



Occurrence of Minor Elements in Water

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Occurrence of Minor Elements in Water

By W. H. Durum and Joseph Haffty



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ABSTRACT

Presented at Conference on Physiological Aspects of Water Quality, September 8, 9, 1960, Washington, D. C.

Three basic studies, using spectrographic methods, have been used to establish the occurrence of minor elements in natural waters. One study, of oceanborne chemicals in principal rivers, has established a method for the quantitative analysis of many minor elements. Strontium, barium, lithium, rubidium, chromium, nickel, copper, lead, boron, titanium, molybdenum, manganese, and vanadium occur most frequently in measurable quantities.

Reconnaissance of the strontium in surface waters of the United States, shows that surface waters in parts of northern and western Texas and southern New Mexico and Arizona are comparatively high in strontium. A study of minor elements in selected waters of California is continuing.

Assessment of preliminary data on uranium and radium in waters is facilitated by grouping data for 10 geotectonic regions of the United States.

THE PROBLEM

In the past few years important advances have been made in the study of minor elements in natural waters. Once considered an area of chemical and geochemical curiosity, but having limited practical application, the study of minor elements is now an integral part of serious investigations of water chemistry. As used herein, minor elements are those dissolved elements that do not generally exceed 1 milligram per liter in natural water. Only a few minor elements are determined in routine water analysis, hence they are often not available in computing the ionic balance.

High on the list of accomplishments is improved methodology, which has provided means for quantitative measurement of elements that are currently of special interest. Of singular importance is the refinement of techniques for sensitive, practical, and reproducible spectrographic determination of minor elements in water.

The principal bulk of dissolved constituents in natural water consists of soluble

products of chemical weathering and soil formation. Thus, factors that control chemical weathering are among those that control the amounts of minor elements available for solution. Some chemical factors that affect release of minor elements from rocks and soils and their stability in solution are solubility of the constituent, pH of the environment, adsorption characteristics of the solid material, hydration, coprecipitation, colloidal dispersion, and complexes.

An important but generally neglected source of minor elements in water is vegetation. Many plants selectively concentrate minor elements, as well as major elements, that become available during the decay and movement of the plant debris in the hydrologic cycle. Decay and solution of organic matter may form metal-organic complexes, an example of which is the stabilization of ferric iron in swamp waters.

Man's activity in mining and manufacturing is an important unmeasured source of minor elements in natural water.

This paper summarizes a few recent studies made by the U.S. Geological Survey on the occurrence of minor elements in water.

THREE STUDIES—THREE METHODS

Three different spectrographic methods have been used in three widely different field programs with different objectives. The 3-prong approach shortened the time required to select adequate tools for each program and thus broadened experience in a relatively short period of investigation.

PRINCIPAL RIVERS

One program (Durum, Heidel, and Tison, 1960) updates basic information in Clarke's

OCCURRENCE OF MINOR ELEMENTS IN WATER

Table 1.—Spectrographic analyses for minor elements in
[Spectrographic analysis in micro-

Date of collection	Discharge (cfs)	Silver (Ag)	Aluminum (Al)	Boron (B)	Barium (Ba)	Beryllium (Be)	Cobalt (Co)	Chromium (Cr)	Copper (Cu)	Iron (Fe)	Lanthanum (La)	Lithium (Li)
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Apalachicola River at State Highway

Dec. 17, 1958	11,000	0.11	73	5.0	42	0	0	2.2	2.1	96	0	0.096
Mar. 30, 1959	54,000	<.058	2,550	11	21	<.058	0	2.2	7.0	1,220	0	.70
Aug. 24	11,900	.098	173	5.5	29	0	<.75	6.9	51	150	0	<.075
Sept. 29	9,030	<.071	135	5.6	26	0	0	7.8	6.2	85	0	.12

Atchafalaya River from railroad bridge, 0.6 mile below

May 10, 1958	323,000	0	-----	14	43	0.X	0.X	2.4	3.6	-----	0	-----
Oct. 14	130,000	.33	725	17	132	0	5.2	30	9.9	1,230	0	4.5
Mar. 13, 1959	276,000	0	1,640	19	52	<.22	0	2.6	3.7	1,240	0	1.9
May 18	166,800	0	462	14	122	0	0	4.9	10	517	0	2.6

Colorado River on bridge on U.S.

Sept. 16, 1958	^b 1,020	1.0	12	52	152	0	0	24	8.8	160	0	35
Jan. 20, 1960		0	153	34	128	0	0	10	8.5	111	0	37

Columbia River below The Dalles Dam,

June 11, 1958	503,000	0.09	-----	11	33	0	0	9.2	3.0	-----	0	-----
Dec. 1	114,000	.15	238	3.9	48	0	0	18	3.8	280	0	3.9
Sept. 8, 1959	124,000	<.11	82	5.0	44	0	<1.1	20	27	131	0	.59

Hudson River at Ford Motor Co. power-

Oct. 29, 1958	23,000	0.15	304	9.0	28	0	0	30	8.6	207	0	2.2
Jan. 22, 1959	63,000	.18	775	15	46	0	<1.3	15	15	650	X.0	1.1
Aug. 17	1,940	.59	251	20	60	0	<1.1	40	44	414	0	.28
Oct. 19	3,790	<.13	225	10	49	0	0	19	4.5	300	0	.89

Mississippi River just above bridge on U.S.

May 10, 1958	865,000	0.13	-----	29	78	0	0	2.6	10	-----	0	-----
Oct. 14	262,000	<.22	1,050	22	127	0	5.8	8.5	6.9	1,670	0	4.9
Mar. 13, 1959	655,000	0	1,010	15	72	0	0	4.6	9.0	828	0	1.8
May 18	415,000	0	281	6.1	84	0	0	84	74	663	0	2.4

Mobile River at Mount

Dec. 16, 1958	^b 24,000	0.13	186	3.3	75	0	0	2.0	3.5	392	0	1.7
Apr. 1, 1959	^b 92,000	.28	818	17	47	0	0	3.4	5.6	735	X.0	2.4
Aug. 25	^b 12,000	<.089	84	1.6	64	0	<.89	6.8	28	125	0	.14
Sept. 30	^b 15,500	<.085	289	4.3	52	0	0	1.9	2.7	204	0	.70

See footnotes at end of table.

waters from principal rivers of the United States and Canada

grams per liter except as indicated]^a

Manga- nese (Mn)	Molyb- denum (Mo)	Nickel (Ni)	Phos- phorus (P)	Lead (Pb)	Rubid- ium (Rb)	Scan- dium (Sc)	Tin (Sn)	Stron- tium (Sr)	Tita- nium (Ti)	Vana- dium (V)	Yttri- um (Y)	Ytter- bium (Yb)	Zinc (Zn)	Zir- co- nium (Zr)
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20, near Blounstown, Fla., U.S.A.

5.0	0	4.6	0	6.2	1.0	0	0	34	<0.80	0	0	0	0	0
25	<.17	2.6	<58	2.1	2.1	.0X	0	7.5	99	2.2	.X	.0X	0	X.0
20	.46	23	0	3.6	<.75	0	0	28	8.3	0	0	0	0	X.0
4.0	.62	34	0	2.7	2.1	0	1.3	25	6.9	0	0	0	0	X.0

bridge on U.S. Highway 190, at Krotz Springs, La., U.S.A.

-----	0	0.X	0	1.1	-----	0	0	11	10	0	0	0	0	0
100	<.93	47	<186	11	2.2	0	0	154	20	0	X.0	0	0	X.0
68	0	6.5	0	2.6	2.4	.X	0	22	107	<6.5	X.0	.X	0	X.0
12	<2.7	10	0	11	<2.7	0	0	139	14	0	0	0	0	0

Highway 80, at Yuma, Ariz., U.S.A.

21	6.9	30	0	<8.0	<8.0	0	0	802	<8.0	0	0	0	0	0
37	6.5	0	0	16	0	0	0	715	10	0	0	0	0	0

about 3 miles above The Dalles, Oreg., U.S.A.

-----	0.X	X.0	0	1.2	-----	0	0	30	2.9	X.0	0	0	0	0
14	2.1	10	0	5.0	1.4	0	0	112	5.2	0	0	0	0	0
5.5	1.0	36	0	3.4	<1.1	0	0	60	2.1	4.0	0	0	0	0

plant, at Green Island, N.Y., U.S.A.

35	0	12	0	2.9	1.9	0	0	106	<1.4	0	0	0	0	0
150	.65	8.6	0	11	1.6	.X	0	84	55	5.6	X.0	.X	<125	X.0
78	1.7	71	0	9.4	<1.1	0	0	72	10	4.3	0	0	0	X.0
56	.55	5.5	0	6.6	2.1	0	0	106	18	3.8	0	0	0	X.0

Highway 190, near Baton Rouge, La., U.S.A.

-----	0	0.X	X00	4.0	-----	0	0	34	62	X.0	0	0	0	X.0
185	<1.1	19	<223	7.8	2.5	0	0	105	6.7	0	X.0	0	0	0
46	0	13	<184	4.0	7.4	0	0	61	72	<5.5	0	0	0	X.0
12	<2.6	33	0	9.4	<2.6	0	0	97	12	0	0	0	0	0

Vernon Landing, Ala., U.S.A.

41	0	6.9	<98	15	1.3	0	0	68	3.6	0	0	0	0	0
20	.28	6.1	<93	3.1	3.9	.X	0	39	38	4.0	X.0	.X	0	X.0
7.4	.35	29	0	1.5	<.89	0	0	59	2.7	0	0	0	0	X.0
6.7	.27	6.8	0	1.2	2.6	0	1.4	51	12	0	0	0	0	X.0

OCCURRENCE OF MINOR ELEMENTS IN WATER

Table 1.—Spectrographic analyses for minor elements in waters

Date of collection	Discharge (cfs)	Silver (Ag)	Aluminum (Al)	Boron (B)	Barium (Ba)	Beryllium (Be)	Cobalt (Co)	Chromium (Cr)	Copper (Cu)	Iron (Fe)	Lanthanum (La)	Lithium (Li)
Sacramento River at tower bridge on												
May 1, 1958	^b 49,900	0	-----	22	9	0	0	<0.72	1.4	-----	0	-----
Nov. 25	^b 13,300	<.086	60	10	31	0	0	4.4	2.9	112	0	2.1
May 1, 1959	^b 11,800	0	286	9.8	25	0	<3.3	2.4	7.0	1,210	0	.77
Sept. 16	^b 9,900	<.16	1,110	25	56	0	<1.6	7.0	14	764	0	.66
Susquehanna River at hydroelectric												
May 7, 1958	126,000	0.29	-----	10	24	0	0.X	1.9	5.1	-----	0	-----
June 10	19,600	0	-----	12	38	0	0	4.5	4.0	-----	0	-----
Sept. 11	10,000	.25	27	16	25	0	0	3.7	5.3	31	0	3.5
June 5, 1959	17,300	<.15	102	4.3	37	0	0	1.3	105	154	X.0	3.4
Yukon River at Mountain												
May 28, 1958	^d 450,000	0.31	-----	11	26	0	0.X	2.3	6.3	-----	0	-----
Jan. 7, 1959	^d 30,000	<.20	82	13	109	0	0	7.0	2.5	1,130	0	2.0
Churchill River east of island off Drachm Point,												
June 24, 1958	^e 40,700	<0.078	148	3.7	19	0	0	5.5	2.0	172	0	1.0
Sept. 25	^e 42,500	.37	103	13	38	0	0	3.6	9.5	79	0	.95
Feb. 20, 1959	^e 27,000	.21	183	16	49	0	0	2.8	8.5	157	0	2.6
June 27	^e 61,000	<.084	134	4.5	33	0	0	12	2.9	185	0	.51
Fraser River at Mission City,												
July 1, 1958	255,000	0	327	2.6	17	0	<1.9	2.9	1.6	1,180	0	0.50
Oct. 1	166,000	<.073	526	11	18	0	1.9	6.0	2.5	635	0	.18
Feb. 12, 1959	37,100	0	261	2.6	20	0	0	23	3.0	363	0	.40
June 12	275,000	0	51	1.4	14	0	0	2.8	.83	52	0	1.3
MacKenzie River about 3 miles upstream from separa-												
July 24, 1958	470,000	0	1,410	13	65	0	5.0	12	11	1,390	0	1.1
Oct. 2	270,000	<.16	440	8.6	70	0	0	5.7	3.9	1,030	0	1.0
June 9, 1959	360,000	0	869	4.7	85	0	0	11	4.2	706	0	2.5
Nelson River near Amery, Manitoba, Canada (observations												
Oct. 5, 1958	^e 85,000	0	226	2.5	45	0	0	5.7	2.3	287	0	2.9
Jan. 29, 1959	^e 49,000	0	664	7.6	50	0	0	2.5	1.0	389	0	4.8
Mar. 9	^e 38,000	0	105	21	58	0	0	1.9	2.5	38	0	7.5
Apr. 9	^e 36,000	0	89	3.6	56	0	0	4.7	4.2	81	0	8.1
May 1	^e 75,000	0	81	7.8	57	0	0	3.4	6.0	198	0	3.9
June 3	^e 84,000	<.18	-----	58	53	0	5.1	21	11	-----	0	1.7

See footnotes at end of table.

from principal rivers of the United States and Canada—Continued

Manganese (Mn)	Molybdenum (Mo)	Nickel (Ni)	Phosphorus (P)	Lead (Pb)	Rubidium (Rb)	Scandium (Sc)	Tin (Sn)	Strontium (Sr)	Titanium (Ti)	Vanadium (V)	Yttrium (Y)	Ytterbium (Yb)	Zinc (Zn)	Zirconium (Zr)
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Capital Street, at Sacramento, Calif., U.S.A.

-----	0	0,X	0	0	-----	0	0	6.3	3.1	0	0	0	0	0
6.3	<.43	7.1	0	4.5	1.0	0	0	46	<.86	0	0	0	<86	0
50	0	6.6	<110	4.2	1.1	0	0	15	14	0	0	0	<110	0
34	<.47	20	0	4.4	<1.6	0	0	61	106	6.7	0	0	0	X.0

plant spillway at Conowingo, Md., U.S.A.

-----	0	X.0	0	3.6	-----	0	0	12	3.2	0	0	0	X00.	0
-----	.X	.X	0	1.1	-----	0	0	40	0	0	0	0	0	0
<2.1	0	11	0	<2.1	<2.1	0	0	25	<2.1	0	0	0	0	0
79	.54	3.9	0	7.2	<1.5	0	0	74	5.7	0	0	0	0	0

Village, Alaska, U.S.A.

-----	0	X.0	X00.	1.5	-----	0	0	15	16	0	0	0	0	0
181	1.2	17	<195	8.6	0	0	0	129	<2.0	0	0	0	0	0

8 miles south of Churchill, Manitoba, Canada

17	0	4.1	0	2.5	<0.78	0	0	22	8.6	0	0	0	0	0
2.6	0	5.6	0	4.0	1.1	0	0	37	3.1	0	0	0	0	0
4.4	.49	11	0	4.3	1.2	0	0	33	7.1	0	0	0	<122	0
8.4	<.25	14	0	2.4	0	0	0	23	5.8	0	0	0	0	X.0

British Columbia, Canada

26	0	5.0	<62	<0.62	2.6	0	0	16	17	0	0	0	0	0
32	0	12	73	1.8	.95	0	0	18	16	0	0	0	0	0
23	.79	13	<79	3.9	.79	0	0	40	18	0	0	0	0	0
3.0	<.21	2.6	0	1.3	.90	0	0	23	2.6	0	0	0	0	0

tion, at Arctic Red River, Northwest Territory, Canada

60	0	36	259	2.9	1.6	0	0	96	8.4	0	0	0	0	0
20	0	8.2	0	6.4	<1.6	0	0	228	6.0	0	0	0	0	0
36	.80	22	0	7.6	2.4	0	0	125	24	0	0	0	0	X.0

on Jan. 20, Apr. 9, and June 3, upstream at Kelsey powersite)

9.6	0	5.9	0	5.3	2.3	0	0	121	9.2	0	0	0	0	0
8.7	.87	4.1	0	0	0	0	0	73	32	0	0	0	0	0
0	1.3	5.5	0	0	0	0	0	105	5.3	0	0	0	0	X.0
<2.8	0	7.8	0	22	<2.8	0	0	86	5.9	0	0	0	0	0
3.4	0	8.8	0	4.9	<2.6	0	0	107	14	0	0	0	0	0
177	<.53	55	425	5.0	5.1	.X	2.1	55	67	5.7	X.0	.X	0	X.0

Table 1.—Spectrographic analyses for minor elements in waters

Date of collection	Discharge (cfs)	Silver (Ag)	Aluminum (Al)	Boron (B)	Barium (Ba)	Beryllium (Be)	Cobalt (Co)	Chromium (Cr)	Copper (Cu)	Iron (Fe)	Lanthanum (La)	Lithium (Li)
St. Lawrence River at water												
Aug. 25, 1958	342,000	0.94	276	13	30	0	0	12	4.3	580	0	0.41
Sept. 3	340,000	0	186	6.3	26	0	0	9.6	4.7	257	0	.40
Sept. 24 ^c	342,000	<.14	1,050	11	46	0	4.0	23	59	1,190	0	.60
Dec. 3	348,000	<.14	828	11	36	0	0	5.8	4.7	718	0	1.1
Apr. 20, 1959 ^c	551,000	<.11	-----	7.8	39	0	<1.1	6.8	-----	-----	0	.27
Apr. 23 ^c	550,000	<.11	-----	5.8	40	0	<1.1	9.7	-----	-----	0	.36
June 16 ^c	404,000	0	206	4.1	29	0	0	7.0	8.1	288	0	.55

^aLooked for but not detected: As, Au, Bi, Cd, Ce, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, Lu, Nb, Nd, Os, Pd, Pr, Pt, Re, Rh, Ru, Sb, Sm, Ta, Tb, Te, Th, Tl, Tm, U, W.

^bDaily mean discharge.

^cAt Quebec.

^dEstimated discharge at Kaltag.

"Data of Geochemistry," and provides current data on rates of continental chemical losses to the oceans. A product of the study of oceanborne chemicals in principal rivers is new and meaningful quantitative data for dissolved minor elements. Samples were obtained in the lower reaches of selected rivers just above tide and were prepared in the field by a unique and simple filter system. Minor elements were retained in solution by addition of concentrated nitric acid. Duplicate residue analyses were made on the spectrograph using regions of the spectrum (2250–4750A and 6250–8750A) in which most of the metals have sensitive analytical lines.

Emission spectrography (Haffty, 1960) using direct-current arc excitation of the water residue is rapid and reliable for quantitative determination of many minor elements commonly found in natural waters. It has been used successfully for samples from principal rivers of the world. Major elements are determined chemically and are not reported in this paper.

Let us look briefly at a few data for the United States and Canada (table 1). Of the alkaline earth metals, barium occurs in all waters examined in concentrations ranging up to about 150 micrograms per liter, and strontium up to about 800 micrograms per liter. Undoubtedly these values are exceeded at very low flows, although barium concentrations seem to be independent of the rate of water discharge.

Generally, there is no well-defined relation between strontium content and streamflow. However, samples from the Mississippi and Atchafalaya Rivers do show an increase in the strontium content and in the ratio of strontium to barium as discharge decreased (fig. 1). Also, the ratios of calcium to strontium and calcium to barium tended to increase with increase in flow of the two river waters (fig. 2). The alkaline earths also increased with an increase in dissolved solids for the Mississippi River (fig. 3), as indicated from observations shown in figure 1.

The occurrence of the metals, cesium, rubidium, and lithium in or below the lower levels of detection suggests that the alkali metals in principal rivers are strongly sorbed by soils and rocks upstream. Zinc and cobalt rarely occur in measurable quantities. Chromium, nickel, copper, lead, and boron were found in most waters, but no relation to streamflow is evident. Titanium occurs in most waters, and at times exceeds 70 micrograms per liter. Molybdenum and vanadium were detected in many samples in low concentrations. The content of copper, manganese, and boron was of the same order as that reported by Konovalov (1959) for major rivers of the U.S.S.R.

The data in table 1 suggest a pattern of occurrence or absence of a particular minor element in waters from a large drainage network. Hydrologic and geologic implications are evident by the relatively wide range in

from principal rivers of the United States and Canada—Continued

Manga- nese (Mn)	Molyb- denum (Mo)	Nickel (Ni)	Phos- phorus (P)	Lead (Pb)	Rubid- ium (Rb)	Scan- dium (Sc)	Tin (Sn)	Stron- tium (Sr)	Tita- nium (Ti)	Vana- dium (V)	Yttri- um (Y)	Ytter- bium (Yb)	Zinc (Zn)	Zir- co- nium (Zr)
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works plant at Levis, Quebec, Canada

21	1.7	13	0	3.7	1.4	0	0	66	21	0	0	0	0	0
6.7	2.4	11	0	4.9	1.4	0	0	92	6.6	0	0	0	0	0
30	2.6	22	173	55	2.9	0	0	78	50	0	0	0	<144	0
18	1.1	13	0	3.2	1.4	0	0	86	51	<4.1	X.0	0	0	X.0
69	<.34	13	<112	7.3	<1.1	0	0	45	-----	<3.6	X.0	.X	<112	X.0
60	.37	12	<112	3.6	<1.1	0	0	58	-----	3.9	X.0	.X	0	X.0
16	.60	16	0	3.6	1.5	0	0	69	12	0	0	0	0	0

^eApproximate.

< Detected, but less than figure indicated.

.. Not determined.

0 Below limit of detection for the specific element in designated sample.

X Refers to semiquantitative determination in the digit order shown.

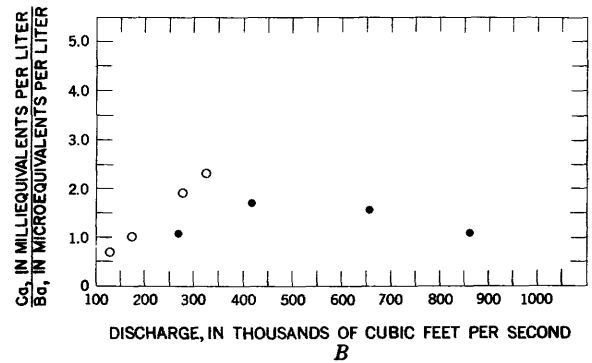
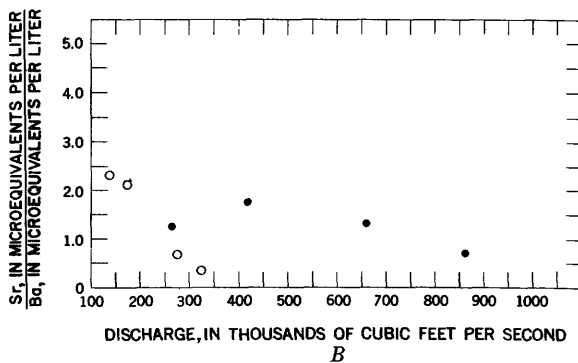
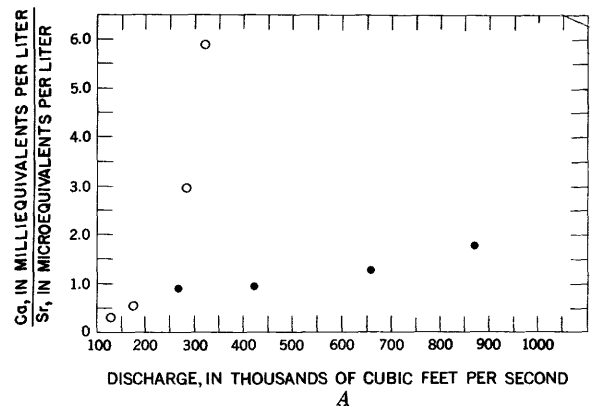
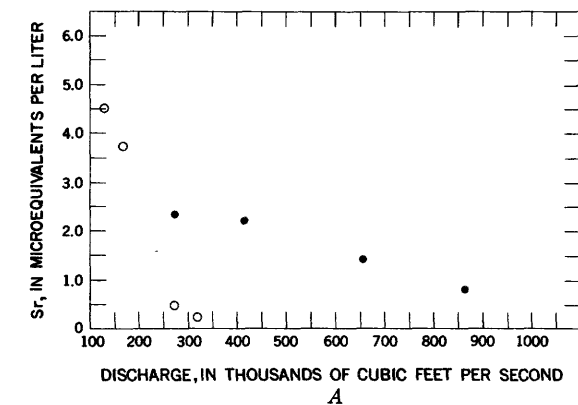


Figure 1.—Strontium and barium in water and water discharge. A, Relation of strontium content to water discharge; B, Ratio of strontium and barium content to water discharge. Open circle, Atchafalaya River at Krotz Springs, La. Closed circle, Mississippi River near Baton Rouge, La.

Figure 2.—Calcium, strontium, and barium in water and water discharge. A, Ratio of calcium and strontium content to water discharge; B, Ratio of calcium and barium content to water discharge. Open circle, Atchafalaya River at Krotz Springs, La. Closed circle, Mississippi River near Baton Rouge, La.

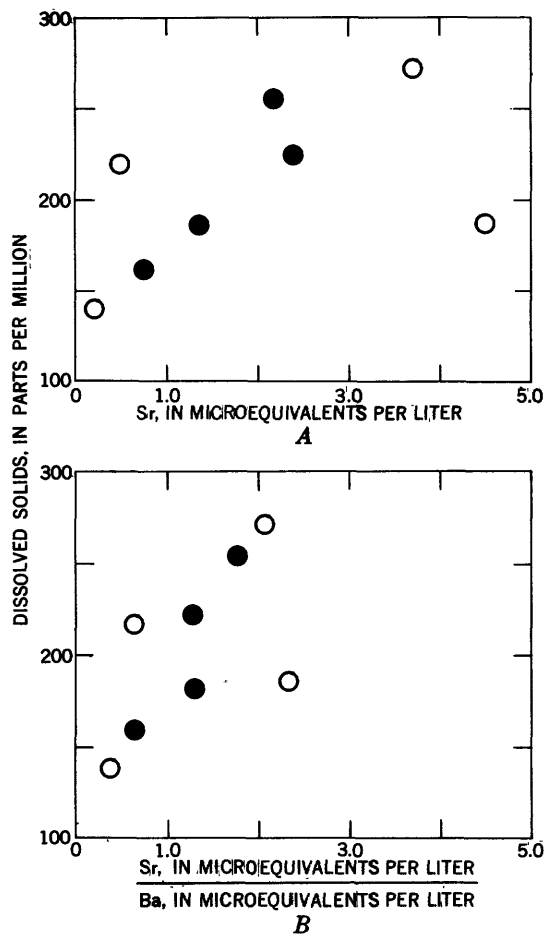


Figure 3.—Strontium, barium, and dissolved solids in water. A, Relation of strontium content to dissolved solids; B, Ratio of strontium and barium content to dissolved solids. Open circle, Atchafalaya River at Krotz Springs, La. Closed circle, Mississippi River near Baton Rouge, La.

content of some elements and the uniform content of others. Waters in the lower reaches of these principal rivers are a meld of many upstream tributaries. Probably much greater divergence in the kinds and amounts of minor elements will be found within the drainage networks than is evident from data for the main stem. This must be kept in mind in assessing current results.

OCCURRENCE OF STRONTIUM

The second approach was used by Skougstad and Horr (1960) in establishing the general occurrence of strontium in natural water of the United States. National interest has been focused on stable strontium and its occurrence and distribution in natural waters. Today, one task confronting the scientist is to assess the relationship of stable elements in

water to their radioactive counterpart in fallout, such as strontium-90.

Skougstad used a Beckman Model DU spectrophotometer with flame attachment for strontium concentrations more than about 0.2 ppm. For greater sensitivity, a spectrographic procedure based on the copper-spark technique of Fred, Nachtrieb, and Tomkins (1947) and Nachtrieb (1950) was used for samples containing less than about 0.2 ppm of strontium.

In the strontium study, surface-water samples were obtained from about 65 places in the United States to represent, insofar as possible, the major streams and drainage areas of the country. At each site, three samples were obtained at intervals of several months to a year, to obtain water during high-, low-, or median-flow conditions for the stream.

The results of the study are summarized by Skougstad and Horr in figure 4. The regions where the natural stable strontium content of surface waters is relatively low (less than 0.50 ppm) include the Pacific Northwest, Northeastern United States, and the Central lowlands, including the lower Mississippi basin and the Western Gulf Coast area. Moderate amounts of strontium (0.50 to 1.5 ppm) are found in streams of Southeastern United States, most of the Great Plains Region, the Western Mountain and Plateau Regions, and California. Surface waters in parts of northern and western Texas and southern New Mexico and Arizona are comparatively high in strontium.

Localized geologic environment such as the extensive celestite deposits in northern Ohio give values for strontium that are uncommonly high for a particular zone shown in figure 4.

STUDIES IN CALIFORNIA

The Geological Survey is studying the distribution and abundance of minor elements in various waters in California in cooperation with the California Department of Water Resources. The spectrographic method (Silvey, W. D., 1960, written communication) used in this study utilizes a chemical enrichment of the minor elements prior to spectrographic analysis of sea water, surface water, ground

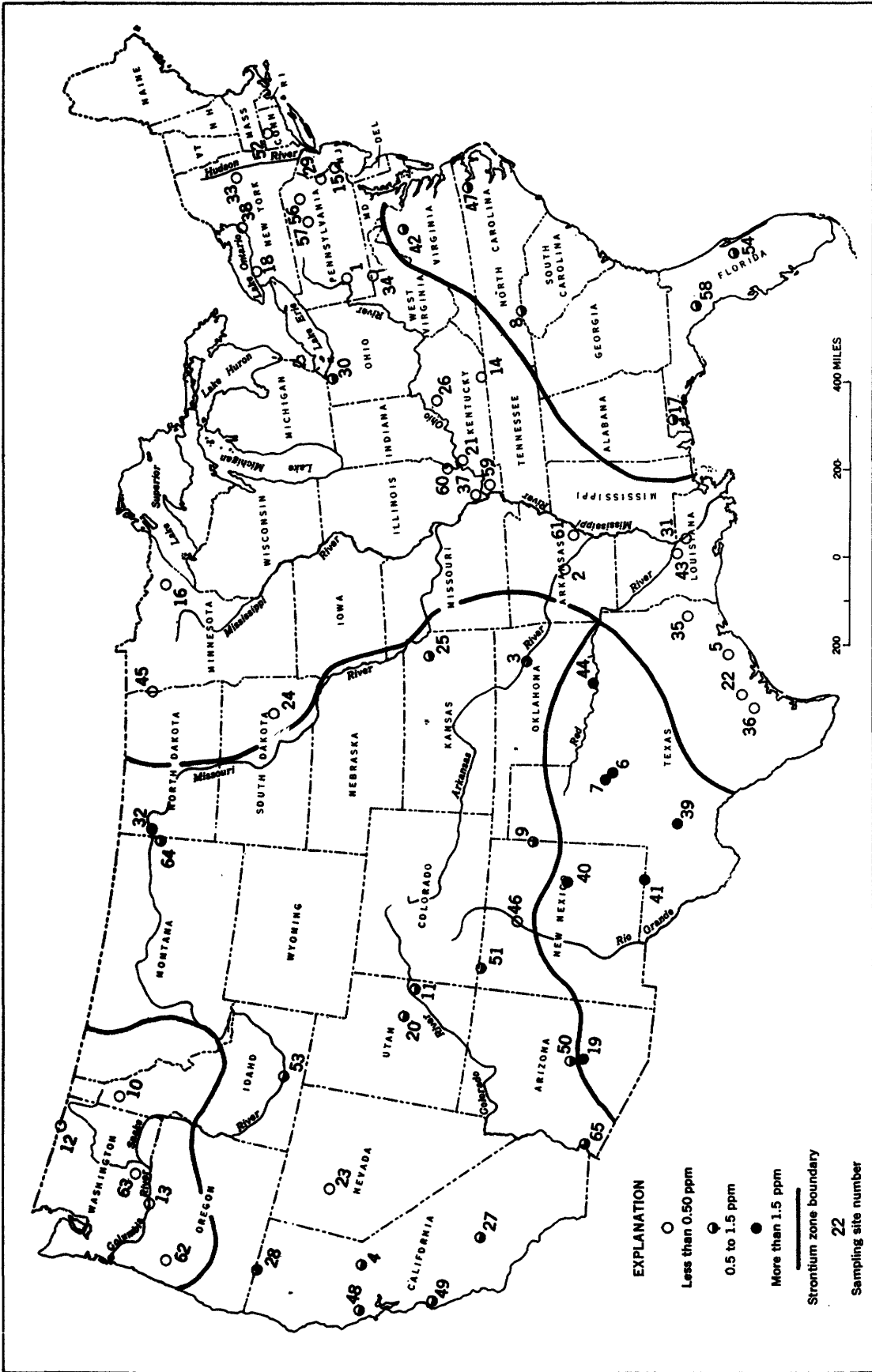


Figure 4.—Map of the United States showing concentration of strontium in surface water at selected sites. (From Skougstad and Horr, 1960.)

waters, including springs, and connate brines. These results will be published in the regular report series of the U.S. Geological Survey.

RADIOELEMENTS

The natural radioelement content of water is a subject receiving wide attention and discussion. For our purpose, however, we may consider natural uranium and radium as important minor elements, and thus emphasize the generalized studies of uranium and radium in the United States, such as the study made by Scott and Barker (1958). In a paper prepared for the United Nations Conference on Peaceful Uses of Atomic Energy (1958) at Geneva, the authors give statistic interpretation of uranium and radium data for 10 geotectonic regions of the United States, which boundaries were established from tectonics, geology, physiography, and ground-water provinces. Table 2 taken from their report, summarizes the then available radioelement data for ground water in the United States. Additional reports are in progress.

Scott and Barker report that neither radium nor uranium concentrations correlate well with concentrations of the more common chemical constituents of ground water, although "uranium concentrations do tend to be somewhat higher in water containing large amounts of bicarbonate ion." Table 2 shows the range, median, and "anomaly threshold" for uranium and radium concentrations, expressed as micrograms per liter ($\mu\text{g}/\text{l}$) and micromicrocuries per liter ($\mu\mu\text{c}/\text{l}$) respectively, for the 10 geotectonic regions. The anomaly threshold represents the lower limit of values which can be considered likely to have come from a population different from the bulk of samples that make up the frequency distribution.

The range and median values for uranium are largest in water samples from Region VI, in West-Central United States, and the largest median value for radium occurs in samples from Region VII, the Ozark-Ouachita Mountains.

A FEW DETAILS ON METHODS

Principal river studies.—Evaporate sample to dryness on a steam bath in fused quartz or

Table 2.—Summation of radioelement data
(From Scott and Barker, 1956)

Geo-tectonic region	No. samples	Uranium ($\mu\text{g U}/\text{l}$)			Conc. factor (U) ($\mu\text{g U}/\text{g dis. solids}$)		Radium ($\mu\mu\text{c Ra}/\text{l}$)			Conc. factor (Ra) ($\mu\mu\text{c Ra}/\text{g dis. solids}$)	
		Range	Median	Anomaly threshold	Maximum	Median	Range	Median	Anomaly threshold	Maximum	Median
I	89	0.1-15	0.2	2.5	62	0.9	0.1-8.6	0.2	4.1	174	1.0
II	78	0.1-24	.6	10	70	4.0	0.1-3.3	.1	2.5	21	.8
III	16	0.1-18	.5	---	72	1.3	0.1-2.1	.1	---	8.4	.2
IV	6	0.2-4.3	1.1	---	10	7.4	0.1-2.6	.1	---	12	.9
V	79	0.1-8.9	.5	4.8	18	.9	0.1-22	.5	7.4	96	.7
VI	74	0.1-120	2.1	45	319	5.9	0.1-11	.3	6.3	25	.9
VII	11	0.1-0.3	.2	---	2.3	1.6	0.1-2.3	1.0	---	13	2.3
VIII	84	0.1-37	1.6	28	60	5.2	0.1-3.4	.1	2.5	12	.1
IX	12	0.1-6.1	.8	---	9.9	2.6	0.1-1.0	.1	---	7.6	.3
X	37	0.1-7.6	.3	7.4	18	1.3	0.1-2.5	.1	1.1	10	(*)

*Below detection limit (Ra 0.1 $\mu\mu\text{c}$ per liter).

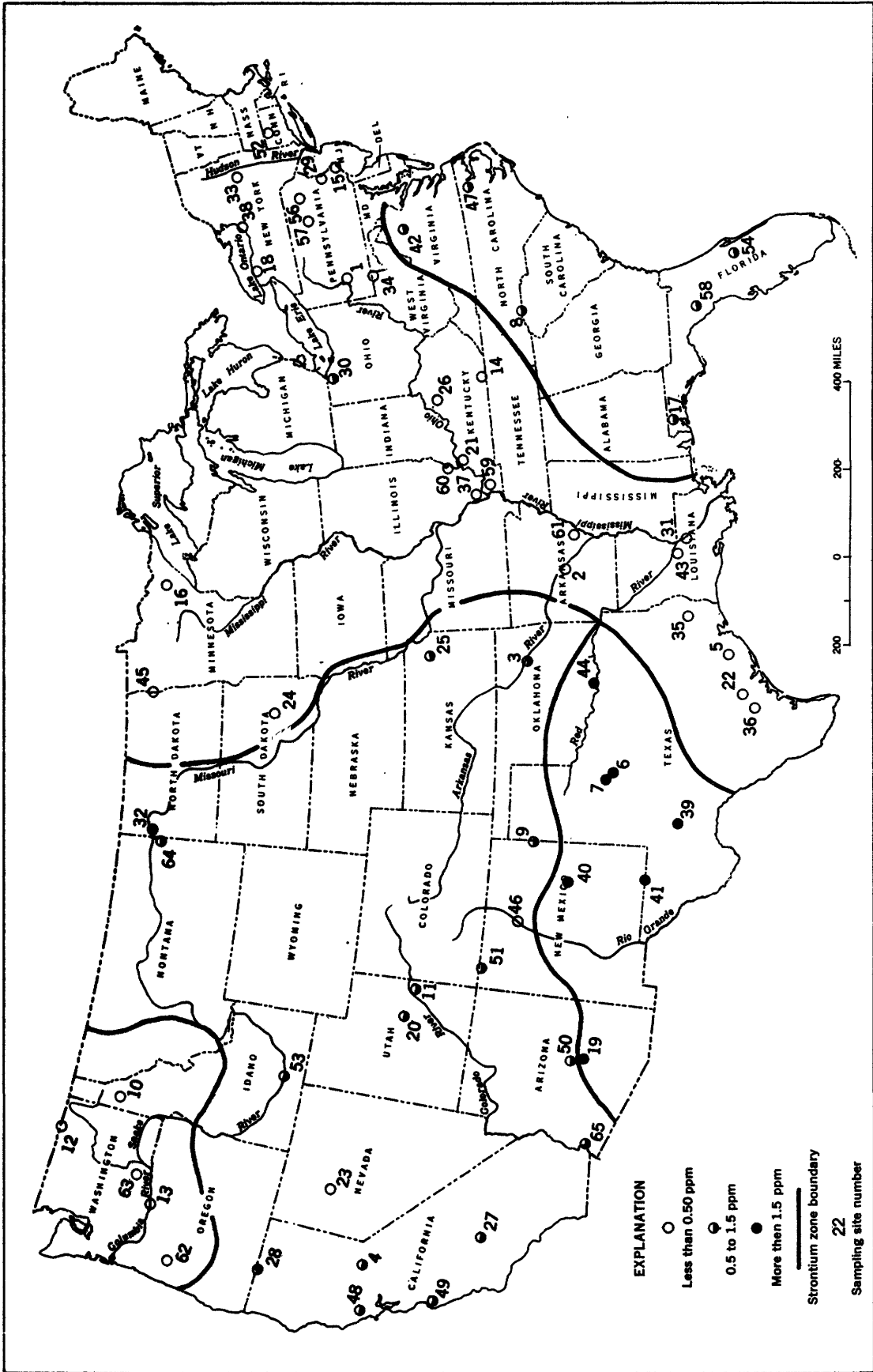


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vydor evaporating dishes. A weighed amount of the residue (12 mg) and synthetic standards mixed with a weighed amount of spectroscopically pure graphite powder (6 mg) is volatilized using a direct-current arc of 16 amperes. The resulting radiant energy is recorded on photographic plates after passing through a dispersing medium (grating), and the intensity of the spectral lines formed is measured by means of a projection comparator-microphotometer. Concentrations of elements in the unknown samples are read from working curves established by the standards arced on the same plate. Concentrations as low as 1 microgram per liter (0.001 ppm for waters considered herein), or less, have been determined by this method.

Strontium studies.—Use Beckman Model DU spectrophotometer with flame attachment, an oxygen-acetylene flame, a photomultiplier tube attachment, and a spectroscopic buffer solution.

The spectrographic copper-spark method requires about 30 ml of water sample and rapidly detects concentrations of strontium to about 5 parts per billion. Probable error of an analysis is about 10 percent of the amount present.

The usual chemical methods for the determination of strontium are not satisfactory when applied to water analysis because of small amounts of strontium present and difficulty in separating a small amount of strontium from much larger amounts of calcium and magnesium normally found in natural water.

California studies.—The chemical procedure uses chelating reagents (8-hydroxyquinoline, thionalide, and tannic acid) to selectively precipitate buffer metals. Indium is used as a radiation buffer, and palladium, the internal standard. The precipitate is ignited in a muffle furnace at a temperature of about 450°C. The ignited precipitate is mixed with "specpure" graphite powder. This mixture is placed in craters of graphite electrodes and subjected to a direct-current arc of 6 amperes. The resulting spectrum formed is recorded on film or photographic plates. Intensities of the spectral lines of the element and indium internal standard are measured

and the concentrations calculated from standard curves. Concentrations of 1 milligram to 1 microgram or less can be determined by use of this method.

SUMMARY

Knowledge of the occurrence of minor elements in water is one additional step in man's continuous probe into the unknown. Only a few of many significant studies are described in this paper. However, the results make clear that a vast frontier in technical studies looms ahead for a better understanding of minor elements—the end products of many earth processes.

REFERENCES CITED

- Braidech, M. M. and Emery, F. H., 1935, The spectrographic determination of minor chemical constituents in various water supplies in the United States: *Am. Water Works Assoc. Jour.*, v. 27, p. 557-580.
- Durum, W. H., Heidel, S. G., and Tison, L. J., 1960, World-wide runoff of dissolved solids: *Internat. Assoc. Sci. Hydrology, Pub. no. 15, General Assembly of Helsinki*, p. 618-628.
- Fred, M., Nachtrieb, N. H., and Tomkins, F. S., 1947, Spectrochemical analysis by the copper spark method: *Optical Soc. America Jour.*, v. 37, no. 4, p. 279-288.
- Haffty, Joseph, 1960, Residue method for common minor elements. *Spectrographic analysis of natural water: U.S. Geol. Survey Water-Supply Paper 1540-A*, 9 p.
- Heggen and Strock, 1953, Determinations of trace elements: *Anal. Chem.* v. 25, p. 859.
- Konovalov, G. S., 1959, The transport of microelements by the most important rivers of the U.S.S.R. *Doklady Akad. Nauk SSSR*, v. 129, no. 4, p. 912-915.
- Nachtrieb, N. H., 1950, Principles and practice of spectrochemical analysis: New York, McGraw-Hill Book Co.
- Scott, R. C. and Barker, F. B., 1958, Radium and uranium in ground water of the United States: *United Nations Peaceful Uses of Atomic Energy. Internat. Conf., 2d, Proc.*, Geneva, v. 2, p. 153-157.
- Skougstad, M. W., and Horr, C. A., 1960, Occurrence of strontium in natural water: *U.S. Geol. Survey Circ. 420*, 6 p.