A Synoptic Survey of Trace Metals in Bottom Sediments of the Willamette River, Oregon

River-Quality Assessment of the Willamette River Basin, Oregon



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By David A. Rickert, Vance C. Kennedy, Stuart W. McKenzie, and Walter G. Hines

RIVER-QUALITY ASSESSMENT OF THE WILLAMETTE RIVER BASIN, OREGON

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FOREWORD

The American public has identified the enhancement and protection of river quality as an important national goal, and recent laws have given this commitment considerable force. As a consequence, a considerable investment has been made in the past few years to improve the quality of the Nation's rivers. Further improvements will require substantial expenditures and the consumption of large amounts of energy. For these reasons, it is important that alternative plans for river-quality management be scientifically assessed in terms of their relative ability to produce environmental benefits. To aid this endeavor, this circular series presents a case history of an intensive river-quality assessment in the Willamette River basin, Oregon.

The series examines approaches to and results of critical aspects of riverquality assessment. The first several circulars describe approaches for providing technically sound, timely information for river-basin planning and management. Specific topics include practical approaches to mathematical modeling, analysis of river hydrology, analysis of earth resources—river quality relations, and development of data-collection programs for assessing specific problems. The later circulars describe the application of approaches to existing or potential river-quality problems in the Willamette River basin. Specific topics include maintenance of high-level dissolved oxygen in the river, effects of reservoir release patterns on downstream river quality, algal growth potential, distribution of toxic metals, and the significance of erosion potential to proposed future land and water uses.

Each circular is the product of a study devoted to developing resource information for general use. The circulars are written to be informative and useful to informed laymen, resource planners, and resource scientists. This design stems from the recognition that the ultimate success of river-quality assessment depends on the clarity and utility of approaches and results as well as their basic scientific validity.

Individual circulars will be published in an alphabetical sequence in the Geological Survey Circular 715 series entitled "River-Quality Assessment of the Willamette River Basin, Oregon."

J. S. Cragwall, Jr. Chief Hydrologist

CONTENTS

Abstra	ct	F 1	Examination of study approaches—Continued	Page
	iction		Fractionation of samples at $20\mu m$	_F11
	illamette River basin		Distinction between natural background and pollution	
Ge	ologic overview	2	Zinc	
Wi	llamette River morphology	2	Lead	13
Pos	ssible sources of trace metals	5	Copper	16
Sampli	ng	7	Chromium	16
	mpling medium		Mercury	16
Sa	mpling approach		Cadmium	17
	mpling locations		Fourth Lake	18
	tory procedures and analytical results		Comparison of results to trace-metal concentrations i	
	ysical procedures		rocks and soils	
	nalysis of metals		Summary and conclusions	
	nalytical results		Acknowledgments	
	nation of study approaches		Glossary of selected terms	
Sa	mpling from the visual center of flow	10	References	21
	II	LLUST	RATIONS	
				Page
FIGURI	1. Map of the Willamette River basin, Oreg.,	showing	mining areas and sediment-sampling sites in the Upstrear	n F3
	9 Man and diagram representing the Willer	ootto Div	er, Oreg., showing distinctive hydrologic reaches and eleva	r o
			er, Oreg., showing distinctive hydrologic reaches and eleva	
	3 Man showing sadiment-sampling sites in t	the Tidel	Reach and the Newberg Pool	9
	4 Graphs showing the relation of trace-meta	d concent	rations in <2-mm materials to the percentage by weight of	of
	<20-um materials (A) copper (B) lea	d (C) zir	nc	12
	5 Normal-probability plots of zinc concentra	tions in	<20-μm materials, (A) all Willamette River basin samples	s.
	(B) unpolluted samples			14
	6. Normal-probability plots of trace-metal co	ncentrat	ions in <20-\mu materials, (A) lead, (B) copper	15
	7. Normal-probability plots of trace-metal co	ncentrat	ions in <20 - μ m materials, (A) chromium, (B) mercury	17
				
		TAB	LES	
				Page
TABLE			Willamette River, Oreg	
			River system	
			s from the Willamette River and adjacent waters	
			ons in the <20-\mu materials of bottom sediments from the	
	5. Comparison of trace-metal concentrations	in center	-of-flow samples to cross-sectional samples for the 2 <20-μn	n
			ace-metal concentrations	
			ocks, and soils	
			ottom sediments from the Willamette River and adjacen	
	- 1 V			
			the Willamette River and adjacent waters	
	•			

			Page
Table	12.	Concentrations of major elements in bottom sediments from the Willamette River and adjacent waters	F25
		Trace elements having concentrations in all sediment samples below detection limits of the emmission	1-
		spectrographic method	_ 26
	14.	Concentrations of trace elements in <20-µm materials of bottom sediments from the Willamette River and	d
		adjacent waters	_ 26
	15.	Uses and sources of selected trace metals	_ 27

CONVERSION FACTORS

[Factors for converting English units to the International System of Units (SI) are given below to four significant figures. However, in the text the metric equivalents are shown only to the number of significant figures consistent with the values for the English units]

English	Multiply by	Metric (SI)
ft (feet) ft/s (feet per second) ft/mi (feet per mile) ft³/s (cubic feet per second) mi (miles) mi² (square miles) ton (short, 2,000 lb)	3.048×10^{-1} 3.048×10^{-1} 1.894×10^{-1} 2.832×10^{-2} 1.609 . 2.590 9.072×10^{-1}	m (metres) m/s (metres per second) m/km (metres per kilometre) m³/s (cubic metres per second) km (kilometres) km² (square kilometres) t (tonne)

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ABSTRACT

During September 1973, 44 bottom sediment samples were collected to assess the concentration and distribution of trace metals in the Willamette River, Oreg. The specific objectives were to provide (1) baseline information for future comparison and (2) a basis for determining whether the analyzed metals were present in high enough concentrations to represent an ecological threat.

Aliquots of the 44 samples were size separated at 2 millimetres to exclude gravel-sized materials and at 20 micrometres (μ m) to obtain fractions containing the clay and fine silt materials. The <20- μ m fractions and aliquots of each whole sample were then analyzed by atomic-absorption spectrophotometry and colorimetry for arsenic, cadmium, chromium, copper, lead, mercury, silver, and zinc. A separate aliquot of each <20- μ m fraction was investigated by semiquantitative emission-spectrographic analysis to detect possible anomalous concentrations of 50 elements.

Trace-metal concentrations in the Willamette were generally indicative of a clean environment. The exceptions were a moderate enrichment of zinc, a slight enrichment of copper and lead, and pollution by several metals in an industrial slough. The zinc enrichment resulted primarily from zinc hydrosulfite used as a brightening agent in ground-wood pulp and paper mills. Upon orders from the Oregon Department of Environmental Quality, all mills will cease using zinc hydrosulfite by July 1977. The lead enrichment appeared to result directly from urban drainage, but causes of the elevated copper levels were not apparent. Fourth Lake, an industrial slough near Albany, showed enrichment of 15 elements including uncommon metals such as zirconium, hafnium, yttrium, ytterbium, and tin. However, none of these metals was present in enriched concentrations at any of the downstream sites.

INTRODUCTION

Many materials discharged into river systems are toxic to aquatic organisms when present in critical concentrations. These materials include numerous trace metals (see "Glossary of Selected Terms") and manmade organic compounds such as insecticides, polychlorinated biphenyls (PCB's), herbicides, and certain industrial or-

ganics. Even though such materials are usually discharged to rivers at subtoxic levels, many are capable of being concentrated at successive steps in aquatic food chains in a process called "biological magnification."

Review of industrial-discharge permits for the Willamette River basin indicates that there is very little possibility of toxic industrial organics entering the Willamette River. Furthermore, over the last 10 years, hard pesticides (such as DDT) have not been used in the basin for disease-vector control nor for widespread plant-pest control. In contrast, there are several industrial sources of potentially toxic trace metals in addition to the metals that undoubtedly enter the river in urban runoff. Thus, if a toxicity problem occurred, it would probably result from the accumulation of trace metals.

Prior to this study, few data existed on the content of trace metals in the water, sediment, and food chains of the Willamette River. Data were so sparse as to preclude even a preliminary assessment of whether metal concentrations were low, moderate, or critically high. To partly fill the void, this report presents information on the concentration and distribution of trace metals in the river-bottom sediments.

The objectives of this trace-metal reconnaissance were to provide (1) baseline information for future comparison and (2) a basis for determining whether the analyzed metals were present in high enough concentrations to represent an ecological threat.

The first goal was fully attainable, the second only partly, because scientists presently lack the ability to relate with confidence the concentrations of trace metals in river sediments to the potential for aquatic organism toxicity. The abil-

ity to define such relationships will require intensive research on the modes and chemical forms of metal transport and on the processes of metal uptake and release by sediments and organisms. In addition, definitive information will be needed on the life cycles of aquatic organisms and on their physiological tolerances.

In the absence of definitive information on toxicity relationships, this circular presents a procedure for identifying those trace metals in bed sediments that are present in concentrations indicative of pollution. The procedure involves (1) physical separation of materials <20- μ m in size from bulk sediment samples, (2) trace-metal analysis of the <20- μ m materials, (3) examination of determined metal concentrations through use of probability plots, and (4) comparison of the concentrations with the metal contents of soils and rocks.

To establish a basis for collecting and assessing trace-metal data, the following section provides background information on the Willamette River basin.

THE WILLAMETTE RIVER BASIN

The Willamette River basin, a watershed of nearly 11,500 mi² (29,800 km²) (fig. 1), is located in northwestern Oregon between the Cascade and Coast Ranges. Within the basin are the State's three largest cities, Portland, Salem, and Eugene, and approximately 1.4 million people, representing 70 percent of the State's population (1970 census). The Willamette River basin supports an economy based on timber, agriculture, industry, and recreation and contains extensive fish and wildlife habitats.

The Willamette River forms at the confluence of the Coast and Middle Forks near Eugene and flows northward for 187 mi (300 km) through the 3,500-mi² (9,100-km²) Willamette Valley floor. Tributaries of the Willamette include the Long Tom, Marys, Luckiamute, Yamhill, and Tualatin Rivers, which flow eastward from the Coast Range, and the McKenzie, Calapooia, Santiam, Molalla, and Clackamas Rivers, which flow west-northwest from the Cascade Range. (See fig. 1.)

GEOLOGIC OVERVIEW

On the basis of physiography and geology, the Willamette River basin can be divided into three

north-south provinces: the Cascade Kange, the Coast Range, and the interlying Willamette Valley (Willamette Basin Task Force, Appendix A, 1969).

The volcanic rocks that compose the Cascade Range can be divided into two major groups. The older group consists of basalt and ardesite together with volcanic debris. These rocks have been folded, faulted, and extensively altered. The younger rocks, which form the High Cascades, are derived from more recent basaltic and andesitic lava flows.

The mountains and foothills of the Ccast Range are formed largely by volcanic rocks and by marine sedimentary rocks derived from them. The older volcanic rocks, consisting of basaltic flows and volcanic debris, are interbedded with continental sedimentary rocks. The marine sedimentary rocks consist of sandstone, shale, and mudstone.

The Willamette Valley is an alluvial lowland framed by the upland volcanic and sedimentary rocks. Much of the valley is covered by sandy to silty terrace deposits that settled from water ponded in a great glaciofluvial lake. Most of the materials in these deposits originated from upstream areas of the Columbia River basin (Glenn, 1965). The alluvial deposits that border existing rivers were derived largely from the surrounding mountains. These deposits consist of interbedded layers of clay, silt, sand, and gravel.

WILLAMETTE RIVER MORPHOLOGY

The bed of the Willamette River drops from an altitude of 435 ft (133 m) at Eugene to slightly below mean sea level at Portland (fig. 2). The river comprises three distinctive reaches whose physical characteristics govern the hydraulics of flow and therefore the patterns of deposition, channel scour, and sediment transport.

The Upstream Reach (fig. 2 and table 1), extending for 135 mi (217 km) from Eugene to above Newberg, is characterized by a meandering channel. The river is shallow and the bed is composed almost entirely of cobbles and gravel which during summer are covered with biological growth. During low-flow conditions, average stream velocity in the Upstream Reach is more than 7 times that of either of the two downstream reaches (table 1). During floods, velocities are

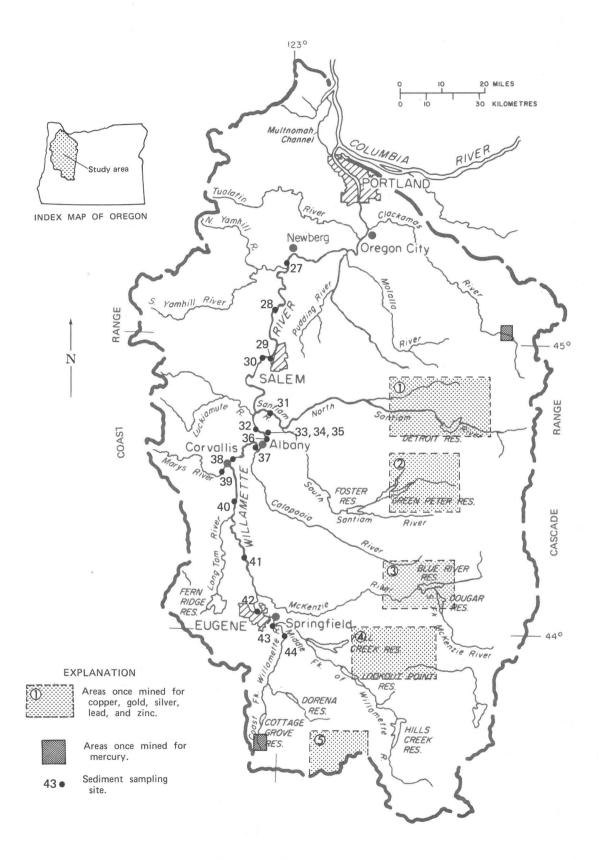


Figure 1.—Map of the Willamette River basin, Oreg., showing mining areas and sediment-sampling sites in the Upstream Reach (above the Newberg Pool).

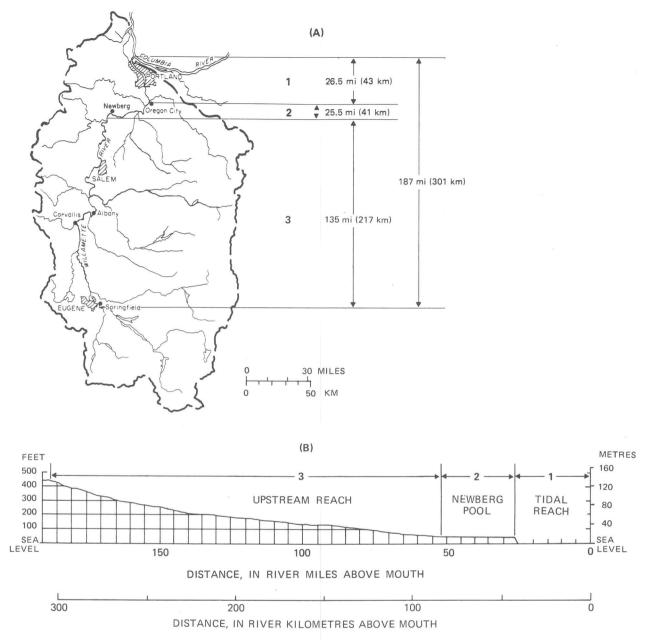


FIGURE 2.—Willamette River, Oreg. A, Distinctive hydrologic reaches. B, Elevation profile.

sufficiently high to transport large quantities of cobbles and gravel as bedload. Morphologically, this upstream section of the Willamette is an "eroding" reach.

The Newberg Pool extends for 25.5 mi (41.0 km) from above Newberg to the Willamette Falls. The deep, slow-moving pool can be characterized hydraulically as a large stilling basin behind a weir (Willamette Falls). The pool is a depositional reach, as evidenced by the elevation profile (fig. 2), average low-flow velocity (table 1),

and the presence of fine bottom sediments.

The Tidal Reach, covering the lower 26.5 mi (42.6 km) of the river, is affected by tides and during spring and early summer by backwater from the Columbia River (Velz, 1961). The Tidal Reach is extensively dredged to maintain a 40-ft (12-m) deep navigation channel from the mouth to about river mile (RM) 14, or river kilometre (RK) 22. During the summer low-flow period, net downstream movement is relatively slow, but tidal effects cause flow reversals twice daily and

Table 1.—Selected physical characteristics of the main stem Willamette River, Oreg. [Characteristics refer to summer low-flow conditions of $6\cdot 10^3$ ft³/s at Salem]

Reach (see fig. 2)		Length	Approximate bed slope (ft/mi)	Bed material	Representative midchannel water depth (ft)	Average velocity (ft/s)	Approximate traveltime in reach (days)
Tidal Reach	(1)	26.5	< 0.1	Intermixed clay, sand, and gravel	40	10.16	10.0
Newberg Pool	(2)	25.5	.12	Intermixed clay, sand, and gravel with	25	¹ .40	3.9
Upstream Reac	h (3)	135	2.8	some cobbles. Mostly cobbles and gravel	7	$^{2}2.9$	2.8

¹Calculated by volume displacement method using channel cross-sectional data. ²Calculated from dye study by U.S. Geological Survey (Harris, 1968).

large changes in velocity. Low-flow hydraulics are most complex in the lower 10 mi (16 km) where, depending on hourly changes in tide- and river-stage conditions, Willamette River water may move downstream or Columbia River water may move upstream. Owing to morphological characteristics and the hydraulic conditions, the subreach between RM's 10 and 3 is the primary depositional area of the Willamette River system.

POSSIBLE SOURCES OF TRACE METALS

Besides natural geological background, the possible sources of trace metals in the Willamette River basin include industrial activities, urban runoff, municipal waste-water discharges, and old mining areas. Table 2 shows the river-mile location on the Willamette of most known or potential sources of metals. The table also indicates the discharge locations of tributaries.

In the Portland metropolitan area, the land corridor along the Willamette is used for many industrial and shipping activities which represent possible direct sources of metals (table 2). In addition, the city of Portland is served by a combined sewerage system that during intense rainfall overflows into the Willamette carrying metals from raw sewage, various industries, and street runoff. (Dry weather flow is diverted via the municipal treatment plant to the Columbia River.) Moreover, between RM's 17 and 27.5, street runoff periodically enters the Willamette through a separate storm-drainage system.

Farther upstream, storm drainage and municipal secondary effluents represent additional trace-metal sources in other urban areas.

Pulp and paper production is a major industry of the Willamette River basin. For many years, zinc hydrosulfite has been used as a brightening agent in the ground-wood pulping process at three large mills (table 2). The three plants and their 1973 zinc loadings to the Willamette were

Publishers Paper Co. at Newberg (RM 49.2), 71 tons (64 t) (Zenon Rozycki, Publishers Paper, oral commun., 1975); Publishers Paper Co. at Oregon City (RM 28.0), 89 tons (81 t); and Crown Zellerbach Corp. at West Linn (RM 27.6), 74 tons (67 t) (Herman Amberg, Crown Zellerbach, oral commun., 1975). In compliance with orders of the Oregon Department of Environmental Quality, Publishers Paper switched to a nonzinc brightening agent at both plants in spring 1974, and Crown Zellerbach will switch by July 1977.

There are seven mineralized areas in the Willamette River basin which at one time or another were commercially mined (Oregon Department of Geology and Mineral Industries, 1951; Willamette Basin Task Force, Appendix A, 1969). Mercury was once mined from the Black Butte area on the Coast Fork above Cottage Grove Reservoir and from the Oak Grove Fork area in the headwaters of the Clackamas River.

The five other areas were mined at various times for copper, gold, lead, silver, and zinc. The areas and their drainage tributaries are (see fig. 1):

- 1. North Santiam district; tributary to the Santiam River.
- 2. Quartzville district; tributary to the Santiam River.
- 3. Blue River district; tributary to the McKenzie River.
- 4. Fall Creek district; tributary to the Middle Fork Willamette.
- 5. Bohemia district; tributary to the Coast Fork Willamette.

No natural deposits of cadmium or chromium are known to exist in the Willamette River basin. No commercially exploitable source of arsenic exists, but high concentrations of this metal do occur in the ground water of Lane County at the southern end of the basin (Goldblatt and others, 1963).

Table 2.—Possible sources of trace metals in the Willamette River system¹

Location ²	Industries and industrial waste-water effluents	Municipal, secondary waste-water effluents ³	Tributaries and urban runoff
0-6.0			Intrusion of Columbia River
Columbia Slough	Calcium carbide and related		sediments.
(1.2).	products. Shipping terminals.		
3.0-8.0	Oil tank forms		
3.3	- Agricultural organic chemicals		Multnomah Channel.
7.0	Agricultural organic chemicals (Cr, Cu, Pb, Ni, Zn).		Carlinal arms
7.4	Chlorine and related products		Combined sewer overflows from Portland (Pb and
Swan Island Channel	(Cr, Zn). Drydocks and ship repairs.		others).
(8.1). 11.0	Coment plant		
13.7	Ship salvage yards.		
17.0–27.5			Urban storm drainage from
		Milwaukie—1.9 Mgal/d (Cr, Ni, and Zn from plating wastes). Oak Lodge—1.8 Mgal/d.	Portland metropolitan area (Pb and others).
		Tryon Creek—3.7 Mgal/d.	
24.1		West Linn—0.7 Mgal/d.	
25.2	Constant	Oregon City—2.8 Mgal/d.	
27.8	Ground-wood pulp and paper mill—13.5 Mgal/d (Zn).	West Linn—0.5 Mgal/d.	
28.0	Ground-wood and magnesium sulfite pulp and paper mill—	Ū	
28.5		Cl 0.2 M1/d	Tualatin River.
35.6		Canby—0.3 Mgal/d.	Molalla River.
48–51			Urban storm drainage from Newberg (Pb and others).
	Ground-wood and magnesium sulfite pulp and paper mill— 11.7 Mgal/d (Zn)		
			Yamhill River.
78.2		Salem—22 Mgal/d.	rammir River.
80.5–87			Urban storm drainage from Salem (Pb and others).
85.2	Ammonium sulfite pulp and		
107.7			Luckiamute River.
108.0	Metal extraction and processing,		Santiam River.
Fourth Bake (117.0).	Kraft pulp and paper mill, resin plant, wood flour mill, oil tank farm (Zr, Hf, Ta, Nb, V, W, Mo, and others).4		
117.9		Albany—5 Mgal/d.	
118-120			Urban storm drainage from Albany (Pb and others).
119.6			Calapooia River.
			Urban storm drainage from Corvallis (Pb and others).
130.8		Corvallis—6 Mgal/d.	
132.0	TT		Marys River.
132.2	Hardboard mill. Kraft pulp and paper mill.		
148.0			Long Tom River.
174–187			Urban storm drainage from Eugene-Springfield (Pb and others).
178.6		Eugene—13 Mgal/d.	McKenzie River.
184.3		Springfield—5 Mgal/d.	
187.0			Confluence of Coast Fork and Middle Fork.

¹Specific metals associated with specific sources are identified in parentheses by their chemical symbols. (See table 11.) ²River-mile location or river-mile interval unless specifically named. ³Approximate flows for summers of 1973 and 1974. ⁴See table 14, samples 33–35.

Fourth Lake, near Albany, is worthy of special mention. The lake, which is actually a slough, receives drainage from 11 industries, including the metal-extraction and processing operations at Teledyne-Wah Chang. Wah Chang extracts zirconjum and hafnium from imported ores and produces various alloys from these metals and from tantalum and niobium, which are purchased in purified form (Tom Nelson, Teledyne-Wah Chang, oral and written communs., 1975). The imported ores also contain scandium, yttrium, lanthanum, and ytterbium. Additional metals used in production of alloys include molybdenum, tungsten, tin, chromium, and nickel. At one time, Wah Chang also used silver in the production of a special tungsten alloy.

From the information in table 2 and figure 1, it can be seen that the potential sources of trace metals to the Willamette River are generally known. To determine the effect of these sources on trace-metal occurrence, it was necessary to develop approaches for the collection and preparation of samples.

SAMPLING

SAMPLING MEDIUM

Bottom sediments have two major characteristics that make them the best sampling medium for conducting a synoptic basinwide study of trace-metal occurrence. First, fine sediments can usually be found and sampled from most reaches of most large rivers. Second, because trace metals associate strongly with particulate materials, bottom sediments can act as metal accumulators during periods of low velocities when the riverbed is not being scoured. During such periods, the riverbed is a depository for incoming sediments, and these, as well as the sediment already in place, can serve as scavengers of dissolved metals from the passing water. Bottom sediments collected during a stable low-flow condition thus provide the opportunity to obtain information on the presence and distribution of metals over an extended period of time. Such information can be used to delineate areas of anomalously high concentrations and possible sources.

Water, suspended sediment, and aquatic organisms (in contrast to bottom sediment) are less desirable as sampling media for a synoptic trace-metal reconnaissance. In some ways, water is the least desirable because a water sample collected from a flowing river represents the condi-

tions that exist at a single instant in time. If the discharge of metal wastes is intermittent (as is often the case), periodic water samples collected downstream may show no pollution. Moreover, even if metal discharge is constant, water samples collected at distant sites may show little or no pollution because the metals could well be adsorbed onto sediment particles during downstream passage.

Suspended sediment can be an excellent medium for determining trace-metal occurrence during specific runoff events. However, suspended sediment is too transitory to provide a sound sampling basis for synoptic basinwide surveys.

Aquatic organisms, although the focus of toxicity studies, represent a poor medium for determining the basinwide occurrence of trace metals. The major drawback to this medium is the improbability of finding enough of specific life stages of selected organisms at all predetermined sampling sites.

Therefore, for this study, bottom sediment was selected as the preferred sampling medium.

SAMPLING APPROACH

Sampling sites were selected to provide (1) general coverage of the entire main stem of the Willamette and (2) specific coverage of locations below possible trace-metal sources (table 2). River-velocity data and low-altitude aerial photographs (U.S. Army Corps of Engineers, 1973) were used to determine areas where fine materials were likely to be found under low-flow conditions.

The objective of field sampling was to obtain sufficient fine-grained material from each site for the laboratory analyses. In the Tidal Reach, satisfactory samples were obtained with a Petersen dredge by compositing two or three bites at the visual center of flow. At two special sites (see "Sampling from the Visual Center of Flow"), additional samples were collected at predetermined cross-sectional points.

The visual center of flow was used in preference to the center of the cross section because, in many subreaches, the channel and most of the flow is near one bank. At each location, the specific sampling site was determined by combining information provided by aerial photographs (U.S. Army Corps of Engineers, 1973) with information attained by visually estimating the water discharge at various points in the cross section.

In many upstream subreaches, the riverbed is almost completely covered with gravel. In these locations, the sampling approach consisted of searching with an Ekman dredge for small areas of fine-grained sediments. The intent was to determine the relative occurrence of metals in each subreach by using the fine materials in bottom sediments as a natural trace-metal concentrator.

SAMPLING LOCATIONS

Bottom-sediment samples were collected from 44 sites (figs. 1 and 3) in late September 1973 after a period of more than 4 months of steady low flow. Thirty-one samples were taken from the Willamette River, and 13 from tributaries, sloughs, and other adjacent waters. Site descriptions and gross physical characteristics of the 44 samples are presented in table 9. (Tables 9–15 are presented at the end of this report.)

Geographically, 19 of the sites were associated with the 26.5-mi (42.6 km) Tidal Reach (see fig. 2 and table 1), 7 with the 25.5-mi (41.0-km) Newberg Pool, and 18 with the 135-mi (217-km) Upstream Reach. The sampling density was designed to be greatest in the Tidal Reach because this section of the river is the most highly urbanized and, as previously noted, the subreach between RM's 10 (RK 16) and 3 (RK 5) is the primary depositional area of the Willamette River system.

LABORATORY PROCEDURES AND ANALYTICAL RESULTS

PHYSICAL PROCEDURES

The 44 samples were sieved through a plastic 2-mm (millimetre) sieve to exclude the coarse materials. The weight, texture, and visual nature of >2-mm materials were recorded; the materials varied from sample to sample but included gravel, wood, paper, and snails. (See table 9.) Aliquots of air-dried <2-mm materials were size fractionated to determine the percentages of sand, silt, and clay and to obtain a $<20-\mu m$ fraction for analysis of metals. A special air-jet device (Chu and Davidson, 1953) was used to physically disperse the sediments and thereby avoid the metal contamination that would result from use of standard pretreatment chemicals (Jackson, 1956). Particle-size analyses were made by the pipette method (Jackson, 1956) and the fractionations at 20 μ m by sedimentation and decantation.

The <20- μ m materials contain the clay and fine-silt fractions from each whole sample. In grain size, these materials are roughly comparable to claystones and shales, and also to the fine fractions of soils. Fractionation at 20 μ m therefore provided a basis for comparing the tracemetal results to existing geochemical data.

ANALYSIS OF METALS

Fifty elements were investigated using a sixstep semiquantitative emission-spectrographic method developed for geochemical exploration (Myers and others, 1961). Emission spectroscopy determines elements within the structure (crystal lattice) of minerals in addition to those held at the surface in exchange sites, oxide coatings, and organometallic complexes. Thus, the method yields trace-metal results higher than the concentrations available to aquatic organisms (biologically available) or those determinable by simple acid extraction. The bulk of many trace metals in sediments is associated with iron and manganese hydrous oxides that coat the sediment particles (Jenne, 1968). However, in uncontaminated sediments, 25 percent or more of certain trace metals could be present within crystal lattices.

Because of the inclusion of crystal-lattice metals and the semiquantitative analyses, the emission-spectrographic method was used primarily for the scanning of trace-metal occurrence. The intent of its use was to determine if any of the wide array of investigated metals was present in anomalously high concentrations. Only the <20- μ m fractions of samples were analyzed by this method.

Atomic-absorption spectrophotometry was used to determine more quantitatively the concentrations of cadmium, chromium, copper, lead, mercury, silver, and zinc; colorimetry was used for arsenic. These eight metals were specifically selected for intensive analysis because they are widespread byproducts of man's activities (table 15) and are potentially toxic to aquatic organisms. The wet chemical methods used to determine the metals were developed for geochemical prospecting (Ward and others, 1963 and 1969). These methods are less sensitive than others presently available but are adequate for a reconnaissance. Both whole samples (<2 mm) and the prepared $<20-\mu m$ fractions were analyzed for the eight metals.

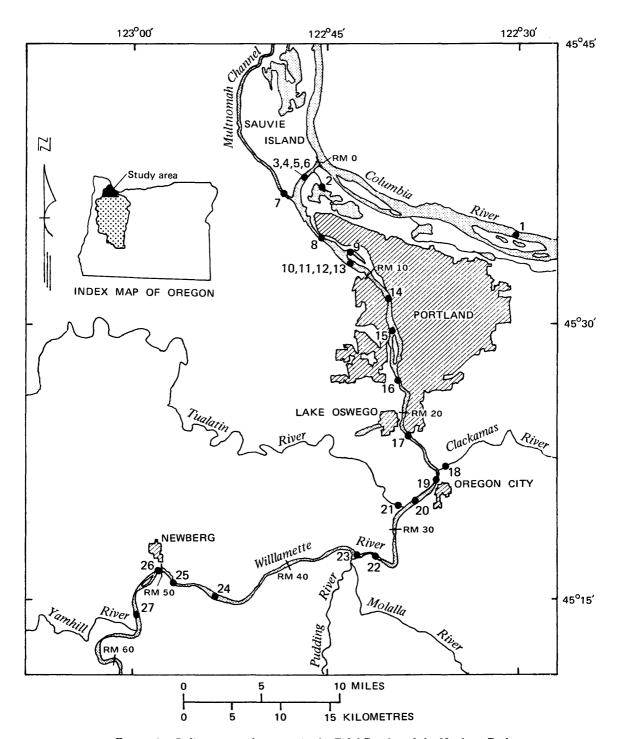


FIGURE 3.—Sediment-sampling sites in the Tidal Reach and the Newberg Pool.

ANALYTICAL RESULTS

Results obtained by the wet chemical methods are presented in table 3 for both the <2-mm and <20- μ m materials. For easier inspection, the | 10 major elements (table 12) and 40 trace ele-

<20- μ m results are geographically summarized as averages and ranges in table 4.

Emission spectroscopy was used to investigate

Table 3.—Concentrations of trace metals in bottom sediments from the Willamette River and adjacent wcters¹ [Concentrations in parts per million²]

				<2-	mm ma	iterials	4					< 20)-μm m:	aterials			
Sample number	Site ³	As	Cd	Cr	Cu	Pb	Hg	Ag	Zn	As	Cd	Cr	Cu	Pb	Нg	Ag	Zn
1	Columbia River	10	1	65	5	5	0.15	< 0.5	75	20	4.5	60	95	70	0.90	1.5	460
2	Columbia Slough	10	1	80	10	5	.17	<.5	140	20	2	60	35	35	.11	.5	270
3	1.5	10	.5	85	10	20	.10	<.5	195	10	2.5	80	40	40	.13	.5	340
4	1.5	<10	.5	90	10	20	.27	<.5	210	10	2	50	40	40	.09	.5	350
5	1.5	<10	5	100	15	10	.09	<.5	215	10	1	70	45	40	.10	.5	340
6	1.5	20	1	90	15	10	.08	<.5	215	20	2	60 60	40 35	35 35	.03 .07	.5 .5	340 370
7	Multnomah Channel	20	.5	55	5	5	.08	<.5	150	$\frac{20}{20}$	1.5	60	35 45	40	.14	.5 .5	310
8 9	6.0 Swan Island Channel	10	.5 1	55	5	10	.14	<.5	$\frac{145}{215}$	20	1	50	60	35	.12	.5	315
10	8.5	$\frac{20}{10}$.5	70 80	25	35	.11	<.5 <.5	185	10	1	50 50	40	25	.03	.5	260
11		10	.5 .5	75	15 15	$\frac{10}{30}$.11	<.5	$\frac{165}{225}$	10	1	50	40	35	.03	.5	315
12	8.5	10	1.5	65	10	20	.13	<.5	205	10	1	50	35	40	.22	.5	335
13	8.5	10	.5	70	15	$\frac{20}{20}$.20	<.5	180	10	.5	60	40	35	.31	.5	260
14	11.7	10	.5	55	5	5	.10	<.5	155	10	1	50	50	90	.34	1	445
15	13.7	10	1.5	65	10	15	.10	<.5	175	10	î	60	50	40	.18	î	395
16	17.0	10	.5	70	10	20	.19	<.5	225	10	ī	50	45	25	.05	ī	470
17	21.1	10	.5	60	10	10	.16	<.5	215	20	[^] .5	60	55	40	.20	ī	1215
18	Clackamas River	10	.5	90	5	5	.07	<.5	70	10	1	60	30	20	.19	.5	135
19	25.6	10	.5	65	5	10	.08	<.5	180	20	.5	50	70	80	.16	.5	475
20	27.9	10	.5	70	5	5	.08	<.5	140	10	1	50	35	20	.11	.5	295
21	Tualatin River	10	1	65	5	15	.17	<.5	85	10	1.5	60	40	70	.31	.5	245
22	34.1	10	.5	75	10	10	.26	<.5	155	10	1	50	35	20	.26	.5	215
23	34.9	10	.5	70	5	5	.15	<.5	110	20	.5	60	35	20	.16	.5	210
24	45.8	10	.5	65	10	10	.13	<.5	130	10	.5	50	35	20	.27	.5	175
25	48.6	10	.5	75	10	10	.16	<.5	120	10	.5	50	35	30	.24	1	185
26	50.2	<10	1	65	15	20	.12	<.5	130	10	.5	50	35	35	.05	1	145
27	54.0	10	.5	80	15	15	.25	<.5	125	10	.5	50	35	30	.26	1_	140
28	69 ()	10	1	70	5	5	.14	<.5	85	10	.5	50	35	20	.29	.5	130
29	Boise Cascade Slough	10	1	65	10	60	.14	<.5	145	10	1_	50	35	80	.08	.5	165
30	86.7	10	.5	60	10	5	.08	<.5	80	10	.5	60	40	40	.09	.5 .5	$\frac{140}{125}$
$\frac{31}{32}$	Santiam River	10	.5	60	5	5	.14	<.5	80	10	.5	40 60	35 30	25 10	.05 .09	.ə .5	135
32 33	112.6Head-Fourth Lake	10	.5	80	5	5	.08	<.5 <.5	80	$\frac{10}{10}$	1 1	80	95	80	.12	4.5	185
33 34	Middle-Fourth Lake	40 60	1 1	95 75	30	65	.12		$\frac{190}{185}$	10	.5	80 80	95 95	120	.09	3	185
35	Fourth Lake near confluence	<10	.5	75 80	30 15	100	.80 .16	<.5 <.5	110	10	.5	50	45	25	.02	1	130
36	117.0	10	.5	75	10	15 5	.20	<.5	110	10	1	50	35	20	.38	.5	145
37	120.0	10	.5 .5	70	5	10	.08	<.5	90	20	1	50	30	15	.31	.5	130
38	130.1	10	.5 .5	85	10	5	.12	<.5	95	10	1	50	30	15	.25	.5	115
39	Marys River	10	.5	135	10	5	.18	<.5	100	10	.5	100	55	15	.10	.5	130
40	141.3	10	.5	75	5	5	.08	<.5	100	10	1	50	35	35	.29	.5	160
41	161 2	10	.5	80	5	10	.26	<.5	85	10	î	60	30	45	.13	.5	175
42	178.1	10	.5	65	5	5	.04	<.5	60	10	î	50	30	25	.30	.5	145
43	185.3	10	.5	65	5	10	.11	<.5	80	$\tilde{20}$	ī	50	40	70	.17	.5	120
44	Coast Fork	10	.5	75	15	35	.08	<.5	140	20	.5	50	40	40	.10	.5	120

Samples collected September 18-29, 1973. Analyses by Kam W. Leong using atomic-absorption spectrophotometry and colorimetry.

²Concentrations in parts per million (ppm) by weight are equivalent to milligrams of metal per kilogram dry sediment.

Numbers refer to river-mile locations. Site descriptions are presented in table 9.

The <2-mm materials include the <20-µm fraction

ments. Of the latter, 19 were not detected in any of the 44 samples (table 13), whereas 21 were detected in at least some of the samples (table 14). The emission-spectrographic data agree with the wet chemical data (table 3) and, with the exception of the Fourth Lake and Marys River samples (table 14), indicate the lack of anomalously high concentrations of the less common trace metals. Certain emission-spectrographic data are described in the text, but the following discussions focus primarily on the more quantitative results obtained by the wet chemical methods (table 3).

EXAMINATION OF STUDY APPROACHES

SAMPLING FROM THE VISUAL CENTER OF FLOW

As previously described, the reconnaissance approach to sampling the Tidal Reach was to collect one sample at each site from the visual center of flow. However, at both RM's 1.5 and 8.5, three

additional samples were collected at the cross-sectional quarter points. (See table 9.) Data for the <20- μ m fractions of these samples are presented in table 5.

For each location, the concentrations of the eight metals in the visual center-of-flow sample is compared to the range and average of the three quarter-point samples. The largest differences between the averages and the center-of-flow samples were for arsenic, cadmium, chromium, and mercury at RM 1.5 and for lead, mercury, and zinc at RM 8.5. However, if each of these relative differences is examined in relation to sample-tosample variation among the 44 samples (table 3), the only values that seem anomalous are for mercury at RM 8.5 and possibly for chromium at RM 1.5. Mercury concentrations were the most variable of the eight metals (table 3); therefore, the wide variation in mercury levels at RM 8.5 are consistent with basinwide results.

Table 4.—Geographic distribution of trace-metal concentrations (parts per million) in the <20-\mu m materials of bottom sediments from the Willamette River and adjacent waters1

			Main stem Wi	illamette River					
Metals	All Willamette River basin samples (43) ²	Main stem. river miles 0–187 (31) ²	Tidal Reach, river miles 0–26.5 (14) ²	Newberg Pool, river miles 26.5–52	Upstream Reach, river miles 52–187 (11) ²	Tributaries ³	Off-river sloughs and channels ⁴	Fourth Lake ⁵	Columbia River ⁶
Arsenic:									
Range	10 – 20	10 - 20	10 - 20	10-20	10-20	10-20	10-20		
Average	13	12	13	12	12	12	18	10	20
Cadmium:									
Range	0.5 – 2.5	0.5 – 2.5	0.5 – 2.5	0.5 - 1.0	0.5 - 1.0	0.5 - 1.0	1.0 – 2.0	0.5 - 1.0	
Average	1.0	1.0	1.2	0.7	0.9	0.8	1.4	0.7	4.5
Chromium:									
Range	40–100	50–80	50-80	50-60	50-60	40-100	50-60	50–8 7	
Average	57	55	57	52	53	62	55	70	60
Copper:									
Range	30 – 95	30–70	35 - 70		30-40	30 - 55	35-60	45-95	
Average	42	39	45	35	34	40	41	78	95
Lead:									
Range	10–120	10–90	25 – 90	20 – 35	10-70	15 - 70	35–80	25 - 120	
Average	38	35	43	24	30	34	46	75	70
Mercury:									
Range	0.02 – 0.38	0.03 – 0.38	0.03 – 0.34	0.05 - 0.27	0.09 – 0.38	0.05 - 0.31	0.07 - 0.12	0.02 - 0.12	
Average	0.16	0.18	0.14	0.18	0.23	0.15	0.10	0.10	0.90
Silver:									
Range	0.5 – 4.5	0.5 - 1.0	0.5 - 1.0	0.5 - 1.0	0.5 - 1.0			1.0 – 4.5	
Average	0.8	0.6	0.6	0.7	0.5	0.5	0.5	2.8	1.5
Zinc:									
Range	115 – 1295	115 – 1295	260-1295	145 – 295	115 – 175	120 – 245	165-370	130 – 185	
Average	249	269	419	204	140	151	280	167	460

¹Individual values reported in table 3.

Table 5.—Comparison of trace-metal concentrations (parts per million) in center-of-flow samples to cross-sectional samples for the <20-µm materials1

		River Mile 1.5		River Mile 8.5			
	Center	Cross-section	on samples³	Center	Cross-section samples ⁵		
Metal	sample ²	Range	Average	sample ⁴	Range	Average	
Arsenic	10	10–20	13	10		10	
Cadmium	2.5	1–2	1.7	1.0	0.5 - 2.0	1.2	
Chromium	80	50-70	60	50	50-60	53	
Copper	40	40-45	42	40	35 – 40	37	
Leâd	40	35-40	38	25	35 – 40	37	
Mercury	.13	0.03 - 0.10	.07	.03	0.03 - 0.31	.19	
Silver	.5		.5	.5		.5	
Zinc	340	340-350	343	260	260-335	303	

 $^{^1\}mathrm{For}$ specific locations and physical data, see tables 9 and 10. Trace-metal data are compiled from table 3. $^3\mathrm{Sample}$ 3. $^3\mathrm{Samples}$ 4-6. $^4\mathrm{Sample}$ 10.

Although based on limited data, the comparisons in table 5 suggest that the sampling approach for the Tidal Reach (one composite sample from the visual center of flow) provided a reasonable basis for describing trace-metal distributions. A similar examination of data from RM's 8.5 and 1.5 was made using the <2-mm results. For most metals, the concentrations showed a greater degree of cross-sectional variability than was observed in the <20- μ m materials. This greater variability was consistent with measured cross-sectional differences in particle-size composition. (See table 10.)

FRACTIONATION OF SAMPLES AT 20 μm

One reason for obtaining $<20-\mu m$ fractions was

²Number of samples. ³Samples 19, 21, 31, 39, and 44.

⁴Samples 2, 7, 9, and 29. ⁵Samples 33, 34, and 35.

⁶Sample 1.

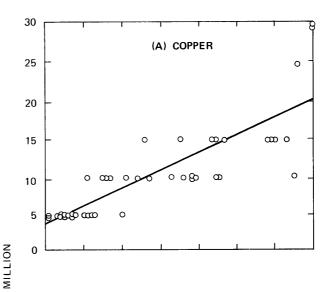
⁵Samples 11-13.

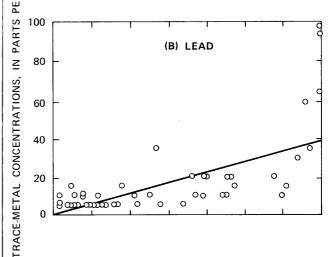
to minimize variations in metal concentrations that normally arise from sample-to-sample differences in the proportion of fine-grained materials. (See above.) This section examines whether or not this objective was achieved.

Table 3 provides a general comparison of metal concentrations in the $<20-\mu m$ materials (clay plus fine silt) with those in the <2-mm materials (combined clay, silt, and sand-sized fractions). The concentrations of chromium, copper, lead, mercury, and zinc are sufficiently above the respective analytical detection limits to permit further comparisons through the computation of ratios. Using all 44 samples, the ratios of the average concentrations in <20-\mu m to <2-mm materials are copper 4.3, lead 2.4, zinc 1.8, mercury 1.2, and chromium 0.8. These ratios suggest that sample-to-sample variations in the proportion of <20-μm materials could largely determine the measured concentrations of copper, lead, and zinc (ratios appreciably different from 1.0), while having little effect on mercury and chromium (ratios close to 1.0).

To investigate this hypothesis, scatter plots (fig. 4) were prepared to show the metal concentrations in the <2-mm samples as a function of the weight percentage of <20-μm materials in each sample (table 10, column 6). As anticipated, the copper, lead, and zinc concentrations show tendencies to increase with increasing percentages of $<20-\mu m$ materials. The scatter of data suggests that the relationship is most definite for copper and somewhat less for lead and zinc. In contrast, similar plots (not shown) for both chromium and mercury showed a random scatter of points. The combined results indicate that sample surface area, as represented by the weight percentage of <20-µm materials, was an important control on the measured concentrations of copper, lead, and zinc but an insignificant control on the occurrence of chromium and mercury.

As further verification, a second set of scatter plots was prepared to relate the concentrations of copper, lead, and zinc in each <20- μ m fraction to the weight percentage of <20- μ m materials in each <2-mm sample. As expected, the plots (not shown) showed a scatter of the 44 points and hence no correlations such as observed for the <2-mm plots (fig. 4). This indicates that the approach of using <20- μ m fractions successfully standardized the variations in metal concentrations that otherwise would have resulted from sample-to-sample differences in the percentages of fine-grained materials. This means that the





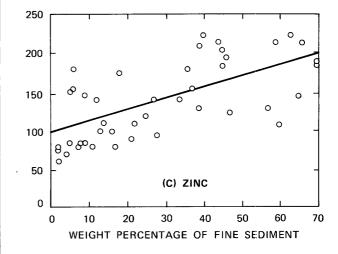


FIGURE 4.—Relation of trace-metal concentrations in <2-mm materials to the percentage by weight of <20-\mu m materials. A, copper, B, lead, and C, zinc.

<20- μ m data can provide a sound comparative basis for detecting trace-metal pollution.

In addition to investigating the effect of particle size, a brief assessment was made of the relationship between selected metals and organic carbon. Scatter diagrams indicated that copper and lead concentrations had some tendency to increase with increasing contents of organic carbon. In contrast, the levels of zinc, mercury, and chromium were not related to organic carbon content.

DISTINCTION BETWEEN NATURAL BACKGROUND AND POLLUTION

If trace metals in Willamette River sediments represented only natural or unpolluted conditions, the concentrations might be expected to follow either a normal or a log-normal distribution (Levinson, 1974). Furthermore, because the fine bottom sediments are derived primarily from the weathering of two chemically related rock types (andesite and basalt), the natural concentrations of the metals might be expected to be distributed as one statistical population.

To test these assumptions for the purpose of distinguishing polluted from unpolluted conditions, the concentrations of chromium, copper, lead, mercury, and zinc in the <20- μ m materials were plotted on probability papers according to the method described by Velz (1970, p. 522–542). Plots were not prepared for arsenic, cadmium, nor silver because the determined concentrations were uniformly low. (See table 3.) In preparing the plots, the Columbia River sample was excluded, providing a total of 43 data points (concentrations) for each metal.

Examination of completed plots showed that the metal concentrations more closely conformed to a normal rather than a log-normal distribution. Normal-probability plots were thus used as the basis of the interpretive approach.

ZINC

The normal-probability plot of zinc concentrations ($<20~\mu m$ materials) defines a two-stage curve with a sharp break at 145 ppm (parts per million) (fig. 5A). The lower segment of the curve represents 15 samples, and the upper segment 27 samples; the concentration of 1,215 ppm from RM 21.1 (table 3) stands by itself far off the upper end of the scale.

From foreknowledge of the potential sources of zinc pollution (see table 2), it was expected that

samples collected downstream from the pulpmill at RM 49.2 would show higher concentrations than those taken from farther upstream. This is confirmed by figure 5A, because the 15 samples represented by the lower segment were collected above RM 50. The concentrations of these samples were replotted in figure 5B, and a well-defined normal distribution was formed, as evidenced by the straight-line fit.

Spatially, the increased levels of zinc in the Newberg Pool and the Tidal Reach corresponded to the locations of the three ground-wood pulpmills (compare tables 2 and 3). The especially high concentrations between RM's 25.6 to 11.7 were below the outfalls of the two mills located between RM's 27 to 28.

The combined knowledge of zinc sources and concentrations indicates that the lower segment in figure 5A represents natural background conditions, whereas the upper segment represents polluted conditions. The spatial distribution of concentrations precludes the possibility that the two-stage curve results from areal differences in geochemistry.

LEAD

Lead concentrations (in <20- μ m materials), like those of zinc, define a two-stage curve when plotted on normal-probability paper (fig. 6A). The lower curve includes concentrations from 10 to 40 ppm and the upper curve concentrations from 45 to 120 ppm. As with zinc, the levels on the upper segment seem to represent pollution.

In contrast to zinc, the enriched lead concentrations occurred at discrete locations (see table 3) rather than in a large downriver zone. Most of the lead-enriched sites were in urban areas suggesting that the pollution resulted largely from storm drainage from streets and roads. (See table 2.) The high-concentration site at RM 185.3 was within the storm-drainage zone of the Eugene-Springfield area, and the sample at RM 161.2 was collected near the highway bridge at Harrisburg. In the Tidal Reach, the samples at both RM's 25.6 and 11.7 were collected just below bridges which cross the Willamette.

Other lead-enriched samples were collected from Fourth Lake, Boise Cascade Slough, and the Tualatin River. Boise Cascade Slough receives garbage-dump leachate which may account for the elevated lead concentration. Also, the elevated lead content of the Tualatin River sample is consistent with the high degree of urban development in the basin.

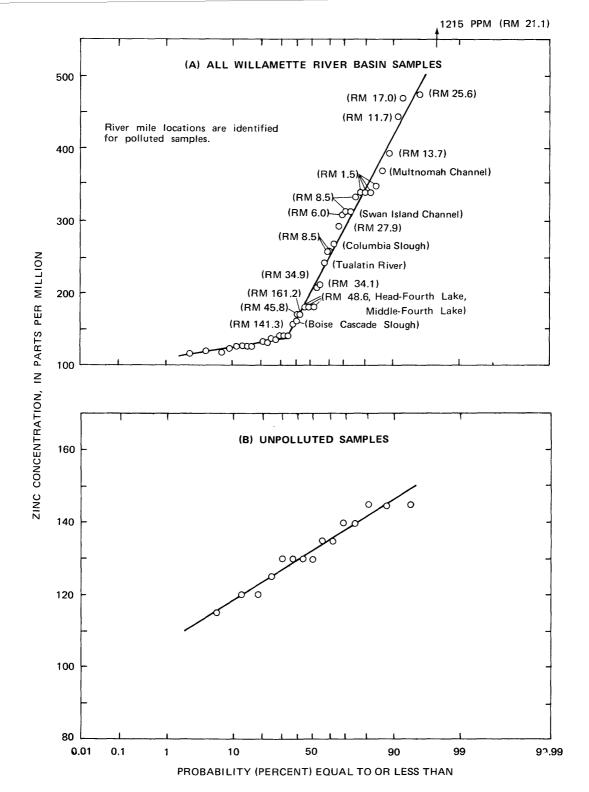


FIGURE 5.—Normal-probability plots of zinc concentrations in <20-µm materials. A, All Willamette River basin samples. B, Unpolluted samples.

lead concentrations >25 ppm are from sites that | suggests that lead concentrations from 10 to 40

Comparison of data in table 3 with possible pol- | receive either urban runoff or storm drainage lution sources shown in table 2 indicates that all | from roads. Thus, although the probability plot

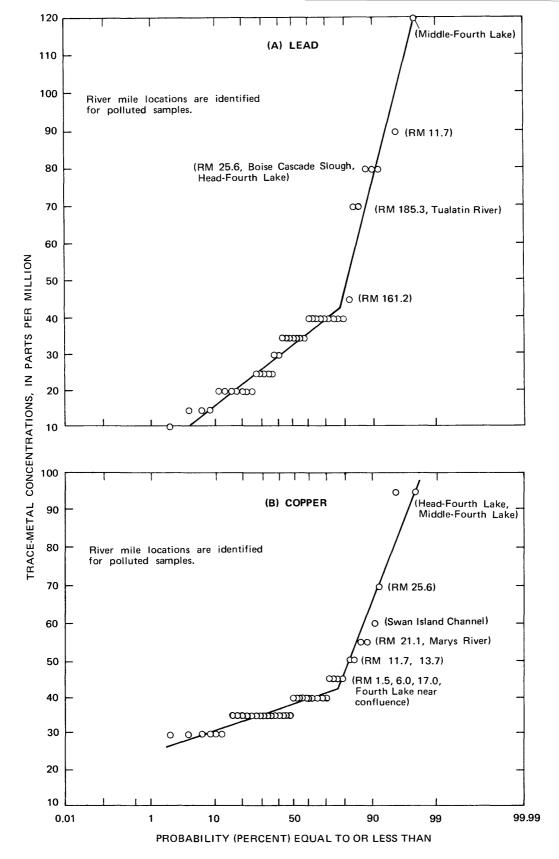


Figure 6.—Normal-probability plots of trace-metal concentrations in <20- μ m materials. A, lead, and B, copper.

ppm are from one population, the comparison suggests that concentrations >25 ppm might constitute pollution. Moreover, as described in a following section (see "Comparison of Results to Trace-Metal Concentrations in Rocks and Soils"), such a delineation is more consistent with lead concentrations in Willamette River basin soils.

Geographically, if we use the 25-ppm value as a breakpoint, zones of lead enrichment occur around Newberg (samples 25 to 27) and in the Tidal Reach (all Tidal Reach samples except RM 17.0). As noted in table 2, the Willamette receives street runoff below RM 27.5, either in the form of urban storm drainage or combined sewer overflows. Samples 25 and 26 from near Newberg were collected in a subreach that receives urban runoff. In addition to the two zones, lead enrichment would also be designated at RM 86.7 (sample 30), which is adjacent to a highway, and at RM 141.3 (sample 40), which is just below the village of Peoria.

Further discussion of the threshold concentration for lead enrichment is presented in "Comparison of Results to Trace-Metal Concentrations in Rocks and Soils."

COPPER

The plot of copper concentrations on normalprobability paper is best fitted by a two-stage curve (fig. 6B). The geographic locations (identified in fig. 6B) of samples on the upper curve are suggestive of pollution. The locations include Fourth Lake (3 samples), the Marys River, a zone between RM's 11.7 and 25.6 (samples 14, 15, 16, 17, and 19 in table 3), and Swan Island Channel plus the immediate downstream site (RM 6.0). The Marys River sample also contained relatively high concentrations of cobalt, nickel, and vanadium (table 14), as well as chromium. (See "Chromium".) The high copper concentrations between RM's 11.7 and 25.6 coincide with the zone of high zinc concentrations (fig. 5) and with elevated levels of lead. The cause of the elevated copper concentrations in this zone is unknown, but possible sources include municipal secondary effluents (table 2) in addition to the urban drainage and the pulp and paper mill effluents.

CHROMIUM

Chromium concentrations also define a twostage curve on normal-probability paper (fig. 7A). Two of the three 80-ppm samples were from Fourth Lake, and the 100-ppm sample was taken from the Marys River. As previously noted, the Marys River sample high levels of cobalt, dium. There is no known cause for the elevated levels of these metals.

In addition, enriched concentrations of 70 and 80 ppm were determined in two of the samples from RM 1.5.

MERCURY

Mercury concentrations (fig. 7B) tend toward one normally distributed population, but there are erratic variations above and below a good straight-line fit. Examination of geographical distributions (table 4) indicates that average mercury concentrations in the <20-μm materials increased slightly in an upriver direction. It was initially considered that the increase might have resulted from enrichment by the old Plack Butte mining area (fig. 1). However, the one sample (number 44) collected below Black Butte on the Coast Fork Willamette had low mercury concentrations in both the <2-mm and <20- μ m samples (table 3). Resolution of whether the Flack Butte area is polluting the Willamette must await further study.

Mercury was once used for slime control by certain pulp and paper mills in the basin. However, this use was discontinued in the late 1960's (A. Caron, Regional Director, National Council for Stream and Air Improvement, personal commun., 1975).

Although none of the <20-\mu m fractions showed definite mercury pollution, the <2-mm sample from site 34 (Fourth Lake) was unquestionably enriched (0.80 ppm). The mercury was associated with the coarse solids of the sample, but the source is unknown. Because the sediments sampled from Fourth Lake may have accumulated over many years, it is also unknown whether the pollution resulted from waste discharges during 1973 or from a previous time.

In summary, based on the lack of a two-stage probability plot and the lack of proven sources, we conclude that mercury concentrations in the $<\!20\text{-}\mu\text{m}$ materials are probably representative of unpolluted conditions. The relatively poor fit of the concentrations to a straight line (in fig. 7B) suggests some possible pollution, but if it exists, it is apparently not very great.

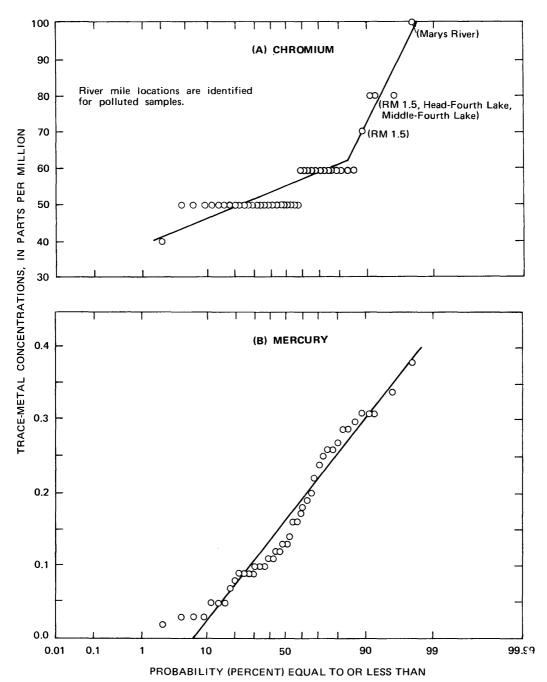


Figure 7.—Normal-probability plots of trace-metal concentrations in <20- μ m materials. A, Chromium, and B, Mercury.

CADMIUM

Cadmium concentrations did not show enough variability to warrant plotting. However, there was a slight increase in cadmium concentrations (<20- μ m materials) in the lower 3 mi (5 km) of the river (table 3). Upstream from this point, cadmium concentrations were reported as either

0.5 or 1.0 ppm in all but one sample (Tualatin River). In contrast, in Multnomah Channel (RM 3.3) the cadmium concentration was 1.5 ppm, at RM 1.5 it averaged 1.9 (four samples), and in the Columbia Slough it was 2.0 ppm.

One possible cause of the increase is admixture of Columbia River sediments which might move

upstream into the Willamette during periods of flow reversal. (See "Willamette River Morphology.") The one sample analyzed from the Columbia had a cadmium content of 4.5 ppm in the <20- μ m materials. However, the Columbia River sample also had elevated contents of copper, lead, and mercury, and no corresponding enrichment of these metals was detected in the lower Willamette.

FOURTH LAKE

The sediments from sites 33 and 34 in Fourth Lake were black, oily, odorous (table 9), and composed entirely of clay and silt-sized materials (table 10). In contrast, sample 35, collected near the confluence of Fourth Lake with the Willamette, showed indications of mixing with coarse river sediments. In reporting the trace-metal data (table 6), the concentrations at sites 33 and 34 are averaged, and the values at site 35 listed separately. For comparison, table 6 also lists the average and modal concentrations of each metal in the other Willamette River basin samples.

Table 6 indicates that the Fourth Lake samples were polluted by a large number of metals. Of the total list of enriched metals, the following 11 can be associated with processes at Teledyne-Wah Chang (see section entitled "Possible Sources of Trace Metals"): chromium, hafnium, lanthanum, molybdenum, niobium, scandium, silver, tin, ytterbium, yttrium, and zirconium.

Arsenic, copper, lead, and mercury were also enriched, but the sources of these metals are unknown. The arsenic and mercury enrichments occurred only in the <2-mm samples.

Although Fourth Lake was heavily polluted, the sample collected just downstream at RM 112.6 (table 3) showed no enrichment of any of the noted metals. Moreover, none of the special metals discharged by Teledyne-Wah Chang was determined at enriched levels in any downstream sample. Thus, it seems that metals discharged into Fourth Lake precipitate and stay within the slough, at least under low-flow conditions. If the metals do flush from the slough at high flows, they must (1) flush entirely from the basin, (2) be diluted to background levels, (3) be annually buried at depths greater than those sampled in the study (improbable), or (4) be affected by some combination of these possibilities. Further work is needed to determine if Fourth Lake is actually a year-round sink of incoming metals and, if so, whether the capacity for storage is still very large or possibly nearing its limit.

COMPARISON OF RESULTS TO TRACE-METAL CONCENTRATIONS IN ROCKS AND SOILS

The approach of using normal-probability plots (figs. 5, 6, 7) provides a means for estimating the natural background concentrations of certain

Table 6.—Concentrations (parts per million) of trace metals in Fourth Lake

Atomic-a	absorption spectrophotom	etry and colorin	netry¹	Emission spectroscopy ²						
Metal	Average of samples 33 and 34	Sample 35	Average for other Willamette River basin samples ³	Metal	Range of samples 33 and 34	Sample 35	Modal value for other Willamette River basin samples ³			
	<2-mm mater	ials			<20-μm mater	ials				
Arsenic Cadmium Chromium Copper Lead Mercury Silver Zinc	1.0 	<10 .5 80 15 15 .16 .5 110	12 .6 74 10 16 .15 .5	Hafnium Lanthanum Molybdenum Nickel Niobium Scandium Tin Ytterbium Zirconium Zirconium	50 7-10 50 200 50-70 150-200 20-50 20-300	150 <50 3 50 70 50 20 15 70 7,000	<100 <50 <3 30 <10 30 <10 30 <20			
Arsenic Cadmium Chromium Copper Lead Mercury Silver Zine	.8 	10 .5 60 45 25 .02 1.0	13 1.0 57 42 38 .16 .8							

Data from table 3.

²Data from table 14

³Forty samples (excluding Columbia River sample).
⁴This value is dominated by the concentration of 0.80 ppm in sample 34.

trace metals in Willamette River sediments. Figure 5B shows the distribution of zinc concentrations in the 15 samples designated as unpolluted. The figure shows that a well-defined normal distribution is formed, which, by graphical analysis (see Velz, 1970, p. 522–542), yields a mean of 133 ppm and a standard deviation of 12 ppm. Similar plots were prepared (not shown) for the graphically defined natural background concentrations of lead, copper, and chromium (<20- μ m materials). The summary data for the four metals are presented in table 7.

Because no definite breakpoint occurs in the mercury plot (fig. 7B), the data are considered as representing unpolluted conditions. The mean of the 43 concentrations is 0.17 ppm, and the standard deviation is 0.11 ppm.

Column 2 of table 8 shows the mean of the mercury samples together with the means (from table 7) of the unpolluted samples of chromium, copper, lead, and zinc. These values represent our initial estimates of the natural background concentrations of the five metals in the $<20-\mu m$ materials.

Table 8 compares these estimated background concentrations to levels for the five metals in rocks and soils of the Willamette Basin and to worldwide averages in claystones and shales. The values shown for Willamette Basin rocks represent uncontaminated consolidated specimens, most of which were basaltic or andesitic in character. The soils data represent "natural" conditions (Shacklette and others, 1971) and were determined on fractionated materials roughly comparable in size to the $<20-\mu m$ materials of the present study. The data for claystones and shales represent worldwide averages for uncontaminated samples and were calculated from the values reported by Parker (1967). Claystones and shales are fine-grained rocks which have formed primarily from consolidation of the sediments carried by ancient rivers. Thus, the chemical composition of these rock types would be expected to resemble that of the finer sediments transported by unpolluted present-day rivers.

Average concentrations for the soils are in remarkable agreement with the mean values for claystones and shales. In comparison to these two sets of values, the concentrations from the Willamette Study are low for chromium, copper, and mercury and somewhat high for lead and zinc. However, as previously discussed (see "Lead"),

Table 7.—Summary data from normal probability plots of trace-metal concentrations (<20-\mu m materials)

Summary data for concentrations below the breakpoint (indicative of

unpolluted or natural background

		conditions)		
Trace metal	Breakpoint concentration (ppm)	Number of samples	Mean (ppm)	Standard deviation (ppm)
Chromium	60	38	53	6
Copper	43	31	35	9
Lead	43	35	30	10
Zinc	145	15	133	12

Table 8.—Trace-metal concentrations (in parts per million) in bottom sediments, rocks, and soils

	Source								
	Willamette Study ¹	Willar Bas							
Metal	<20-μm materials	Rocks ²	Soils ³	Claystones and shales ⁴					
Chromium	53	<1-500	70	95					
Copper	35	5-300 (30)	50	51					
Lead	30	<10-15 (<10)	15	20					
Mercury Zinc		<25–159 (<25)	68 ^{.2}	.4 88					

¹Average concentrations for "unpolluted" samples (table 7). See text for discussion of lead in "unpolluted" samples.

²Values represent concentration ranges and modes in 36 rock samples from throughout the Willamette River basin (R. Mendes, U.S. Geol. Survey, written commun., 1975)

³Values for chromium, copper, and lead represent modal concentrations of 50 soils; values for mercury and zinc represent the average concentration of 3 soils (R. Mendes, written commun., 1975; T. H. Shacklette, U.S. Geol. Survey, written commun., 1975).

⁴Values represent averages from Parker (1967, table 19).

the upper end of the range for unpolluted lead concentrations may be 25 ppm. On the basis of this breakpoint, the average concentration of the unenriched lead samples is 20 ppm. This value is consistent with the data for soils and claystonesshales. It therefore supports the selection of 25 ppm as the breakpoint concentration.

The average zinc concentration in table 8 for Willamette sediments is considerably greater than the averages for soils and for the claystones and shales. We previously noted that old mining areas represent possible sources of zinc pollution in the upper Willamette (see "Possible Sources of Trace-Metal Pollution"); however, examination of table 3 indicates that above RM 50 zinc concentrations varied randomly and were unaffected by the discharge of tributaries (fig. 1) which drain the mineralized areas. We therefore believe that the average zinc concentration of 133 ppm (<20-\mum materials) represents the natural background level for Willamette River sediments.

SUMMARY AND CONCLUSIONS

This study developed and applied a procedure for identifying trace metals in river-bottom sediments that are present in concentrations indicative of pollution. The procedure involves (1) physical separation of materials $<\!20~\mu\mathrm{m}$ in size from bulk sediment samples, (2) trace-metal analysis of the $<\!20~\mu\mathrm{m}$ materials, (3) examination of the determined metal concentrations through use of probability plots, and (4) comparisons of the concentrations with the metal contents of soils and rocks. The procedure could be used intact or in modified form for the study of other rivers.

Use of the procedure in the Willamette River basin revealed a clean environment with the exception of a moderate enrichment of zinc, slight enrichment of copper and lead, and pollution by several metals in Fourth Lake.

The zinc enrichment resulted primarily from use of zinc hydrosulfite as a brightening agent in three ground-wood pulp and paper mills. As a result of orders from the Oregon Department of Environmental Quality, the mills will cease using zinc hydrosulfite by July 1977. The lead enrichment appeared to be related directly to urban drainage, but no specific source was identified for copper. Fourth Lake, an industrial slough, showed enrichment of 15 elements including uncommon metals such as zirconium, hafnium, yttrium, ytterbium, and tin. However, none of these metals was present in enriched concentrations at any downstream site.

The study results suggest that no metals were accumulated in Willamette River sediments at concentrations which might represent an immediate ecological threat. However, from a resource management standpoint, further studies are needed to determine (1) how zinc concentrations in the Tidal Reach respond to the ban on zinc hydrosulfite, (2) how much lead is annually reaching the river from urban drainage and combined sewer overflows, and (3) the ultimate fate of metals discharged to Fourth Lake. Answers to these questions still will not define the relationship of trace-metal concentrations in Willamette sediments to possible long-range potentials for toxic effects. It is hoped that basic knowledge of aquatic ecosystems will advance rapidly in the near future so studies can be initiated in the Willamette and in other United States rivers to assess this critical relationship.

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GLOSSARY OF SELECTED TERMS

Aliquot. A known exact part of a whole sample. **Alluvial.** Deposited by a stream or running water.

Andesite. A dark-colored fine-grained rock formed by the cooling of extruded volcanic magma.

Background. The abundance of an element or substance in an area in which the concentration is not anomalous.

Basalt. A dark- to medium-dark-colored rock commonly formed by the cooling of extruded volcanic magma.

Baseline information. Information that describes an environmental condition or parameter at the time of study that will permit future comparisons to be made as changes occur.

Bedload. The part of the total sediment of a stream that is moved on or near the streambed. In many streams sand is the main component of bedload.

Bottom sediment. The sediment deposited at the bottom of a water body.

Claystone. An earthy fine-grained sedimentary rock formed by the consolidation of primarily clay-sized particles.

Clay sized. Soil or sediment particles having a diameter of less than 0.002 mm (2 μ m).

Detection limit. The lowest concentration of a substance that can be measured by a given

- analytical method. The term is synonymous with sensitivity.
- **Enrichment.** An increase in the concentration of a substance over the natural background concentration. As used in this paper, the term is synonymous with pollution.
- **Geochemistry.** The study of the distribution, amounts, and circulation of the chemical elements in minerals, rocks, soils, water, and the atmosphere.
- Glaciofluvial. Pertaining to the melt-water streams flowing from wasting glacier ice and especially to the deposits produced by such streams.
- **Gravel.** An unconsolidated natural accumulation of rounded rock fragments resulting from erosion, consisting predominantly of particles having a diameter of greater than 2 mm.
- **Micrometre** (μ m). A conventional unit for expressing the diameter of small particles. One micrometre is equal to one thousandth of a millimetre, or 1/25,400 inch.
- **Modal.** Pertaining to the predominant or most frequent magnitude.
- **Normal probability.** A distribution of different values of a variable which follows the Gaussian or "bell shaped" curve.
- **Organic.** Pertaining or relating to a compound containing carbon.
- **Organometallic complex.** A special form of chemical combination between a metal and organic molecules.
- Parts per million (ppm). A conventional unit for expressing concentration. For describing the concentration of metals in sediment, the unit expresses the number of parts by weight of the metal per million parts of dry sediment weight. This is equivalent to milligrams of metal per kilogram of dry sediment.
- **Pollution.** Any substance introduced into water that changes the natural quality of the water or associated aquatic system. As used in this paper, the term is synonymous with enrichment.
- **Reconnaissance.** A type of sample or program designed to determine the present status of something; a preliminary survey.
- **River morphology.** The pattern and geometry of a river channel, including the network of tributaries within the drainage basin.
- **Sand sized.** Soil or mineral particles having a diameter in the range of 0.05–2 mm.

- **Sediment.** Fragmental material, both mineral and organic, that is in suspension or is being transported by the water mass or has been deposited on the bottom of the aquatic environment.
- **Sensitivity.** The term is synonymous with detection limit.
- **Shale.** A fine-grained sedimentary rock formed by the consolidation of clay- and silt-sized particles and characterized by a fine parallel structure along which the rock breaks into thin layers.
- **Silt sized.** Soil or sediment particles having a diameter in the range of 0.002–0.05 mm (2–50 μ m).
- **Slough.** A section of an abandoned river channel containing stagnant or slowly moving water.
- **Synoptic.** The distribution of conditions over a wide area at a given time.
- **Toxicity.** The ability of a substance to cause injury to living tissue once it reaches a susceptible site in or on the organism.
- **Trace metal.** A metal present in minor amounts in the Earth's crust; that is, less than about 0.01 percent.

REFERENCES

- Chu, T. Y., and Davidson, D. T., 1953, Simplified air-jet dispersion apparatus for mechanical analysis of soils: Highway Board Proc., v. 32, p. 441-457.
- Glenn, J. L., 1965, Late Quaternary sedimertation and geologic history of the north Willamette Valley, Oregon: Ph.D. thesis submitted to the Graduate School of Oregon State Univ., Corvallis, Oreg., 231 p.
- Goldblatt, E. L., Van Denburgh, A. S., and Marsl land, R. A., 1963, The unusual and widespread occurrence of arsenic in well waters of Lane County, Oregon: Eugene, Oreg., Lane County Dept. Public Health, 24 p.
- Harris, D. D., 1968, Travel rates of water for selected streams in the Willamette River basin, Oregon: U.S. Geol. Survey Hydrol. Inv. Atlas HA–273.
- Jackson, M. L., 1956, Soil chemical analysis—advanced course [published by author]: Madison, Wisconsin Univ., 991 p.
- Jenne, E. A., 1968, Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides: Trace inorganics in water, in Advances in chemistry series No. 73, p. 337–387.
- Levinson, A. A., 1974, Introduction to exploration geochemistry: Calgary, Canada, Applied Publ. Co., Ltd., 612 p.
- Myers, A. T., Havens, R. G., and Dunton, P. J., 1961, A spectrochemical method for the semiquantitative analysis of rocks, minerals, and ores: U.S. Geol. Survey Bull. 1084–I, p. 207–229.
- Oregon Department of Geology and Mineral Industries, 1951, Oregon metal mines handbook—northwestern Oregon:

- Oregon Dept. Geology and Mineral Industries Rept. 14–D, 166 p.
- Parker, R. L., 1967, Composition of the earth's crust, *in* Fleischer, Michael, tech. ed., Data of geochemistry (6th ed.): U.S. Geol. Survey Prof. Paper 440-D, 19 p.
- Shacklette, H. T., Hamilton, J. C., Boerngen, J. G., and Bowles, J. M., 1971, Elemental composition of surficial materials in the conterminous United States: U.S. Geol. Survey Prof. Paper 545–D, 71 p.
- U.S. Army Corps of Engineers, 1973, Aerial mosaics, Willamette River, May 2, 1972: Portland, Oreg., U.S. Army Engineer Dist., 57 p.
- Velz, C. J., 1961, Supplementary report on lower Willamette River waste assimilation capacity: Natl. Council for Stream Improvement of Pulp, Paper, and Paperboard In-

- dustries, Inc., School of Public Health, Michigan Univ., Ann Arbor, 28 p.
- ——1970, Applied stream sanitation: New York, John Wiley & Sons, Inc., 619 p.
- Ward, F. N., Lakin, H. W., Canney, F. C., and others, 1963, Analytical methods used in geochemical exploration by the U.S. Geological Survey: U.S. Geol. Survey Bull. 1152, 100 p.
- Ward, F. N., Nakagawa, H. M., Harms, T. F., and Van Sickle G. H., 1969, Atomic-absorption methods of analysis useful in geochemical exploration: U.S. Geol. Survey Bull. 1289, 45 p.
- Willamette Basin Task Force, 1969, Willamette Basin comprehensive study of water and related land resources, Appendix A, Study area: Pacific Northwest River Basins Comm. rept., 103 p.

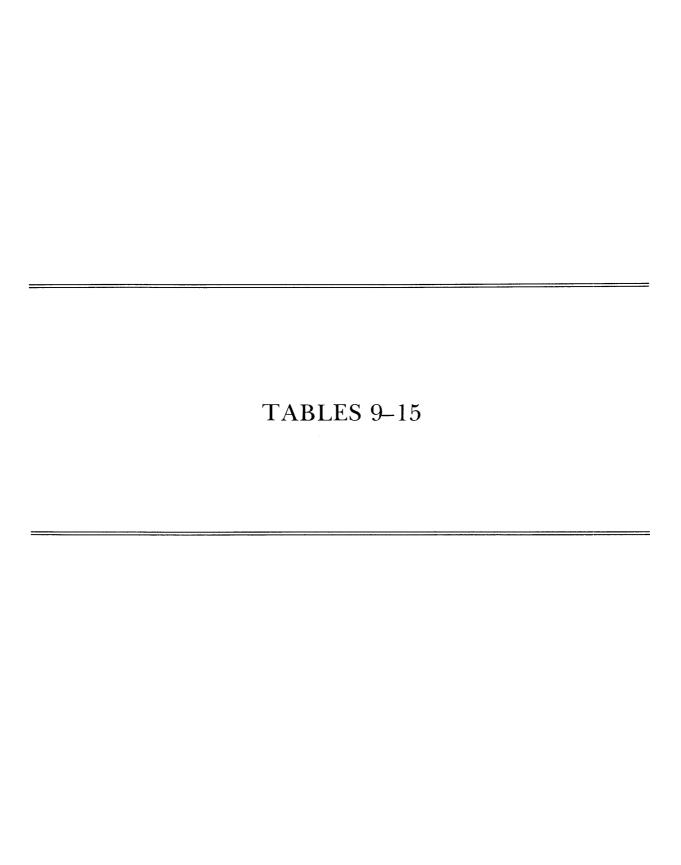


Table 9.—Site descriptions and physical characteristics of bottom sediments from the Willamette River and adjacent waters

Sample number		Location in cross section ²	Water depth (ft)	Field observations	Weight percentage >2 mm	Description >2-mm materials
1	Columbia River; 1/8 mi below Portland sewage treatment plant	1/4	33	Sandy		Gravel.
2	Columbia Slough; 1/4 mi from Willamette River	1/2	10	Fine materials, dark color		Wood.
3	1.5; opposite G. Grebe's house	1/3	43	Fine materials		
4	do	1/4	40	do		
5	do	1/2	40	do		
6	do	3/4	40	do		
7	Multnomah Channel; 14 mi below Gray's Moorage	1/3 and 1/2	20	Sandy, some gravel		Gravel.
8	6.0; just below St. Johns Bridge	1/2	43	do	8	Do.
9	8.1; 300 yards inside Swan Island Channel	1/2	36	Fine materials		
10	8.5; off Swan Island	1/2	60	do	0	
11	do	1/4	30	do		
12	do	1/2	60	do		
13	do	3/4	30	do		Gravel.
14	11.7; below Broadway Bridge	1/2	42	Sandy		Gravel and wood.
15	13.7; above Marquam Bridge	1/3	22	Sand and fine materials		Wood.
16	17.0; 12 mi above Sellwood Bridge	1/2	66	Fine materials, odorous		Wood.
17	21.1; 200 yards above Lake Oswego confluence	1/2	60	Gravelly and sandy		Gravel.
18	Clackamas River; 1000 ft below bridge on State Hwy. 99 E	1/10	1	Sandy	1	Do.
19	25.6; opposite Sportcraft Landing	1/2	15	Very gravelly	76	Do.
20	27.9; just below Oregon City Marina	1/3	27	Gravelly	49	Do.
21	Tualatin River; 500 ft from Willamette River	1/20	3	Sandy	18	Gravel and wood.
22	34.1; 4 mi below Canby ferry	1/3	60	Very gravelly	81	Gravel.
23	34.9; 12 mi above Canby ferry	1/4	25	Sandy, black, gas bubbles	0	
24	45.8; just below Champoeg Park	1/4	30	Fine materials	0	
25	48.6; 500 ft above New Newberg Bridge	1/4	15	Fine materials, odorous	1	Gravel and wood.
26	50.2; just above Publishers Paper outfall. 54.0; about 1 mi below confluence of Yamhill River.	2/3	33	Sludgy, fine materials	0	
27	54.0; about 1 mi below confluence of Yamhill River	4/5	22	Fine materials, odorous		Gravel.
28	69.0; near Tompkins Bar	1/10 and 9/10	5-10	Sandy		Wood.
29	Boise Cascade Slough; 500 ft from Willamette River	1/2	14	Fine materials, black, gas bubbles.		Wood and paper.
30	86.7; above Boise Cascade outfall	9/10	6	Gravelly and sandy		Gravel.
31	Santiam River; at railroad bridge	5/6	7	do	7	Do.
32	112.6; Spring Hill Rocks near Conser Road	1/10 and 9/10	2-3	do	13	Do.
33	Head of Fourth Lake	1/2	3	Black and oily, gas bubbles	0	
34	Center of Fourth Lake	1/2	10	do	0	
35	Fourth Lake near confluence with Willamette River	1/2	10	do	<1	Wood.
36	117.0; below Albany sewage-treatment plant	1/10 and 9/10	2	Sand and fine materials		Gravel and wood.
37	120; above Calapooia River	1/10 and 4/5	3-12	do		Wood.
38	130.1; below Corvallis	9/10	6	Fine materials		Gravel and wood.
39	Marys River; beneath highway bridge near Willamette River	1/2 and 4/5	6-8	Sandy	3	Do.
40	141.3; just below Peoria	9/10	2	do	2	Do.
41	161.2: near highway bridge at Harrisburg	4/5	12	do	2	Do.
42	178.1; near Beltline Bridge below Eugene	9/10	3	Gravelly and sandy		Gravel.
43	185.3; near bridge on State Hwy. 126	1/10	4	Very gravelly	56	Gravel, some snails.
44	Coast Fork near bridge on State Hwy. 58	9/10	4	do	79	Gravel.

 $^{^1\}mathrm{River}$ mile locations in Willamette River according to revised U.S. Army Corps of Engineers index system. $^2\mathrm{From}$ left bank.

Table 10.—Particle-size composition of bottom sediments from the Willamette River and adjacent waters

]	Particle-size	composition	ıi				Particle-size	e compositio	n¹
Sample number Site	Sand (2 mm– 50 µm)	Silt (50 μm– 2 μm)	Clay (<2 µm)	$<20~\mu\mathrm{m}^2$	Sample number		Sand (2 mm– 50 μm)	Sılt (50 μm– 2 μm)	Clay (<2 µm)	$<$ 20 $\mu\mathrm{m}^2$
1 Columbia River	96 39 22 30 30 13 91 89 5 22 3 24 37 88 87 67 28 81 93 94 88 44 43 77	3 56 70 64 62 78 8 10 84 71 89 69 51 13 65 18 7 6 65 18 7 6	1586689111778751377100221552	2 34 46 39 44 59 5 8 66 45 63 45 66 45 61 12 4 6 12 4 5 37	25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44	48.6 50.2 54.0 69.0 Boise Cascade Slough 86.7 112.6 Head of Fourth Lake Middle of Fourth Lake. Fourth Lake near confluence. 117.0 120.0 130.1 Marys River 141.3 161.2 178.1 185.3 Coast Fork at Highway 58.	63 23 37 86 12 75 82 89 0 0 10 67 65 52 72 81 87 94 91 61	33 67 56 13 77 23 16 10 85 85 82 30 31 43 24 17 11 5 8	10 7 1 11 2 2 1 15 15 15 8 3 4 4 2 2 1 1 5 5	25 57 47 9 65 117 70 70 60 22 21 28 16 13 8 2 2 27

Table 11.—Checklist of element names and symbols

Element	Symbol	Element	Symbol	Element	Symbol
Aluminum	Al	Indium	In	Silicon	Si
Antimony	Sb	Iron	Fe	Silver	A.g
Arsenic	As	Lanthanum	La	Sodium	Na
Barium	Ba	Lead	Pb	Strontium	Sr
Beryllium	Be	Lithium	Li	Tantalum	Та
Bismuth	Bi	Magnesium	Mg	Tellurium	Te
Boron	B	Manganese		Thallium	Tl
Cadmium	Cd	Mercury	Hg	Thorium	Th
Calcium	Ca	Molybdenum	Mo	Tin	Sn
Cerium	Ce	Nickel		Titanium	Ti
Chromium	Cr	Niobium		Tungsten	V ⁷
Cobalt	Co	Palladium		Uranium	
Copper	Cu	Phosphorus		Vanadium	V
Gallium	Ga	Platinum		Ytterbium	Yb
Germanium	Ge	Potassium	К	Yttrium	Y
Gold	Au	Rhenium	Re	Zinc	Zn
Hafnium	Hf	Scandium	Sc	Zirconium	7.r

 $\textbf{Table } 12. \\ -Concentrations \ (percentage \ by \ weight) \ of \ major \ elements \ in \ bottom \ sediments \ from \ the$ Willamette River and adjacent waters1

-					Emi	ssion sp	ectrosco	py²					Atomic absorption spectrophotometry			
					<20)-μm m	aterials			<2 mm ⁴				<20 μm		
Sample Number	Site	Si	Al	Ca	Mg	Na	К	Ti	P	Fe	Mn	Fe	Mn	Fe	Mn	
1 2 3	Columbia River	>10 >10 (5)	10 10	3 2	1.5 1.5	2 1.5	3 3	0.7	<0.2 <.2	7 7	0.15 .1	0.8 1.9 2.3	0.012 .040 .048	3.6 2.4 2.5	0.087 .062 .069	
3 4 5	1.5 1.5 1.5	>10	10	2	1.5	1.5	2	.7	<.2	7	.1	$\frac{2.3}{2.7}$.042 $.054$	$\frac{3.0}{3.6}$.062 .065	
6 7	1.5 Multnomah Channel	>10 >10	10 10	2	1.5 1.5	1 1	$\frac{2}{1.5}$.7 .7	<.2 <.2	7 10	.1 .3 .15	$\frac{2.6}{1.5}$ $\frac{1.4}{1.4}$.062 .045 .027	3.6 4.4 4.4	.073 .260 .110	
8 9 10	6.0 Swan Island Channel 8.5	$^{>10}_{>10}$	10 10	$\frac{2}{2}$	1.0 1.5	1	$\frac{2}{1.5}$	1.0	<.2 <.2	7 7	.15	$\frac{1.4}{3.1}$ $\frac{2.8}{2.8}$.062 .072	$\frac{4.4}{2.7}$ $\frac{3.0}{3.0}$.061 .086	
11 12	8.5	>10 >10	10 10	2 2	1.5 1.5	1 1	1.5	.7 .7	<.2 <.2	7 7	.1 .1	$\frac{3.0}{2.4}$.059 .044	2.7 3.1	.065 .068	
13 14 15	8.5 11.7 13.7	>10 >10 >10	>10 10 10	$\frac{2}{2}$	1.5 1.5 1.5	1.5 1 1	1.5 1.5 1	.7 .7 .7	<.2 <.2 <.2	7 7 7	.1 .15 .15	$\frac{2.8}{1.4}$ $\frac{1.8}{1.8}$.053 .022 .034	3.4 3.9 3.7	.067 .096 .086	
16 17	17.0	>10 >10 >10	10 10 10	1.5 1.5	1.5 1.5	.7 .7	1	.7 .7	< .2 $< .2$	7	.15 .15	$\frac{2.5}{1.9}$.075 .050	$\frac{3.4}{3.6}$.110 .130	
18 19 20	Clackamas River 25.6 27.9	>10 >10 >10	10 10 10	$\frac{2}{2}$	1.5 1.5 1.5	1 .7 1	1.5 1 1	.7 1.0 .7	<.2 <.2 <.2	7 7 7	.15 .15 .15	$1.7 \\ 1.7 \\ 2.2$.029 .037 .044	$\frac{3.8}{2.6}$ $\frac{4.2}{4.2}$.120 .130 .120	
21 22	Tualatin River	>10	10	2	1.5	i	1.5	.7	<.2	7	.15	$\frac{2.0}{2.6}$.045 .066	3.5	.110	
23 24 25	34.9 45.8	>10 >10 >10	10 10 10	$\frac{2}{2}$	1.5 1.5 1.5	1 1 .7	1.5 1 .7	.7 .7 .7	<.2 <.2 <.2	7 7 5	.15 .1 .15	$2.1 \\ 2.9 \\ 2.3$.034 .073 .049	$\frac{4.1}{3.6}$ $\frac{3.7}{3.7}$.089 .089 .110	
26 27	48.6 50.2 54.0	>10 >10 >10	10 10	1.5 1.5	1.5 1.5	1 1	1 .7	.7 .7	< .2 < .2	5 7	.1 .15	$\frac{2.8}{2.6}$.080 .097	$\frac{3.2}{3.6}$.092 $.120$	
28 29	69.0 Boise Cascade Slough	>10 >10	10 >10	$\frac{1.5}{1}$	1.5 1.5	1.5 1	1 1.5 .7	.7 .7 .7	<.2 <.2 <.2	7 7 7	.1 .07 .15	$2.0 \\ 2.6 \\ 2.1$.036 .046 .051	4.8 3.5 4.3	.076 .056 .120	
$\frac{30}{31}$	86.7 Santiam River	>10 >10 >10	10 10 10	2 2 3	1.5 1.5 1.5	.7 .7 1		.7 .7	<.2 <.2	7 7	.1 .15	2.0 .93	$.040 \\ .023$	4.1 3.9	.089 .110	
33 34	Head-Fourth Lake Middle-Fourth Lake	>10 >10	7 7	1.5 1.5	.7 .7	1	1 1 .7	.3 .3 .5	<.2 <.2 <.2	3 3 5	.07 .07 .05	.19 .69 1.5	.070 .037 .020	$3.9 \\ 3.1 \\ 2.9$.052 .052 .026	
35 36 37	Fourth Lake near confluence 117.0	>10 >10 >10	10 10 10	$\frac{2}{2}$ 1.5	1.5 1.5 1.5	.7 .7 1	.7 .7	.7 .7	<.2 <.2	7 7	.1 .1	1.8 1.5	.030	$\frac{3.9}{3.1}$.062 .084	
38 39	130.1 Marys River	>10 >10	10 10	2 1.5	1.5 2	1.7	1 1.5 1	.7 .7 .7	<.2 <.2 <.2	7 7 7	.07 .2 .1	1.1 1.5 1.4	.021 .090 .021	$\frac{6.0}{2.9}$ $\frac{3.9}{3.9}$.300 .037 .071	
40 41 42	141.3 161.2 178.1	>10 >10 >10	10 10 10	$\frac{2}{2}$	1.5 1.5 1.5	1 1.5 1	1 .7	.7 .7	< .2 < .2	7	.15 .15	$\frac{1.4}{1.3}$	$.028 \\ .027$	4.2 2.8	.970	
43 44	185.3 Coast Fork	>10 >10	7	1 .7	1.0 .7	.5 .5	< .7 < .7	.5 .5	<.2 <.2	7 5	.15 .2	$\frac{1.3}{1.9}$.034 $.120$	$\bar{3.3}$.250	

 $[^]t$ To obtain concentrations in parts per million, multiply weight percentages by 10,000. 2 Emission spectroscopy includes metals contained in crystal lattices. Analyses by Ray G. Havens. 3 Analyses by Kam W. Leong. 4 The $^{<2}$ -mm materials contain the $^{<20-\mu m}$ fraction. 5 Not determined.

Table 13.—Trace metals having concentrations in all sediment samples below detection limits of the emission-spectrographic method¹

Metal	Dection limit (parts per million)	Metal	Detection limit (parts per million
Antimony Beryllium Bismuth Cerium Germanium Gold Indium Lithium	1.5 10 200 10 20 10	Palladium Platinum Rhenium Tantalum Tellurium Thallium Thorium Tungsten Uranium	50 50 500 2,000 50 200 100

¹Arsenic and cadmium were below the detection limits but were later determined by wet chemical methods. (See table 3.) Spectrographic analyses were by Ray G. Havers.

Table 14.—Concentrations (in parts per million) of trace elements in <20-\mu materials of bottom sediments from the Willamette River and adjacent waters

[All analyses by emission spectroscopy]¹

Sample number		Ba	В	Cr	Co	Cu	Ga	Hf	La	Pb	Mo	Ni	Nb	Sc	Ag	Sr	Sn	v	Yb	Y	Zn	Zr
1	Columbia	1,000	700	70	30	150	15	<100	< 50	100	<3	50	<10	30	3.0	700	<10	150	5	50	700	200
2	River. Columbia Slough.	700	50	70	20	70	15	<100	< 50	70	<3	30	<10	30	<.5	500	<10	150	3	30	<300	150
3 4	1.5	(²) 700	$\bar{20}$	$\bar{70}$	$\bar{20}$	$\bar{7}\bar{0}$	$\bar{15}$	<100	<50	$\bar{70}$	<3	30	<10	$\bar{30}$.5	$5\bar{0}\bar{0}$	< 10	$1\bar{50}$	3	$\bar{30}$	300	150
5 6	1.5	$7\bar{0}\bar{0}$	$<\bar{20}$	$\bar{70}$	$\bar{20}$	$\hat{70}$	15	<100	< 50	$7\overline{0}$	<3	30	<10	30	.5	700	< 10	150	3	30	300	150
7	Multnomah Channel.	700	150	70	50	70	15	<100	< 50	70	<3	50	<10	30	<.5	300	<10	150	3	30	500	200
8 9	6.0 Swan Island Channel.	700 500	$^{100}_{<20}$	70 70	$\frac{30}{20}$	$\begin{array}{c} 70 \\ 100 \end{array}$	15 15	<100 <100	<50 <50	70 70	<3 <3	30 30	<10 <10	30 30	.5 .5	300 500	<10 <10	$\frac{150}{150}$	3 3	30 30	300 <300	200 200
$\frac{10}{11}$	8.5	$5\bar{0}\bar{0}$	$<\hat{20}$	$\bar{70}$	$\tilde{20}$	$\bar{70}$	15	<100	< 50	$\bar{7}\bar{0}$	$\stackrel{-}{<} 3$	$\bar{30}$	$<\bar{10}$	$\bar{30}$	5	500	< 10	$1\overline{50}$	-â	30	300	150
12	8.5	700	20	70	20	70	15	<100	< 50	70	<3	30	<10	30	.5 .5	500	<10	150	3	50	300	200
$\frac{13}{14}$	8.5 11.7	500 500	30 150	70 70	$\frac{20}{20}$	70 70	15 15	<100 <100	<50 <50	70 150	<3 <3	30 30	<10 <10	30 30	.5 1.5	700 500	<10 <10	150 150	3	30 30	<300 500	200 200
15	13.7	500	50	70	20	70	15	<100	< 50	70	<3	30	<10	30	1.0	300	< 10	150	3	30	500	200
$\frac{16}{17}$	17.0 21.1	500 500	20 50	70 70	$\frac{20}{20}$	70 100	15 15	<100 <100	<50 <50	50 70	<3 <3	30 30	<10 <10	30 30	1.0 1.5	300 200	<10 <10	150 150	3	30 30	700 700	200 200
18	Clackamas River.	700	300	70	30	70	15	<100	<50	30	<3	30	<10	30	1.0	300	<10	150	3	30	<300	200
19 20	25.6	500 500	150	70	20	50	15	<100	< 50	150	<3	30	<10	30	1.0	300	15	150	3	30	<300	200
21	Tualatin River.	700	100 300	70 70	30 30	70 70	15 15	<100 <100	<50 <50	$\begin{array}{c} 20 \\ 100 \end{array}$	<3 <3	30 30	<10 <10	30 30	<.5 .5	300 300	<10 <10	150 150	3 3	30 30	<300 <300	200 150
$\frac{22}{23}$	34.1	500	70	70	00	Ξô	î	-100	- 50	ĒŌ		20	-10	ôô	175	500	-10	150	^-		<300	200
24	34.9 45.8	500 500	20	70 70	$\frac{20}{20}$	70 70	15 15	<100 <100	<50 <50	$\frac{50}{20}$	<3 <3	30 30	<10 <10	30 30	1.5 .7	300	<10 <10	$\frac{150}{150}$	3	30 30	<300	200 200
25	48.6	500	20	70	20	70	15	< 100	< 50	50	<3	30	<10	30	1.5	200	<10	150	3	30	< 300	200
$\frac{26}{27}$	50.2 54.0	500 500	$^{<20}$	70 70	15 15	70 70	15 15	<100 <100	< 50 < 50	50 50	<3 <3	30 30	<10 <10	30 30	$\frac{1.5}{1.5}$	300 300	<10 <10	$\frac{150}{150}$	3	30 30	<300 <300	150 200
28	69.0	500	70	70	20	70	15	<100	<50	30	<3	30	<10	30	.5	500	<10	150	3	30	<300	150
29	Boise Cas- cade Slough.	500	<20	70	20	70	15	<100	< 50	150	<3	30	<10	30	<.5	300	<10	150	3	30	<300	150
$\frac{30}{31}$	86.7 Santiam River.	500 300	30 50	70 50	$\frac{30}{20}$	70 70	15 15	<100 <100	<50 <50	70 30	<3 <3	30 30	<10 <10	30 30	.5 <.5	300 300	<10 <10	$\frac{150}{100}$	3 3	30 30	<300 <300	$\frac{200}{150}$
32 33	112.6 Head-Fourth	500 500	$^{150}_{<20}$	70 100	30 10	70	15	< 100	< 50	20 100	<3	30 50	<10 200	30 50	<.5 10	500 150	$^{<10}_{200}$	100 70	$\frac{3}{20}$	30 200	<300 <300	150 20,000
34	Lake. Middle-	500	<20	100	10	150 150	15 15	700 500	50 50	150	10 7	50	200	70	10	150	150	70	50	300	<300	15.000
35	Fourth Lake. Fourth Lake near	500	20	70	15	100	15	150	< 50	30	3	50	70	50	2	300	20	100	15	70	<300	7,000
	confluence.																					
36 37	117.0 120.0	500 500	30 30	70 70	30 30	70 70	15 15	<100 <100	<50 <50	$\frac{20}{20}$	<3 <3	30 30	<10 <10	50 30	.5 .5	300 300	<10 <10	150 150	3 3	30 30	<300 <300	200 200
38	130.1	500	20	70	20	70	15	<100	< 50	15	<3	30	<10	30	.5	300	<10	150	3	30	<300	150
39	Marys River.	700	50	150	70	100	15	<100	< 50	20	<3	70	<10	30	<.5	150	<10	200	3	30	<300	150
40	141.3	500	70	70	30	70	15	<100	< 50	70	<3	50	<10	30	.5	300	<10	150	3	30	< 300	150
$\frac{41}{42}$	161.2	500 500	$\frac{100}{200}$	70 70	30 20	70 70	15 15	<100 <100	<50 <50	70 50	<3 <3	50 30	<10 <10	30 30	<.5 <.5	500 500	$^{15}_{<10}$	150 150	3	30 30	<300 <300	150 200
42	178.1 185.3	300	< 20	30	15	70 70	15	<100	< 50 < 50	100	<3	30	<10	20	<.5 <.5	200	<10	100	3	30	<300	200
44	Coast Fork	300	30	50	20	100	15	<100	< 50	70	<3	20	<10	30	<.5	150	<10	150	3	30	< 300	200

¹Emission spectroscopy includes metals contained in crystal lattices. Analyses by Ray G. Havens. ²Not determined.

Table 15.—Uses and sources of selected trace metals

Metal	Use or source
Arsenic	Coal, petroleum, detergents, pesticides, dyes and pigments, pottery and porcelain, wood preservation, glass industry, dye and tanning industry, various chemical production industries.
Cadmium	Batteries, tires, motor oils, heating oils, paints, plastics, coal, water mains and pipes, photography, various chemical production industries.
Chromium	Alloys, refractories, catalysts, photography, paints, bacteriocides, electroplating industry, pulp and paper mills, dye and tanning industry.
Copper	Ink manufacturing, dyes and pigments, electroplating industry, pharmaceutical industry, textile industry, tanning industry, various chemical production industries.
Lead	Batteries, dyes and paints, auto exhaust, photography, textile plants.
Mercury	Coal, fungicides, electrical batteries, embalming, ink manufacturing, electroplating industry, pharmaceutical industry, pulp and paper mills, dye and tanning industry, textile plants, various chemical production industries.
Silver	Photography, alloys.
Zinc	Embalming, wood preservation, water mains and pipes, paints, electroplating industry, pulp and paper mills, dye and tanning industry, various chemical production industries.

