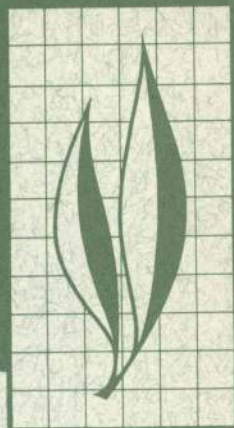


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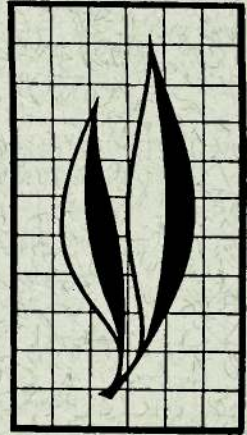


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Trace Elements in the Water Resources of California

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Trace element concentration ranges, means, medians, and number of positive occurrences are listed for 383 water samples from various sources in California. Data are compared to accepted public water supply and irrigation water standards. Municipal and industrial waste water and water extracts from Suisun Bay sediments contained the greatest number of trace elements at concentrations suggesting likely deleterious effects on aquatic life.

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TRACE ELEMENTS IN THE WATER RESOURCES OF CALIFORNIA¹

INTRODUCTION

WATER IS A VITAL STATE RESOURCE. The U. S. Department of the Interior, FWPCA Technical Advisory Committee (1968) lists five general areas of water use: 1. recreation and aesthetics; 2. public water supplies; 3. fish, other aquatic life and wildlife; 4. agriculture; and 5. industry. One of the most serious problems in maintaining good quality water for these general areas of use and reuse is pollution with heavy metals such as arsenic, lead, cadmium, zinc, silver, mercury, and copper.

The significance of trace elements (those elements occurring in small concentrations) in water is emphasized through knowledge of their mode of action in plant and animal metabolism. Most of the trace elements readily react with proteins and especially the enzymes. A slight excess of these elements in solution readily poisons vital metabolic reactions. Several of these elements are essential and/or toxic over low narrow concentration ranges to plant and animal life. For example, boron, molybdenum, zinc, copper, iron and manganese are required at low concentrations in higher green plants, and the same elements, except boron, are essential to most vertebrate animals (Albritton, 1953). At solution concentrations slightly higher than the re-

quired minimum, most of these elements become toxic to plants and animals. It is well known that the heavy metal ions or compounds are highly toxic to animals. Low level increases of these toxic heavy metals in water become more significant when we understand that at some stage in nearly every use and reuse of our water resources, they adversely affect biological systems important to man.

When heavy metals are added to a body of water, a potential pollution problem exists indefinitely. They can form stable compounds and remain in solution or form insoluble compounds subject to resolution with a slight change in pH of the environment. The equilibrium solution concentrations of some heavy metal compounds are toxic to aquatic organisms exposed over a long-time interval which permits the organism to concentrate the elements from solution. The problem is accentuated in mammals where some heavy metals, such as cadmium and arsenic, are cumulative poisons.

This project was undertaken to provide data for interpretations of the increasing number of experiments concerning low concentration effects of heavy metals on biological systems.²

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MATERIALS AND METHODS

Three hundred and eighty-three water samples were collected between January 1966 and July 1970 from miscellaneous sources and analyzed for their contents of trace elements. The samples were collected in one-gallon acid-cleaned polyethylene containers, and handled with care to avoid contamination. Samples of well waters were taken after allowing free flow for some time to flush the water that had been standing in the casing.

Samples were analyzed by a spectrochemical method (Bradford *et al.*, 1968): Each sample was divided into two aliquots, the volume depending on the salt content; viz. less for samples of greater total salt content. The method applies to samples having an electrical conductivity ($EC \times 10^8$) of less than 1.5 millimhos/cm. One 20-ml aliquot was evaporated to dryness in a Teflon beaker immersed in a hot water bath. The residue was dissolved in 1 ml of 2N hydrochloric acid containing 100 ppm Pd as an internal standard. One-half ml was analyzed with a Jarrell-Ash 3.4 meter Ebert direct-reading spectrograph using a rotating disc solution spark technique. A 1-liter aliquot was evaporated to approximately 100 ml in a large Pyrex crystallizing dish and any organic matter was oxidized with hydrogen peroxide in the presence of a high intensity ultraviolet light. Two ml of a 5 per cent aqueous solution of ammonium pyrrolidine dithiocarbamate (APDC-chelate) were then added to the sample solution and the pH adjusted within the range from 5 to 7 with 6N KOH or HCl. After standing $\frac{1}{2}$ hour the pH was again adjusted to the same range and the solution transferred to a 250 ml separatory funnel. Ten ml of chloroform were then added and the funnel shaken vigorously for 30 seconds. After the layers separated, the lower chloroform layer was drained

into a 60 ml silica dish. The process was repeated with a 5 ml volume of chloroform. Four drops of 6N HCl and $\frac{1}{2}$ ml of APDC solution were added to the aqueous solution which was then extracted with two 3-5 ml volumes of chloroform. All chloroform fractions were combined and the chloroform evaporated by heating the silica dish over a hot water bath. The residue was

TABLE 1
DETECTION LIMITS*
IN WATER SAMPLE

Metal	ppm	Metal	ppm
	mg/l		mg/l
Aluminum.....	0.1	Manganese.....	0.001
Arsenic.....	0.3	Molybdenum.....	0.001
Barium.....	0.05	Nickel.....	0.001
Boron.....	0.1	Silicon.....	0.3
Chromium.....	0.001	Silver.....	0.0001
Cobalt.....	0.001	Strontium.....	0.01
Copper.....	0.001	Vanadium.....	0.001
Iron.....	0.001	Zinc.....	0.001
Lead.....	0.001		

* For water samples with conductivity ($EC \times 10^8$) of less than 1.5 millimhos/cm. Values for detection limits are increased for samples with higher salt contents.

muffled at 450°C for three hours to destroy organic matter and dissolved in 2 ml of 6N HCl by heating the covered silica dish over a boiling water bath for $\frac{1}{2}$ hour. The cover was removed and the contents heated to dryness. The residue was dissolved in 1 ml of 2N HCl containing 75 ppm as an internal standard and 400 ppm K to increase sensitivity.. One-half ml of this solution was analyzed with the direct reader. The other $\frac{1}{2}$ ml was rerun with the direct reader in the photographic mode and the spectrum recorded on Number 3 spectrum analysis film. Quantitative data were then available from both the direct reader results and the photographic record. Visual comparison was made of spectrum line densities on the film with direct reader

values for all elements programmed on the direct reader. Elements not determined by the direct reader were measured by examination of the film record.

Pretreatment of the 1-liter aliquot of the sample with the chelate effectively concentrates zinc, iron, molybdenum, manganese, copper, nickel, cobalt, chromium⁺⁶, lead, vanadium, cadmium, and silver. Direct-reader analyses of the two sample aliquots provide quantitative detection limits as shown in table 1.

One-liter aliquots of sampled waste water containing large concentrations of organic matter were evaporated to dryness and muffled to 450°C for two hours to destroy organic matter. The residue was then dissolved in hydrochloric acid, filtered, treated with the chelate, etc.

None of the samples were filtered through micropore filters to remove colloidal or other material, since this fraction of the sample was considered part of the aqueous biological system.

RESULTS AND DISCUSSION

Table 2 lists the trace element concentration ranges, means, medians and numbers of positive occurrences in 383 water samples from various sources in California. The problem of setting concentration limits of trace elements in water is complicated by the fact that the same or different aquatic species react differently at different stages of development to the different soluble trace elements. Other dissolved minerals may either accentuate or mitigate the tolerance or sensitivity of a given species to a particular trace element. Plant reaction to trace elements in irrigation water is variable. Recognizing these and other problems, the Technical Advisory Committee (U. S. Department of the Interior, 1968) defined separate water quality criteria for the more important general areas of water use. Tables 3 and 4 are to assist the reader in interpreting the data presented in table 2. Not all elements are listed in every table but only those for which data were available.

Table 5 lists the number of samples with concentrations of elements in excess of the minimum permissible levels for public water supplies and irrigation waters, as shown in tables 3 and 4. A comparatively high number of surface water samples had concentrations of barium, boron, manganese and molybdenum in excess of recommended

standards. Boron, manganese and molybdenum are the elements which most often exceeded the permissible standards. As one might expect, the waste waters contained a greater variety of elements at concentrations more frequently exceeding the permissible limits accepted for public water supply (U. S. Department of the Interior, 1968).

The relatively high concentrations of strontium found in the drainage waters from Coachella Valley, where Colorado River water is used for irrigation, are in agreement with the report of high strontium in the Colorado River by Kopp and Kroner (1970).

The geothermal brine has by far the highest concentrations of barium, boron, copper, iron, lead, manganese, silver, strontium, and vanadium of all samples analyzed including municipal and industrial waste waters. This emphasizes the need for concern and control of all sources of pollution.

The data in table 2 are probably more significant when analyzed in relation to trace element toxicities as reviewed by Wilber (1969) and U. S. Department of the Interior (1968). They discuss the incipient lethal levels or the concentrations of toxic trace elements below which the experimental organism survives indefinitely. There is increasing experimental proof that concentrations of Ag, Cd, Cr, Cu, Hg,

TRACE ELEMENT CONCENTRATION RANGES, MEANS, MEDIANS, AND NUMBER

Sample Sources	Number of samples	Ag	Al	B	Ba	Cd	Co	Cr
Surface Waters								
Number of positive occurrences.....	165	37	48	134	153	0	0	20
Range*.....		<0.0001-0.003	<0.05-1.2	<0.02-11.0	<0.01-12.0	<0.005	<0.0005	<0.0005
Mean*.....		0.0003	0.6	1.37	0.65	—	—	0.0
Median*.....		0.0001	<0.10	0.11	0.09	—	—	<0.0
Well Waters from San Joaquin Valley								
Number of positive occurrences.....	82	51	6	63	69	0	0	55
Range.....		<0.0001-0.0004	<0.02-0.2	<0.02-8.5	<0.01-1.2	<0.005	<0.0005	<0.0005
Mean.....		0.0002	0.15	0.71	0.31	—	—	0.0
Median.....		<0.0001	<0.06	0.12	0.08	—	—	<0.0
Agricultural Drainage Waters from Coachella Valley								
Number of positive occurrences.....	22	22	4	20	1	0	0	1
Range.....		0.0005-0.0010	<0.2-0.8	<0.2-6.0	<0.1-2.2	<0.020	<0.002	<0.002
Mean.....		0.0008	0.45	1.20	2.2	—	—	0.0
Median.....		0.0008	<0.2	0.70	<0.1	—	—	<0.0
Domestic Waste Waters from California Cities								
Number of positive occurrences.....	22	22	5	22	20	2	18	13
Range.....		0.0006-0.004	<0.1-0.38	0.2-1.3	0.01-0.57	<0.005-0.007	<0.001-0.007	<0.001-0.007
Mean.....		0.0020	0.15	0.54	0.13	0.0065	0.0037	0.0
Median.....		0.0020	<0.1	0.52	0.10	<0.005	0.004	0.0
Spring and Well Waters Surrounding the Salton Sea								
Number of positive occurrences.....	22	12	2	21	15	0	1	8
Range.....		<0.0001-0.0004	<0.05-0.8	<0.02-11.4	<0.02-3.7	<0.005	<0.0005-0.005	<0.0005
Mean.....		0.0002	0.5	2.60	0.30	—	—	0.0
Median.....		0.0002	<0.1	0.64	0.02	—	—	<0.0
Food Processing—Plant 1†								
Number of positive occurrences.....	5	4	5	5	5	0	4	4
Range.....		<0.0001-0.0008	0.9-2.2	0.4-0.7	0.1-0.27	<0.005	<0.001-0.006	<0.001
Mean.....		0.0006	1.6	0.54	0.19	—	0.004	0.0
Median.....		0.0005	1.7	0.50	0.22	—	0.003	0.0
Food Processing—Plant 2†								
Number of positive occurrences.....	5	5	5	5	5	0	5	4
Range.....		0.0005-0.0035	14.0-50.0	0.4-0.8	0.1-0.27	<0.005	<0.005-0.008	<0.001
Mean.....		0.0013	25.0	0.58	0.18	—	0.006	0.0
Median.....		0.001	16.0	0.60	0.15	—	0.007	0.0
Metal and Chemical Processing								
Plant 1†								
Number of positive occurrences.....	5	5	3	5	2	0	5	5
Range.....		0.0004-0.0010	<0.1-0.7	0.7-1.9	<0.05-0.04	<0.005	<0.005-0.03	0.005
Mean.....		0.00060	0.50	1.58	0.04	—	0.015	0.0
Median.....		0.0005	0.60	1.70	<0.05	—	0.011	0.0
Plant 2.....	1	0.008	<2.0	<2.0	<1.0	0.20	0.013	<0.1
Plant 3.....	1	0.0006	<2.0	<2.0	<1.0	<0.01	<0.002	0.0
Plant 4.....	1	0.0006	<2.0	4.6	<1.0	<0.01	0.004	0.0
Plant 5.....	1	0.0006	<2.0	<2.0	<1.0	<0.01	0.006	0.0
Plant 6.....	1	0.0006	<2.0	<2.0	5.8	<0.01	0.002	0.0
Oil Well Brines								
Composite of 8 Producing Wells.....	1	<0.0001	<0.2	0.4	0.09	<0.001	<0.001	<0.0
Brines from Desert Wells								
Imperial Valley Geothermal Brine.....	1	1.0	<100.0	570.0	1100.	<1.0	<1.0	<4.0
Amboy Salt Well.....	1	<0.001	<0.05	7.5	<0.2	<0.001	<0.001	<0.0
Various Water Samples from Casa Diablo (Includes hot and cold springs, lake waters and streams from area of volcanic activity)†								
Number of positive occurrences.....	27	Not determined	0	20	15	0	0	4
Range.....			<0.2	<0.02-35.0	<0.02-0.9	<0.001	<0.001	<0.0005
Mean.....			—	8.41	0.29	—	—	0.0
Median.....			—	0.63	<0.02	—	—	<0.0
Suisun Bay—Lower San Joaquin River Water Samples								
Number of positive occurrences.....	10	10	0	2	2	0	0	3
Range.....		0.0002-0.0005	<2.0	<2.0-0.7†	<1.0-0.4	<0.01	<0.02	<0.002
Mean.....		0.0003	—	0.65	0.3	—	—	0.0
Median.....		<0.0003	—	<2.0	<1.0	—	—	<0.0
Suisun Bay—Lower San Joaquin River sediment saturation extracts								
Number of positive occurrences.....	10	10	0	0	2	0	7	1
Range.....		0.01-0.03	<2.0	<2.0	<1.0-2.4	<0.01	<0.002-0.055	<0.005
Mean.....		0.013	—	—	1.3	—	0.027	0.0
Median.....		0.013	—	—	<1.0	—	0.021	<0.0

* Given as mg/l.

† Data from five samples taken at monthly intervals

‡ Number of positive occurrences, 0; Range, <0.04-12; Mean, 0.62; Median, <0.08.

¶ Boron detected in two samples after concentration five-fold by evaporation.

CONTINUED OCCURRENCES IN 383 WATER SAMPLES FROM MISCELLANEOUS SOURCES

	Cu	Fe	Ga	Mn	Mo	Ni	Pb	Si	Sr	V	Zn
0.0065	150	0	154	149	123	110	164	159	160	164	
0.006	0.0013-0.38	<0.0005	0.0005-1.5	<0.0005-0.130	<0.0005-0.025	0.0005-0.018	<0.02-36.4	<0.02-1.8	<0.0005-0.085	0.0005-0.4	
0.003	0.057		0.028	0.009	0.003	0.002	9.6	0.43	0.005	0.018	
	0.02		0.004	0.003	0.001	0.001	7.5	0.24	0.003	0.01	
0.0047	82	0	70	78	52	78	82	79	78	82	
0.006	0.0006-0.5	<0.0005	<0.0005-0.66	<0.0005-0.015	0.0005-0.007	<0.0005-0.01	0.2-28.0	<0.02-1.0	<0.0005-0.06	0.0005-3.0	
0.003	0.029		0.042	0.004	0.002	0.003	8.5	0.37	0.012	0.125	
	0.005		0.003	0.003	0.0006	0.002	6.9	0.22	0.006	0.006	
0.018	22	0	13	22	22	22	21	22	22	22	
0.007	0.005-0.048	<0.002	<0.002-1.2	0.007-0.088	0.002-0.008	0.003-0.014	0.7-19.0	0.2-17.2	0.005-0.047	0.005-0.02	
0.006	0.061		0.159	0.030	0.004	0.005	7.3	3.21	0.011	0.009	
	0.008		0.002	0.026	0.004	0.004	6.8	2.50	0.01	0.009	
0.065	22	1	22	22	22	21	22	22	22	22	
0.024	0.025-1.4	<0.001-0.001	0.002-0.25	0.002-0.012	0.003-0.6	<0.001-0.35	2.3-7.5	0.12-1.2	0.003-0.021	0.017-0.22	
0.022	0.27	—	0.036	0.006	0.047	0.034	4.4	0.39	0.008	0.067	
	0.128	—	0.015	0.005	0.007	0.01	4.0	0.30	0.007	0.047	
0.028	22	6	22	21	17	22	22	21	18	22	
0.022	0.003-0.44	<0.0005-0.003	0.0006-0.24	<0.002-0.12	<0.0005-0.007	0.0008-0.006	1.2-12.0	<0.02-19.0	<0.001-0.085	0.001-0.21	
0.009	0.063	0.0012	0.025	0.024	0.003	0.002	5.8	2.2	0.013	0.033	
	0.032	<0.005	0.004	0.012	0.001	0.002	4.8	0.60	0.005	0.018	
0.038	5	5	5	4	5	5	5	5	5	5	
0.025	1.4-10.5	0.001-0.1	0.003-0.036	<0.001-0.014	0.018-0.09	0.006-0.015	4.3-9.0	0.35-0.85	0.008-0.016	0.03-0.095	
0.028	3.54	0.029	0.018	0.008	0.046	0.01	5.6	0.64	0.010	0.053	
	2.10	0.001	0.015	0.015	0.044	0.009	5.1	0.70	0.01	0.045	
0.040	5	5	5	5	5	5	5	5	5	5	
0.272	1.2-2.7	<0.001-0.1	0.012-0.047	0.01-0.026	0.023-0.05	0.018-0.027	1.6-30.0	0.57-1.1	0.015-0.08	0.048-0.100	
0.030	1.96	0.041	0.030	0.016	0.035	0.020	9.8	0.89	0.032	0.076	
	2.0	0.003	0.03	0.017	0.034	0.018	4.1	0.98	0.024	0.075	
0.031	5	2	5	5	5	5	5	5	5	5	
0.026	0.075-0.62	<0.001-0.035	0.017-0.055	0.017-0.034	0.004-0.016	0.009-0.040	5.9-25.0	0.30-0.35	0.004-0.008	0.026-0.24	
0.038	0.39	0.035	0.035	0.027	0.009	0.020	12.7	0.32	0.005	0.094	
0.002	0.5	<0.001	0.041	0.031	0.01	0.018	12.0	0.32	0.004	0.07	
0.070	40.0	0.001	0.040	0.012	0.053	2.0	<2.0	3.2	0.009	4.0	
0.013	0.062	0.001	0.003	0.002	0.004	0.003	<2.0	<2.0	0.003	0.003	
0.006	0.0175	<0.001	0.065	<0.001	0.011	0.033	<2.0	<2.0	<0.001	1.3	
0.002	0.019	<0.001	0.003	<0.001	0.021	0.003	<2.0	<2.0	<0.001	2.8	
	0.037	<0.001	0.005	0.001	0.013	0.006	<2.0	<2.0	<0.001	0.034	
0.008	0.031	<0.001	0.010	0.006	0.001	0.005	68.0	0.64	<0.001	0.002	
0.008	1200	<1.0	2000	<1.0	<4.0	70.0	<30.0	610.0	6.0	600	
	0.35	<0.001	0.095	0.27	0.002	0.001	5.0	15.0	0.0043	0.8	
0.004	27	0	27	27	21	22	26	12	24	25	
0.004	0.003-0.9	<0.001	0.001-0.57	0.005-0.023	<0.0005-0.006	<0.0005-0.014	0.06-68.0	<0.02-0.35	0.0001-0.008	0.0003-0.32	
	0.09	—	0.032	0.005	0.001	0.003	31.2	0.13	0.004	0.054	
	0.014	—	0.0036	0.003	0.001	0.001	31.0	<0.04	0.003	0.012	
0.015	10	0	10	9	10	10	4	5	10	10	
0.005	0.005-0.037	<0.01	0.002-0.006	<0.001-0.008	0.003-0.014	0.002-0.007	<2.0-3.4	<2.0-3.0	0.006-0.010	0.005-0.024	
0.009	0.016	—	0.003	0.003	0.005	0.004	3.0	1.7	0.007	0.012	
	0.014	—	0.003	0.002	0.003	0.003	<2.0	<2.0	0.006	0.008	
0.020	10	5	10	10	10	10	10	5	10	10	
0.013	0.03-27.0	<0.01-0.01	0.7-30.0	0.007-0.026	0.007-0.033	0.019-0.130	2.0-58.0	<2.0-5.2	0.013-0.029	0.020-0.038	
0.014	14.4	0.01	6.9	0.016	0.018	0.056	17.0	3.6	0.021	0.027	
	4.4	<0.01	2.0	0.016	0.017	0.038	14.0	<2.0	0.019	0.027	

TABLE 3
SURFACE WATER CRITERIA FOR
TRACE ELEMENTS IN
PUBLIC WATER SUPPLIES

Metal	Permissible criteria	Desirable criteria*
	mg/l	
Arsenic.....	0.05	Absent
Barium.....	1.0	Absent
Boron.....	1.0	Absent
Cadmium.....	0.01	Absent
Chromium ⁺⁺	0.05	Absent
Copper.....	1.0	Virtually absent
Iron (filterable).....	0.3	Virtually absent
Lead.....	0.05	Absent
Manganese.....	0.05	Absent
Selenium.....	0.01	Virtually absent
Silver.....	0.05	Virtually absent
Zinc.....	5	Virtually absent

Source: U.S. Department of the Interior, FWPCA, 1968, table II-1 p. 20. Virtually the same as drinking water standards (U.S. Department of Health, Education, and Welfare, 1962).

* Absent means that the most sensitive analytical procedure in Standard Methods (1965) or other approved procedures does not show the presence of the subject constituent.

Virtually absent implies that the substance is present in very low concentrations and is used where the substance is not objectionable in these barely detectable concentrations.

Mo, Ni, and Pb as low as 0.01 ppm in water may have serious deleterious effects on different species of aquatic life. For example, Soyer (1963) found that concentrations of silver nitrate from 0.01 to 0.1 ppm caused abnormal or inhibited development of eggs of *Paracentrotus* (sea urchin). His comparative experimental data showed that silver is about 80 times as toxic as zinc, 20 times as toxic as copper and 10 times as toxic as mercury. Sprague (1964) found that the incipient lethal level of copper is 0.048 ppm for young Atlantic Salmon, *Salmo salor*. He also found that the avoidance level for salmon is 0.0023 ppm Cu and 0.053 ppm Zn. Jones' (1938, 1939) experimental results with sticklebacks showed that one-week survival concentrations are 0.0067 ppm Cu, 0.014 ppm Hg, and 0.0025 ppm Ag. U. S. Department of the Interior (1968) discussed unpublished results indicating mortality of oysters resulting from two-year ex-

TABLE 4
TRACE ELEMENT TOLERANCES
FOR IRRIGATION WATERS

Element	For water used continuously on any soil	For short-term use on only fine-textured soils
	mg/l	mg/l
Aluminum.....	1.0	20.0
Arsenic.....	1.0	10.0
Beryllium.....	0.5	1.0
Boron.....	0.75	2.0
Cadmium.....	0.005	0.05
Chromium.....	5.0	20.0
Cobalt.....	0.2	10.0
Copper.....	0.2	5.0
Fluorine.....	*	*
Iron.....	*	*
Lead.....	5.0	20.0
Lithium.....	5.0	5.0
Manganese.....	2.0	20.0
Molybdenum.....	0.005	0.05
Nickel.....	0.5	2.0
Selenium.....	0.05	0.05
Tin.....	*	*
Tungsten.....	*	*
Vanadium.....	10.0	10.0
Zinc.....	5.0	10.0

Source: U.S. Department of the Interior, FWPCA, 1968, table IV-15 p. 152.

* The authors (Technical Advisory Committee, 1968) make the following comments: The most serious effects of excess fluoride are not on plants but on animals including man consuming them. (Bollard and Butler, 1966) Iron is not likely to be a problem with irrigation waters. Tin, tungsten and titanium are effectively excluded by plants. (Stolbova and Sharshukova, 1962)

posures to 0.010 to 0.012 ppm Cr, Mo, or Ni.

Pollution problems, even at these low concentrations, are made more acute by additive and synergistic effects where several elements occur together. Skidmore (1964) found in experiments with trout that zinc and cadmium acted additively to produce their toxic effects while zinc and nickel, and zinc and copper acted synergistically. The synergistic effect of zinc and copper demonstrated up to five times the toxicity anticipated from the combined effects.

Wilber (1969) discussed the similarity of clinical symptoms of lead poisoning and multiple sclerosis and suggested that the not uncommon reports of muscular dystrophy occurring naturally in fishes and amphibians may perhaps be associated with some metal poison (e.g., lead) in the environment.

TABLE 5
 NUMBER OF SAMPLES WITH CONCENTRATIONS OF ELEMENTS IN EXCESS OF MINIMUM
 PERMISSIBLE LEVELS LISTED IN TABLES 3 AND 4

Water source	Number of samples	Elements													
		Ag	Al	As	B	Ba	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
Surface waters.....	165				I-12 D-6	D-17				D-3	D-14	I-53			
Well waters from San Joaquin Valley.....	82				I-21 D-6	D-1				D-1	D-4	I-12			
Agricultural drainage water from Coachella Valley.....	22				I-10 D-7	D-1				D-1	D-2	I-22			
Waste waters from California cities.....	22				I-4 D-1	D-1	I-2			D-6	D-2	I-13	I-1		
Spring and well waters surrounding Salton Sea.....	22				I-9 D-9	D-1			I-1	D-1	D-6	I-10			D-2
Miscellaneous industrial waste waters.....	20		I-2		I-2 D-2	D-1	I-1 D-1	D-2	I-2	D-4	D-2	I-5			D-1
Oil well brines (composite of 8 samples).....	1				I-2	D-2			I-1		I-1	I-1			I-1
Brines from desert wells.....	2	D-1			D-2 I-13	D-2			D-1	D-2	D-2	I-2			D-1
Various water samples from Casa Diablo area.....	27				D-3 *	D-3			I-1	D-2	D-2	I-8			D-1
Suisun Bay and lower San Joaquin River water.....	10				*										
Suisun Bay and lower San Joaquin sediment saturation extracts.....	10				*	D-1				D-8	I-10 D-10	I-10			D-4

Symbols:
 D—Number of samples with concentrations of elements in excess of drinking water standards.
 I—Number of samples with concentrations of elements in excess of irrigation water standards.
 * Small sample volumes increased detection limits for boron above minimum standards listed in tables 3 and 4.

TABLE 6
NUMBERS OF WATER SAMPLES WITH CONCENTRATION OF ELEMENTS
IN EXCESS OF 0.01 ppm

Water source	Number of samples	Elements									
		Ag*	As	Cd	Cr	Cu	Mo	Ni	Pb	V	Zn
Surface waters	165			1	2	11	26	5	4	11	77
Well waters from San Joaquin Valley . .	82					6	4	1	2	25	17
Agricultural drainage waters from											
Coachella Valley	22					4	20		1	12	10
Waste waters from California cities . . .	22	8				17	3	9	13	6	22
Spring and well waters surrounding											
Salton Sea	22						5			1	1
Miscellaneous industrial waste waters . .	20	2		1	6	16	14	13	13	8	19
Oil well brines (composite of 8 samples) .	1										
Brines from desert wells	2	1				1			1	1	1
Various water samples from											
Casa Diablo area	27		9			6	5		1	1	16
Suisun Bay and lower San Joaquin											
River water	10					3		1		2	5
Suisun Bay and lower San Joaquin											
River sediment saturation extracts . .	10	10				10	9	9	10	10	10

* Ag concentration in excess of 0.003 ppm.

Deleterious effects of trace elements on aquatic life at low solution concentrations suggest that the data collected for this study may have greater significance if compared to a low reference concentration. Table 6 lists the number of samples with concentration of elements in excess of 0.01 ppm.

It is apparent from table 6 that municipal and industrial wastes and particularly the sediment solutions contain more elements at higher concentrations than occur in samples from other sources. The occurrences of a few well and surface water samples with concentrations of elements in excess of 0.01 ppm is probably the result of waste water contamination of surface waters and metal plumbing contamination of well waters.

Relatively high concentrations of molybdenum and vanadium in several sample sources is probably due to the naturally higher geochemical solution concentrations of these elements.

Comparatively high levels of several elements in the sediment solutions are especially significant for the following reasons: The concentrations found in the sediment saturation extracts are probably much lower than would be expected if only the first few centimeters of sediment had been sampled. The sediment samples were collected using a Peterson dredge with no provision to restrict the sample to a few centimeters in depth. Lee (1970) concluded from water chemistry studies that the upper layer of sediments over which exchange reactions and mixing may take place is in the order of a few centimeters in thickness. It is within this zone of the sediment water interface that many aquatic species are confined or frequent during their life span. It is likely that they are exposed to toxic concentrations of heavy metals several times higher than those listed in table 2.

LITERATURE CITED

- ALBRITTON, ERRET C.
1953. Standard values in nutrition and metabolism. American Inst. Bio. Sci. Nat. Res. Council.
- BOLLARD, E. G., and G. W. BUTLER
1966. Mineral nutrition of plants. Ann. Rev. Plant Physiol. 17:77-112.
- BRADFORD, G. R., F. L. BAIR, and V. HUNSAKER
1968. Trace and major element content of 170 High Sierra lakes in California. Limnology and Oceanography 13(3):526-30.
- JONES, J. R. E.
1938. The relative toxicity of salts of lead, zinc, and copper to stickleback (*Gasterosteus aculeatus* L.) and the effect of calcium on the toxicity of lead and zinc salts. Jour. Exp. Biol. 15:394-407.
1939. Relation between electrolytic solution pressures of the metals and their toxicity to the stickleback (*Gasterosteus aculeatus* L.). Jour. Exp. Biol. 16:425-37
- KOPP, JOHN F., and ROBERT C. KRONER
1970. Trace metals in waters of the United States. U. S. Dept. of the Interior, Federal Water Pollution Control Administration. Cincinnati, Ohio.
- LEE, FRED G.
1970. Factors affecting the transfer of materials between water and sediments. Literature Review No. 1, The University of Wisconsin Water Resources Center.
- SKIDMORE, J. F.
1964. Toxicity of zinc compounds to aquatic animals with special reference to fish. Quart. Rev. Biol. 39(3):227-48.
- SOYER, J.
1963. Contribution a l'etude des effets biologiques du mercure et de l'argent dans l'eau de Mer. Vie et Milieu 14:1-36.
- SPRAGUE, J. G.
1964. Lethal concentrations of copper and zinc for young Atlantic Salmon. Jour. Fish Res. Bd. Canad. 21:17-26.
- STANDARD METHODS FOR THE EXAMINATION OF WATER AND WASTE WATER
1965. 12th Edition, APHA, Inc. N.Y.
- STOLBOVA, E. P., and N. V. SHARSHUKOVA
1962. Effect of intoxication with tungsten compounds on ascorbic acid metabolism in animals. Sb. Nauchn. Tr. Ryazansk, Med. Inst. 15:129-31.
- U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
1962. Public Health Service "Drinking Water Standards." Revised 1963. U. S. Gov't. PHS Pub. 956. Washington, D.C.
- U. S. DEPARTMENT OF THE INTERIOR, FWPCA
1968. Water quality criteria. Report of the National Technical Advisory Committee. Washington, D.C.
- WILBER, CHARLES G.
1969. The biological aspects of water pollution. Charles C. Thomas Publisher. Springfield, Ill., U.S.A.

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