per liter for Cd and 38,160 micrograms per liter for Zn) by laboratories participating in the USGS interlaboratory evaluation program. Data from Long and Farrar (1994).

highly variable. Most of the reported concentrations range from 63 percent to 180 percent of the most probable value (MPV; the median of interlaboratory determinations) and a substantial number of outliers differ by an order of magnitude from the MPV (Long and Farrar, 1994). This variability in interlaboratory analytical results is noteworthy in light of the fact that all of the MPVs are at least an order of magnitude above the detection limits for the analysis of whole-water samples (Garbarino and Struzeski, 1998), and that these laboratories, by participating in an interlaboratory comparison, have some components of a QA/QC system (Jones, 1999) in place. Therefore, the digestion method and laboratory performance must be properly documented through a QA/QC program to ensure comparability of data from sample to sample and among data collected from different studies.

Differences in digestion procedures may also affect measured trace element concentrations. For example, whole-water sample digestions have been historically prepared in laboratories without any special precautions to control the potential for airborne contamination. In developing a new in-bottle digestion method for whole-water samples, Hoffman and others (1996) showed that this newer technique had lower blank concentrations and improved reproducibility when compared to the existing open-beaker method. Therefore, historical whole-water data may be affected by these processing artifacts and may not be directly comparable with more recent data.

Historically, the USEPA has recommended the "total recoverable method" of sample preparation as an indication of bioavailability of trace elements (U.S. Environmental Protection Agency, 1986a). There are, however, no universal and robust methods to relate concentrations of total recoverable trace elements to ecosystem effects. Therefore, total recoverable concentrations of trace elements in water samples are at best one of many explanatory variables to be measured in addition to more direct measurements of the ecological effects of runoff on aquatic biota (Buckler and Granato, 1999). Also, use of whole-water samples does not address the issue of speciation, which may provide information about processes that control transport and

fate of trace elements that may be useful for understanding and potentially mitigating the adverse effects of trace elements in receiving waters (Horowitz, 1991).

Use of the whole-water matrix may present problems if trace-element concentrations in the dissolved matrix are low, because the water may dilute concentrations of the trace elements in the whole-water sample below detection limits even if the sediment is highly contaminated (Horowitz, 1991; Hem, 1992). If the concentrations of trace elements in samples collected from highways and structural BMPs are to be compared with those in samples from relatively uncontaminated receiving waters (in which many of the trace elements are associated with the suspended solids), detection limits also may pose problems. Trace-element concentrations below detection limits for whole-water samples (Garbarino and Struzeski, 1998) are important at the watershed scale because, annually, substantial loads of trace elements may go undetected (Horowitz, 1991; Hem, 1992). Also, many of the trace elements associated with highway operations (table 1) that were not detected in historical whole-water sample analyses may now be measured because of the lower detection limits associated with improvements in analytical techniques. Knowledge of historical and current method-detection limits, therefore, is needed to compare the results of whole-water analysis.

Three examples are presented to illustrate the potential suitability of whole-water sampling for monitoring highway and urban runoff in terms of the aforementioned detection-limit problems. In a "worst case scenario," it is assumed that all trace elements associated with sediment and trace-element concentrations in the dissolved phase are zero. Sediment-associated trace-element concentrations are from the analysis of sediment samples from highways, urban areas, and U.S. rivers by Kobriger and Gienoplos (1984), K.C. Rice (USGS, written commun., 1999) and Rice (1999), respectively. Hypothetical concentrations of suspended-sediment from one to 1,000 mg/L are used in calculations because this range includes many concentrations reported in highway runoff (Driscoll and others, 1990), urban runoff (Athayde and others, 1983) and stream water in most of the conterminous United

States (Smith and others, 1993). Using these assumptions, hypothetical whole-water concentrations of trace elements in highway runoff, urban receiving water, and relatively uncontaminated receiving water-samples are calculated by means of equation 1:

$$C_{ww} = C_{ss} * C_{stm} * U , \quad (1)$$

where

C_{ww} is the hypothetical whole water-concentration of trace elements in micrograms per liter;

C_{ss} is the hypothetical suspended-sediment concentration in milligrams per liter;

C_{stm} is the range of measured trace element concentrations from analysis of sediment samples in milligrams of the trace element (TE) per kilogram of sediment (S); and

U is the unit conversion factor (kg(S)(μ g(TE)/1000 mg(S)(mg(TE))).

The amount of suspended sediment required to produce detectible whole-water trace-element concentrations can be examined in terms of current whole-water detection limits (Garbarino and Struzeski, 1998). Figure 5 indicates the relations between sediment concentrations, the range of trace elements measured on potential source sediment, and method detection limits for Cd, Cr, Ni and Zn. More specifically, the calculated concentrations (equation 1) associated with the minimum, 25th percentile, median, 75th percentile, and maximum trace-element concentrations measured in sediment samples are shown in figure 5 as a function of suspended sediment concentrations in the hypothetical whole-water samples. The results of this method applied to concentrations of trace elements associated with fine sediment (grain sizes less than 74 μ m) from the highway surface (Kobriger and Gienoplos, 1984) are demonstrated in figure 5A. This figure indicates that for Cd, Cr, Ni and Zn, the contribution of sediment would not be detectable until suspended-sediment concentrations are about 7 mg/L, 20 mg/L, 3 mg/L, and less than 1 mg/L, respectively. In comparison, a similar calculation uses measured concentrations of trace elements in

the fine fraction (grain sizes less than 64 μ m) of 91 urban streambed sediment samples collected by the U.S. Geological Survey's (USGS) National Water Quality Assessment (NAWQA) Program (K.C., Rice, written commun., 1999) in equation 1. Figure 5B indicates that minimum suspended sediment concentrations of about 60 mg/L, 25 mg/L, 10 mg/L, and about 2 mg/L are necessary for detection of Cd, Cr, Ni and Zn, respectively. Finally, the third example uses concentrations of trace elements in the fine fraction of streambed sediment samples collected by NAWQA in the conterminous United States (Rice, 1999). Cd, Cr, Ni and Zn would not be detectable until suspended-sediment concentrations were about 125 mg/L, 30 mg/L, 10 mg/L, and 4, mg/L respectively (fig 5C).

These examples suggest that that the ability to detect sediment-associated trace elements depends on the constituent of interest and the concentration of suspended sediment in the whole-water sample. Median suspended-sediment concentrations characteristic of "rural" and "urban" highways monitored in the 1970s and 1980s were about 50 and 140 mg/L, respectively (Driscoll and others, 1990) and median sediment concentrations measured by NURP were 101, 67, 69, and 70 mg/L for residential, mixed use, commercial, and open/nonurban land uses, respectively. Therefore, the detection-limit issue is not as critical a concern for highway- and urban-runoff studies as it may be when monitoring relatively uncontaminated receiving waters. These examples also indicate, however, that it may be imprudent to declare that a certain trace element is not present in runoff on the basis of whole-water analysis unless the detection limits and suspended-sediment concentrations also are published. Also, these examples are based only upon the contribution of sediment-associated trace elements and do not include concentrations of dissolved trace elements, which may be substantial given the unique geochemical environment on the road surface.

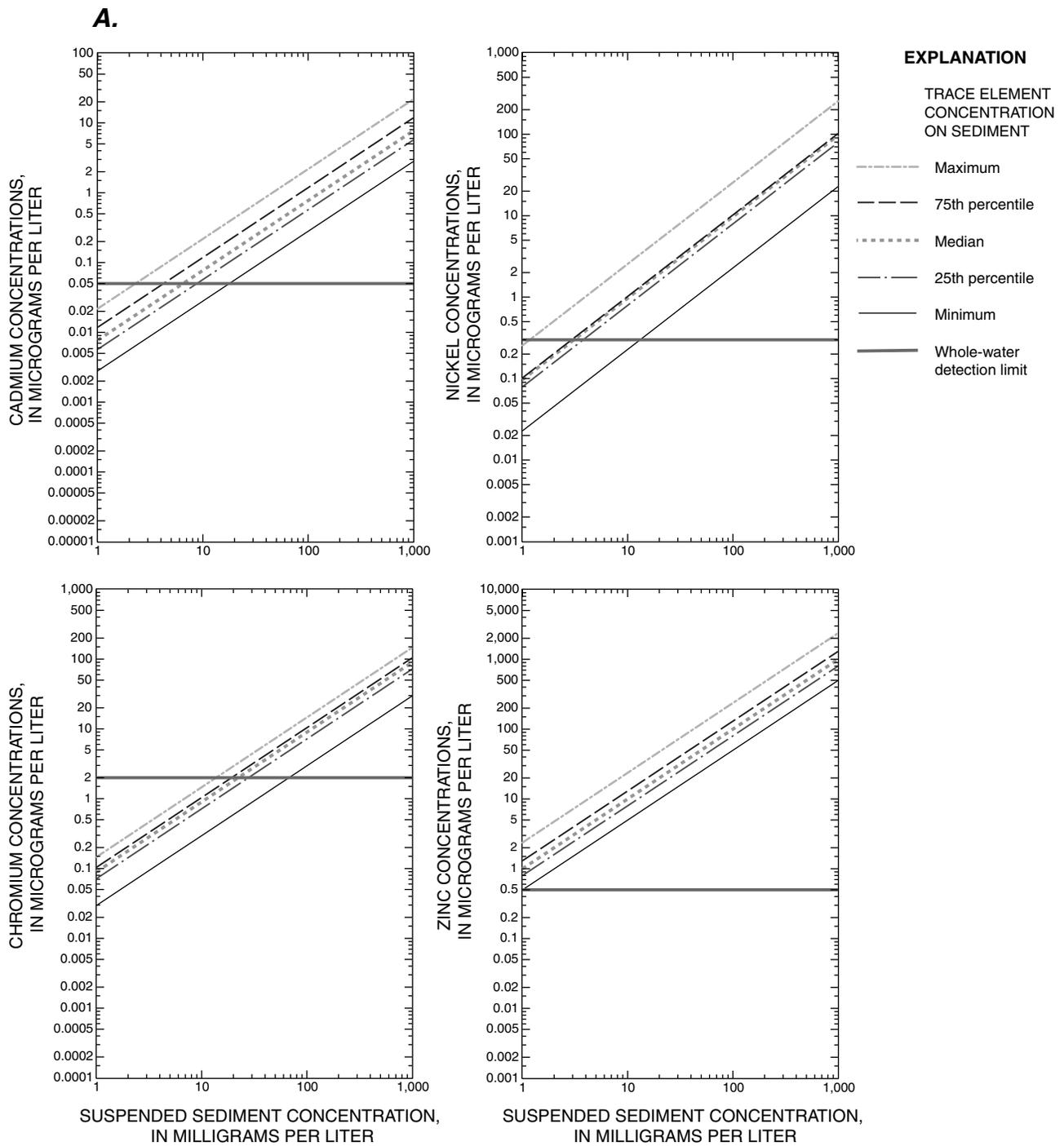


Figure 5. Method detection limits (MDLs) for analysis of whole-water samples (Garbarino and Struzeski, 1998) in comparison to whole-water trace-element concentrations calculated from measured trace-element concentrations in fine-grained (A) highway-surface sediments (Kobriger and Geinopolos, 1984) and hypothetical suspended-sediment concentrations in highway runoff; (B) urban stream-bed sediments (Rice, K.C., USGS NAWQA Trace Element Synthesis Project, written commun.) and hypothetical suspended-sediment concentrations in urban-stream runoff; and (C) stream-bed sediments (Rice, 1999) and hypothetical suspended-sediment concentrations in receiving waters.

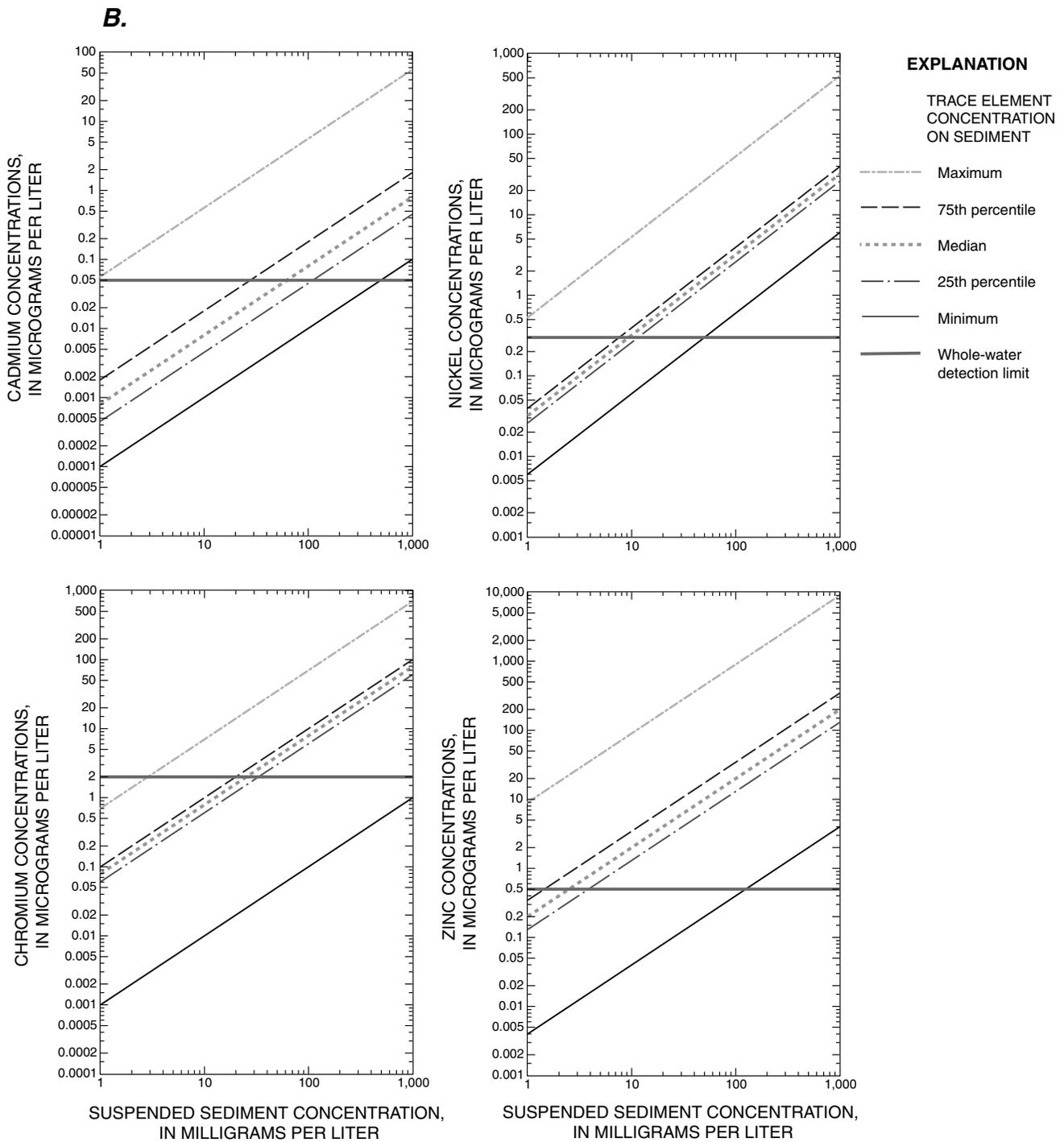


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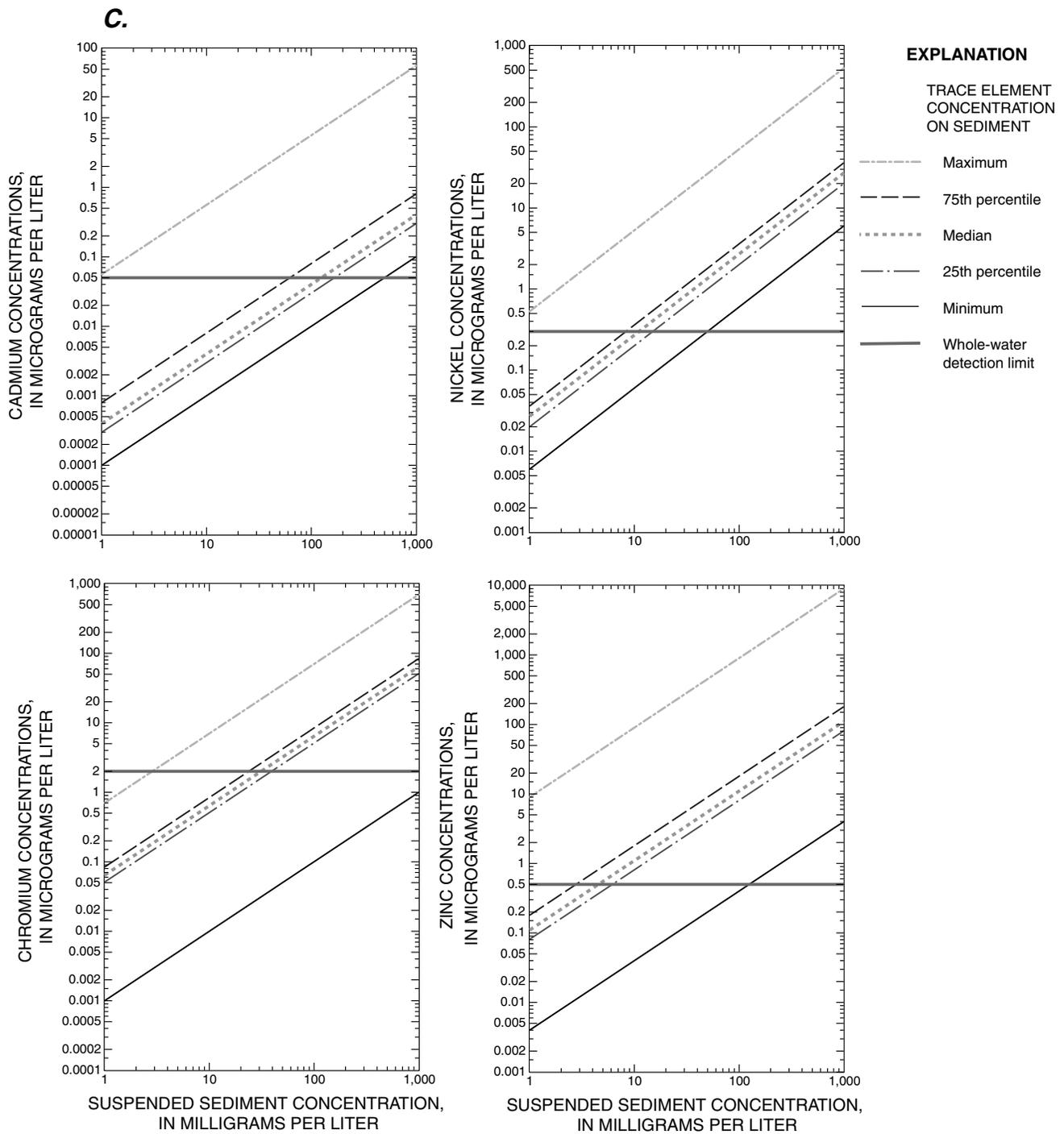


Figure 5. Method detection limits (MDLs) for analysis of whole-water samples (Garbarino and Struzeski, 1998) in comparison to whole-water trace-element concentrations calculated from measured trace-element concentrations in fine-grained (A) highway-surface sediments (Kobriger and Geinopolos, 1984) and hypothetical suspended-sediment concentrations in highway runoff; (B) urban stream-bed sediments (Rice, K.C., USGS NAWQA Trace Element Synthesis Project, written commun.) and hypothetical suspended-sediment concentrations in urban-stream runoff; and (C) stream-bed sediments (Rice, 1999) and hypothetical suspended-sediment concentrations in receiving waters—*Continued*.

Dissolved (Filtered Water)

The dissolved phase is, theoretically, the material that forms a uniformly homogeneous solution of water and solute molecules. The solute molecules are surrounded by solvent (water) molecules and do not contact other solute molecules except in collisions during migration through solution (Hem, 1992). Chemically, the theoretical definition of the dissolved phase would include trace elements that exist as neutral atoms, electrically charged ions, neutral or charged complexes (containing two or more associated ions), and multi-elemental molecules. The amount of each trace element dissolved in solution may be estimated using geochemical models based on the thermodynamics of each constituent in solution (Bricker, 1999), but the information needed to construct such a model is dependent upon water-quality data that can be obtained only from complete analysis of appropriate water samples. Physically, the operational definition of the dissolved phase includes all the material that would never settle out of solution by gravity. Consideration of colloidal particles, however, reveals a fundamental inconsistency in this definition. Colloidal particles (particles having diameters that range from about 0.001 to 1 micrometers) are agglomerations of molecules that are not viewed as chemically dissolved, but that still will not settle from solution, even under favorable conditions (Hem, 1992; Buffle and Leppard 1995a; 1995b).

Difficulties in separating colloids from water have led to the somewhat arbitrary definition of dissolved as those constituents that pass through a 0.45-micron (μm) or a 0.40- μm filter (U.S. Environmental Protection Agency, 1983; U.S. Geological Survey, 1984; American Public Health Association-American Water Works Association-Water Pollution Control Federation (APHA-AWWA-WPCF), 1989; American Society for Testing and Materials (ASTM), 1995). The USEPA Office of Water has defined the dissolved phase as the standard by which compliance with water-quality criteria should be measured (U.S. Environmental Protection Agency, 1996). The use of this operational definition has been codified because it is believed that this "dissolved trace element" definition more closely approximates the bioavailable fraction of trace elements in the water column than does the definition of total recoverable elements (40 CFR Part 131, 1995;

Horowitz and others, 1996; Sansalone and Buchberger, 1997). There also are other methods to measure "dissolved" concentrations, such as "exhaustive filtration," which removes colloids from solution by utilizing a filter's tendency to clog to achieve very fine pore sizes (approaching 0.005 micrometers) to remove colloids from solution (Taylor and Shiller, 1995); tangential filtration and centrifugation, which also may be used to separate particulates and colloids from the dissolved phase (Buffle and Leppard, 1995b); and chemical speciation methods such as potentiometry or ion exchange resin removal (Morrison and others, 1984a,b; Morrison and others, 1987; Breault and others, 1996). These methods are much less prevalent than the USEPA standard, so in most cases a reference to a "dissolved constituent" is in reality a reference to an analysis of a filtered water sample.

Benefits

Monitoring the dissolved phase of runoff may provide an abundance of information that is potentially useful for highway and urban runoff studies. Dissolved trace-element concentrations are expected to provide more reliable correlations with toxicity than total-recoverable, or sediment-associated trace-element concentrations (U.S. Environmental Protection Agency, 1992c; Stumm and Morgan, 1996). If the dissolved phase is monitored in conjunction with the whole-water and(or) suspended-sediment phases, more detailed information about the partitioning of trace elements of interest (in time and space) can be obtained. The mechanisms that control partitioning (sorption reaction rates), however, are poorly understood and require further study (Davis and Kent, 1990). Repeated sampling of runoff and analysis of the dissolved matrix to evaluate the chemical behavior of trace elements on the pavement, in drainage structures, BMPs, and receiving water may provide information necessary to evaluate the effectiveness of BMPs (including retention) for toxicity reduction of effluent (Sansalone and Buchberger, 1997). Relevant information about the dissolved phase in conjunction with information about the physical and chemical characteristics of suspended solids can provide distribution coefficients between the dissolved, suspended-sediment, and ultimately the bottom-sediment phases. These coefficients may be

used to estimate the effects of runoff at unmonitored sites on receiving waters (Yousef and others 1985a, 1985b; Sansalone, Buchberger, and Al-Abed, 1996; Sansalone, and Buchberger, 1997; Radovanovic and Koelmans, 1998; Sigg, 1998).

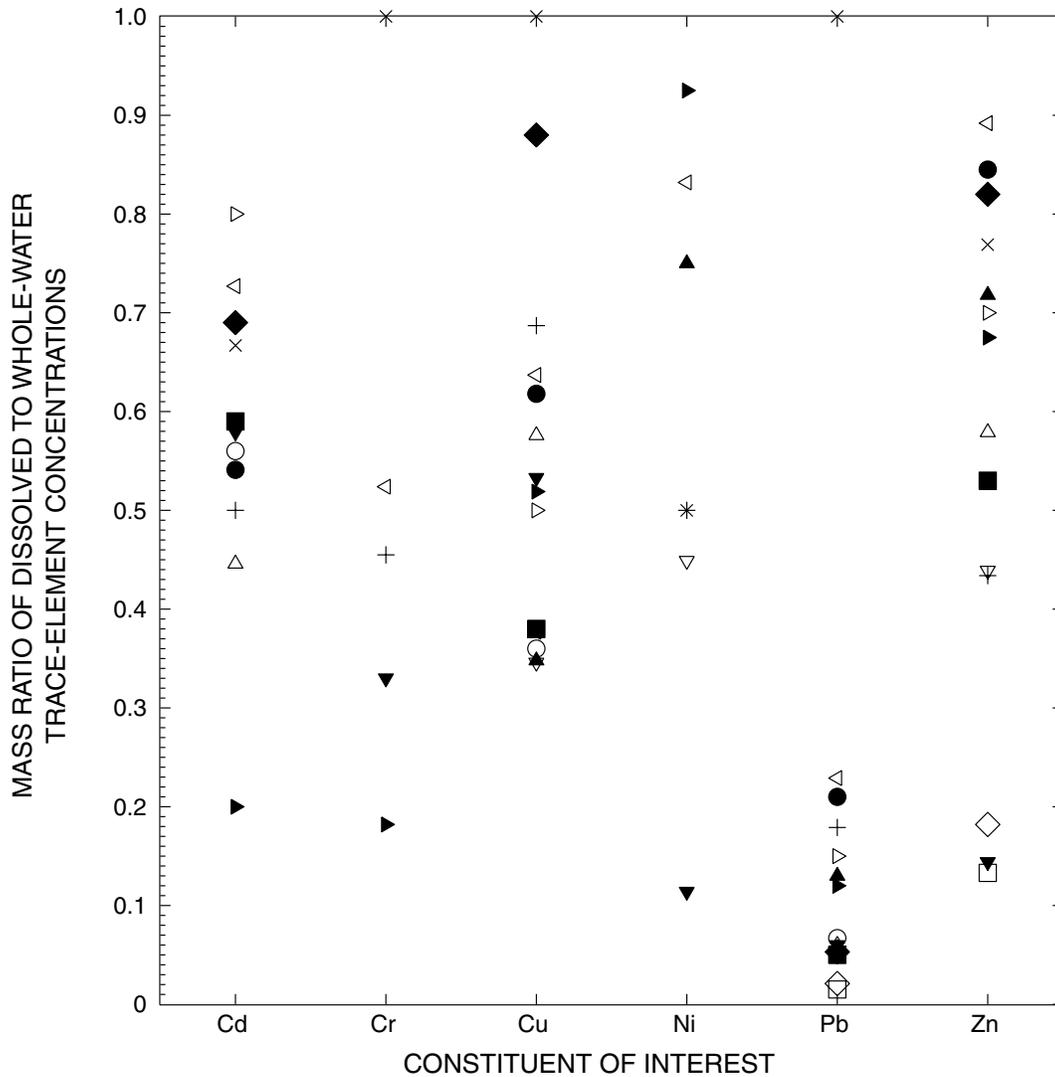
Monitoring of dissolved trace-element concentrations in runoff samples has been incorporated into recent highway-runoff studies in response to scientific and regulatory information needs and for evaluating the potential toxicity of highway-runoff (Dupuis and others, 1985; Marsalek and others, 1997; Sansalone and Buchberger, 1997). Highway runoff data sets that include analysis of comparable dissolved and whole-water samples indicate that a substantial proportion of the trace elements measured in the whole-water samples may be associated with the dissolved matrix (fig. 6). The relatively high proportion of dissolved trace elements (medians from fig 6 being about 55-, 45-, 52-, 60-, 12-, and 65-percent dissolved for Cd, Cr, Cu, Ni, Pb, and Zn, respectively) would at first seem to contradict the paradigm that almost all trace elements are associated with the suspended-sediment matrix (table 2). Consideration of the unique geochemistry of the highway environment, however, would suggest that a relatively higher proportion of some trace elements may be dissolved in pavement runoff than in river water. For example, data from a very low-flow snowmelt event (Dupuis and others, 1985), which indicated that 100 percent of the Cr, Cu, and Pb was in the dissolved phase, is logical given the fact that this water had relatively high ionic strength but insufficient volume and flow velocity to entrain suspended solids (Dupuis and others, 1985, reported an EMC of 7 mg/L for suspended solids and a corresponding specific conductance of 3,450 μ S/cm during this "event"). Although this may be an extreme case, figure 6 indicates that speciation of the individual constituents may be variable and may depend upon the chemistry of the constituent of interest, and potentially many site specific variables. More specifically, table 3 indicates that the relative solubility of trace elements differs from constituent to constituent among available results from highway-runoff studies. Studies of dissolved trace elements also suggest the potential for removal of trace elements by sedimentation. For example, Pb—being the least soluble among these trace elements—may be

more efficiently removed using BMPs that employ sedimentation processes than would trace elements with greater relative solubilities.

Study of the dissolved matrix also provides information about trace-element mobilization and transport processes that may be valuable for characterizing highway runoff, evaluating the potential effectiveness of BMPs, and identifying possible environmental effects. Studies indicate that whereas a high proportion of the trace elements in runoff on the pavement are dissolved, geochemical effects such as pH buffering by reaction with suspended and bottom sediment and by the concrete in drainage structures tends to drive speciation toward the solid phase (Revitt and Morrison, 1987; Morrison and others, 1990). Conversely, other biochemical and(or) geochemical conditions that exist in drainage structures and BMPs can reverse this process, thereby increasing concentrations of dissolved trace elements. For example, both Ellis and others, (1987) and Morrison and others, (1990) measured increases in dissolved concentrations of Cd, Cu, Pb, and Zn in "gully-pot liquor" (catch-basin water) between storms that was caused by conditions of low pH and anoxia resulting from decomposition of organic matter in the sump sediment.

Technical Concerns

Although analysis of the dissolved sampling matrix may provide information about the speciation of trace elements, improper sampling, processing, and preservation is of particular concern when using this matrix in trace-element monitoring programs. Recent studies have shown that the currently accepted operational definition of dissolved constituents (passing unspecified volumes of whole water through unspecified 0.45- μ m membrane filters) is inadequate due to sampling and processing artifacts (Kennedy and others, 1974; Shiller and Boyle, 1987; Horowitz and others, 1992; Taylor and Shiller, 1995). It is difficult and expensive to process and preserve filtered samples under field conditions without affecting sample integrity (contributing or attenuating trace elements of interest) through the extensive contact with pumps, tubing, filters, and sample bottles used in the filtration process.



EXPLANATION

- | | |
|---------------------------------------|----------------------------------|
| + Dupuis and others, 1985 | ▷ Morrison and others, 1990 |
| × Dupuis and others, 1985 (snow melt) | ■ Morrison and others, 1987 |
| □ Gupta and others, 1981 (composite) | ◆ Revitt and others, 1990 |
| ◇ Gupta and others, 1981 (discrete) | ● Sansalone and Buchberger, 1997 |
| ○ Harrison and Wilson, 1985 | ▲ Schiffer, 1989 |
| △ Legret and Pagotto, 1999 | ◄ Speiran, 1998 |
| ◁ Legret and others, 1995 | ▼ Yousef and others, 1985 |
| ▽ Marsalek and others, 1997 | ▶ Yousef and others, 1984 |

Figure 6. The mass ratio of dissolved to whole-water concentrations measured in pavement runoff.

Table 3. Hierarchy of the relative solubility of trace elements commonly studied in highway runoff

[The percent dissolved of each constituent's total concentration decreases from left to right, the greater than symbol (>) indicates a difference of at least 10 percent between adjacent constituents; ≈, a difference that is less than 10 percent. Cd, cadmium; Cr, Chromium; Cu, Copper; Ni, nickel, Pb, lead; Zn, zinc]

Highway-runoff study	Relative solubility
Dupuis and others, 1985	Cu>Cd≈Ni>Cr>Zn>Pb
Ellis and Revitt, 1982	Cd>Zn≈Cu>Pb
Gupta and others, 1981	Zn>Pb
Harrison and Wilson, 1985c	Cd>Cu>Pb
Laxen and Harrison, 1977	Cd>Zn>Pb
Legret and Paggotto, 1999	Zn≈Cu>Cd>Pb
Legret and others, 1995	Zn>Ni>Cd>Cu>Cr>Pb
Marsalek and others, 1997	Ni≈Zn>Cu
Morrison and others, 1990	Cd>Zn>Cu>Pb
Morrison and Florence, 1990	Cd>Zn>Cu>Pb
Morrison and others, 1987	Cd>Zn>Cu>Pb
Morrison and others, 1984b	Zn>Cd>Cu>Pb
Revitt and others, 1990	Cu>Zn>Cd>Pb
Revitt and Morrison, 1987	Cd≈Zn>Cu>Pb
Sansalone and Buchberger, 1997	Zn>Cu>Cd>Pb
Sansalone and others, 1995	Cr>Cd>Cu≈Zn>Pb
Schiffer, 1989	Ni≈Zn>Cu>Pb
Sperian, 1998	Zn>Cu>Pb
Yousef and others, 1985b (runoff)	Cd≈Cu>Cr>Zn≈Ni>Pb
Yousef and others, 1985b (pond)	Zn≈Cu>Cd≈Ni>Pb≈Cr
Yousef and others, 1984	Ni>Zn>Cu>Cd>Cr>Pb

Laboratory and field evaluations of the filtration process indicate that measured trace-element concentrations in filtered water samples are affected by both environmental and procedural factors (Horowitz and others, 1992). Defining environmental factors, both natural and anthropogenic, include local geochemistry, suspended-sediment concentration, grain-size distribution in suspended sediment, concentration of colloids, and the amount of organic material present in the sample. These factors will be highly variable from storm to storm and site to site, and therefore, these variables need be documented for use of dissolved matrix data (especially for eventual use in a regional or national synthesis). Procedural factors, such

as filter pore size, filter type, surface area, method of filtration, and the volume of sample processed also influence the proportion of the total trace-element concentration that will be measured as "dissolved" in the filtrate (Martin and Meybeck, 1979; Horowitz and others, 1992; Karlsson and others, 1994). Filtration-rate reductions commonly are observed as water flows through a filter. These reductions are due to clogging of the filter by organic and inorganic material, which effectively reduces the pore size of the filter and likely increases the quantity of trace-element-rich colloidal material retained by the filter (Kennedy and others, 1974; Wagemann and Brunskill, 1975; Martin and Meybeck, 1979; Hoffman and others, 1981; Ledin, 1993; Nriagu and others, 1993; Karlsson and others, 1994). For example, in a controlled experiment, Horowitz and others (1992) determined that concentrations of dissolved Fe (and other trace elements) in filtrates were affected by pore size, filter diameter, and the total volume processed (fig. 7). In a subsequent study, Horowitz and others (1996) evaluated the performance of different filters commonly used for sampling the dissolved matrix (Shiller and Boyle, 1987; Windom and others, 1991; Nriagu and others, 1993; Benoit, 1994; Horowitz and others, 1994; Taylor and Shiller, 1995; USEPA, 1996) and found that trace-element concentrations appear to be proportional to the surface areas of the filters. Horowitz and others (1996) recommended use of the Gelman filter for minimizing filtration artifacts because of its large surface area and because the necessary QA/QC data (Windom and others, 1991; Horowitz and others, 1994; Horowitz and others, 1996; U.S. Environmental Protection Agency, 1996) are available for this filter.

Aspects of the filtration process other than the pore size and type of filter must also be considered if artifacts are to be reduced or eliminated and concentration data for dissolved constituents are to be considered reliable and comparable. In some studies, trace elements were shown to sorb to the filter during initial processing, and, once all the potential sorption sites were filled, higher concentrations were measured in subsequent aliquots of the filtrate (Horowitz and others, 1994). One should be aware that the presence of

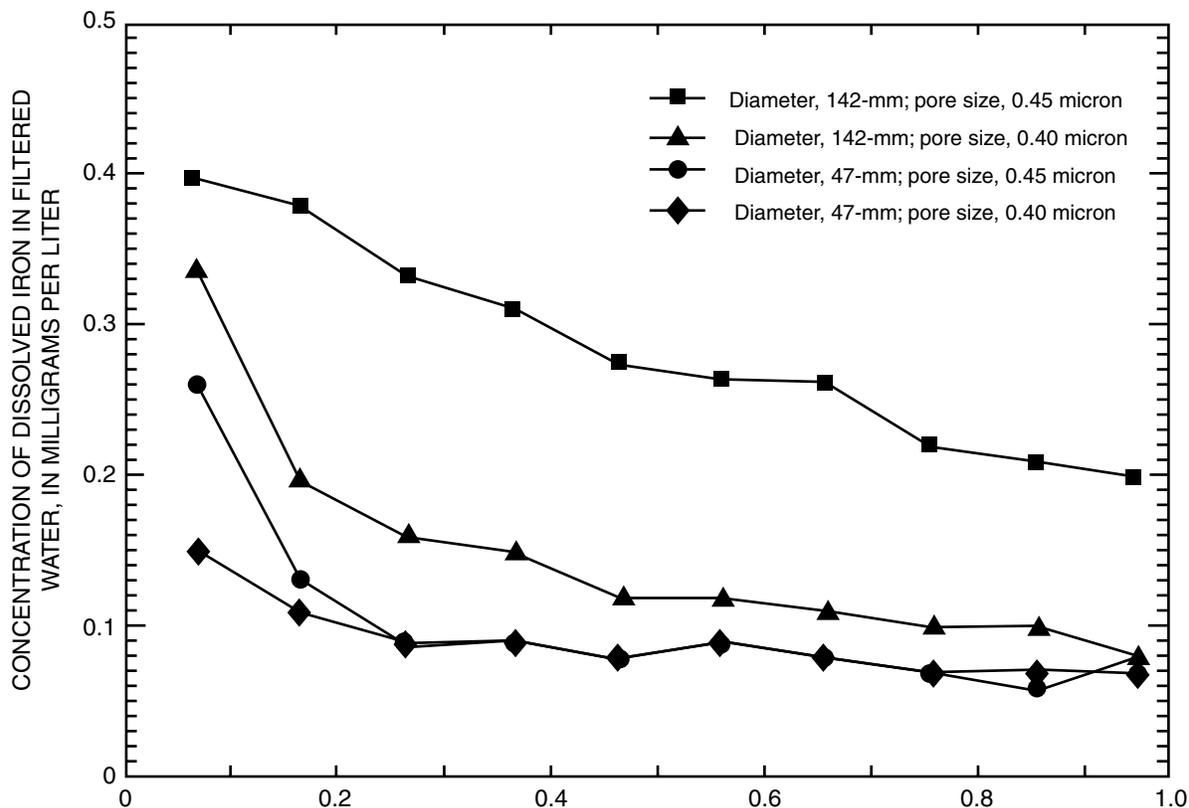


Figure 7. The effect of filter diameter, pore size, and total volume of water processed, on measured concentrations of dissolved iron (from Horowitz and others, 1992).

deionized water that was used to condition the filters could also result in a similar pattern of increasing concentrations with subsequent aliquots of the filtrate because the initial aliquots could be diluted by this deionized water (Horowitz and others, 1994).

Chemical-speciation kinetics may be a major issue affecting measured dissolved concentrations in highway runoff samples. Several physical and chemical processes affect the speciation of trace elements at different time scales, including complexation, flocculation, chemical precipitation, biological reactions, and sorption-desorption reactions (Revitt and Morrison, 1987; Davis and Kent, 1990; Sansalone, Buchberger, and Al-Abed, 1996; Sansalone and Buchberger, 1997). All these reactions are complex, variable, and interdependent, with reaction rates that are different for each trace element. Furthermore, mechanisms that control reaction rates are poorly understood and require further study (Davis and Kent, 1990; Stumm and Morgan, 1996). A few examples are examined to estimate the

order of magnitude of the time scales at which these reactions may proceed. In one case, Hering and Morel (1988) measured the complexation rate of Cu and found that more than half of the free Cu had complexed within a two-hour period. In a highway-runoff study, Sansalone and Buchberger (1997) reported that dissolved concentrations of trace elements in highway runoff samples were affected by flocculation of fine particulates during the initial six to eight hours of holding time. Therefore, they did a partitioning experiment and measured substantial changes in the partitioning of trace elements that are neither predominantly dissolved nor associated with suspended solids (Cu and Ni) but did not detect substantial changes for trace elements that were either primarily associated with suspended solids (Al, Fe, and Pb) or primarily dissolved (Zn, Mn, and Cd) over 24 hours. Davies (1986) monitored the chemical precipitation of dissolved Cd in a previously filtered hard-water solution. Cd concentrations were reduced by about 20 percent within 10 hours and 40

percent within in 20 hours. This test solution reached equilibrium at about 50 hours with an overall reduction in the dissolved phase concentration of about 85 percent. Ellis and others (1987) and Morrison and others, (1990) measured increases in dissolved trace-element concentrations caused by biochemical processes in a road-side catchbasin, during a period of a few days. These examples, however, indicate only the order-of-magnitude of potential reaction rates because the actual reaction rates depend upon conditions that will differ between storms and between samples collected within each storm. More specifically, geochemical changes on the pavement, in the drainage structures (during and between flow events) and in the sample collection bottles (until the samples are processed and or preserved) will effect these reaction rates and the apparent speciation observed in the partitioned samples.

Partitioning rates between the dissolved and suspended-solids phases are of particular concern when sampling the dissolved matrix in urban- and highway-runoff studies, because logistics may preclude sample filtering during a storm, and suspended sediment concentrations can vary by orders of magnitude within and between storms. Wood and others (1995) published reaction-rate equations and rate constants for several trace elements under different conditions of suspended sediment and salinity. These equations, reformulated in terms of the proportions of dissolved and solid-phase trace elements to the total (whole water concentration) are summarized as

$$[TE_d/TE_w]_t = 1 + k_b*[TE_s/TE_w]_{t-1} - k_f*[SSC]*[TE_d/TE_w]_{t-1}, \quad (2)$$

where

- $[TE_d/TE_w]_t$ is the ratio of the dissolved (TE_d) to total trace element (TE_w) concentration at time step t ;
- $[TE_s/TE_w]_{t-1}$ is the ratio of the sediment associated (TE_s) to total trace element (TE_w) concentration during the previous time step $t-1$;
- $[TE_d/TE_w]_{t-1}$ is the ratio of the dissolved (TE_d) to total trace-element (TE_w) concentration during the previous time step $t-1$;
- $[SSC]$ is the concentration of solids in the sample container;

k_b is the backward rate constant indicating the rate of desorption from solids; and

k_f is the forward rate constant indicating the rate of sorption to solids.

Using this equation, and rate constants for Cu in a fresh-water solution containing natural particles, three hypothetical examples are presented to illustrate the potential effect of solid-solution partitioning on dissolved trace-element concentrations with time in the absence of competing reactions. The median national EMC for total Cu (0.039 mg/L) and various suspended-sediment concentrations representing a range of typical highway-runoff sediment concentrations (from Driscoll and others, 1990) are used to examine potential rates of sorption to sediment as a function of the time from sample collection (assuming all the Cu in solution is initially dissolved). Figure 8 indicates that the proportion of measured dissolved Cu will be a function of the time between sample collection and filtration and of the concentration of solids in the sample container. Within the first six hours, about 15, 80, and more than 99 percent of the initial dissolved Cu concentrations are expected to be sorbed by the solid matrix when suspended-sediment concentrations are 10, 100, and 1,000 mg/L, respectively. Therefore, it is difficult to interpret the data on dissolved concentrations unless dissolved samples are processed shortly after sample collection because the relation between a measured dissolved concentration and the actual concentration of any given trace element in the runoff at the sampling point is unknown. This consideration is important in runoff studies, especially in terms of the collection and use of composite samples for analysis of a single EMC value for each storm, because the median of national storm-event durations reported by Driscoll and others, (1990) is about 5 hours and the median of national storm-event durations reported by the USEPA (1992a) is about 9 hours. Furthermore, Sansalone and Buchberger (1997) noted that, in many runoff-monitoring programs, samples may not be retrieved and subsequently filtered within 24 hours. Also, many programs do not collect samples from pavement sheet flow (where geochemical conditions are expected to favor the dissolved phase), but rather from drainage systems in which considerable residence times and mixing can favor partitioning to the solid phase (Sansalone and Buchberger, 1997). It is for these

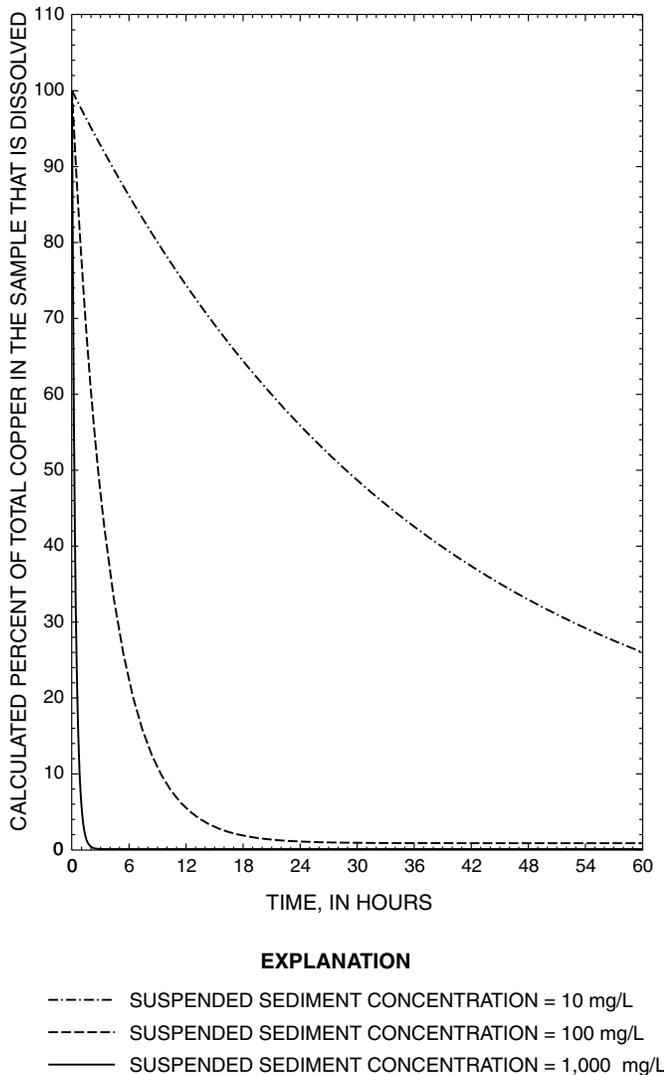


Figure 8. The percent of total copper that is dissolved in a hypothetical two-phase (water and sediment) highway-runoff sample with the median national event mean copper concentration (0.039 mg/L) and various suspended-sediment concentrations (representing a range of typical highway runoff sediment concentrations; Driscoll and others, 1990) as a function of the time from sample collection using published rate equations and rate constants for natural particles in fresh water (Wood and others, 1995) assuming that all of the copper is initially in the dissolved state.

reasons that contemporary trace-element sampling protocols require immediate filtration of samples upon collection (Horowitz and others, 1994; Radtke and others, 1998).

The existence of dissolved-matrix sampling artifacts raises serious questions about the generation of accurate, precise, and comparable dissolved trace-element data and casts doubt on the utility of

substantial amounts of historical data, especially in the context of a regional or national-runoff monitoring program. It is unlikely that correction factors can be developed and applied to filtered-water data to eliminate the effects of processing artifacts, because differences in background geochemical conditions and suspended-sediment concentrations vary widely at regional and national scales. Three methods, however, are proposed to minimize filtration artifacts and enhance the comparability of dissolved (filtered) trace element data for national monitoring programs:

- use of large-surface area filters and collection of the initial aliquots for analysis (Windom and others, 1991; Horowitz and others, 1994; U.S. Environmental Protection Agency, 1996);
- precentrifugation to remove sediment and colloids followed by filtration through a 0.45-micrometer membrane filter (Horowitz and others, 1996); and
- exhaustive filtration with more complex filtering assemblies that are designed to remove all colloids and to measure only the trace elements that are chemically dissolved (Martin and Meybeck, 1979; Hoffman and others, 1981; Taylor and Shiller, 1995).

The effects of filtration artifacts may be limited by employing one of these three methods but data from analysis of samples processed with different methods may not be comparable. Detailed documentation of all sampling and processing procedures is necessary to assess dissolved trace-element data in terms of the potential for filtration artifacts (Horowitz and others, 1996).

For regional or national runoff-monitoring programs, the dissolved matrix may provide valuable information about the chemistry of runoff speciation, but use of this matrix alone may lead to an underestimation of the effects of highway runoff on receiving waters. For example, Yousef and others (1985a; 1985b) measured both dissolved and whole-water concentrations in highway runoff and the retention basin receiving that runoff. Analysis of samples collected from the retention basin indicated that reductions in concentrations of dissolved Cd, Cr, Cu, Ni, Pb, and Zn, were on the order of 30-, 30-, 56-, 44-, 63-, and 88-percent, respectively compared to dissolved concentrations measured in the highway runoff. Analysis of whole-water samples collected from the retention basin, however, indicated that reductions in concentrations of Cd, Cr, Cu, Ni, Pb, and Zn, were on the order of

47-, 66-, 73-, 92-, 97-, and 98-percent, respectively, compared to whole-water concentrations measured in the highway runoff. The reductions in trace element concentrations for whole-water samples were generally 1.5 to 2 times greater than for the dissolved trace element samples because the difference in dissolved concentrations did not account for the relatively large effect of the removal of sediment and associated trace elements by settling in the pond (Yousef and others, 1985a; 1985b).

Suspended Sediment

Suspended sediment, also referred to as suspended solids and suspended particulate matter, is operationally defined as the material that is collected with the water phase in the water column that does not pass through a 0.45-micrometer or a 0.40-micrometer filter. Methods used to separate the suspended solids from the water matrix prior to chemical analysis include filtration, gravity dewatering, and centrifugation. Each of these methods has been used extensively in water-quality and geochemical studies. Samples are filtered by in-line filtration using membrane filters or by tangential filtration using a stack of membrane filters (Horowitz, Elrick and Hooper, 1989a). The gravity-dewatering method is accomplished by allowing the entrained suspended sediment to settle out over time in a sealed bottle at room temperature (Jenne and others, 1980; Horowitz, 1986). In the centrifugation method, centripetal force is used to accelerate the separation of the solid from the liquid phase (Horowitz, Elrick and Hooper, 1989a). Typically, the separated solids are then chemically processed to extract trace elements for chemical analysis. The two types of sediment-digestion techniques, operationally defined as "total recoverable" and "total" (Fishman and Friedman, 1989), were discussed previously in the section on whole-water analysis. A number of sequential extraction methods can be used to evaluate the potential bio-availability and environmental behavior of trace elements present in sediment by measuring the ease of release of trace elements into solution (Tessier and others 1979; Hamilton and others 1984; Fiedler and others, 1994; Kane, 1995).

Properties of suspended-sediment particles, including specific surface area, number and type of surface groups, and surface charge, as well as geochemical characteristics of the solution will influence how trace

elements partition between the dissolved and suspended-sediment matrixes (Sigg, 1998). Partitioning is also a function of the chemical characteristics of each trace element. In natural waters, the relative affinity of trace elements for the solid matrix generally decreases in the order $Pb > Zn > Cd \approx Cu$ (see table 3). This order, however, is not absolute. For example, in waters in which iron oxides predominate, the order is $Pb > Cu > Cd \approx Zn$ (Sigg, 1998); but high concentrations of dissolved organic matter (DOM) may cause a redistribution of trace elements such that the order would be $Pb > Cd > Zn > Cu$ because Cu and Zn are complexed by DOM (Breault and others, 1996; Radovanovic, and Koelmans, 1998). Also, anthropogenic and natural organic material (such as tire particles, vegetation, and biota) commonly are separated with and analyzed as a component of the suspended sediment. These organic materials can have high trace-element affinities. For example, algae can become enriched with trace elements and can be measured as part of a suspended-sediment load (Sigg, 1998).

Benefits

Monitoring the suspended-sediment matrix in highway and urban runoff may provide information for trace-element studies that have various objectives. Historically, chemical analysis of suspended sediment has provided information for the study of geochemical cycling, contaminant transport, trace-element loads, temporal variability and trend analysis, as well as the study of biological effects of sediment-associated trace elements (Horowitz, 1995; Buckler and Granato, 1999). Although analysis of this matrix provides data suitable for meeting these objectives, chemical analysis of suspended sediment is particularly suited for studying short-term spatial and temporal variability in trace-element concentrations. Use of this matrix, therefore, may provide useful information as a component of storm-runoff monitoring studies.

Fewer data sets are available for trace metals in the suspended-sediment matrix than for whole- or filtered-water samples because (with the exception of Canada; Persaud and others, 1993) currently there are few Federal, State, or local water-quality criteria or regulatory limits based on sediment-associated trace-element concentrations. The lack of sediment-associated water-quality criteria is due in part to substantial disagreements over how to estimate the bio-availability of sediment-associated trace elements

(Forstner and Wittmann, 1981; Salomons and Forstner, 1984; Horowitz, 1991). Similarly, use of the suspended sediment-sampling matrix for chemical analysis of trace elements is not as prevalent in the highway runoff literature as either whole- or filtered-water matrix sampling. Historically, however, many highway- and urban-runoff studies have noted correlations between suspended solid and trace element concentrations from the analysis of whole-water samples (Gupta and others 1981; Harrison and Wilson, 1985a; Driscoll and others, 1990; Sansalone, J.J., Buchberger, S.G., and Koechling, M.T., 1995).

When chemical analysis of suspended sediment has been included in runoff studies, use of this matrix has yielded information about trace-element speciation, the distribution among different grain sizes, and the source, fate, and transport of trace elements. Highway- and urban-runoff studies in which sequential extraction schemes are used to differentiate the suspended-sediment-associated trace elements among chemical fractions (including: ion exchangeable; acid soluble; reducible—associated with Fe- and Mn-oxides; reducible—associated with an organic fraction; and residual—associated with the mineral matrix) commonly provide valuable information about the physical and chemical mechanisms within and between storms that influence the quality of runoff and the potential effect on receiving waters (Wilber and Hunter, 1979; Harrison and others, 1981; Ellis and Revitt, 1982; Hamilton and others, 1984; Harrison and Wilson, 1985b; Yousef and others, 1990; Flores-Rodriguez and others, 1994). For example, Harrison and Wilson (1985b) utilized sequential extraction of suspended solids separated from highway runoff by centrifugation to show that the sediment had chemical characteristics similar to those of road-surface dusts. Flores-Rodriguez and others (1994) demonstrated that structural changes in the solids and chemical changes in the associations between trace elements and solids reduced the chemical availability of some trace elements as stormwater runoff moved through an urban drainage system. Also, several studies have shown that differences in the intensity, duration, and type of storm affect the grain-size distribution of suspended sediment, which in turn affects the total load and partitioning of trace elements between the dissolved and suspended matrixes (Harrison and Wilson, 1985c;

Sansalone and others 1995; Sansalone and Buchberger, 1996; Sansalone and others, 1998). Further study of the suspended sediment-sampling matrix may provide the basis for quantification of transport processes, which may explain some of the wide variability that is characteristic of measured highway- and urban-runoff concentration data sets. Marsalek and others (1997) showed that trace-element concentrations in the fine (less than 45 μm) size fraction of suspended sediment in bridge runoff were greater than in corresponding bulk suspended-sediment samples. This enrichment, however, was considered insignificant in terms of the bulk sediment load because the fine fraction represented less than one percent of the total mass of solids at that site. Although the concentrations of trace elements in the bulk suspended sediment were only 43-, 44-, 76-, and 61-percent of the fine-fraction concentrations of Cu, Ni, Pb, and Zn, respectively, bulk suspended-sediment trace-element concentrations exceeded Canadian aquatic sediment-quality guidelines. If these discharges are uncontrolled they could substantially reduce receiving water quality (Marsalek and others, 1997).

Information gained from analysis of the grain-size distribution of sediment-associated trace elements as a function of geology, climate, land use, and environmental practices could aid in the development, design, implementation, and evaluation of BMPs. For example, Harrison and Wilson (1985b) measured higher concentrations of trace elements in suspended-sediment samples than in street-dust samples. They determined that the apparent enrichment per unit mass was caused by selective removal of the larger grain sizes in the roadside catchbasins, which shifted the grain-size distribution in suspended-sediment samples toward the trace-element-rich fine fractions. More recently, while investigating the trace-element composition and speciation in street sediment, Stone and Marsalek (1996) found that silt and clay (less than 63 microns), fine sands (63 to less than 250 microns), medium sand (250 to less than 500 microns) and coarse sand (500 to less than 2000 microns) accounted for about 4, 27, 30, and 39 percent of the total trace-element load, respectively. The fine fractions tend to stay in suspension in retention facilities and are hard to remove by street cleaning operations. They concluded that the measurement of bulk

sediment-associated trace-element concentrations is adequate for determining total loads, but the measurement of concentrations as a function of grain size is necessary to assess remedial options.

In receiving waters, the role of suspended sediment in the biological and geochemical cycling of trace elements in fluvial systems is well established (Forstner and Wittmann, 1981; Salomons and Forstner, 1984). Even in natural-waters with suspended-sediment concentrations as low as 10 mg/L, the sediment may be a substantial source for many trace elements. For example, Horowitz (1991, 1995) demonstrates the potential effect of different sediment concentration on the solid phase contribution to whole-water trace-element concentrations (table 4). As suspended-sediment concentrations approach 100 mg/L, the solid phase may be the dominant source of trace elements in natural waters Horowitz (1991, 1995). The percentiles of different suspended-sediment concentrations reported by the USGS NASQAN program from 1974 to 1981 indicate their frequency of occurrence: 18 mg/L (25th percentile), 67 mg/L (50th percentile), and 193 mg/L (75th percentile; Smith and others, 1987). In comparison, the range of suspended-solids concentrations in highway runoff was reported as 4.0 to 1,160 mg/L (Smith and Lord, 1990), while the range of suspended-solid concentrations for urban runoff was reported as 1.0 to 36,200 mg/L (Makepeace and others, 1995). Suspended sediment from runoff discharges may also settle to the bottom sediment in receiving waters and may interact with natural sediment in the deposition and resuspension cycles of natural streams. For example, Harrison and Wilson (1985c) noted the resuspension of previously deposited runoff-derived sediment near an outfall when they measured upstream suspended-sediment concentrations that were less than 2.0 mg/L, highway-runoff outfall concentrations of about 100 mg/L, and downstream suspended-sediment concentrations that were about 230 mg/L.

Technical Concerns

Although chemical analysis of the suspended-sediment matrix may provide information about the physical and chemical processes that influence the quality and potential effects of runoff on the aquatic

environment, the potential for improper sampling and processing are of concern when using this matrix in trace-element-monitoring programs. The highly heterogeneous lateral and vertical distribution of suspended sediment in the water column (caused by differences in grain size, density, and the distribution of kinetic energy in the flowing water) makes it difficult to collect a representative sediment sample. This difficulty may be the largest potential source of bias in measurements of sediment-associated trace-element concentrations (Webb and others, 1999). Methods for the physical collection of representative samples of suspended sediment from fluvial systems and from runoff drainage structures are described by Edwards and Glysson (1999) and Bent and others (2001), respectively. Although the "contamination problem" is perceived to be relatively minor for sampling the suspended-sediment matrix, the potential for sampling artifacts from extensive contact with pumps, tubing, filters, and other equipment used in the separation process must be recognized and addressed with QA/QC measures.

When monitoring highway and urban drainages, rapid changes in flow and concentrations of sediment and trace elements in runoff may complicate efforts to obtain sufficient sediment mass in individual aliquots to represent in-storm processes using standard automatic sampling techniques. If suspended-sediment concentrations are low (less than about 100 mg/L), physical and chemical limitations of the separation and analysis process may affect the quality and reproducibility of measured trace-element concentrations because replicate analyses of small aliquots of suspended-sediment can display marked variability (Horowitz, 1995). Although a sediment mass as small as 50 mg may be sufficient for trace element analysis, a single grain of unusual composition in a 50 mg sample may generate a non-reproducible analytical result (Horowitz, 1995). In comparison, Standard Reference Materials (SRMs) produced by the National Institute of Science and Technology (NIST), which have been exhaustively processed and tested for chemical content and homogeneity prior to distribution, are distributed with a "Certificate of Analysis" that indicates a minimum sample size for aqueous sediment (commonly 250 to 500 mg) that is typically five to ten times the minimum possible sample size (NIST, 1998; 2000).

Table 4. Solid-phase contributions to whole-water trace-element concentrations of rivers in the conterminous United States and Canada for various suspended-sediment concentrations

[Modified from Horowitz, 1991. **Dissolved concentration:** Dissolved trace-element concentration values are averages from such sources as Shiller and Boyle (1987); Taylor and Shiller (1995); Windom and others (1991); Krabbenhoft (unpublished data). **Bed sediment trace-element concentration:** Fine-grained (<63 µm) bed sediment chemical data from unimpacted areas (Horowitz, 1991). **SSATEC:** Suspended sediment-associated trace-element concentration (µg/L) = [Bed sediment trace-element concentration (µg/g) x Suspended-sediment concentration (g/L)]. **Total concentration:** Total concentration (µg/L) = [SSATEC (µg/L)] + [Dissolved concentration (µg/L)]. **Percent of total:** Percent of total trace-element concentration that is associated with suspended sediment. g/L, gram per liter; mg/L, milligrams per liter; µg/g, microgram per gram; µg/L, microgram per liter; µm, micrometer]

Element	Dissolved concentration (µg/L)	Bed sediment trace-element concentration (µg/g)	Suspended-sediment concentration (10 mg/L)			Suspended-sediment concentration (100 mg/L)		
			SSATEC (µg/L)	Total concentration (µg/L)	Percent of total	SSATEC (µg/L)	Total concentration (µg/L)	Percent of total
Antimony	0.05	0.6	0.006	0.056	11	0.06	0.11	55
Arsenic.....	.5	7	.07	.57	12	.7	1.2	58
Cadmium01	.6	.006	.016	38	.06	.07	86
Chromium.....	.07	20	.2	.27	74	2.0	2.07	97
Cobalt05	18	.18	.23	78	1.8	1.85	97
Copper2	25	.25	.45	56	2.5	2.7	93
Lead05	50	.5	.55	91	5.0	5.05	99
Mercury006	.05	.0005	.0065	8	.005	.011	46
Nickel.....	.3	25	.25	.55	46	2.5	2.8	89
Selenium08	.4	.004	.084	5	.04	.12	33
Zinc.....	.2	90	.9	1.1	82	9.0	9.2	98

Element	Dissolved concentration (µg/L)	Bed sediment trace-element concentration (µg/g)	Suspended-sediment concentration (500 mg/L)			Suspended-sediment concentration (1,000 mg/L)		
			SSATEC (µg/L)	Total concentration (µg/L)	Percent of total	SSATEC (µg/L)	Total concentration (µg/L)	Percent of total
Antimony	0.05	0.6	0.3	0.35	86	0.6	0.65	92
Arsenic.....	.5	7	3.5	4.0	88	7.0	7.5	93
Cadmium01	.6	.3	.31	97	.6	.61	>99
Chromium.....	.07	20	10	10.07	>99	20	20.07	>99
Cobalt05	18	9.0	9.05	>99	18	18.05	>99
Copper2	25	12.5	12.7	98	25	25.2	>99
Lead05	50	25	25.05	>99	50	50.05	>99
Mercury006	.05	.025	.031	81	.05	.056	89
Nickel.....	.3	25	12.5	12.8	98	25	25.3	>99
Selenium08	.4	.2	.28	71	.4	.48	83
Zinc.....	.2	90	45	45.2	>99	90	90.2	>99

Also, the NIST typically supplies a sample volume (usually about 50 grams) that is about 1,000 times the minimum sample volume needed for analysis to provide for replicate analysis to address potential problems in the digestion process and(or) for repeat quality assurance and quality control measurements. Also, when suspended-sediment concentrations are low, the filter pad may contain a substantial proportion of the material that is digested and analyzed. In this case, the sediment should be removed from the filter pad prior to actual chemical analysis (Tramontano and Church, 1984). If discrete samples are combined for analysis of a composite sample, however, limitations caused by low sediment concentrations can be surmounted by collecting a large sample volume and concentrating the sediment to achieve the necessary sample volumes for analysis of the recovered sediments (Horowitz, 1995).

Although there are several ways to collect and process sufficient amounts of suspended sediment to compensate for sample inhomogeneity and detection limit problems, these procedures are difficult in terms of the logistics (Carpenter and others, 1975; Etchebar and Jouanneau, 1980; Ongley and Blachford, 1982; Horowitz, 1986; Horowitz, Elrick, and Hooper, 1989a; 1989b). Composite samples can also be collected in order to surmount potential problems caused by inhomogeneities among aliquots. The production and use of composite samples, however, leads to certain limitations and tradeoffs, such as a substantial loss of temporal resolution. The importance of such a tradeoff must be evaluated in the context of the particular problem being addressed to determine if the loss in temporal resolution is scientifically acceptable.

The time between collection and processing of trace elements in the suspended-sediment matrix can substantially affect the total concentration of trace elements that may be attributed to the solid phase. For example, figure 8 indicates that a substantial proportion of a trace element (Cu) that is initially in the dissolved phase may partition toward the solid phase in as little as one hour after a sample is collected. Furthermore, the total time between collection and the completion of

the separation process may affect the redistribution of trace elements among grain-size fractions and may affect the chemical speciation in the solid matrix. If grain-size specific determination of trace element concentrations or chemical partitioning (for example, partial chemical extractions) are of interest, then this redistribution can be important.

As with whole-water samples, many of the sediment-associated trace-element concentrations reported as "total" are actually "total recoverable," and the proportion digested by a specific technique is in part dependent upon the geochemistry of local sediment. Therefore, it is important to document the digestion method, especially in the context of a regional or national monitoring program. Potential differences in performance among nominally equivalent digestion methods may be a substantial source of uncertainty in available data on concentrations of sediment-associated trace elements. For example, Siaka and others (1998) used four different digestion mixtures including HNO₃-HCl (3:1 and 1:3), HNO₃-H₂O₂ (1:1), and HNO₃-H₂SO₄ (1:1) and found that measured trace element concentrations were different among the acid mixtures used, and varied among the different trace elements. Combined results for three trials for each of the four mixtures are summarized in figure 9, which indicates the population statistics of the combined trials with respect to certified total recoverable and total digestion concentrations for the standard reference materials used in the experiment. A comparison of the medians indicate that these four mixtures can produce large differences in analytical results and that are largely trace-element specific. Siaka and others (1998) also found substantial variation in measured concentrations that were caused by differences in the type of heating used in their experiments (hotplate versus microwave digestion), the power setting of the microwave (from 40- to 100-percent of the maximum power), digestion time (from 5 to 75 minutes in different trials), and other factors. These results demonstrate that the details of the digestion procedure need to be specified, documented, and verified by a QA/QC program to produce accurate and comparable results.

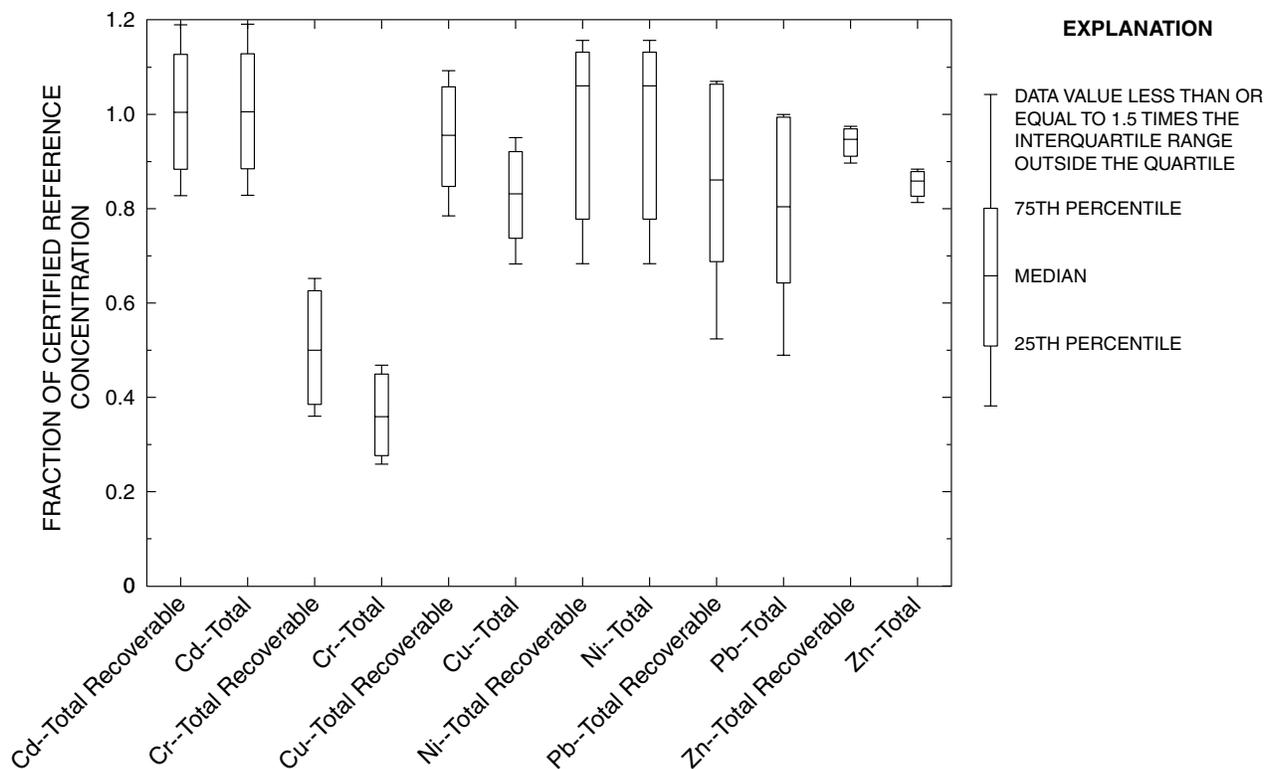


Figure 9. The distribution of variability in median trace-element concentrations measured when different mixtures of digestive agents are used in a standard reference sediment matrix as compared to certified total recoverable and total digestion values (data from Siaka and others, 1998).

Digestion procedure-specific factors are compounded when using sequential extraction to evaluate the potential bioavailability and environmental behavior of sediment-associated trace elements, because several chemical digestion procedures are used in series to determine trace-element concentrations in the different chemical fractions. Lack of uniform protocols for each step of the extraction is a potential source of variability, which precludes direct comparability among results from laboratories that use even slightly different methods and(or) reagents (Fiedler and others, 1994; Quevauviller, 1998). Moreover, variability in results from use of sequential extraction is compounded by the extraction procedures, because each result in the sequence is dependent upon the residual from the previous extraction step.

Potential differences in performance among laboratories are an issue with both suspended and bottom sediment because of sample inhomogeneities and differences in laboratory techniques. The results of an

interlaboratory comparison (fig.10) of analyses of a well-mixed sediment sample by more than 25 professional water-quality laboratories indicates that laboratory performance can be highly variable. The bulk of data ranges from 42 percent to 190 percent of the MPV, and a number of outliers differ by orders of magnitude from the MPV (Long and Farrar, 1995). The large variability in the results of analysis are noteworthy in light of the fact that all of the MPVs are well above current USEPA detection limits for analysis of sediment samples (Dowling, 1999), and that these laboratories, by participating in an interlaboratory comparison, have some components of a QA/QC system (Jones, 1999) in place. Therefore, laboratory performance must be properly documented through a QA/QC program to ensure comparability of data from sample to sample within a study and among data collected from different studies.

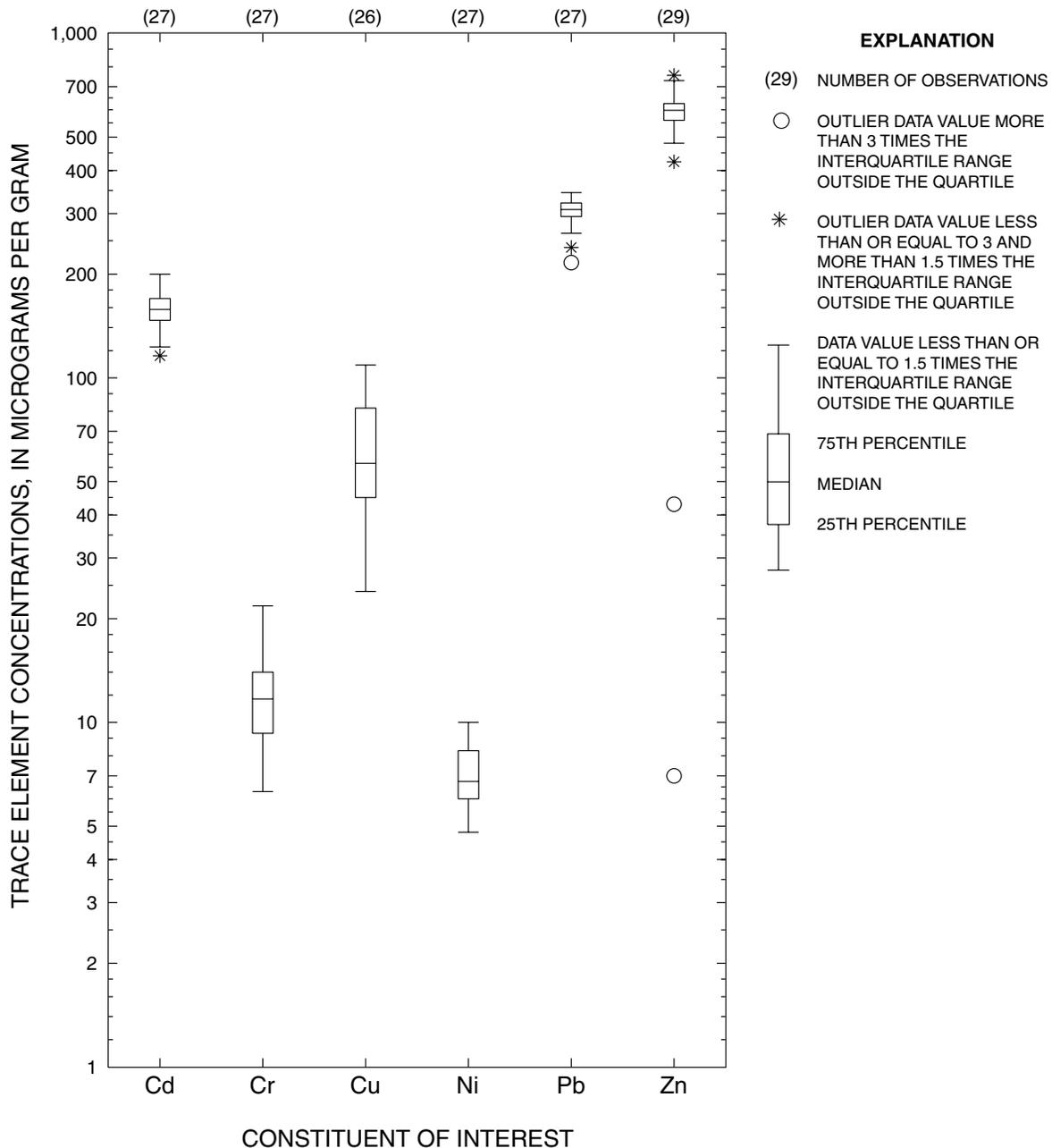


Figure 10. The distribution of total-recoverable trace-element concentrations measured in a standard reference sample of bed material (excluding a far outlier of 0.6 micrograms per kilogram for Cr) by laboratories participating in the USGS interlaboratory evaluation program. Data from Long and Farrar (1995).

Bottom Sediment

Bottom sediment is also referred to as bed sediment, bottom or bed material, bottom or bed solids, mud, muck, or simply just sediment. Bottom sediment consists of the geological, anthropogenic, and biological

material that has been deposited and retained within a sampling site at the time of collection. Unlike the dissolved or the suspended-sediment matrixes, the bottom sediment matrix is not operationally defined by a particle-size separation technique. Although not operationally defined on a physical basis, measured trace

element concentrations are defined by the chemical separation of a digestion or extraction process. As for whole water and suspended sediment, results of chemical analysis of bottom sediment are dependent upon chemical processing (such as total-recoverable digestions, total digestions, and sequential extraction techniques) to extract trace elements for chemical analysis (Tessier and others 1979; Hamilton and others, 1984; Fishman and Friedman, 1989; Fiedler and others, 1994; Kane, 1995). Also, for bottom sediment, the USEPA Toxicity Characteristics Leaching Procedure (TCLP) is sometimes used as a digestion/extraction procedure to assess the capacity for trace elements to leach from bottom sediment (U.S. Environmental Protection Agency, 1992b) and the results of this process may vary from other analytical techniques.

The distribution of trace elements within the bottom sediment of drainage structures, structural BMPs, and receiving waters depends partly upon the chemical and physical processes that control sediment-particle transport. Sediment-bound trace elements can dissolve into the water column, enter the food chain, and have other environmental effects when geochemical conditions (for example, pH, redox, dissolved oxygen, bacterial action) change. Trace elements from bottom sediment can be dispersed over a wide geographical area when hydraulic conditions change. For example, during high flows, water velocities may be sufficient to mobilize the sediment and associated trace elements and move them downstream, where they are redeposited in low-energy depositional zones (Horowitz, 1991; Breault and others, 2000). Therefore, bottom sediment also may be regarded as a major source of suspended-sediment associated trace elements.

In depositional zones affected by highway and/or urban runoff, bottom sediment is commonly characterized as having: a high water content; a distinctive grey to black color; a high organic-matter content —commonly measured as total organic carbon (TOC); a density lower than that of local natural geologic material; and a relatively fine grain-size distribution (Mudre and Ney, 1986; Breault and others, 2000). In contrast, relatively coarse-grained sediment with lower concentrations of TOC and trace elements, which are more characteristic of local natural geologic material, are found in non-depositional environments and in erosional areas (Breault and others, 1998; Breault and Harris, 1997). Consequently, the hydraulic characteristics of the depositional environment define the physical

and chemical characteristics of the bottom-sediment profile. Therefore, the focus of individual studies tend to be grouped into investigations of bulk surficial-sediment quality (usually defined as the top 3-20 centimeters of the sediment profile); bulk core-sediment quality (which generally includes surficial sediment and sediment at depth —below 20 centimeters in the profile); and discrete vertical-profile studies (which are usually used to define the distribution of constituents at depth within the profile).

Benefits

Monitoring the bottom-sediment matrix may provide information for trace-element studies with various objectives. Historically, chemical analysis of bottom sediment has provided information for the study of geochemical cycling, temporal variability, and trend analysis (on the order of months to years), as well as the study of biological effects of sediment-associated trace elements (Horowitz, 1995; Buckler and Granato, 1999). Surficial sampling of the sediment column is used primarily in studies of the spatial distribution of trace elements. Sediment samples at depth may be used to establish local trace-element baseline levels, to delineate historical changes in sediment-associated trace-element concentrations, or to determine average sediment and sediment-associated trace-element loading and(or) deposition rates. Bottom-sediment sampling can provide regional geochemical reconnaissance data for use in identifying environmental effects of point and nonpoint sources of contamination (Webb, 1978; Fauth and others, 1985).

The use of bottom-sediment samples offers several logistical advantages over sampling water and(or) suspended sediment as a trace-element-monitoring matrix. When compared to suspended-sediment monitoring, it is easier to collect the requisite mass of bottom sediment required for an analysis, especially when suspended-sediment concentrations are less than 100 mg/L in the water column. Because bottom-sediment samples may represent a time-integrated history of local deposition, a single core may represent water-quality conditions on a time scale from weeks to years. A single water or suspended sediment sample, on the other hand, may represent water-quality conditions only on a time scale from minutes to hours. For example, Callender and Van Metre (1997), analyzed sediment cores from a number of lakes and reservoirs across the midwest and southeast United

States. They measured Pb concentrations in vertical sediment-core-profiles that recorded the history of the use and subsequent ban of leaded gasoline between the early 1900s and the mid-1990s. Furthermore, concentrations and accumulation rates of Pb in cores collected at different sites showed the effects of surrounding land use. Pb accumulation rates in cores from urban sites were about 20, 10, and 5 times the Pb accumulation rates measured in cores from rural, agricultural, and suburban sites, respectively. Use of bed sediment, therefore, may provide useful information as a reconnaissance tool to identify potential sites for more intensive stormwater monitoring efforts, and as a time-integrating component of storm-runoff monitoring studies to put results from short-term runoff monitoring programs into historical perspective.

The merits of monitoring trace elements by sampling bottom-sediment are apparent from information available in the highway- and urban-runoff literature. The effectiveness of BMPs commonly can be inferred from examination of bottom-sediment quality within the drainage systems and receiving waters. For example, Yousef and others (1984) found that bottom sediment under a bridge with scuppers that drain directly to a lake had concentrations of Cr, Cu, Ni, Pb, and Zn that were about 2 to 4 times the concentrations in bottom sediment under a second bridge, which had drains diverting runoff to the local land surface. These two bridges were along the same and highway over the same lake. Dupuis and others (1985) also detected enriched metal concentrations in bottom sediment near highway outfalls. Schiffer (1989) determined that bottom-sediment samples collected in wetlands near highways with structural BMPs, such as holding ponds, showed lower concentrations of trace elements than samples collected in wetlands near highways without structural BMPs. Legret and others (1995) measured trace elements in runoff and in surficial- and core-sediment samples from a detention pond. They found that concentrations of Cd, Cr, Cu, Ni, Pb, and Zn were 2-10 times higher in runoff than in surficial sediment, which in turn had concentrations 2-5 times higher than deeper sediment. These results indicate that this detention pond was only partially effective. Guo, (1997) measured the depth and sediment chemistry of an 18-year-old detention basin to determine the efficiency of the basin for removing trace elements and sediment. He found that the basin was effective in removing sedi-

ment, but not as effective in removing trace elements in comparison to predicted removal efficiencies for these constituents in the detention basin (Guo, 1997).

Use of the bottom-sediment matrix also can provide information about the effects of trace elements in highway runoff on the watershed scale. Mudre and Ney (1986) studied sediment deposition in six small watersheds in Virginia crossed by a relatively low-traffic-volume highway (6,000 to 15,000 vehicles per day). They found that concentrations of trace elements in bottom sediment downstream of the highway outfall were controlled by explanatory factors including overland-flow distance from the pavement to the stream, stream velocity, and organic content of the sediment. Also, they found that high flows during a wet year washed away local contaminated deposits, and concluded that trace-element concentrations vary with precipitation totals from year to year. Callender and Rice (2000) examined correlations between population density, traffic density, and concentrations of Pb and Zn in bottom-sediment samples from the Chattahoochee River Basin that has an urban-to-suburban-to-rural-land use gradient. They found that traffic density can be used as a predictor of sediment-associated Pb and Zn concentrations. This is particularly interesting given the fact that the effects of local traffic density were apparent in downstream sediment concentrations measured in this large watershed (52,840 square kilometers) that stretches from the Atlanta Georgia Metropolitan Area to the Gulf of Mexico. Tuit and others (2000) found that concentrations of platinum-group elements (PGEs) in Boston Harbor sediment were five times greater than background PGE concentrations in sediment and concluded that this enrichment was caused by uncontrolled runoff from roads and highways that carry residuals from automotive catalytic converters.

In a review of available studies on the effects of runoff on aquatic biota, Buckler and Granato (1999) determined that sediment deposits from highway outfalls correlated with measured concentrations of trace elements in biological tissue and with effects on biodiversity in receiving waters. For example, van Hassel and others (1980) found direct correlations among traffic density, trace-element concentrations in stream sediment, and trace-element concentrations in benthic insects and fish. Breault and others (2000), using Canadian sediment-quality guidelines (Ecosystem Conservation Directorate Evaluation and Interpretation Branch, 1995), found that concentrations of trace

elements were in the "probable range" for adverse effects on benthic organisms at 77 percent of 135 surficial-sediment-sampling sites in the Lower Charles River Basin, Massachusetts, where the source of sediment is largely urban and highway runoff. Among the trace elements studied by Breault and others (2000) at 135 sites, Pb, with 123 sites (91 percent); Cd, with 113 sites (84 percent); Zn, with 112 sites (83 percent); Cu, with 99 sites (73 percent); Ni, with 85 sites (63 percent); and Cr, with 72 sites (53 percent) exceeded the highest tier "probable range" concentrations as defined by the Canadian sediment-quality guidelines.

Technical Concerns

Although chemical analysis of the bottom-sediment matrix has many benefits, large spatial and temporal variability at the sampling site and improper sampling and processing also are of concern when this matrix is used in trace-element-monitoring programs. Differences in the physical and chemical characteristics of bottom sediment from place to place and at different depths are expected, because a variety of hydrologic and chemical processes can affect deposition, resuspension, and chemical partitioning of trace elements (Baudo, 1990; Forstner, 1990; Allen, 1995; Stumm and Morgan, 1996). Measuring trace-element concentrations that are representative of a sampling site, therefore, requires a number of sediment samples from different points within a site. The choice of a statistical procedure for characterizing the site with a finite data set depends on the degree of confidence required to meet particular program goals (Keith and others, 1983; Hakanson, 1984; Baudo, 1990). The confidence limit is affected by the number of samples to be collected in a particular study area, how the data are to be used, and the level of chemical detail required. Regardless of the requisite degree of confidence, it is better to collect a group of subsamples to generate a final composite sample than to collect a single arbitrary sample as being representative of a sampling site. Methods for the physical collection of representative bottom-sediment samples with the associated trace elements are described by USEPA (1982), Baudo (1990), Mudroch and MacKnight (1991), Shelton and Capel (1994), and Radtke (1997).

Once representative sediment samples are collected, appropriate laboratory techniques must be applied to ensure that measured trace-element concentrations are unbiased, representative of the sample, and comparable. As for whole-water and suspended-sediment samples, there are a number of digestion techniques, including total and total recoverable, that may cause systematic differences in measured concentrations of trace elements in the same sample. Also, as for suspended-sediment samples, there are a number of accepted (but unstandardized) sequential-extraction techniques that may cause systematic differences in measured concentrations of trace elements in the same sample. Even when comparable digestion-extraction methods are used, the artifacts cause by interlaboratory variability (fig. 10) may be expected to introduce additional uncertainty when different data sets are combined for regional or national synthesis. Also, there are a number of technical issues that may confound the interpretation of trace-element data from the bottom-sediment matrix, even when appropriate protocols and QA/QC systems are used.

Sediment-associated trace-element concentrations commonly are a function of the grain-size distribution in sediment samples (Forstner and Wittmann, 1981; Salomons and Forstner, 1984; Horowitz and Elrick, 1987, 1988; Horowitz, 1991). The effect of grain size on sediment trace-element chemistry is so substantial that, if grain-size variations amongst samples are not taken into account, a study may produce misrepresentative spatial distributions (Horowitz and Elrick, 1987; Horowitz, 1991). There is a long-standing controversy over what represents the most appropriate grain-size range for mapping trace-element distributions in bottom sediments in various depositional environments (Banat and others, 1972; Copeland, 1972; Renzoni and others, 1973; Cameron, 1974; Chester and Stoner, 1975; Webb, 1978; Jenne and others, 1980; deGroot and others, 1982; Ackermann and others, 1983; Beeson, 1984; Horowitz and Elrick, 1987, 1988). The two size ranges most commonly used for trace-element analysis are less than 180- μm (typical for geochemical exploration surveys) and less than 63- μm (typical for water-quality studies). For example, the USGS NAWQA program analyzed the less than 63- μm fraction in bottom-sediment samples collected from 20 different study

units across the conterminous United States in order to increase the comparability among trace-element analyses of sediment samples from rivers with widely varying grain-size distributions (Gilliom and others, 1995; Rice, 1999).

For highway- and urban-runoff studies, however, analysis of unsieved bulk samples and(or) a variety of different size fractions (including the large grain size fractions) may provide information necessary for evaluating the potential effectiveness of structural BMPs and the effect of highway runoff on receiving waters. Information about the mass distribution of different grain sizes (and associated trace-element concentrations) provides information about the potential for removal of sediment and associated trace elements by BMPs that utilized physical sedimentation for water-quality treatment (Harrison, and Wilson, 1985b; 1985c; Legret and others, 1995; Stone and Marsalek, 1996; Marsalek and others, 1997; Roger and others 1998). Unsieved bulk samples may be appropriate for reconnaissance studies because the full spectrum of the grain-size distribution commonly is transported in highway and urban runoff, and because high concentrations of trace elements are typically measured throughout the grain-size spectrum in suspended and bottom sediments (Legret and others, 1995; Sansalone, Buchberger, and Al-Abed 1996; Sansalone, Buchberger, Koran, and Smithson, 1996; Roger and others, 1998). For example, Kobriger and Geinopolos (1984) used manual street sweeping and subsequent wet vacuuming (to obtain ultrafine sediment samples) a number of times at sites on four different highways to collect road dust as part of an investigation of the sources and migration of highway-runoff constituents. They found that concentrations of Cd, Cr, Cu, Ni, Pb, and Zn were relatively consistent among different grain-size fractions (with the exception of the fraction that was larger than 3,350 μm). Therefore, bulk trace-element concentrations may be considered representative and comparable for runoff studies (fig. 11) and the use of bulk-sediment samples for analysis of trace elements could reduce potential artifacts introduced by a sieving process. If properly done, sieving samples to obtain grain-size specific trace-element concentrations provides more quantitative information at each site. In reconnaissance studies, however, use of bulk samples

may allow for more spatial definition at and between sites because of the reduced processing and analysis cost for each sample collected.

Undisturbed bottom sediment can contain a historical record of sediment quality if a sufficiently large and stable depositional zone can be found, sampled, and chemically analyzed (Forstner and Wittmann, 1981; Horowitz, 1991). Typically, the ages of different strata (sediment layers) within a core are estimated using techniques such as radiometric age dating (Horowitz, 1991). Physical and chemical factors such as resuspension, bioturbation, diagenesis, and sediment focusing, however, if unaccounted for, can bias the interpretation of trace-element profiles. High flow velocities during the period thought to be represented by the core potentially can resuspend and thereby remove and(or) mix a number of strata (Lick, 1994). Resuspension, therefore, can confound meaningful interpretation of trace-element-concentration data from core samples. Bioturbation or the mixing of strata by organisms living in and on the sediment also can affect the distribution of sediment-associated trace elements (Baudo, 1990). Chemical and biological reactions that alter sediment after deposition (diagenesis) can affect the distribution of trace elements. For example, Callender (2000) measured sediment accumulation rates and Fe concentrations in interstitial waters from the upper 9 cm of two sediment cores collected from the Cheyenne River in South Dakota. One core was collected during a year of relatively high sediment deposition (more than one centimeter per year) and the other during a year of lower sediment deposition. Fe concentrations in the interstitial water were found to be higher from the core collected during the period of lower sediment deposition than they were in the rapid deposition sample (fig. 12). Higher concentrations of Fe in the interstitial waters indicate increased reduction of ferromanganese oxyhydroxides by microbiologically mediated reactions that take place in the absence of oxygen. Trace elements commonly are associated with ferromanganese oxyhydroxides in bottom sediment and can be released upon their reduction. Low sediment-accumulation rates, which allow sufficient time for oxygen depletion, reduction of ferromanganese oxyhydroxides, and subsequent redistribution of trace elements, therefore, must be considered for interpretation of trace-element-concentration data from core samples. In urban and highway runoff BMPs, which

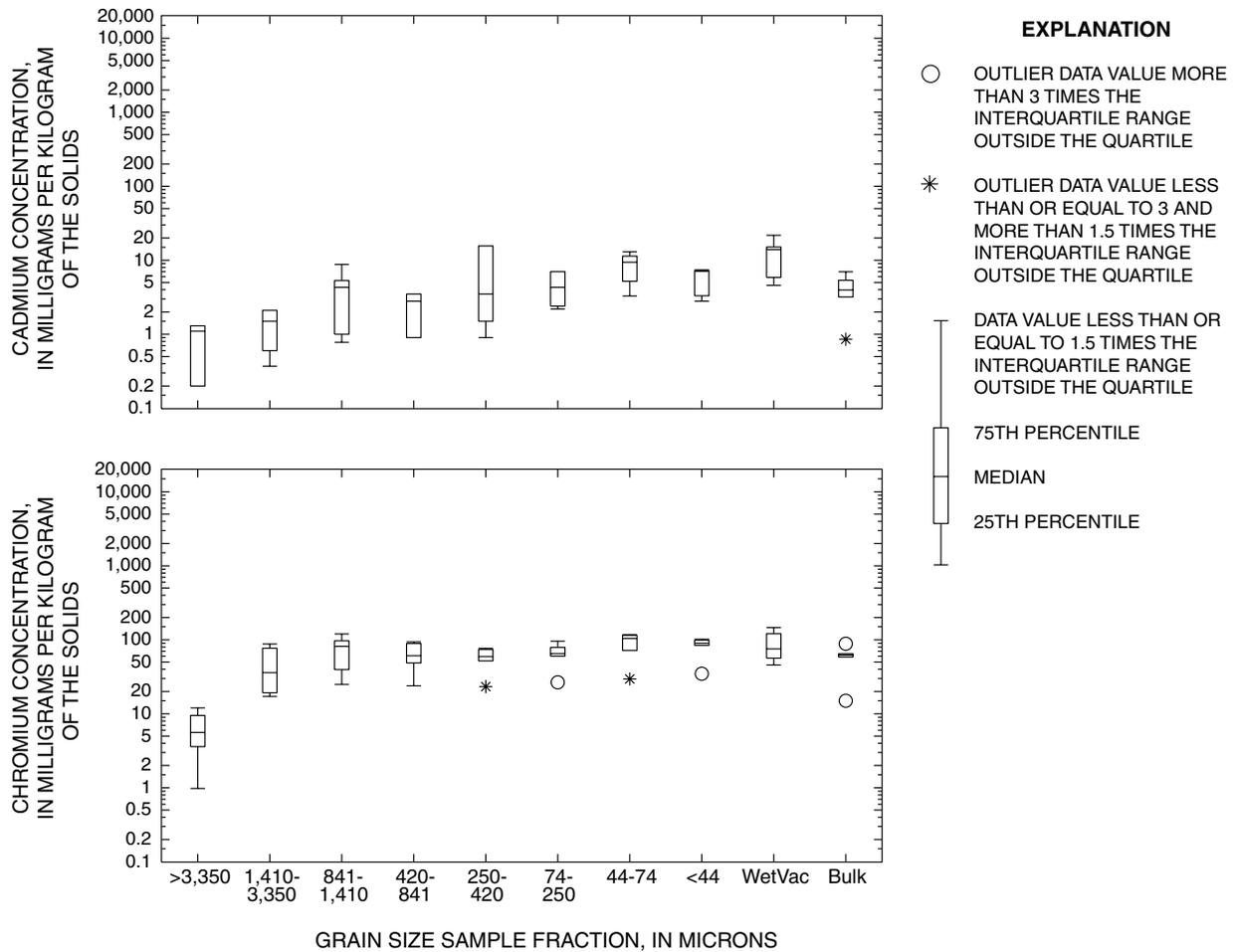


Figure 11. The distribution of total recoverable trace-element concentrations measured in road-dust samples collected by manual street sweeping and subsequent wet vacuuming (to obtain ultrafine sediment samples) at four highways in the conterminous United States by the FHWA. Data from Kobriger and Geinopolos, (1984).

are designed to treat stormwater by sedimentation, the potential for the redistribution of trace elements in the sediment column may be minimized by high-sediment deposition rates. Trace-element data from core samples collected from sedimentation structures and receiving waters may not be comparable because sedimentation rates may be very different. Differences in effective sediment-deposition rates within a water body also may be a potential source of error in the interpretation of profile data for trace-element concentrations. For example, sediment focusing is the process by which fine-grain sediment and associated chemical constituents are resuspended and redistributed spatially from

shallow to deeper zones by currents and episodic storms. Researchers typically use the ratio of the measured ^{137}Cs and (or) ^{210}Pb isotope(s) in the sediment to concentrations expected from atmospheric deposition as a measure of the sediment focusing factor to correct for this phenomenon (Wong and others, 1995; Callender and Van Metre, 1997). Finally, to compare the historical trace-element profile to background trace-element concentrations (with respect to potential anthropogenic inputs in the area of interest), it is necessary to obtain trace-element concentrations in soils that are representative of the watershed of interest (Callender and Rice, 2000).

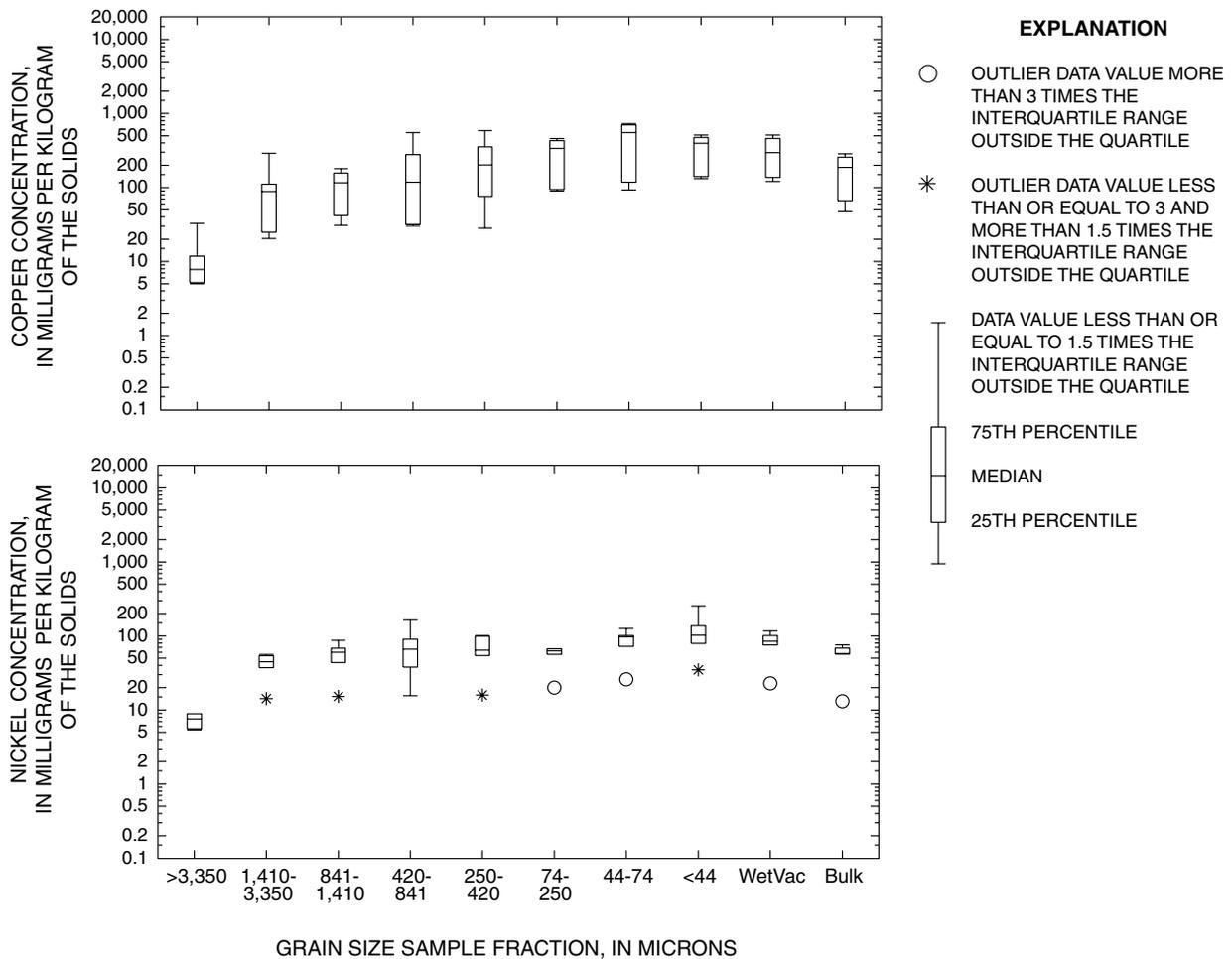


Figure 11. The distribution of total recoverable trace-element concentrations measured in road-dust samples collected by manual street sweeping and subsequent wet vacuuming (to obtain ultrafine sediment samples) at four highways in the conterminous United States by the FHWA. Data from Kobriger and Geinopolos, (1984)— *Continued*.

Biological Tissue

Collection and chemical analysis of biological tissues may represent one of the most direct measures of trace-element bioavailability in an aquatic ecosystem (Crawford and Luoma, 1993; Meador and Gurtz, 1994; Buckler and Granato, 1999). Trace-element concentrations in tissue are dependent upon concentrations of trace elements in sediment and the water column as well as on the local geochemistry (Luoma and Fisher, 1997; Bricker, 1999), habitat (Meador and Gurtz, 1994), and many other physical and biological factors (Crawford and Luoma, 1993; Meador, Hupp, and

others, 1993; Luoma and Fisher, 1997). Chemical analysis of tissues has been used in local, regional, and national water-quality studies in conjunction with the analysis of water and sediment quality to examine the relations between trace constituents in the environment and bioaccumulation in aquatic organisms (Crawford and Luoma, 1993; Gurtz and Muir, 1994; Meador and Gurtz, 1994). When chemical data from the analysis of tissues, water, and sediment are used in conjunction with other biological indicators (such as community assessments), effects on individuals and populations of aquatic biota also can be examined.

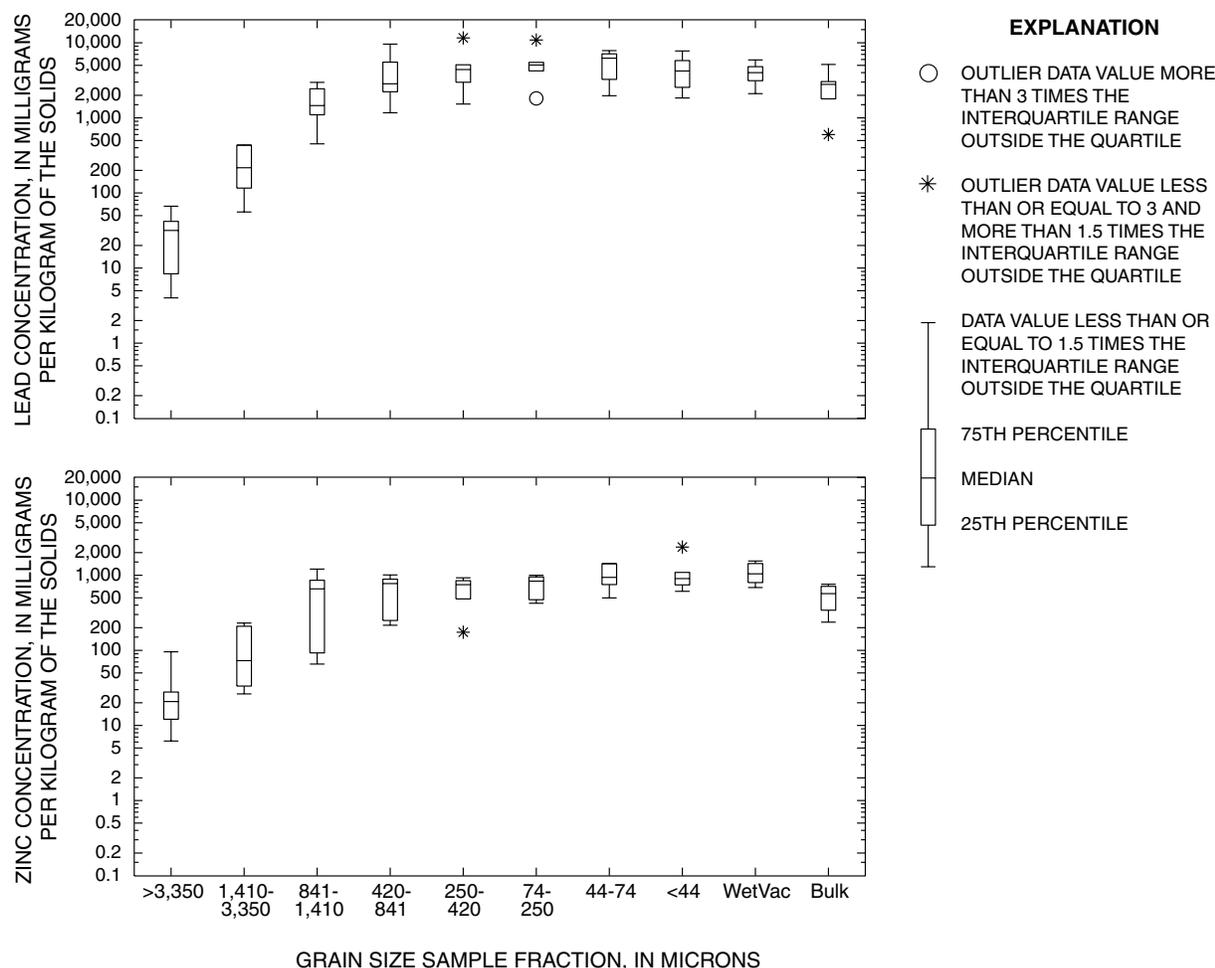


Figure 11. The distribution of total recoverable trace-element concentrations measured in road-dust samples collected by manual street sweeping and subsequent wet vacuuming (to obtain ultrafine sediment samples) at four highways in the conterminous United States by the FHWA. Data from Koberger and Geinopolos, (1984)— *Continued*.

Benefits

Studies that utilize the chemical analysis of tissue samples from different organisms provide information about cause-and-effect relations because each taxon responds differently to changes in local geochemistry, habitat, food, mobility, physiology, and life history (Gurtz, 1994). The size, weight, and life stage of available organisms vary seasonally and from year to year with natural conditions. For example, comparison of the characteristics of algae, aquatic invertebrates (including aquatic insects, mollusks, crustaceans, and worms), and fish indicates the different types of information that can be obtained from different biological tissue matrixes. Algae have a short life span (days to weeks), they readily exchange constituents with the water column and sediment, and being

sedentary, reflect local water and sediment quality in the short term (Porter and others, 1993, Gilliom and others, 1995). In comparison, aquatic invertebrates have longer life spans (months to years) than algae, are abundant at many sites, accumulate trace elements proportionally to environmental concentrations, live in close association with bottom sediment, and are not highly mobile from area to area. Therefore, aquatic invertebrates also are good indicators of local water and sediment quality (Crawford and Luoma, 1993; Cuffney and others, 1993a, 1993b; Gilliom and others, 1995). Fish have relatively long life spans (years to decades), can be highly mobile, and therefore, may be indicative of long-term watershed health (Meador, Cuffney, and Gurtz, 1993, Gilliom and others, 1995).

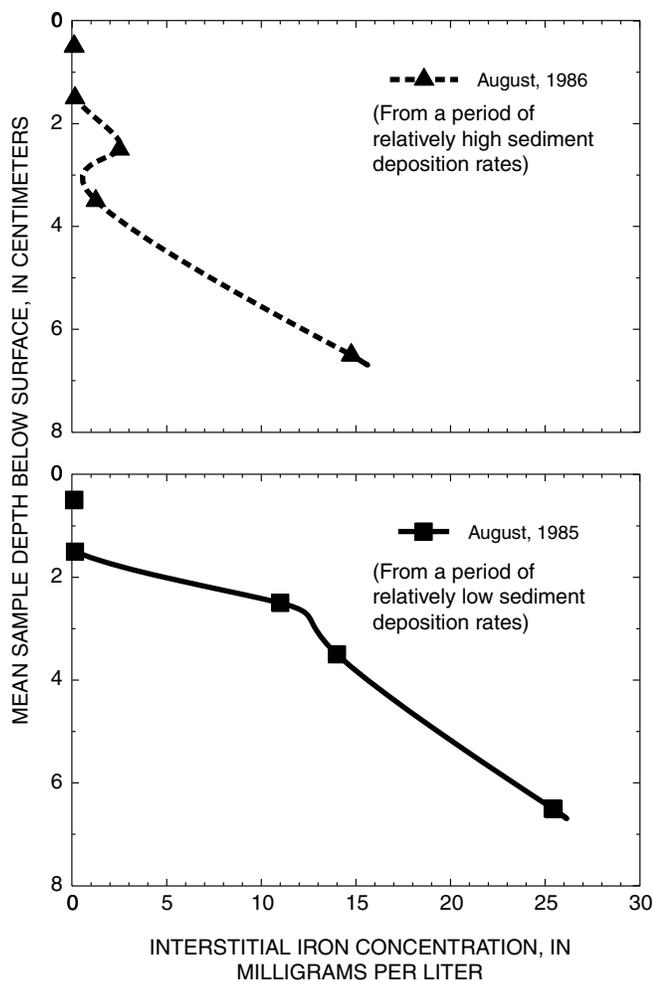


Figure 12. The vertical profiles of interstitial iron concentrations for two annual sampling dates at a site in the Cheyenne River Embayment of Lake Ohae, South Dakota, indicating the effect of sediment deposition rates on phase transformation and subsequent redistribution (modified from Callender, 2000).

Therefore, it is important to consider the characteristics of different organisms when evaluating biological tissue matrix-data.

Tissue analysis has been used successfully as a component of highway- and urban-runoff-quality monitoring to assess the effects of highway runoff on aquatic biota (Buckler and Granato, 1999). In many studies, increased trace-element concentrations were detected in the tissues of animals and plants exposed to soils and sediment in highway environments, even from sites near highways with low traffic volumes (Gish and Christensen, 1973; Dupuis and others, 1985; Birdsall and others, 1986; Davis and George, 1987; Baekken, 1994, Cooper and others, 1996; Dupuis and

others, 1999). Trace-element concentrations in tissue samples collected from aquatic communities near highway outfalls were elevated above background concentrations in the same species, but elevated concentrations commonly represented local "hot spots" near discharges rather than widespread downstream contamination (van Hassel and others, 1980; Dupuis and others, 1985; Baekken, 1994; Maltby and others, 1995; Cooper and others, 1996). For example, Yousef and others (1984) studied the effects of runoff from two bridges for a busy highway (with an average daily traffic volume of 50,000 vehicles per day) across a lake in Florida. In this study, trace-element concentrations in tissues of *Spirogyra* (an alga) and *Hydrilla* (an aquatic plant) were about 150 to 320 percent greater under the bridge that drained directly to the lake than under the bridge that drained to the local land surface (fig. 13).

Review of available highway-runoff-quality literature (Buckler and Granato, 1999) indicates that highway studies can successfully utilize trace analysis of tissues from many of the same organisms used in other national, regional, and local water-quality studies, including algae (Dupuis, others, 1985; McHardy and George, 1985), aquatic invertebrates (van Hassel and others, 1980; Dupuis and others, 1985; Mudre, 1985; Madigosky and others, 1991), and fish (van Hassel and others, 1980; Ney and van Hassel, 1983; Dupuis and others, 1985; Mudre, 1985). Although tissue analysis does not explicitly define the toxicity of trace constituents to the organisms sampled in these runoff studies, several studies noted the potential for bioaccumulation of trace elements higher in the food chain (Gish and Christensen, 1973; Birdsall and others, 1986, Cooper and others, 1996). Although the tissue matrix would seem to provide a simple answer to the question of bioavailability, many chemical and biological factors complicate representative monitoring of this matrix.

Technical Concerns

As for other matrixes used for analysis of trace elements, appropriate sample collection and processing methods are necessary to ensure that the data collected are representative and comparable. Organisms must be collected using appropriate biosampling methods, and the tissues collected from these organisms must be handled using suitable trace-element-sampling methods. To ensure the quality of data collected, it is important to ensure that sampling crews are properly trained in

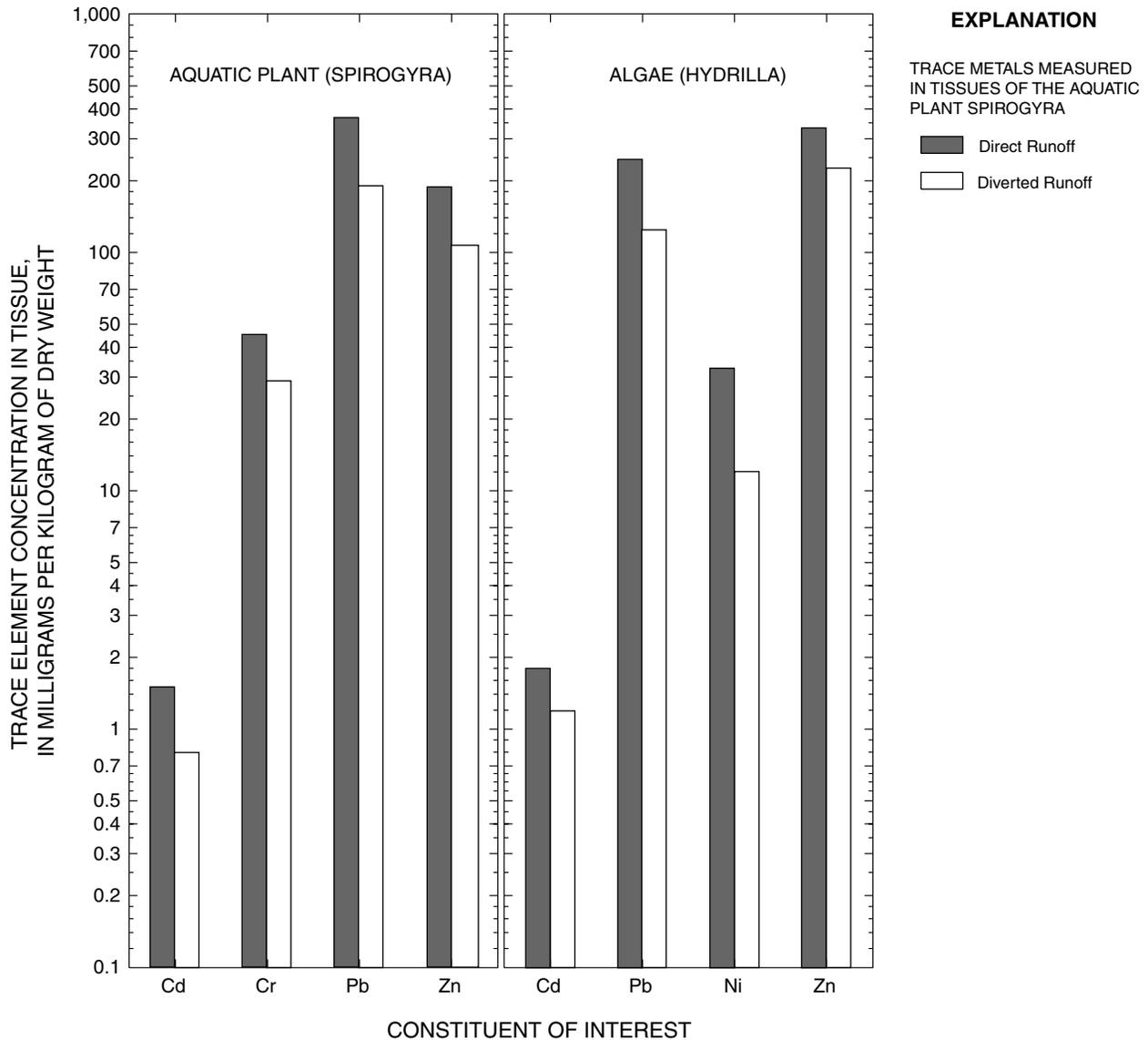


Figure 13. The concentrations of trace elements measured in tissue samples collected from a lake in Florida at two bridge sites: one with scuppers—which drain to the lake (direct runoff)—and one with a drainage system that discharges runoff to the local land surface (diverted runoff). Data from Yousef and others (1984).

biological sample-collection-methods; that samples are processed using clean methods; and that equipment, storage containers, and preservation methods and materials do not affect trace-element concentrations in biological tissues (Katz, 1984; Crawford and Luoma, 1993; Hoffman, 1996). The potential for trace-element contamination during collection, processing, shipment, sample preparation, and storage may be considerable for biological tissues (Crawford and Luoma, 1993). Also, it is important to use appropriate and consistent laboratory methods for matrix digestion

and analysis of tissues, and to be aware that different digestion or extraction methods are available (Hoffman, 1996).

Biological factors to consider when evaluating the possible use of tissue analysis of one or more organisms include:

- measurable tissue concentrations that vary with environmental concentrations and exposure,
- uptake of constituents that is relatively rapid in comparison to release,

- tissue concentrations with low variability among individuals collected in order to be representative of site conditions at a given time period,
- availability of organisms that are hardy enough to withstand contaminant concentrations of interest,
- organisms that do not commonly travel beyond the immediate area,
- organisms that are abundant and widespread in the study area, so that they can be repeatedly harvested for analyses,
- organisms that can be collected, and that are large enough to meet sample-size requirements;
- organisms that are easy to find and hardy enough to withstand captivity during controlled laboratory studies, and
- a species for which biological and toxicological information is available for comparison (Crawford and Luoma, 1993).

Biological characteristics of the different organisms selected for use in a monitoring program determine the suitability of the tissues collected to determine food-chain concentrations and accumulation rates. Also, contaminant concentrations in tissues only are comparable within the same species, and for organisms at the same life stage, reproductive condition, size, weight, and sex. For example, to address comparability problems among available test species, the USGS NAWQA program developed a National Target Taxa List (NATT) to define the organisms that local teams could target for biological monitoring efforts, and a decision tree to prioritize choices among available organisms within the context of regional and national sampling objectives (Crawford and Luoma, 1993).

Different tissues within each organism accumulate different constituents selectively, so the type of tissue used for analysis is a major factor for consideration in the interpretation of tissue matrix data and is as important as variations among organisms. For example, Ney and van Hassel (1983) noted that the amount of trace-element uptake by organisms in streams affected by highway runoff depended upon the various site characteristics controlling the availability of trace elements in the local environment, on the species (because fish species associated with sediment had higher trace-element body-burdens than species associated with the water column), and on the specific affinities of the different tissues within a fish. To establish that tissue concentrations are in fact affected by a runoff source, it

also is important to establish background tissue concentrations with a local control and to compare both concentrations with natural baseline concentrations in tissues of similar organisms from streams with minimal anthropogenic influences (Buckler and Granato, 1999).

Variation in habitats and the diversity of biological communities adds uncertainties to comparisons of tissue concentrations from site to site, especially at regional and(or) national scales (Meador, Hupp, and others, 1993, Crawford and Luoma, 1993). The complexity of the nation's freshwater environments; variations in flow, temperature, and water quality from season to season; and differences in surrounding land use, physical and hydrologic features, complicate the use of tissue analysis in a consistent manner on a national or regional scale (U.S. Environmental Protection Agency, 1986b). Therefore, extensive field records, including information such as sampling location, the date, the organism, physical characteristics (such as age, size, tissue type, and sex) are necessary to identify the many explanatory variables that can affect the concentrations of trace elements in tissue samples (Crawford and Luoma, 1993). As with other trace-element-monitoring matrixes, it is important to employ a comprehensive program of QA/QC (U.S. Environmental Protection Agency, 1986b; Buckler and Granato, 1999).

Sources

Source-matrix monitoring is the practice of collection, processing, and chemical analysis of materials that may contribute constituents to highway and urban runoff. If a comprehensive analysis of constituents in stormwater and potential source materials is available, the concentrations of certain indicator constituents may indicate the relative magnitude of different sources. Qualitatively, source matrixes for highway and urban runoff include atmospheric deposition, soil, highway-construction materials, vehicle contributions, highway-maintenance materials, natural (from animals and plants) debris, and anthropogenic litter. These sources commonly are integrated on paved surfaces as dust and dirt accumulations that provide a primary source of trace elements in runoff. Source-matrix monitoring is a valuable method for identifying contaminants of concern, fingerprinting different potential sources, identifying the relative magnitude of potential sources, and estimating loads of constituents from these

sources. The value of source-matrix-monitoring information is indicated by the fact that many of the original studies that examined sources of runoff constituents (Sartor and others, 1972; Shaheen and Boyd, 1975; Christensen and Guinn, 1979) still are cited widely more than 20 years after publication (Brinkmann, 1985; Barrett and others, 1993; Armstrong, 1994; Young and others, 1996; Callender and Rice, 2000).

It is important to note that the physical and chemical properties of source matrixes commonly change with time. Since the early 1970s, many source matrixes have changed, and implementation of environmental legislation has resulted in the improvement of air quality, the quality of atmospheric deposition, and the quality of receiving waters (U.S. Environmental Protection Agency, 1997, 1999). During the past 30 years, changes also have been made in highway construction materials, highway-maintenance materials (pesticides, herbicides, and deicers), and maintenance practices that affect the environmental availability of these materials (Barrett and others, 1993; Armstrong, 1994; Young and others, 1996). Materials used in fuels, lubricants, automotive parts, and exhaust systems also have been changing to improve performance, meet changing safety criteria, and reduce emissions of priority pollutants (U.S. Environmental Protection Agency, 1999). A number of studies have detected trace elements that are not commonly studied in water-resource investigations. For example, Ti and tungsten (W) from studded tires (Bourcier and others, 1980); trace elements from automotive catalysts—including Pt, Pt, rhodium (Rh), cerium (Ce), lanthanum (La), neodymium (Nd), and zirconium (Zr)—(Helmers, 1996; Zereini and others, 1997; Tuit and others, 2000); and Cu, Sb and tin (Sn) from asbestos-free brake linings (Armstrong, 1994; Reifenhauer and others, 1995) have been detected in runoff, receiving waters, and biota. Concentrations and potential loads of trace elements from various sources differ among studies, but similar source matrixes commonly are identified as primary contributors of trace elements in highway and urban runoff. If comprehensive and timely analysis of trace elements from various potential sources is available, this information can be used to identify emerging contaminants; to identify likely sources of trace elements detected in water, sediment, and biota; and to estimate relative contributions from different sources.

It is especially important to apply good sampling and analytical design as well as an extensive QA/QC program to the analysis and interpretation of the results of source-monitoring programs. Small errors in the measurement of contaminant sources can be magnified by many times when estimates of annual and(or) areal loads are calculated. Confidence in the results of source-matrix monitoring depends on many of the same factors that are necessary for quantification of trace elements in other matrixes. It is necessary to collect samples representative of the source; to collect, process, and analyze the samples in a way that will not introduce sampling artifacts; and to collect and publish information on a substantial QA/QC program (Jones, 1999). If reliable source-matrix-monitoring data are available within the context of a national or regional highway-runoff database, quantification of potential sources may be useful in explaining some of the large variations in concentrations and the loads of highway-runoff constituents from site to site and season to season and year to year.

Vehicular Sources

Fuel and vehicle exhaust contain a number of trace elements that may be entrained in runoff and transported to receiving waters. The most obvious example is the dramatic increase and decrease of aquatic Pb concentrations, which correspond to the use and subsequent elimination of leaded fuels (Callender and Van Metre, 1997). Similarly, in a recent highway-runoff study, Marsalek and others (1997) found that Pb concentrations in bridge runoff were about 10 percent of the average Pb EMCs recorded in earlier runoff studies, whereas the EMCs for Cd, Ni, and Zn were comparable to historical values. Marsalek and others (1997) reported, however, that EMCs for Cu were about twice the historical values. Source-matrix studies (Hillemann and others, 1991; Hee, 1994) reveal that fuels and exhaust contain a number of elements in measurable concentrations (including Al, Br, calcium (Ca), cobalt (Co), Fe, potassium (K), lithium (Li), Mg, Mn, Na, Pt, Sb, strontium (Sr), Ti, and V), in addition to the commonly studied trace elements (Cd, Cr, Cu, Ni, Pb, and Zn). Knowledge of the chemical constituents in fuel and exhaust also can indicate the potential speciation of trace elements in precipitation and runoff. For example, Laxen and Harrison (1977) noted that auto exhaust contains inorganic complexes as well as metal

chlorides, bromides, oxides, sulfides, and ammonium halides, most of which have relatively high water solubility.

Lubricants, including motor oil and grease, are also a potential source of trace elements in runoff. Hunter and others (1982) measured trace elements in used crankcase oil and found relatively high concentrations of Cr (11–16 mg/kg), Cu (32–190 mg/kg), Ni (9–12 mg/kg), Pb (10,500–16,600 mg/kg), and Zn (860–6,280 mg/kg). Concentrations of Zn are expected to be relatively high in lubricants because Zn commonly is used as a stabilizing additive (Yousef and others, 1985b). Concentrations of Cd in motor and lubricating oils are expected to be about 0.2 and 0.1 mg/kg, respectively (Lagerwerff and Specht, 1970; Falahi-Ardakani, 1984). In a review of semivolatile and volatile organic compounds in highway and urban runoff, Lopes and Dionne (1998) reported that oil and grease concentrations in urban stormwater ranged from about 1 to 480 mg/L, and concentrations of oil and grease associated with suspended sediment, bottom sediment, and urban soils ranged from about 8 to 507,000 mg/kg. Therefore, the use of organic tracers may be useful in assessing the predominance of lubricants as a potentially substantial source of trace elements in runoff. Technical concerns for monitoring organic chemicals in runoff are discussed by Lopes and Dionne (1998).

The contributions of trace elements from automotive brake materials depend upon the brake design, the road geometry and traffic intensity. The composition of automotive brakes has been changing throughout the period of record for highway-runoff studies because of regulatory changes (Armstrong, 1994). Hildemann and others (1991) reported measurable concentrations of a number of elements in brake-dust samples (including Al, Br, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Ni, Pb, Pt, Sb, Sr, Ti, V, and Zn). Helmers (1996) reported measurable concentrations of Sb and Sn in the roadside environment and attributed the presence of these trace elements to the increased use of asbestos-free brake linings. Legret and Pagotto (1999) reported Cd, Cu, Pb, and Zn concentrations in European brakes of about 2.7; 142,000; 3,900; and 21,800 mg/kg, respectively. In comparison, Armstrong (1994) analyzed 20 different brake pads from vehicles in the United States and found concentration ranges of about 200–205,000; 100–119,000; and 100–188,000 mg/kg for Cu, Pb, and Zn, respectively. Although these concentrations are high, and may represent a substantial source of trace elements in

urban runoff, the geometry of limited-access highways should minimize brake use between exits unless traffic volumes are high. For example, Legret and Pagotto (1999) calculated loads from different sources and noted that concentrations of brake-associated trace elements were lower than expected (on the basis of brake-life data for different vehicle types) because of the relatively low braking frequency on the section of limited-access highway that they studied. This case indicates the influence of highway characteristics on potential brake-associated trace-element loads and the potential for variability in measured trace-element concentrations with the proximity of a given highway site to an exit.

Tire-wear particulates are a noted constituent of road dust and of suspended sediment in runoff; these particulates contribute trace elements to runoff and receiving waters. As with brakes, Hildemann and others (1991) reported concentrations of a number of elements in tire-wear particulates including Al, Br, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Pt, Sb, Sr, Ti, V, and Zn. Legret and Pagotto (1999) reported Cd, Cu, Pb, and Zn concentrations in tire material of about 2.6, 1.8, 6.3, and 10,250 mg/kg, respectively. In comparison, Falahi-Ardakani (1984) reported much higher concentrations of Cd (about 20–90 mg/kg) in tire material. To put these concentrations in context, Christensen and Guinn (1979) calculated tread wear to estimate Zn loads from tires. They estimated that a typical tire (of diameter 65 cm and width 15 cm) would produce about 3,200 grams of tire particulates and (using a concentration of 7,300 mg/kg of Zn in tire rubber) about 23,360 mg of Zn over a 32,000-kilometer tread life. They calculated that each vehicle, therefore, would be expected to produce about 400 mg of tire particulates, including 3 mg of Zn, per kilometer. As with brakes, tire loads also are expected to vary with road geometry and traffic intensity.

Sources in the Highway Environment

Pavement, bridges, safety structures, and other materials may be a potential source of trace elements in highway runoff (Hopke and others, 1980; Gupta and others 1981; Kobriger and Geinopolos, 1984; Legret and Pagotto, 1999). For example, Faure and others (2000) used the organic chemical signature of asphalt to determine that pavement materials constitute a substantial proportion of bottom sediment in depositional

areas affected by highway and road runoff. Dupuis and others (1999) reported that blasting abrasives and chips of leaded paint generated by bridge maintenance activities may have adverse effects on receiving waters. Legret and Pagotto (1999) estimate the annual Zn load from galvanized road barriers to be 950 g/km/y from a one-year-long experiment in which a piece of barrier was mounted on a roof and rain running off the barrier was collected for analysis. Data describing the chemical composition of most road-construction materials may be available from manufacturers and suppliers, but this information has not been systematically catalogued in an accessible publication. The availability of such information would be a boon for interpretation of runoff data by transportation agencies. Estimating the contribution of highway-construction materials to runoff, however, raises many technical concerns that must be addressed on a case-by-case basis.

Road dust contains a number of materials that may contribute trace elements (table 1). Hopke and others (1980) identified soil, pavement particulates, vehicle-exhaust emissions, rust from vehicles and highway structures, tire-wear particulates, and salt as primary components of road dust. Gupta and others (1981) noted that local soils constitute a considerable proportion of highway-runoff solids. Kobriger and Geinopolos (1984) noted that soil, cement, vehicle exhaust, rust, tire wear, and deicing agents are the primary sources of particulates. Furthermore, they estimated that among vehicle-derived particulates, tire wear (37 percent), direct pavement wear (37 percent), engine and brake wear (18 percent), and settleable exhaust particulates (7 percent) were primary sources. Beckwith and others (1986) studied trace-element and magnetic relationships for urban-source sediment and identified exhaust particles, wheel-hub particulates, and corroded bodywork as source matrixes. Hildemann and others (1991) measured a number of source materials, including exhaust from vehicles with and without catalytic converters, brake dust, tire dust and road dust. In this study, Al concentrations in road dust were between one and two orders of magnitude higher than in the direct vehicular sources, and were similar to geologic materials (as described in table 1), thus indicating that local soil may constitute a significant proportion of road dust. Rogge and others (1993) used analyses of organic chemicals characteristic of each potential source to estimate that fine road dust consists of vehicular exhaust particulates (7 percent), vehicular aerosol emissions (5 percent), tire particles (5 percent), and

vegetative detritus (2 percent). They also concluded that atmospheric aerosols in the urban environment are, chemically, similar to road dust. More recently, Sansalone, Buchberger, Koran, and Smithson (1996) also indicated that deposition and accumulation of solids on road surfaces is caused by traffic, vehicular-component wear, pavement degradation, roadway maintenance, littering, and atmospheric deposition.

Local soils represent a substantial proportion of the road dust that may be entrained by stormwater runoff (Gupta and others, 1981; Kobriger and Geinopolos, 1984). Shacklette and Boerngen (1984) measured concentrations of soil-associated trace elements in runoff at more than 1,300 sampling points across the conterminous United States (fig. 14). They found that natural concentrations of many trace elements varied by one or more orders of magnitude. Therefore, the trace-element contribution of natural soils may introduce a potentially large source of variability from site to site in trace-element concentrations measured in runoff samples. This variability may not be explained without soil-matrix-monitoring data. Also, in some mineral-rich areas of the United States, small concentrations of natural soils in runoff may substantially increase trace-element loads in highway runoff, urban runoff, and receiving waters. Measurements of soil-associated trace-element concentrations also can be used to establish baseline (or background) concentrations for the assessment of anthropogenic inputs (Shacklette and Boerngen, 1984). For example, Ames (1994) compared concentrations of trace elements in soils and bottom sediment in several watersheds in Washington state and found that concentrations of the elements Al, Ba, Cr, Fe, Ni were similar in soils and sediment, but concentrations of Cu, Hg, Mn, Pb and Zn in streambed sediment were two or more times the watershed soil concentrations. Callender and Rice (2000) used soil samples and natural streambed-sediment samples to establish baseline-background trace-element concentrations as an indication of the natural and anthropogenic trace-element inputs along a rural-to-urban land-use gradient in the Apalachicola-Chattahoochee-Flint River Basin in the southeastern United States. In a study of watershed soils and streambed sediment, Prych and others (1995) found that concentrations of trace elements and organic carbon were higher in bottom sediment than in local soils. One soil sample from a highway right of way was enriched in Cu, Hg, Mn, Pb, Sb, Zn and other trace elements. Enriched trace elements in soils near highways are

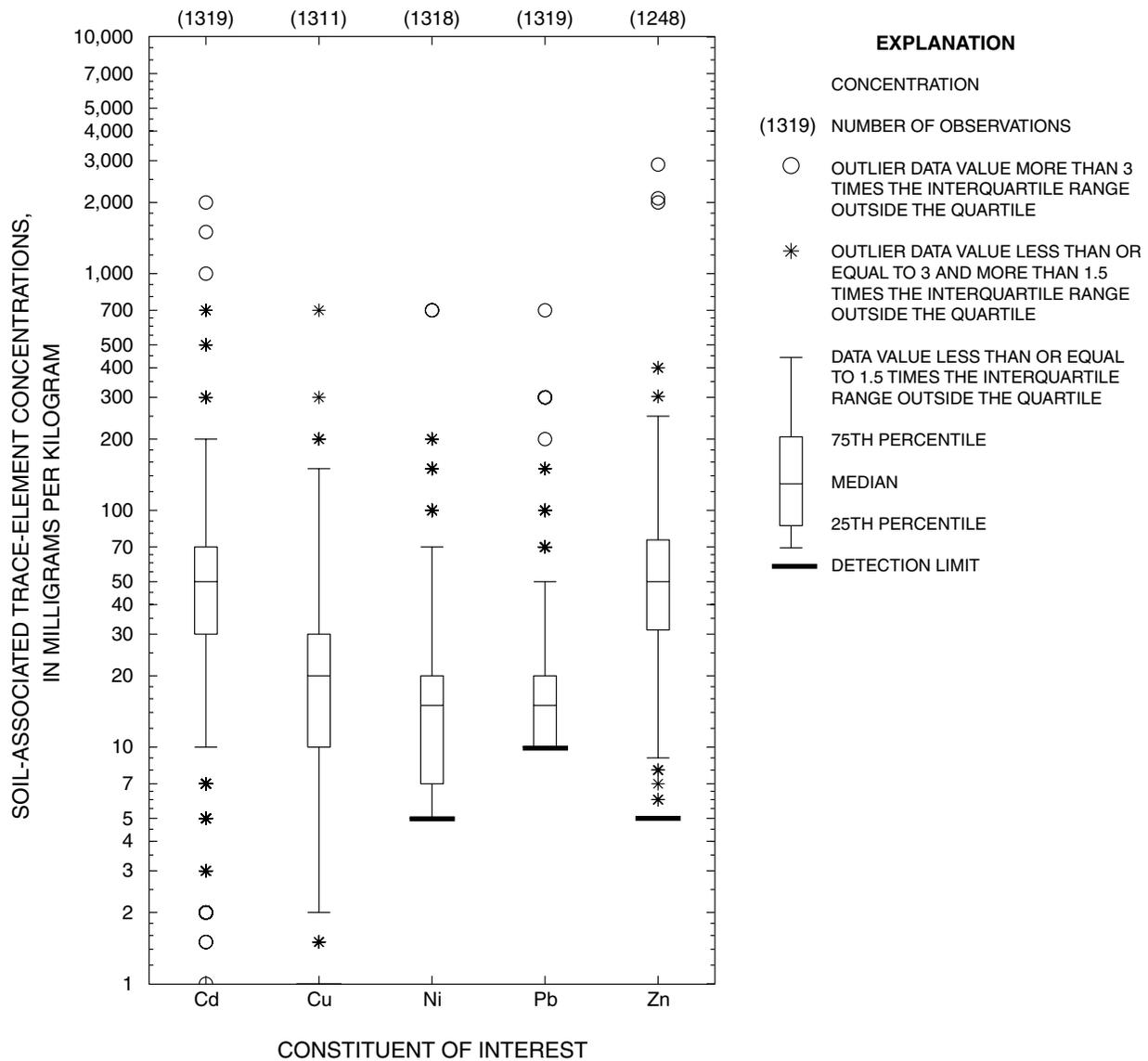


Figure 14. The distribution of natural soil-associated trace-element concentrations from sampling sites near highways across the conterminous United States. Data from Shacklette and Boerngen (1984).

typical, commonly with exponential decays in surface-soil concentrations with increasing distance from the highway (Kobriger and Geinopolus, 1984; Speiran, 1998). Flores-Rodriguez and others (1994) compared trace-element concentrations from natural soils and from highway and urban sediment. They found that trace-element concentrations were enriched by factors of 26, 2, 79, and 11, for Cd, Fe, Pb, and Zn, respectively, in highway sediment, and 1-24, 1-2, 2-106, and 1-18, for Cd, Fe, Pb, and Zn, respectively, in urban sediment when compared to concentrations in natural soil.

Technical concerns related to soil sampling are similar to those for sampling bottom sediment. Areal variability is an important concern, and the chemistry of surface soils is more variable than that of soils at depth because the upper soils are affected by anthropogenic inputs (Ames and Prych, 1995; Prych and others, 1995). To obtain soil samples representative of the natural geology, it is advisable to collect and composite three or more samples from a depth that represents material deposited and(or) formed in the selected plot before widespread industrial influences (Ames and Prych, 1995; Prych and others, 1995). A QA program

is important to assess field variability, repeatability of the laboratory measurements, and differences among digestions-recovery methods. Results of soil analysis also are affected by the digestion or sequential extraction methods used. Ames and Prych, (1995) noted that for Washington-State soils, total-recoverable trace-element concentrations were about 7 to 56 percent of concentrations from the total digestion method, and concentrations derived from partial-extraction procedures were about 1 percent of concentrations from the total digestion method.

The potential effect of atmospheric deposition on the pavement and on local soils (which may be entrained in stormwater) has long been a concern for highway and urban runoff studies (Gupta and others, 1981; Brinkmann, 1985; J.A. Colman, K.C. Rice, and T.C. Willoughby, USGS, written commun., 2000). Warren and Birch (1987) noted that trace-element concentrations in road dust and local soils increase with increasing local airborne metal concentrations. Local sources of trace elements potentially can confound site comparisons in the context of a regional or national synthesis. For example, Driscoll and others (1990) noted the effect of one site on population statistics. This site had a median EMC for Zn that was more than 10 times the median of that for the other 20 sites used in the synthesis. Driscoll and others (1990) noted that Zn concentrations characteristic of runoff from the relatively low-volume highway at this site, which is affected by a local zinc-smelting operation, would indicate an inverse relation between Zn concentrations and average daily traffic if they were included in the synthesis. When data from this site are omitted from the national data set, however, there is a significant (r -squared=0.7) relation between increasing average daily traffic and increasing Zn concentrations among the remaining sites used in the analysis (Driscoll and others, 1990).

Although local sources can have important effects on measured runoff quality, studies indicate that the highway is commonly a local net contributor to atmospheric deposition because measured trace-element concentrations commonly decrease with distance from the road surface (Kobriger and Geinopolos, 1984; Falahi-Ardakani, 1984, Harrison and Johnston, 1985; Speiran, 1998; Legret and Pagotto, 1999). Hildemann and others (1991) sampled and analyzed sources such as domestic heating appliances; exhaust from catalyst- and non-catalyst-equipped vehicles; diesel trucks; and fine particulates (less than 2 micrometers) of paved road dust, brake dust, and tire dust. These

and other values were then used to estimate local air-pollution loads in Los Angeles by source type on the basis of estimates of the relative use of each source. The estimates made by Hildemann and others (1991) indicated that vehicular sources (including paved road dust, brake dust, tire dust, exhaust from diesel trucks, and exhaust from vehicles) would contribute between 38- and 44-percent of the contaminants found in urban air. In another example, Ondov and others (1982) measured concentrations of trace metals in urban air and the Baltimore Harbor Tunnel (presumably affected by vehicle exhaust) and found that the air in the tunnel was enriched in trace-element concentrations—Br and Pb (about 20 times); Cu and Mg (5–10 times); Al, Cd, Cr, Fe, Sb, and Zn (2–5 times); and Mn and Ni (1–2 times)—as compared to urban air. Measured concentrations and loading rates of trace elements at most highway sites reflect variations in dustfall, average daily traffic and, land use in the area, as well as many other contributing parameters (Yousef and others, 1985b). Also, monitoring atmospheric deposition as a source for constituents in highway runoff is difficult and involves many technical concerns that are addressed by J.A. Colman, K.C. Rice, and T.C. Willoughby, USGS, written commun., (2000). Therefore, the assumption that constituent concentrations in atmospheric deposition samples collected on the highway right-of-way may be subtracted from constituent concentrations in runoff is questionable.

Deicing chemicals also have been studied as potential sources of trace elements in runoff (Kobriger and Geinopolos, 1984; Brinkmann, 1985; Granato, 1996; Legret and Pagotto, 1999). In these studies, many elements have been measured as components of deicing chemicals (including boron (B), Br, Ca, Cl, Cr, Cu, Fe, K, Mg, sodium (Na), Ni, Pb, Sr, V, and Zn). Deicing chemicals are a source of major ions that can affect the geochemistry of runoff and receiving waters. Deicing chemicals, however, are not a major source of trace elements in highway runoff, but they are not a trivial source either, especially because they are widely applied to many impervious surfaces (roads, driveways, walkways and parking lots) on the watershed scale, particularly in urban catchments (Granato, 1996). Deicing chemicals are different from other sources because they are applied purposefully to maintain safe travel conditions at prescribed application rates, which depend on climate, pavement area, and environmental concerns. The variation in annual deicing-chemical loads at a single site can be substantial. During a 5-year road-salt study in southeastern Massachusetts, total

annual deicing-chemical loads (and therefore the associated trace-element loads) varied by a factor of four from year to year depending on the severity of winter weather (Granato, 1996). It is expected that this variability would be even greater among different sites with different climates, and that differences in the use of deicing chemicals may contribute to differences in measured trace-element concentrations.

DATA-QUALITY ISSUES FOR REGIONAL OR NATIONAL SYNTHESIS

The quality of available data is a primary concern for evaluation of trace-element-monitoring data, especially in terms of a regional or national synthesis, because results of water-quality studies may be used as the basis for the formulation of agency policies and may, therefore, have substantial economic and environmental implications. To assess the potential precision, accuracy, representativeness, completeness, and comparability of trace-element data, it is necessary to evaluate the availability, suitability and completeness of documentation necessary to establish that data-quality objectives necessary for a regional or national synthesis are fulfilled. The necessary documentation includes information about monitoring protocols, QA/QC efforts, and ancillary data.

The Intergovernmental Task Force on Monitoring Water Quality (ITFM, 1995a,b) noted that among existing environmental-monitoring programs, the lack of consistent water-quality-monitoring protocols is "one of the biggest barriers to sharing water monitoring data," especially within the context of a regional or national synthesis. The ITFM has not established a single monitoring protocol; however, use of performance-based methods systems (PBMS) for field and laboratory work is recommended. PBMS accommodate the use of different collection, processing, and analysis protocols as long as the accepted methods produce a sample population of results that are within levels of confidence defined by data-quality objectives. To assess different field methods, side-by-side sampling is done (using identical laboratory methods). To assess different laboratory methods, field duplicates, and analytical reference materials are used. Efforts to establish a set of protocols within a PBMS, however, are not trivial, so it is

advisable to use established protocols that are suitable for the collection of trace-element data (ITFM, 1995a,b).

Even when using proven monitoring protocols, a well-designed QA/QC program is a critical component of the documentation necessary to establish the validity, scientific defensibility, and utility of trace-element data. Jones (1999) describes principles and practices for QA/QC in terms of a regional and(or) national runoff-quality-monitoring data set. Briefly, use of standard protocols are necessary to ensure that the quality of data collected and information gained from the use of various blank samples, replicate samples, split samples, spiked samples, synthetic samples, and standard reference samples are used to document the quality of data collected. These activities must be carried out within a system of data validation, data-quality assessment, and independent quality audits (Jones, 1999). QA/QC programs are especially important for trace-element monitoring because trace elements are ubiquitous in the environment, they are present in low concentrations in environmental samples, and the partitioning of trace elements between sampling matrixes and sample collection and processing equipment can be considerable.

Ancillary information also is needed to evaluate available data for a national synthesis because this information may provide explanatory variables that can be used to standardize data to a common basis for comparison, or to account for some of the otherwise unexplainable variability in the data. Many of the site characteristics that have been used in the FHWA's evaluations of highway-runoff quality, including information about the highway, local land use, geology, and climate (Granato and others, 1998), are especially relevant to interpretation of trace-element data on a national or regional scale. Currently, however, there are no established national formats for documentation and exchange of ancillary information and data from highway-runoff research studies (Transportation Research Board, 1997).

Documentation of monitoring protocols, QA/QC efforts, and ancillary data is especially important for the evaluation of historical trace-element monitoring data because monitoring and analysis methods have changed considerably over the past 30 years. Quantitative use of historical data collected during different time periods from different sites may be difficult, because changes in methods and long-term trends in diffuse trace-element contamination from anthropogenic sources would tend to obscure relations between

explanatory variables and measured trace-element concentrations. Within this context, historical changes in detection limits are a particularly vexing problem for the interpretation of trace-element-monitoring data sets. For example, in compiling the master data file for evaluation of contaminant loadings and environmental effects from highway stormwater runoff, Driscoll and others (1990) noted, "it was virtually impossible to unequivocally determine the actual detection limit associated with each contaminant concentration." They could not determine the detection limits because this information was not explicitly documented in available ancillary data and because the data were produced by a number of different analytical laboratories over an extended period of time.

Detection limit artifacts affect the accuracy and precision of individual values as well as the statistical characteristics of entire data sets. Uncertainty in the accuracy and precision of individual values tends to increase as concentrations approach the lower analytical detection limit. For example, in an assessment of interlaboratory evaluation data, Granato and others (1998) noted that uncertainties (expressed as relative percent error) in measured trace-element concentrations in standard reference solutions (SRS) increased exponentially with decreasing concentrations. The most probable value (MPV) of trace-element concentrations in SRS samples that are near detection limits have uncertainties of about plus or minus 100 percent for the "best" (the top 5 percent) laboratories, and uncertainties of about plus or minus 400 percent for "most" (the top 95 percent) laboratories. In comparison, when the MPV concentrations of reference solutions are about two orders of magnitude above detection limits, uncertainties in the populations of MPV concentrations from interlaboratory studies are generally reduced to within plus or minus 10 percent (Granato and others, 1998). Even when nominal laboratory detection limits are available, effective detection limits for individual data sets may vary because of operational differences in analytical techniques, which are necessitated by variations in the chemical characteristics of individual samples. For example, Granato (1996) found that in a study to examine deicing chemicals as a source of trace constituents in highway runoff, Ba, Co, Li, Mn and Zn were detected in the more dilute (0.001 percent) solutions but not in the more concentrated (0.5 percent) solutions. This detection-limit artifact was caused by laboratory procedures that necessitated dilution of the more concentrated samples

because of the high salinity. Therefore, although both samples were analyzed by the same method (with the same nominal detection limit), the dilution produced a much higher effective detection limit for the more concentrated sample. The statistical characteristics of entire data sets can be affected when a significant number of values are below one or more detection limits. Driscoll and others (1990) noted that, depending upon the method of statistical analysis, an overestimation of measures of central tendency and an underestimation of measures of spread are caused by a significant number of values below the detection limit that are omitted or set equal to the detection value. Different methods for dealing with the effects of one or more detection limits within a data set are available, but utilization of the various methods requires knowledge of the different detection limits within the data (Helsel, 1990; Helsel and Hirsch, 1992). Therefore, it is necessary to document detection limits and use caution when interpreting trace-element data that are at or near the detection limit, especially when different data sets are combined for regional or national synthesis.

SUMMARY

Trace elements have been a primary focus of most highway- and urban-runoff studies because stormwater runoff may be a source of trace elements that are regulated for aquatic-life protection. There are many technical issues of concern for monitoring trace elements in highway and urban runoff. Trace elements, by definition, are difficult to quantify, especially in stormwater-runoff studies. Trace elements in highway runoff accumulate on the road surface as a result of local and regional atmospheric deposition and regular highway operation and maintenance activities. The Federal Highway Administration and State Transportation Agencies are concerned about the potential effects of highway runoff on the watershed scale and for the management and protection of watersheds. Information that is documented as valid, current, and scientifically defensible is needed by transportation agencies to support necessary planning and management decisions. Currently, because of many technical concerns, most trace-element monitoring data are considered to be suspect, and the responsibility to provide published data-quality information to support the validity of reported results rests with the data-collection agency.

Paved surfaces are fundamentally different physically, chemically and hydraulically from the natural freshwater systems that have been the focus of most trace-element-monitoring studies. Therefore, existing scientific conceptions of the behavior of trace elements in the environment are based largely upon research on natural systems, not on systems typical of pavement runoff. Paved surfaces are characterized by extreme conditions of temperature, kinetic energy, chemistry, and hydraulics. Furthermore, the logistics of sampling runoff in the highway and urban environment are different than the logistics of sampling many natural freshwater systems. Therefore, trace-element-monitoring programs may benefit if conducted within the framework of automated monitoring and sampling programs that standardize the process and provide a record of the variations in flow and water-quality characteristics.

Trace elements have both natural and anthropogenic sources, including the sample collection, processing, and handling materials used in many trace-element-monitoring studies. Trace elements also react with these materials within the time scales typical for collection, processing, and analysis of runoff samples. The relative effect of potential contamination and(or) attenuation of trace elements in runoff samples is a function of the concentration of major and trace elements, organic chemicals, and sediment in solution. Sampling artifacts are especially important when measured concentrations are at or near analytical detection limits. Historically, anthropogenic sources in developed areas were thought to produce trace-element concentrations high enough to obscure the effects of contamination from sample collection and processing procedures, but studies show that even trace-element data from urban-runoff studies may be affected by sampling artifacts. Without sufficient supporting documentation, however, it is impossible to determine how sampling artifacts affect monitoring data sets. Therefore, great care is required to collect and process samples in a manner that will minimize potential sample contamination and variability in the sampling process. Standardization of sampling protocols designed to minimize these sampling artifacts for each matrix of interest will maximize the comparability and technical defensibility of data used in a regional or national synthesis.

A wide spectrum of geochemical conditions commonly precludes the definitive physical and chemical characterization of aqueous systems. To study the

characteristics and potential effects of trace elements in highway and urban runoff, six matrixes are typically sampled—whole water, dissolved (filtered water), suspended sediment, bottom sediment, biological tissue, and sources (from vehicles and the highway environment). These matrixes are operationally defined in an effort to maximize comparability of data sets. Each matrix, however, is associated with a number of technical concerns that must be understood and addressed through use of proper sampling protocols designed to minimize inherent problems and maximize the accuracy, precision, comparability, and representativeness of data collected. The whole-water matrix appears to be the most appropriate for monitoring runoff quality at a given site because of the unique nature of the monitoring environment, the range of trace-element concentrations expected in runoff samples, and the logistics of sampling stormwater. If it is possible to separate filtered water and suspended sediment immediately at the time of sample collection, information about the chemical partitioning of trace elements in runoff and receiving waters may be gained. The bottom-sediment matrix appears to be an appropriate reconnaissance tool for identifying past and present trace-element contamination in drainage systems and receiving waters. The biological-tissue matrix appears to be appropriate for measuring the potential effect of trace element contamination when used in conjunction with community assessments and trace-element concentrations derived from the analysis of bottom sediment and(or) whole water-samples from runoff. The source-monitoring matrix appears to be appropriate for identification of emerging contaminants and estimation of relative loads from different potential sources.

Results of water-quality studies are used as the basis for the formulation of agency policies and can have substantial economic and environmental implications. Therefore, the data quality is a primary concern for evaluation of trace-element monitoring data, especially in terms of a regional or national synthesis. Documentation necessary to establish data quality includes information about monitoring protocols, quality assurance and quality control efforts, and ancillary data. This documentation is especially important for the evaluation of historical trace-element-monitoring data because trace-element monitoring and analysis methods have been in constant flux over the past 30 years.

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