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METALS IN
POWER PLANT COOLING
WATER DISCHARGES

Cooling water from coastal power plants is the largest type of discharge to the Southern California Bight. The average annual flow from the fifteen major electrical generating stations in southern California during 1970-71 was 7.7×10^{12} liters/year, approximately seven times the corresponding rate for municipal wastewater discharged via submarine outfalls. In recent years, there has been growing concern that these very large thermal discharges could be raising the levels of certain toxic trace metals, such as copper, in the nearshore waters. However, because of the extremely low concentrations of such metals in seawater and in the discharges, there is little reliable information as to whether or not the effects of the discharges are significant. Therefore, we have conducted an investigation into the levels of six trace metals in both seawater influent and effluent of eight major generating stations located along the Ventura, Los Angeles, and Orange County coastlines. Our findings to date indicate that, although increased levels of some metals are found in certain near-shore regions (particularly harbors), the power plants studied do not appear to be an important source.

PROCEDURES

In February 1977, with the support and assistance of the Southern California Edison Company (SCE), we initiated a study of dissolved and particulate (greater than 0.4 micron) cadmium, chromium, copper, nickel, lead, and zinc in the influents and effluents of eight of SCE's coastal generating stations (Figure 1). During 1970-71, these plants had a total annual discharge of 5.3×10^{12} liters/year (3,800 million gallons per day), which constituted approximately 70 percent of the total thermal discharge to the Bight; in 1976, the discharge rate for these plants was 6.8×10^{12} liters/year.

In view of the difficulty of establishing net differences in trace metals at levels below a part per billion, it was necessary to be extremely careful about the cleanliness of sampling and replication and the determination of procedural blank and recovery values. Because cooling water is generally taken into and released from a given power plant at a depth of about 10 meters, and ports for obtaining representative samples of influent and effluent are not available, we developed an all-plastic subsurface seawater pumping

system patterned after that of Prof. John Martin (Moss Landing Marine Station).

Before the day of sampling, arrangements were made with operators of each plant so that no retention basin water (consisting of acid-cleaning wastes, fireside boiler wash water, and floor drainings) was discharged with the effluent on the day of sampling. This procedure was adopted because the concentrations of metals in basin waters are highly variable, often ranging over four orders of magnitude, and only the effect of the cooling process itself was to be investigated in this study.

Early on the day of sampling, the intake structure to be sampled was located with a fathometer, and the boat was moored directly above the end of the structure. The sampling hose was lowered to within 1 meter of the intake structure, the pump was engaged, and the samples were collected.

To sample the effluent, divers descended with the sampling hose and a piece of 1/4-inch polypropylene line. One end of this line was attached to a corner of the discharge structure. The line was then pulled taut across the orifice of the pipe, and the sampling hose was attached to the center of the line. The divers pulled themselves along the taut line and ascended along the sampling hose, making sure there were no constrictions. The divers then boarded the boat, and sampling commenced.

Samples were collected in duplicate, and in triplicate whenever practical. To obtain a sample, a precleaned, capped 4-liter Nalgene bottle was removed from double plastic bags, the cap was removed, and the bottle was filled from the seawater stream without touching the pump line to the inner neck of the bottle. Care was taken not to contaminate the bottle cap during this process. The sample bottles were then tightly recapped, placed in double, clean polyethylene bags, and returned to the laboratory within a few hours of collection.

In the laboratory, the samples were filtered without delay through prewashed 0.4-micron Nuclepore filters, and the filtrates were acidified to pH of about 2. Aliquots of both influent and effluent filtrates were spiked with standard solutions of the six target metals to monitor ionic recovery. Two procedural blanks (prepared by filtering 1 liter of deionized distilled water) were run with each sample set, which consisted of eight individual samples and two recovery aliquots.

Because levels of trace metals in seawater are usually very low, and the relatively large amounts of salts in seawater can cause serious Interferences in detection by atomic absorption spectroscopy, samples must be treated to concentrate the dissolved metals and, at the same time, remove the bulk salts. For this purpose, two techniques-organic solvent extraction and ion exchange—were applied in this study. To prepare a sample for analysis for dissolved chromium, copper, nickel, and lead, 200 ml of the sample were first treated with 2 ml of 1 percent ammonium pyrrolidine dithiocarbamate at a pH of about 4.0 and then heated to incipient boiling. After the sample had cooled to room temperature, 5.5 ml of methyl isobutyl ketone were added to the mixture, and it was shaken for 25 minutes. After the organic phase had

separated, it was saved for trace metals measurement against a set of internal standards that were prepared following the same procedure. For the determination of dissolved cadmium and zinc, 1 liter of water sample was adjusted to a pH of about 7.6 and passed through a 2-cm-diameter Pyrex glass column, which was fitted with a 4-cm-deep bed of ammonium-form Chelex 100 resin. After the column was washed with 150 ml of deionized distilled water, the trace metals were collected by passing 25 ml of 4N nitric acid solution through the column; the metals concentrations were then measured against the standards prepared in deionized distilled water.

The fraction of a metal retained by the 0.4-micron filter, and thus defined as in the particulate state, was determined by digesting the filter pad with 10 ml of 8N nitric acid solution for 2 hours. After adding 10 ml of deionized distilled water to the residue, the supernatant was removed by filtration, and the trace metals were measured against the standards prepared in deionized distilled water.

RESULTS

At three of the stations (Ormond Beach, Long Beach, and San Onofre), 3 to 4 replicate samples of both influent and effluent were collected and analyzed. This provided us an opportunity to determine the precision or repeatability of our measurements, as indicated by the overall percentage coefficient of variation, or CV (define as the standard deviation divided by 100 times the mean). The results are listed in Table 1. In general, the average CV for a given metal and state is well below ±50 percent, which is quite satisfactory when working at levels below a part per billion.

In view of the large amount of data obtained and the fact that replicate grab samples were collected only once from each site, we have grouped the data from the eight generating stations to characterize the overall effect of SCE's use of nearshore seawater on the metals balance in the Bight. To accomplish this, each available mean effluent concentration was compared to the corresponding influent mean concentration, and the difference (positive or negative) was calculated. Because more than one effluent was sampled at several of the plants, ten to thirteen "delta" values were obtained for each state of each metal; Table 2 lists the medians of the delta values and, for comparison, median influent concentrations.

To obtain estimates of the yearly input of the metals to the Bight via SCE's cooling process, the median "delta" values were multiplied by the average total discharge from the eight plants (6.8 x 1012 liters/year). The combined mass emission rates (dissolved plus particulate) for each metal are presented in Table 3. For comparison. Table 3 also gives available estimates of the magnitude of metal inputs from three other types of sources in the study area (Ventura, Los Angeles, and Orange Counties). These are municipal wastewaters, dry aerial fallout, and storm runoff.

DISCUSSION

The results of Table 2 show that, in 11 of the 12 cases, the median difference between effluent and influent concentration was positive, suggesting a net addition of the metals to the seawater during its use for cooling. However, it should be noted that none of the increases exceeds 0.2 ppb, and 10 of the 12 values are less than 0.1 ppb. Thus, although some metals contamination of the influent seawater is occurring, it is generally occurring at exceedingly low levels. There are several possible explanations for the increases. It has been our experience that the collection and transport of seawater invariably results in higher metals levels, unless extraordinary pre-cautions (such as washing equipment with ultrapure acid) are taken. For example, in the Project's natural seawater aquaria system, levels of dissolved chromium are about 0.6 ppb, three times the concentration of coastal seawater. Part of the additional metals measured in the thermal effluent may be contributed by organisms swept into the plant intake systems. If the whole body levels of copper in these organisms are on the order of 10 ppm or 10~5 (a typical value), and the concentration of such organisms in the influent is also 10 ppm (or 1 part organism per 105 parts seawater), extraction of the copper from organisms during the cooling process would raise the level of dissolved copper in the coolant seawater by 10"10, or 0.1 ppb.

The data of Table 3 also help to place these results in perspective. Comparison of estimated annual mass emission rates of the six metals to the general study area indicates that the use of nearshore seawater by the SCE system con- tributes only 0.06 to 0.4 percent of the combined input from municipal wastewater, aerial fallout, storm runoff, and thermal discharge.

As stated earlier, the retention basin waters from generating stations were not discharged during the time that samples were being taken for this study. It would seem appropriate to determine if the periodic discharges of these basin waters add additional trace metal contaminants to the effluent cooling water.

ACKNOWLEDGMENT

REFERENCES

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Table 1. Coefficients of variation (%) for dissolved and particulate metals concentrations measured in the influents and effluents of three SCE generating stations. Each value is based on the analysis of three or four replicate samples.*

	Ormond Beach		Long Beach		San Onofre	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
Cadmium						
Dissolved	48	17	6.2	62	102	61
Particulate	52	39	ND	ND	82	79
Chromium						
Dissolved	40	17	5.9	5.4	22	5.7
Particulate	12	28	2.2	7.1	18	31
Copper						
Dissolved	37	26	9.9	14	22	14
Particulate	17	2.5	3.6	1.4	13	23
Nickel						
Dissolved	37	27	12	5.0	15	7.1
Particulate	17	18	13	5.2	64	27
Lead						
Dissolved	ND	ND	3.3	27	ND	83
Particulate	1.3	45	36	5.0	103	19
Zinc						
Dissolved	ND	ND	31	21	ND	ND
Particulate	33	6.2	2.8	8.4	12	21

*ND indicates insufficient data.

Table 2. Median concentrations (ppb) of six metals in the influents of eight SCE generating plants and median difference (ppb) between effluent and influent concentrations.

	Median Influent Concentration		Median Difference Between Effluent and Influent Concentrations	
	Dissolved	Particulate	Dissolved	Particulate
Cadmium	0.06	0.006	0.034	0.005
Chromium	0.16	0.20	(0.01)	0.097
Copper	0.80	0.32	0.21	0.10
Nickel	0.44	0.16	0.10	0.004
Lead	0.14	0.24	0.04	0.07
Zinc	<0.2	0.48	0.09	0.17

Table 3. Estimated annual inputs (metric tons/year) of six metals to the Southern California Bight from eight SCE generating stations and three other sources.

	Municipal Wastewater[1]	Dry Aerial Fallout[2]	Storm Runoff[3]	SCE Cooling Waters[4]	Sum	SCE Cooling Waters (% of Sum)
Cadmium	41	0.8	1	0.3	43	0.7
Chromium	576	6.6	25	0.6	608	0.1
Copper	472	31	18	2.1	523	0.4
Nickel	307	12	17	0.7	337	0.2
Lead	161	240	90	0.8	492	0.2
Zinc	1,010	150	100	1.8	1,260	0.1

1. Based on 1976 data on total metals in effluents of the Oxnard, Hyperion (Los Angeles City), JWPCP (Los Angeles County), and Orange County treatment plants.

2. The estimated input in a 100- by 100-km zone off Los Angeles and Orange Counties in 1975. From Young and Jan 1977.

3. The estimated input of dissolved and particulate metals to the study area during 1971, an abnormally dry year. From Young et al. 1973.

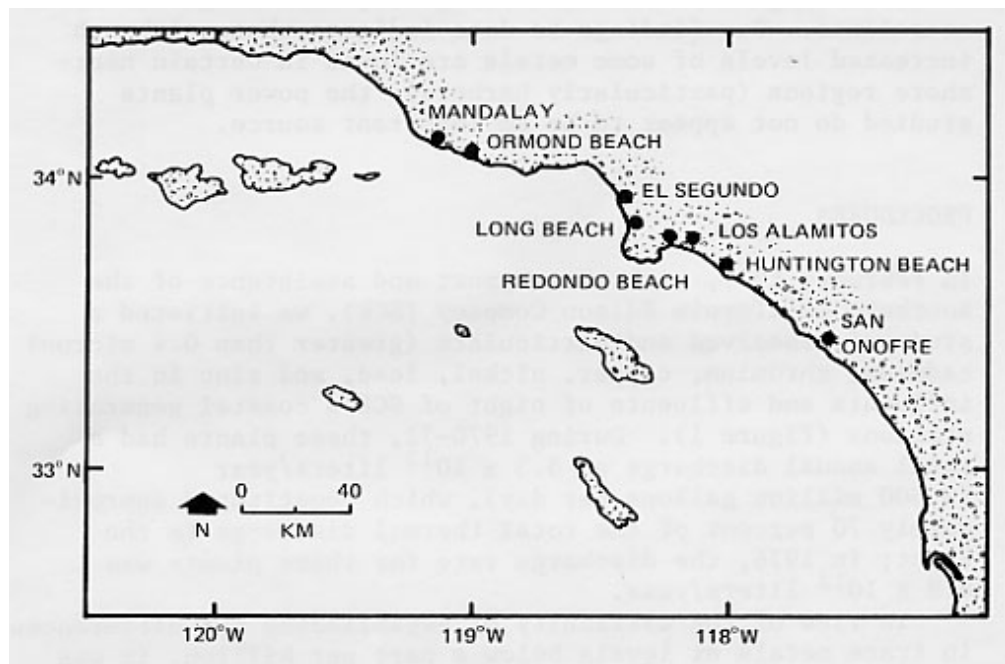4. Based on sum of dissolved and particulate metals concentrations.

Figure 1. Location of Southern California Edison electrical generating stations.