

CHROMIUM SPECIATION IN MUNICIPAL WASTEWATER AND SEAWATER

Over the last 2 years, the Project has studied the forms in which chromium is found in wastewater and seawater as part of our investigations into the marine toxicity of this metal. This has required the development of techniques of analysis that are sensitive to variations in chromium in seawater at the 10 parts-per-trillion level (0.01 pg/liter). Here we briefly discuss important aspects of these techniques and results of their application to questions on the physical/ chemical state of chromium in major municipal wastewaters and coastal seawater from outfall discharge sites and control stations in the Southern California Bight.

ANALYTICAL TECHNIQUES

As shown in Table 1, four methods are involved in our chromium speciation technique. Because of the relatively high concentrations of total dissolved chromium in wastewater, these measurements can be made by directly injecting the sample (which has been filtered through a 0.4-micron filter) into the graphite furnace of the atomic absorption spectrometer. However, the dissolved chromium in seawater must be concentrated before analysis by first complexing it with ammonium pyrrolidine dithiocarbamate (APDC) and then extracting it with the organic solvent methyl isobutyl ketone (MIBK). Seawater and wastewater samples to be analyzed for dissolved hexavalent chromium are treated by first complexing the hexavalent chromium with sodium diethyldithiocarbamate (NaDDC) and then extracting it into MIBK. A ferric hydroxide coprecipitation method is used to separate dissolved trivalent chromium from both wastewater and seawater.

Table 1 also gives recovery efficiencies and average blank values obtained in the analysis of eight wastewater and six seawater samples. To determine recovery, a known amount of the appropriate form of chromium was spiked into an aliquot of a sample immediately after filtering. The spiked samples were analyzed by the same procedures used for the nonspiked samples, and the recovery efficiencies were then calculated. Process blanks were determined by filtering double distilled water through a 0.4-micron filter and then processing it with the regular samples. The only significant blank values are those for trivalent chromium, which accounts for approximately 30 percent of the total signal for surface coastal water and certain wastewater samples; this is mainly due to contaminant levels in one of the reagents (ferric chloride).

Particulate chromium compounds are separated from samples by vacuum filtration through a 0.4-micron Nuclepore membrane filter followed by nitric acid digestion. All our chromium measurements are conducted by furnace atomic absorption spectrophotometry.

CHROMIUM IN MUNICIPAL WASTEWATER

In 1975, four grab samples of wastewaters were collected at Los Angeles City's Hyperion Treatment Plant. Replicates of these samples were analyzed for dissolved and particulate chromium (the usual sample size was 50 ml); the results are given in Table 2.

Trivalent chromium was the predominant dissolved species in all samples and accounted for more than 97 percent of the total dissolved chromium. The predominance of this form of chromium is probably a reflection of the high reducing environment of the organic-rich wastewater.

We also collected single grab samples of the primary-treated final effluents at four other southern California treatment plants; results of the analyses of replicates of these samples are shown in Table 3. Trivalent chromium again dominated the dissolved portions of the effluents.

When the data on Tables 2 and 3 are compared, it is apparent that the fractions of chromium compounds associated with particulates varied considerably from effluent to effluent. Los Angeles County's JWPCP effluent had the highest average concentration of particulate chromium compounds (747 ppb); relatively lower mean values of 27 to 88 ppb were measured in the other four primary effluents. The results also indicate that the average level of particulate chromium compounds in the November 1975 samples of Hyperion primary effluent (88 ppb) was reduced to 5 ppb by secondary treatment.

Equilibrium considerations suggest that, at a pH value of about 8 (the pH of the most wastewaters), a hydroxide complex is the predominant species of trivalent chromium, with Cr^{+3} , $\text{Cr}(\text{OH})^{+2}$, $\text{Cr}(\text{OH})_2^{+}$, and $\text{Cr}(\text{OH})_3$ being the four major species. By selecting equilibrium constants from McDuff and Morel (1973) and using the ionic strength value (10-2 M) suggested by Morgan,* we calculate the equilibrium concentration of trivalent chromium in wastewater at pH 8 to be 6.3×10^{-7} M/liter, or about 45 ppb. The dissolved trivalent chromium in three Hyperion effluents were all measured at about this level, agreeing with this equilibrium model within about 15 percent. The trivalent chromium levels in the samples of the other four municipal wastewaters ranged from 10 to 16 ppb, approximately one-quarter to one-third the predicted concentration.

Because disinfection by chlorination is widely used in some wastewater treatment plants, we conducted tests to determine if this procedure could oxidize trivalent chromium to the much more toxic dissolved hexavalent state. Test and control samples of Hyperion secondary-treated effluent and JWPCP primary-treated effluent were collected during 1975, and the test samples were treated with hypochlorite solution, producing representative dissolved chlorine concentrations of 2.5 and 36 mg/liter, respectively. The samples were stirred for more than 4 hours in the dark; they were then filtered and analyzed for dissolved trivalent chromium and hexavalent chromium. The mean concentrations were as follows:

	<u>Chlorinated</u>	<u>Unchlorinated</u>
JWPCP primary treated effluent		
Trivalent chromium	12.7	14.1
Hexavalent chromium	0.41	0.39
Hyperion secondary treated effluent		
Trivalent chromium	55.1	55.7
Hexavalent chromium	0.24	0.24

These results indicate that chlorination of municipal waste-water does not significantly increase effluent levels of dissolved hexavalent chromium.

COASTAL SEAWATER

We have initiated a study of the concentrations, and dominant physical/chemical states, of chromium in seawater away from discharge sites. During 1975, we collected replicate samples of surface seawater from three coastal stations beyond the immediate influence of wastewater discharges. These collections were made with an acid-washed plastic bucket from the bow of a small vessel that was moving slowly into the current. Stations 1 and 2 were located approximately 6 and 18 km to the southeast of the JWPCP outfalls off Palos Verdes Peninsula, while Station 3 was located on Cortes Bank, 150 km south-west of the Peninsula at the edge of the Bight. A fourth pair of samples was collected from Malibu Pier (Station 4) at the northern end of Santa Monica Bay. The usual size of the samples processed for analysis for dissolved trivalent chromium and particulate chromium compounds was 1 liter; 0.2-liter samples were used in analyses for dissolved hexavalent chromium. Results are given in Table 4.

The median concentrations measured for dissolved trivalent and hexavalent chromium in six offshore water samples were 0.045 and 0.14 pg/liter, respectively—in good agreement with the median value of 0.19 pg/liter obtained for total dissolved chromium. In comparison, the median concentration observed for particulate chromium (particles larger than 0.4 microns) was 0.017 pg/liter, less than 10 percent of the total chromium measured. Most of the Malibu Pier values (except those for dissolved hexavalent chromium) were higher than the medians for the offshore stations, perhaps reflecting the influence of the pier itself or another local source.

On 2 February 1976, we collected subsurface samples from two depths (25 m and 40 m) at a station located approximately 1.5 km to the northwest (downcurrent) of the JWPCP outfalls using a nonmetallic pumping system. The samples were filtered through 0.4-µm Nuclepore filters aboard ship and preserved, and the laboratory analyses were begun the following day.

Transmissometer readings at 25 and 40 m at the time of collection indicated light attenuation values of 25 and 75 percent per meter, respectively. (For comparison, in February of the previous year, the value at 25 m at a control station off Palos Verdes Peninsula was only 5 percent per meter.) In addition, the concentrations of ammonium-nitrogen at the two depths were 0.04 and 0.17 mg/liter, respectively (the

value at the control station in 1975 was 0.015 mg/liter). Thus, it appears that the 25 and 40 m 1976 collections represented different dilutions of the JWPCP effluent plume.

The results of our chromium analyses of the seawater at the two depths are presented in Table 5. The most important finding from this portion of the study is that the median concentrations of dissolved hexavalent chromium (0.15 and 0.16 ug/liter, respectively) were not significantly greater than the median of values measured elsewhere in the Bight (0.14 ug/liter). In comparison, the particulate chromium compound values at 25 and 40 m were elevated by one and two orders of magnitude, respectively, and the dissolved trivalent chromium levels were 2 to 4 times the estimated controls. The median concentrations of dissolved trivalent chromium in the 40-m depth JWPCP plume samples and offshore waters were 0.11 and 0.045 ug/liter, respectively (Tables 4 and 5). The difference (0.065 ug/liter) appears to be due to contamination from the submarine discharge. Combination of this value and the dissolved trivalent chromium concentration (14 ug/liter) in JWPCP primary effluent (Table 3) indicates a dilution factor for dissolved effluent materials exceeding 200 at the 40-m plume station. In comparison, median particulate chromium concentrations for the plume (1.1 ug/liter) and effluent (750 ug/liter) samples suggest a dilution factor of roughly 700 for suspended effluent materials at the 40-m station.

SUMMARY

Chromium compounds occur principally in the particulate state in municipal wastewaters of southern California. Of the fraction that is dissolved, 97 to 99 percent is in the trivalent form; the measured concentrations of dissolved trivalent chromium agree quite well with those predicted from equilibrium calculations. In contrast, hexavalent chromium—by far the most toxic form—generally constitutes less than 1 percent of the total chromium found in these wastewaters. Chlorination does not significantly increase these hexavalent chromium concentrations.

The majority of dissolved chromium found in clean coastal seawater off southern California is hexavalent chromium. The sums of the concentrations of dissolved trivalent and hexavalent chromium measured in our samples are in good agreement with the values for total dissolved chromium measured by an independent process.

Subsurface seawater samples, known by their high levels of turbidity, ammonium-nitrogen, and particulate metals to have come from within the JWPCP wastewater plume, contained concentrations of particulate chromium up to 50 times control levels. In contrast, the concentrations of dissolved trivalent chromium in the plume samples were only 2 to 4 times background values, and those of dissolved hexavalent chromium showed no significant enhancements. There appears to be a relatively high natural background of dissolved hexavalent chromium in coastal seawater. The low percentage of municipal wastewater chromium that occurs in this toxic form (plus the apparent lack of conversion of other forms of chromium to it) indicate that significant increases in seawater concentrations of hexavalent chromium do not result from ocean discharge of these wastewaters.

REFERENCE

McDuff, R.E., and F.M.M. Morel. 1973. Description and use of the chemical equilibrium program REDEQL2. Rept. EQ-73-02, W.M. Keck Laboratory of Environmental Engineering Science, Calif. Institute of Technol. Pasadena, Calif.

Table 1. Methods of analysis for dissolved chromium.

Sample	Sample Treatment	Blank *		Recovery *	
		µg/liter	CV ** (%)	%	CV ** (%)
Total chromium					
200 ml seawater	APDC/MIBK extraction	0.045	78	61	30
2.5 µl wastewater	Direct injection	—	—	—	—
Trivalent chromium					
1,000 ml seawater	Fe(OH) ₃ coprecipitation	0.019	21	70	41
50 ml wastewater	Fe(OH) ₃ coprecipitation	6.2	61	99	8
Hexavalent chromium					
200 ml seawater	NaDDC/MIBK extraction	0.015	33	98	12
50 ml wastewater	NaDDC/MIBK extraction	0.08	25	87	22

*Averaged from analysis of 8 wastewater and 6 seawater samples.

**Coefficient of variation.

Table 2. Chromium concentration (ug/liter) in four grab samples of wastewater collected in 1975 from Hyperion Treatment Plant.

Sample	Dissolved Chromium			Particulate Chromium	
	Trivalent	Hexavalent	Total*	Concentration	% of Total Cr
Primary treated wastewater, November					
Replicate 1	45.1	0.38	53.0	86.2	62
Replicate 2	52.3	0.21	NA **	89.6	63
Secondary treated wastewater					
June					
Replicate 1	52.7	0.25	65.1	12.1	16
Replicate 2	58.6	0.22	61.5	14.7	19
November					
Replicate 1	48.7	0.19	40.9	4.9	11
Replicate 2	47.8	0.19	NA	4.4	9.6
Final 5-mile outfall effluent, November					
Replicate 1	47.8	0.19	52.1	47.9	48
Replicate 2	50.0	0.13	NA	44.2	46

*Direct measurements; compare with sum of measurements of trivalent and hexavalent.
 **NA = not analyzed.

Table 3. Chromium concentrations (ug/liter) in grab samples of primary-treated effluents collected in 1975-76 from four southern California treatment plants.

Sample	Dissolved Chromium			Particulate Chromium	
	Trivalent	Hexavalent	Total*	Concen- tration	% of Total Cr
Los Angeles County, Joint Water Pollution Control Plant (JWPCP), June 1975					
Replicate 1	13.6	0.35	16.2	936	98
Replicate 2	14.5	0.43	15.6	557	97
Orange County, June 1975					
Replicate 1	15.3	0.10	14.2	46.5	76
Replicate 2	16.4	0.12	13.9	50.4	79
San Diego City, January 1976					
Replicate 1	11.1	<0.08	12.7	61.5	83
Replicate 2	12.3	0.08	NA**	62.9	83
Oxnard City, January 1976					
Replicate 1	9.9	<0.08	13.6	27.0	66
Replicate 2	10.3	<0.08	NA**	26.7	67

*Direct measurement; compare with sum of measurements of trivalent and hexavalent.
 **NA = not analyzed.

Table 4. Chromium concentrations (ug/liter) in southern California seawater from four locations away from municipal wastewater outfalls, 1975.

Sample	Dissolved Chromium			Particulate Chromium
	Trivalent	Hexavalent	Total*	
Offshore waters				
Station 1, 6 km SE of JWPCP outfalls				
Replicate 1	0.048	0.13	0.17	0.017
Replicate 2	0.029	0.14	0.21	0.027
Station 2, 18 km SE of JWPCP outfalls				
Replicate 1	0.056	0.16	0.25	0.012
Replicate 2	0.062	0.16	0.27	0.017
Station 3, Cortes Bank				
Replicate 1	0.032	0.13	0.11	0.011
Replicate 2	0.041	0.12	0.09	0.022
Median	0.045	0.14	0.19	0.017
Surf zone				
Station 4, Malibu Pier				
Replicate 1	0.25	0.18	0.56	0.18
Replicate 2	0.25	0.17	0.46	0.14

*Direct measurement; compare with sum of measurements of trivalent and hexavalent.

Table 5. Chromium concentrations (ug/liter) in two samples of seawater taken at two depths in the Los Angeles County outfall system, 2 February 1976.*

Dissolved Chromium				Particulate Chromium
Sample	Trivalent	Hexavalent	Total**	
25-m depth				
Replicate 1	0.074	0.15	0.16	0.15
Replicate 2	0.078	0.15	0.27	0.24
Replicate 3	0.064	0.14	0.22	0.28
40-m depth				
Replicate 1	0.104	0.15	0.19	1.41
Replicate 2	0.110	0.16	0.20	1.14
Replicate 3	0.135	0.17	0.16	0.95

*For comparison, the concentrations of dissolved and particulate total chromium of a Palos Verdes control station in February 1975 were 0.23 and 0.03 $\mu\text{g/liter}$, respectively.

**Direct measurement; compare with sum of trivalent and hexavalent measurements.