SURFACE-WATER-QUALITY ASSESSMENT OF THE YAKIMA RIVER BASIN IN WASHINGTON: ANALYSIS OF MAJOR AND MINOR ELEMENTS IN FINE-GRAINED STREAMBED SEDIMENT, 1987

By Gregory J. Fuhrer, Stuart W. McKenzie, Joseph F. Rinella,
Richard F. Sanzolone, and Kenneth A. Skach

With sections on:

Geology,
By Marshall W. Gannett, U.S. Geological Survey

U.S. GEOLOGICAL SURVEY
Open-File Report 93-30

Portland, Oregon
1994

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FOREWORD

One of the great challenges faced by the Nation's water-resources scientists is providing reliable water-quality information to guide the management and protection of our water resources. That challenge is being addressed by Federal, Tribal, State, Interstate, and local water-resources agencies and by academic institutions. Many of these organizations are collecting water-quality data for a host of purposes, including compliance with permits and water-supply standards; development of remediation plans for specific contamination problems; operational decisions on industrial, wastewater, or water-supply facilities; and research to advance our understanding of processes that affect water quality. In fact, during the past two decades, tens of billions of dollars have been spent on water-quality data-collection programs. Unfortunately, the utility of these data for present and future regional and national assessments is limited by such factors as the areal extent of the sampling network, the frequency of sample collection, the varied collection and analytical procedures, and the types of water-quality characteristics determined.

In order to address this deficiency, Congress appropriated funds for the U.S. Geological Survey (USGS), beginning in 1986, to test and refine concepts in a pilot program for a National Water-Quality Assessment (NAWQA) Program that would:

1. Provide a nationally consistent description of water-quality conditions for a large part of the Nation's water resources;

2. Define long-term trends (or lack of trends) in water quality; and

3. Identify, describe, and explain, as possible, the major factors that affect observed water-quality conditions and trends.

Four surface-water projects, including the Yakima NAWQA project, and three ground-water projects were conducted as part of the pilot program to test and refine the assessment methods and to help determine the need for and the feasibility of a full-scale program. Results are presented in individual reports for specific topics and for each project. In 1991, USGS began a 4-year transition from a pilot program to a full-scale program. The design concepts to be implemented are based, in part, on the pilot program that began in 1986.

NAWQA studies depend heavily on cooperation and information from many Federal, Tribal, State, Interstate, and local agencies. The assistance and suggestions of all are gratefully acknowledged.

Philip Cohen
Chief Hydrologist

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[Plates are in back pocket]

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CONVERSION FACTORS AND VERTICAL DATUM

To convert from	To	Multiply by
inch (in)	millimeter (mm)	25.40
foot (ft)	meter (m)	0.3048
mile (mi)	kilometer (km)	1.609
square mile (mi^2)	square kilometer (km^2)	2.590
acre	square meter	4,047.
acre-feet (acre-ft)	cubic meter (m^3)	1,233.
ton, short (T)	megagram (Mg)	0.9072
cubic foot per second (ft^3/s)	cubic meter per second (m^3/s)	0.02832
ounce, avoirdupois (oz)	gram (g)	28.35
ounce per square inch	grams per square centimeter	4.394
pound, avoirdupois (lb)	kilogram (kg)	4.536
gallon (gal)	cubic decimeter $(dm)^3$	3.785
gallons per minute (gal/min)	cubic decimeter per second (dm^3/s)	0.06309

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

$$°F = (°C/0.555)+32$$

SEA LEVEL: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

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With sections on geology by Marshall W. Gannett

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ABSTRACT

In 1986, the U.S. Geological Survey implemented a pilot program to test and refine concepts for a National Water Quality Assessment (NAWQA) program. On the basis of water use, the Yakima River Basin, Washington, was selected as one of four surface-water pilot studies.

One of the objectives of the NAWQA program, and the subject of this report, is to determine the occurrence and distribution of major and minor chemical elements in streambed sediment. The terms major and minor were applied to elements that typically exist in concentrations greater than 1,000 parts per million and less than 1,000 parts per million, respectively. In 1987, fine-grained (less than 62 micrometer in diameter) streambed-sediment samples were obtained from 448 locations in the Yakima River Basin. These samples represent a variety of large and small streams, and include limited samplings of urban-storm-water drains and agricultural soils. Sediment was analyzed for 45 elements using a total-digestion procedure that dissolves elements in the sediment matrix.

Results of this study, along with those of other Yakima NAWQA studies which include analyses of minor elements in water (dissolved), suspended sediment, and aquatic tissue, will provide multiple lines of evidence to:

- o Define spatial and temporal variability;
- o Identify sources and describe the transport and fate of minor elements;
- o Evaluate the effects of minor elements on fish, benthic invertebrates, and algae.

The Yakima NAWQA data will be compatible with data collected at 59 other NAWQA basins throughout the United States, so that the status of trace elements in the Nation's water can be assessed.

Anomalous major- and minor-element concentrations in streambed sediment were determined by constructing normal probability plots of the element concentrations in the Yakima River Basin. The large concentrations that formed a distinctive curve or distribution were termed anomalous. Baseline concentrations were derived by locating the element concentration that corresponded to the point of intersection between the anomalous distribution and the remainder of the data. Anomalous data may result from point-source discharges and human caused

as well as naturally occurring nonpoint sources. The largest number of anomalies were found for antimony, arsenic, cerium, copper, and zinc; at least 10 percent of these element concentrations exceeded the baseline value of 0.7 µg/g, 8.5 µg/g, 57, µg/g, 40 µg/g, and 120 µg/g, respectively.

The largest anomalous antimony concentration (4.8 µg/g) occurred in streambed sediment originating from the pre-Tertiary metamorphic and intrusive rocks geologic unit in the Cle Elum Subbasin and was attributed to the presence of antimony-bearing minerals pyrite, galena, and sphalerite. Antimony concentrations as large as 3.0 µg/g were found in lower-order-streambed sediment originating from the Miocene and older volcanic rocks geologic unit in the upper Naches Subbasin and was attributed to hydrothermally altered and mineralized andesitic rock located in the headwaters of the American River.

Streambed sediment concentrations of arsenic in lower-order streams of the pre-Tertiary metamorphic and intrusive rocks geologic unit in the upper basin were as large as 31 µg/g; in addition, concentrations in the nonmarine sedimentary rock geologic unit were as large as 61 µg/g. Streambed sediment formed from these geologic units were likely sources of arsenic to the higher-order Teanaway River (30 µg/g) and Cle Elum River (81 µg/g) as well as to the upper reaches of the Yakima River (7.9 µg/g). The downstream-order decrease in arsenic concentrations in the main stem of the upper basin probably results from arsenic-rich sediment (from lower-order streams within the Teanaway River and Cle Elum River drainages) mixing with incoming arsenic-poor sediment from Wilson Creek. Streambed sediment from Wilson Creek originates from the Quaternary deposits and loess geologic unit that contained only 2.0 µg/g arsenic. Geologic sources of arsenic were small in land-use areas designated as agriculture; however, concentrations of arsenic as large as 140 µg/g were found in soils that have historically been treated with the lead-arsenate pesticide. In addition, concentrations of lead, as large as 890 µg/g, were found in these pesticide-treated soils.

Lower-order streams in the pre-Tertiary metamorphic and intrusive rocks geologic unit of the upper and middle basin contain anomalous concentrations as large as 1,700 µg/g for chromium, 140 µg/g for cobalt, 13 percent for magnesium, and 1,900 µg/g for nickel. These anomalies were associated with the mineral chromite; the iron-rich soil, ferruginous laterite; and the rock dunite, all present in the pre-Tertiary rocks geologic unit. Chromium enrichment in sediment of higher-order streams results from geologic sources, rather than anthropogenic sources. Like arsenic, the downstream-order decrease in chromium concentrations (in addition to mercury and nickel) in the main stem of the upper basin probably result from chromium-rich sediment (from lower-order streams within the Teanaway River and Cle Elum River drainages) mixing with incoming chromium-poor sediment from Wilson Creek.

Concentrations of copper are enriched at urban drain sites in the cities of Selah (67 µg/g) and Ellensburg (65 µg/g); however, the concentration of copper at Ellensburg was measurably lower (25 µg/g) near the mouth of Wilson Creek prior to entering the main stem. Anomalous concentrations of zinc also were found at urban drain sites in the cities of Ellensburg (190 μg/g), Yakima (220 μg/g and 310 μg/g), and Prosser (260 μg/g); however, no measurable enrichment was observed in the main stem downstream. Application of zinc sulfate to orchards is probably responsible for concentrations of zinc as large as 150 μg/g in soils, and 180 μg/g in streambed sediment in agricultural land-use areas. Although placer-gold mining (ores deposited by alluvial action) is a potential source of mercury within the Swauk Creek drainage, only one site within the drainage had a large concentration of mercury (0.18 μg/g). A near anomalous 0.24 μg/g mercury was detected in Wide Hollow Creek, an urbanized and industrialized creek draining lowlands near the city of Yakima.

Streambed sediment formed from Quaternary flood deposits have significant-positive associations ($\rho \leq 0.05$) among the elements cerium, lanthanum, neodymium, thorium, and potassium. These associations result from granitic-rich flood deposits in the Yakima River Basin that were scoured from the Columbia Plateau following the failure of the Lake Missoula ice dam in the Pleistocene Epoch.

Anomalous concentration of zinc were found in several geologic units. Concentrations of zinc in streambed sediment formed from the Quaternary and Pliocene volcanic rocks geologic unit, however, were shown by analysis of variance to be statistically larger than concentrations originating from most of the other geologic units. Nearly one-half the sites sampled within this unit had anomalous concentrations of zinc. In addition to geologic sources of zinc in the basin, the practice of adding zinc-sulfate to apple orchards to retain blossoms and promote overall yields appears to be a nonpoint source of zinc to streambed sediment. Concentrations of zinc in soils collected from sites that were formerly apple orchards and in streambed sediment collected at sites located downstream of present and former apple orchards range from 140 μg/g to 180 μg/g. These concentrations exceed the 90th percentile zinc concentration in the present study as well as zinc concentrations attributable to geologic sources upstream from apple orchards.

INTRODUCTION

Concern about the effects to the aquatic environment from major and minor elements[1] present in streambed sediment has increased over the past several decades. Many minor elements such as arsenic, cadmium, copper, lead, and mercury can be toxic to aquatic biota. These elements are ingested from particulate matter (in streambed sediment or suspended in the water column) by a wide variety of benthic organisms; moreover, these

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[1] Although definitions of the terms "major" and "minor" with reference to elements in sediment are not precise, substances typically occurring in concentrations of less than 1,000 parts per million (<0.1 percent) are considered minor or trace elements (Forstner and Wittmann, 1979, p. 5). Elements typically occurring in concentrations of greater than 1,000 parts per million are considered major elements. In this report major elements are reported in concentration units of percent and minor elements are reported in concentration units of micrograms per gram. For convenience, inorganic carbon is listed along with total-organic carbon, under the heading of "Major Elements."

elements may accumulate in biota and move up the food chain. The biological importance of trace elements in particulate matter may be due principally to the manner in which particulate forms of trace elements regulate dissolved forms of trace elements at equilibrium (Jenne and Luoma, 1977). These equilibrium processes include sorption-desorption and dissolution-precipitation reactions (Jenne and Luoma, 1977). Minor elements in sediment are known to be concentrated three orders of magnitude or more, in comparison with minor elements in aqueous phases (Jenne and others, 1980). Elements in streambed sediment enter the environment from natural and anthropogenic sources. Water managers cannot effectively mitigate issues relating to minor-element concentrations until natural and anthropogenic element sources are identified. Major elements, unlike minor elements, generally are not a threat to aquatic life; rather, the magnitude of their concentrations is a useful measure for determining the type of rock that contributes to or constitutes the geochemical character of streambed sediment. Evaluating the occurrence and distribution of elements in streambed sediment is an initial step in understanding the effect of element concentration on the aquatic environment.

Beginning in 1986, Congress authorized funds for the U.S. Geological Survey to implement a pilot program to test and refine concepts for a National Water Quality Assessment (NAWQA) program (Hirsch and others, 1988). The Yakima River Basin was one of four surface-water-study units selected to test NAWQA concepts (McKenzie and Rinella, 1987). The Yakima River Basin pilot program began in 1986 with a planning phase and a historical-data analysis phase; from 1987 to 1990, a data-collection phase took, and in 1991, the report-writing phase began. This report, one of the major topical reports from the Yakima NAWQA study, describes the occurrence and distribution of major and minor elements in streambed sediment.

The full scale NAWQA program, begun in 1991, entails operation of 60 combined surface- and ground-water-study units and covers about 60 to 70 percent of the Nation's water use (Leahy and others, 1990). The NAWQA program will provide results that are useful in understanding and managing water resources, as well as addressing national water-quality issues. Specifically, the goals of the NAWQA program are to:

(1) Provide a nationally consistent description of current water-quality conditions for a large part of the Nation's water resources;

(2) Define long-term trends (or lack of trends) in water quality; and

(3) Identify, describe, and explain, as possible, the major factors affecting observed water-quality conditions and trends.

The program is perennial and will involve a cyclic pattern of 4 to 5 years of continuous and intensive data collection and analysis followed by 5 years of less intensive assessment activities. This cyclic pattern of sampling is sufficient to define long-term trends in water quality. The water-quality issues addressed in the program are broad, covering topics such as euthrophication, pesticides, major and minor elements, sanitary quality in surface water, and aquatic biota.

Purpose and Scope

The purposes of this report are to:

(1) Determine the occurrence and distribution of major and minor elements in streambed sediment in the Yakima River Basin;

(2) Provide background data to determine long-term trends for future measurements of streambed sediment chemistry;

(3) Relate minor elements in streambed sediment to geologic and anthropogenic sources; and

(4) Disscuss the implications of the assessment study and how they may affect monitoring activities, assessment studies, and management activities in the future.

Sources and Characteristics of Streambed Sediment

Streambed sediment is derived primarily from the physical and chemical weathering of rocks at the earth's surface. Initially, solid rocks are transformed into an aggregate of loose material by physical weathering processes, such as the action of frost. The freshly disaggregated rock surfaces are subject to chemical-weathering processes when sources of water are present. Chemical-weathering processes (hydration and hydrolysis, oxidation and reduction, and the action of carbon dioxide) enable some of the physically disaggregated rocks to dissolve in water. In addition, other rocks may be altered chemically by reacting with ions present in water or may remain totally unaltered by the action of water. The physically and sometimes chemically disaggregated rocks ultimately are transported by the action of flowing water, ice, wind, and animals (including man) to surface waters, where they may be deposited as streambed sediment.

Many processes, usually taking place simultaneously, can alter the chemical characteristics of streambed sediment. As a result, streambed sediment consists primarily of resistates, hydrolyzates, oxidates, reduzates, precipitates, and evaporites Rankama and Sahoma (1950).

Resistates are chemically unchanged mineral residue from weathering and typically occur as gravel, sand, and silt (Folk, 1974). Many, elements that are found primarily in minerals resistant to weathering, increase in concentration in streambed sediment because other elements found in less resistant minerals are leached from sediment and transported. One element that commonly increases in concentration due to weathering is titanium, which is found primarily in the resistate mineral rutile (TiO_2). Hydrolyzates are the insoluble particles that remain after other elements have dissolved into solution as ions and colloids. They differ from resistates by their decidedly smaller particle size, which includes clay and colloidal-size particles. Dominant elements forming the hydrolyzates are aluminum, silica, iron, and potassium. Oxidates are formed in oxygenated-surface water by precipitation reactions which form hydroxides with iron, manganese, and aluminum ions. Unlike the resistates and hydrolyzates, which are transported as particles of varying size (suspended in water), ions or colloids are transported in solution to sites of deposition where oxidation and precipitation form the oxidates. Reduzates are sediment particles formed in strongly reducing environments (absence of oxygen) that are typically enriched in organic carbon. The absence of free oxygen inhibits the oxidation of sulfur to sulfate while promoting the formation of hydrogen sulfide. The presence of even trace quantities of hydrogen sulfide in sediment pore water can sorb minor elements, such as copper, nickel, mercury, and zinc (present in surface and ground water as ions) to streambed sediment (Forstner and Wittmann, 1979). Precipitates form sediment particles from dissolved ions present in surface waters. This occurs when water becomes saturated with dissolved ions, such as calcium and magnesium, for reasons other than simple evaporation. Subsequent additions of calcium or magnesium ions, for example, to the water (increases in ion concentration above the saturation indices of mineral precipitates) are removed by precipitation. Evaporites include elements contained in precipitates and oxidates; however, unlike these latter forms, evaporites cannot form sediment until extensive water loss or evaporation has occurred. Common evaporite-forming ionic species are calcium, potassium, magnesium, sodium, bicarbonate, borate, chloride, and sulfate.

Acknowledgments

The authors wish to acknowledge the aid and advice provided by members of the Yakima NAWQA Liaison Committee. During 1992, this committee included:

David W. Zimmer, U.S. Bureau of Reclamation
Don Schram, U.S. Bureau of Reclamation
Richard Albright, U.S. Environmental Protection Agency
William Garrigues, U.S. Forest Service
Terry W. Berkompas, U.S. Bureau of Indian Affairs
Kate Benkert, U.S. Fish and Wildlife Service
Wendell Hanigan, Yakima Indian Nation
Jannine Jennings, Yakima Indian Nation
Bob Barwin, Washington State Department of Ecology
Perry Harvester, Washington State Department of Fisheries
Brent Renfrow, Washington State Department of Wildlife
Glen Patrick, Washington State Department of Health
Dr. L. Clint Duncan, Washington Water Research Center, Central Washington State University
Skip Steinmetz, Yakima County Health Department
Ronald L. Van Gundy, Yakima River Basin Association of Irrigation Districts
Ray L. Wondercheck, U.S. Soil Conservation Service, District Conservationist
Elaine Taylor, Yakima Valley Conference of Governments
Don Chaplin, County Extension Service
Mike Tobin, North Yakima Conservation District
Richard C. Bain Jr., Kittitas County Conservation District

Special thanks to Steve Smith (U.S. Geological Survey, Geologic Division) for assistance and advice in interpreting streambed sediment data in addition to providing a comprehensive colleague review of the manuscript.

DESCRIPTION OF THE YAKIMA RIVER BASIN

The Yakima River Basin, located on the eastern slope of the Cascade Mountains, drains an area of 6,155 mi^2 [square miles] (Columbia Basin Inter-agency Committee, 1964) and contains about 1,900 miles of perennial streams (when mapped at a scale of 1:250,000 by the U.S. Geological Survey). The Yakima River, referred to as the "main stem," originates at the outlet of Keechelus Lake in the eastern Cascades, flows southeastward a distance of 214.5 river miles, and empties into the Columbia River (fig. 1). Numerous tributaries drain to the main stem. Major tributaries include: Cle Elum River at Yakima (river mile [RM] 185.6), Teanaway River (RM 176.1), Wilson Creek (RM 147.0), Naches River (RM 116.3), Moxee Drain (RM 107.6), Wide Hollow Creek (RM 107.4), Ahtanum Creek (RM 106.9), Granger Drain (RM 82.8), Marion Drain (RM 82.6), Toppenish Creek (RM 80.4), Satus Creek (RM 69.6), Sulphur Creek Wasteway (RM 61.0), and Spring and Snipes Creeks (RM 41.8).

The climate of the Yakima River Basin varies from maritime along the crest of the Cascade Mountains to arid in the lower valley. Mean annual precipitation ranges from less than 10 inches in the southern part of the basin to about 140 inches in the higher mountains of the northwestern part of the basin (U.S. Weather Bureau, 1965). Most of the precipitation (61 to 81 percent) falls in both the maritime and arid parts of the basin from October to March. Over the last century, the population of the basin has increased from less than 70,000 in 1910 to more than 300,000 in 1980 (Onni Perala, U.S. Bureau of Reclamation, written commun., 1990). The county populations in 1983--incorporated (urban) and unincorporated (rural)--were: Kittitas County, 15,730 and 9,170, respectively; Yakima County, 88,800 and 88,200, respectively; and Benton County, 77,600 and 31,100, respectively, (Washington Office of Financial Management, 1984). The largest cities and 1990 populations in Kittitas, Yakima, and Benton Counties are Ellensburg (11,300), Yakima (50,610), and Kennewick (35,700), respectively. The combined urban area of all cities in the basin is about 59 mi^2 and contains about 58 percent of the basin's population. For a detailed description of climate, population, water use, water-resource development, surface-water hydrology, crop production, and population, see Rinella and others (1992).

The Yakima River and most of its major tributaries have perennial streamflow as a result of ground-water inflow, May-June snow melt, and summertime glacial melt. Peak runoff generally occurs during May and June in streams receiving snow melt; moreover, streamflows decrease in snow-melt streams from November to January as snow and glacial melting is abated by lower air temperatures. The streamflow in the main stem and in many tributaries to the main stem is augmented by reservoirs during the May-October irrigation season; however, streamflow varies in accordance with the location of major diversions. Streamflows during the irrigation season in the main stem can range from several thousand cubic feet per second upstream of irrigation diversions to several hundred downstream of diversions, but upstream of irrigation return flows.

The Yakima River Basin is intensively irrigated and managed over an area of 465,000 acres that extends along both sides of the Yakima River (U.S. Bureau of Reclamation, 1983). More than 1 million acre-feet of water, collected from rainfall and snow melt for irrigation and flood control, is stored in six reservoirs and distributed through 14

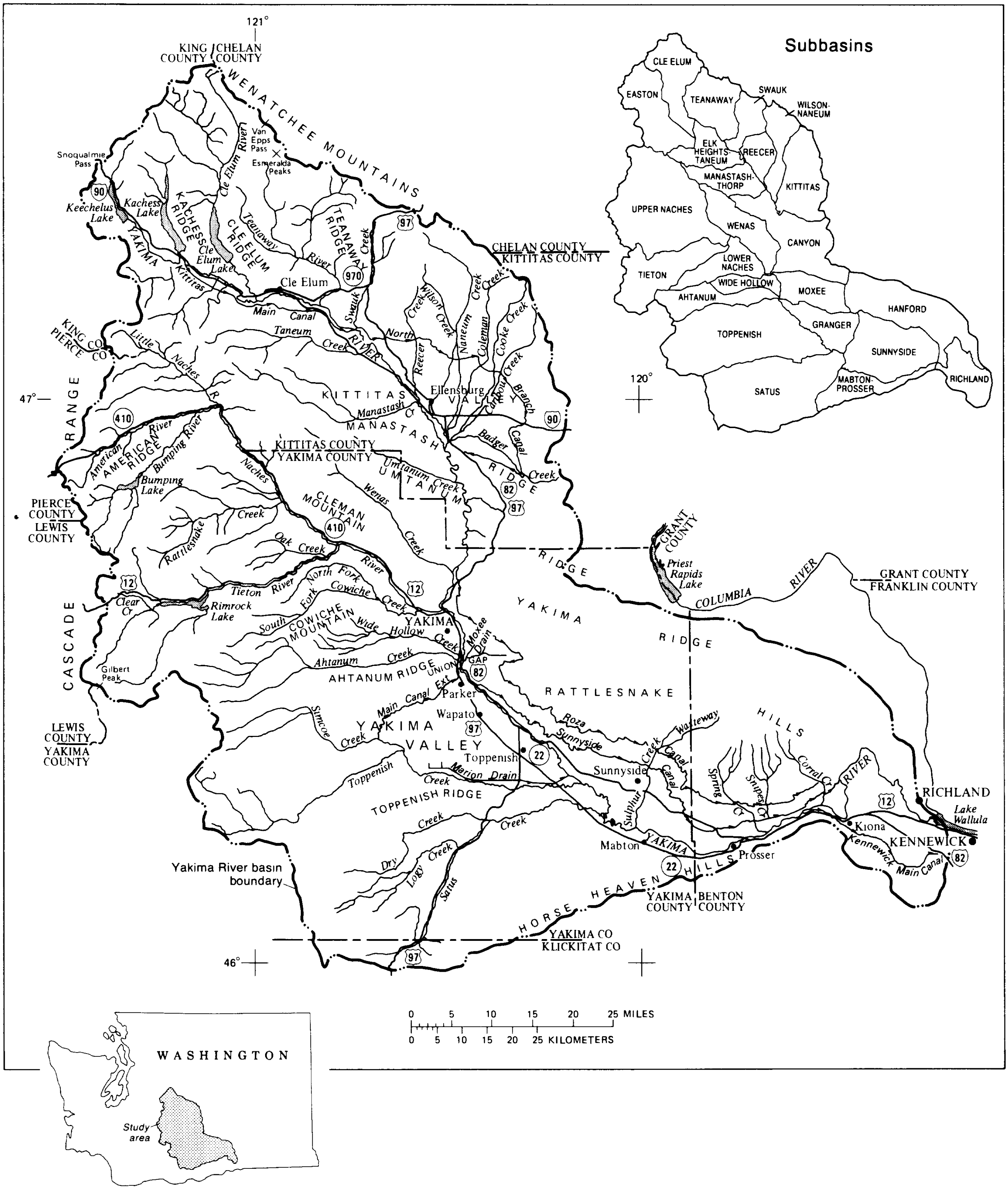

Figure 1. The Yakima River Basin, Washington.

diversions and more than 1,900 mi of canals to seven irrigation divisions. Reservoirs are regulated to provide an adequate water supply for instream habitat in addition to augmenting streamflow. Surface water from the Naches River and Yakima River, respectively, also is used as a public water supply for the cities of Yakima and Cle Elum.

The extensive irrigation system in the Yakima River Basin has transformed this near-desert region into one of the most productive agricultural regions in the United States. Often called the "Fruit Bowl of the Nation," the Yakima River Basin supports many varieties of fruit, vegetable, seed, grain, forage, and specialty crops valued at one-half billion dollars annually (U.S. Bonneville Power Administration, 1988). Yakima County ranks first in the United States in the production of apples, mint, and hops and fifth in total agricultural production. Such productivity, however, has not been without cost. The Yakima River, prior to 1880, was one of the most productive salmon rearing streams in the Columbia Basin; adult salmon returned to the Yakima River in numbers as large as 600,000 per year. However, with the advent of storage dams, irrigation canals, and ditches along the Columbia and Yakima Rivers, as well as increased fishing off the Pacific coast, spawning runs on the Yakima River in the early 1980's averaged fewer than 4,000 adult salmon per year (U.S. Bonneville Power Administration, 1988).

Geologic Overview

By Marshall W. Gannett, U.S. Geological Survey

The Yakima River Basin comprises parts of the Columbia Plateau and the Cascade geologic provinces. The largest segment of the basin, including the entire southern and eastern parts, is in the Columbia Plateau, a province that consists primarily of basaltic lava flows with minor interbedded and overlying sediment. The western and northern margins of the basin are in the Cascade Range (see fig. 1). The Cascade Mountains in the basin consist of a complex assemblage of volcanic, sedimentary, metamorphic and intrusive rocks.

Approximately two-thirds of the Yakima River Basin is in the Columbia Plateau province. This province is dominated by lavas of the Columbia River Basalt Group, which, in the Yakima River Basin, include the Grande Ronde, Wanapum, and Saddle Mountain Basalts (Walsh and others, 1987). The basalt exists as multiple layers consisting of individual flows ranging generally from 10 to over 100 feet (ft) thick. Compressional forces in the Earth's crust during and after the emplacement of Columbia River Basalt Group lavas have warped and faulted the basalt into a series of east-northeast to east-southeast trending valleys and ridges. The ridges include the Horse Heaven Hills, the Rattlesnake Hills, and Toppenish, Ahtanum, Umtanum, Manastash, Naneum, and Yakima Ridges (see fig. 1). Some of the lowlands between these basalt highlands have accumulated significant amounts of sediment. Major sediment accumulations, such as the Ellensburg Formation, are in structural lows of the Kittitas, Selah, Yakima, and Toppenish sedimentary basins according to Smith and others (1989).

Basalt flows of the Columbia River Basalt Group are overlain by, and locally interbedded with, sedimentary deposits. The major sedimentary unit in the Columbia Plateau province, in the Yakima River Basin, is the

Ellensburg Formation, which consists chiefly of volcaniclastic material derived from the Cascade Range. Smith and others (1989) report that more than 1,000 ft of coarse-grained volcaniclastic sediment has accumulated over many parts of the Yakima River Basin.

A variety of unconsolidated surficial deposits of Quaternary age is present on the Columbia Plateau in the Yakima River Basin. These deposits include alluvial deposits along rivers and streams, alluvial terrace deposits, loess, and deposits resulting from catastrophic glacial outburst floods which inundated the lower part of the basin during the Pleistocene Epoch (Waitt, 1985). These catastrophic flood deposits are present up to an altitude of about 1,000 feet in parts of the basin (Waitt, 1985).

Approximately one-third of the Yakima River Basin is located in the Cascade Range geologic province. The Cascade Province includes parts of the western and northern margins of the basin. The southern part of the Cascade Range in the basin, south of the Naches River, is dominated by Tertiary volcanic rocks, which include basalt and andesite flows, flow breccias, and related pyroclastic and volcaniclastic rocks (Walsh and others, 1987). Tertiary volcanic units are predominant in the middle part of the Tieton drainage, the upper part of the Rattlesnake Creek drainage and most of the American River, Bumping River, and Crow Creek drainages. Older Jurassic to early Cretaceous marine sedimentary rocks are present in the Cascades south of the Naches River, most notably in the upper Tieton River drainage. These nonvolcanic rocks consist of sandstone and mudstone with lesser conglomerate (Walsh and others, 1987).

North of the Naches River, the Cascade province in the Yakima River Basin is dominated by Tertiary nonmarine sedimentary rocks, and pre-Tertiary metamorphic and intrusive rocks with lesser amounts of Tertiary volcanic rocks. Major sedimentary units in this area include the Eocene Roslyn and Swauk Formations.

The Roslyn Formation, which underlies a large part of the Teanaway River drainage, consists primarily of nonmarine sandstone with lesser conglomerate and thin coal seams (Tabor and others, 1982). The Swauk Formation, which is older than the Roslyn Formation, is present in the upper parts of the Teanaway River, Cle Elum River, and Swauk Creek drainages. The Swauk Formation consists primarily of nonmarine sandstone with lesser siltstone, shale, and conglomerate. The Swauk and Roslyn Formations are separated by the Teanaway Formation, which consists primarily of basaltic flows, tuff, and breccia.

The upper parts of the south fork of Manastash Creek and the north and south forks of Taneum Creek drain areas where pre-Tertiary metamorphic rocks are found, including gneiss, schist, phyllite and amphibolite. These metamorphic rocks are surrounded and locally overlain by Tertiary volcanic rocks and nonmarine sedimentary rocks similar to the Swauk and Roslyn Formations.

In the far northern part of the basin, the uppermost sections of the Cle Elum River and the north fork of the Teanaway River drain an area underlain by ultramafic rocks adjacent to the Mount Stuart batholith. These ultramafic rocks include serpentinite, serpentinized peridotite, metaserpentinite, metaperidotite, diabase, and gabbro (Tabor and others 1982).

Unconsolidated surficial deposits in the Cascade Province in the Yakima River Basin include alluvium along rivers and streams, alluvial fans, landslides, and glacial drift and outwash.

Stream Reaches

The Yakima River descends from a water-surface altitude of 2,449 ft at the foot of Keechelus Dam to 340 ft at its mouth, downstream of Horn Rapids Dam near Richland (fig. 2a). The headwater of Keechelus Lake and other tributaries flowing to the lake range in altitude from about 2,500 ft to more than 6,000 ft on the eastern slopes of the Cascade Mountains. Because of physical characteristics, the Yakima River Basin can be divided into three distinctive river reaches (fig. 2b). In the upper reach (Kittitas Valley), the Yakima River is high gradient with an average streambed slope of 14 feet per mile (ft/mi) that extends 67.5 mi from the foot of Keechelus Dam to just upstream of Wilson Creek (RM 147). The river is shallow and the streambed is composed mostly of cobble and large gravel with some boulders, sand, and silt. Rocks in the upper reach are covered with light coatings of periphyton and are embedded slightly with sediment.

In the middle reach (mid-valley), the Yakima River extends a distance of 39.5 mi from below Wilson Creek to Union Gap (RM 107) and is also high gradient, with an average streambed slope of 11 ft/mi (see fig. 2a). Located along the Yakima River in the mid-valley are the Roza (RM 127.9), Wapato (RM 106.6), and Sunnyside (RM 103.8) Dams that raise the hydraulic head of the river to divert water into irrigation canals. Upstream of the aforementioned irrigation diversion dams, small stream segments of 1 river mile or less are in backwater and accumulate fine-fraction sediment. During the irrigation season (April through October), several waterways including Wilson Creek and Moxee Drain carry sediment-laden, irrigation-return flow to the middle reach. Typical suspended-sediment concentrations during the irrigation season were about 100 mg/L (milligrams per liter) and 650 mg/L for Wilson Creek at Mouth and Moxee Drain, respectively. Some of this sediment-laden water is, in turn, diverted into the Roza, Wapato, and Sunnyside irrigation canals, or the sediment is deposited in low-velocity backwaters of the middle reach. Other sediment, especially the fine fraction, is transported farther down the main stem. Similar to the upper reach, the middle reach is shallow and the streambed is composed mostly of cobble and large gravel with some boulders, sand, and silt. In general, the streambed is covered with light coatings of periphyton, and is free of rooted aquatic plants. Conversely, physical characteristics in reaches affected by backwaters of diversion dams are notably different. For example, the substrate in the backwaters of the Roza Dam is predominantly silt/clay with some organic matter and supports rooted aquatic plants.

The Naches River, a major tributary with 1,106 mi^2 of drainage area, flows into the middle reach at RM 116.3. The Naches River is a high-gradient stream with an average streambed slope of 36 ft/mi. It ranges in altitude from 2,560 ft, at the confluence of the Little Naches and Bumping Rivers, to 1,070 ft at its mouth (headwaters of the Naches River have water-surface altitudes as high as 6,000 ft). The river is shallow and the streambed is composed mostly of cobble and large gravel with some boulders, sand, and silt. Rocks are covered with light to medium coatings of periphyton and are slightly embedded with sediment. The vegetative

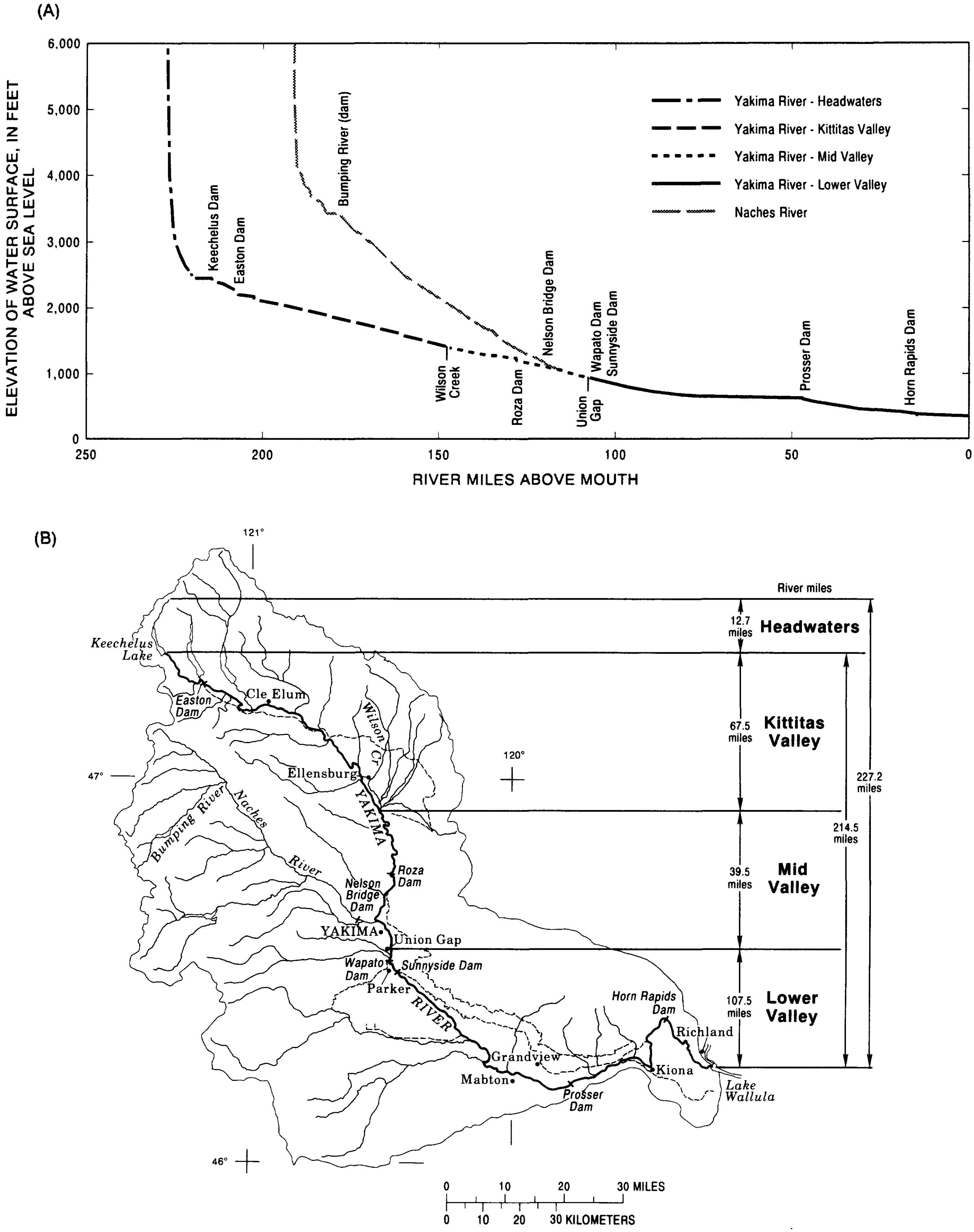

Figure 2. Elevation profile (A), and distinctive-hydrologic reaches (B) of the Yakima River, Washington.

cover and thin soil mantle of the upper Naches Subbasin limit the amount of suspended sediment in the stream. Moreover, the steep river gradient tends to keep most sediment entrained until the Naches River flows into the middle reach of the main stem where velocities decrease in the backwater of the Wapato and Sunnyside Diversion dams.

The lower reach of the Yakima River has an average streambed slope of 7 ft/mi and extends for 107.5 mi from the city of Union Gap to its mouth (fig. 2). The streambed slope is highly variable through this reach, as is streamflow and average velocity. During the irrigation season, streamflow in the main stem below the Wapato and Sunnyside Diversions commonly is less than a few hundred cubic feet per second; streamflows remain small until irrigation waters are returned to the main stem by waterways between Parker (RM 104.6) and Mabton (RM 59.8). During the 1974-81 irrigation seasons, as much as 80 percent of the mean-monthly streamflow at Kiona was from tributaries carrying irrigation-return flow between Parker and Kiona (Rinella and others, 1992). The upstream end of the lower reach has a steep channel slope (12.8 ft/mi) which decreases midway through the reach (0.9 ft/mi) and results in a slow moving, meandering pool. The pool is hydraulically characterized as a stilling basin behind a bedrock control, and is located upstream of the Euclid Street bridge which serves the city of Grandview (RM 55). The pool is a depositional reach and contains predominantly silt/clay, with some small gravel and organic matter. The substrate within the higher gradient sections, preceding and following the pool, is similar to that of the upper and middle reaches. Numerous rooted aquatic plants exist along the lower reach, especially in the vicinity of Horn Rapids Dam (RM 18.0).

Land Use

Land use in the Yakima River Basin is governed by geology, topography, climate, and soils. Mountainous terrain receives most of the precipitation and is the dominant land form in all but the lower valley. Most of the nonmountainous terrain in the Yakima River Basin is arid with sparse vegetative cover and is generally rangeland. A small part of the basin, which has been reclaimed from the arid basin floor and serviced with irrigation systems, supports intensively farmed, agricultural land. It is this agricultural land that has earned Yakima River Basin the title "The Nation's Fruit Bowl."

Land use in the basin (fig. 3) is classified as forest (40.3 percent), rangeland (37.4 percent), agriculture (19.2 percent), urban (1.6 percent), water bodies and wetlands (1.2 percent) and other (0.3 percent). Land-use data are based on 1981 data (U.S. Geological Survey, 1986). Streambed sediment chemistry of higher-order streams can be affected by irrigated agriculture and urban-land-use activities. Although small in area, these land-use activities can be large in terms of intensity. Sunnyside Subbasin contains only 76 mi^2 of irrigated land and is drained by Sulphur Creek Wasteway. During the irrigation season (instantaneous sample collected on June 21, 1988), Sulphur Creek Wasteway transported 190 tons per day (t/d) of suspended sediment in comparison to the nonirrigation season (instantaneous sample collected on February 16, 1988), when only 6.6 t/d of suspended sediment was transported to the Yakima River. Cultivation practices are undoubtedly paramount to irrigation-agriculture soil loss; for example, practices used for growing hops and corn which remove vegetative cover to create furrows for the delivery of irrigation water tend to easily erode top soils. The sediment chemistry of lower-order streams (headwaters) is

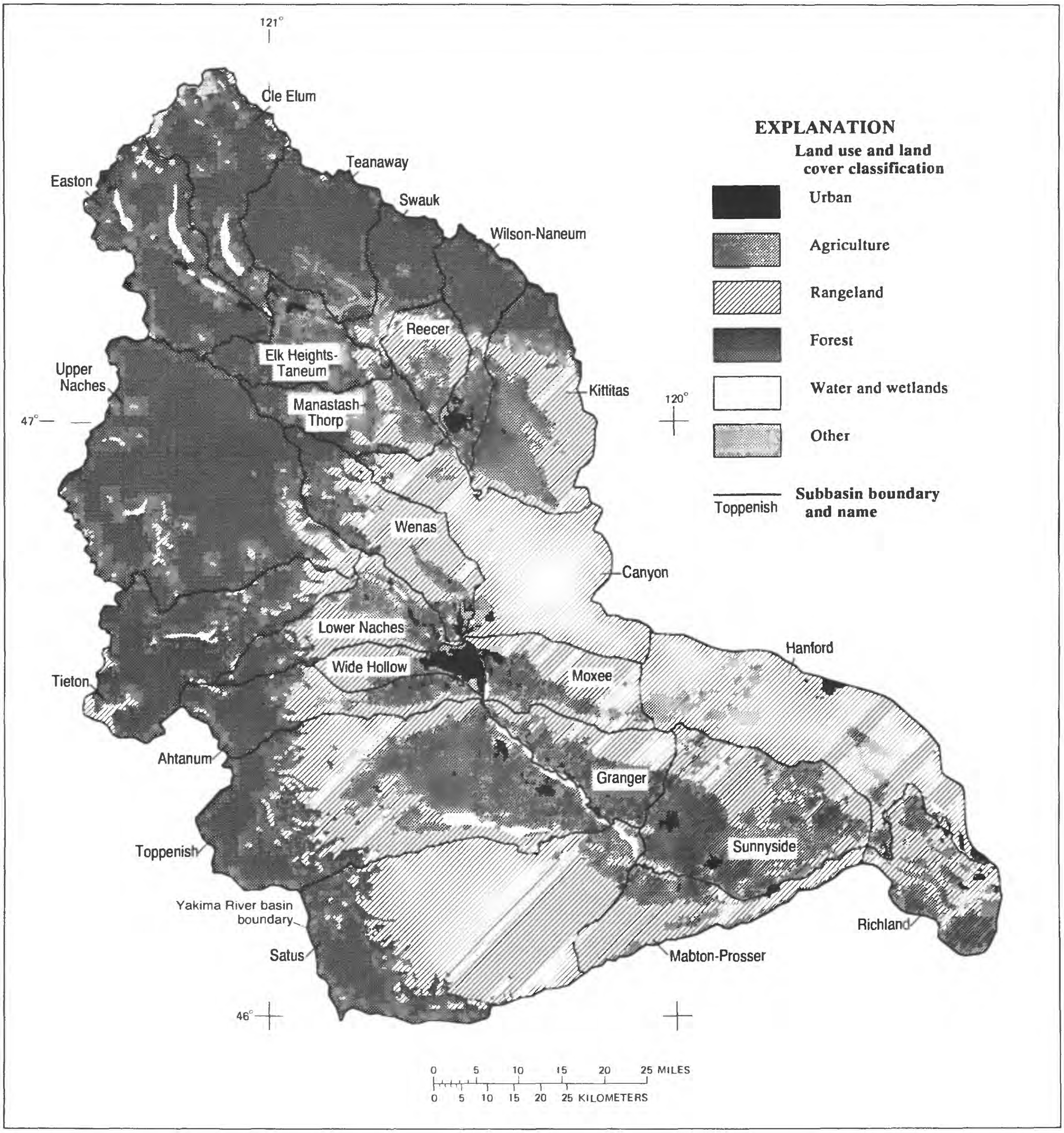

Figure 3. Land use and land cover by subbasin in the Yakima River Basin, Washington, 1981. (U.S. Geological Survey, 1986.)

susceptible to effects from forest and rangeland activities. In lower-order streams[2], for example, timber harvesting may affect sediment chemistry by increasing peak runoff, which, in turn, may destabilize stream channels and increase soil erosion and sedimentation.

Possible Sources of Major and Minor Elements

Major and minor elements in streambed sediment can exist as a result of both natural and anthropogenic sources. In many places, these sources are inseparable when bed-sediment chemistry is determined solely in anthropogenically affected areas of higher-order streams[2]. As an example, the arsenic content of streambed sediment in higher-order streams may locally reflect arsenic-bearing mineralization (a natural geologic source) or the applications of arsenic based pesticides (a known anthropogenic source) or both.

In this report, point sources of waters containing major and minor elements are defined as pipe discharges or outfall discharges, or both. Point-source discharges are from municipalities and industries and are placed directly into waterways. Nonpoint-source discharges are from activities including farming, timber harvesting, mining, construction and manufacturing, as well as from sources including atmospheric deposition, urban runoff, and underlying geology. Other nonpoint sources include storm runoff from the transport of rain-washed pollutants to storm drains, sewer systems, and eventually waterways.

The Washington State Department of Ecology, Industrial Permit Division, as of 1991, has no National Pollutant Discharge Elimination System (NPDES) permits on file for the discharge of minor elements within the Yakima River Basin (Rick Frye, oral commun., 1990). There are, however, about 300 point-source permits (related to fruit processing) and about 150 point sources without permits (Rick Frye, Washington State Department of Ecology, oral commun., 1990). The Yakima-Kittitas Resource Conservation and Development Project determined that food processing and wood products account for more than 50 percent of the basin's industry; metal products account for less than 12 percent (U.S. Department of Agriculture, 1974).

There were a few plating, casting, and placer-gold mining facilities listed in the mid-1970's Yakima River Basin Water Quality Management Plan (CH2M Hill, 1975) that presently (1991) are not listed in the NPDES permit register (Rick Frye, oral commun., 1990) and are assumed to no longer be in operation. These facilities included metallic mining, plating, and casting operations (table 1). In addition, at the turn of the century, a number of arsenopyrite workings in the Cle Elum Subbasin were in operation and a stamp mill was constructed to process ore (U.S. Geological Survey, 1989). This site may have been a point source of arsenic to streambed sediment of the Cle Elum River.

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[2] In this report, lower-order streams are defined as first- or second-order tributaries and higher-order streams are defined as third order or larger tributaries--the largest being the main stem of the Yakima River. The smallest unbranched mapped (1:24,000-scale map) tributaries are first-order tributaries, streams receiving only first-order tributaries are second-order tributaries, larger streams receiving only first- and second-order tributaries are third order (Horton, 1945).

Table 1.--Inventory of industrial facilities producing metallic products, Yakima River Basin, Washington, 1974

[RM = River Mile, data from Yakima Basin Water Quality Management Plan (CH2M Hill, 1975)]

Industry name	Products	Subbasin	Receiving water
Miners Mining	Placer gold	Swauk Creek	Williams Creek[1]
Bay Zinc	Zinc sulfate fertilizer	Ahtanum Creek and Moxee Drain	na
Cascade Casting	Metallic castings	Moxee Drain	Yakima RM 110
Masco Products	Chrome/nickel plating	Ahtanum Creek and Moxee Drain	Ground water
Yakima Plating	Bumper rebuilding	Ahtanum Creek and Moxee Drain	Ground water

[1] Confluence with Swauk Creek at Swauk Creek river mile 11; Swauk Creek flows into the Yakima River at river mile 169.9.

Noteworthy among NPDES permits is the city of Yakima sewage-treatment plant (STP) which in 1980 discharged an average of 11.0 million gallons per day (Mgal/d). The Yakima STP, which services the major population center of the basin, is the largest point-source discharger, of the basin's 12 STPs. The river-mile location of possible sources of major and minor elements in the Yakima River Basin is listed in table 2.

Metallic wastes (dissolved and suspended) passing through municipal waste-treatment plants may be a source of minor elements to streambed sediment (Forstner and Whittmann, 1979). Whole-water (dissolved plus suspended) concentrations of several minor elements which include arsenic, antimony, copper, lead, mercury, nickel, silver, zinc, and the ionic compound cyanide were detected in an August 1988 effluent survey of the city of Ellensburg's STP (Reif, 1989). In this survey, silver equaled the U.S. Environmental Protection Agency (EPA) acute freshwater-aquatic-life criterion of 4.1 μg/L (micrograms per liter) [U.S. Environmental Protection Agency, 1986] and was 33 times the chronic-aquatic-life criterion (0.12 μg/L); mercury was seven times the chronic criterion (0.012 μg/L) and cyanide was twice the chronic criterion (5.2 μg/L); effluent hardness was used to calculate aquatic-life criteria (Reif, 1989). Similarly, whole-water concentrations of several minor elements which include copper (8 to 33 μg/L), nickel (30 to 90 μg/L), and zinc (42 to 110 μg/L) were detected in effluent surveys between 1989 and 1991 of the city of Yakima's STP (J. Schnebly, City of Yakima Wastewater Treatment Plant, written commun., 1990). In the above surveys, four of five copper determinations exceeded the EPA chronic-freshwater-aquatic-

Table 2.--Possible sources of major and minor elements in the Yakima River Basin, Washington

[Effluent discharges are the average-daily discharge for 1987 (from Washington State Department of Ecology); Cr = Creek; Mgal/d = million gallons per day; DID = Drainage Irrigation District; E = east]

Yakima River mile location	Waste water		Sewage treatment		Major nonpoint sources
	Industry	Effluent discharge (Mgal/d)	Plant	Effluent discharge (Mgal/d)	
0-4.0	--	--	--	--	Intrusion of Columbia River sediment
28.6	--	--	Benton	0.325	--
Spring Cr at 41.8	--	--	--	--	Agricultural runoff
Snipes Cr at 41.8	--	--	--	--	Agricultural runoff
45.7	Seneca1/	0.14			
46.5	--	--	Prosser	.62 (contains industrial wastes)	--
Satus Drain at 60.2	--	--	--	--	Agricultural runoff
60.5	--	--	Mabton	.090	--
Sulphur Cr at 61.0	--	--	Sunnyside	1.46	Agricultural and urban runoff
DID # 7 at 65.1	--	--	--	--	Agricultural runoff
South Drain at 69.3	--	--	--	--	Agricultural runoff
Satus Cr at 69.6	--	--	--	--	Agricultural runoff
Coulee Drain at 77.0	--	--	--	--	Agricultural runoff
Toppenish Cr at 80.4	--	--	--	--	Agricultural runoff
Marion Drain at 82.6	Endurance Fruit1/	.008	Wapato	.496	Agricultural runoff
	--	--	Harrah	.039	--
	Washington Beef Products (industrial)	.09	--	--	--
Granger Drain at 82.8	--	--	Granger	.172	Agricultural runoff and dairy related animal wastes
Sub 35 Drain at 83.2	--	--	--	--	Agricultural runoff
E. Toppenish Drain at 86.0	--	--	Toppenish	.956	Agricultural runoff
89.2	--	--	Zilla	.819	--
Wide Hollow Cr at 107.4	--	--	--	--	Urban and industrial runoff
Moxee Drain at 107.6)	--	--	Moxee	.066	Agricultural runoff and urban
111	--	--	Yakima	12.48 (contains industrial wastes)	--
113.1	Snokist1/	1.5	--	--	--
114.2	Boise Cascade #1 (plywood plant)	.559	--	--	--
114.5	Boise Cascade #2 (lumber plant)	.365	--	--	--
Naches River at 116.3	--	--	Naches	.074	Agricultural runoff
117	--	--	Selah	.976	Urban runoff
Wenas Cr at 122.4	--	--	--	--	Agricultural runoff
151.5	--	--	Ellensburg	3.26	--
Manastash Cr	--	--	--	--	Agricultural runoff
166	--	--	--	--	Old municipal land fill
Taneum Cr at 166.1	--	--	--	--	Agricultural runoff
Swauk Cr at 169.9	--	--	--	--	Mining runoff
180.5	--	--	Cle Elum	.609	--
183.1	--	--	--	--	Cle Elum; urban runoff Rosyln; mine runoff

1/ Industrial and municipal data are maximum allowable discharges listed on National Pollutant Discharge Elimination System Waste Discharge Permits active between 1987-91, (Kim Shidell, Washington State Department of Ecology, written commun., 1990).

life criterion (8.2 μg/L); two of five copper determinations exceeded the EPA acute-freshwater-aquatic-life criterion (12 μg/L); and one of six zinc determinations exceeded both the chronic and acute aquatic-life criterion of 74 and 82 μg/L, respectively; effluent hardness was used to calculate aquatic-life criteria (U.S. Environmental Protection Agency, 1986). Most of the elements present in Yakima River Basin STP effluents coincide with elements reported by Forstner and Whitmann (1979, p. 44) to be present in typical STP solids.

Runoff from urban areas can contain a broad array of minor elements including cadmium, lead, silver, and zinc (Forstner and Wittmann, 1979). Local enrichment of streambed sediment may occur in the vicinity of urban outfalls; for example, those outflows that flow into Wide Hollow Creek and Sulphur Creek (see table 2).

Early farming practices may be a significant source of minor elements to waterways receiving agricultural return flow. Before the introduction of DDT in 1947, lead arsenates were the primary pesticides used for the control of codling moth in apples. In eastern Washington, from 1908 to 1947, lead-arsenate applications increased from 50 lb (pounds) of lead and 18 lb of arsenic to 192 lb of lead and 71 lb of arsenic per acre (Peryea, 1989). These minor elements accumulate in top soil where present day fertilizing practices tend to bind lead to soil and dissolve arsenic into shallow ground water (Peryea, 1989). Thus, soil erosion and ground-water seepage from agricultural regions treated with lead arsenate must be considered nonpoint sources of lead and arsenic.

Several mineralized areas have been mined in the Yakima River Basin (fig. 4); presently (1991), there are no active mining operations (Washington State Department of Natural Resources, 1990). Substantial quantities of placer and lode gold have been mined along the Swauk Creek drainage (U.S. Geological Survey, 1989). Other metallic deposits in Yakima and Kittitas Counties are largely undeveloped and include small quantities of chromium, copper, iron, manganese, mercury, and silver along the Cle Elum River drainage, in addition to small deposits of copper, mercury, and tungsten in the Tieton River and Bumping Lake drainages (U.S. Department of Agriculture, 1974; Moen, 1978; Simmons and others, 1983). These mineralized areas represent geologic nonpoint sources (naturally affected) of minor elements to overlying soils and streambed sediment.

The action of man often augments the natural dispersion of minor elements from mineralized areas into streambed sediments. Increased erosion of soils in areas with natural enrichment of metals and associated minor elements results from mineral exploration (drill road construction) and timbering practices (clear cuts, selective cuts, road construction, and log handling). Hard-rock mining, the extraction of metal-rich deposits from bedrock, can increase the quantities of metals and other minor elements available for natural dispersion into streambed sediments; mine-waste dumps are easily eroded and directly add metal-rich sediment. The oxidation of freshly exposed sulfide minerals in mine dumps creates weak sulfuric acid solutions which leach additional elements and transport them into the local ground water. The milling and extraction of metallic ores is an additional potential source of minor

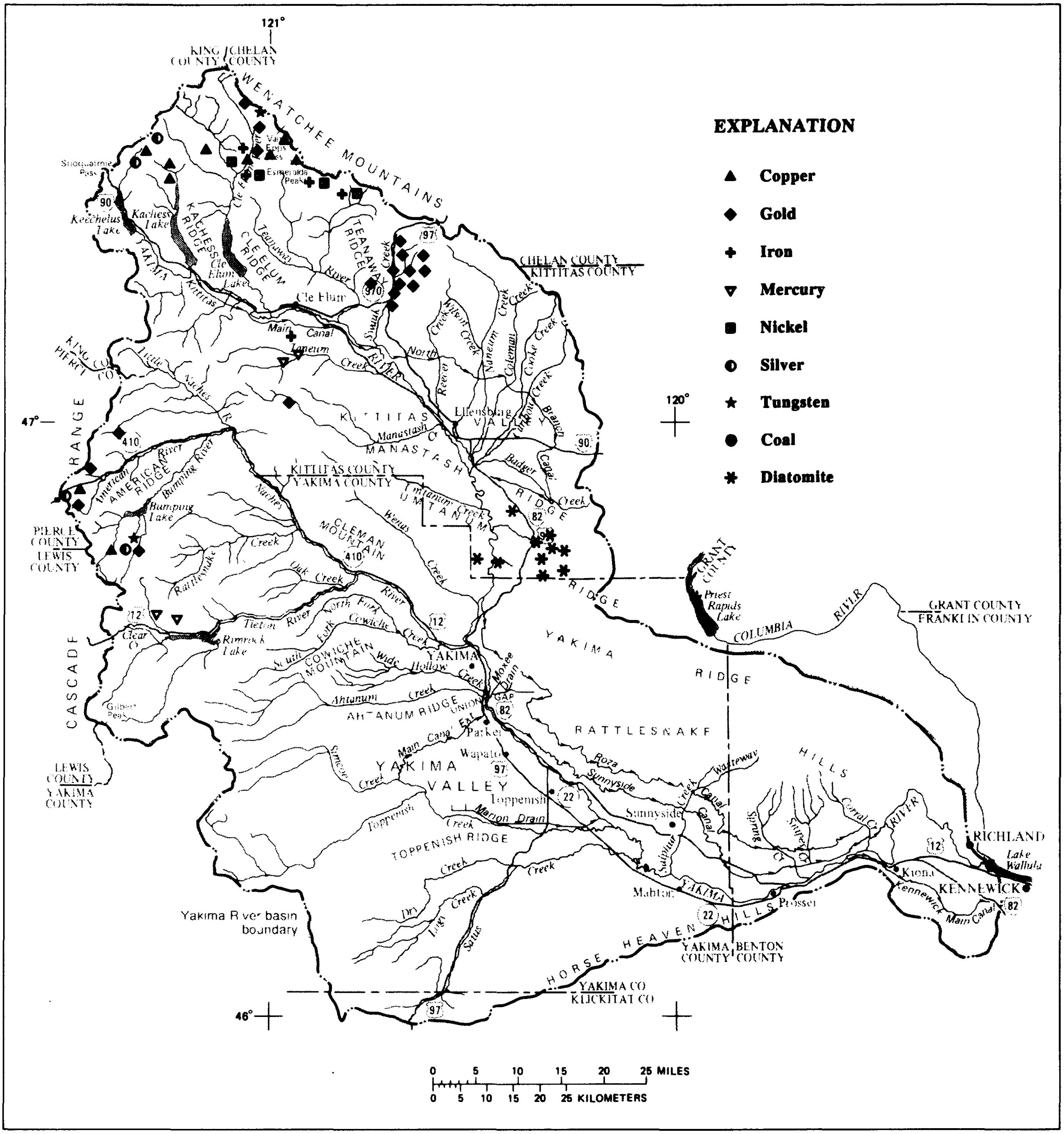

Figure 4. Mined metallic- and nonmetallic-mineral deposits in the Yakima River Basin, Washington, 1972. (Modified from U.S. Department of Agriculture, Soil Conservation Service, 1974.)

elements to streambed sediment, and when situated on higher-order streams, can enrich sediment that was originally unaffected by the natural minor element dispersion. Historic placer mining operations, such as those along the Swauk Creek drainage, commonly are sources of mercury because of the traditional use of quicksilver to extract gold from auriferous sediment (Wise, 1964).

A significant atmospheric source of major and minor elements in the Yakima River Basin was the May 18, 1980, eruption of Mount St. Helens in southwestern Washington. Ash falling in the Yakima River Basin ranged from 0.001 grams per square centimeter (g/cm^2) to 5 g/cm^2. The heaviest ash deposition (4 to 5 g/cm^2) fell in the Tieton Subbasin (see fig. 3); the lightest ash deposition fell in the northern (0.01 g/cm^2) and southern (0.001 g/cm^2) extremes of the basin. Two subsequent eruptions of Mount St. Helens, July 22, 1980 and August 7, 1980, deposited ash within the basin; however, deposition from these events was insignificant compared to the May 18, 1980, eruption.

Samples of volcanic ash from the May 18, 1980, eruption were collected in the Yakima River Basin and analyzed by several researchers. The composition of these volcanic-ash deposits was reported by Taylor and Lichte (1980), Hinkley and others (1987), Fruchter and others (1980), and Sarna-Wojcicki, Meyer and others (1981).

In general, the ash from Mount St. Helens deposited on the Yakima River Basin in 1980 was of dacitic composition (Fruchter and others, 1980). Ash-fall deposits from the May 18 eruption were collected and analyzed by Fruchter and others (1980) at Tieton Ranger Station, Ahtanum, Yakima, and Richland; by Taylor and Lichte (1980) at Tampico, and Tieton; by Sarna-Wojcicki and others (1981) at a site located 17 mi northeast of Yakima; and by Hinkley and others (1987) at Richland. The average chemical concentration of the ash sampled was determined and concentration ranges were reported (in percent) as follows: silica 59 to 63 percent; aluminum oxide 16.4 to 18.6 percent; iron oxide 5.24 to 6.64 percent; magnesium oxide 2.7 to 4.1; calcium oxide 5.14 to 6.72 percent; and sodium oxide 4.3 to 4.8 percent. In addition, element concentrations of copper ranged from 32 to 48 $\mu g/g$, lead ranged from 5.8 to 13 $\mu g/g$, and zinc ranged from 54 to 92 $\mu g/g$ among these same sites within the Yakima Basin.

Previous Studies

Sediment-chemistry studies in the Yakima River Basin historically have focused on mineral-resource studies, and mostly cover mountainous regions of the northern and southwestern Yakima River Basin. Noteworthy, among these studies, are the Alpine Lakes Wilderness area (Gualtieri and Simmons, 1989), the mineral resource studies of the upper Yakima and Naches Rivers (Moen, 1969), Goat Rocks Wilderness area (Church and others, 1983), mineral resource studies of upper Cle Elum and Teanaway Rivers (Lucas, 1975), and mineral resource studies of the Cougar Lakes-Mount Aix areas (Simmons and others, 1983). The locations of these study areas are shown in figure 5.

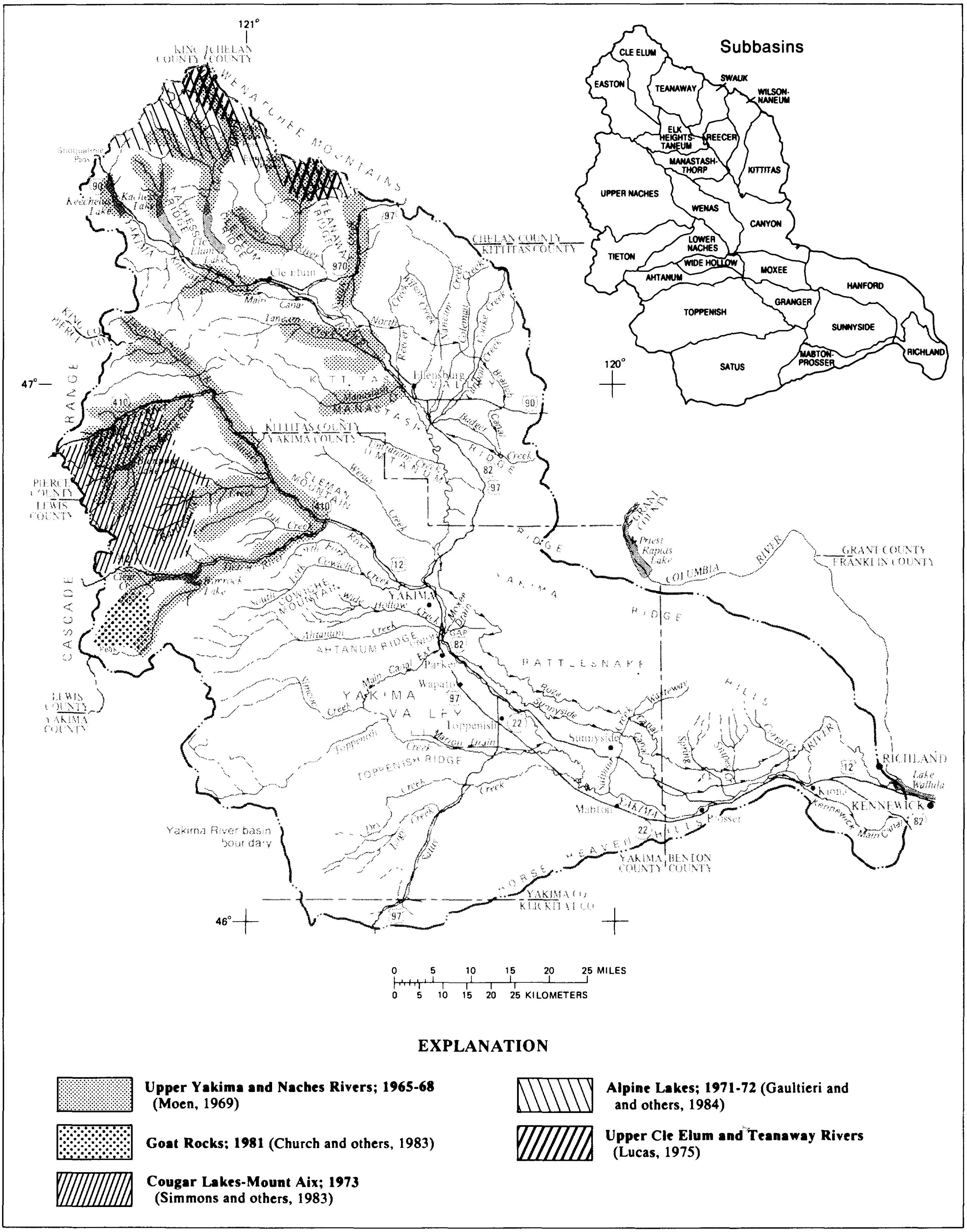

Figure 5. Sampling locations of previous studies of minor elements in streambed sediment and rock in the Yakima River Basin, Washington, 1965-81.

The Alpine Lakes study (Gualtieri and Simmons, 1989), with boundaries beyond that of the Yakima River Basin, encompasses a small part of the northern basin. Although during this 1971-72 study 2,657 streambed-sediment samples (finer than 0.018 millimeters, in diameter) were collected, only 38 samples are in proximity of streambed samples collected in the NAWQA study. The Alpine Lakes report contains geology, mineral resource information, geochemical data, and a detailed chronology of historical mining activities. Alpine Lakes samples were screened by semiquantitative-spectrographic analysis for 30 elements--including environmentally significant elements such as antimony, arsenic, barium, cadmium, copper, chromium, nickel, silver, and zinc. Anomalously large concentrations were re-determined by atomic absorption.

Several lower-order streams in the upper Cle Elum River were extensively prospected in the early 1900's and are still considered to have unexplored mineral potential (Gualtieri and Simmons, 1989). Streambed sediment samples collected from these lower-order streams were considered by Gualtieri and Simmons (1989) to be enriched in zinc (200-300 μg/g) and silver (0.5-1.0 μg/g). Zinc enrichment probably results from mineralization associated with the geologic contact between the Wenatchee Mountains and local ultramafic rocks. Streambed-sediment samples collected from lower-order streams of the North Fork Teanaway River were enriched in zinc (120-200 μg/g). Rock samples collected along lower-order streams of the North Fork Teanaway River were enriched in copper (300-20,000 μg/g) and zinc (200-500 μg/g). Streambed sediment of lower-order streams flowing into Keechelus and Cle Elum Lakes were enriched in copper (100-700 μg/g), silver (0.5-2 μg/g), and molybdenum (5-30 μg/g). Most of the anomalously large element concentrations in streambed sediment of lower-order streams flowing into Keechelus Lake reflect the presence of altered and mineralized rock (Gualtieri and Simmons, 1989). Also notable in the Alpine Lake Study were enriched chromium, cobalt, and nickel concentrations in mineralized rock samples of the Cle Elum River drainage.

A previous study of the Upper Yakima and Naches Rivers (Moen, 1969), the largest historical streambed sediment sampling of the basin, entailed the collection of 182 streambed sediment samples between 1965-68. The study covered eight Yakima subbasins: Cle Elum, Easton, Upper Naches, Tieton, Teanaway, Elk Heights-Taneum, Manastash-Thorp, and Swauk in the northwest part of the Yakima River Basin (see fig. 5). Samples were analyzed for copper, molybdenum, lead, and zinc by atomic adsorption and colorimetry. These data were summarized statistically by Fries and Ryder (in Rinella and others, 1992), and were considered anomalous when concentrations exceeded the 95-percent range shown for soils in the Western United States (R.C. Severson, U.S. Geological Survey, written commun., 1987, based on data in Shacklette and Boerngen, 1984). Concentrations of copper (206 μg/g in Easton Subbasin), and zinc (330 μg/g in the Upper Naches Subbasin and 120 μg/g in the Tieton Subbasin) were classified as anomalous by Fries and Ryder (in Rinella and others, 1992).

The Goat Rocks study (Church and others, 1983) was conducted in the area of Old Snowy Mountain, southwest of Rimrock Lake in the Tieton Subbasin, and entailed collection of 43 streambed-sediment samples in 1981. Although the Goat Rocks area received ash fall (primarily dacite) from the May 18, 1980 eruption of Mount St. Helens, Church and others

(1983) concluded that minor-element concentrations present in ash fall were insufficient to cause anomalies in streambed-sediment chemistry. Streambed-sediment samples were analyzed for 31 elements using a direct-current, arc-emission, spectrographic method. Data from Church and others (1983) also were summarized by Fries and Ryder (in Rinella and others, 1992). The 90-percentile concentrations of copper (50 μg/g), vanadium (300 μg/g), and zinc (200 μg/g) in the Tieton Subbasin were classified as anomalous by Fries and Ryder (in Rinella and others, 1992).

From a study of mineral deposits in Kittitas County (Lucas, 1975), chromium- and nickel-bearing deposits were noted in the upper Cle Elum and Teanaway Rivers. The Cle Elum deposit, located on the east bank of the Cle Elum River between RM 24.1 and RM 25.6, is described as a highly weathered ferruginous laterite enriched in nickel, chromium, and iron. This deposit lies along 20 mi (miles) of the contact between the Swauk Formation and an adjacent periodotite. The bulk of the deposit also lies adjacent to the Cle Elum River. Concentrations of nickel, chromium, and iron as large as 7,000, 16,400, and 480,000 μg/g, respectively, were found in the Cle Elum deposit (Lucas, 1975). The Denny deposit, drained by lower-order streams about 2 mi east of the Cle Elum deposit, is enriched in chromium. The Mount Hawkins deposit, similarly enriched, is located along a tributary to the North Fork of the Teanaway River. The chromium contained in the Hawkins and Denny deposits is not related to the nearby Cle Elum laterite; rather, it is found in serpentinite--a metamorphic rock formed from peridotite.

In the Cougar Lake-Mount Aix area (Simmons and others, 1983), which lies east of Mount Rainier, 779 streambed sediment samples were collected in 1973. Sediment passing through a 0.018 millimeter mesh sieve were screened by semiquantitative-spectrographic analysis for 30 elements including environmentally significant elements, such as antimony, arsenic, barium, cadmium, copper, chromium, nickel, and zinc. Anomalously large concentrations were re-determined by atomic adsorption. Streambed sediment of lower-order streams flowing to the Bumping River are enriched in copper (100-500 μg/g) and zinc (200-500 μg/g). Sediment of lower-order streams flowing to the American River and Rattlesnake Creek are enriched in lead (30-50 μg/g). Mercury enrichment (0.7-10 μg/g) was found in sediment of lower-order streams flowing into the Tieton River, upstream of Rimrock Lake. Natural sources of minor-element enrichment are generally attributed to mineralization associated with andesitic rock of the Ohanapecosh Formation and local granitic plutons.

ASSESSMENT APPROACH

To accurately determine element sources that contribute to the streambed-sediment chemistry, as well as to qualitatively evaluate the transport of elements, basin-wide sampling of lower- and higher-order streams is required. In many instances, element concentrations in streambed sediment from lower-order streams in the Yakima River Basin are controlled principally by elements from local geologic sources. In other instances, however, element concentrations in streambed sediment from lower-order streams are affected by human activities; these effects generally are confined to the agricultural lands of the middle and lower valley. When areas draining lower-order streams are affected by several sources and (or) activities, higher-order streams integrate element concentrations in the streambed. Sampling lower- and higher-order streams can aid in determining the relative contributions of elements (for example, from geologic sources and agricultural activities) to the streambed sediment chemistry of higher-order streams.

Sampling Medium

Fine-fraction-streambed sediment (finer than 63 µm [micrometer] in diameter) is an ideal sampling medium for a basinwide assessment of major- and minor-element distributions. Apart from usually being found and sampled along most stream reaches, fine-fraction sediment tends to concentrate major and minor elements, and thus, improves the likelihood of detecting the presence of elements in streambed sediment (Horowitz, 1991). Fine-fraction-streambed sediment accumulates--especially along low-gradient reaches--during periods of sustained low streamflow when most streambed sediment is not being resuspended and transported.

Site Selection

Streambed-sediment samples were collected from 448 sites in the basin. Of the 448 sites, 41 were sufficiently close to one another--within 300 ft--and were assigned single map numbers on plate 1 (a "#" symbol appears next to site-reference numbers on plate 1 where an additional site, in close proximity, was sampled). The additional sites were sampled for quality-assurance purposes. Thus, 407 (448-41) site-reference numbers are listed on plate 1 and statistically summarized and interpreted in this report. Streambed-chemical data and quality-assurance data were published by Ryder and others (1992). The 407 sampling sites represent a variety of environments, which were divided into seven different "site classifications" for subsequent use in tables and illustrations. Site classifications were categorized as:

(1) los--lower-order streams: 332 sites are located on lower-order streams (first- or second-order streams) at a map scale of 1:24,000;

(2) Totm--tributaries to other than the main stem: 19 sites are third-, fourth-, or higher-order streams that do not directly flow into the the Yakima River;

(3) tmna--tributaries to main stem; naturally affected: 11 sites are located on higher-order streams that flow directly to the main stem of the Yakima River, but lack major known anthropogenic sources;

(4) tma--tributaries to main stem; anthropogenically affected: 19 sites are located on higher-order streams that flow directly to the Yakima River and are affected by sources which include agricultural-return flow, urban runoff and STP effluents;

(5) m--main stem: 16 sites are located on the main stem of the Yakima River;

(6) ss--soil samples: four sites represent soils from pesticide-contaminated orchards; and

(7) ud--urban storm water drains: six sites (see pl. 1).

Site classification 1 represents "lower-order streams" and site classifications 2 through 5 represent "higher-order streams." Site names are given to higher-order streams, urban drains, and soil samples (table 3).

Sampling sites classified as "lower-order streams" were selected using a random-sampling design described by Ryder and others (1992); in addition, some lower-order sites were intentionally selected for quality assurance measurements. The random-sampling design, initially developed for geochemical exploration, entails the random selection of a site from within a "square sample grid" (4.7 mi per side) that has been placed over a 1:24,000-scale base map; 270 of the 332 lower-order stream sites were selected in this manner. Sites not randomly sampled were intentionally selected and sampled for quality-assurance purposes. Lower-order stream sites were selected in the vicinity of known mineralization (based on previous geochemical studies) to determine appropriate analytical methods, and to evaluate variability associated with field collection, sample processing, and sample analysis.

Sites selected by the random-sampling design represent stream reaches no more than 2 mi in length and drainages of no greater than 6 mi^2; additionally, drainages do not originate from lakes or impoundments--any condition that might serve to impede the downstream movement of streambed sediment. Several lower-order stream sites characteristically have intermittent streamflow and were dry during the period of sampling. Streambed sediment was formed in single bedrock units for most of the small drainage areas selected using the random-sampling design. The presence of anomalous element concentrations in streambed sediment under these conditions commonly reflects a geologic source of enrichment to streambed sediment such as: (1) element-enriched ground water, (2) element-enriched runoff, and (3) physically weathered, detrital mineral grains (Levenson, 1980). Data from these sites may be used to relate the spatial distribution of element concentrations to specific bedrock units. In addition, the chemistry of lower-order sites in agricultural areas (where element concentrations exceed those of surrounding geology) may be used to identify elements associated with agricultural activities; for example, lead arsenate.

The 19 sampling sites classified as "tributaries to other than the main stem" were not randomly selected; instead, they were located in areas removed from agricultural land-use activity and represent much larger drainage areas than their lower-order counterparts. Because these sites represent larger drainage areas, the geochemistry of the streambed sediment is a chemical aggregate of multiple-geologic sources. These sites generally occur in the upper and middle reach of the basin--particularly within the Naches River drainage which flows into the middle reach and comprises the Lower Naches, Upper Naches, and Tieton Subbasins (see fig. 1). These sites were selected to indicate if element-enriched sediment of lower-order streams is transported to higher-order streams. If so, the observed enrichment may be related to a particular geologic unit or land use that has been chemically characterized from samplings of lower-order streams.

The 11 sampling sites classified as "tributaries to the main stem; naturally affected" are located near the mouths of tributaries that flow directly to the Yakima River. Streambed sediment at these large drainage

Table 3.--Sample-site locations of higher-order streams, urban drains, and soils in the Yakima River Basin, Washington, 1987

[Agency identification numbers for lower-order-stream sites are equal to the 15 digit latitude and longitude, as shown on plate 1. Some higher-order-stream sites were assigned an eight digit number (downstream order number) for retrieval purposes. Site names were not assigned to lower-order streams. 1/ = computer retrieval of chemical data by either the U.S. Geological Survey's (USGS) WATSTORE (a WAter Data STOrage and REtrieval System) or U.S. Environmental Protection Agency's STORET (STOrage and RETrieval System) cen be made using the USGS identification number]

Site reference number (plate 1)	Site name	USGS 1/ identification number	Latitude	Longitude
27	Cle Elum River above Cle Elum Lake near Roslyn, WA	4721191210621	472119	1210621
32	Jungle Creek at Pines Campground, WA	4720111205129	472011	1205129
35	Box Canyon Campground near mouth of Lodge Creek, WA	4719571211521	471957	1211521
56	North Fork Teanaway River, WA	4715271205244	471527	1205244
57	Middle Fork Teanaway River, WA	4715331205349	471533	1205349
58	West Fork Teanaway River, WA	4715321205412	471532	1205412
65	Lodge Creek near mouth, WA	4714261211326	471426	1211326
70	Swauk Creek downstream of First Creek, WA	4712301204156	471230	1204156
76	Yakima River at Cle Elum, WA	12479500	471135	1205655
90	Naneum Creek near Ellensburg, WA	4707241202843	470724	1202843
95	Taneum Creek at Taneum Campground, WA	4706281205117	470628	1205117
119	Little Naches River above Quartz Creek, WA	4701431210912	470143	1210912
121	Yakima River at Evergreen Farm near Ellensburg, WA	12482780	470107	1203628
126	Wilson Creek at 6th and Pine Street	4659521203245	465952	1203245
127	Little Naches River near Highway 410, WA	4659291210559	465929	1210559
131	American River near Cedar Springs, WA	4658401211004	465840	1211004
136	Manastash Creek ebove diversions near Reed Canyon, WA	4658021204103	465802	1204103
141	Cherry Creek above Wipple Wasteway at Thrall, WA	12484440	465544	1202948
142	Wilson Creek above Cherry Creek at Thrall, WA	12484100	465535	1203001
144	Bumping River at Soda Springs, WA	4655271211249	465527	1211249
164	Yakima River at Umtanum, WA	12484500	465146	1202844
169	Umtanum Creek at mouth, WA	4651191202902	465119	1202902
178	Bumping River above Bumping Lake, WA	4650101212208	465010	1212208
180	Squaw Creek below Scorpion Coulee Creek, WA	4649191202702	464919	1202702
181	Wenas Creek upstream of Wenas Lake, WA	4649161204128	464916	1204128
183	Rattlesnake Creek at mouth, WA	4649091205601	464909	1205601
201	Yakima River at Roza Dam, WA	4645041202751	464504	1202751
202	Naches River upstream of Tieton River, WA	4644471204714	464447	1204714
207	Tieton River at mouth, WA	4643361204834	464336	1204834
209	Irrigation canal intake at Naches, WA	4642551204156	464255	1204156
213	Selah Creek at mouth at Ponoma, WA	4642291202803	464229	1202803
224	Former apple orchard site near Naches, WA	4639331203557	463933	1203557
229	Selah urban drain, WA	4638551203130	463855	1203130
233	Clear Creek inflow to Clear Lake, WA	4638171211704	463817	1211704
235	Naches River near North Yakima, WA	12499000	463742	1203110
236	Cowiche Creek near mouth, WA	4637401203436	463740	1203436
237	South Fork Tieton at inflow to Rimrock Lake, WA	4637321210754	463732	1210754
241	North Fork Tieton near Clear Lake, WA	4637001211856	463700	1211856
248	Yakima urban drain #1, WA	4635071202744	463507	1202744
252	Yakima urban drain #2, WA	4634001202816	463400	1202816
256	Former apple orchard near Ahtanum, WA	4633511203726	463351	1203726
258	Former apple orchard near Ahtanum, WA	4633381203730	463338	1203730
259	Former apple orchard near Ahtanum, WA	4633381203731	463338	1203731
265	Moxee Drain at Thorpe Road near Union Gap, WA	12500430	463218	1202719
266	Wide Hollow Creek near mouth, WA	4632181202817	463219	1202817
270	Ahtanum Creek at Union Gap, WA	12502500	463210	1202820
272	Yakima River above Ahtanum Creek at Union Gap, WA	12500450	463204	1202758
281	Yakima River at Parker, WA	4629471202624	462947	1202624
311	Yakima River at Zillah, WA	4624071201654	462407	1201654
318	East Toppenish Drain at Wilson Road, WA	4622031201500	462203	1201500
329	Yakima River at Granger, WA	4620161201147	462016	1201147
330	Granger Drain at mouth at Granger, WA	12505460	462010	1201138
331	SUB 35 Drain at Parton Road, WA	4620111201347	462011	1201347
337	Marion Drain at Indian Church Road at Granger, WA	12505510	461952	1201154
344	Toppenish Creek at Indian Church Road near Granger, WA	12507508	461852	1201153
346	Urban Sunnyside Washout Drain, WA	4618361195925	461836	1195925
347	Toppenish Creek near Fort Simcoe, WA	4618421204713	461842	1204713
348	Toppenish Creek at Toppenish National Wildlife Refuge, WA	4618331201952	461833	1201952
351	Yakima River at Van Geison Bridge, WA	4617521191955	461752	1191955
355	Drain containing Sunnyside Sewage Treatment Plant effluent, WA	4617281200105	461728	1200105
356	Corral Creek near Benton City, WA	4616461193217	461646	1193217
361	Satus Creek at gage at Satus, WA	12508620	461626	1200832
367	Yakima River above Chandler Pump, WA	4615581193519	461558	1193519
374	Yakima River at River Mile 4, WA	4615081191700	461508	1191700
375	Yakima River at Kiona, WA	12510500	461513	1192837
376	Yakima River below Satus Creek, WA	4615061200544	461506	1200544
377	Satus Creek below Dry Creek near Toppenish, WA	12508500	461500	1202240
382	Snipes Creek at mouth at Whitstran, WA	12509829	461402	1194037
386	Spring Creek at mouth at Whitstran, WA	12509710	461400	1194038
388	Yakima River at Mabton, WA	4613531195954	461353	1195954
390	Yakima River below Prosser Dam and Sewage Treatment Plant, WA	4613251194346	461325	1194346
391	Grandview Drain below gravel pit, WA	4613281195548	461328	1195548
395	Yakima River at Euclid Bridge at River Mile 55 near Grandview, WA	12509050	461301	1195500
396	Satus Drain 303 at Highway 22 near Mabton, WA	4613031200107	461303	1200107
402	Urban catch basin in Prosser, WA	4611531194704	461153	1194704

sites could be affected by several lower-order streams in specific geologic units. Where large element concentrations were found at sites classified as tributaries to the main stem, "naturally affected", they were related to specific geologic sources from lower-order streams.

Nineteen sampling sites were classified as "tributaries to the main stem; anthropogenically affected" and were located at the mouths of anthropogenically affected tributaries that flow directly to the Yakima River. These sites are affected by sources such as nonpoint-agricultural runoff, STP-point-source effluents, and urban runoff. The sites were sampled to assess the chemical character of anthropogenically affected streambed sediment in addition to characterizing the chemical quality of sediment (suspended sediment and bed load) that may transport to the main stem.

Sixteen sampling sites were classified as "main stem." They were located about 10 mi from one another and often were situated downstream of major tributaries to the main stem. The streambed-sediment chemistry of the main stem represents the cumulative sum of the natural chemical characteristics from various geologic units plus the effects from upstream land-use activities, which include a variety of point and nonpoint sources.

A limited number of surficial soil samples were collected from agricultural plots formerly treated with lead arsenate to estimate the potential effect of erosion on streambed-sediment chemistry. These plots had been apple orchards and were converted to row crops. Historically, three of the four former apple orchards were treated with lead-arsenate pesticides to eradicate codling moths. All four sampling sites were located in areas where peas were being grown at the time of sampling in 1987. Growth of pea crops at three of the four sites was described by the land owner as "poor or retarded," possibly an effect of prior pesticide applications. The fourth site was in an area exhibiting no growth retardation. One of the three affected sites was sampled at a depth of 1 foot in addition to the surficial sample; thus, a total of five determinations were made from four sampling sites.

Sampling sites were located in urban storm-water drains from the cities of Ellensburg, Selah, Yakima, Sunnyside, and Prosser. Six samples were collected to chemically characterize streambed sediment that directly received urban-nonpoint-source runoff. Data collected from urban drains may be used to explain element enrichment at downstream, main-stem sites.

Sample Collection and Processing

Streambed-sediment samples were collected during the low-flow period in late summer and fall of 1987. Sample-collection techniques were described by Ryder and others (1992). Techniques were similar in lower- and higher-order streams, differing only in sieving methodology--wet sieving for higher-order streams and dry sieving for lower-order streams. Dry sieving was used for lower-order streams because of the large number (332) of lower-order sites and because it is an automated laboratory procedure in comparison to the time intensive, field, wet-sieving method. In addition, dry sieving was used because 60 percent of lower-order sites were dry at collection time. All sampling equipment was washed with Liquinox and rinsed with distilled-deionized water prior to sample collection.

Streambed sediment was collected from five to seven points in each cross section of the stream channel; sampling was confined to surficial-oxic sediment usually present within the upper one-half inch of the streambed. Samples generally were collected in higher-order streams by dipping a polyethylene 100 mL (milliliter) beaker into the streambed; in deeper water, samples were collected by coring the streambed with a butyrate-acetate cylinder. Samples were collected in lower-order streams using a polyethylene scoop.

All streambed sediment samples were wet sieved through a 2-mm mesh stainless-steel sieve using a minimum amount of stream-site water. Following the initial sieving, higher-order streambed sediment was wet sieved through a 0.063-mm-mesh-polyethylene sieve using stream-site water. The supernatant was decanted (after overnight settling in 2-L glass bottles) and the sediment was dried at room temperature and placed in plastic containers for shipment to the laboratory. Following the initial sieving, sediment from lower-order streams was dewatered and air dried by transferring the sample from the stainless-steel-catchment pan to a 6-by-10-inch Hubco sample bag. In both wet and dry sieving, about 3.5 grams of the fine-fraction (less than 0.063-mm-diameter size) sediment was collected for chemical analysis. Soil samples from former orchard sites were wet sieved using distilled-deionized water.

Samples were submitted to the U.S. Geological Survey's Branch of Geochemistry in Denver, Colorado, and were processed by methods described by Arbogast (1990). The higher-order stream samples, which had been sieved through a 0.063-mm-mesh sieve, were processed through a jaw crusher to break up large aggregates that formed during the drying period; about 25 percent of the sample was archived. The remainder of the sample was processed using a ceramic-plate pulverizer to disaggregate and homogenize the sample prior to analysis. The lower-order stream samples, which had been sieved through a 2-mm-mesh sieve, were initially disaggregated using a jaw crusher and processed by a ceramic "juicer" (Mechanical Nasco-Asplin Soil Grinder) which further disaggregates the sample with minimal particle disintegration--again, about 25 percent of the sample was archived. The remainder of the sample was dry sieved through a 0.063-mm-mesh, stainless-steel sieve prior to analysis. The variability associated with sample collection and processing (including use of wet- and dry-sieving techniques) is presented in appendixes A and B.

Geologic Classification of Lower-order Stream-sampling Sites

By Marshall W. Gannett

The probable geologic source of 270 randomly selected, lower-order streambed samples was determined to evaluate the relation between sediment chemistry and geology. In some drainages, particularly small ones, there may be only one bedrock unit present and the probable source of the sediment, or alluvium, can be identified. In other drainages, however, where multiple bedrock units are present, the sediment probably includes material from a number of sources.

To identify probable sediment sources, individual sampling sites were plotted on geologic maps. Geologic maps by Walsh and others (1987), Tabor and others (1982), Frizzell and others (1984), and Myers and Price (1979) were considered to be the best maps available at scales appropriate for this study (1:100,000 to 1:250,000). For this analysis, the most likely sources for the surficial deposits sampled were identified. Though all stream-sediment samples are technically alluvium, because of scale limitations, alluvium is often not mapped on lower-order streams of small-scale maps. Although alluvium is present, the stream is shown to flow directly on bedrock.

In the classification scheme presented in this report, samples were assigned to a particular geologic unit or, if no single unit could be identified, designated as Quaternary alluvium. If one bedrock unit covered or dominated the entire drainage from which a sample was taken, that bedrock unit was considered the source for the sample. If the sample was from an area mapped as alluvium within a drainage underlain entirely or predominantly by one bedrock unit, that bedrock unit was considered the source for the sample. If a sample was from a drainage where multiple bedrock units were present and the sediment sample was considered to include material from multiple geologic sources, the sample was designated as Quaternary alluvium whether or not the sample site actually was mapped as alluvium. In this scheme, samples for which no probable single source could be identified were lumped as Quaternary alluvium.

Samples from areas mapped as alluvial fans or landslides that occurred entirely in one bedrock unit were assigned to that bedrock unit. Samples from areas mapped as loess were designated Quaternary alluvium because the origin of the loess could not be readily identified. Sediment deposited by catastrophic Pleistocene floods, which have a probable origin outside the Yakima Basin, was classified separately from other Quaternary alluvial deposits.

Compared to the number of sediment samples, the number of geologic map units in the Yakima Basin is too large to allow for meaningful statistical analysis. The geologic map units, therefore, were combined into nine generalized categories used to depict the generalized-surficial geology of the Yakima River Basin (see pl. 1). Each of the nine categories are intended to represent materials of similar origin, mineralogy, or chemistry. The nine categories--used repeatedly in tables, illustrations, and statistical analyses of this report--are henceforth termed Yakima River Basin geologic units and are as follows:

(1) pTmi--Pre-Tertiary metamorphic and intrusive rocks (146 mi^2): Ten sediment samples were collected from areas underlain by bedrock units in this group.

This category includes a variety of rock types from pre-Tertiary units, such as the Mount Stuart batholith, which encompass only small areas in the basin. Rocks in this category include phyllite, schist, diabase, gabbro, peridotite, and serpentinite.

(2) ms--Marine sedimentary rocks (86 mi^2): Six samples are from areas underlain by units in this category.

The marine sedimentary rocks that compose this group consist primarily of sandstones and conglomerates. Deposition and diagenesis of sediment in the marine environment are sufficiently different from the nonmarine environment to justify separate marine and nonmarine sediment categories.

(3) nms--Nonmarine sedimentary rocks, exclusive of Quaternary deposits (640 mi^2): 30 samples are from areas underlain by units in this category.

This group includes geologic units mapped as nonmarine or continental sediment, such as the Swauk, Roslyn, and Ellensburg Formations. These units include a variety of sedimentary rock types deposited in a variety of depositional environments. Some of the sedimentary units are interbedded with volcanic flows. Even though much of this sedimentary material is volcanic in origin, the processes of erosion, transportation, redeposition and diagenesis have undoubtedly modified the chemistry and mineralogy of these materials sufficiently to warrant placing them in a group separate from other volcanic materials.

(4) Tgii--Tertiary granitic and intermediate intrusive rocks (73 mi^2): Only three sediment samples are from areas underlain by units in this category.

This group includes Tertiary intrusive rocks of silicic to intermediate composition. These intrusives were considered to be sufficiently mineralogically and chemically unique to constitute their own generalized group.

(5) Mov--Miocene and older volcanic rocks, exclusive of the Columbia River Basalt Group (685 mi^2): 34 samples are from areas underlain by units in this category.

Flows, tuffs and other volcaniclastic deposits of predominantly basaltic to andesitic composition, such as the Teanaway Formation, are included in this category. This is, to a certain extent, a "lumped" category which includes Tertiary volcanic and volcanic-derived rocks of Miocene age and older. Many of the geologic-map units contained within this category include a variety of rock compositions and textures. At the scale of available mapping (and for this study), there was insufficient information for a more refined subdivision of these units.

(6) crb--Columbia River Basalt Group rocks (2,551 mi^2): 100 samples were located in Miocene-Epoch-flood basalts of the Columbia River.

Rocks of the Columbia River Basalt Group were placed in their own category separate from other Tertiary volcanics because they represent a very large area of relatively uniform lithology and rock chemistry. The Columbia River Basalt Group constitute the largest bedrock map unit in the basin. More sediment was sampled from areas underlain by Columbia River Basalt Group than from any of the other generalized geologic units.

(7) QPlv--Quaternary and Pliocene volcanic rocks (274 mi^2): 11 samples were located in the Cascade Range geologic province.

This group includes Pliocene to Quaternary basalt and andesite flows and is separated from other Tertiary volcanics on the basis of age.

(8) Qfd--Quaternary flood deposits (566 mi^2): 29 samples were located in Quaternary surficial deposits from catastrophic floods.

This group includes deposits resulting from catastrophic, glacial-outburst floods during the Pleistocene (Waitt, 1985). These deposits generally are found at altitudes below 1,000 feet. A large part of the material included in this group probably originated outside the region and, therefore, may have a distinct chemical signature.

(9) Qdl--Quaternary deposits and loess (1,104 mi^2)[3]/ : 47 samples were located in Quaternary surficial deposits including loess and excluding catastrophic flood deposits.

This category includes alluvial deposits along rivers and streams, eolian materials, and other Quaternary sedimentary materials for which no single bedrock source can be identified.

Analytical Methods

Fine-fraction-streambed sediment was analyzed for 45 elements including two forms of carbon. Analytical methods and method-reporting levels for each element are shown in table 9, at the back of the report. Analytical methods and quality-assurance practices have been described by Arbogast (1990) and Sanzolone and Ryder (1989) and have been summarized together with method reporting levels in table 9 (at back of report).

Thirty-eight elements were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES), while arsenic and antimony were determined by hydride generation with atomic adsorption (AA) spectrometry. Total carbon and sulfur were determined as carbon dioxide and sulfur dioxide after combustion and measured by infrared and titration techniques, respectively. Inorganic carbon was determined by titration. Mercury was determined using the cold vapor technique with atomic-adsorption spectrometry, and uranium was determined by fluorimetry. Digestion methods for ICP-AES and AA are "total" (greater than 95-percent analyte recovery), as are the combustion methods for

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[3]/ The sum of the areas for the nine-geologic units (based on digitized data stored in the geographical-information system data base is 30 mi^2 smaller than the 6,155 mi^2 reported by the Columbia Basin Inter-Agency Committee (1964).

total carbon and sulphur determinations, and the titration method for inorganic carbon. The digestion method for uranium is considered a partial extraction technique (less than 95-percent analyte recovery).

Statistical Methods

The statistical tests used in this report are nonparametric (with the exception of factor analysis) and are appropriate for water-quality data because the population of data does not need to be normally distributed and, in a natural environment, element concentrations in streambed-sediment rarely comprise a normal distribution.

Geologic factor analysis, as described by Joreskog and others (1976), was used as an exploratory data-analysis technique to examine relations among groups of elements, and the Kendall Tau B test (PSTAT, 1989) for correlation (a nonparametric test) was used on ranked data to further verify relations between elements. Prior to factor analysis, element data were logarithmically transformed to approximate a normal distribution. A five-factor model using a varimax projection has been selected for the streambed sediment chemistry data of the Yakima Basin. Factor analysis compares various groupings of major and minor elements under what is known as "factors." Each sampling site in the above example of a five-factor model receives five "factor scores." Factor scores increase, either in a positive or negative direction, as the significance level increases among a defined suite of elements at a particular sampling site.

To confirm relations observed among elements by factor analysis, Kendall's Tau B test for correlation was used on ranked data (SAS Institute, 1982; version 5.16). Analysis of variance (ANOVA) and Tukey's studentized range test, a nonparametric procedure, was used to test for significant difference ($\rho = 0.1$) between mean ranks of element concentrations among the nine generalized geologic units of the Yakima River Basin (SAS Institute, 1982). The mean ranks for the element concentrations were determined by first placing all the concentrations for each element into one group. The element concentrations within the group were ranked in ascending order. The ranked values were then placed into nine subgroups--each subgroup represents a geologic unit. For each subgroup, the mean of the ranks (not the element concentrations) was calculated and henceforth will be referred to as "the mean ranks of the element concentrations." For each element, nine mean ranks were computed and tested to determine if one or more of the mean ranks were significantly different from one another.

As a simple example, consider the following hypothetical data set that is based on three geologic units or subgroups:

Geologic unit	Element concentration		Rank
1	0.1		1
1	.2		2
1	.3		3
		Mean rank	2
2	.4		4
2	.5		5
2	.6		6
		Mean rank	5
3	.7		7
3	.8		8
3	.9		9
		Mean rank	8

The mean rank of the element concentrations for each geologic unit is calculated by summing the ranks and dividing by the number of element concentrations within each geologic unit. For geologic unit number 1, the mean rank is equal to:

$$\frac{1 + 2 + 3}{3} = 2.$$

The mean rank for geologic unit 2 is equal to 5, and the mean rank for geologic unit 3 is 8.

Graphical distributions of major and minor elements were made using Tukey's modified boxplots (Helsel and Hirsch, 1992, p. 25) and cumulative frequency plots (Veltz, 1984).

VARIABILITY OF MAJOR- AND MINOR-ELEMENT CONCENTRATIONS ATTRIBUTABLE TO ANALYTICAL METHODS AND FIELD-COLLECTION AND PROCESSING TECHNIQUES

Differences in streambed-sediment chemistry among sampling sites cannot be determined without first defining the variability of the element concentration resulting from the analytical method and the field-collection and processing technique. The above factors that affect element-concentration variability, collectively termed "chemical variability," were defined in terms of (1) analytical variability (splitting a homogeneous sample into two fractions and analyzing each fraction independently, (2) cross-section variability (variability of the element concentration within the stream cross section), (3) on-site variability (variability of the element concentration between a randomly selected sampling site and a second site, located 300 feet upstream), (4) within-sample-grid variability (variability of the element concentration between two sampling sites, within a single-sampling grid [4.7 mi per side]), and (5) sample-collection and processing variability (additional variability of the element concentration attributed analytical precision, cross section variability, on-site variability, and the use of different sieving techniques--dry sieving for lower-order streams and wet sieving for higher-order streams).

The types of chemical variability described above are not mutually exclusive. By sampling design, analytical variability was present in the measurement of cross-section variability, on-site variability, within-sample grid variability, and sample-processing variability. In addition to analytical variability, cross-section variability and on-site variability also were present in the measurement of sample-collection and processing variability. Thus, sample-collection and processing variability should not be used as a direct measure of variability between wet- and dry-sieved samples.

On the basis of an evaluation of the various types of chemical variability (app. A and B), on-site variability and sample-collection and processing variability were used throughout this report as quality-assurance guidelines for making intersite comparisons of element concentrations. The guidelines were derived by computing statistical tolerance intervals (app. B) for on-site variability and sample-processing variability measurements. Intersite comparisons were qualified or censored, when the difference in element concentrations between sites falls within the statistical tolerance intervals calculated from on-site variability and sample-processing variability measurements. When this occurs, differences in element concentrations between sites may not be any larger than on-site variability or sample-processing variability, or both.

EFFECTS OF MOUNT ST. HELENS ASH FALL ON THE CHEMISTRY OF STREAMBED SEDIMENT IN THE YAKIMA RIVER BASIN

The eruption of Mount St. Helens on May 18, 1980 deposited volcanic ash over the entire Yakima River Basin. The extent to which this ash may have enriched or diluted various elements in the streambed sediment, and thus affected comparisons between streambed-sediment sampling sites, was explored using ANOVA (analysis of variance, see statistical methods section).

Two groups of streambed-sediment sampling sites were selected on the basis of the amount of ash deposited. Using the ash-fall maps of Sarna-Wojcicki, Shipley, and others (1981), sites that received greater than 1.0 gram per square centimeter (g/cm^2) of ash (high-ash-fall sites) and those sites that received less than 0.5 g/cm^2 (low-ash-fall sites) were identified. To minimize the influence of many uncontrollable factors, such as the influence of point sources on higher-order streams, only sites on lower-order streams were used. Also to minimize the effects of different rock types, only sites in the Columbia River Basalt Group rocks geologic unit were included in the high-ash-fall and low-ash-fall groups. Of the 100 lower-order stream sites in the Columbia River Basalt Group rocks geologic unit, 28 were high-ash-fall sites, and

56 were low-ash-fall sites. Those sites that received between 0.5 and 1.0 g/cm^2 of ash were ignored to emphasize the difference between areas that receive high-ash fall and low-ash fall (fig. 6).

An assumption was made that streams draining basalts will have sediment of similar chemical compositions. This may seem a questionable assumption, because the Columbia River Basalt Group rocks geologic unit includes three major formations, each composed of members or geologic units having chemical variations. Substantial variations, however, were not evident in the streambed sediment sampled for this study, as will be discussed in a later section on spatial distribution of major and minor elements in streambed sediment.

The ANOVA test (table 4) was used to determine if statistically significant differences in element concentration existed for high- and low-ash-fall groups. The hypothesis is that if ANOVA found a statistical difference ($\rho \leq 0.05$) between the two groups, then that difference is due to the effects of the Mount St. Helens ash deposited in 1980.

The ANOVA tests indicated that for 10 elements, the high- and low-ash-fall groups represented statistically different populations ($\rho \leq 0.05$). Calcium, sodium, and copper showed enrichment in the high-ash-fall area, while seven elements showed dilution in the high-ash-fall area (table 4). By comparing the ranges of concentrations for the elements in the reported ash samples with the median concentrations in the low- and high-ash-fall groups, it appears that all 10 of these elements fit the hypothesis. Where the ash concentrations are higher than the low-ash-fall group median, the high-ash-fall group median also is higher, apparently elevated by the ash fall. Similarly, for the seven "diluted" elements, the ash concentrations are lower than the low-ash-fall group median, and the ash has apparently lowered the median concentration in the high-ash-fall group. If these differences were due to chemistry of basalt instead of the ash, one would expect some of these ash concentrations not to correspond to the change (dilution or enrichment) in the medians of the two groups. Instead, all 10 of these elements show correspondence.

For 12 elements, the ANOVA tests showed no significant difference between the high- and low-ash-fall groups, and for one element, mercury, no conclusion can be made because the medians of both groups are below the detection limit. Six elements, potassium, cobalt, lead, nickel, vanadium, and zinc, have median concentrations in the low-ash-fall group that lie within the ranges of reported ash concentrations (see table 4). Thus, ash fall would not be likely to affect the median concentration for the low-ash-fall group.

The lower concentrations of titanium and arsenic in the ash could have lowered the median concentrations in the high-ash-fall group, but the difference was not significant ($\rho \leq 0.05$). Arsenic, however, was significant at $\rho \leq 0.1$.

Concentrations in ash samples and in streambed sediment for only four elements failed to meet the hypothesis. Comparing concentrations in ash to the median element concentrations in streambed sediment from

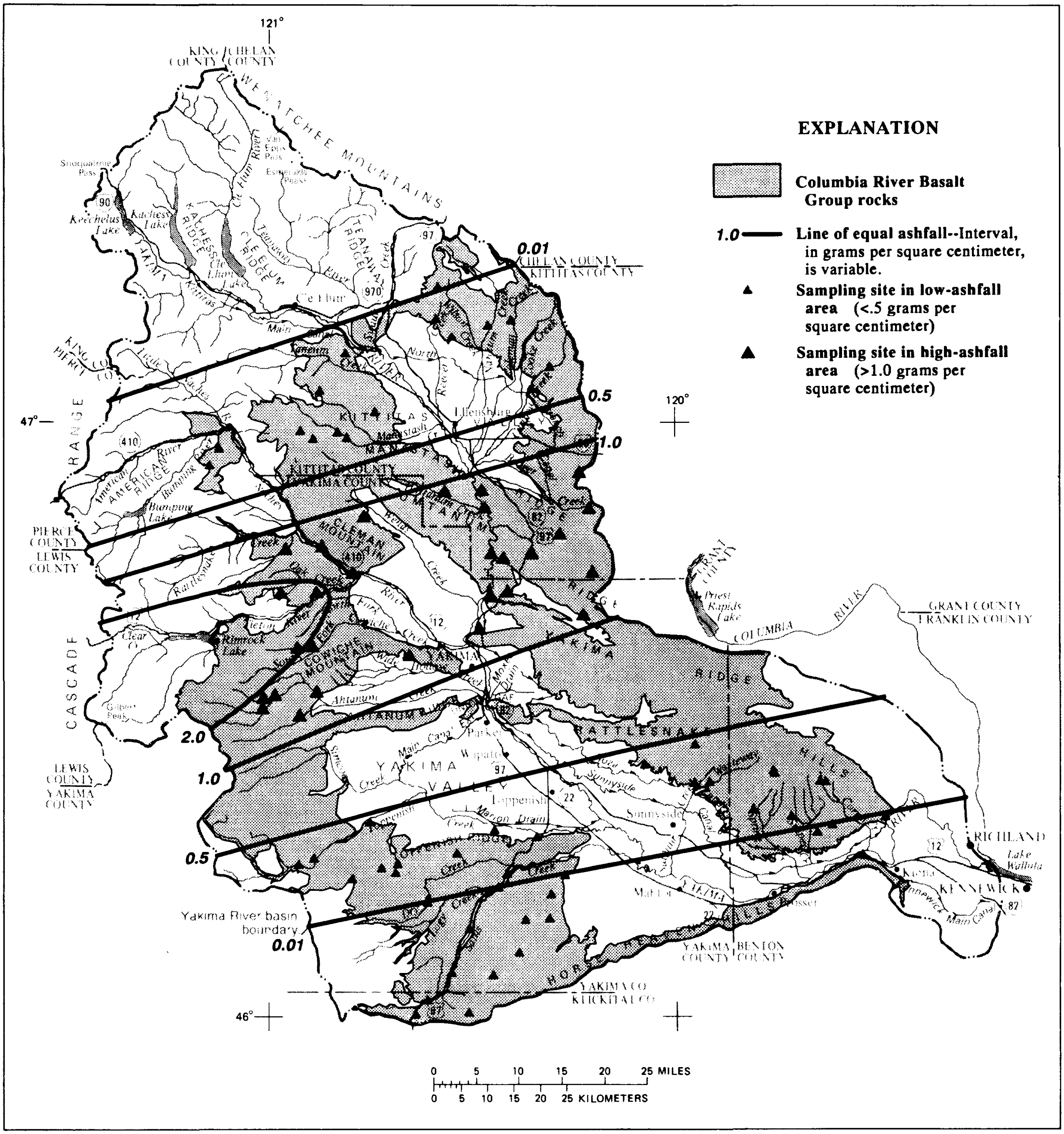

Figure 6. Locations of streambed-sediment sampling sites in the Yakima River Basin, Washington, in 1987 that occur in areas of high- and low-ash fall from the 1980 eruptions of Mount St. Helens.

Table 4.--Tukey's studentized range test on analysis of variance for major- and minor-element concentrations in streambed sediment of high- and low-ash-fall sites in the Columbia River Basalt Group rocks geologic unit, Yakima River Basin, 1987

[High-ash-fall sites received greater than 1.0 grams of ash per square centimeter, and low-ash-fall sites received less than 0.5 grams of ash per square centimeter]

Element	Concentration range in ash samples	Source of data1/	Effect of high-ash fall (range of dilution or enrichment2/)	Median concentration in streambed sediment originating from ash-fall sites	
				Low	High
Major elements, in units of grams per 100 grams (percent)					
Calcium	3.7-4.8	FHTS	Enrichment (0.3-0.4)	2.8	3.0
Iron	3.7-4.6	FHTS	None	5.3	5.6
Magnesium	1.6-2.5	FHTS	None	1.2	1.1
Potassium	0.73-1.3	FHTS	None	1.1	1.1
Sodium	3.2-3.6	FHTS	Enrichment (0.3-0.4)	1.8	2.2
Titanium	0.42-0.53	FHTS	None	.85	.82
Minor elements, in units of micrograms per gram					
Antimony	7.5	H	None	.30	.30
Arsenic	<2-2.6	F	None	3.2	2.2
Barium	218-320	FHTS	Dilution (40-60)	530	480
Beryllium	0.5-0.75	HT	Dilution (0.5-1)	2.0	1.0
Cerium	13-26	HT	Dilution (6-20)	52	43
Chromium	11-45	FHTS	Dilution (6-10)	50	44
Cobalt	15-28	FHT	None	20	22
Copper	25-48	FHT	Enrichment (6-7)	24	30
Lanthanum	15	H	Dilution (4-10)	30	24
Lead	5.8-13	FHT	None	12	12
Mercury	0.0070-0.0088	F	Unknown	<.02	<.02
Neodymium	7.7	H	Dilution (3-80)	30	24
Nickel	13-32	FHTS	None	19	17
Scandium	11-13	TH	None	18	18
Thorium	<2.7	H	Dilution (1.5-3.0)	7.0	5.0
Vanadium	100-169	FHT	None	165	170
Zinc	54-92	FHT	None	86	90

1/ Sources of data are F = Fruchter and others (1980) [four sites], T = Taylor and Lichte (1980) [two sites], H = Hinkley and others (1987) [one site] S = Sarna-Wojcicki, Meyer, and others (1981) [one site].

2/ Dilution = element concentrations in streambed sediment of high-ash-fall groups are statistically smaller ($p \leq 0.05$) than concentrations in low-ash-fall groups; Enrichment = element concentrations in streambed sediment of high-ash-fall groups are statistically larger ($p \leq 0.05$) than concentrations in low-ash-fall groups; None = no statistical difference ($p \leq 0.05$) between groups. Values in parentheses represent the range of differences between streambed-sediment concentrations at the standard quartiles [25, 50th (median), and 75th percentiles] of the high- and low-ash-fall groups.

the high- and low-ash-fall groups, iron and scandium would be expected to be diluted, and magnesium and antimony would be expecte to be enriched. Instead the high-and low-ash-fall medians were not statistically different ($\rho \leq 0.05$), even though they appeared slightly different. Reasons why these four elements did not affect the streambed sediment are unknown.

Because most of the 23 elements analyzed with the ANOVA test fit the hypothesis, the 1980 deposition of Mount St. Helens ash may have affected the chemistry of 10 elements in the streambed sediment of the Yakima River Basin, while 12 other elements were unaffected. These dilutions and enrichments attributed to Mount St. Helens ash fall have been considered in the spatial comparisons of concentrations made in this report. For example, the median and upper quartile for chromium in the high-ash-fall group were both 6 μg/g lower than their counterparts in the low-ash-fall group, while the lower quartile was 10 μg/g lower. Thus, streambed sediment in areas of high-ash fall may be diluted in chromium from 6 to 10 μg/g (see table 4, "effect of high-ash fall"), compared to sediment that received low-ash fall.

BASELINE VALUES FOR MAJOR- AND MINOR-ELEMENT CONCENTRATIONS IN STREAMBED SEDIMENT

The identification of anomalous major- and minor-element concentrations is often accomplished by noting element concentrations that exceed a baseline concentration (Severson and others, 1987; Sinclair, 1974).

A derivation of the baseline concentration concept has been adopted for major- and minor-element concentrations in streambed sediment of Yakima River Basin. For streambed sediment data in this report, the term baseline is applied to an element concentration that separates an upper or anomalous data set from a lower or background data set. The anomalous data set may result from one or more factors which include point-source discharges, urban runoff, hydrothermally altered and mineralized deposits, and allochthonous-element deposits.

Baseline concentrations are listed in table 5 along with percentiles for major and minor elements, and baseline element concentrations typical for soils in the Western United States. Baseline concentrations were selected for Yakima River Basin streambed sediment by plotting element concentrations on normal probability paper (cumulative frequency plots), according to the method described by Veltz (1984, p. 712-721). Most cumulative frequency plots in this report were either monotonic (constant slope) or bimodal (two distinct slopes). Baseline concentrations were identified by locating the point of maximum curvature from a bimodal-cumulative frequency plot of element concentrations. Baseline concentrations for monotonic cumulative frequency plots were arbitrarily selected at a concentration equal to the 95th percentile. For some elements, baseline values could not be determined because nearly all element concentrations were censored--smaller than the analytical method reporting level.

Element concentrations, in this report, were considered anomalous when they exceed the specified baseline concentration for major and minor elements in streambed sediment of the Yakima River Basin. For most of the elements, baseline concentrations were determined from abnormal breaks in

Table 5.--Baseline concentrations and distributions of concentrations for major and minor elements in streambed sediment of the Yakima River Basin, Washington, 1987

[na = data not available; ___ = value at indicated percentile equals or exceeds the baseline concentration. Elements in capital letters = U.S. Environmental Protection Agency Priority Pollutants (Chapman and others, 1982); * = baseline concentration equal to the 95th percentile]

	Yakima River Basin streambed sediment										Western United States soils[1]		
	Number of obser-vations	Minimum	Value at indicated percentile 10	25	50 (median)	75	90	98	Maximum	Base-line concen-tration[2]	Number of obser-vations	Expected 95 percent range baseline soils[3]	Maximum
Chemical													
Major elements, in units of grams per 100 grams (percent)													
aluminum	407	2.7	6.6	7.1	7.7	8.3	8.8	9.7	13	10	770	1.5 - 23	na
calcium	407	.6	1.8	2.2	2.6	3.0	3.4	4.1	4.9	*3.8	777	.19 - 17	32
carbon, inorganic	407	.01	.01	.01	.02	.04	.09	.19	.62	*.14	na	na	na
carbon, total	407	.23	.58	.97	1.8	2.9	4.6	7.6	16	*5.8	na	na	na
IRON	407	2.7	3.9	4.4	5.1	5.9	6.8	8.3	9.8	*7.4	777	.55 - 8.0	>10
magnesium	407	.4	.8	1	1.2	1.4	1.6	5.9	13	2	778	.15 - 3.6	>10
phosphorus	407	.02	.07	.08	.10	.12	.14	.17	.27	.17	524	.006 - .17	.45
potassium	407	.13	.74	.90	1.1	1.3	1.5	1.8	2.2	2.8	777	.38 - 3.2	6.3
sodium	407	.4	1.4	1.6	1.8	2.0	2.3	2.8	3.8	*1.7	774	.26 - 3.7	10
sulfur	407	.01	.01	.01	.02	.03	.05	.09	.36	*.07	2.8	na	na
titanium	407	.14	.46	.59	.71	.86	1.1	1.4	1.8	*1.3	777	.069 - .70	2.0
Minor elements, in units of micrograms per gram													
ANTIMONY	404	.1	.2	.3	.4	.5	.8	2.0	4.8	.7	na	na	na
ARSENIC	404	.7	1.6	2.3	3.9	5.9	11	66	310	8.5	730	1.2 - 22	97
BARIUM	407	55	370	440	500	560	610	790	1,000	650	778	200 - 1,700	5,000
BERYLLIUM	407	<1	<1	<1	<1	2	2	2	4	3	778	.13 - 3.6	15
bismuth	407	<10	<10	<10	<10	<10	<10	<10	10	na	na	na	na
boron	387	<.4	<.4	.4	.7	1.3	2.2	--	8.3	4.0	na	na	na
CADMIUM	407	<2	<2	<2	<2	<2	<2	<2	2	na	na	na	na
cerium	407	5	33	39	45	56	69	100	120	57	683	22 - 190	300
CHROMIUM	407	14	32	44	54	74	110	554	1,800	320	778	8.5 - 200	2,000
cobalt	407	10	15	17	20	24	30	57	140	40	778	1.8 - 28	50
COPPER	407	13	20	24	28	34	46	96	190	40	778	4.9 - 90	300
europium	407	<2	<2	<2	<2	2	2	3	4	na	na	na	na
gallium	407	2	17	18	19	21	23	26	35	*24	776	5.7 - 45	70
gold	407	<8	<8	<8	<8	<8	<8	<8	<8	na	na	na	na
lanthanum	407	3	19	22	25	30	37	53	62	38	777	8.4 - 110	200
LEAD	407	2	9	11	13	17	25	130	890	20	778	5.2 - 55	700
lithium	407	12	18	20	23	27	37	53	110	42	731	8.8 - 55	130
MANGANESE	407	420	660	770	950	1200	1400	1,968	2,900	1,600	777	97 - 1500	5,000
MERCURY	406	<.02	<.02	<.02	.02	.08	.16	.48	3.1	.30	733	.008 - .25	4.6
molybdenum	407	<2	<2	<2	<2	<2	<2	2	8	na	774	.18 - 4.0	7
neodymium	407	<4	19	23	26	31	38	51	66	*45	538	12 - 110	300
NICKEL	407	4	13	17	21	32	53	690	1,900	120	778	3.4 - 66	700
niobium	407	2	2	5	8	10	13	19	35	16	na	na	na
scandium	407	7	13	15	18	21	25	30	40	*27	778	2.7 - 25	50
SELENIUM	99	<.1	<.1	.2	.4	.6	1.0	1.3	1.4	.7	733	.04 - 1.4	4.3
SILVER	407	<2	<2	<2	<2	<2	<2	<2	<2	na	na	na	na
strontium	407	48	218	270	310	340	370	430	620	*400	778	43 - 930	3,000
thorium	407	<4	<4	5	6	8	10	15	20	*12	195	4.1 - 20	31
tin	407	<10	<10	<10	<10	<10	<10	<10	10	na	na	na	na
uranium	407	.10	.55	.70	1	1.3	1.9	6	74	5	224	1.2 - 5.3	7.9
vanadium	407	62	95	120	150	180	220	270	330	*250	778	18 - 270	500
ytterbium	407	<1	2	2	3	3	4	5	6	*4	764	.98 - 6.9	20
yttrium	407	6	17	19	22	25	31	43	61	*35	778	8.0 - 60	150
ZINC	407	32	71	80	93	110	130	220	710	120	766	17 - 180	2,100

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[1] Soils data may offer a regional perspective or framework for gaging Yakima River Basin, streambed-sediment chemistry. Several noteworthy limitations apply when making comparisons between soils and streambed-sediment data--see section titled "Baseline values for major- and minor-element concentration in streambed sediment."

[2] The term baseline was applied to a concentration that separates and upper or anomalous data set from a lower or background data set.

[3] Baseline values were arbitarily selected to coincide with the expected 95-percent range. For log-transformed date, the upper and lower limit of the expected 95-percent range were determined as the geometric mean divided by the geometric standard deviation and the geometric mean multiplied by the square of the geometric standard deviation, respectively.

the cumulative frequency plot of the data. Of the elements whose baseline concentrations were determined in this manner, antimony, arsenic, cerium, copper, and zinc had the largest number of anomalies. At least 10 percent of the element concentrations exceeded the baseline values. Selected anomalies, in addition to selected priority-pollutant trace elements (Chapman and others, 1982), will be evaluated in subsequent sections of this report relative to spatial occurrence, relations with other elements, generalized-surficial geology, and where appropriate, anthropogenic sources. Sampling sites with data anomalies were evaluated by the Yakima NAWQA staff as potential sites for measuring trace elements in tissues of aquatic life.

Comparing the streambed-sediment chemistry of the Yakima River Basin to baseline element concentrations in soils of the Western United States may further substantiate anomalous element concentrations in streambed sediment from the Yakima River Basin. In addition, the soils data base provides a larger, geologically-diverse and regional-orientated perspective of major- and minor-element chemistry. However, use of soils data as a surrogate for comparison to streambed data have several limitations. First, baseline soil concentrations--derived from sampling soils within the B horizon--are not comparable directly to element concentrations in streambed sediment. Though, in a geologic framework, streambed sediment is derived from soils and rocks, comparison of the two media is tenuous because soils may not be subjected to the same degree of geochemical weathering as streambed sediment. Second, baseline-element concentrations in soils are derived from particle sizes of <2 mm in diameter; the data in this report are derived from particle sizes of <0.063 mm. Particle-size effects, therefore, were a factor hampering the comparison of major- and minor-element concentrations from the two sample mediums (Horowitz and Elrick, 1987). Preliminary evaluations of soils (<2 mm and <0.063 mm size fractions) in the Western United States show an enrichment of the <0.063 mm size fraction, relative to the <2 mm size fraction. This enrichment ranged from 30 to 50 percent for chromium, copper, nickel, vanadium, and zinc and there was nearly equal enrichment between size fractions for arsenic, barium, potassium, and lead (R.C. Severson, U.S. Geological Survey, written commun., 1987, based on data in Shacklette and Boerngen, 1984). If some similarities exist between the geochemical weathering of fine-grained sediment and soils, comparison of elements in <2 mm baseline soils to elements in <0.063 mm streambed sediment may overestimate the number of chromium, copper, nickel, vanadium, and zinc anomalies in fine-fraction streambed sediment. These comparisons, however, were likely to be an accurate estimate of arsenic, barium, potassium, and lead anomalies. Data relating particle-size effects to different size classes were not available for all elements determined in the present study.

SPATIAL DISTRIBUTION OF MAJOR AND MINOR ELEMENTS IN STREAMBED SEDIMENT RELATIVE TO GEOLOGY AND LAND USE

To the extent possible, the spatial distribution of elements has been described relative to geologic sources and land-use activities. Lower-order stream sites were used in this report to denote geologic-element sources because they represent small, well-defined drainage areas. This also is true, but to a lesser extent, for lower-order sites with sources attributed to particular land-use practices (for example, the use of pesticides or soil amendments in agricultural areas) may affect some lower-order sites. In contrast, higher-order stream sites may reflect the cumulative effects that multiple-geologic sources and land-use practices had on streambed-sediment chemistry. However, the streambed-sediment chemistry of some higher-order sites may have well- defined element signatures originating from chemical anomalies within lower-order streams. Such sites were particularly useful in illustrating element transport from lower- to higher-order streams, as well as concentration attenuation or sediment dilution. Sediment dilution occurred when sediment enriched in elements from lower-order sites was mixed with sediment that was not similarly enriched from higher-order sites. In addition to locating element sources, relations among elements were examined as they relate to geology (occurrence of minerals or rocks) and land use (occurrence of specific pesticides). Element concentrations were statistically summarized according to site classifications and geologic units (tables 10 and 11, at back of report).

Selected Target Elements in the National Water Quality Assessment Program (NAWQA)

Streambed sediment chemistry may be characterized by chemical measurements of numerous major and minor elements. One key component of the NAWQA program design was the selection of target elements that were relevant to important water-quality issues (Hirsch and others, 1988).

For discussion in this report, target elements are presented alphabetically (singularly or in groups). Elements are grouped in instances where several elements had similar spatial distributions. For example, chromium, cobalt, magnesium, and nickel are grouped together because all were spatially related as a result of a common mineralogic source. The target elements, cadmium and silver, are omitted because their chemical concentrations were below analytical method reporting levels (MRL's). The target element cadmium is omitted because only one detectable concentration existed out of 407 determinations (see table 5). It is important to note, however, that the MRL for cadmium (2.0 μg/g) is approximately an order of magnitude larger than the concentration of cadmium in basalt (0.19 μg/g; Parker, 1967).

With the exception of thallium, the NAWQA target-minor elements correspond to minor elements listed as U.S. Environmental Protection Agency's priority pollutants (Chapman and others, 1982; see capitalized elements in table 5).

Antimony

In the Yakima River Basin, approximately 10 percent of the sites sampled had anomalous concentrations (≥0.7 μg/g) of antimony. Some of the larger anomalies, those exceeding the range of concentration (0.1 to 2.0 μg/g) reported by Parker (1967) for igneous and sedimentary rocks on the earth's surface, were found in streambed sediment of lower-order streams (sites 8, 21, 158, 177, 205, 206, and 296; pl. 1). These streams originated from the Quaternary deposits and loess, Miocene and older volcanic rock, nonmarine sedimentary rocks, marine sedimentary rocks, and pre-Tertiary metamorphic and intrusive rocks geologic units (table 11 at back of report).

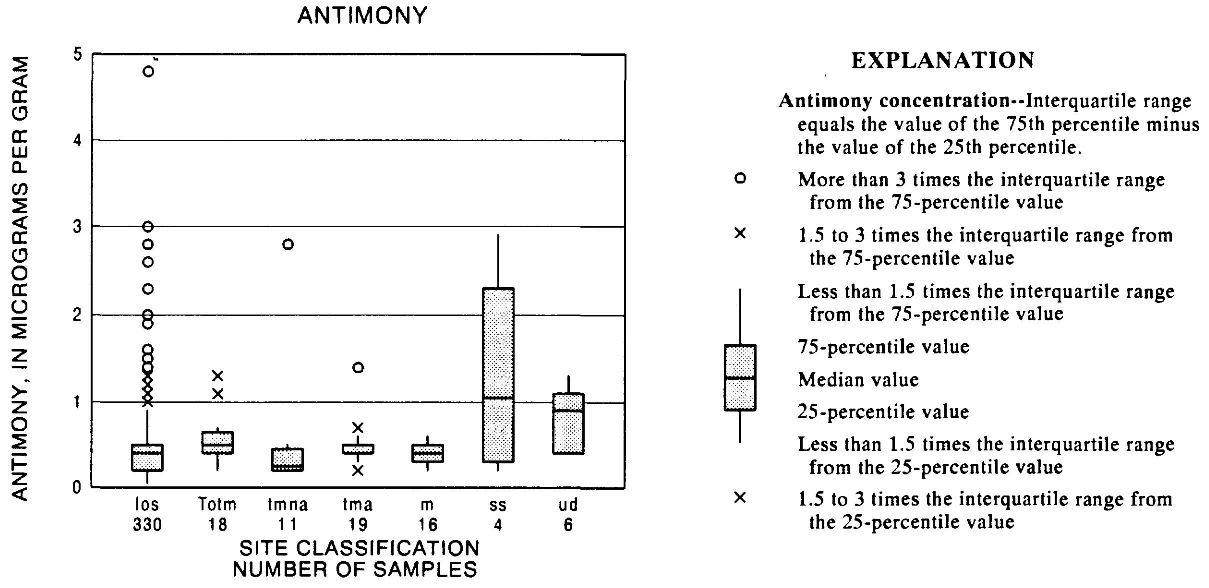
Antimony-bearing minerals weather slowly and large concentrations are not uncommon in soil and streambed sediment in the vicinity of mineralization (Levinson, 1980). The largest concentration of antimony (4.8 μg/g) was at lower-order-stream site 8, which is located in the pre-Tertiary metamorphic and intrusive rocks geologic unit in the Cle Elum River drainage (pl. 1). Geochemical exploration studies by Gualtieri and Simmons (1989) reported that mineralization in the vicinity of site 8 was the result of pyrite (iron sulfide, FeS_2), galena (lead sulfide, PbS), and sphalerite (zinc sulphide, ZnS), all known carriers of antimony (Levinson, 1980; Boyle and Jonasson, 1984).

Streambed sediment at site 8 also contained an anomalous arsenic concentration of 31 μg/g which is consistent with a geologic source of antimony. Site 10 also is located in the pre-Tertiary metamorphic and intrusive rocks geologic unit of the Cle Elum River drainage and contains anomalous concentrations of antimony (2.6 μg/g) and arsenic (220 μg/g).

Large antimony concentrations occurred in lower-order streams of the Upper Naches Subbasin (sites 158, 177, and 197) and had a geologic source of antimony. For example, lower-order stream site 158, located in the headwaters of the American River, contained 3.0 μg/g antimony--the second largest concentration in this report. Streambed sediment at site 158 originates from the Miocene and older volcanic rocks geologic unit and, like sites in the pre-Tertiary metamorphic and intrusive rocks geologic unit, contains anomalous concentrations of arsenic (310 μg/g) in addition to lead (60 μg/g) and zinc (180 μg/g). These anomalies were consistent with the geochemical character of antimony (Levinson, 1980; Boyle and Jonasson, 1984) and coincide with anomalous concentrations of lead and zinc in mineralized areas associated with hydrothermally-altered-andesitic rock in the headwaters area of the American River (Simmons and others, 1983; Schasse, 1987).

Antimony has a variety of industrial sources and uses that include mining, smelting or refining, use in alloys (battery plates, solder, and bearings), abrasives, paints, and explosives (Sittig, 1981). Industrial point sources and urban runoff may be the reason that the median antimony concentration in urban-storm-water drains (0.9 μg/g) exceeded the median in lower-order streams (0.4 μg/g). However, it is important to note that the entire range of concentrations for antimony (0.4 to 1.3 μg/g) at urban storm-water-drain sites (table 10 at back of report) is smaller than the enrichment of antimony attributed to geologic sources. In the Yakima River Basin, the largest concentrations of antimony in this report were in streambed sediment derived from geologic sources rather than urban sources.

With a few exceptions, antimony concentrations at higher-order sites (sites classified as tributaries to other than the main stem and tributaries to the main stem, nonanthropogenic; fig. 7) were found to be smaller than concentrations at urban-drain sites (see table 10 at back of report, and fig. 7). In the few instances where antimony concentrations in higher-order streams are large, urban sources of antimony were absent, and antimony enrichment probably resulted from a geologic source. For example, the 1.1 μg/g of antimony in the Bumping River (site 144) probably resulted from larger concentrations of antimony (1.6 μg/g; site 177) in streambed sediment originating from mineralization associated with the Tertiary granitic and intermediate intrusive rocks geologic



	Site classification
los	Lower-order streams
Totm	Tributaries to other than the main stem
tmna	Tributaries to main stem; naturally affected
tma	Tributaries to main stem; anthropogenic
m	Main stem
ss	Soil samples
ud	Urban-storm-water drains

Figure 7. Distribution of antimony concentrations in streambed sediment of lower- and higher-order streams, soil samples, and urban-storm-water drains, Yakima River Basin, Washington, 1987. Higher-order streams include Totm, tmna, tma, and m.

unit. It should be noted, however, that sample-collection and processing variability for antimony was large (see app. B, table B2) and at least some of the variation in antimony concentrations between sites was the result of sample-collection and processing variability. In the above example, if the mean of the relative differences for the 24 antimony, sample-collection and processing replicates (30 percent) was used to estimate sample-collection and processing variability (see app. B, table B2), then the upper limit for the 1.1 μg/g antimony is 1.5 μg/g and the lower limit for the 1.6 μg/g antimony is 1.2 μg/g. Thus, the concentrations of antimony for the Bumping River site and the mineralized, lower-order stream site overlap one another slightly when sample-processing variability was determined from equation 1 and table B2 in appendix B.

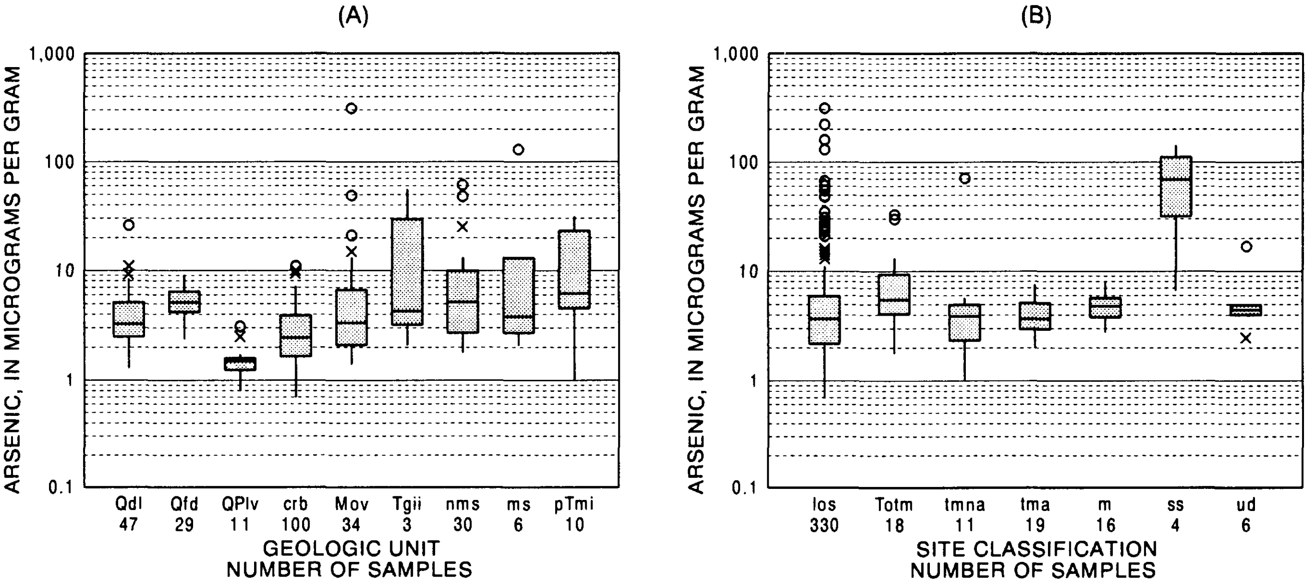
A local source of antimony exists at some soil sites in the Ahtanum and Lower Naches Subbasins (see fig. 1). These sites are located in the nonmarine sedimentary rocks and Quaternary deposits and loess geologic units, and contain concentrations of antimony as large as 2.9 μg/g (site 224), 1.7 μg/g (site 256), and 1.3 μg/g (site 259). The large antimony concentrations coincide with anomalous concentrations of arsenic and lead (described in the following section) that result from historical applications of lead-arsenate pesticides in the basin. Antimony may reside as an impurity in the formulation of lead-arsenate pesticides. Lead-arsenate formulations could contain residual antimony, because domestic production of antimony consists almost entirely of by-product antimony from lead-silver mines (U.S. Geological Survey, 1969, p. 94).

The large concentrations of antimony at these soil sites probably do not result from the nonmarine sedimentary rocks or the Quaternary deposits and loess and geologic units. Median antimony concentrations in these geologic units are 0.5 μg/g and 0.4 μg/g, respectively, and are markedly smaller than concentrations at soil sites. Further substantiation occurs at soil site 258 that was not historically treated with lead-arsenate pesticides and consequently contain a small antimony concentration of 0.4 μg/g.

Arsenic and Lead

The median arsenic concentrations were larger in streambed sediment of lower-order streams originating from pre-Tertiary metamorphic and intrusive rocks (6.2 μg/g), nonmarine sedimentary rocks (5.2 μg/g), and Quaternary flood deposits (5.1 μg/g) in comparison to the other six geologic units in the basin (fig. 8A). Conversely, arsenic concentrations were generally small at sites located in the Quaternary and Pliocene volcanic rocks geologic unit and the Columbia River Basalt Group rocks geologic unit. Anomalous concentrations of arsenic as large as 31 μg/g (site 8) occur in streambed sediment of the pre-Tertiary metamorphic and intrusive rocks geologic unit and probably result from the presence of arsenopyrite (FeAsS). Arsenopyrite has been identified in rock samples within small drainage basins of southwest-flowing tributaries to the Cle Elum River (upstream of Tucquala Lake). Arsenic concentrations in these rocks ranged from 300 to 10,000 μg/g (Gualtieri and Simmons, 1989). Enrichment of arsenic sediment of the pre-Tertiary rocks geologic unit was concurrent with enrichment of nickel and cobalt. Although, arsenopyrite minerals commonly incorporate trace elements (preferably nickel and cobalt) into their structure during formation (Rankama and Sahama, 1950), the proportions of nickel and cobalt are too large for arsenopyrite to be a sole source of nickel and cobalt.

Anomalously large arsenic concentrations were found at lower-order sites 158 (310 μg/g) and 197 (49 μg/g) in the Miocene and older volcanic rocks geologic unit in the western part of the basin (fig. 8A and pl. 2). Mineralization in this area is associated with older volcanic rocks that have been intruded by granitic rocks and by rhyodacite, an extrusive igneous rock (Simmons and others, 1983). A few large arsenic concentrations occur at lower-order sites 26 (21 μg/g) and 31 (15 μg/g) in the Miocene and older volcanic rocks geologic unit in the Easton Subbasin (pl. 2). According to Gualtieri and Simmons (1989), this unit contains hydrothermally altered volcanic and granitic rock with arsenic concentrations in rock as large as 7,000 μg/g.



EXPLANATION

Arsenic concentration--Interquartile range equals the value of the 75th percentile minus the value of the 25th percentile.

o	More than 3 times the interquartile range from the 75-percentile value
×	1.5 to 3 times the interquartile range from the 75-percentile value
|	Less than 1.5 times the interquartile range from the 75-percentile value
▭	75-percentile value
	Median value
	25-percentile value
|	Less than 1.5 times the interquartile range from the 25-percentile value
×	1.5 to 3 times the interquartile range from the 25-percentile value

Geologic unit

Qdl	Quaternary deposits and loess
Qfd	Quaternary flood deposits
QPlv	Quaternary and Pliocene volcanic rocks
crb	Columbia River Basalt Group rocks
Mov	Miocene and older volcanic rocks
Tgii	Tertiary granitic and intermediate intrusive rocks
nms	Nonmarine sedimentary rocks
ms	Marine sedimentary rocks
pTmi	Pre Tertiary metamorphic and intrusive rocks

Site classification

los	Lower-order streams
Totm	Tributaries to other than the main stem
tmna	Tributaries to main stem; naturally affected
tma	Tributaries to main stem; anthropogenic
m	Main stem
ss	Soil samples
ud	Urban-storm-water drains

Figure 8. Distribution of arsenic concentrations in streambed sediment of lower-order streams by geologic units (A), and distribution of arsenic concentrations in lower- and higher-order streams, soil samples, and urban-storm-water drains (B), Yakima River Basin, Washington, 1987. Higher-order streams include Totm, tmna, tma, and m.

Large concentrations of arsenic at many lower-order stream sites in the pre-Tertiary metamorphic and intrusive rocks and the nonmarine sedimentary rocks geologic units of the northern part of the Yakima River Basin were likely sources of arsenic to higher-order streams, including the main stem. However, arsenic concentrations rapidly attenuate on the main stem, downstream of Wilson Creek (RM 147). Concentrations of arsenic in sediment originating from the pre-Tertiary metamorphic and intrusive rocks geologic unit were as large as 31 $\mu g/g$ (site 8) in the headwaters of the Cle Elum River and as large as 61 $\mu g/g$ (site 27) in streambed sediment originating from the nonmarine sedimentary rocks geologic unit in the lower Cle Elum River (pl. 2). Similar enrichment also exists in lower-order streambed sediment formed from nonmarine sedimentary rock in the Upper Teanaway River (sites 17 and 18; pl. 2).

Concentrations of arsenic at higher-order sites along the Cle Elum River and the Teanaway River were as large as 81 $\mu g/g$ (site 27) and 30 $\mu g/g$ (site 32), respectively. Concentrations of arsenic on the main stem below the Cle Elum River and the Teanaway River were 7.9 $\mu g/g$ (site 76) and 5.5 $\mu g/g$ (site 121), respectively, and decrease to 2.8 $\mu g/g$ (site 164) downstream of Wilson Creek. The concentration of arsenic in Wilson Creek is 2.0 $\mu g/g$ (site 142), and the sharp decline in concentration in the main stem below Wilson Creek is believed to result from sediment dilution--the mixing of arsenic-poor sediment from Wilson Creek with arsenic-rich sediment from upstream sources. (See the "Chromium, cobalt, magnesium, and nickel" section of this report for a detailed example of sediment dilution in the main stem.) Concentration variations along the main stem, downstream of Wilson Creek, were small (2.8 $\mu g/g$ to 6.8 $\mu g/g$ of arsenic) and most of the data remain within the interquartile range of arsenic concentrations measured at lower-order stream sites (fig. 8B, and table 10 at back of report). In addition, arsenic contributions from tributaries to the main stem (tributaries to main stem; nonanthropogenic and tributaries to main stem; anthropogenic) as well as urban drains were generally small, and again, most of the data remained within the interquartile range of arsenic concentrations measured at lower-order-stream sites (see fig. 8B, and table 10 at back of report).

The presence and distribution of arsenic in lower-order-streambed sediment, originating from the nonmarine sedimentary rocks and the Quaternary deposits and loess geologic units, is explained partly by considering areas of land use designated as agriculture. In eastern Washington, beginning in 1908, the pesticide lead arsenate was applied to control codling moths in apples and this practice continued until the introduction of DDT (dichlorodiphenyldichloroethane) in 1947. From 1908 to 1947, the application of the lead-arsenate pesticide increased from 50 pounds (lb) of lead and 18 lb of arsenic to 192 lb of lead and 71 lb of arsenic per acre (Peryea, 1989). The land-use-classification scheme (see fig. 3) was from 1981 and did not separate orchard from nonorchard land use. However, it is known that approximately 3,000 acres of apple orchards existed in the Yakima River Basin (primarily in the middle and lower valley) prior to 1955 (U.S. Dept. of Agriculture, 1986). Two geologic units which represent a large proportion of the agricultural land-use areas in the middle and lower valley are the Quaternary deposits and loess and the nonmarine sedimentary rocks geologic units. Using the available land-use scheme and given that a proportion of the land use designated as agriculture represent orchards, concentrations of arsenic in streambed sediment formed from these two geologic units were larger for land use designated as agriculture than for land use designated as nonagriculture (fig. 9 A and B). Several of these arsenic concentrations from agricultural lands also were larger than the median arsenic concentration in streambed sediment formed from the Quaternary deposits and loess and nonmarine sedimentary rocks geologic units (table 11, at back of report).

Results from factor analysis show a positive relation between arsenic and lead at many sampling sites in the Quaternary deposits and loess and the nonmarine sedimentary rocks geologic units. In addition, the relation between arsenic and lead was further verified as significant ($\rho = 0.03$; n = 77) using Kendall's Tau-B test for correlation. At many agricultural land-use sites, the concurrent increase in lead and arsenic concentrations may be attributed to the historical use of the lead-arsenate pesticide.

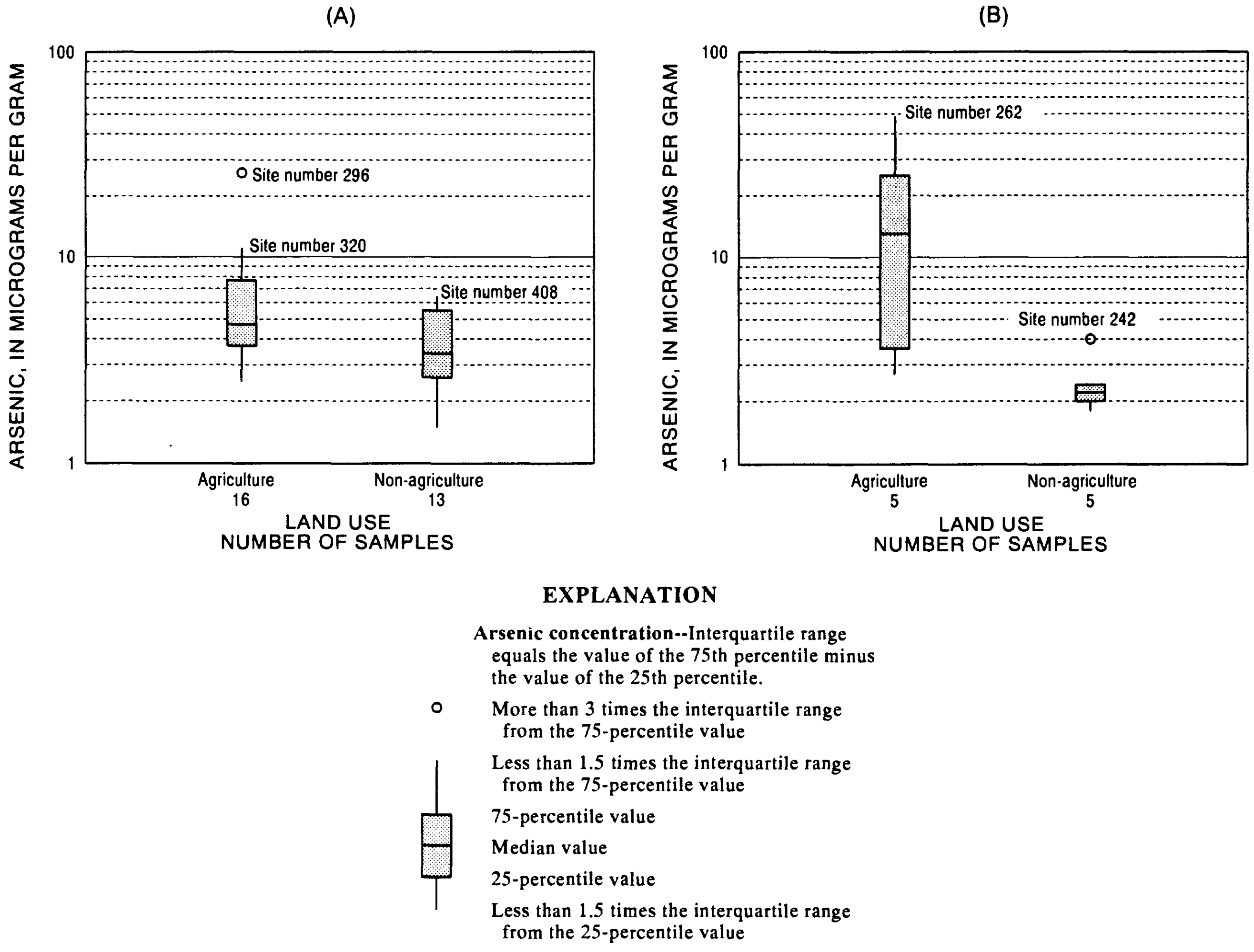


Figure 9. Arsenic concentrations in agricultural and nonagricultural land uses for streambed sediment of lower-order streams in Quaternary deposits and loess geologic unit (A), and in the nonmarine sedimentary rocks geologic unit (B), Yakima River Basin, Washington, 1987.

A local source of arsenic is further substantiated based on soil samples collected from agricultural plots located within the nonmarine sedimentary rock and Quaternary deposits and loess geologic units in the basin. The distribution of arsenic concentrations from a limited soil sampling is shown on plate 2. Two composite soil samples were collected from two agricultural plots (sites 256 and 259), located in the Ahtanum Subbasin, that were known to historically have been used to grow apples and treated with the lead-arsenate pesticide. Each soil sample represents a composite of several subsamples collected at a depth of 1 inch. Soils from the first plot (site 256) retarded the growth of hay and contained arsenic and lead concentrations of 140 µg/g and 890 µg/g, respectively. The second plot (site 259) appeared to retard the growth of peas and contained arsenic and lead concentrations of 82 µg/g and 350 µg/g, respectively. Two composite soil samples were collected from the lower Naches Subbasin within a plot (site 224) used to grow apples and known to have historically been treated with the lead-arsenate pesticide. The first composite sample was collected at a depth of 1 inch and the second was collected at a depth of 12 inches. The near-surface concentrations of arsenic and lead (57 µg/g and 490 µg/g, respectively) exceeded concentrations determined from the deeper composite sample (44 µg/g and 360 µg/g). Peryea (1989) and Gough and others (1979) also have reported near-surface enrichment (upper 8 inches) of arsenic and lead in unproductive orchards in the Yakima River Basin and in eastern Washington (fig. 10). A soil sample was collected from a nearby agricultural plot (site 258) where peas were grown with no indication of growth retardation. This site had only 22 µg/g lead and 6.7 µg/g arsenic.

Considering the persistence of arsenic and lead in surficial soils of some orchards--coupled with approximately 3,000 acres of apple orchards in the Yakima River Basin prior to 1955 (U.S. Dept. of Agriculture, 1986)--agricultural activities that may potentially erode

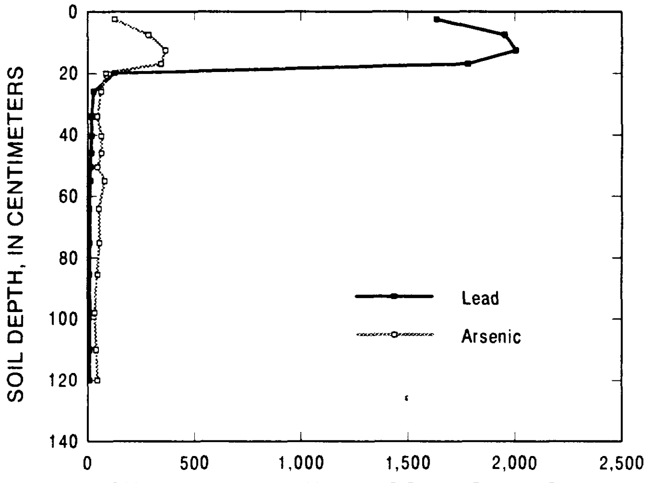


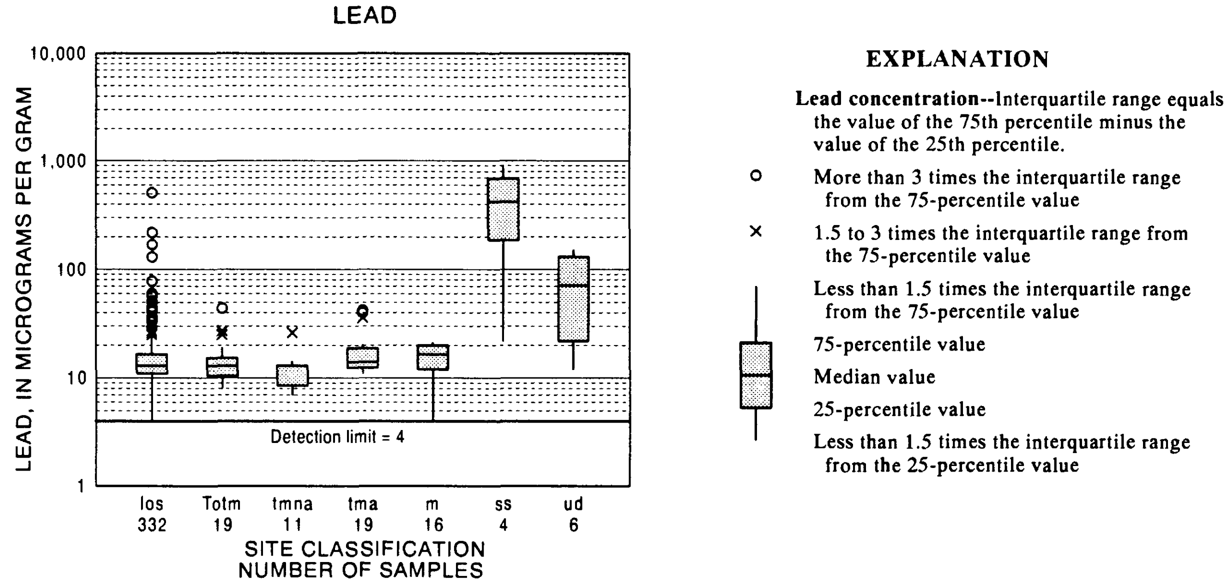
Figure 10. Depth profile of lead and arsenic concentrations in soils of a Washington State apple orchard, 1988. Data are from Peryea (1989).

soils may be a significant source of arsenic and lead to streambed sediment. In addition, use of this pesticide also may affect shallow ground water. Findings of Peryea (1989) suggest that present day phosphate-fertilizer applications to soils formerly treated with lead arsenate may release arsenic from soils to shallow ground water. Thus, arsenic may not only occur in streambed sediment from the erosion of lead-arsenate treated soil, it also may be discharged to waterways in dissolved form and subsequently attach to streambed sediment by adsorption or coprecipitation reactions with hydrous iron oxides where ground water contributes to streamflow (Hem, 1989, p. 144).

Arsenic was similar to antimony in that sample-collection and processing variability for arsenic was large (app. B, table B2) and at least some of the variation in arsenic concentrations between sites was the result of sample-collection and processing variability. Intersite comparisons of arsenic were hampered most when the differences were small between concentrations of arsenic. For example, comparison of arsenic concentrations between lower-order streams--in particular, those affected by the historical application of the lead-arsenate pesticide--and higher-order streams were hampered when differences were small between concentrations. Arsenic anomalies occur in soils (sites 256 and 259) and lower-order stream sites (sites 261 and 262) in the Ahtanum Subbasin, and arsenic concentrations were slightly enriched at the mouth of Wide Hollow Creek (site 266; tributary to the main stem; anthropogenic), but not at the mouth of Ahtanum Creek (site 270)--although both creeks drain the Ahtanum Subbasin (pl. 2). The slight enrichment measured at the mouth of Wide Hollow Creek (5.4 μg/g), after accounting for sample-collection and processing variability, may not be any greater than that of Ahtanum Creek (2.3 μg/g), which was typical of streambed sediment originating from the Quaternary deposits and loess geologic unit.

In streambed sediment of the Yakima River Basin, arsenic is derived from geologic and anthropogenic sources; however, in higher-order streams, it is difficult to separate one from the other. For example, consider the natural enrichment of arsenic in sediment originating from the pre-Tertiary metamorphic and intrusive rocks geologic unit in the vicinity of the Cle Elum River (pl. 2). Numerous lower-order-stream sites in the Cle Elum River Basin were enriched as was the downstream higher-order tributary to the main-stem site (site 27) and the higher-order, main-stem site (site 76). Concentrations of arsenic at these downstream sites were 81 μg/g and 7.9 μg/g, respectively. In addition to a natural source, Thurber and others (1984) state that arsenopyrite ores were processed in the early 1900's at a stamp mill erected near Tucquala Lake on the Cle Elum River (RM 29.6). Thus, the head waters of the Cle Elum River cannot be totally discounted as a potential point source of arsenic. Anomalies at other sites are undoubtedly attributed to geologic sources; for example, the anomalous 33 μg/g of arsenic downstream of Bumping Lake Reservoir (site 144, pl. 2)--a site classified as a tributary to other than the main stem (fig. 8B). Upstream lower-order-stream sites of the Upper Naches Subbasin have concentrations of arsenic as large as 55 μg/g. This streambed sediment originated from the Tertiary granitic and intermediate intrusive rocks geologic unit and mineralization is affected within the unit (pl. 2).

Sediment from urban-storm-water drains in addition to urban soils are probable nonpoint sources of lead in the Yakima River Basin (fig. 11). Lead is a highly versatile element and is formulated in a broad array of products that include pesticides, fuel additives, soldering compounds, metal alloys, domestic piping, batteries, and rubber; consequently, lead is likely to occur in urban-storm-water drain and agricultural soil sites in the basin. The interquartile range of lead concentrations in urban-storm-water-drain sites (20 μg/g to 135 μg/g) exceeds that of lower-order-stream sites (11 μg/g to 17 μg/g) shown in table 10 at back of report and figure 11. Likewise, lead concentrations at soil sites--known to have been historically treated with the pesticide lead arsenate--exceeded the interquartile range of lead concentrations measured at lower-order-stream sites. Sample-collection and processing variability was considered in making these comparisons among percentile distributions. Using the mean relative difference for the 24 lead,



	Site classification
los	Lower-order streams
Totm	Tributaries to other than the main stem
tmna	Tributaries to main stem; naturally affected
tma	Tributaries to main stem; anthropogenic
m	Main stem
ss	Soil samples
ud	Urban-storm-water drains

Figure 11. Distribution of lead concentrations in streambed sediment of lower- and higher-order streams, soil samples, and urban-storm-water drains, Yakima River Basin, Washington, 1987. Higher-order streams include Totm, tmna, tma, and m.

sample-processing replicates (15 percent; app. B, table B2), and equation number 1 (app. B), there was slight overlap between lead distributions of lower-order sites and urban-storm-water drains and no overlap between lower-order sites and soil sites. A few natural sources of lead exist; however, there was little evidence to suggest that sediment from naturally enriched lower-order-stream sites affected the sediment quality of higher-order streams (pl. 2).

It is often difficult to determine the degree to which specific nonpoint sources of lead affect sediment chemistry of higher-order streams. Consider, for example, the difficulty of determining the proportion of lead in sediment at a higher-order stream site that was attributed to agriculture compared with urban nonpoint sources. Wide Hollow Creek (site 266) is a good example of a tributary-to-main-stem, anthropogenic site that probably is affected by different nonpoint sources. Natural sources were of less concern in the Wide Hollow Basin because its drainage, for the most part, is confined to the Quaternary deposits and loess geologic unit. The use of lead-arsenate pesticide, as discussed earlier, has enriched lead concentrations in soils and streambed sediments of lower-order streams in the Wide Hollow Subbasin (pl. 2). In addition, lead in urban runoff and effluent from the city of Union Gaps STP (closed in 1979), should be considered a probable source of lead to streambed sediment in Wide Hollow Creek. Thus, the lead concentration of 56 μg/g measured at the mouth of Wide Hollow Creek (site 266) probably reflects multiple point and nonpoint sources that are not easily differentiated (pl. 2).

A similar situation to that of Wide Hollow Creek exists in the Naches River. There was evidence of some lead enrichment in the upper Naches Subbasin; however, there was no indication that these natural sources affected lead concentrations of higher-order streams in the lower Naches Subbasin (pl. 2). For example, the Naches River above the Tieton River, a higher-order stream, had a lead concentration (15 μg/g, site 202) that was smaller than that of the upstream, lower-order-stream site lead concentration (51 μg/g, site 154). Thus, geologic sources within lower-order streams--although present--do not appreciably affect the concentrations of lead in streambed sediment in the Naches River.

The lead concentration at the mouth of the Naches River (22 μg/g, site 235) also was similar to the upstream lead concentration on the Naches River above the Tieton River. The similarity between concentrations suggests the absence of an appreciable anthropogenic source of lead in the lower Naches Subbasin. The mouth of Cowiche Creek, a tributary to the Naches River (RM 2.7), had the largest streambed-sediment, lead concentrations (25 μg/g, site 236) in the lower Naches Subbasin. This concentration, although considered small in comparison to typical anthropogenic-lead enrichments measured in Willamette River bottom material in Oregon (Rickert and others, 1977) may account for the slight enrichment at the mouth of the Naches River. It should be noted that differences between lead concentrations are small and could easily be accounted for by considering sample-collection and processing variability or subtle variations in grain size between sites.

Barium

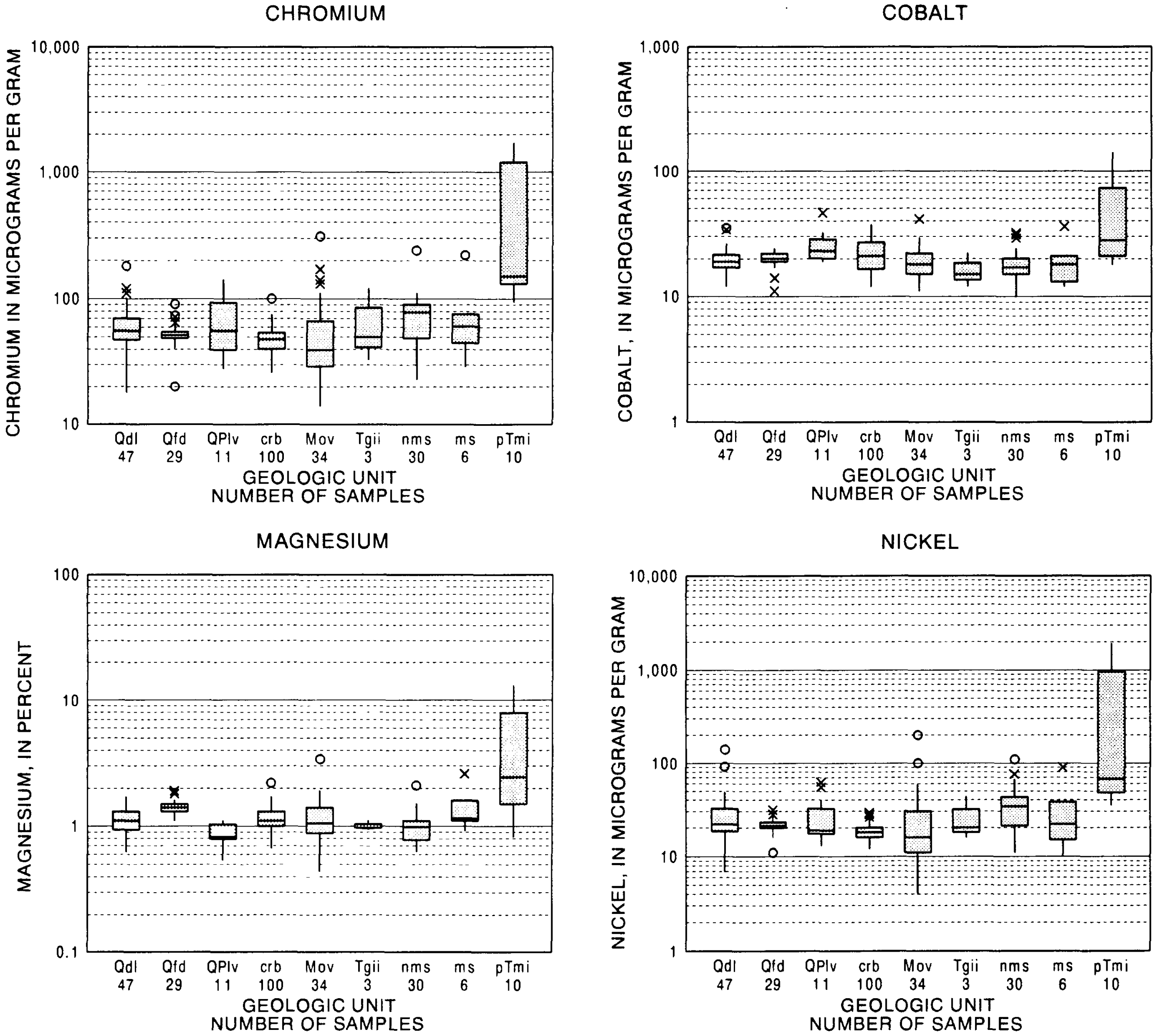
In the Yakima River Basin, approximately 2 percent of the sites sampled had anomalous ($\geq$ 650 mg/g) concentrations of barium. Several of these anomalies (sites 37, 38, and 44) occur in or near arkosic sandstone formations which comprise a part of the Swauk Formation. In this report, the Swauk Formation has been grouped into the nonmarine sedimentary rocks geologic unit. The source of enriched barium within the Swauk Formation is unknown, but possibly may be attributed to the presence of abundant potassium feldspar (a family of minerals having the same chemical composition -$KALSi_3O_8$ identified in the Swauk Formation (Tabor and others, 1982). Feldspar minerals are able to substitute barium for potassium thereby becoming enriched in barium (Levinson, 1980). This is particularly true for sandstone that is enriched with feldspar; for example, the arkosic sandstone formations of the Swauk Formation. Feldspar can contain 900-14,000 μg/g barium (Goldschmidt, 1958; calculated from barium oxide values in table LVII, p. 252) by substituting barium for potassium in the crystal structure. Factor analysis and Kendall's Tau-B correlation testing further support the feldspathic component in the Swauk Formation. Aluminum, potassium, and barium for sites in the nonmarine sedimentary rocks geologic unit were grouped together by factor analysis and also were shown to have significant positive relations ($\rho \leq 0.1$; n = 30) by the Kendall's Tau-B correlation test.

Another noteworthy mechanism for enrichment of barium in streambed sediment in areas removed from direct geologic sources (for example, the main stem) involves the adsorption of dissolved barium on clay mineral surfaces (Jenne, 1977). Clay minerals are the insoluble products from the chemical weathering of rock and particulate clay and they provide an excellent surface for adsorption of alkaline cations including barium (Levinson, 1980).

Chromium, Cobalt, Magnesium, and Nickel

In the Yakima River Basin, approximately 10 percent of the sites sampled had anomalous concentrations of chromium, cobalt, magnesium, and nickel (see table 5). Though covering only a small northeastern part of the Yakima River Basin, a number of these anomalies occurred in lower-order streambed sediment originating from the pre-Tertiary metamorphic and intrusive rocks geologic unit (pl. 2, and table 11 at back of report). These anomalous concentrations also were large in comparison to element concentrations in other geologic units (fig. 12) and in soils of the Western United States (see table 5). In addition, many of the aforementioned element concentrations in the pre-Tertiary metamorphic and intrusive rocks geologic unit within the Cle Elum River drainage (sites 2, 5, 7, and 8, pl. 2) fell well outside the expected 95-percent range of concentration for these elements in soils in the Western United States. Chromium concentrations at these sites ranged from 1,200 to 1,700 μg/g (Ryder and others, 1992); in comparison, the 95-percent range of concentration in Western United States soils is 8.5 to 200 μg/g.

The pre-Tertiary metamorphic and intrusive rocks geologic unit is undoubtedly paramount in contributing to the enrichment of cobalt, chromium, magnesium, and nickel in streambed sediment. As an example, large concentrations of chromium in streambed sediment coincide with the distribution of the ultramafic rock "periodotite." Peridotite--a rock



EXPLANATION

Element concentration--Interquartile range equals the value of the 75th percentile minus the value of the 25th percentile.

o More than 3 times the interquartile range from the 75-percentile value

× 1.5 to 3 times the interquartile range from the 75-percentile value

Less than 1.5 times the interquartile range from the 75-percentile value

75-percentile value

Median value

25-percentile value

Less than 1.5 times the interquartile range from the 25-percentile value

× 1.5 to 3 times the interquartile range from the 25-percentile value

o More than 3 times the interquartile range from the 25-percentile value

	Geologic unit
Qdl	Quaternary deposits and loess
Qfd	Quaternary flood deposits
QPlv	Quaternary and Pliocene volcanic rocks
crb	Columbia River Basalt Group rocks
Mov	Miocene and older volcanic rocks
Tgii	Tertiary granitic and intermediate intrusive rocks
nms	Nonmarine sedimentary rocks
ms	Marine sedimentary rocks
pTmi	Pre Tertiary metamorphic and intrusive rocks

Figure 12. Distribution of chromium, cobalt, magnesium, and nickel concentrations in streambed sediment of lower-order streams, relative to geologic units, Yakima River Basin, Washington, 1987.

called "dunite" when composed primarily of the mineral olivine [$(Mg,Fe)_2SiO_4$], or "harzburgite" when primarily composed of the minerals olivine and orthopyroxene--can be metamorphosed to serpentinized peridotite, a variety of serpentinite. Exposures of dunite and serpentinite are commonly found in the pre-Tertiary metamorphic and intrusive rocks geologic unit of the basin. According to the geologic mapping of Tabor and others (1982), the element-enriched samples collected during this study are located in the midst of dunite. Although dunite commonly contains chromium, in the form of the accessary mineral chromite [$(Fe,Mg)(Cr,Al)_2O_4$], it is unknown whether or not dunite in the Yakima River Basin is similarly enriched. Known mineral deposits of chromium have been identified in layered structures termed "chromite pods" within the serpentinite (Tabor and others, 1982). In addition, Lucas (1975) has described the 1.5 mi stream segment of the Cle Elum River between Big Boulder Creek and Camp Creek (upstream of Cle Elum Lake and in the pre-Tertiary metamorphic and intrusive rocks geologic unit) as a principal zone containing outcrops of nickel-chromium-bearing ferruginous laterite (highly weathered, iron-rich subsoil), which was developed on the surface of an intrusive pre-Tertiary peridotite body. The laterite was, subsequently, partially eroded, transported, and deposited along the margins of the peridotite body in contact with the Eocene Swauk Formation.

The nickel-chromium deposits, in addition to covering the 1.5 mi stream segment of the Cle Elum River, are said to be scattered along 20 mi of the peridotite contact between the pre-Tertiary rocks geologic unit (serpentinized peridotite) and the nonmarine sedimentary rocks geologic unit (Swauk Formation)--nickel enrichment related to this contact will be discussed later in the report. Thus, anomalous chromium concentrations of lower-order streams are attributable directly to natural sources and are in agreement with average concentrations (1,600 μg/g) in ultramafic rocks reported by Parker (1967).

Large concentrations of nickel, although not anomalous, also are found in lower-order streambed sediment derived from sandstone of the Swauk Formation which forms the upper drainages of the Cle Elum River, Teanaway River, and Swauk Creek, and has been categorized as nonmarine sedimentary rocks in this report study. Concentrations in sediments from the nonmarine sedimentary rocks geologic unit, however, were not as pronounced as in the pre-Tertiary metamorphic and intrusive rocks geologic unit. For example, enrichment at sites 17 (76 μg/g) and 21 (59 μg/g) in the nonmarine sedimentary rocks geologic unit was smaller than enrichment at sites 8 (1,800 μg/g) and 2 (1,900 μg/g) in the pre-Tertiary metamorphic and intrusive rocks geologic unit. Enrichment at sites 17 and 21 was attributed to the peridotite contact between the pre-Tertiary rocks geologic unit and the nonmarine sedimentary rocks geologic unit.

Anomalous concentrations of cobalt in streambed sediment of the pre-Tertiary metamorphic and intrusive rocks geologic unit ranged from 73 to 120 μg/g (sites 2, 5, 7, and 8, pl. 2). Enrichment of cobalt within this geologic unit, as with chromium and nickel, is attributed to the exposures of dunite and serpentinite and the common geochemical associations among the elements chromium, cobalt, and nickel in ultramafic rocks like dunite and serpentinite (Levinson, 1980). As expected, nickel and cobalt were significantly positively correlated ($\rho = 0.03$) with one another in streambed sediment of the pre-Tertiary metamorphic and intrusive rocks geologic unit. In addition, the ANOVA procedure shows that the mean rank of the nickel concentrations in the pre-Tertiary metamorphic and intrusive rocks geologic unit was not only the largest mean rank, but is significantly different ($\rho = 0.1$) than the mean rank of the nickel concentrations in the other geologic units--except for the nonmarine sedimentary rocks geologic unit (table 12 at back of report).

The presence of cobalt in streambed sediment of the pre-Tertiary metamorphic and intrusive rocks geologic unit was attributed to incomplete weathering of the streambed sediment. Once weathered, however, cobalt tends to enter the aqueous phase and generally remains dissolved until encountering reducing conditions where cobalt forms sulfides (Rankama and Sahama, 1950).

The enrichment of magnesium at anomalous sites was related to exposures of dunite and serpentinite in the pre-Tertiary metamorphic and intrusive rocks geologic unit. This relation was further borne out by a significant positive relation ($\rho = 0.01$) between magnesium and chromium in streambed sediment originating from the pre-Tertiary rocks geologic unit.

As with chromium, cobalt, magnesium, and nickel enrichment were directly attributable to natural sources. The enrichment of chromium, in addition to cobalt, magnesium, and nickel, in ultramafic rocks like peridotite has long been recognized by mineral explorationists as a geochemical association and a pathfinder for mineralization (Levinson, 1980). The observed chromium, cobalt, magnesium, and nickel enrichment at sites located in pre-Tertiary rock geologic units was verified by an earlier study (Gualtieri and Simmons, 1989). In the earlier study, eight anomalous samples with concentrations ranging from 700 to 3,000 μg/g for chromium, 50 to 100 μg/g for cobalt, 5 to 8.2 percent for magnesium, and 350 to 1,500 μg/g for nickel were reported in streambed sediment of tributaries flowing west to the Cle Elum River and south to the Teanaway River in the vicinity of Van Epps Pass.

Although the element chromium is well known in an industrial setting as a plating and anodizing agent, and although it is commonly associated with anthropogenic point and nonpoint source discharges, it is doubtful whether the industrial use of chromium has any measurable effect on the sediment chemistry of higher-order streams in the Yakima River Basin. Rather, concentrations of chromium in higher-order streams result from geologic sources and exhibit signs of sediment dilution--element concentrations decrease by mixing with less enriched sediment from other geologic sources. As an example, consider site 27 located on the Cle Elum River (a site classified as a tributary to the main stem; naturally affected) and site 56 located on the north fork of the Teanaway River (a site classified as a tributary to other than the main stem, pl. 2). Chromium enrichment at these sites (620 μg/g and 210 μg/g, respectively) is probably a direct result of suspended-sediment transport of chromium-enriched sediment, derived from the upstream pre-Tertiary metamorphic and intrusive rocks geologic unit, to streambed sediment of higher-order streams (pl. 2).

Chromium concentrations at some main-stem sites also are affected by upstream geological sources. Chromium concentrations decrease down the main stem, from a maximum concentration of 210 μg/g at the Yakima River at Cle Elum (RM 183.1; site 76; downstream of the Cle Elum River) to 160 μg/g at the Yakima River at Evergreen Farm (RM 157.5; site 121), and again to 64 μg/g at the Yakima River at Umtanum (RM 140.4; site 164; downstream of Wilson Creek) as shown in figure 13. The chromium concentration decreased sharply between the Yakima River at Evergreen Farm and at Yakima River at Umtanum. The sharp decrease in chromium concentration is likely the result of sediment dilution from chromium-poor sediment transported to the main stem from Wilson (site 142) and Cherry (site 141) Creeks. Sediment formed in these creeks originates from the Quaternary deposits and loess geologic unit, and Quaternary flood deposits geologic unit and contained only 84 μg/g and 54 μg/g chromium, respectively. These units form the soil associations of agricultural lands that drain to the upper reach of the Yakima River. Rinella and others (1992) showed that median concentrations of suspended sediment in the main stem increased by 5 mg/L downstream of Wilson Creek during the irrigation season for the period 1974-81.

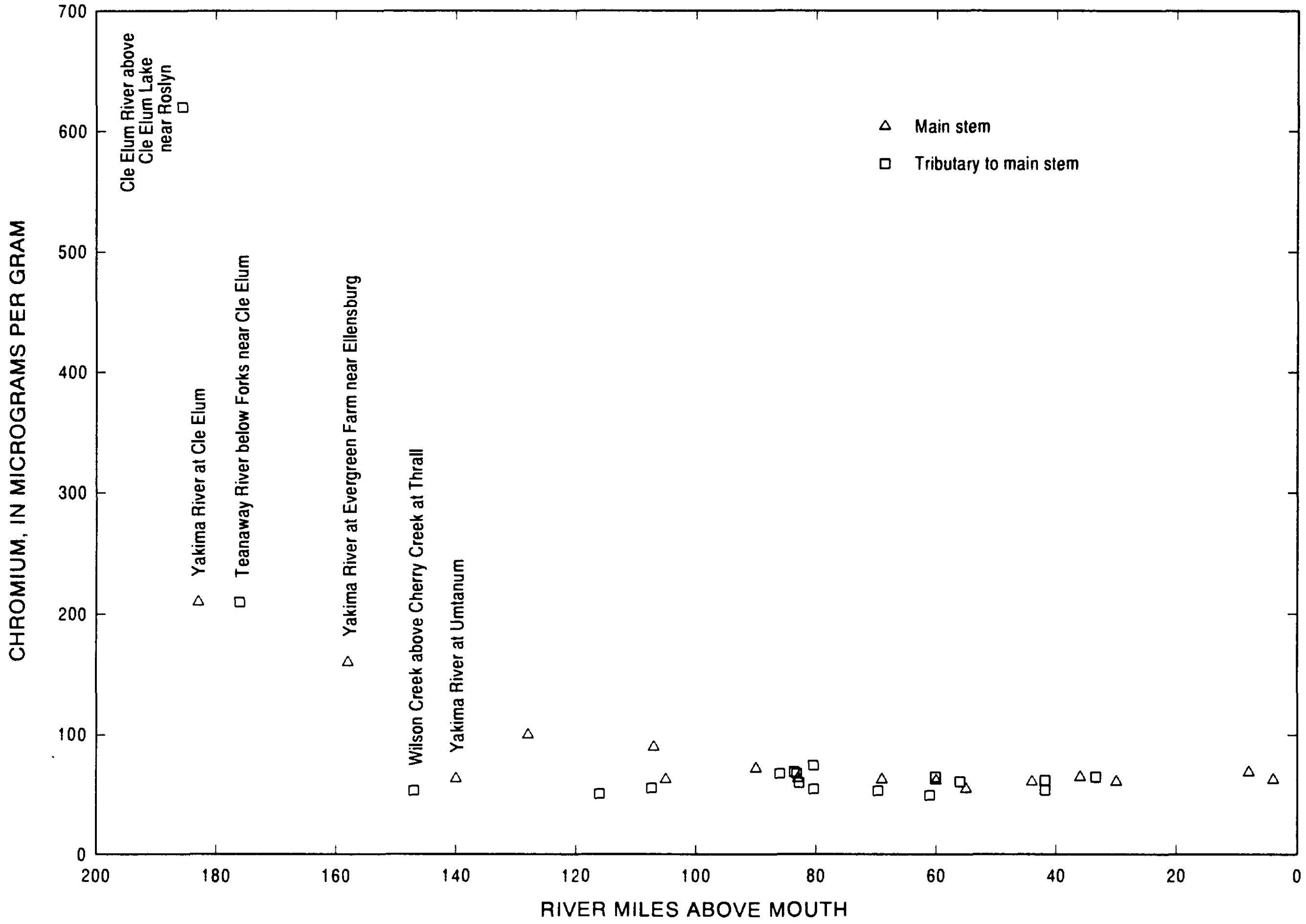


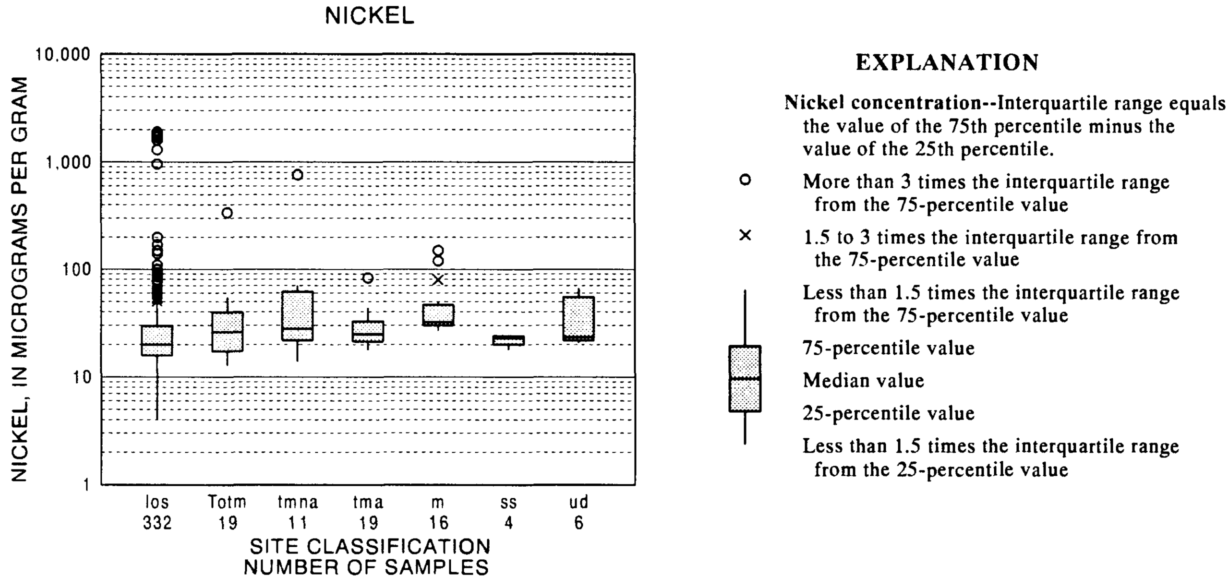
Figure 13. Chromium concentrations in streambed sediment of the main stem and selected tributaries, Yakima River Basin, Washington, 1987.

Sediment transported from Wilson Creek probably accounts for the sediment dilution of chromium observed in the main stem downstream of Wilson Creek. Chromium concentrations were diluted to the minimum concentration at the Yakima River at Grandview (RM 55; site 395). This site is located downstream of Sulphur Creek, the largest conveyance of irrigation-return flow and canal-return flow in the basin.

The behavior of nickel in the main stem is similar to that of chromium, which is not unexpected considering the geochemical relation between nickel and chromium in streambed sediment originating from the pre-Tertiary metamorphic and intrusive rocks geologic unit. For example, the nickel concentration for the Cle Elum River (site 27; a tributary to the main stem, naturally affected site) and the north fork of the Teanaway River (site 56; tributary to other than main-stem site) was 780 μg/g and 340 μg/g, respectively, and probably results from transport of nickel-enriched suspended sediment originating from the pre-Tertiary metamorphic and intrusive rocks geologic unit (pl. 2). Concentrations of nickel in the main stem, downstream of the Cle Elum River (site 76) and Teanaway River (site 121), are small (150 μg/g and 120 μg/g, respectively), relative to nickel concentrations in the tributaries. However, they are large (outside the interquartile range; 30 to 47 μg/g for main-stem sites) in comparison to other main-stem sites (fig. 14, and table 10 at back of report). Again, as with chromium, the concentration of nickel (48 μg/g) at the Yakima River at Umtanum (site 164) is reduced by sediment dilution with sediment from Wilson Creek (site 142) and Cherry Creek (site 141). The concentration of nickel at main-stem sites downstream of Wilson Creek remains small relative to natural sources in pre-Tertiary rock forming parts of the Cle Elum River and Teanaway River drainages. In addition, the interquartile range of nickel concentrations at main-stem sites are small (28.8 to 45.8 μg/g) and reflect an absence of large point and (or) nonpoint sources of nickel to the main stem. This is not unexpected considering the small nickel concentrations associated with soil and urban-storm-water-drain sites (fig. 14).

Copper and Molybdenum

In the Yakima River Basin, approximately 10 percent of the sites sampled had anomalous concentrations (≥ 40 μg/g) of copper (see table 5). In comparison to soils in the Western United States, concentrations of copper fall within the expected 95-percent range of concentration. Copper anomalies exist at lower-order sites in the pre-Tertiary metamorphic and intrusive rocks geologic unit (sites 12 and 16) and in the marine sedimentary rocks geologic unit (site 205). Anomalous concentrations of copper at these sites range from 92 to 150 μg/g. The largest anomaly (150 μg/g), was on a tributary to Rattlesnake Creek (site 205) in the Upper Naches Subbasin. This tributary also contained anomalous concentrations of arsenic and zinc in what has been described by Simmons and others (1983) as andesitic tuff and breccia of the Ohanapecosh Formation, which underlies this area. The remaining anomalies (92 μg/g, site 12 and 110 μg/g, site 16), as well as larger concentrations of copper, were in streambed sediment originating from the pre-Tertiary metamorphic and intrusive rocks geologic unit in the Cle Elum Subbasin. Ultramafic rocks, like peridotite commonly found within this unit (Tabor and others, 1982), are commonly enriched with copper as well as cobalt, chromium, and nickel (Levinson, 1980).



EXPLANATION

Nickel concentration--Interquartile range equals the value of the 75th percentile minus the value of the 25th percentile.

○ More than 3 times the interquartile range from the 75-percentile value

× 1.5 to 3 times the interquartile range from the 75-percentile value

Less than 1.5 times the interquartile range from the 75-percentile value

75-percentile value

Median value

25-percentile value

Less than 1.5 times the interquartile range from the 25-percentile value

	Site classification
los	Lower-order streams
Totm	Tributaries to other than the main stem
tmna	Tributaries to main stem; naturally affected
tma	Tributaries to main stem; anthropogenic
m	Main stem
ss	Soil samples
ud	Urban-storm-water drains

Figure 14. Distribution of nickel concentrations in streambed sediment of lower- and higher-order streams, soil samples, and urban-storm-water drains, Yakima River Basin, Washington, 1987. Higher-order streams include Totm, tmna, tma, and m.

Geochemical associations or enrichment of copper along with chromium, cobalt, and nickel were noted at several sites within this geologic unit as well as in earlier samplings by Gualtieri and Simmons (1989).

Although copper has a great number of agricultural uses in the basin, including fertilizers, fungicides, and insecticides, and although it is known to readily associate with clay and organic matter in streambed sediment, copper concentrations at higher-order stream sites are within the expected 95-percent range of copper concentrations for soils in the Western United States. Relative to streambed sediment in the basin, however, the concentrations of copper at the urban-storm-water-drain sites in the city of Yakima (site 252, 67 μg/g) and Ellensburg (site 126, 65 μg/g) were anomalous. Concentrations of copper at these urban-storm-water-drain sites exceeded those of the local geology (Quaternary deposits and loess geologic unit) and probably represent small anthropogenic sources. Although not anomalous in comparison to soils in the Western United States, copper concentrations at Yakima and Ellensburg urban-storm-water drains exceed concentrations at higher-order-stream sites, soil sites, and approximately 95 percent of the basin's lower-order-stream sites. The 65 μg/g copper from Ellenburg's urban-storm-water-drain site (Wilson Creek at 6th and Pine, RM 10.5) was diluted to 25 μg/g near the mouth (Wilson Creek above Cherry Creek at Thrall Road, site 142) by mixing with sediment-laden, irrigation-return flow received by Wilson Creek prior to entering the main stem. The behavior suggests that urban sources of copper are small and readily attenuated as sediment passes to the main stem.

Molybdenum anomalies were few in number but are noteworthy because of molybdenum's role as a pathfinder for copper. It is also important to note that the analytical-method reporting level for molybdenum in this report (2 μg/g) was larger than the average concentration of molybdenum (1.5 μg/g) reported for basalt by Parker (1967). Thus, nearly all the molybdenum concentrations determined in this report were below the minimum reporting level for molybdenum.

Anomalies were found at lower and higher-order sites 205 and 178, respectively. Streambed sediment at these sites were similarly enriched in copper and zinc which is consistent with known geochemical associations (Levinson, 1980) as well as an earlier study by Simmons and others (1983). For example, the large concentration of molybdenum at site 205, located on the Bumping River upstream of Bumping Lake, is in the vicinity of a contact between the andesitic rock of the Ohanapecosh Formation and a granitic pluton. Simmons and others (1983) reported molybdenum anomalies along this contact. Interestingly, the higher-order-stream site 144, located downstream of Bumping Lake, had a molybdenum concentration of 2 μg/g in addition to copper and zinc enrichment. Enrichment of molybdenum, copper, and zinc along the higher-order Bumping River sites probably emulate from weathering of mineralized zones of the aforementioned geologic contact.

Manganese

In the Yakima River Basin, slightly less than 10 percent of the sites sampled had anomalous concentrations ($\geq$ [greater than or equal to] 1,600 μg/g) of manganese. The baseline concentration for manganese generally coincides with the upper limit (1,500 μg/g) for the expected 95-percent range of concentration for soils in the Western United States (see table 5). Manganese concentrations at anomalous lower-order stream sites (sites 109, 114, 138, 150, and 187) range from 2,000 to 2,900 μg/g and probably result from natural-geologic processes. One of the larger anomalies (2,700 μg/g) was in the headwaters of the American River (site 150) in streambed sediment formed from andesitic rock of the Miocene and older volcanic rocks geologic unit.

Concentrations of manganese at lower-order-stream sites were larger in streambed sediment originating from the Miocene and older volcanic rocks geologic unit than in most of the other geologic units (table 11). These findings were verified by ANOVA, which shows that the concentration of manganese in the Miocene and older volcanic rocks geologic unit represents a significantly ($\rho \leq 0.1$) different population (mean ranks of manganese concentrations were larger) than concentrations in the aforementioned geologic units (table 12 at back of report).

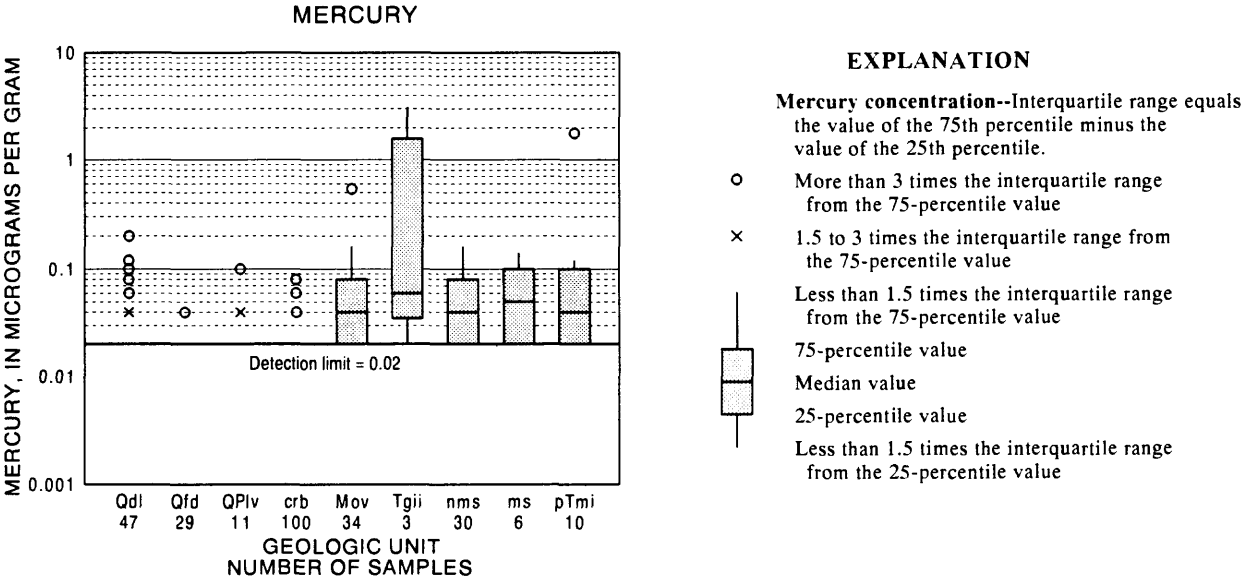
Concentrations of manganese in higher-order streams, soils, and urban-storm-water drains were not large relative to concentrations in lower-order streams (table 10 at back of report). For example, the median concentration of manganese in urban-storm-water drains was 845 μg/g and the median in lower-order streams was 930 μg/g.

The similarity of manganese concentrations between lower-and higher-order streams, in contrast to the large differences noted earlier for elements like chromium and nickel, may reflect the chemical nature of manganese. As described in the introduction of this report, manganese is formed in streambed sediment as an oxidate--oxidates are transported as ions or colloids to sites of deposition where oxidation and sedimentation occur. Thus, with the exception of sites near locally rich manganese deposits, the spatial distribution of manganese in streambed sediment is governed by factors which include pH, redox, and dissolved-organic matter (Rankama and Sahama, 1950, p. 647-653; Hem, 1965). There were exceptions, however, regarding similarities among manganese concentrations along the main stem between Reecer Creek (RM 153.7) and Umtanum Creek (RM 139.8). The concentration of manganese on the main stem increases from 1,300 μg/g upstream of Reecer Creek (site 121; RM 153.7) to 1,700 μg/g upstream of Umtanum Creek (site 164; RM 139.8). This concentration increase may result from an anomalous concentration of manganese (2,900 μg/g) in a lower-order tributary to Reecer Creek (site 114) in addition to manganese contributions (1,700 μg/g) from Wilson Creek (site 142) at RM 147.0.

Mercury

In the Yakima River Basin, more than 2 percent of the sites sampled had anomalous concentrations (≥ 0.30 μg/g) of mercury. Concentrations of mercury in streambed sediment were similar to concentrations in soils of the Western United States (see table 5). Mercury anomalies along lower-order-stream sites 177, 218, and 421 were likely the result of natural geologic processes. For example, a mercury concentration of 3.1 μg/g was measured in streambed sediment of a low-order tributary to Bumping Lake (site 177). Streambed sediment in this tributary originated from Tertiary granitic and intermediate intrusive rocks geologic unit south of Bumping Lake in an area shown by Moen (1978) to contain deposits of copper, gold, and mercury. This area was later described by Simmons and others (1983) as hydrothermally altered and iron-stained rhydodacite that contains anomalous concentrations of copper, lead, silver, tin, and other metals. Hydrothermally altered rock is a natural source of mercury that cannot be discounted in the Yakima River Basin considering that hydrothermal alteration commonly is associated with volcanic regions like the Cascade Mountains. Mercury deposition in the vicinity of hydrothermally altered rock also has been documented by Ellis and Mahon (1977). In addition, the presence of mercury in rock, soil, plant, and streambed sediment has been used as a geochemical indicator of mineralization associated with hydrothermal alteration (Jonasson and Boyle, 1972) and for active geothermal systems (Zhu and others, 1986).

The anomalous concentration of mercury (1.8 μg/g) at site 218 was on a lower-order tributary to Indian Creek, which flows into Rimrock Lake (pl. 2). This site is located in the pre-Tertiary metamorphic and intrusive rocks geologic unit. Mercury in the form of cinnabar is widespread in the Indian Creek drainage in altered pre-Puget Group rocks and to a lesser extent in granodiorite that intrudes the pre-Puget Group rocks (Simmons and others, 1983). Concentrations of mercury (fig. 15 and pl. 2) at lower-order-stream sites are larger in streambed sediment originating from this first group of geologic units (Miocene and older volcanic rocks, Tertiary granitic and intermediate intrusive rocks, pre-Tertiary metamorphic and intrusive rocks, nonmarine sedimentary rocks, and marine sedimentary rocks) than from this second group (Quaternary flood deposits and Columbia River Basalt Group). The concentrations of mercury in the first group represent a significantly different population (mean ranks are significantly smaller) than concentrations



Geologic unit	
Qdl	Quaternary deposits and loess
Qfd	Quaternary flood deposits
QPlv	Quaternary and Pliocene volcanic rocks
crb	Columbia River Basalt Group rocks
Mov	Miocene and older volcanic rocks
Tgii	Tertiary granitic and intermediate intrusive rocks
nms	Nonmarine sedimentary rocks
ms	Marine sedimentary rocks
pTmi	Pre Tertiary metamorphic and intrusive rocks

Figure 15. Distribution of mercury concentrations in streambed sediment of lower-order streams, relative to geologic units, Yakima River Basin, Washington, 1987.

of mercury in the second group (table 12 at back of report). Although mercury concentrations in the first group exceed those of the second group, they cannot be considered enriched relative to concentrations found in rock and soil. The average crustal abundance of mercury in sandstone and igneous rock is 0.03 μg/g and 0.08 μg/g (Parker, 1967), respectively, and the concentration of mercury in 95 percent of soils in the Western United States range from 0.008 to 0.25 μg/g. The small mercury concentrations associated with basalt sites are not surprising. Basalts are considered early differentiate of magma and, according to Rankama and Sahama (1950), mercury is almost completely absent in early magma.

As noted above, large concentrations of mercury in addition to some anomalies exist at numerous lower-order-stream sites in the first group of geologic units. Numerous higher-order streams draining these enriched geologic units are similarly enriched; thus, mercury appears to be transported from lower-order streams to higher-order streams (pl. 2). Mercury transport is a potentially important mechanism because zones of deposition/accumulation for solid forms of mercury may chemically degrade aquatic habitat. The north (site 56), middle (site 57), and west (site 58) forks of the Teanaway River, located in the northeastern part of the basin, have mercury concentrations of 0.16 μg/g, 0.14 μg/g, and 0.14 μg/g, respectively, and reflect enrichment from upstream sources located along lower-order streams (pl. 2). The upstream concentrations of mercury measured at lower-order streams flowing to the north (site 32), middle (site 42), and west (site 47) forks of the Teanaway River were 0.20 μg/g, 0.54 μg/g, and 0.70 μg/g, respectively.

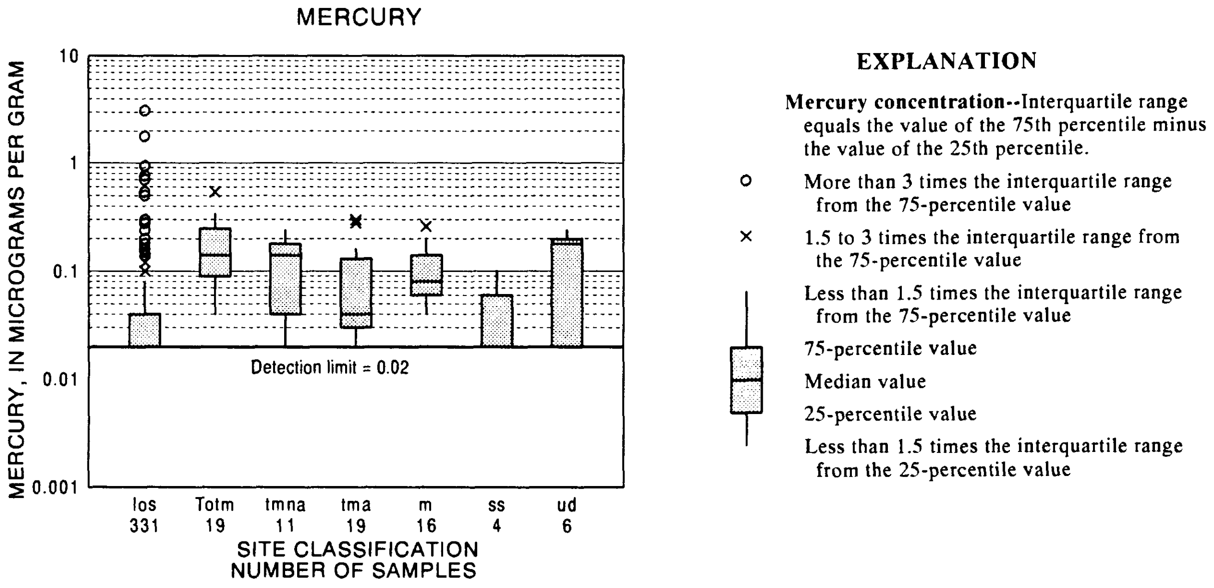
The Naches River drainage is another example of how naturally enriched lower-order streams can enrich streambed sediment of higher-order streams (pl. 2). As discussed earlier in this section, natural sources of mercury in the Naches River drainage occur in Miocene and older volcanic rocks, Tertiary granitic and intermediate intrusive rocks, and marine sedimentary rocks geologic units. Numerous samples were collected from higher-order-stream sites that are tributaries to the Naches River (sites 119, 127, 183, and 207). A sample also was collected at the mouth of the Naches River (site 235). All these samples contained mercury concentrations equal to or greater than the maximum concentration observed in streambed sediment formed from local Quaternary deposits and loess, and Columbia River Basalt Group geologic units--the dominant geology contributing to streambed sediment of higher-order streams in the Naches River drainage. Thus, the enrichment of mercury at the mouth of the Naches River probably was caused by contributions of lower-order tributaries that were affected by natural sources of mercury. For example, streambed sediment at the mouth of the Naches River contained 0.24 μg/g of mercury.

Bumping River also is located within the Naches River drainage. The mercury concentration of 0.5 μg/g at site 144 of the Bumping River (a site classified as a tributary to other than the main stem) may be a result of the mercury anomaly (3.1 μg/g) at site 177, a lower-order tributary to Bumping Lake. Mercury's tendency to sorb readily onto particulate matter suspended in water and onto streambed sediment (U.S. Geological Survey, 1970), suggests storm events are important mechanisms in the transport of mercury to high-order streams. Transport of mercury by storm runoff is reasonable because concentrations of mercury are small at neighboring lower-order-stream sites (adjacent to and immediately upstream of the Bumping River site) draining to the Bumping River (pl. 2).

Placer-gold mining was considered a potential source of mercury to streambed sediment. Placer miners commonly used "quicksilver" in various methods to recover gold. One such method was to coat the bottom of gold pans and riffles in sluices with mercury before placing them into the stream. Gold-bearing sands and gravel were then washed across the treated surface. The gold particles which stick to the mercury-coated surfaces (and are partly dissolved in mercury to form amalgam) then could be recovered. These methods often released large quantities of mercury into the streams. The Swauk Creek drainage, located in the northeastern part of the basin, was heavily mined for gold (see fig. 4). Small pools and droplets of mercury have been observed along the streambed and are thought to be associated with small-claim mining (Russ Raylor, Washington State Department of Ecology, written commun., 1987). Although substantial amounts of mercury were used in mining gold from Swauk-Creek-placer deposits, only one large mercury concentration (0.18 μg/g) occurred in Swauk Creek (site 70, a higher-order stream site). This site was located downstream of a tributary (Williams Creek) known to have received effluent from a placer-gold operation (see table 1 and pl. 2). The concentration of mercury at site 70 was larger than that measured in lower-order streambed sediment originating from upstream sites in the nonmarine sedimentary rocks geologic unit sites in the Swauk Creek drainage. The mercury enrichment at site 70 was probably a result of the upstream placer operation on Williams Creek and, to a lesser extent, a result of geologic sources.

Large concentrations of mercury, relative to the median concentration (<0.02 μg/g) in lower-order streams, also exist at some sites classified as tributaries to the main stem, anthropogenic (see table 10, and fig. 16). Wide Hollow Creek is a good example of anthropogenic-mercury enrichment along a higher-order tributary to the main stem (pl. 2, site 235). The concentration of mercury measured near its mouth (0.24 μg/g) was probably anthropogenically derived because Wide Hollow Creek drains urbanized and industrialized lowlands (predominantly streambed sediment derived from Quaternary deposits and loess) of the mid-valley and lacks the geologic mercury sources known to exist in streambed sediment derived from Miocene and older volcanic rocks, Tertiary granitic and intermediate intrusive rocks, and marine sedimentary rocks geologic units (fig. 16).

In addition to nonpoint sources of mercury, such as those affecting streambed sediment in Wide Hollow Creek, point sources such as STP's may increase concentrations of mercury in streambed sediment. As stated earlier, detectable concentrations of several minor elements including mercury were emitted from STP's in the basin. Point-source effluents may explain the presence of the 0.12 μg/g of mercury in East Toppenish Drain (site 318), downstream of the Toppenish STP. Point sources of mercury were not directly determined in this report. The Toppenish STP, however, may be a point-source contributor of mercury, because geological sources (primarily loess) of mercury in East Toppenish drainage were generally too small (<0.02 μg/g) to account for the observed enrichment.



	Site classification
los	Lower-order streams
Totm	Tributaries to other than the main stem
tmna	Tributaries to main stem; naturally affected
tma	Tributaries to main stem; anthropogenic
m	Main stem
ss	Soil samples
ud	Urban-storm-water drains

Figure 16. Distribution of mercury concentrations in streambed sediment of lower- and higher-order streams, soil samples, and urban-storm-water drains, Yakima River Basin, Washington, 1987. Higher-order streams include Totm, tmna, tma, and m.

Although, anthropogenic sources of mercury exist in the basin, they are small in comparison to geologic sources of mercury.

Selenium

Few selenium determinations were made, but those few are included in this report because of selenium's significance as a priority pollutant (Chapman and others, 1982). On the basis of historical data, numerous mineralized sites were purposely sampled for elements including selenium during the present study (1987). This was done to ensure the presence of quantifiable element concentrations in order to select analytical methods appropriate for the main sampling effort. Thus, many of the sites sampled for selenium were not randomly selected and are not summarized in table 11, at back of report. Although the selenium data are not representative of the entire basin, the data are used in discussing selenium mineralization in lower-order streams.

In the Yakima River Basin, approximately 15 percent of the sites sampled had anomalous concentrations ($\geq$ 0.7 μg/g) of selenium (table 5). When compared to soils data, concentrations of selenium in the basin did not exceed the expected 95-percent range of concentration for soils in the Western United States.

Notable selenium anomalies exist along lower-order stream sites 225 and 260 in the marine sedimentary rocks geologic unit and site 10 in the pre-Tertiary metamorphic and intrusive rocks geologic unit (pl. 1). For example, a selenium concentration of 1.4 μg/g was measured for a lower-order tributary (site 225) to Indian Creek which flows into Rimrock Lake. Site 225 is a nonrandomly selected site located in the marine sedimentary rocks geologic unit. Rocks in the Indian Creek drainage were hydrothermally altered and mineralized as a result of the emplacement of granitic intrusions (Simmons and others, 1983). Hydrothermally derived minerals common to this drainage include pyrite (FeS_2), arsenopyrite (FeAsS), and chalcopyrite ($CuFeS_2$).

Selenium is preferentially enriched in hydrothermal sulfides formed at elevated temperatures (Rankama and Sahama, 1950). Thus, sulfide minerals were a probable source of selenium in streambed sediment of the Indian Creek drainage.

Concentrations of selenium were similarly enriched in lower-order streams of the Cle Elum River (sites 7, 10, 13, 19 and 21) and Teanaway River (site 57) drainages, located in the northern portion of the Yakima River Basin. Again, selenium concentrations were large in the vicinity of areas reported by Gualtieri and Simmons (1989) to be composed of hydrothermally altered and mineralized rock containing sulfide minerals such as arsenopyrite.

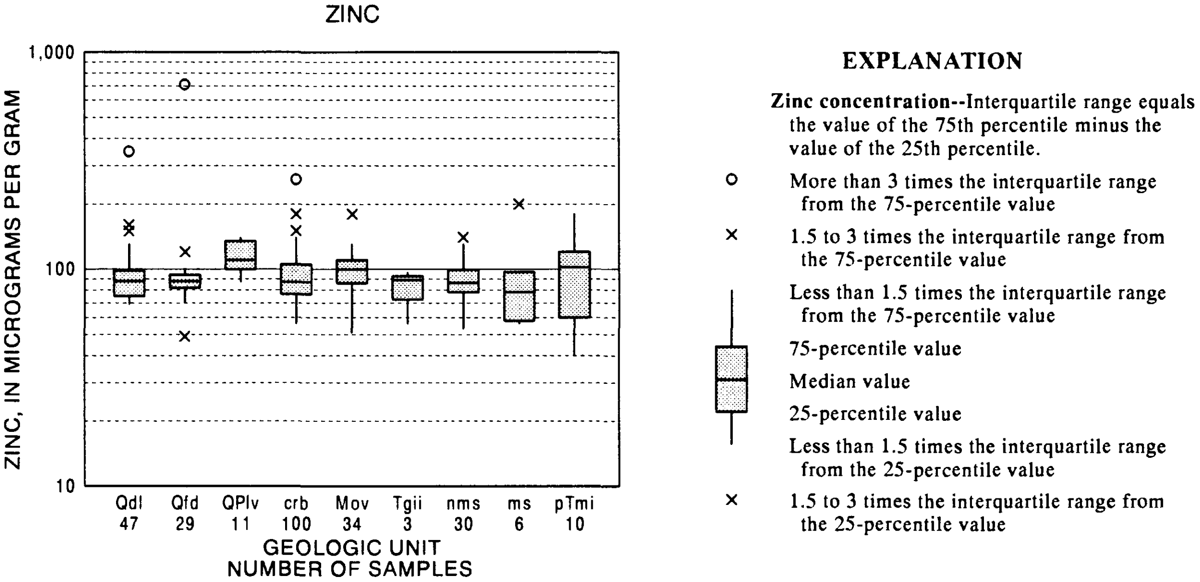
With the exception of lower-order sites within the immediate vicinity of mineralized deposits, large selenium concentrations were found at the middle fork of the Teanaway River (site 57) and at the mouth of Rattlesnake Creek (site 183). These sites were located downstream of previously identified, hydrothermally altered and mineralized rocks (Simmons and others, 1983; Gualtieri and Simmons, 1989) and probably are enriched from suspension, transport, and deposition of mineralized sediment from lower-order streams.

The only notable selenium concentration (0.6 μg/g) in the main stem was in the upper basin at the Yakima River at Evergreen Farm near Ellensburg (site 121). The concentration of selenium at the main stem site was about one-half that measured from mineralized, lower-order-stream sites. The Evergreen Farm site is located downstream of sources of mineralized rock within the Cle Elum River and the Teanaway River drainages (Gualtieri and Simmons, 1989).

Zinc

In the Yakima River Basin, approximately 10 percent of the sites sampled had anomalous concentrations ($\geq$ 120 μg/g) of zinc (table 5). Anomalous concentrations of zinc were distributed over several geologic units, particularly noteworthy were sites located in the Quaternary and Pliocene volcanic rocks, the Miocene and older volcanic rocks, and the pre-Tertiary metamorphic and intrusive rocks geologic units (fig. 17 and pl. 2). Nearly one-half the zinc determinations of lower-order sites in the Quaternary and Pliocene volcanic rocks geologic unit were anomalous (fig. 17 and pl. 2). Quaternary and Pliocene volcanic rocks comprise the recent basalt of the Simcoe Mountains in the southeastern part of the basin.

The ANOVA procedure shows that the mean rank of the zinc concentrations from the 11 streambed-sediment samples collected in the Quaternary and Pliocene volcanic rocks were significantly ($\rho \leq 0.1$) larger than the mean rank of the zinc concentrations in streambed sediment originating from most of the other geologic units in the basin (table 12, at back of report). Although zinc concentrations in streambed sediment originating from Quaternary and Pliocene volcanic rocks were large relative to most of the other geologic units in the basin, they were within the 100 to 300 μg/g of zinc reported by Goldschmidt (1958) for basalt and gabbro.



Geologic unit	
Qdl	Quaternary deposits and loess
Qfd	Quaternary flood deposits
QPlv	Quaternary and Pliocene volcanic rocks
crb	Columbia River Basalt Group rocks
Mov	Miocene and older volcanic rocks
Tgii	Tertiary granitic and intermediate intrusive rocks
nms	Nonmarine sedimentary rocks
ms	Marine sedimentary rocks
pTmi	Pre Tertiary metamorphic and intrusive rocks

Figure 17. Distribution of zinc concentrations in streambed sediment of lower-order streams, relative to geologic units, Yakima River Basin, Washington, 1987.

Several anomalous concentrations of zinc exist in streambed sediment of other geologic units, particularly at some sites located in the pre-Tertiary metamorphic and intrusive rocks and Miocene and older volcanic rocks geologic units (pl. 2). As an example, consider site 12 located in pre-Tertiary metamorphic and intrusive rocks geologic unit upstream of Little Kachess Lake in the northern basin (pl. 1). Streambed sediment at this site originated predominantly from the metamorphic rock phyllite (Frizzell and others, 1984) and had a zinc concentration of 180 μg/g. Another large concentration of zinc, one that relates well to the historical zinc data (pl. 2) and one that illustrates the extreme variability that can occur within the pre-Tertiary metamorphic and intrusive rocks geologic unit was at a lower-order-headwater tributary to the Cle Elum River (site 5). This site was not selected using the random-sampling design; rather, it was intentionally sampled as part of the quality-assurance program. Streambed sediment at this site originates from the metamorphic rock serpentinite (Frizzell and others, 1984) and had a zinc concentration of 160 μg/g. Neighboring lower-order-stream sites had zinc concentrations of less than 71 μg/g and were similar in concentration to many of the data reported by Moen (1969). Even when sample-collection variability is accounted for (app. B, equation number 1, table B1) before making intersite comparisons, substantial differences remain between the large concentration of zinc at site 5 and the smaller concentrations at neighboring sites. The large concentration of zinc at site 5 was in agreement with anomalous zinc concentrations of 200 to 300 μg/g, reported by Gualtieri and Simmons (1989) from samples collected along the same lower-order headwater tributary to the Cle Elum River. Thus, data in this report and historical data indicate a strong heterogeneous distribution of zinc concentrations in streambed sediment originating from the pre-Tertiary metamorphic and intrusive rocks geologic unit in the northern part of the Yakima River Basin. This heterogeneity probably results from the presence of small and scattered gold and minor-element mineralization documented within this region (Gualtieri and Simmons, 1989; Thurber and others, 1984).

An anomalous concentration of zinc exists in streambed sediment originating from the Miocene and older volcanic rocks geologic unit of Gold Creek (site 20)--inflows to Keechelus Lake, located in the northeastern part of the basin (pl. 2). The streambed sediment concentration of zinc at this site is 180 μg/g. Anomalous zinc concentrations reported by Gualtieri and Simmons (1989) in nearby streambed sediment, ranged from 200 μg/g to 390 μg/g (pl. 2). These anomalies occur approximately 2 mi upstream of the present study site and, according to the geologic mapping of Gualtieri and Simmons (1989), were formed in an area containing hydrothermally altered and mineralized rock, with zinc concentrations ranging from 200 μg/g to 7,000 μg/g.

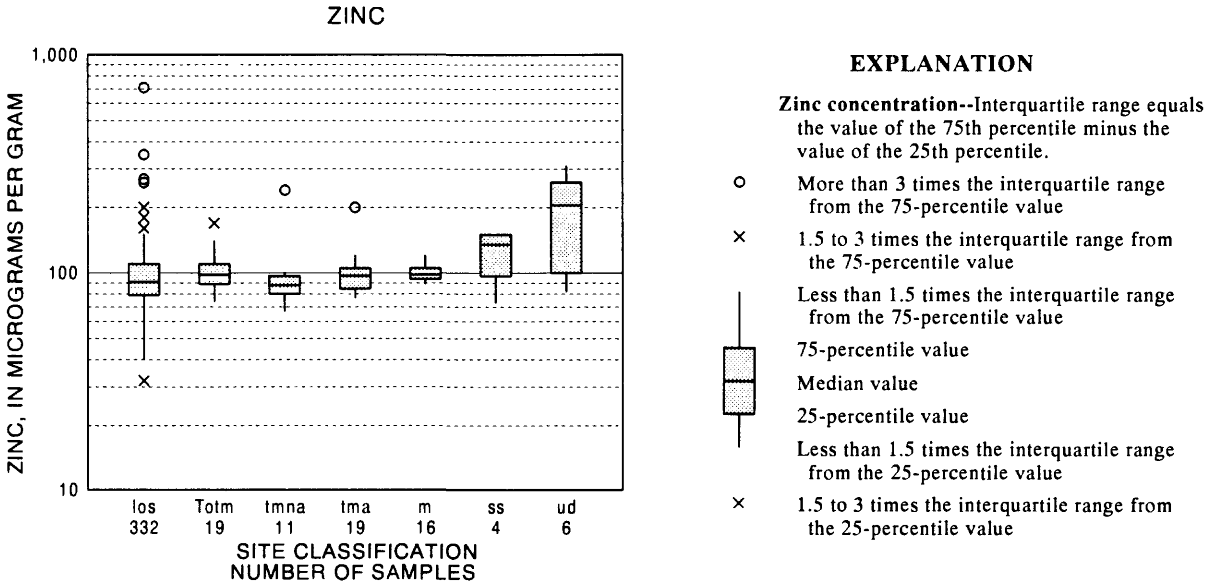
Large zinc concentrations also were found at some sites located in the Miocene and older volcanic rocks geologic unit. Streambed-sediment samples at sites 150 and 158 were collected on tributaries to the American River in the western basin and had zinc concentrations of 150 μg/g and 180 μg/g, respectively, (pl. 2). Streambed sediment at both sites originated from Miocene and older volcanic rocks--specifically Oligocene rocks immediately east of Mount Rainier. Oligocene rocks comprise the Ohanapecosh Formation and are composed of dacitic to basaltic-andesitic rock which has undergone extensive hydrothermal alteration (Schasse, 1987). The large concentrations of zinc in streambed sediment originating from the Miocene and older volcanic rocks geological unit is probably a result of mineralization associated with hydrothermally altered rock in the Upper Naches Subbasin. Zinc enrichment also was reported at numerous historical streambed-sediment sampling sites in the Naches River Basin. In the immediate vicinity of sampling sites 150 and 158, Moen (1969) reported zinc concentrations that ranged from 205 μg/g to 1,000 μg/g (pl. 2), and in the vicinity of Bumping Lake, Simmons and others (1983) reported that zinc concentrations ranged from 200 μg/g to 300 μg/g.

The maximum zinc concentration (710 μg/g) for all sites sampled in this report, including urban-storm-water drains, occurred in streambed sediment of an intermittent lower-order stream (site 298) formed from the Quaternary flood deposits geologic unit. This concentration is larger than concentrations measured in the other geologic units (fig. 17). This site probably has an anthropogenic source because it is downstream of numerous apple orchards and is in the vicinity of several rural roadways. Zinc is commonly applied to apple trees of the Yakima River Basin in the form of zinc sulfate, a spray used to retain apple blossoms and promote overall yields (Robert Wample, University of Washington, Prosser Experimental Station, oral commun., 1991). Concentrations of zinc in zinc sulphate sprays applied to apple trees are as large as 600 mg/L (Severson and Shacklette, 1988). Zinc enrichment also may result from the interaction of streambed sediment with galvanized-road culverts, which are common throughout the basin.

Agricultural practices associated with orchard crops may represent a nonpoint source of zinc to streambed sediment. Several zinc anomalies exist in soils (sites 256 and 259) and streambed sediment (sites 243, 255, and 262) of the Ahtanum Subbasin which is located in the mid-valley and supports a large number of apple orchards (pl. 2). Of the aforementioned sites, concentrations of zinc in soils (150 μg/g and 150 μg/g, respectively) and streambed sediment (180 μg/g, 150 μg/g, and 140 μg/g, respectively) exceed the 90th percentile concentration (130 μg/g) of all samples in this report (see table 5). In addition, they exceed concentrations found outside agricultural areas, further up the Ahtanum Creek drainage, where only geologic sources would be expected to affect local concentrations (pl. 2). Thus, it is unlikely that geologic sources are accounting for the observed enrichment; rather, enrichment probably is from a local nonpoint source. As described earlier, the above two soil samples (enriched in zinc) were collected from two agricultural plots that were formerly apple orchards. A third soil sample, collected from a nonorchard site (pea field), contained only 73 μg/g of zinc. The latter concentration is in close agreement with the median concentration (88 μg/g) found in streambed sediment formed from the Quaternary deposits and loess geologic unit (table 11, at back of report). Thus, soils in agricultural plots not used for growing apples have concentrations of zinc that were similar to the geologic sources, whereas soils in apple orchards and lower-order streambed sediments in the vicinity of apple orchards contain concentrations of zinc that are larger than nearby geologic sources. A likely nonpoint source of zinc is the use of the chemical zinc sulfate.

Anomalous concentrations of zinc also were found at urban-storm-water-drain sites. The median zinc concentration at urban-storm-water drains is twice that of higher-order streams (fig. 18). For example, zinc concentrations in urban-storm-water drains of the cities of Ellensburg (site 126), Yakima (sites 248 and 252), and Prosser (site 402) were 190 μg/g, 220 μg/g, 310 μg/g, and 260 μg/g, respectively. Zinc commonly is associated with urban runoff and is used in a broad array of industrial and household items including: wood preservatives, metallic plating, battery cells, and disinfectants (Sittig, 1981). Many of these uses could result in the sorption of zinc to sediment of urban-storm-water drains.

It is doubtful that the anomalous zinc concentrations in urban-storm-water drains are notably enriching zinc concentrations along the main stem. If urban-storm-water drains were causing enrichment then zinc would be expected to vary in concentration along the main stem. Zinc concentrations, however, are relatively consistent down the main stem; the interquartile (difference between the 25th and 75th percentile) is only 15 μg/g (table 10 at back of report, and fig. 18).



Site classification

los	Lower-order streams
Totm	Tributaries to other than the main stem
tmna	Tributaries to main stem; naturally affected
tma	Tributaries to main stem; anthropogenic
m	Main stem
ss	Soil samples
ud	Urban-storm-water drains

Figure 18. Distribution of zinc concentrations in streambed sediment of lower- and higher-order streams, soil samples, and urban-storm-water drains, Yakima River Basin, Washington, 1987. Higher-order streams include Totm, tmna, tma, and m.

Selected Nontarget Elements in the National Water Quality Assessment Program

Nontarget elements, although not usually a concern to aquatic health, provide important ancillary data. In rock, the relative concentrations of nontarget major elements calcium, iron, potassium, and sodium serve to identify specific types of igneous rock comprising a geologic unit (Plummer and McGeary, 1982). Because the chemistry of streambed sediment is affected by major elements originating from rock, the relative concentrations of the major, nontarget elements are important in determining origins of the streambed sediment. This section of the report examines some nontarget elements in streambed sediment and their relations to the local geology.

Relations among Selected Rare Earth Elements, Potassium, and Thorium in the Quaternary Flood Deposits Geologic Unit

Streambed sediment collected at lower-order streams draining the Quaternary flood deposits geologic unit (pl. 3) are enriched in the rare earth elements cerium, lanthanum, and neodymium, the actinide thorium, and the alkali earth element potassium as determined by factor analysis, correlation testing, and ANOVA. Factor analysis shows that many sites have significant-positive associations or factor scores among the elements cerium, lanthanum, neodymium, and potassium. The same relations among the aforementioned elements were further verified by use of the nonparametric Kendall Tau-B test for correlation--again significant (ρ = 0.0001) relations exist. The ANOVA procedure shows that the mean rank of the cerium, lanthanum, neodymium, and potassium concentrations in streambed sediment originating from flood deposits was significantly different (ρ = 0.1) than the mean rank of like elements in the other geologic units. This is true except for cerium, lanthanum, and neodymium in the Quaternary and Pliocene volcanic rocks geologic unit (table 12, at back of report). In addition, the mean ranks for concentrations of the above elements in flood deposits are generally larger than the mean ranks for concentrations in other geologic units in the basin.

Spatially, enrichment is notable in numerous samples within the Quaternary flood deposits geologic unit (pl. 3). Petrographic data show that flood deposits with a heavy mineral suite, similar to that of Yakima River Basin flood deposits, exist in other river basins connected to the Columbia River Basin; for example, the Willamette River Basin in western Oregon and the Walla Walla River Basin in eastern Washington (Glenn, 1965). Streambed sediment within the Quaternary flood deposits geologic unit were chiefly silt and clay that originated from loess of the Palouse Formation--part of the Columbia Plateau in eastern Washington (Glenn, 1965). This loess was scoured by water through the failure of the Lake Missoula ice dam in the Pleistocene Epoch (Glenn, 1965). Loess of the Palouse Formation was formed from granitic and metamorphic rock (Glenn, 1965). From a geochemical perspective, these flood deposits have imparted a unique geochemical character to Yakima River Basin streambed sediment of the lower valley. Specifically, the geochemistry of streambed sediment originating from Quaternary flood deposits reflects the granitic character of the loess of the Palouse Formation. Granitic rock is known to be a source of the rare-earth elements cerium, lanthanum, and neodymium, the actinide thorium, and the alkaline earth element potassium (Rankama and Sahama, 1950).

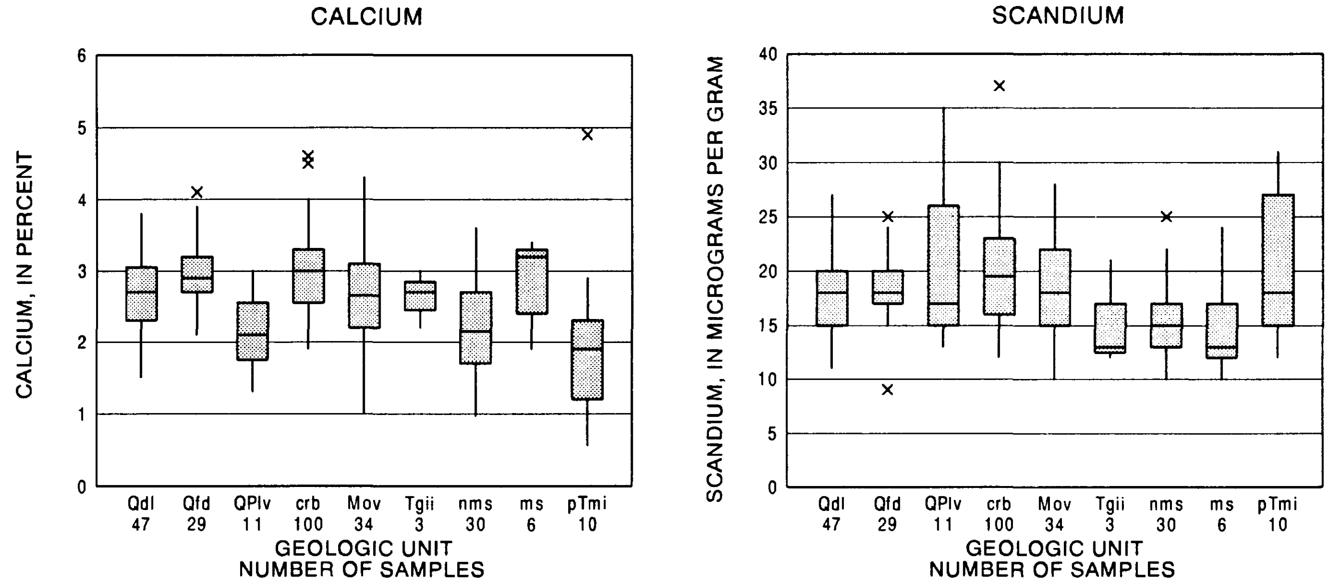
Although the mean ranks for cerium, lanthanum, neodymium, and potassium concentrations were significantly different between the Quaternary flood deposits geologic unit and the Columbia River Basalt Group rocks geologic unit, factor analysis shows that many sites in the latter geologic unit also have significant-positive associations among the rare-earth elements, potassium, and thorium. These sites are located within the lower valley where the Columbia River Basalt Group boarders the Quaternary flood deposits geologic unit. Element enrichment at these sites probably resulted from eolian (wind blown) deposits from the Quaternary flood deposits geologic unit.

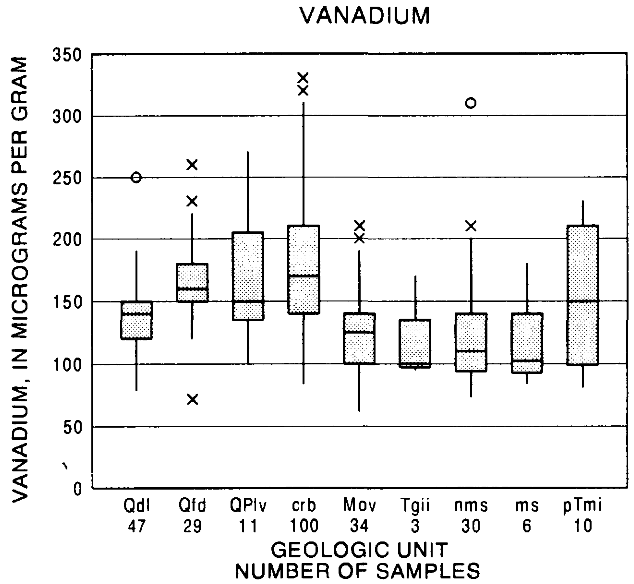
Relations among Selected Transition Metals, Calcium, Iron, and Scandium in the Columbia River Basalt Group Rocks Geologic Unit

A large number of randomly selected, lower-order stream sites (100 out of 270) are located in the Columbia River Basalt Group because of the large area represented by this geologic unit. Many of these sites have significant positive factor scores, or associations, among the elements calcium, iron, scandium, titanium, and vanadium. These same relations were verified as highly significant ($\rho = 0.0001$) using the Kendall Tau-B test for correlation. The ANOVA procedure (table 12 at back of report) shows that the mean rank of calcium concentrations in streambed sediment formed from the Columbia River Basalt Group was significantly different ($\rho \leq 0.1$) than the mean rank of calcium concentrations in streambed sediment of the other geologic units, except Quaternary flood deposits and marine sedimentary rocks geologic units.

Many of the following relations among the aforementioned elements are commonly recognized by geochemists--for a detailed explanation see Krauskopf (1979). Streambed sediment originating from the Columbia River Basalt Group was notably enriched (median element concentration generally exceeds that of other geologic units) in calcium, scandium, and vanadium--all common elements within basaltic rocks (fig. 19, and table 11 at back of report). Calcium in the Columbia River Basalt Group results from calcium-rich plagioclase feldspar, an aluminosilicate mineral (Plummer and McGeary, 1982). Scandium is found commonly in the ferromagnesian minerals of basalt rock (Rankama and Sahama, 1950) and because of its abundance has been used as a tracer to identify Tertiary Columbia River Basalt in the coastal range of northwestern Oregon (Moinoddin and others, 1983). Vanadium is enriched in basalt rock because of its ability to substitute into ferromagnesian mineral assembledges of basalt in exchange for iron and aluminum (Rankama and Sahama, 1950).

Titanium concentrations also were large in the Columbia River Basalt Group and Quaternary and Pliocene volcanic rocks. During weathering, titanium minerals are known to form resistates and consequently remain unchanged in the resultant sediment (Rankama and Sahama, 1950, p. 563). Concentrations of titanium in streambed sediment



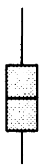


EXPLANATION

Element concentration--Interquartile range equals the value of the 75th percentile minus the value of the 25th percentile.

○ More than 3 times the interquartile range from the 75-percentile value

× 1.5 to 3 times the interquartile range from the 75-percentile value



Less than 1.5 times the interquartile range from the 75-percentile value

75-percentile value

Median value

25-percentile value

Less than 1.5 times the interquartile range from the 25-percentile value

× 1.5 to 3 times the interquartile range from the 25-percentile value

Geologic unit

Qdl	Quaternary deposits and loess
Qfd	Quaternary flood deposits
QPlv	Quaternary and Pliocene volcanic rocks
crb	Columbia River Basalt Group rocks
Mov	Miocene and older volcanic rocks
Tgii	Tertiary granitic and intermediate intrusive rocks
nms	Nonmarine sedimentary rocks
ms	Marine sedimentary rocks
pTmi	Pre Tertiary metamorphic and intrusive rocks

Figure 19. Distribution of calcium, scandium, and vanadium concentrations in streambed sediment of lower-order streams, relative to geologic units, Yakima River Basin, Washington, 1987.

originating from Columbia River Basalt Group rocks and Quaternary and Pliocene volcanic rocks geologic units are in agreement with those in basalt (0.8 to 1.38 percent), reported by Parker (1967). Thus, the observed titanium concentrations were probably weathering products of basaltic origin.

CONSIDERATIONS FOR FUTURE STREAMBED-SEDIMENT-SAMPLING PROGRAMS

Sampling Lower-order Streams

Random sampling is probably the best sampling method for exploration geochemists because this sampling scheme affords a large number of samples in lower-order streams for typically small, mineralized subbasins. However, in large river basins (typical of those considered the NAWQA program), considerable resources of time and money are required to achieve an appropriate sampling density to spatially portray streambed chemistry. It is suggested, therefore, that sediment be sampled from lower-order streams using a sequential combination of random sampling and stratified-random sampling. Random sampling is described in the "Site selection section" of this report and stratified-random sampling is an adaptation of the method described by Slack and others (1973, p. 17). Stratified random sampling is suggested when the strata (for example, geologic units) are distinct, have known sizes, and are more homogeneous than the population as a whole. In the Yakima River Basin, the logical sampling stratum is geology. In other basins, however, geology may not be an appropriate stratum. Basins affected by glaciation, for example, may have geologic strata which are poorly defined and chemically heterogenous and representatively sampling a geologic stratum might not be possible. Under such circumstances, other divisions, such as land use, should be considered for stratified-random sampling. If distinct divisions or strata are unavailable, random sampling is suggested in place of stratified-random sampling. Stratified-random sampling has particular application to streambed sampling, because sampling sites among strata are distributed in accordance with the variance (rather than evenly, as in random sampling) in each stratum and the area in each stratum.

The primary difference between sampling methods is the grid size in which a sample site is randomly selected. Grid size in random sampling is fixed; for example, 270 sites were randomly selected in the Yakima River Basin from a sample grid of 270 squares (4.7 miles per side) placed over a 1:24,000 scale map. Grid size in stratified random sampling varies between strata; for example, if geologic units are used to subdivide an area into strata, then grid size could vary for each geologic unit or stratum. More precisely, in stratified random sampling, grid size for each stratum is determined by three factors: (1) total number of proposed sampling sites in the basin, (2) standard deviation of the targeted element concentration (because the sampling medium is streambed sediment, it is recommended using the standard deviation of the log-transformed-element concentrations to approximate a normal distribution), and (3) the areas of the various strata. Because the standard deviation for each element may vary, compute standard deviations for several target elements. Select the target element with the largest standard deviation to ensure population variance is minimal and that an adequate number of samples are collected for all elements that is the most representative of the data as a whole. This standard deviation is used to determine the appropriate number of samples to be collected from each stratum.

In most streambed sampling investigations, the standard deviation of the targeted element concentrations is unknown. To circumvent this problem, first conduct a random sampling for the entire basin, using a subset of the total number of proposed sampling sites. From this sampling, an estimate of standard deviation for the target element will be obtained for each proposed geologic stratum.

In the following example, a hypothetical river basin has (1) a drainage area of 6,000 mi^2, (2) a geologic strata composed of four geologic units (geologic units 1-4), and (3) a total proposed number of sites equaling 200. A subset of the total number of proposed sampling sites is selected for random sampling. This subset will be used to obtain an estimate of standard deviation for each proposed geologic stratum. Initially, 50 samples (25 percent of the proposed number) were alloted to the random-sampling subset (table 6). This number was multiplied by the area within each stratum and divided by the total drainage area of the basin to obtain the number of "samples per stratum" (table 6). The samples per stratum in some cases were increased to a minimum of 15 to obtain a reasonable estimate of standard deviation. These increases resulted in a subset sample size of 68. Of the 68 random-sampling sites, geologic units 1, 2, 3, and 4 were alloted 15, 21, 15, and 17 sites, respectively (table 6). In some instances, it may be possible to use the following U.S. Geological Survey data base: Rock Analysis and Storage System (RASS), National Uranium Resource Evaluation (NURE), and PLUTO data to make these estimates.

After obtaining an estimate of standard deviation for each geologic unit strata, calculate the appropriate number of samples within each geologic unit for a random-stratified sampling (table 7). Even though geologic unit 1 is four times smaller than geologic unit 4, it receives an equal number of sampling sites because its standard deviation is four times larger than that of geologic unit 4. The advantage of stratified random sampling is that more sampling sites are alloted to chemically-heterogeneous strata than are alloted to chemically-homogeneous strata. Thus, the likelihood of over sampling some strata and under sampling other strata are greatly reduced relative to simple random sampling.

Other Sampling Considerations

Some higher-order streams and possibly a few lower-order streams should be re-sampled when seasonally induced changes are expected in the concentration of elements in the streambed. For example, concentrations of arsenic and chromium in streambed sediment of the Yakima River at Umtanum were diluted by sediment present in incoming-irrigation-return flow from Wilson Creek. Streambed sediment at Umtanum was collected near the end of the irrigation season when the river was wadeable. Quite possibly, larger concentrations of arsenic and chromium may have been present if the streambed had been sampled during the period following winter storms, but prior to irrigation.

Table 6.--Use of random sampling as input to the design of a stratified-random-sampling scheme

[A (area) of river basin = 6,000 square miles; Ai = area of geologic unit; N = number of sites to randomly sample; (15) = suggested minimum number of samples per stratum; Si = standard deviation of log-transformed-element concentrations for each stratum]

Stratum geologic unit	$\frac{Ai \times N}{A}$	Samples per stratum	Minimum 1/ samples per stratum	Si 2/ ($\log_{10}$)
1	$\frac{500 \times 50}{6,000}$	4	(15)	2.0
2	$\frac{2,500 \times 50}{6,000}$	21	21	.5
3	$\frac{1,000 \times 50}{6,000}$	8	(15)	1.7
4	$\frac{2,000 \times 50}{6,000}$	17	17	.5
	(total)	50	68	--

1/ The total number of random samples has increased from 50 to 68 (an addition of 11 sites in geologic unit 1 and 7 sites in geologic unit 3) because a minimum of 15 samples per stratum is recommended for estimating standard deviation.

2/ The suggested minimum samples per stratum, where used to calculate Si.

Table 7.--Calculating the appropriate number of sampling sites within strata based on a stratified-random-sampling scheme

[Ai = area of geologic unit; Si = standard deviation of log-transformed element concentrations; N = 200, total proposed number of sampling sites; Σ = sum; mi2 = square miles]

Stratum geologic unit	Ai x Si	Samples per stratum 1/ $\frac{Ai \times Si \times N}{\Sigma\ (Ai \times Si)}$	Size of sample grids (mi2)
1	1,000	40	12.5
2	1,250	51	49
3	1,700	69	14.5
4	1,000	40	50
(total)	4,950	200	--

1/ Note, although 200 sample sites are shown, 68 have already been sampled by random sampling; only 132 sampling sites remain. For example, 21 sites were previously sampled from geologic unit 2 in order to estimate standard deviation; thus only 30 of the 51 sites in geologic unit 2 remain to be sampled.

Because wet- and dry-sieving techniques were not directly compared in this report, it is not possible to suggest a particular technique. However, the following factors need to be considered in the selection of sieving technique. Wet sieving reduces the potential for the loss of fine-fraction sediment when samples are placed into kraft paper bags to dewater, prior to disaggregation and dry sieving. The wet-sieving technique provides an accurate representation of fine-grained sediment because the streambed-sediment is passed directly through a 63 μm-pore diameter sieve. The dry-sieve sample may have two potential problems that stem from sample collection and processing. Fine-grained sediment was observed passing through the cloth sample bag as the water-sediment slurry dewatered; thus, concentrations of trace elements associated with a portion of the fine-grained sediment may be lost. Prior to dry sieving, the sediment sample was processed through a jaw crusher followed by a ceramic-plate pulverizer to disaggregate and homogenize the sample. This sample-disaggregation technique, used prior to sieving, may generate newly formed fine-grained sediment that is different in chemical composition to that of wet-sieved sediment.

A limited number of soil samples should be collected to verify hypotheses as to sources of anomalous element concentrations. Soil sampling has been especially useful in this report in regard to identifying agricultural sources of arsenic, lead, and zinc in the Yakima River Basin.

SUMMARY AND CONCLUSIONS

The Yakima River Basin was one of four surface-water-pilot project areas selected to test and refine concepts for implementing the U.S. Geological Survey's National Water Quality Assessment program. As part of the pilot project, streambed sediment was collected from 448 locations throughout the Yakima River Basin to help determine the occurrence and spatial distribution of potentially toxic major and minor elements. Streambed sediment is an ideal sampling medium for an area-wide assessment of elements in aquatic systems. Concentrations of many of these elements in water generally are small. In addition, nonpoint-source contributions of elements may be intermittent or storm related; and, as a result, may not be detected in single or periodic water samples. Streambed sediment is derived primarily from the weathering of the earth's surface. Weathered materials, especially particulate matter, ultimately are transported through the action of flowing water, ice, wind, and animals (including man) to surface waters, where they may be deposited as streambed sediment. Because the chemistry of streambed sediment is dynamic, some ions may dissolve into surrounding water while others (including environmentally important elements like cadmium, mercury, and lead) may attach (sorb) to streambed sediment. Streambed sediment can accumulate these constituents during periods of low stream velocity, when the streambed is not being scoured. During these periods, the streambed becomes a depository for incoming sediment. This sediment, as well as sediment already in place, can accumulate dissolved metals and other elements from sources related to natural processes, as well as to man's activities. Thus, streambed sediment is an ideal medium in which to measure the distribution of elements that have come in contact with streambed sediment over an extended period of time. More importantly, the concern associated with elements sorbed to sediment is that many important aquatic species and food-chain organisms spend a major part of their life cycle living in or on aquatic sediment. Through this contact, a pathway exists for these elements to be consumed by higher aquatic life and wildlife, including birds and man.

This report presents the results of the 1987 occurrence and distribution survey of potentially toxic major and minor elements in streambed sediment of the Yakima River. More specifically, this report provides information about the:

(1) Ranges of concentrations of selected major and minor elements in streambed sediment in the Yakima River Basin, and identifies elements that are unusually large or anomalous, and

(2) Areal distribution of concentrations of selected major and minor elements and their relation to man's activities and naturally occurring sources.

The sediment sampled in the basin represents a variety of environments that covers lower- to higher-order streams, and includes some agricultural soils and urban drains. Fine-fraction sediment (that passing through a 63- micrometer pore-size sieve) was analyzed for 44 major and minor elements, including two forms of organic carbon.

Concentrations of selected major and minor elements in streambed sediment--Large or anomalous element concentrations were identified by establishing baseline concentrations for sediment in the Yakima River Basin (table 8).

The largest number of anomalies was measured for antimony, arsenic, cerium, copper, lead, and zinc. At least 10 percent of these element concentrations exceeded the baseline value derived for streambed sediment in the Yakima River Basin. Additionally, several of these element concentrations are high in comparison to element concentrations present in soils of the Western United States. Streambed sediment concentrations for several elements, including arsenic, chromium, cobalt, copper, lead, mercury, nickel, and zinc exceeded concentrations measured for 95 percent of the soils in the Western United States.

Sources of major and minor elements in streambed sediment--Most of the element anomalies resulted from the presence of geologic sources within the basin. Elements with geologic sources include antimony, arsenic, chromium, copper, mercury, selenium, and zinc. The predominant subbasins containing geologic sources of anomalous element concentrations were the Cle Elum, Upper Naches, and Tieton. Anomalous concentrations of arsenic, cobalt, chromium, nickel, and zinc as large as 61, 120, 1,700, 1,900, and 180 micrograms per gram, respectively, were derived from geologic sources in the Cle Elum Subbasin. In addition, anomalous element concentrations of copper, mercury, and selenium as large as 150, 3.1, and 1.4 micrograms per gram, respectively, were derived from geologic sources in the Upper Naches Subbasin. Concentrations of the above elements equaled or exceeded concentrations measured for 95 percent of the soils in the Western United States. Several of these elements, including arsenic, chromium, and nickel, leave chemical signatures or markers that were measurable in

Table 8.--Concentrations of selected elements in soils of the Western United States and in fine-grained stream sediment of the Yakima River Basin, Washington, 1987

[na = data not available; ___ = value at indicated percentile equals or exceeds the baseline concentration]

	Yakima River Basin streambed sediment										Western United States soils[1]		
Chemical	Number of observations	Minimum	Value at indicated percentile 10	25	50 (median)	75	90	98	Maximum	Baseline concentration [2]	Number of observations	Expected 95 percent range baseline soils [3]	Maximum
Major elements, in units of percent													
Aluminum	407	2.7	6.6	7.1	7.7	8.3	8.8	9.7	13	10	770	1.5 - 23	na
Calcium	407	.6	1.8	2.2	2.6	3.0	3.4	4.1	4.9	*3.8	777	.19 - 17	32
Carbon, inorganic	407	.01	.01	.01	.02	.04	.09	.19	.62	*.14	na	na	na
Carbon, total	407	.23	.58	.97	1.8	2.9	4.6	7.6	16	*5.8	na	na	na
Iron	407	2.7	3.9	4.4	5.1	5.9	6.8	8.3	9.8	*7.4	777	.55 - 8.0	>10
Magnesium	407	.4	.8	1	1.2	1.4	1.6	5.9	13	2	778	.15 - 3.6	>10
Phosphorus	407	.02	.07	.08	.10	.12	.14	.17	.27	.17	524	.006 - .17	.45
Potassium	407	.13	.74	.90	1.1	1.3	1.5	1.8	2.2	2.8	777	.38 - 3.2	6.3
Sodium	407	.4	1.4	1.6	1.8	2.0	2.3	2.8	3.8	*1.7	774	.26 - 3.7	10
Sulfur	407	.01	.01	.01	.02	.03	.05	.09	.36	*.07	2.8	na	na
Titanium	407	.14	.46	.59	.71	.86	1.1	1.4	1.8	*1.3	777	.069 - .70	2.0
Minor elements, in units of micrograms per gram													
Antimony	404	.1	.2	.3	.4	.5	.8	2.0	4.8	.7	na	na	na
Arsenic	404	.7	1.6	2.3	3.9	5.9	11	66	310	8.5	730	1.2 - 22	97
Barium	407	55	370	440	500	560	610	790	1,000	650	778	200 - 1,700	5,000
Beryllium	407	<1	<1	<1	<1	2	2	2	4	3	778	.13 - 3.6	15
Bismuth	407	<10	<10	<10	<10	<10	<10	<10	10	na	na	na	na
Boron	387	<.4	<.4	.4	.7	1.3	2.2	--	8.3	4.0	na	na	na
Cadmium	407	<2	<2	<2	<2	<2	<2	<2	2	na	na	na	na
Cerium	407	5	33	39	45	56	69	100	120	57	683	22 - 190	300
Chromium	407	14	32	44	54	74	110	554	1,800	320	778	8.5 - 200	2,000
Cobalt	407	10	15	17	20	24	30	57	140	40	778	1.8 - 28	50
Copper	407	13	20	24	28	34	46	96	190	40	778	4.9 - 90	300
Europium	407	<2	<2	<2	<2	2	2	3	4	na	na	na	na
Gallium	407	2	17	18	19	21	23	26	35	*24	776	5.7 - 45	70
Gold	407	<8	<8	<8	<8	<8	<8	<8	<8	na	na	na	na
Lanthanum	407	3	19	22	25	30	37	53	62	38	777	8.4 - 110	200
Lead	407	2	9	11	13	17	25	130	890	20	778	5.2 - 55	700
Lithium	407	12	18	20	23	27	37	53	110	42	731	8.8 - 55	130
Manganese	407	420	660	770	950	1200	1400	1,968	2,900	1,600	777	97 - 1,500	5,000
Mercury	406	<.02	<.02	<.02	.02	.08	.16	.48	3.1	.30	733	.008 - .25	4.6
Molybdenum	407	<2	<2	<2	<2	<2	<2	2	8	na	774	.18 - 4.0	7
Neodymium	407	<4	19	23	26	31	38	51	66	*45	538	12 - 110	300
Nickel	407	4	13	17	21	32	53	690	1,900	120	778	3.4 - 66	700
Niobium	407	2	2	5	8	10	13	19	35	16	na	na	na
Scandium	407	7	13	15	18	21	25	30	40	*27	778	2.7 - 25	50
Selenium	99	<.1	<.1	.2	.4	.6	1.0	1.3	1.4	.7	733	.04 - 1.4	4.3
Silver	407	<2	<2	<2	<2	<2	<2	<2	<2	na	na	na	na
Strontium	407	48	218	270	310	340	370	430	620	*400	778	43 - 930	3,000
Thorium	407	<4	<4	5	6	8	10	15	20	*12	195	4.1 - 20	31
Tin	407	<10	<10	<10	<10	<10	<10	<10	10	na	na	na	na
Uranium	407	.10	.55	.70	1	1.3	1.9	6	74	5	224	1.2 - 5.3	7.9
Vanadium	407	62	95	120	150	180	220	270	330	*250	778	18 - 270	500
Ytterbium	407	<1	2	2	3	3	4	5	6	*4	764	.98 - 6.9	20
Yttrium	407	6	17	19	22	25	31	43	61	*35	778	8.0 - 60	150
Zinc	407	32	71	80	93	110	130	220	710	120	766	17 - 180	2,100

1/ Soils data may offer a regional perspective or framework for gaging Yakima River Basin, streambed-sediment chemistry. Several noteworthy limitations apply when making comparisons between soils and streambed-sediment data--see section titled "Baseline values for major- and minor-element concentration in streambed sediment."

2/ The term baseline was applied to a concentration that separates and upper or anomalous data set from a lower or background data set.

3/ Range of concentration encompassing 95 percent of Western United States soils (R.C. Severson, U.S. Geological Survey written commun., 1987, based on data in Shacklette and Boerngen, 1984). Soil data were listed as an ancillary data base which may offer a regional perspective.

streambed sediment of higher-order streams, including the main stem. Concentrations of geologically derived arsenic, for example, ranged from 31 to 61 micrograms per gram in lower-order streams of the Cle Elum Subbasin--similarly enriched arsenic concentrations were found in higher-order tributaries in the Cle Elum Subbasin. These concentrations, once in the Yakima River and after mixing with arsenic-poor sediment in irrigation return flow from the Kittitas Subbasin, decreased to 2.8 micrograms per gram, which is equivalent to background conditions.

Some element anomalies have sources that are related to man's activities, in addition to natural geologic sources. Elements with sources related to man's activities include arsenic, copper, lead, mercury, and zinc. The subbasins containing predominately anthropogenic sources of these elements are Ahtanum, Lower Naches, Wenas, Wilson-Naneum, Wide Hollow, and Swauk. All of these subbasins, except for Swauk, are affected by agricultural- and urban-land-use activities--Swauk is affected by past gold-mining activities. Pesticide formulations containing minor elements, including antimony, arsenic, lead, and zinc, have been used in the past on agricultural lands of the basin. Additionally, the elements in these formulations have been detected in concentrations which exceed that of geologic sources in areas of agricultural land use. For example, geologic sources of arsenic and zinc were small in streambed sediment formed from the Quaternary deposits and loess and nonmarine sedimentary rocks--two geologic units that represent most of the agricultural-land-use areas in the mid and lower Yakima Valley. However, concentrations of arsenic in streambed sediment formed from the nonmarine sedimentary rocks, for example, was about six times larger for land use designated as agricultural than for land use designated as nonagricultural. These differences, which are not attributable to geologic sources, likely resulted from applications of lead-arsenate pesticides. In addition, concentrations of arsenic and lead were as large as 140 and 890 micrograms per gram, respectively, in soils treated with the lead-arsenate pesticide. These soil concentrations of lead and arsenate exceed the maximum concentration measured in more than 700 soil samples from the Western United States.

Past gold-mining activities can be sources of mercury. The historical use of mercury to form amalgams for recovering gold was probably the source of mercury in the Swauk Subbasin. A mercury concentration of 0.18 micrograms per gram was measured downstream from a tributary known to have received effluent from a placer-gold-mining operation.

Urban drains are sources, although small, of elements such as copper, lead, and zinc. Urban drains were not considered large sources because main-stem sites, downstream of urban areas, were not similarly enriched. Apart from agricultural soils affected by past lead-arsenate applications, concentrations of lead in streams receiving urban runoff (in all but one case) exceeded lead concentrations in sediment of lower-order streams. The median concentration of lead in urban drains (an anomalous 71 micrograms per gram) was 5.5 times larger than the median lead concentration from 332 lower-order streams. Anomalous concentrations of copper also were found in urban drains in the city of

Selah (67 micrograms per gram) and the city of Ellensburg (65 micrograms per gram). These concentrations were more than twice the median concentration found in sediment formed from geologic sources. The concentration of copper from Ellensburg's urban drain site was diluted more than two fold after mixing with sediment laden, irrigation-return flow in Wilson Creek, prior to entering the main stem. The median concentration of zinc in urban drains (an anomalous 205 micrograms per gram) was twice the median concentration of higher-order streams.

Anomalous mercury concentrations of 0.24 and 0.12 micrograms per gram were found in Wide Hollow Creek and East Toppenish Drain, respectively. These concentrations are at least six times larger than the median concentration found in sediment formed from geologic sources. Probable anthropogenic sources of mercury in these subbasins are not known with certainty; however, both subbasins are urbanized (for example, Wide Hollow Subbasin has the highest urban density in the basin) and highly agriculturalized.

Implication for water-resource monitoring and regulation--On the basis of results of the occurrence and distribution survey, elements to consider as part of future water-resource monitoring in the Yakima River Basin include arsenic, chromium, copper, nickel, mercury, selenium, and zinc. Some of these elements (for example, chromium) are present in streams primarily as a result of geologic sources, some elements (for example, lead) primarily are present because of anthropogenic sources, and other elements (for example, arsenic, copper, and zinc) are present because of both sources. Because sources of elements may differ, monitoring-design strategies need to be tailored to specific subbasin(s) based on findings from the occurrence and distribution survey. Furthermore, regardless of the source, the implications of anomalous element concentrations to the health of aquatic organisms cannot be assessed only by streambed sediment chemistry. Rather, anomalous concentrations are best viewed as environmental flags or indicators of a need for further study. Researchers may want to consider designing sampling strategies to determine the effects to water, suspended sediment, and aquatic biota, from element sources in geologic and anthropogenic settings. For example, an appropriate geologic setting for determining the potential effects of chromium on water, suspended sediment, and aquatic biota would be found in the upper Yakima Valley near the geologic source. Subbasins for special consideration include Cle Elum and Teanaway.

For arsenic, the potential effects on water, suspended sediment, and aquatic biota also are best measured in the upper Yakima Valley (again, near the geologic source in the Cle Elum and Teanaway Subbasins), and additionally in the mid and lower valley where agricultural sources exist. The occurrence of anomalous concentrations of arsenic and lead in streambed sediment of agricultural lands and soils in the mid and lower valley indicates that past agricultural practices may still be a source of arsenic and lead to streambed sediment--particularly, agricultural practices which tend to facilitate soil loss or erosion. An ideal sampling strategy would target orchard sites established between 1907 and 1947--the application period for lead-arsenate pesticides--in the Wide Hollow and Ahtanum Subbasins. Zinc anomalies also occurred in soils and streambed sediment of lower-order streams of the Ahtanum Subbasin--again, these anomalies were prominent in agricultural-land-use areas. Zinc needs to be considered in water-resource-monitoring strategies.

The elements found in higher-order streams receiving urban runoff included copper, lead, and zinc. At some urban-affected sites, these elements were found in anomalous concentrations; however, concentrations in the main stem were not anomalous, and did not vary in the vicinity of anthropogenic sources. The difference between the 25th and 75th percentile value for main stem concentrations of zinc, for example, was only 15 micrograms per gram. Larger differences would have been expected if large quantities of urban runoff were passing from urban-affected sites to the main stem. Thus, elements in urban runoff, like copper, lead, and zinc, do not appreciably affect sediment quality in the main stem.

The occurrence and distribution survey succeeded in characterizing spatial patterns of element concentrations in terms of geologic and anthropogenic sources. These efforts serve as a foundation for future assessment studies and water-resource-monitoring activities to delineate specific anthropogenic sources. For example, efforts of future studies to delineate the effects of agricultural practices, urban runoff, and municipal sources on streambed-sediment quality, at the subbasin level, may assist water-quality managers in allocating element loads to conform to sediment-quality guidelines.

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SUPPLEMENTAL DATA TABLES

Table 9.--Analytical methods and method reporting levels

[HCl = hydrochloric acid; HNO_3 = nitric acid; $HClO_4$ = perchloric acid; HF = hydrofluoric acid; $Na_2Cr_2O_7$ = sodium dichromate; ICP-AES = inductively coupled plasma-atomic emission spectrometry; AAS = atomic absorption spectrometry]

Element	Digestion method	Method of determination	Method reporting level
Major elements and carbon [All values are reported in units of grams per 100 grams (percent)]			
Aluminum	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	0.005
Calcium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	.005
Carbon, inorganic	($HClO_4$)	Titration	.01
Carbon, total	(combustion)	Infrared	.01
Iron	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	.005
Magnesium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	.005
Phosphorus	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	.005
Potassium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	.01
Sodium	(HCl, HNO_3, $HCLO_4$, HF)	ICP-AES	.005
Sulfur	(combustion)	Titration	.01 and .05
Titanium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	.005
Minor elments [All values are reported in micrograms per gram]			
Antimony	(HF, HNO_3, $HClO_4$)	Hydride-AAS	0.1
Arsenic	(HF, HNO_3, $HClO_4$)	Hydride-AAS	.1
Barium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	1
Beryllium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	1
Bismuth	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	10
Boron	(Hot water soluble)	ICP-AES	.4
Cadmium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2
Cerium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4
Chromium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	1
Cobalt	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	1
Copper	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	1

Table 9.--Analytical methods and method reporting levels--Continued

Element	Digestion method	Method of determination	Method reporting level
Minor elments [All values are reported in micrograms per gram]			
Europium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2
Gallium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4
Gold	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	8
Lanthanum	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2
Lead	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4
Lithium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2
Manganese	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4
Mercury	(HNO_3, $Na_2Cr_2O_7$)	Cold vapor-AAS	.02
Molybdenum	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2
Neodymium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4
Nickel	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2
Niobium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4
Scandium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2
Selenium	(HF, HNO_3, $HClO_4$)	Hydride-AAS	.1
Silver	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2
Strontium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2
Thorium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	4
Tin	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	10
Uranium	(HNO_3); partial extraction	Fluorimetry	.05
Vanadium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2
Ytterbium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	1
Yttrium	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2
Zinc	(HCl, HNO_3, $HClO_4$, HF)	ICP-AES	2

Table 10.--Distributions of major- and minor-element concentrations in streambed sediment relative to site classifications, Yakima River Basin, Washington, 1987

[los = lower-order streams; totm = tributaries to other than the naturally affected main stem; tmna = tributaries to main stem; tma = tributaries to main stem, anthropogenic; m = main stem; ss = soil samples; ud = urban storm drains; < = less than; totm, tmna, tma, and m = higher-order streams]

Stream class1/	Number of samples	Minimum value	Value at indicated percentile							Maximum value
			10	25	50	75	90	95	98	
MAJOR ELEMENTS, IN UNITS OF GRAMS PER 100 GRAMS (PERCENT)										
Aluminum										
los	332	2.7	6.7	7.3	7.9	8.4	8.8	9.4	10.0	13.0
totm	19	6.6	6.7	7.0	7.6	7.9	8.8	9.0	9.0	9.0
tmna	11	4.3	4.5	6.0	7.2	7.6	8.2	8.4	8.4	8.4
tma	19	6.2	6.3	6.5	6.8	7.1	7.5	7.5	7.5	7.5
m	16	5.9	6.4	6.6	6.8	7.0	7.3	7.5	7.5	7.5
ss	4	7.4	7.4	7.4	7.6	8.0	8.2	8.2	8.2	8.2
ud	6	6.5	6.5	6.6	7.6	8.2	8.5	8.5	8.5	8.5
Calcium										
los	332	.6	1.7	2.2	2.7	3.1	3.4	3.8	4.1	4.9
totm	19	.9	1.6	1.9	2.4	2.6	3.4	3.4	3.4	3.4
tmna	11	1.3	1.4	2.0	2.5	2.8	3.5	3.6	3.6	3.6
tma	19	2.2	2.4	2.5	2.8	3.1	3.2	4.4	4.4	4.4
ms	16	1.7	1.8	2.1	2.5	2.6	2.7	2.8	2.8	2.8
ss	4	2.1	2.1	2.1	2.3	2.5	2.6	2.6	2.6	2.6
ud	6	2.4	2.4	2.5	2.9	2.9	3.1	3.1	3.1	3.1
Carbon, Inorganic										
los	332	<.01	<.01	.01	.02	.04	.08	.14	.19	.45
totm	19	<.01	<.01	.02	.03	.04	.08	.09	.09	.09
tmna	11	<.01	<.01	.02	.04	.05	.12	.14	.14	.14
tma	19	<.01	<.01	.02	.02	.10	.14	.62	.62	.62
m	16	<.01	<.01	.02	.03	.07	.14	.14	.14	.14
ss	4	<.01	<.01	<.01	.01	.03	.04	.04	.04	.04
ud	6	.01	.01	.02	.03	.11	.16	.16	.16	.16
Carbon, Total Organic										
los	332	.23	.57	.94	1.74	2.87	4.60	6.01	7.86	16.20
totm	19	.90	1.11	2.24	3.00	4.55	7.32	7.61	7.61	7.61
tmna	11	.88	.93	1.24	3.14	4.77	5.26	5.31	5.31	5.31
tma	19	.42	.48	.62	1.73	2.14	2.54	3.21	3.21	3.21
m	16	1.19	1.25	1.88	2.33	2.86	4.07	4.11	4.11	4.11
ss	4	.96	.96	1.05	1.47	1.97	2.09	2.09	2.09	2.09
ud	6	.44	.44	.79	1.91	2.54	3.10	3.10	3.10	3.10
Iron										
los	332	2.7	3.7	4.4	5.0	6.0	7.0	7.6	8.3	9.8
totm	19	3.6	4.6	4.8	5.4	5.7	6.3	6.8	6.8	6.8
tmna	11	4.7	4.7	4.9	5.2	5.5	7.1	7.4	7.4	7.4
tma	19	4.2	4.3	4.8	5.1	5.5	5.9	6.4	6.4	6.4
m	16	4.3	4.4	4.9	5.1	5.2	5.3	5.4	5.4	5.4
ss	4	3.9	3.9	3.9	3.9	4.4	4.5	4.5	4.5	4.5
ud	6	5.1	5.1	5.3	5.7	6.2	6.5	6.5	6.5	6.5
Magnesium										
los	332	.4	.8	1.0	1.1	1.4	1.6	2.1	8.3	13.0
totm	19	.8	.9	1.0	1.2	1.4	1.9	2.6	2.6	2.6
tmna	11	.8	.8	1.1	1.5	1.7	5.4	6.3	6.3	6.3
tma	19	1.2	1.2	1.3	1.4	1.5	1.7	2.1	2.1	2.1
m	16	1.2	1.2	1.4	1.4	1.5	1.8	2.1	2.1	2.1
ss	4	.8	.8	.9	.9	1.0	1.0	1.0	1.0	1.0
ud	6	1.2	1.2	1.3	1.4	1.4	1.5	1.5	1.5	1.5

Table 10.--Distributions of major- and minor-element concentrations in streambed sediment relative to site classifications, Yakima River Basin, Washington, 1987--Continued

Stream class1/	Number of samples	Minimum value	Value at indicated percentile							Maximum value
			10	25	50	75	90	95	98	
MAJOR ELEMENTS, IN UNITS OF GRAMS PER 100 GRAMS (PERCENT)										
Phosphorous										
los	332	0.02	0.07	0.08	0.10	0.11	0.14	0.15	0.17	0.27
totm	19	.08	.08	.10	.12	.13	.16	.19	.19	.19
tmna	11	.07	.07	.10	.11	.11	.14	.14	.14	.14
tma	19	.05	.06	.08	.10	.11	.13	.14	.14	.14
m	16	.09	.10	.10	.12	.15	.16	.16	.16	.16
ss	4	.07	.07	.07	.08	.13	.14	.14	.14	.14
ud	6	.11	.11	.11	.12	.19	.21	.21	.21	.21
Potassium										
los	332	.13	.73	.89	1.10	1.30	1.50	1.60	1.80	2.20
totm	19	.67	.70	.81	1.00	1.10	1.20	1.30	1.30	1.30
tmna	11	.56	.58	.74	.90	1.00	1.24	1.30	1.30	1.30
tma	19	.92	.94	1.00	1.10	1.40	1.50	1.50	1.50	1.50
m	16	.88	.90	1.02	1.20	1.30	1.40	1.40	1.40	1.40
ss	4	1.20	1.20	1.22	1.30	1.37	1.40	1.40	1.40	1.40
ud	6	.99	.99	1.00	1.15	1.45	1.60	1.60	1.60	1.60
Sodium										
los	332	.4	1.5	1.7	1.9	2.1	2.3	2.6	3.0	3.8
totm	19	.8	1.1	1.3	1.5	1.7	2.1	2.3	2.3	2.3
tmna	11	1.0	1.0	1.3	1.5	1.7	1.9	2.0	2.0	2.0
tma	19	1.5	1.5	1.6	1.7	1.8	2.0	2.0	2.0	2.0
m	16	1.2	1.3	1.4	1.5	1.6	1.7	1.7	1.7	1.7
ss	4	1.8	1.8	1.8	1.9	2.1	2.1	2.1	2.1	2.1
ud	6	1.5	1.5	1.6	1.7	1.7	1.9	1.9	1.9	1.9
Sulfur										
los	332	<.01	<.01	.01	.02	.02	.04	.06	.08	.36
totm	19	<.01	<.01	<.01	.03	.05	.08	.08	.08	.08
tmna	11	<.01	<.01	.02	.02	.07	.11	.12	.12	.12
tma	19	<.01	<.01	.02	.02	.04	.06	.09	.09	.09
m	16	.02	.02	.02	.04	.04	.05	.05	.05	.05
ss	4	<.01	<.01	<.01	<.01	.02	.02	.02	.02	.02
ud	6	.01	.01	.02	.03	.08	.12	.12	.12	.12
Titanium										
los	332	.14	.44	.60	.72	.89	1.10	1.30	1.43	1.80
totm	19	.46	.46	.57	.66	.74	.87	1.10	1.10	1.10
tmna	11	.26	.31	.54	.66	.74	1.03	1.10	1.10	1.10
tma	19	.51	.58	.63	.73	.84	1.00	1.10	1.10	1.10
m	16	.50	.56	.60	.66	.70	.73	.74	.74	.74
ss	4	.50	.50	.50	.55	.61	.62	.62	.62	.62
ud	6	.67	.67	.69	.71	.90	1.10	1.10	1.10	1.10
MINOR ELEMENTS, IN UNITS OF MICROGRAMS PER GRAM										
Antimony										
los	330	<.1	.2	.2	.4	.5	.7	1.1	1.9	4.8
totm	18	.2	.3	.4	.5	.8	1.1	1.3	1.3	1.3
tmna	11	.2	.2	.2	.4	.5	2.3	2.8	2.8	2.8
tma	19	.2	.3	.3	.4	.5	.7	1.4	1.4	1.4
m	16	.2	.3	.4	.5	.5	.6	.6	.6	.6
ss	4	.4	.4	.6	1.5	2.6	2.9	2.9	2.9	2.9
ud	6	.4	.4	.4	.9	1.1	1.3	1.3	1.3	1.3

Table 10.--Distributions of major- and minor-element concentrations in streambed sediment relative to site classifications, Yakima River Basin, Washington, 1987--Continued

Stream class1/	Number of samples	Minimum value	Value at indicated percentile							Maximum value
			10	25	50	75	90	95	98	
			MINOR ELEMENTS, IN UNITS OF MICROGRAMS PER GRAM							
			Arsenic							
los	330	0.7	1.5	2.2	3.7	5.9	11.0	23.4	57.3	310.0
totm	18	1.8	1.9	4.3	5.5	9.7	30.3	33.0	33.0	33.0
tmna	11	1.0	1.1	1.9	3.9	4.5	57.9	71.0	71.0	71.0
tma	19	2.0	2.2	2.6	3.7	5.1	6.4	7.4	7.4	7.4
m	16	2.8	3.4	3.8	4.8	5.7	6.8	7.9	7.9	7.9
ss	4	6.7	6.7	19.3	69.5	125.5	140.0	140.0	140.0	140.0
ud	6	2.5	2.5	3.6	4.4	7.9	17.0	17.0	17.0	17.0
			Barium							
los	332	55	360	440	510	570	620	700	793	930
totm	19	310	350	400	440	490	540	610	610	610
tmna	11	320	328	370	430	450	568	580	580	580
tma	19	400	420	460	500	530	560	560	560	560
m	16	440	447	472	505	530	533	540	540	540
ss	4	460	460	470	510	528	530	530	530	530
ud	6	400	400	490	545	708	1,000	1,000	1,000	1,000
			Beryllium							
los	332	<1	1	1	1	2	2	2	2	4
totm	19	1	1	1	1	1	2	2	2	2
tmna	11	<1	<1	1	1	1	2	2	2	2
tma	19	1	1	1	2	2	2	2	2	2
m	16	1	1	1	2	2	2	2	2	2
ss	4	1	1	1	2	2	2	2	2	2
ud	6	1	1	2	2	2	2	2	2	2
			Bismuth							
los	332	<10	<10	<10	<10	<10	<10	<10	<10	10
totm	19	<10	<10	<10	<10	<10	<10	<10	<10	<10
tmna	11	<10	<10	<10	<10	<10	<10	<10	<10	<10
tma	19	<10	<10	<10	<10	<10	<10	<10	<10	<10
m	16	<10	<10	<10	<10	<10	<10	<10	<10	<10
ss	4	<10	<10	<10	<10	<10	<10	<10	<10	<10
ud	6	<10	<10	<10	<10	<10	<10	<10	<10	<10
			Boron							
los	317	<.5	<.5	.5	.7	1.2	2.1	2.6	4.0	8.3
totm	16	<.5	.5	.6	.8	2.0	2.8	4.1	4.1	4.1
tmna	10	<.5	<.5	<.5	.6	1.4	3.1	3.3	3.3	3.3
tma	19	<.5	<.5	.5	.8	1.5	3.4	4.0	4.0	4.0
m	16	.5	.5	.6	1.1	1.7	3.4	4.0	4.0	4.0
ss	3	.7	.7	.7	.8	2.3	2.3	2.3	2.3	2.3
ud	6	<.5	<.5	<.5	.5	1.0	1.8	1.8	1.8	1.8
			Cadmium							
los	332	<2	<2	<2	<2	<2	<2	<2	<2	<2
totm	19	<2	<2	<2	<2	<2	<2	<2	<2	<2
tmna	11	<2	<2	<2	<2	<2	<2	<2	<2	<2
tma	19	<2	<2	<2	<2	<2	<2	<2	<2	<2
m	16	<2	<2	<2	<2	<2	<2	<2	<2	<2
ss	4	<2	<2	<2	<2	<2	<2	<2	<2	<2
ud	6	<2	<2	<2	<2	<2	2	2	2	2

Table 10.--Distributions of major- and minor-element concentrations in streambed sediment relative to site classifications, Yakima River Basin, Washington, 1987--Continued

Stream class1/	Number of samples	Minimum value	Value at indicated percentile 10	25	50	75	90	95	98	Maximum value
MINOR ELEMENTS, IN MICROGRAMS PER GRAM										
Cerium										
los	332	5	33	39	46	57	69	84	103	120
totm	19	30	36	38	42	47	49	50	50	50
tmna	11	28	28	33	38	46	54	56	56	56
tma	19	35	38	41	47	82	94	110	110	110
m	16	33	35	41	52	56	57	57	57	57
ss	4	42	42	42	46	52	53	53	53	53
ud	6	38	38	47	52	72	85	85	85	85
Chromium										
los	332	14	31	42	52	71	110	174	837	1,800
totm	19	39	42	44	64	100	120	210	210	210
tmna	11	32	34	44	67	130	508	600	600	600
tma	19	52	54	55	64	69	84	160	160	160
m	16	57	60	62	64	90	175	210	210	210
ss	4	48	48	50	56	62	63	63	63	63
ud	6	41	41	47	74	86	110	110	110	110
Cobalt										
los	332	10	14	16	20	24	31	35	74	140
totm	19	15	17	18	22	24	27	33	33	33
tmna	11	17	17	19	22	26	54	59	59	59
tma	19	16	17	19	21	22	23	26	26	26
m	16	17	18	19	20	20	26	28	28	28
ss	4	14	14	14	16	16	16	16	16	16
ud	6	19	19	20	24	26	27	27	27	27
Copper										
los	332	13	20	23	27	33	44	66	98	190
totm	19	24	27	30	39	43	59	60	60	60
tmna	11	22	22	26	32	43	43	43	43	43
tma	19	15	17	22	25	33	41	46	46	46
m	16	25	26	27	29	36	43	43	43	43
ss	4	25	25	26	32	34	34	34	34	34
ud	6	21	21	28	56	66	67	67	67	67
Europium										
los	332	<2	<2	<2	<2	<2	2	2	3	4
totm	19	<2	<2	<2	<2	<2	<2	<2	<2	<2
tmna	11	<2	<2	<2	<2	<2	<2	<2	<2	<2
tma	19	<2	<2	<2	<2	<2	2	2	2	2
m	16	<2	<2	<2	<2	<2	<2	<2	<2	<2
ss	4	<2	<2	<2	<2	<2	<2	<2	<2	<2
ud	6	<2	<2	<2	<2	<2	2	2	2	2
Gallium										
los	332	<4	17	18	19	21	23	25	26	35
totm	19	15	17	17	19	21	22	22	22	22
tmna	11	12	12	14	18	20	21	21	21	21
tma	19	15	15	16	18	18	19	19	19	19
m	16	10	14	17	18	19	19	19	19	19
ss	4	18	18	18	18	20	21	21	21	21
ud	6	17	17	18	20	22	23	23	23	23

Table 10.--Distributions of major- and minor-element concentrations in streambed sediment relative to site classifications, Yakima River Basin, Washington, 1987--Continued

Stream class1/	Number of samples	Minimum value	Value at indicated percentile							Maximum value
			10	25	50	75	90	95	98	
MINOR ELEMENTS, IN UNITS OF MICROGRAMS PER GRAM										
Gold										
los	332	<8	<8	<8	<8	<8	<8	<8	<8	<8
totm	19	<8	<8	<8	<8	<8	<8	<8	<8	<8
tmna	11	<8	<8	<8	<8	<8	<8	<8	<8	<8
tma	19	<8	<8	<8	<8	<8	<8	<8	<8	<8
m	16	<8	<8	<8	<8	<8	<8	<8	<8	<8
ss	4	<8	<8	<8	<8	<8	<8	<8	<8	<8
ud	6	<8	<8	<8	<8	<8	<8	<8	<8	<8
Lanthanum										
los	332	3	18	22	25	31	37	44	53	62
totm	19	16	19	21	23	25	26	27	27	27
tmna	11	16	16	18	22	24	30	31	31	31
tma	19	19	21	23	25	42	51	58	58	58
m	16	18	19	23	28	29	30	31	31	31
ss	4	22	22	23	26	29	30	30	30	30
ud	6	22	22	24	29	37	45	45	45	45
Lead										
los	332	<4	9	11	13	17	23	35	58	510
totm	19	8	9	10	13	16	27	44	44	44
tmna	11	7	7	8	13	13	24	26	26	26
tma	19	11	11	12	14	20	40	42	42	42
m	16	<4	7	12	16	20	21	21	21	21
ss	4	22	22	104	420	790	890	890	890	890
ud	6	12	12	20	71	135	150	150	150	150
Lithium										
los	332	12	18	20	23	28	39	43	57	110
totm	19	18	21	24	28	34	38	39	39	39
tmna	11	13	14	19	23	31	32	32	32	32
tma	19	19	19	20	21	22	23	25	25	25
m	16	20	21	23	24	25	26	26	26	26
ss	4	20	20	21	24	26	26	26	26	26
ud	6	19	19	21	23	26	27	27	27	27
Manganese										
los	332	420	640	760	930	1,100	1,400	1,500	1,868	2,900
totm	19	660	840	1,000	1,100	1,500	1,600	2,000	2,000	2,000
tmna	11	550	588	780	820	1,200	1,700	1,800	1,800	1,800
tma	19	660	710	770	960	1,100	1,700	1,800	1,800	1,800
m	16	700	756	820	1,250	1,600	1,790	2,000	2,000	2,000
ss	4	710	710	715	730	730	730	730	730	730
ud	6	660	660	742	845	932	1,000	1,000	1,000	1,000
Mercury										
los	331	<.02	<.02	<.02	<.02	.04	.12	.16	.51	3.10
totm	19	.04	.04	.10	.16	.26	.34	.54	.54	.54
tmna	11	.02	.02	.04	.08	.18	.23	.24	.24	.24
tma	19	<.02	<.02	.02	.04	.14	.28	.30	.30	.30
m	16	.04	.04	.06	.08	.14	.22	.26	.26	.26
ss	4	<.02	<.02	<.02	<.02	.08	.10	.10	.10	.10
ud	6	<.02	<.02	<.02	.18	.21	.24	.24	.24	.24

Table 10.--Distributions of major- and minor-element concentrations in streambed sediment relative to site classifications, Yakima River Basin, Washington, 1987--Continued

Stream class1/	Number of samples	Minimum value	Value at indicated percentile							Maximum value
			10	25	50	75	90	95	98	
MINOR ELEMENTS, IN UNITS OF MICROGRAMS PER GRAM										
Molybdenum										
los	332	<2	<2	<2	<2	<2	<2	<2	2	8
totm	19	<2	<2	<2	<2	<2	2	4	4	4
tmna	11	<2	<2	<2	<2	<2	<2	<2	<2	<2
tma	19	<2	<2	<2	<2	<2	<2	2	2	2
m	16	<2	<2	<2	<2	<2	<2	<2	<2	<2
ss	4	<2	<2	<2	<2	<2	<2	<2	<2	<2
ud	6	<2	<2	<2	<2	<2	<2	<2	<2	<2
Neodymium										
los	332	<4	19	22	26	32	38	46	51	66
totm	19	18	21	22	24	26	28	28	28	28
tmna	11	17	17	20	23	24	29	29	29	29
tma	19	22	22	23	25	41	45	60	60	60
m	16	19	20	23	27	30	30	31	31	31
ss	4	23	23	24	26	28	28	28	28	28
ud	6	23	23	26	28	39	44	44	44	44
Nickel										
los	332	4	13	16	20	30	48	91	1,076	1,900
totm	19	15	16	18	26	43	54	340	340	340
tmna	11	13	13	14	28	68	622	760	760	760
tma	19	18	19	21	25	33	43	83	83	83
m	16	27	28	30	32	47	129	150	150	150
ss	4	18	18	19	23	24	24	24	24	24
ud	6	21	21	22	24	58	65	65	65	65
Niobium										
los	332	<4	<4	6	8	11	13	14	21	35
totm	19	<4	<4	<4	6	9	14	17	17	17
tmna	11	<4	<4	<4	6	9	11	11	11	11
tma	19	<4	<4	<4	<4	8	13	14	14	14
m	16	<4	<4	<4	6	9	10	11	11	11
ss	4	<4	<4	<4	8	10	10	10	10	10
ud	6	4	4	7	10	11	13	13	13	13
Scandium										
los	332	7	13	15	17	22	25	28	30	40
totm	19	13	13	18	19	23	26	27	27	27
tmna	11	14	14	17	20	22	26	27	27	27
tma	19	14	15	18	19	21	22	22	22	22
m	16	14	16	18	18	19	20	21	21	21
ss	4	14	14	14	14	15	15	15	15	15
ud	6	18	18	18	19	21	23	23	23	23
Selenium										
los	62	<.1	<.1	.2	.5	.7	1.1	1.3	1.4	1.4
totm	9	.1	.1	.4	.5	1.0	1.2	1.2	1.2	1.2
tmna	5	<.1	<.1	<.1	.1	.4	.4	.4	.4	.4
tma	8	<.1	<.1	<.1	.2	.4	.5	.5	.5	.5
m	7	.3	.3	.4	.5	.5	.6	.6	.6	.6
ss	3	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1
ud	5	.1	.1	.1	.2	.3	.4	.4	.4	.4

Table 10.--Distributions of major- and minor-element concentrations in streambed sediment relative to site classifications, Yakima River Basin, Washington, 1987--Continued

Stream class1/	Number of samples	Minimum value	Value at indicated percentile 10	25	50	75	90	95	98	Maximum value
MINOR ELEMENTS, IN MICROGRAMS PER GRAM										
Silver										
los	332	<4	<4	<4	<4	<4	<4	<4	<4	<4
totm	19	<4	<4	<4	<4	<4	<4	<4	<4	<4
tmna	11	<4	<4	<4	<4	<4	<4	<4	<4	<4
tma	19	<4	<4	<4	<4	<4	<4	<4	<4	<4
m	16	<4	<4	<4	<4	<4	<4	<4	<4	<4
ss	4	<4	<4	<4	<4	<4	<4	<4	<4	<4
ud	6	<4	<4	<4	<4	<4	<4	<4	<4	<4
Strontium										
los	332	48	220	280	310	340	377	410	437	620
totm	19	150	190	220	250	280	380	380	380	380
tmna	11	170	172	210	250	270	300	300	300	300
tma	19	240	250	270	290	310	330	350	350	350
m	16	210	210	232	250	268	280	280	280	280
ss	4	290	290	298	325	338	340	340	340	340
ud	6	230	230	260	300	328	350	350	350	350
Thorium										
los	332	2	2	5	6	8	10	12	15	19
totm	19	2	2	2	4	6	7	7	7	7
tmna	11	2	2	2	4	6	7	7	7	7
tma	19	4	4	5	7	11	15	20	20	20
m	16	2	2	4	6	8	8	8	8	8
ss	4	5	5	5	6	7	7	7	7	7
ud	6	5	5	6	6	9	14	14	14	14
Tin										
los	332	<10	<10	<10	<10	<10	<10	<10	<10	40
totm	19	<10	<10	<10	<10	<10	<10	<10	<10	<10
tmna	11	<10	<10	<10	<10	<10	<10	<10	<10	<10
tma	19	<10	<10	<10	<10	<10	<10	<10	<10	<10
m	16	<10	<10	<10	<10	<10	<10	<10	<10	<10
ss	4	<10	<10	<10	<10	<10	<10	<10	<10	<10
ud	6	<10	<10	<10	<10	18	40	40	40	40
Uranium										
los	332	.10	.55	.70	.90	1.30	1.90	2.57	7.01	74.00
totm	19	.40	.60	.70	.90	1.50	3.10	3.90	3.90	3.90
tmna	11	.55	.58	.75	.90	1.10	1.34	1.40	1.40	1.40
tma	19	.55	.60	.80	1.20	1.50	2.00	2.40	2.40	2.40
m	16	.50	.60	.92	1.10	1.50	1.70	1.70	1.70	1.70
ss	4	.75	.75	.81	1.05	1.10	1.10	1.10	1.10	1.10
ud	6	.75	.75	.79	1.20	1.80	2.70	2.70	2.70	2.70
Vanadium										
los	332	62	93	110	140	180	220	250	277	330
totm	19	100	110	130	140	170	180	220	220	220
tmna	11	84	91	130	150	170	240	250	250	250
tma	19	130	130	140	150	190	210	210	210	210
m	16	110	117	132	140	150	173	180	180	180
ss	4	99	99	99	105	118	120	120	120	120
ud	6	120	120	142	155	182	220	220	220	220

Table 10.--Distributions of major- and minor-element concentrations in streambed sediment relative to site classifications, Yakima River Basin, Washington, 1987--Continued

Stream class[1]	Number of samples	Minimum value	Value at indicated percentile 10	25	50	75	90	95	98	Maximum value
MINOR ELEMENTS, IN UNITS OF MICROGRAMS PER GRAM										
Ytterbium										
los	332	<1	2	2	3	3	4	4	5	6
totm	19	2	2	2	3	3	4	4	4	4
tmna	11	1	1	2	3	3	3	3	3	3
tma	19	2	2	3	3	3	3	4	4	4
m	16	2	2	3	3	3	3	3	3	3
ss	4	2	2	2	2	3	3	3	3	3
ud	6	3	3	3	3	3	4	4	4	4
Yttrium										
los	332	6	16	19	22	25	31	37	48	61
totm	19	16	17	22	24	26	31	35	35	35
tmna	11	13	14	20	21	25	27	27	27	27
tma	19	19	19	21	23	24	25	29	29	29
m	16	19	20	21	23	23	24	24	24	24
ss	4	17	17	17	18	20	20	20	20	20
ud	6	22	22	23	24	28	30	30	30	30
Zinc										
los	332	32	70	79	91	110	130	150	187	710
totm	19	74	78	86	97	110	140	170	170	170
tmna	11	67	69	78	88	100	214	240	240	240
tma	19	77	78	82	97	110	120	200	200	200
m	16	89	90	93	98	108	113	120	120	120
ss	4	73	73	85	135	150	150	150	150	150
ud	6	82	82	96	205	272	310	310	310	310

[1] Distributions of element concentrations for low-order streams represent 332 sites, 270 were randomly sampled and the remainder were intentionally sampled for quality assurance measures described in the "Variability of major- and minor-element concentrations attributable to analytical methods and field-collection techniques" section of this report.

Table 11.--Distributions of major- and minor-element concentrations in streambed sediment of randomly sampled lower-order streams, relative to geologic units,Yakima River Basin, Washington, 1987

[Qdl = Quarternary deposits and loess;
Qfd = Quarternary flood deposits;
QPlv = Quarternary and Pliocene volcanic rocks;
crb = Columbia River Basalt group rocks;
Mov = Miocene and older volcanic rocks;
Tgii = Tertiary granitic and intermediate intrusive rocks;
nms = nonmarine sedimentary rocks;
ms = marine sedimentary rocks;
pTmi = pre-Tertiary metamorphic and intrusive rocks;
All major element values are reported in units percent;
All minor element values are reported in microgram per gram;
< = less than; -- = no data available;
Percentile summaries in this table represent data from
270 randomly sampled lower-order streams]

Simple geology	Number of samples	Minimum value	Value at indicated percentile							Maximum value
			10	25	50	75	90	95	98	
MAJOR ELEMENTS, IN UNITS OF GRAMS PER 100 GRAMS (PERCENT)										
Aluminum										
Qdl	47	6.6	6.9	7.2	7.6	7.9	8.0	8.2	8.3	8.3
Qfd	29	6.0	6.2	6.7	7.0	7.2	7.4	8.4	8.5	8.5
QPlv	11	8.1	8.1	8.3	8.6	9.2	9.9	10.0	10.0	10.0
crb	100	6.2	6.8	7.3	7.9	8.3	8.7	8.9	9.4	13.0
Mov	34	6.6	7.3	7.9	8.5	8.8	9.0	9.7	9.8	9.8
Tgii	3	7.3	7.3	7.3	8.2	8.5	8.5	8.5	8.5	8.5
nms	30	6.1	6.5	7.5	8.0	8.5	8.9	9.7	9.8	9.8
ms	6	7.4	7.4	7.6	7.9	8.3	8.3	8.3	8.3	8.3
pTmi	10	2.7	3.0	5.7	7.3	9.4	10.9	11.0	11.0	11.0
Calcium										
Qdl	47	1.5	1.9	2.3	2.7	3.1	3.3	3.4	3.8	3.8
Qfd	29	2.1	2.2	2.6	2.9	3.2	3.8	4.0	4.1	4.1
QPlv	11	1.3	1.3	1.7	2.1	2.6	2.9	3.0	3.0	3.0
crb	100	1.9	2.3	2.5	3.0	3.3	3.7	3.9	4.5	4.6
Mov	34	1.0	1.4	2.2	2.7	3.1	3.5	4.2	4.3	4.3
Tgii	3	2.2	2.2	2.2	2.7	3.0	3.0	3.0	3.0	3.0
nms	30	1.0	1.3	1.7	2.2	2.7	3.0	3.3	3.6	3.6
ms	6	1.9	1.9	2.3	3.2	3.3	3.4	3.4	3.4	3.4
pTmi	10	.6	.6	1.2	1.9	2.5	4.7	4.9	4.9	4.9
Carbon, Inorganic										
Qdl	47	<.01	<.01	.01	.02	.04	.11	.18	.24	.24
Qfd	29	<.01	.01	.02	.04	.13	.29	.41	.45	.45
QPlv	11	<.01	<.01	.01	.03	.03	.04	.04	.04	.04
crb	100	<.01	<.01	.01	.02	.02	.06	.08	.13	.20
Mov	34	<.01	.01	.02	.03	.04	.06	.07	.09	.09
Tgii	3	.01	.01	.01	.02	.04	.04	.04	.04	.04
nms	30	<.01	<.01	.01	.02	.04	.09	.12	.14	.14
ms	6	.02	.02	.03	.03	.05	.05	.05	.05	.05
pTmi	10	<.01	<.01	.02	.03	.03	.08	.09	.09	.09
Carbon, Total Organic										
Qdl	47	.38	.57	.94	1.51	2.56	4.62	6.19	7.55	7.55
Qfd	29	.32	.36	.60	.77	1.07	1.39	1.98	2.22	2.22
QPlv	11	1.12	1.12	1.56	2.44	3.75	4.41	4.42	4.42	4.42
crb	100	.23	.45	.67	1.27	2.05	3.07	4.08	6.06	6.43
Mov	34	.59	.93	2.02	2.89	4.11	5.32	5.67	5.75	5.75
Tgii	3	.29	.29	.29	2.01	3.99	3.99	3.99	3.99	3.99
nms	30	.55	.79	1.13	1.98	3.70	7.79	10.43	12.90	12.90
ms	6	.91	.91	1.08	4.12	6.80	7.93	7.93	7.93	7.93
pTmi	10	1.26	1.28	1.56	2.48	3.12	6.13	6.39	6.39	6.39

Table 11.--Distributions of major- and minor-element concentrations in streambed sediment of first- and second-order streams, relative to geologic units, Yakima River Basin, Washington, 1987--Continued

Simple geology	Number of samples	Minimum value	Value at indicated percentile							Maximum value
			10	25	50	75	90	95	98	
MAJOR ELEMENTS, IN UNITS OF GRAMS PER 100 GRAMS (PERCENT)										
Iron										
Qdl	47	2.9	3.9	4.3	4.9	5.1	5.6	5.8	7.4	7.4
Qfd	29	3.2	4.6	4.8	5.2	5.6	6.6	6.9	7.2	7.2
QPlv	11	4.7	4.7	5.0	5.7	6.8	9.3	9.8	9.8	9.8
crb	100	3.4	4.3	4.7	5.5	6.5	7.3	8.0	8.9	9.0
Mov	34	3.5	3.7	4.2	4.9	6.0	7.0	7.8	7.9	7.9
Tgii	3	3.5	3.5	3.5	4.2	5.7	5.7	5.7	5.7	5.7
nms	30	2.7	2.9	3.5	4.1	4.4	6.1	7.2	8.3	8.3
ms	6	3.4	3.4	3.6	3.8	5.3	6.0	6.0	6.0	6.0
pTmi	10	4.4	4.4	4.7	5.8	6.8	7.9	7.9	7.9	7.9
Magnesium										
Qdl	47	.7	.7	.9	1.1	1.3	1.5	1.6	1.7	1.7
Qfd	29	1.1	1.2	1.3	1.4	1.5	1.6	1.9	1.9	1.9
QPlv	11	.5	.6	.8	.8	1.1	1.1	1.1	1.1	1.1
crb	100	.7	1.0	1.0	1.1	1.3	1.5	1.6	1.7	2.2
Mov	34	.4	.8	.9	1.1	1.4	1.7	2.3	3.4	3.4
Tgii	3	.9	.9	.9	1.0	1.1	1.1	1.1	1.1	1.1
nms	30	.6	.7	.7	.9	1.1	1.4	1.8	2.1	2.1
ms	6	.9	.9	1.1	1.2	1.9	2.6	2.6	2.6	2.6
pTmi	10	.8	.8	1.4	2.5	8.2	12.6	13.0	13.0	13.0
Phosphorus										
Qdl	47	.05	.06	.08	.10	.11	.13	.15	.15	.15
Qfd	29	.06	.08	.10	.11	.13	.15	.16	.17	.17
QPlv	11	.03	.04	.09	.11	.14	.19	.20	.20	.20
crb	100	.04	.07	.08	.09	.11	.13	.16	.17	.17
Mov	34	.05	.07	.09	.10	.11	.14	.19	.27	.27
Tgii	3	.07	.07	.07	.08	.12	.12	.12	.12	.12
nms	30	.04	.05	.08	.09	.10	.11	.13	.14	.14
ms	6	.06	.06	.07	.08	.10	.11	.11	.11	.11
pTmi	10	.02	.02	.05	.08	.12	.19	.19	.19	.19
Potassium										
Qdl	47	.72	.89	.97	1.10	1.30	1.42	1.50	1.50	1.50
Qfd	29	1.20	1.30	1.35	1.50	1.60	1.80	1.80	1.80	1.80
QPlv	11	.61	.63	.73	1.00	1.10	1.36	1.40	1.40	1.40
crb	100	.52	.74	.81	1.00	1.30	1.50	1.60	1.70	1.70
Mov	34	.48	.67	.79	.94	1.10	1.20	1.40	1.40	1.40
Tgii	3	.90	.90	.90	1.10	1.50	1.50	1.50	1.50	1.50
nms	30	.65	.81	.93	1.10	1.30	1.49	1.69	1.80	1.80
ms	6	.95	.95	.96	1.05	1.12	1.20	1.20	1.20	1.20
pTmi	10	.13	.15	.46	1.05	1.52	2.17	2.20	2.20	2.20
Sodium										
Qdl	47	.9	1.6	1.7	1.9	2.0	2.2	2.4	2.7	2.7
Qfd	29	1.5	1.5	1.6	1.7	1.9	2.0	2.8	3.3	3.3
QPlv	11	1.0	1.1	1.6	1.8	2.1	2.2	2.2	2.2	2.2
crb	100	1.0	1.6	1.8	2.0	2.1	2.4	2.7	3.1	3.8
Mov	34	.5	1.2	1.5	1.9	2.1	2.4	3.0	3.1	3.1
Tgii	3	1.9	1.9	1.9	2.0	2.5	2.5	2.5	2.5	2.5
nms	30	1.7	1.7	1.7	2.0	2.2	2.4	2.5	2.6	2.6
ms	6	1.5	1.5	2.0	2.3	2.7	2.8	2.8	2.8	2.8
pTmi	10	.3	.4	1.2	1.6	1.8	2.0	2.0	2.0	2.0

Table 11.--Distributions of major- and minor-element concentrations in streambed sediment of first- and second-order streams, relative to geologic units, Yakima River Basin, Washington, 1987--Continued

Simple geology	Number of samples	Minimum value	Value at indicated percentile 10	25	50	75	90	95	98	Maximum value
MAJOR ELEMENTS, IN UNITS OF GRAMS PER 100 GRAMS (PERCENT)										
Sulfur										
Qdl	47	<0.01	<0.01	0.02	0.02	0.04	0.07	0.10	0.14	0.14
Qfd	29	<.01	<.01	.01	.02	.02	.05	.06	.07	.07
QPlv	11	<.01	<.01	.01	.01	.02	.02	.02	.02	.02
crb	100	<.01	<.01	<.01	.02	.02	.03	.05	.06	.36
Mov	34	<.01	<.01	.01	.02	.02	.03	.04	.04	.04
Tgii	3	<.01	<.01	<.01	.03	.05	.05	.05	.05	.05
nms	30	<.01	<.01	.01	.02	.03	.04	.06	.07	.07
ms	6	.01	.01	.02	.03	.06	.08	.08	.08	.08
pTmi	10	<.01	<.01	.02	.02	.03	.12	.13	.13	.13
Titanium										
Qdl	47	.39	.57	.61	.68	.77	.91	1.06	1.10	1.10
Qfd	29	.42	.64	.68	.78	.87	1.20	1.30	1.40	1.40
QPlv	11	.92	.94	1.10	1.20	1.40	1.74	1.80	1.80	1.80
crb	100	.46	.62	.72	.85	.98	1.30	1.40	1.60	1.60
Mov	34	.42	.52	.62	.70	.79	.98	1.10	1.10	1.10
Tgii	3	.48	.48	.48	.55	.81	.81	.81	.81	.81
nms	30	.32	.40	.44	.54	.66	.86	1.20	1.60	1.60
ms	6	.45	.45	.46	.55	.90	.93	.93	.93	.93
pTmi	10	.18	.19	.34	.49	.58	.64	.64	.64	.64
MINOR ELEMENTS, IN UNITS OF MICROGRAMS PER GRAM										
Antimony										
Qdl	47	.1	.2	.3	.4	.4	.5	.6	2.8	2.8
Qfd	29	.2	.3	.4	.5	.6	.6	.8	.8	.8
QPlv	11	.1	.1	.1	.2	.2	.3	.3	.3	.3
crb	100	<.1	.1	.2	.3	.4	.5	.5	.6	.6
Mov	34	.1	.2	.2	.4	.5	1.1	1.8	3.0	3.0
Tgii	3	.4	.4	.4	.5	1.6	1.6	1.6	1.6	1.6
nms	30	.2	.2	.3	.5	.8	1.2	2.1	2.3	2.3
ms	6	.3	.3	.3	.5	.8	1.3	1.3	1.3	1.3
pTmi	10	.2	.2	.3	.5	1.1	4.5	4.8	4.8	4.8
Arsenic										
Qdl	47	1.3	1.8	2.5	3.4	5.3	7.3	10.3	26.0	26.0
Qfd	29	2.4	3.3	4.1	5.1	6.5	8.2	8.9	9.0	9.0
QPlv	11	.8	.8	1.1	1.5	1.7	3.0	3.1	3.1	3.1
crb	100	.7	1.3	1.6	2.5	3.9	4.6	6.6	10.0	11.0
Mov	34	1.4	1.7	2.1	3.4	6.7	18.0	114.3	310.0	310.0
Tgii	3	2.1	2.1	2.1	4.3	55.0	55.0	55.0	55.0	55.0
nms	30	1.8	2.0	2.7	5.2	10.2	23.8	53.9	61.0	61.0
ms	6	2.1	2.1	2.6	3.8	42.3	130.0	130.0	130.0	130.0
pTmi	10	1.0	1.2	4.2	6.2	24.3	30.7	31.0	31.0	31.0
Barium										
Qdl	47	400	420	470	520	560	592	606	630	630
Qfd	29	350	500	555	580	600	630	690	700	700
QPlv	11	380	386	410	470	520	538	540	540	540
crb	100	320	440	470	500	550	590	610	610	900
Mov	34	200	305	360	420	480	615	758	930	930
Tgii	3	360	360	360	450	580	580	580	580	580
nms	30	330	354	455	560	643	757	804	820	820
ms	6	280	280	310	360	433	440	440	440	440
pTmi	10	55	65	188	465	645	795	800	800	800

Table 11.--Distributions of major- and minor-element concentrations in streambed sediment of first- and second-order streams, relative to geologic units, Yakima River Basin, Washington, 1987--Continued

Simple geology	Number of samples	Minimum value	Value at indicated percentile 10	25	50	75	90	95	98	Maximum value
MINOR ELEMENTS, IN UNITS OF MICROGRAMS PER GRAM										
Beryllium										
Qdl	47	<1	1	1	1	2	2	2	2	2
Qfd	29	1	1	2	2	2	2	2	2	2
QPlv	11	2	2	2	2	2	3	4	4	4
crb	100	1	1	1	2	2	2	2	2	2
Mov	34	<1	1	1	1	2	2	2	2	2
Tgii	3	1	1	1	1	2	2	2	2	2
nms	30	1	1	1	1	2	2	2	2	2
ms	6	1	1	1	1	1	1	1	1	1
pTmi	10	<1	<1	1	1	2	2	2	2	2
Bismuth										
Qdl	47	<10	<10	<10	<10	<10	<10	<10	<10	<10
Qfd	29	<10	<10	<10	<10	<10	<10	<10	<10	<10
QPlv	11	<10	<10	<10	<10	<10	<10	10	10	10
crb	100	<10	<10	<10	<10	<10	<10	<10	<10	<10
Mov	34	<10	<10	<10	<10	<10	<10	<10	<10	<10
Tgii	3	<10	<10	<10	<10	<10	<10	<10	<10	<10
nms	30	<10	<10	<10	<10	<10	<10	<10	<10	<10
ms	6	<10	<10	<10	<10	<10	<10	<10	<10	<10
pTmi	10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Boron										
Qdl	46	<.5	<.5	.5	.8	1.1	1.5	1.9	2.2	2.2
Qfd	29	<.5	<.5	<.5	.6	.8	1.6	2.7	3.0	3.0
QPlv	11	<.5	<.5	<.5	<.5	1.1	2.2	2.3	2.3	2.3
crb	100	<.5	<.5	<.5	.6	1.0	1.5	2.1	3.8	4.3
Mov	30	<.5	<.5	<.5	1.3	1.9	2.3	3.0	3.3	3.3
Tgii	3	.5	.5	.5	.6	1.2	1.2	1.2	1.2	1.2
nms	27	<.5	<.5	.6	.9	2.1	2.8	4.2	4.6	4.6
ms	6	<.5	<.5	<.5	.8	2.6	3.1	3.1	3.1	3.1
pTmi	10	<.5	<.5	<.5	.7	1.2	2.0	2.1	2.1	2.1
Cadmium										
Qdl	47	<2	<2	<2	<2	<2	<2	<2	<2	<2
Qfd	29	<2	<2	<2	<2	<2	<2	<2	<2	<2
QPlv	11	<2	<2	<2	<2	<2	<2	<2	<2	<2
crb	100	<2	<2	<2	<2	<2	<2	<2	<2	<2
Mov	34	<2	<2	<2	<2	<2	<2	<2	<2	<2
Tgii	3	<2	<2	<2	<2	<2	<2	<2	<2	<2
nms	30	<2	<2	<2	<2	<2	<2	<2	<2	<2
ms	6	<2	<2	<2	<2	<2	<2	<2	<2	<2
pTmi	10	<2	<2	<2	<2	<2	<2	<2	<2	<2
Cerium										
Qdl	47	30	37	40	43	51	58	68	73	73
Qfd	29	29	50	60	68	78	110	110	110	110
QPlv	11	45	46	54	59	69	89	92	92	92
crb	100	27	36	40	46	59	73	96	110	120
Mov	34	26	31	37	42	47	52	57	57	57
Tgii	3	40	40	40	49	56	56	56	56	56
nms	30	27	31	40	46	54	63	86	100	100
ms	6	23	23	26	36	42	42	42	42	42
pTmi	10	5	6	17	30	46	68	69	69	69

Table 11.--Distributions of major- and minor-element concentrations in streambed sediment of first- and second-order streams, relative to geologic units, Yakima River Basin, Washington, 1987--Continued

Simple geology	Number of samples	Minimum value	Value at indicated percentile							Maximum value
			10	25	50	75	90	95	98	
MINOR ELEMENTS, IN UNITS OF MICROGRAMS PER GRAM										
Chromium										
Qdl	47	18	37	47	56	70	85	116	180	180
Qfd	29	20	43	48	52	55	72	83	91	91
QPlv	11	28	29	38	56	99	136	140	140	140
crb	100	26	31	40	48	54	63	68	75	100
Mov	34	14	25	29	40	71	135	205	310	310
Tgii	3	33	33	33	50	120	120	120	120	120
nms	30	23	37	48	79	91	109	169	240	240
ms	6	29	29	41	61	112	220	220	220	220
pTmi	10	94	95	122	150	1,250	1,670	1,700	1,700	1,700
Cobalt										
Qdl	47	12	15	17	19	22	24	30	35	35
Qfd	29	11	17	19	20	22	23	24	24	24
QPlv	11	19	19	20	23	30	43	46	46	46
crb	100	12	15	17	21	27	32	35	37	37
Mov	34	11	13	14	18	22	27	32	41	41
Tgii	3	12	12	12	15	22	22	22	22	22
nms	30	10	12	15	17	21	29	32	32	32
ms	6	12	12	12	18	24	36	36	36	36
pTmi	10	18	18	21	28	74	134	140	140	140
Copper										
Qdl	47	13	21	24	27	32	35	40	67	67
Qfd	29	17	18	20	23	26	32	49	66	66
QPlv	11	21	21	23	26	40	45	47	47	47
crb	100	16	19	22	26	30	34	38	45	47
Mov	34	15	21	25	30	38	54	65	89	89
Tgii	3	19	19	19	61	72	72	72	72	72
nms	30	17	20	23	27	31	36	39	39	39
ms	6	24	24	26	39	77	150	150	150	150
pTmi	10	13	14	37	47	65	108	110	110	110
Europium										
Qdl	47	<2	<2	<2	<2	<2	<2	<2	<2	<2
Qfd	29	<2	<2	<2	<2	<2	2	3	3	3
QPlv	11	<2	<2	2	2	3	3	4	4	4
crb	100	<2	<2	<2	<2	<2	2	2	3	3
Mov	34	<2	<2	<2	<2	<2	<2	2	2	2
Tgii	3	<2	<2	<2	<2	<2	<2	<2	<2	<2
nms	30	<2	<2	<2	<2	<2	<2	2	2	2
ms	6	<2	<2	<2	<2	<2	<2	<2	<2	<2
pTmi	10	<2	<2	<2	<2	<2	2	2	2	2
Gallium										
Qdl	47	17	17	18	19	20	20	21	22	22
Qfd	29	16	17	17	18	19	20	21	21	21
QPlv	11	19	19	21	24	27	29	30	30	30
crb	100	16	17	18	20	22	24	25	26	35
Mov	34	18	19	20	21	21	23	24	24	24
Tgii	3	17	17	17	19	21	21	21	21	21
nms	30	14	17	18	19	21	22	25	25	25
ms	6	17	17	17	19	20	20	20	20	20
pTmi	10	<4	<4	10	19	23	26	26	26	26

Table 11.--Distributions of major- and minor-element concentrations in streambed sediment of first- and second-order streams, relative to geologic units, Yakima River Basin, Washington, 1987--Continued

Simple geology	Number of samples	Minimum value	Value at indicated percentile							Maximum value
			10	25	50	75	90	95	98	
MINOR ELEMENTS, IN UNITS OF MICROGRAMS PER GRAM										
Gold										
Qdl	47	<8	<8	<8	<8	<8	<8	<8	<8	<8
Qfd	29	<8	<8	<8	<8	<8	<8	<8	<8	<8
QPlv	11	<8	<8	<8	<8	<8	<8	<8	<8	<8
crb	100	<8	<8	<8	<8	<8	<8	<8	<8	<8
Mov	34	<8	<8	<8	<8	<8	<8	<8	<8	<8
Tgii	3	<8	<8	<8	<8	<8	<8	<8	<8	<8
nms	30	<8	<8	<8	<8	<8	<8	<8	<8	<8
ms	6	<8	<8	<8	<8	<8	<8	<8	<8	<8
pTmi	10	<8	<8	<8	<8	<8	<8	<8	<8	<8
Lanthanum										
Qdl	47	17	20	22	24	27	31	35	39	39
Qfd	29	16	26	32	36	43	55	58	58	58
QPlv	11	29	29	29	32	38	44	45	45	45
crb	100	18	22	23	26	33	40	50	59	62
Mov	34	16	17	19	22	24	27	29	32	32
Tgii	3	23	23	23	27	29	29	29	29	29
nms	30	16	18	22	23	27	33	43	52	52
ms	6	13	13	16	20	25	28	28	28	28
pTmi	10	3	4	10	14	24	32	33	33	33
Lead										
Qdl	47	7	9	12	14	16	32	44	170	170
Qfd	29	9	11	14	17	19	27	40	43	43
QPlv	11	<4	<4	8	10	13	21	23	23	23
crb	100	6	9	11	12	15	23	34	50	220
Mov	34	6	8	9	11	14	21	54	60	60
Tgii	3	12	12	12	13	41	41	41	41	41
nms	30	8	10	11	13	18	73	301	510	510
ms	6	7	7	7	10	11	14	14	14	14
pTmi	10	9	9	9	14	18	24	24	24	24
Lithium										
Qdl	47	13	19	20	22	24	31	43	47	47
Qfd	29	19	20	22	22	27	28	29	29	29
QPlv	11	19	19	20	21	25	39	42	42	42
crb	100	15	18	18	21	22	24	26	29	30
Mov	34	15	17	23	26	35	40	45	55	55
Tgii	3	20	20	20	24	30	30	30	30	30
nms	30	16	19	21	29	40	48	58	64	64
ms	6	20	20	23	36	38	38	38	38	38
pTmi	10	12	12	18	32	44	105	110	110	110
Manganese										
Qdl	47	550	576	690	850	1,000	1,400	1,840	2,900	2,900
Qfd	29	540	610	770	890	1,000	1,100	1,150	1,200	1,200
QPlv	11	510	542	750	930	1,100	1,420	1,500	1,500	1,500
crb	100	480	690	760	920	1,100	1,400	1,495	1,500	1,800
Mov	34	630	775	958	1,100	1,300	1,450	1,700	2,000	2,000
Tgii	3	540	540	540	780	920	920	920	920	920
nms	30	430	534	698	850	1,125	1,390	2,005	2,500	2,500
ms	6	610	610	625	910	1,300	1,600	1,600	1,600	1,600
pTmi	10	710	713	823	1,000	1,250	1,400	1,400	1,400	1,400

Table 11.--Distributions of major- and minor-element concentrations in streambed sediment of first- and second-order streams, relative to geologic units, Yakima River Basin, Washington, 1987--Continued

Simple geology	Number of samples	Minimum value	Value at indicated percentile							Maximum value
			10	25	50	75	90	95	98	
MINOR ELEMENTS, IN UNITS OF MICROGRAMS PER GRAM										
Mercury										
Qdl	47	<0.02	<0.02	<0.02	<0.02	0.02	0.08	0.17	0.20	0.20
Qfd	29	<.02	<.02	<.02	<.02	<.02	.02	.04	.04	.04
QPlv	11	<.02	<.02	<.02	<.02	.02	.09	.10	.10	.10
crb	100	<.02	<.02	<.02	<.02	<.02	.04	.04	.08	.08
Mov	34	<.02	<.02	<.02	.04	.08	.14	.25	.54	.54
Tgii	3	<.02	<.02	<.02	.06	3.1	3.1	3.1	3.1	3.1
nms	30	<.02	<.02	<.02	.04	.08	.14	.16	.16	.16
ms	6	<.02	<.02	.02	.05	.11	.14	.14	.14	.14
pTmi	10	<.02	<.02	<.02	.04	.10	1.6	1.8	1.8	1.8
Molybdenum										
Qdl	47	<2	<2	<2	<2	<2	<2	<2	<2	<2
Qfd	29	<2	<2	<2	<2	<2	<2	<2	<2	<2
QPlv	11	<2	<2	<2	<2	<2	<2	2	2	2
crb	100	<2	<2	<2	<2	<2	<2	<2	<2	<2
Mov	34	<2	<2	<2	<2	<2	<2	<2	<2	<2
Tgii	3	<2	<2	<2	<2	3	3	3	3	3
nms	30	<2	<2	<2	<2	<2	<2	2	4	4
ms	6	<2	<2	<2	<2	<2	3	3	3	3
pTmi	10	<2	<2	<2	<2	<2	<2	2	2	2
Neodymium										
Qdl	47	16	21	22	24	27	32	37	39	39
Qfd	29	17	25	32	35	40	49	58	58	58
QPlv	11	23	24	31	38	43	50	52	52	52
crb	100	14	22	24	27	33	39	48	51	58
Mov	34	17	19	20	24	28	31	33	33	33
Tgii	3	25	25	25	27	28	28	28	28	28
nms	30	15	18	21	24	27	33	42	49	49
ms	6	15	15	17	22	26	29	29	29	29
pTmi	10	<4	<4	11	18	26	39	41	41	41
Nickel										
Qdl	47	7	16	18	22	33	44	74	140	140
Qfd	29	11	17	20	21	23	27	30	31	31
QPlv	11	13	13	17	19	39	60	62	62	62
crb	100	12	14	16	18	20	22	25	28	29
Mov	34	4	8	11	16	31	53	125	200	200
Tgii	3	16	16	16	20	43	43	43	43	43
nms	30	11	15	20	34	43	65	91	110	110
ms	6	10	10	13	22	51	90	90	90	90
pTmi	10	35	35	45	68	1,170	1,890	1,900	1,900	1,900
Niobium										
Qdl	47	<4	<4	4	8	9	11	11	13	13
Qfd	29	<4	<4	5	10	12	14	16	17	17
QPlv	11	<4	<4	4	19	24	33	35	35	35
crb	100	<4	<4	6	9	12	14	14	14	16
Mov	34	<4	<4	6	8	11	13	14	17	17
Tgii	3	5	5	5	7	10	10	10	10	10
nms	30	<4	5	6	7	9	10	11	13	13
ms	6	<4	<4	5	8	10	16	16	16	16
pTmi	10	<4	<4	<4	4	8	11	11	11	11

Table 11.--Distributions of major- and minor-element concentrations in streambed sediment of first- and second-order streams, relative to geologic units, Yakima River Basin, Washington, 1987--Continued

Simple geology	Number of samples	Minimum value	Value at indicated percentile							Maximum value
			10	25	50	75	90	95	98	
MINOR ELEMENTS, IN UNITS OF MICROGRAMS PER GRAM										
Scandium										
Qdl	47	11	14	15	18	20	22	23	27	27
Qfd	29	9	15	17	18	20	22	25	25	25
QPlv	11	13	13	14	17	28	33	35	35	35
crb	100	12	15	16	20	23	27	29	30	37
Mov	34	10	13	15	18	22	27	28	28	28
Tgii	3	12	12	12	13	21	21	21	21	21
nms	30	10	11	13	15	17	21	23	25	25
ms	6	10	10	12	13	18	24	24	24	24
pTmi	10	12	12	14	18	28	30	31	31	31
Selenium										
Qdl	3	<.1	<.1	<.1	.2	.4	.4	.4	.4	.4
Qfd	3	.2	.2	.2	.2	.9	.9	.9	.9	.9
QPlv	1	.2	.2	.2	.2	.2	.2	.2	.2	.2
crb	8	<.1	<.1	<.1	<.1	.2	.5	.5	.5	.5
Mov	4	.5	.5	.5	.6	.8	.8	.8	.8	.8
Tgii	0	--	--	--	--	--	--	--	--	--
nms	5	<.1	<.1	<.1	.3	.8	1.1	1.1	1.1	1.1
ms	0	--	--	--	--	--	--	--	--	--
pTmi	2	.3	.3	.3	.5	.7	.7	.7	.7	.7
Silver										
Qdl	47	<4	<4	<4	<4	<4	<4	<4	<4	<4
Qfd	29	<4	<4	<4	<4	<4	<4	<4	<4	<4
QPlv	11	<4	<4	<4	<4	<4	<4	<4	<4	<4
crb	100	<4	<4	<4	<4	<4	<4	<4	<4	<4
Mov	34	<4	<4	<4	<4	<4	<4	<4	<4	<4
Tgii	3	<4	<4	<4	<4	<4	<4	<4	<4	<4
nms	30	<4	<4	<4	<4	<4	<4	<4	<4	<4
ms	6	<4	<4	<4	<4	<4	<4	<4	<4	<4
pTmi	10	<4	<4	<4	<4	<4	<4	<4	<4	<4
Strontium										
Qdl	47	210	260	290	310	330	370	380	390	390
Qfd	29	250	260	280	300	310	340	405	430	430
QPlv	11	200	214	290	310	340	348	350	350	350
crb	100	220	290	310	330	350	380	420	449	620
Mov	34	150	165	210	295	330	390	440	470	470
Tgii	3	320	320	320	350	350	350	350	350	350
nms	30	210	270	300	320	345	407	415	420	420
ms	6	260	260	283	335	363	400	400	400	400
pTmi	10	48	57	148	190	230	269	270	270	270
Thorium										
Qdl	47	2	2	5	6	7	8	9	12	12
Qfd	29	2	7	9	10	12	15	18	19	19
QPlv	11	4	4	5	7	8	11	12	12	12
crb	100	2	4	5	6	8	11	14	16	18
Mov	34	2	2	4	5	6	6	8	9	9
Tgii	3	6	6	6	7	10	10	10	10	10
nms	30	2	2	4	6	8	10	14	16	16
ms	6	2	2	2	5	6	6	6	6	6
pTmi	10	2	2	2	4	7	10	10	10	10

Table 11.--Distributions of major- and minor-element concentrations in streambed sediment of first- and second-order streams, relative to geologic units, Yakima River Basin, Washington, 1987--Continued

Simple geology	Number of samples	Minimum value	Value at indicated percentile 10	25	50	75	90	95	98	Maximum value
					MINOR ELEMENTS, IN UNITS OF MICROGRAMS PER GRAM					
					Tin					
Qdl	47	<10	<10	<10	<10	<10	<10	<10	40	40
Qfd	29	<10	<10	<10	<10	<10	<10	<10	<10	<10
QPlv	11	<10	<10	<10	<10	<10	<10	<10	<10	<10
crb	100	<10	<10	<10	<10	<10	<10	<10	<10	<10
Mov	34	<10	<10	<10	<10	<10	<10	<10	<10	<10
Tgii	3	<10	<10	<10	<10	20	20	20	20	20
nms	30	<10	<10	<10	<10	<10	<10	<10	<10	<10
ms	6	<10	<10	<10	<10	<10	<10	<10	<10	<10
pTmi	10	<10	<10	<10	<10	<10	<10	<10	<10	<10
					Uranium					
Qdl	47	.30	.50	.70	.90	1.30	1.92	2.50	6.60	6.60
Qfd	29	.20	.55	.72	1.00	1.40	2.40	2.85	3.30	3.30
QPlv	11	1.10	1.10	1.30	1.30	1.60	2.36	2.40	2.40	2.40
crb	100	.25	.55	.70	.80	1.17	1.49	1.70	2.10	2.30
Mov	34	.20	.55	.60	.85	1.10	1.70	3.07	6.30	6.30
Tgii	3	.50	.50	.50	.70	12.00	12.00	12.00	12.00	12.00
nms	30	.35	.60	.70	1.10	1.50	3.27	5.93	7.80	7.80
ms	6	.15	.15	.52	1.00	15.62	55.00	55.00	55.00	55.00
pTmi	10	.10	.11	.29	.52	1.50	1.50	1.50	1.50	1.50
					Vanadium					
Qdl	47	79	96	120	140	150	182	190	250	250
Qfd	29	72	120	145	160	185	220	245	260	260
QPlv	11	100	102	130	150	210	264	270	270	270
crb	100	84	120	140	170	210	250	289	329	330
Mov	34	62	81	100	125	145	185	203	210	210
Tgii	3	95	95	95	100	170	170	170	170	170
nms	30	74	78	94	110	140	198	255	310	310
ms	6	84	84	90	103	150	180	180	180	180
pTmi	10	81	82	98	150	213	229	230	230	230
					Ytterbium					
Qdl	47	2	2	2	3	3	3	4	4	4
Qfd	29	2	3	3	3	3	4	4	4	4
QPlv	11	3	3	3	4	5	5	6	6	6
crb	100	2	2	3	3	3	4	5	6	6
Mov	34	2	2	2	3	4	5	5	5	5
Tgii	3	2	2	2	2	3	3	3	3	3
nms	30	2	2	2	2	2	3	3	3	3
ms	6	2	2	2	3	4	4	4	4	4
pTmi	10	<1	<1	1	2	2	2	2	2	2
					Yttrium					
Qdl	47	14	17	18	22	23	28	33	36	36
Qfd	29	13	20	22	24	26	29	30	31	31
QPlv	11	22	22	24	30	42	52	53	53	53
crb	100	16	19	21	23	26	33	39	48	61
Mov	34	13	18	20	24	29	35	37	40	40
Tgii	3	18	18	18	21	24	24	24	24	24
nms	30	13	15	17	18	21	24	30	31	31
ms	6	13	13	13	19	29	30	30	30	30
pTmi	10	6	6	11	17	20	21	21	21	21

Table 11.--Distributions of major- and minor-element concentrations in streambed sediment of first- and second-order streams, relative to geologic units, Yakima River Basin, Washington, 1987--Continued

Simple geology	Number of samples	Minimum value	Value at indicated percentile 10	25	50	75	90	95	98	Maximum value
MINOR ELEMENTS, IN UNITS OF MICROGRAMS PER GRAM										
Zinc										
Qdl	47	69	71	75	88	99	122	156	350	350
Qfd	29	49	75	82	88	94	100	415	710	710
QPlv	11	87	88	99	110	140	140	140	140	140
crb	100	56	70	77	87	108	110	140	179	260
Mov	34	51	73	85	100	110	115	143	180	180
Tgii	3	56	56	56	89	96	96	96	96	96
nms	30	53	62	77	87	99	130	135	140	140
ms	6	56	56	58	78	122	200	200	200	200
pTmi	10	40	42	59	102	125	176	180	180	180

Table 12.--Results of Tukey's studentized range test on analysis of variance for major- and minor-element concentrations in streambed sediment of different geologic units, Yakima River Basin, Washington, 1987

[Median values are in concentration units of grams per 100 grams (percent) for major elements and micrograms per gram for minor elements, -- = no significant (= 0.1) difference; * = significant difference (= 0.1) exists between mean concentration ranks; number in parenthesis = number of observations]

Geologic unit, median value, and rank	Geologic units							
	Quaternary[1/] deposits and loess (47)	Quaternary flood deposits (29)	Quaternary and Pliocene volcanic rocks (11)	Columbia River Basalt Group rocks (100)	Miocene[2/] and older volcanic rocks (34)	Nonmarine sediment-ary rocks (30)	Marine sediment-ary rocks (6)	Pre-Tertiary metamorphic and intrusive rocks (10)
				MAJOR ELEMENTS				
				Calcium				
Median value[3/]	2.7	2.9	2.1	3.0	2.7	2.2	3.2	1.9
Quaternary deposits and loess		--	--	*	--	*	--	--
Quaternary flood deposits	--		*	--	--	*	--	*
Quaternary and Pliocene volcanic rocks	--	*		*	--	--	--	--
Columbia River Basalt Group rocks	*	--	*		*	*	--	*
Miocene and older volcanic rocks	--	--	--	*		--	--	--
Nonmarine sedimentary rocks	*	*	--	*	--		*	--
Marine sedimentary rocks	--	--	--	--	--	*		*
Pre-Tertiary metamorphic and intrusive rocks	--	*	--	*	--	--	*	
				Potassium				
Median value[3/]	1.1	1.5	1.0	1.1	.94	1.1	1.1	1.1
Quaternary deposits and loess		*	--	--	*	--	--	--
Quaternary flood deposits	*		*	*	*	*	*	*
Quaternary and Pliocene volcanic rocks	--	*		--	--	--	--	--
Columbia River Basalt Group rocks	--	*	--		--	--	--	--
Miocene and older volcanic rocks	*	*	--	--		--	--	--
Nonmarine sedimentary rocks	--	*	--	--	--		--	--
Marine sedimentary rocks	--	*	--	--	--	--		--
Pre-Tertiary metamorphic and intrusive rocks	--	*	--	--	--	--	--	
				Titanium				
Median value[3/]	.68	.78	1.2	.85	.70	.54	.55	.49
Quaternary deposits and loess		*	*	*	--	*	--	*
Quaternary flood deposits	*		*	--	--	*	--	*
Quaternary and Pliocene volcanic rocks	*	*		*	*	*	*	*
Columbia River Basalt Group rocks	*	--	*		*	*	*	*
Miocene and older volcanic rocks	--	--	*	*		*	--	*
Nonmarine sedimentary rocks	*	*	*	*	*		--	--
Marine sedimentary rocks	--	--	*	*	--	--		--
Pre-Tertiary metamorphic and intrusive rocks	-- *	-- *	-- *	-- *	-- *	--	--	

Table 12.--Results of Tukey's studentized range test on analysis of variance for major- and minor-element concentrations in streambed sediment of different geologic units, Yakima River Basin, Washington, 1987--Continued

Geologic unit, median value, and rank	Quaternary[1/] deposits and loess (47)	Quaternary flood deposits (29)	Quaternary and Pliocene volcanic rocks (11)	Columbia River Basalt Group rocks (100)	Miocene[2/] and older volcanic rocks (34)	Nonmarine sedimentary rocks (30)	Marine sedimentary rocks (6)	Pre-Tertiary metamorphic and intrusive rocks (10)
MINOR ELEMENTS								
Arsenic								
Median value[3/]	3.4	5.1	1.5	2.4	3.4	5.2	3.8	6.2
Quaternary deposits and loess		*	*	*	--	--	--	--
Quaternary flood deposits	*		*	*	--	--	--	
Quaternary and Pliocene volcanic rocks	*	*		--	*	*	*	*
Columbia River Basalt Group rocks	*	*	--		*	*	--	*
Miocene and older volcanic rocks	--	--	*	*		--	--	--
Nonmarine sedimentary rocks	--	--	*	*	--		--	--
Marine sedimentary rocks	--	--	*	--	--	--		--
Pre-Tertiary metamorphic and intrusive rocks	--	--	*	*	--	--	--	
Cerium								
Median value[3/]	43	68	59	46	42	46	36	30
Quaternary deposits and loess		*	*	--	--	--	--	--
Quaternary flood deposits	*		--	*	*	*	*	*
Quaternary and pliocene volcanic rocks	*	--		*	*	*	*	*
Columbia River Basalt Group rocks	--	*		*	--	*	*	
Miocene and older volcanics	--	*	*	*		--	--	--
Nonmarine sedimentary rocks	--	*	*	--	--		--	--
Marine sedimentary rocks	--	*	*	*	--	--		--
Pre-Tertiary metamorphic and intrusive rock	--	*	*	*	--	--	--	
Chromium								
Median value[3/]	56	52	56	48	40	78	60	150
Quaternary deposits, loess	--	--	--	*	--	--	--	*
Quaternary flood deposits	--		--	--	--	--	--	*
Quaternary and Pliocene volcanic rocks	--	--		--	--	--	--	*
Columbia River Basalt Group rocks	*	--	--		--	*	--	*
Miocene and older volcanic rocks	--	--	--	--		*	--	*
Nonmarine sedimentary rocks	--	--	--	*	*		--	*
Marine sedimentary rocks	--	--	--	--	--	--		--
Pre-Tertiary metamorphic and intrusive rocks	*	*	*	*	*	*	--	

Table 12.--Results of Tukey's studentized range test on analysis of variance for major- and minor-element concentrations in streambed sediment of different geologic units, Yakima River Basin, Washington, 1987--Continued

Geologic unit, median value, and rank	Geologic units: Quaternary[1/] deposits and loess (47)	Quaternary flood deposits (29)	Quaternary and Pliocene volcanic rocks (11)	Columbia River Basalt Group rocks (100)	Miocene[2/] and older volcanic rocks (34)	Nonmarine sedimentary rocks (30)	Marine sedimentary rocks (6)	Pre-Tertiary metamorphic and intrusive rocks (10)
MINOR ELEMENTS								
Lanthanum								
Median value[3/]	24	36	32	26	22	23	20	14
Quaternary deposits and loess		*	*	--	*	--	--	*
Quaternary flood deposits	*		--	*	*	*	*	*
Quaternary and Pliocene volcanic rocks	*	--		*	*	*	*	*
Columbia River Basalt Group rocks	--	*	*		*	--	*	*
Miocene and older volcanic rocks	*	*	*	*		--	--	--
Nonmarine sedimentary rocks	--	*	*	--	--		--	--
Marine sedimentary rocks		*	*	*	--			--
Pre-Tertiary metamorphic and intrusive rocks	*	*	*	*	--	--	--	*
Lead								
Median value[3/]	14	17	10	12	11	13	9.5	14
Quaternary deposits and loess		--	--	--	*	--	*	--
Quaternary flood deposits	--		*	*	*	--	*	--
Quaternary and Pliocene volcanic rocks	--	*		--	--	--	--	--
Columbia River Basalt Group rocks	--	*	--		--	--	--	--
Miocene and older volcanic rocks	*	*	--	--		--	--	--
Nonmarine sedimentary rocks	--	--	--	--	--		--	--
Marine sedimentary rocks	*	*	--	--	--	--		--
Pre-Tertiary metamorphic and intrusive rocks	--	--	--	--	--	--	--	
Mercury								
Median value[3/]	<.02	<.02	<.02	<.02	.04	.04	.05	.04
Quaternary deposits and loess		--	--	--	*	*	*	--
Quaternary flood deposits	--		--	--	*	*	*	*
Quaternary and Pliocene volcanic rocks	--	--		--	--	--	--	--
Columbia River Basalt Group rocks	--	--	--		*	*	*	*
Miocene and older volcanic rocks	*	*	--	*		--	--	--
Nonmarine sedimentary rocks	*	*	--	*	--		--	--
Marine sedimentary rocks	*	*	--	*	--	--		--
Pre-Tertiary metamorphic and intrusive rocks	--	*	--	*	--	--	--	

Table 12.--Results of Tukey's studentized range test on analysis of variance for major- and minor-element concentrations in streambed sediment of different geologic units, Yakima River Basin, Washington, 1987--Continued

Geologic unit, median value, and rank	Quaternary[1/] deposits and loess (47)	Quaternary flood deposits (29)	Quaternary and Pliocene volcanic rocks (11)	Columbia River Basalt Group rocks (100)	Miocene[2/] and older volcanic rocks (34)	Nonmarine sedimentary rocks (30)	Marine sedimentary rocks (6)	Pre-Tertiary metamorphic and intrusive rocks (10)
				Geologic units				
				MINOR ELEMENTS				
				Manganese				
Median value[3/]	850	890	930	920	1,100	850	910	1,000
Quaternary deposits and loess		--	--	--	*	--	--	--
Quaternary flood deposits	--		--	--	*	--	--	--
Quaternary and Pliocene volcanic rocks	--	--		--	--	--	--	--
Columbia River Basalt Group rocks	--	--	--		*	--	--	--
Miocene and older volcanic rocks	*	*	--	*		*	--	--
Nonmarine sedimentary rocks	--	--	--	--	*		--	
Marine sedimentary rocks	--	--	--	--	--	--		--
Pre-Tertiary metamorphic and intrusive rocks	--	--	--	--	--	--	--	
				Neodymium				
Median value[3/]	24	35	38	27	24	24	22	18
Quaternary deposits and loess		*	*	*	--	--	--	--
Quaternary flood deposits	*		--	*	*	*	*	*
Quaternary and Pliocene volcanic rocks	*	--		*	*	*	*	*
Columbia River Basalt Group rocks	*	*	*		*	*	--	*
Miocene and older volcanic rocks	--	*	*	*		--	--	--
Nonmarine sedimentary rocks	--	*	*	*	--		--	--
Marine sedimentary rocks	--	*	*	--	--	--		--
Pre-Tertiary metamorphic and intrusive rocks	--	*	*	*	--	--		
				Nickel				
Median value[3/]	22	21	19	18	16	34	22	68
Quaternary deposits and loess		--	--	*	*	--	--	*
Quaternary flood deposits	--		--	*	--	--	--	*
Quaternary and Pliocene volcanic rocks	--	--		--	--	--	--	*
Columbia River Basalt Group rocks	*	*	--		--	*	--	*
Miocene and older volcanic rocks	*	--	--	--		*	--	*
Nonmarine sedimentary rocks	--	--	--	*	*		--	--
Marine sedimentary rocks	--	--	--	--	--	--		*
Pre-Tertiary metamorphic and intrusive rocks	*	*	*	*	*	--	*	

Table 12.--Results of Tukey's studentized range test on analysis of variance for major- and minor-element concentrations in streambed sediment of different geologic units, Yakima River Basin, Washington, 1987--Continued

Geologic unit, median value, and rank	Geologic units							
	Quaternary[1] deposits and loess (47)	Quaternary flood deposits (29)	Quaternary and Pliocene volcanic rocks (11)	Columbia River Basalt Group rocks (100)	Miocene[2] and older volcanic rocks (34)	Nonmarine sediment-ary rocks (30)	Marine sediment-ary rocks (6)	Pre-Tertiary metamorphic and intrusive rocks (10)
MINOR ELEMENTS								
Strontium								
Median value[3]	310	300	310	330	295	320	335	190
Quaternary deposits and loess		--	--	*	--	--	--	*
Quaternary flood deposits	--		--	*	--	*	--	*
Quaternary and Pliocene volcanic rocks	--	--		--	--	--	--	*
Columbia River Basalt Group rocks	*	*	--		*	--	--	*
Miocene and older volcanic rocks	--	--	--	*		*	--	*
Nonmarine sedimentary rocks	--	*	--	--	*		--	*
Marine sedimentary rocks	--	--	--	--	--	--		*
Pre-Tertiary metamorphic and intrusive rocks	*	*	*	*	*	*	*	
Thorium								
Median value[3]	6.0	10	7	6	5	6	4.5	4
Quaternary deposits and loess		*	--	--	--	--	--	--
Quaternary flood deposits	*		*	*	*	*	*	*
Quaternary and Pliocene volcanic rocks	--	*			*	--	--	--
Columbia River Basalt Group rocks	--	*	--		*	--	--	--
Miocene and older volcanic rocks	--	*	*	*		--	--	--
Nonmarine sedimentary rocks	--	*	--	--	--		--	--
Marine sedimentary rocks	--	*	--	--	--	--		--
Pre-Tertiary metamorphic and intrusive rocks	--	*	--	--	--	--	--	
Vanadium								
Median value[3]	140	160	150	170	125	110	100	150
Quaternary deposits and loess	*	--	*	--	--	--	--	
Quaternary flood deposits	*		--	--	*	*	*	--
Quaternary and Pliocene volcanic rocks	--	--		--	--	*	--	--
Columbia River Basalt Group rocks	*	--	--		*	*	*	--
Miocene and older volcanic rocks	--	*	--	*		--	--	--
Nonmarine sedimentary rocks	--	*	*	*	--		--	--
Marine sedimentary rocks	--	*	--	*	--	--		--
Pre-Tertiary metamorphic and intrusive rocks	--	--	--	--	--	--	--	

Table 12.--Results of Tukey's studentized range test on analysis of variance for major- and minor-element concentrations in streambed sediment of different geologic units, Yakima River Basin, Washington, 1987--Continued

Geologic unit, median value, and rank	Quaternary[1] deposits and loess (47)	Quaternary flood deposits (29)	Quaternary and Pliocene volcanic rocks (11)	Columbia River Basalt Group rocks (100)	Miocene[2] and older volcanic rocks (34)	Nonmarine sedimentary rocks (30)	Marine sedimentary rocks (6)	Pre-Tertiary metamorphic and intrusive rocks (10)
MINOR ELEMENTS								
Zinc								
Median value[3]	88	88	110	87	99	86	78	102
Quaternary deposits and loess		--	*	--	--	--	--	--
Quaternary flood deposits	--		*	--	--	--	--	--
Quaternary and Pliocene volcanic rocks	*	*		*	--	*	*	--
Columbia River Basalt Group rocks	--	--	*		--	--	--	--
Miocene and older volcanic rocks	--	--	--	--		--	--	--
Nonmarine sedimentary rocks	--	--	*	--	--		--	--
Marine sedimentary rocks	--	--	*	--	--	--		--
Pre-Tertiary metamorphic and intrusive rocks	--	--	--	--	--	--	--	--

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[1] Excluding Quaternary flood deposits.

[2] Excluding Miocene Columbia River Basalt Group rocks.

[3] Median values were determined only for randomly selected lower-order streams.

APPENDIX A

ANALYTICAL PRECISION AND ACCURACY

In this report, analytical precision data are important when comparing element concentrations between sites (intersite comparisons). Analytical precision was determined for elements with concentrations above method reporting limits (MRL's). Sediment samples were analyzed in batches of 40. Analytical precision "within" each batch was determined by splitting one randomly selected sample from within each batch (within-batch precision). Analytical precision "among" the different batches was determined by randomly selecting a second sample from each batch. The second sample was split, one-half remaining within the batch and the second half was removed from the batch, placed with similarly collected samples from other batches, and randomly distributed "among" the different sample batches (among-batch precision).

Analyses of within-batch quality-control samples represent analytical precision over a short period of time, usually a day. Conversely, because among-batch quality-control samples were randomly distributed among the different batches, the analyses of these samples represent analytical precision ranging from a short to a long period of time--usually weeks. Analytical precision was evaluated by determining the relative difference between the split samples--the absolute value of the difference divided by the mean of the split-sample concentrations times 100. The relative differences were plotted for selected percentiles using box plots. The within-batch precision is better than the among-batch precision (fig. A1). In addition, for most among-batch precision data, relative differences generally decreased as element concentrations increased. For example, relative differences computed from among-batch precision data for native streambed samples and standard reference samples of antimony, arsenic, and lead generally decreased as element concentrations increased (fig. A2). Larger variability associated with among-batch precision may be a result of subtle differences in daily instrument calibration, operations, and sample digestive procedures.

Analytical accuracy is important when comparing data from different studies. Analytical accuracy is assessed by analyzing geochemical-reference samples that have interlaboratory-consensus means--concentrations that have been verified by several independent laboratories. Geochemical-reference samples also are used to characterize positive or negative analytical bias.

To determine the accuracy of chemical analyses in this study, two geochemical-reference samples GSD-6 (geochemical standard six) and GXR-2 (geochemical exploration reference sample two) were submitted concurrently for analysis with native streambed-sediment samples. Each batch or group of 40 samples contained two standard reference samples. All element determinations of GSD-6, a copper and molybdenum enriched reference sample from clastic, volcanic, and basaltic rock (Xie and others, 1985), fell within two standard deviations of the consensus mean

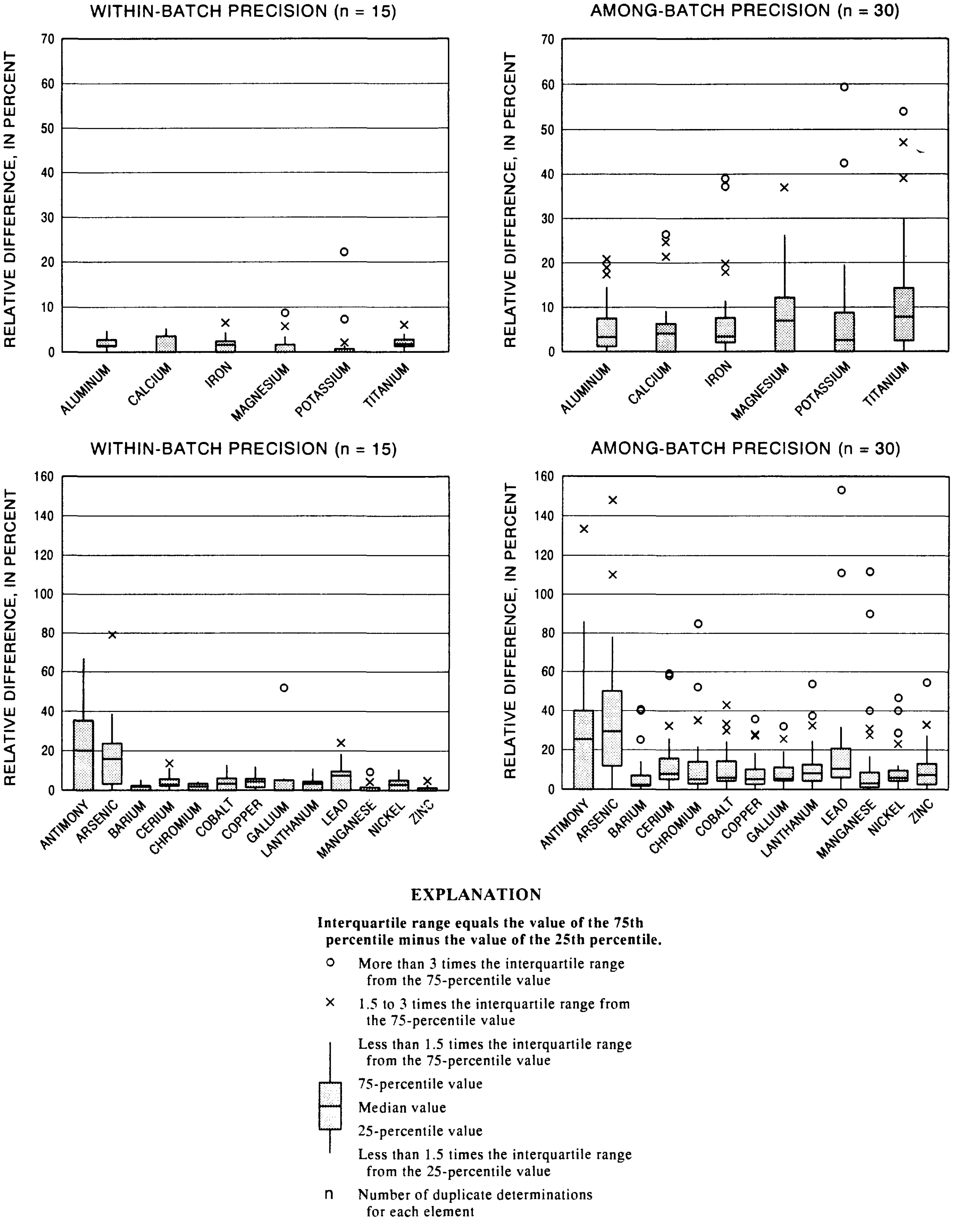

Figure A1. Analytical precision of selected elements from duplicate samples analyzed at the same time (within-batch precision) and at different times (among-batch precision), Yakima River Basin, Washington, 1987.

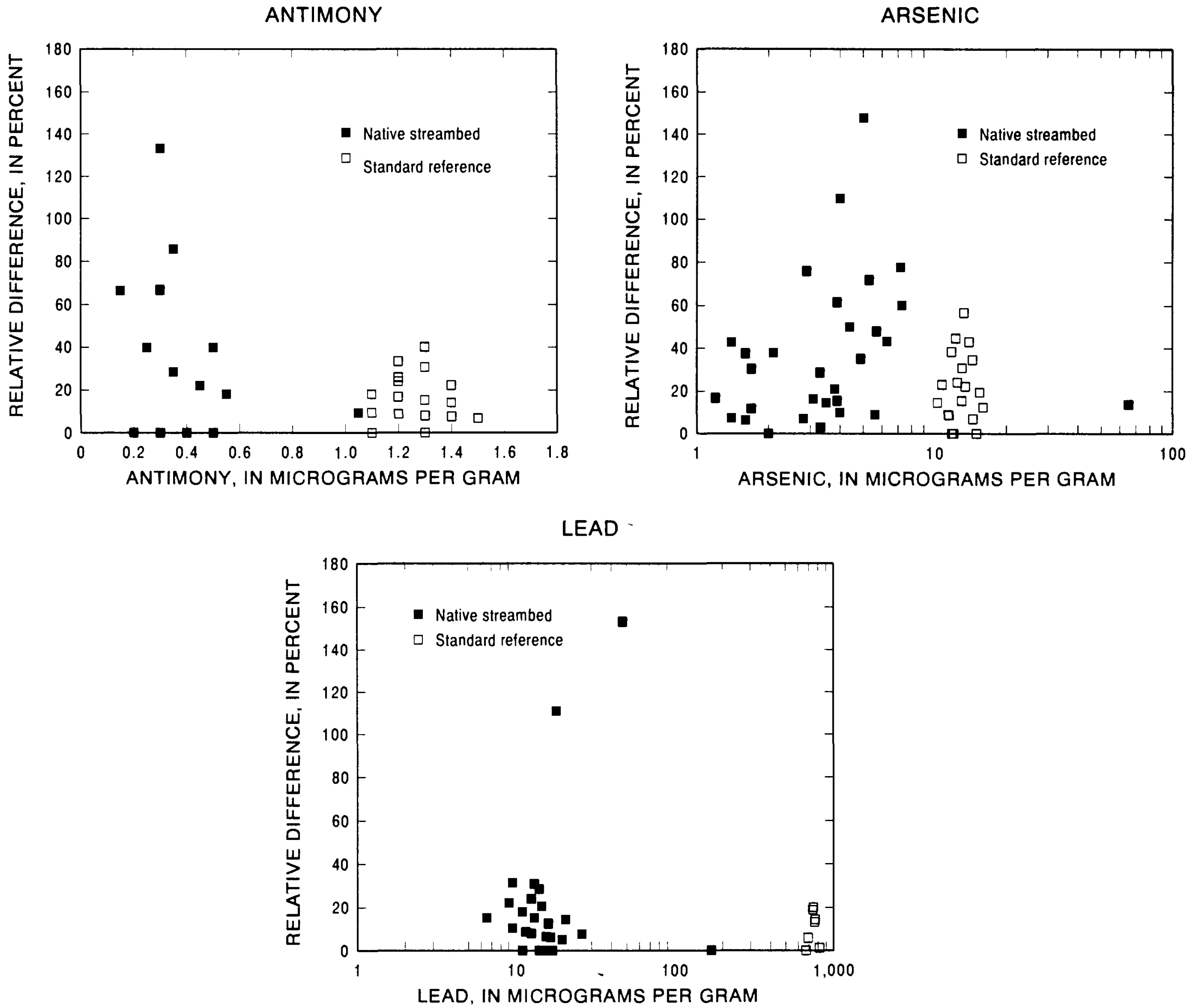

Figure A2. Analytical precision of antimony, arsenic, and lead from duplicate analyses of geochemical-reference and streambed-sediment samples, Yakima River Basin, Washington, 1987.

(Sanzolone and Ryder, 1989, table 2b). A small percentage of element determinations of GXR-2, a lead, zinc, silver, and copper enriched reference sample from residual, gray-brown loams (Allcott and Lakin, 1975), fell beyond two standard deviations from the consensus mean (R. Sanzolone, U.S. Geological Survey, written commun., 1988). Cadmium, the only significant GXR-2 outlier, exceeded two standard deviations from the consensus mean (4.1 μg/g) 17 percent of the time. Because nearly all cadmium determinations of Yakima River Basin streambed sediment are less than the 2 μg/g method reporting level (MRL), the poor analytical accuracy of cadmium is of little significance. The percentage of other elements falling outside the consensus mean is small; most occur less than 5 percent of the time and none occurs more than 10 percent of the time.

Although most GSD-6 and GXR-2 determinations reflect acceptable analytical precision and accuracy, it is important to determine the magnitude and direction of the analytical bias. The average analytical bias (determined from concurrent analysis of GSD-6, GXR-2 and Yakima River Basin native-streambed sediment) is generally small and of similar value and direction between the two different types of reference materials (table A1). Noteworthy exceptions (mean-analytical bias exceeded 20 percent of the standard-reference sample consensus values) and mean analytic bias for GSD-6 and GXR-2 samples are as follows: aluminum (-11.9 percent; GXR-2), antimony (-13 μg/g; GXR-2), cobalt (2 μg/g; GXR-2), gallium (-18 μg/g; GXR-2), lithium (14 μg/g; GXR-2), mercury (-0.01 μg/g; GSD-6), molybdenum (-2 μg/g; GSD-6), niobium (-5 μg/g; GSD-6 and -3 μg/g; GXR-2), uranium (-1.3 μg/g; GSD-6), yttrium (-5 μg/g; GXR-2) and zinc (101 μg/g; GXR-2). Although the digestion procedures (with the exception of uranium) used in this study are described as "total" (see Analytical Methods), analytical digestion methods recover less than 100 percent of the sought for element in a sample. These reduced recoveries usually result from either the presence of highly insoluble mineral phases or problems associated with an analytical method. For example, the extraction efficiency of the decomposition technique used to extract aluminum markedly decreases in the presence of corundum--an aluminum-oxide mineral phase found in GXR-2 but not in GSD-6. The negative bias of antimony is attributed to analytical-method design. Similar to aluminum, the negative bias of uranium is attributed to a partial digestion technique.

Table A1.--Analytical accuracy based on the analysis of standard geochemical-reference samples

[Geochemical-reference samples were analyzed concurrent with Yakima Basin streambed-sediment samples; 4 and 30 analyses were made of GSD-6 (geochemical standard six) and GXR-2 (geochemical exploration reference sample two), respectively; -- = data not available; + = positive-analytical bias; - = negative-analytical bias; Sd = standard deviation]

Chemical	Geochemical reference sample GSD-6[1]/					Geochemical reference sample GXR-2[2]/				
	Mean			Max	Sd	Mean			Max	Sd
	SRS[3]/	Lab[4]/	Bias[5]/	bias[6]/	lab	SRS[3]/	lab[4]/	bias[5]/	bias[6]/	lab
Major elements [All values are reported in units of percent]										
Aluminum	7.5	7.5	0.0	-0.1	0.05	18.6	6.7	-11.9	-12.3	0.24
Calcium	2.8	2.8	.0	.1	.05	.9	.9	.0	.0	.2
Carbon, inorganic	.55	.54	-.01	-.02	.01	.02	--	--	--	.004
Carbon, total	1.17	.96	-.21	-.24	.02	2.5	2.9	.4	.5	.05

Table A1.--Analytical accuracy based on the analysis of standard geochemical-reference samples--Continued

	Geochemical reference sample GSD-6[1]					Geochemical reference sample GXR-2[2]				
Chemical	Mean			Max	Sd	Mean			Max	Sd
	SRS[3]	Lab[4]	Bias[5]	bias[6]	lab	SRS[3]	lab[4]	bias[5]	bias[6]	lab
Major elements [All values are reported in units of percent]										
Iron	4.1	4.1	.0	-.1	.05	1.8	1.9	.1	.2	.06
Magnesium	1.8	1.8	.0	.0	.00	.9	.8	.1	.0	.03
Phosphorus	.1	.1	.0	.0	.00	.07	.07	.00	.01	.006
Sodium	1.7	1.7	.0	.0	.00	.5	.6	.1	.1	.02
Sulfur	.08	.08	.0	±.004	.00	.03	.03	.00	.02	.026
Titanium	.46	.43	-.03	-.04	.01	.29	.26	-.03	-.05	.01
Minor elements [All values are reported in units of micrograms per gram]										
Antimony	1.2	1.1	-0.1	-0.2	.1	47	34	-13	-36	4.4
Arsenic	13.6	11.8	-1.8	-2.6	.5	21.0	20.1	-0.9	-2.2	1.3
Barium	330	307	-23	-30	5	2210	2160	50	90	70
Beryllium	1.7	2	.3	.3	.0	1.6	2	0	--	.3
Cadmium	--	--	--	--	--	4.1	4	0	-1	0
Cerium	68	64	-4	-6	2	50	51	1	4	2
Chromium	190	205	15	30	24	34	39	5	9	2
Cobalt	24.4	27	3	4	1	9.0	11	2	9	0
Copper	383	395	12	37	2.0	70	81	11	19	4.2
Gallium	16.7	17	0	1	1	37	18	-18	-21	1
Lanthanum	39	34	-5	6	1	25	26	2	4	1
Lead	27	26	-2	-3	1	670	688	18	110	44
Lithium	40	42	2	3	1	48	62	14	17	2
Manganese	970	965	-5	-20	13	980	1035	55	120	51
Mercury	.04	.03	-.01	-.02	.01	2.7	3.1	.40	.50	.10
Molybdenum	7.7	6	-2	-2.7	1	--	--	--	--	--
Neodymium	33	31.2	-1.8	-2	0	--	--	--	--	--
Nickel	78	76	-2	-2	1	20	17.5	-2	-3	1
Niobium	12	7	-5.2	6	1	9	6	-3	-5.0	1
Scandium	17	15	-2	-2	0	7.2	6	-1	-1.2	0

Table A1.--Analytical accuracy based on the analysis of standard geochemical-reference samples--Continued

Chemical	Geochemical reference sample GSD-6[1]					Geochemical reference sample GXR-2[2]				
	Mean			Max	Sd	Mean			Max	Sd
	SRS[3]	Lab[4]	Bias[5]	bias[6]	lab	SRS[3]	lab[4]	bias[5]	bias[6]	lab
Minor elements [All values are reported in units of micrograms per gram]										
Strontium	266	280	14	14	0	152	164	12	18	5
Thorium	9.0	8	0	-2	1	8.6	8	0	-2	1
Uranium[7]	2.4	1.1	-1.3	-1.4	1.4	2.0	2.0	.0	.8	0.4
Vanadium	142	140	-2	-2	0	61	50	-11	14	2
Ytterbium	2.1	2	0	0	0	2	2	0	-1	0
Yttrium	20.2	16	-4	-5	2	19	14	-5	-5	0
Zinc	144	140	-4	-4	0	460	561	101	140	22

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[1] Sample composed of clastic, volcanic and granodiorite rocks from a copper and molybdenum enriched area of China. Mean values were derived from 41 participating laboratories (Xie and others, 1985).

[2] Sample composed of residual, gray-brown loams from a lead, zinc, silver, and copper_rich mining district in Summit County, Utah. Mean values were derived from 109 participating laboratories (Allcott and Lakin, 1975).

[3] Standard-reference-sample mean or consensus value from GSD-6 or GXR-2 multiple-laboratory determinations.

[4] Standard-reference-sample mean determined concurrent with Yakima Basin, native-streambed sediment, by U.S. Geological Survey, Branch of Geochemistry.

[5] Sum of the standard-reference-sample mean minus the element concentration of standard-reference sample (determined by the Branch of Geochemistry), divided by the number of determinations.

[6] Difference between the maximum element concentration, in the direction of the mean bias, and the standard-reference-sample mean determined from multiple laboratory determinations.

[7] Partial extraction method.

APPENDIX B

QUALITY-ASSURANCE GUIDELINES

Field collection and sample-processing variability, in addition to analytical variability (as discussed in appendix A), needs to be considered when evaluating the occurrence and distribution of elements among sites. Guidelines are presented in this appendix that allow for meaningful comparisons of intersite-chemical data for lower-order streams.

Field Collection and Sample Processing

Sample-collection and processing variability has been used to establish quality-assurance guidelines for making intersite comparisons for element concentrations. These guidelines will help to determine if differences in element concentrations between sites were real or if the the differences were within the variability associated with the sample-collection and sample-processing techniques. Separate guidelines were derived for making intersite comparisons between lower-order stream sites and for making intersite comparisons between lower-order stream sites and higher-order stream sites. The latter are more complicated, however, because sieving techniques differ between lower- and higher-order streams. Techniques to adjust for sample-collection and processing variability will be presented in the following sections of this appendix.

Sample-Collection Variability

Sample-collection variability has been used to develop quality assurance guidelines for making intersite comparisons of element concentration for lower-order stream sites. Sample-collection variability was estimated by calculating the mean-relative difference and the statistical-tolerance interval from the on-site variability (relative difference, in percent, between an element concentration from a randomly selected sampling site and a second site located 300 ft upstream) quality-assurance data. On-site variability was selected over analytical precision and cross-section variability as an estimate of sample-collection variability, because it represents the variation in element concentrations that occur in the vicinity of lower-order-stream sampling sites. As would be expected, the chemical variability within a sampling grid generally increases as follows: cross-section variability is less than on-site variability which is less than within-sample-grid variability (fig. B1). Although the within-sample-grid variability generally exceeds on-site variability, within-sample-grid variability was eliminated as a potential quality-assurance guideline. The large within-sample-grid variability was commonly attributed to the second (within-sample-grid) random sample falling within a different geologic unit or within localized areas of mineralization within the same geologic unit.

On-site variability was selected after first determining it was independent from the geology in which the sampling site resides as well as being independent from changes in element concentration at the sampling sites. The independence of on-site variability relative to small, medium, and large element concentrations as well as to geologic units is typified by antimony, arsenic, chromium, and zinc (fig. B2).

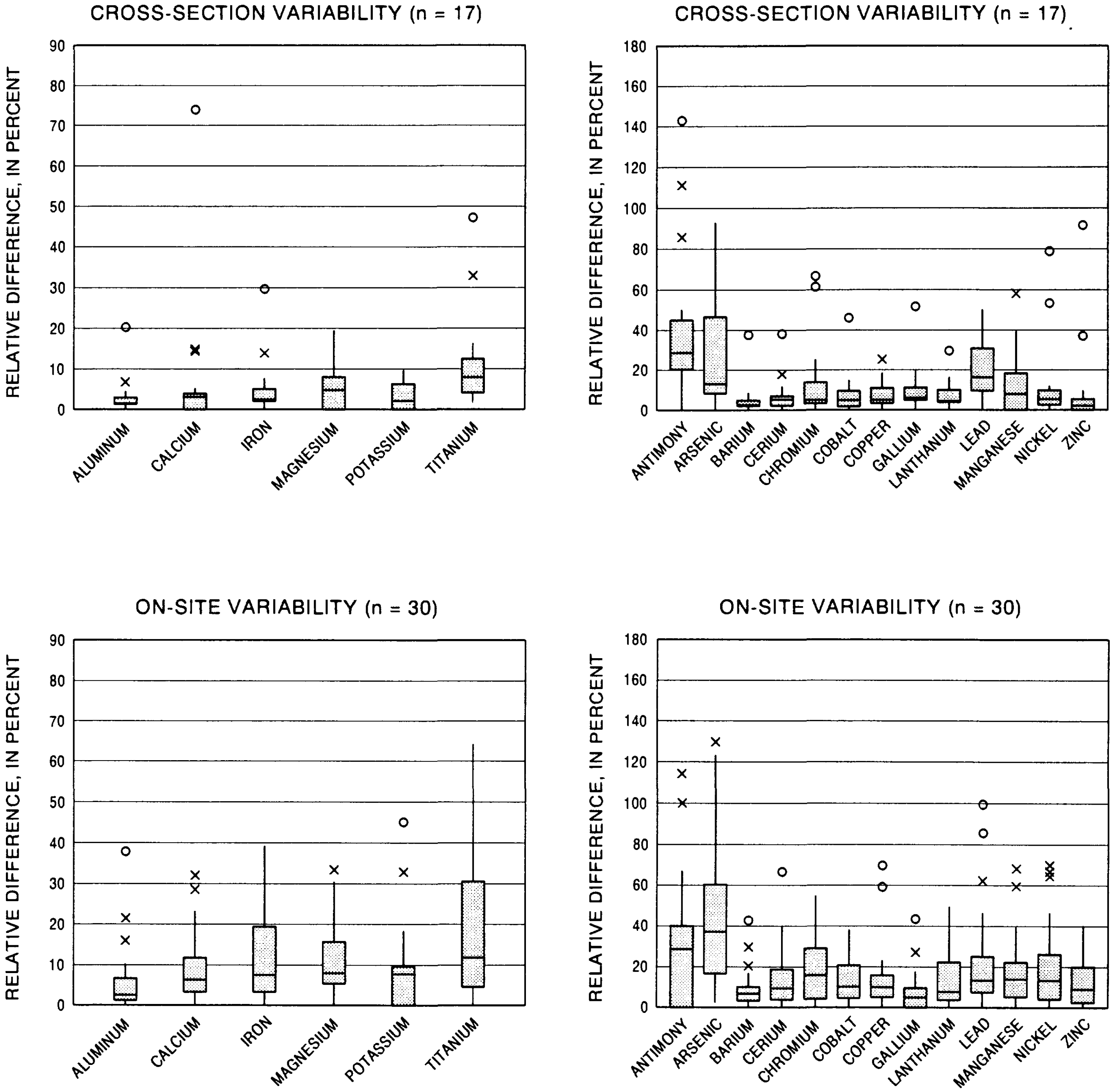
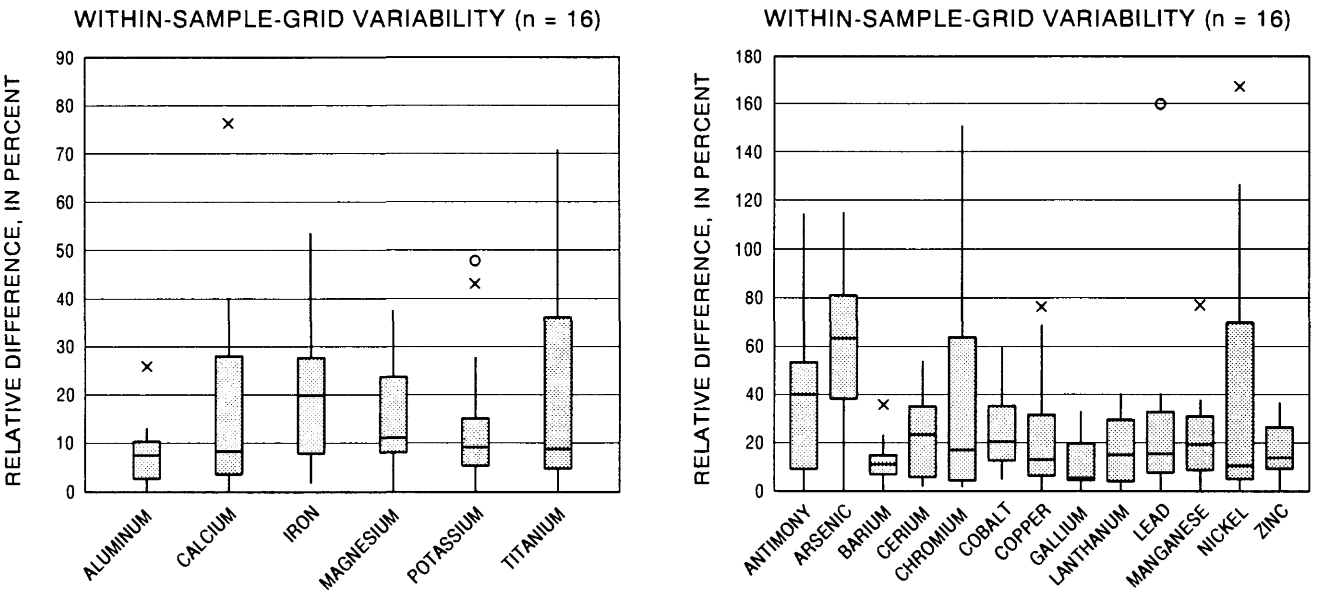


Figure B1. Variability of major- and minor-element concentrations from duplicate samplings of streambed sediment, Yakima River Basin, Washinton, 1987. (Cross-section variability equals duplicate samplings of a single cross section; on-site variability equals variability between a randomly selected site and

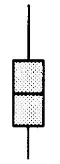


EXPLANATION

Element concentration--Interquartile range equals the value of the 75th percentile minus the value of the 25th percentile.

o More than 3 times the interquartile range from the 75-percentile value

× 1.5 to 3 times the interquartile range from the 75-percentile value



Less than 1.5 times the interquartile range from the 75-percentile value

75-percentile value

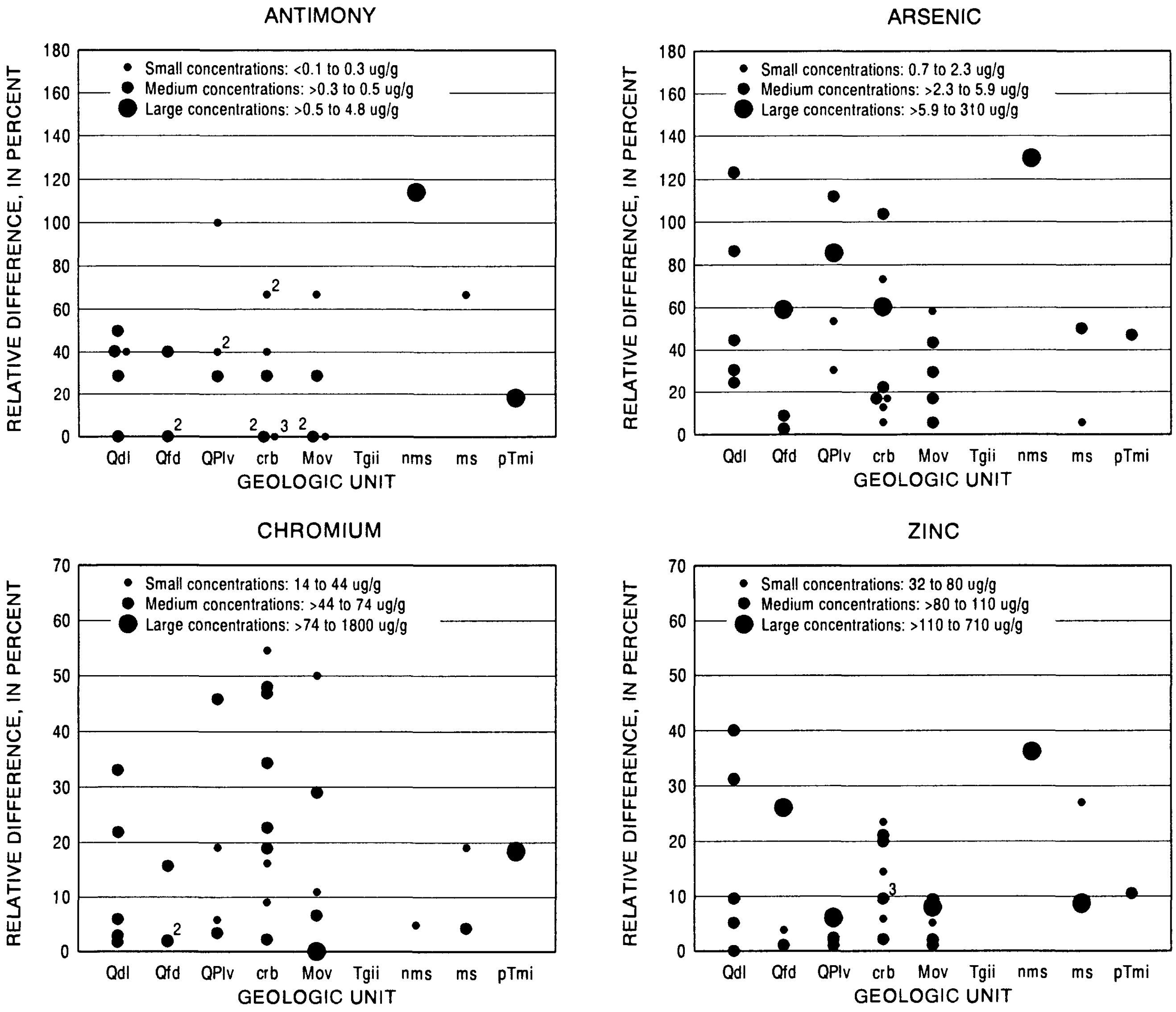
Median value

25-percentile value

Less than 1.5 times the interquartile range from the 25-percentile value

n Number of duplicate determinations for each element

a site located 100 meters up-stream; within-sample-grid variability equals variability from sampling two random locations within one sampling grid.)



EXPLANATION

	Geologic unit
Qdl	Quaternary deposits and loess
Qfd	Quaternary flood deposits
QPlv	Quaternary and Pliocene volcanic rocks
crb	Columbia River Basalt Group rocks
Mov	Miocene and older volcanic rocks
Tgii	Tertiary granitic and intermediate intrusive rocks
nms	Nonmarine sedimentary rocks
ms	Marine sedimentary rocks
pTmi	Pre Tertiary metamorphic and intrusive rocks

ug/g equals micrograms per gram

Numbers which have been placed next to symbols represent cases where more than one data pair was used to calculate relative difference.

Figure B2. On-site variability of antimony, arsenic, chromium, and zinc, relative to geology and element concentration, Yakima River Basin, Washington, 1987. (On-site variability equals relative difference in percent between a randomly selected site and a site located about 300 feet upstream; small concentrations represent the minimum to 25th percentiles, medium concentrations represent the 25th to 75th percentiles, and large concentrations represent the 75th to 100th percentiles of the on-site variability data.)

Comparisons between "among-batch precision" (see app. A, fig. A1) and "on-site variability (see fig. B1) data show that "among-batch precision" (split samples, randomly submitted among sample batches) data account for approximately two-thirds of the "on-site variability"--at the 75th percentile, percent-relative difference. For example, the 75th percentile, percent-relative difference for arsenic "among-batch precision" data is 50 percent (see app. A, fig. A1), whereas, the corresponding value for "on-site variability" is 60 percent (fig. B1). Thus, analytical precision accounts for most of the on-site variability.

Relative differences were calculated for each of the 30 on-site variability data pairs. Relative differences were made to approximate a "normal distribution" by log transformation. For each element, relative difference has been expressed as a mean relative difference and as a statistical tolerance interval (table B1). The statistical tolerance interval has been described by Taylor (1987, p. 31) and is used in this report as a method of calculating the minimum and maximum relative difference (in percent) that brackets at least 90 percent of the distribution of relative differences at a significance level of $\rho = 0.1$. The magnitude of the range for the statistical tolerance interval is indicative of the amount of on-site variability. For example, the large ranges, as well as the large means, for the on-site variability of relative differences for arsenic, antimony, and cerium indicate considerable on-site variability for concentrations of the aforementioned elements.

Meaningful comparisons of intersite data for lower-order streams require that estimates of sample-collection variability be applied to element concentrations measured in this study. This is accomplished by using either the mean relative difference or the maximum value from the statistical tolerance interval to estimate sample-collection variability(table B1). The selection of the latter would yield the most stringent guideline for making intersite comparison. The X term in equation 1 below is the measured element concentration at a lower-order site and the Y term is the concentration limit for the measured element concentration X.

$$\text{Sample-collection variability} = \left[\frac{|X - Y|}{\left(\frac{X + Y}{2} \right)} \right] \text{x } 100 \qquad (1)$$

Because the numerator of equation 1 contains an absolute value term, an upper and lower concentration limit exists for each measured element concentration. As an example, consider the intersite comparison of arsenic concentrations at sites A and B. The sites have arsenic concentrations of 5.0 and 20.0 μg/g, respectively. The estimate for sample-collection variability for each concentration is 30 percent (table B1). Thus, the site A upper and lower concentration limits were calculated by solving for X in equations 2 and 3, respectively.

$$\text{Site A; upper limit:} \quad \left[\frac{X\ \mu g/g - 5.0\ \mu g/g}{\left(\frac{X \mu g/g + 5.0\ \mu g/g}{2} \right)} \right] \text{x } 100 = 30 \text{ percent} \qquad (2)$$

Table B1.--Estimates of sample-collection variability for lower-order streams in the Yakima River Basin, Washington, 1987

[Estimates are based on the relative difference, computed from 30 "on-site variability" data pairs; "on-site variability" = relative difference between a randomly selected site and a site located about 300 feet upstream]

Chemical	Relative difference, in percent Mean	 Statistical tolerance interval 1/
Major elements		
Aluminum	5	1 - 25
Calcium	5	1 - 50
Iron	5	1 - 70
Magnesium	5	1 - 60
Potassium	5	4 - 56
Titanium	10	1 - 120
Minor elements		
Antimony	10	0 - 510
Arsenic	30	4 - 250
Barium	5	1 - 41
Cerium	10	1 - 385
Chromium	10	1 - 120
Cobalt	10	1 - 80
Copper	10	1 - 65
Gallium	5	1 - 40
Lanthanum	10	1 - 90
Lead	10	1 - 190
Manganese	10	1 - 105
Nickel	10	1 - 160
Zinc	5	1 - 70

1/ Range of relative differences containing 90 percent of the on-site variability at a significance level of 0.1.

The upper concentration limit for X equals 6.8 µg/g (arsenic),

$$\text{Site A; lower limit:} \quad \left[\frac{5.0\ \mu g/g - X\ \mu g/g}{\left(\frac{X\ \mu g/g + 5.0\ \mu g/g}{2} \right)} \right] \times 100 = 30 \text{ percent} \tag{3}$$

and the lower concentration limit for X equals 3.7 µg/g (arsenic). Similarly solving equation 1, for site B upper and lower concentration limits, yields 27.0 µg/g and 14.8 µg/g arsenic, respectively. Site A and B arsenic concentrations (5.0 µg/g and 20.0 µg/g, respectively) are different because the upper concentration limit (6.8 µg/g) at site A does not overlap the lower concentration limit (14.8 µg/g) at site B.

Sample-Collection and Processing Variability

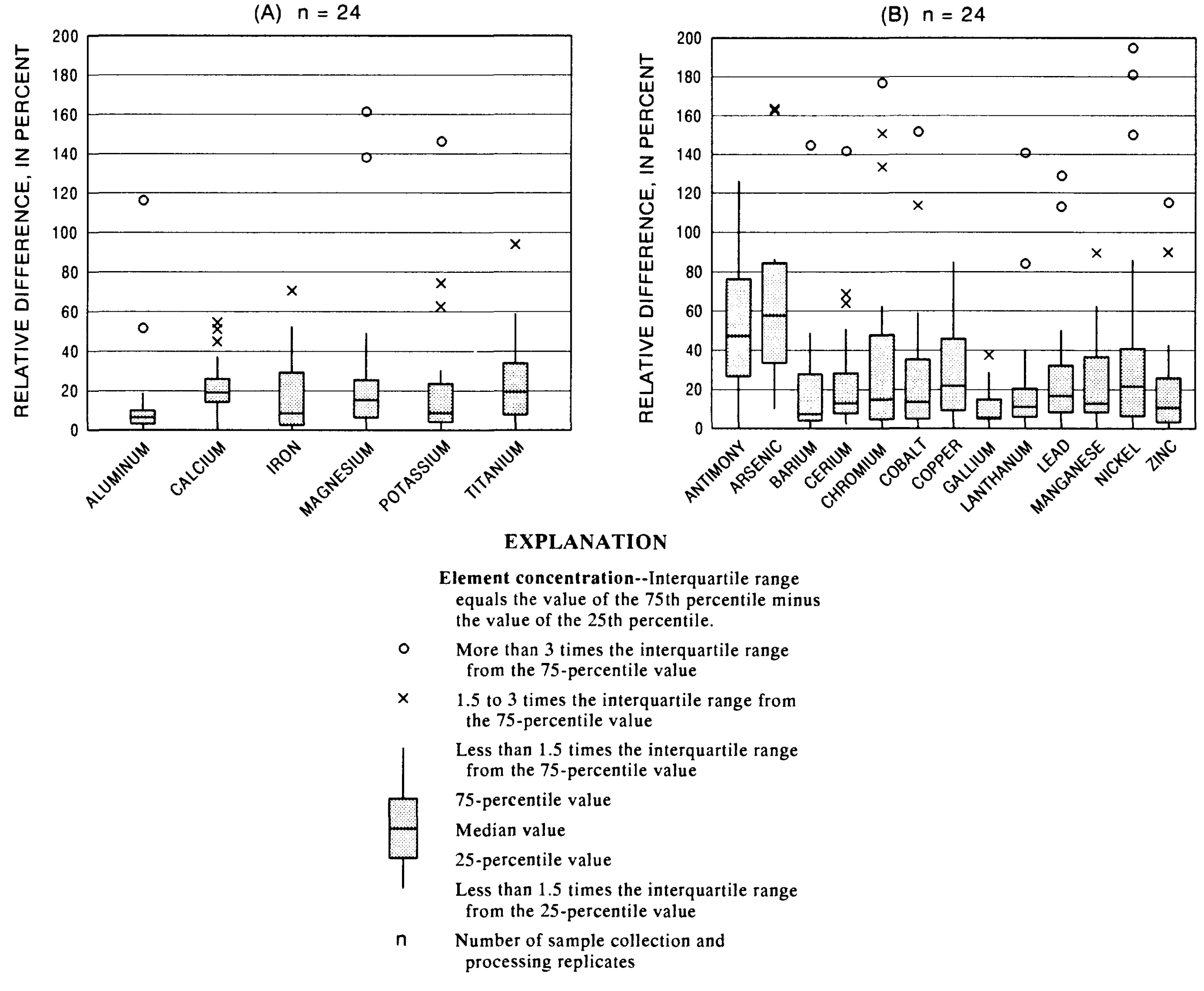
Sample-collection and processing variability has been used to develop quality-assurance guidelines for making intersite comparisons between lower-order-stream sites and higher-order-stream sites. Sample-collection and processing variability included differences attributed to the use of dry sieving for lower-order streambed sediment and wet sieving for higher-order streambed sediment (see approach and methodology sections). It also included, by sample design, analytical variability and cross-section variability. Additionally, lower-order-stream data pairs also included on-site variability. Sample-collection and processing variability should not be used as a direct measure of variability between wet- and dry-sieving techniques.

Sample-processing variability was evaluated from replicate samples collected at 11 lower- and 13 higher-order streams. The lower-order stream replicates consisted of the dry-sieved sample, in addition to a second wet-sieved sample. Conversely, the higher-order stream replicate consisted of the wet-sieved sample, in addition to a second dry-sieved sample. A slightly smaller analytical suite of elements was determined in the sieving comparability study, and all censored data were excluded from analysis.

In an effort to achieve element concentrations that are above MRL's, samples were collected from lower-order sites historically known to be enriched based on data from (Moen, 1969). Conversely, samples collected along depositional reaches of higher-order streams had unknown degrees of enrichment at the time of sampling.

Determining the sample-processing variability for several minor-elements was hampered by large numbers of qualified or censored data. Elements hampered in this way include: beryllium, boron, lithium, neodymium, niobium, scandium, strontium, thorium, titanium, uranium, vanadium, ytterbium, and yttrium. Of the few available uncensored data, only the relative differences between sample-processing replicates for boron and uranium suggest that sample-processing variability may be large.

Sample-collection and processing variability (fig. B3) was found generally to be larger than on-site variability (see fig. B1). Because of these differences, some adjustment is required in order to make intersite comparisons between lower- and higher-order streams. The technique used to make this adjustment differs in one respect from that used to estimate sample-collection variability. The mean-relative difference and statistical-tolerance interval from the 24 replicate samples were used (instead of the 30 on-site variability data pairs) to develop guidelines for sample-collection and processing variability (table B2 and fig. B3). Quality-assurance guidelines were estimated by substituting either the mean-relative difference or the maximum value for the statistical-tolerance interval in place of sample-collection variability in equation number 1. The selection of the maximum value from the statistical-tolerance interval would yield the most stringent guideline for making intersite comparisons. Upper- and lower-concentration limits can be calculated in the manner described earlier for sample-collection variability in appendix B.



EXPLANATION

Element concentration--Interquartile range equals the value of the 75th percentile minus the value of the 25th percentile.

○ More than 3 times the interquartile range from the 75-percentile value

× 1.5 to 3 times the interquartile range from the 75-percentile value

Less than 1.5 times the interquartile range from the 75-percentile value

75-percentile value

Median value

25-percentile value

Less than 1.5 times the interquartile range from the 25-percentile value

n Number of sample collection and processing replicates

Figure B3. Variability of selected major- and (A) minor-element (B) concentrations from sample collection and processing replicates, Yakima River Basin, Washington, 1987. Sample collection and processing variability included differences attributed to the use of dry sieving for lower-order streambed sediment and wet sieving for higher-order streambed sediment. In addition, sample collection and processing variability also included analytical variability and cross-section variability. Relative differences calculated for lower-order streams also include on-site variability.

Table B2.--Estimates of sample-collection and processing variability between lower- and higher-order streams, Yakima River Basin, Washington, 1987

[Estimates are based on relative difference, computed from 24 sample-processing replicates data pairs; estimates for arsenic and mercury were computed from 11 sample-processing replicates for lower-order streams; lower-order-stream sediment was dry sieved, higher-order-stream sediment was wet sieved--see "Sample-collection and processing" section in this report]

Chemical	Relative difference, in percent Mean	 Statistical tolerance interval 1/
	Major elements	
Aluminum	5	0 - 40
Calcium	5	3 - 105
Iron	10	1 - 155
Magnesium	10	1 - 230
Potassium	10	1 - 155
Titanium	15	1 - 215
	Minor elements	
Antimony	30	1 - 860
Arsenic	50	7 - 380
Barium	5	1 - 135
Cerium	15	2 - 130
Chromium	15	1 - 420
Cobalt	10	1 - 270
Copper	15	1 - 240
Gallium	5	1 - 70
Lanthanum	10	1 - 170
Lead	15	1 - 240
Manganese	15	1 - 165
Mercury	50	2 - 1,700
Nickel	15	1 - 375
Zinc	10	1 - 170

1/ Range of relative differences containing 90 percent of the sample-collection and processing variability at a significance level of 0.1.

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