

CHROMIUM IN MUNICIPAL WASTEWATER AND SEAWATER

The toxicity of an element often depends on its physical and chemical state in the environment. As discussed in the Biology Section of this report, we are trying to identify the forms and concentrations of chromium that are deleterious to marine organisms. A parallel objective of this research is to identify the forms and concentrations of chromium that occur in municipal wastewaters of southern California. Here we report the progress we have made to date in reaching this objective.

We determined in previous experiments that, on the average, approximately 85 percent of the total chromium in major municipal wastewaters discharged to the Bight is associated with particulate material retained on a 0.45-micron filter. To learn more about the chemical forms of the "dissolved" chromium in wastewater, meaning all chromium that passes the filter, we conducted a pilot test with replicate grab samples of Hyperion final effluent collected on 24 November 1974, just prior to discharge via the 5-mile outfall in Santa Monica Bay.

One pair of the 1-liter effluent replicates was filtered immediately upon collection. A second and third pair of replicates were spiked with 10,000 ppb chromium as the trivalent (Cr^3) and hexavalent (Cr^{+6}) forms, respectively. (These are the two principal oxidation states of chromium believed to exist in solution in the environment.) These samples were well mixed and then capped and allowed to sit overnight at room temperature before being filtered. A fourth and fifth pair of replicates were also spiked in this manner, but instead of being filtered on the second day, they were diluted 100-fold with unfiltered seawater, allowed to sit overnight, and filtered on the third day.

The liquid fractions (filtrates) of these samples were analyzed for three classes of dissolved chromium. Trivalent chromium concentrations were determined using an $\text{Fe}(\text{OH})_3$ coprecipitation technique, which, at the 50-ppb level, appears to recover more than 95 percent of the trivalent chromium and less than 20 percent of the hexavalent chromium in the filtrate. Hexavalent chromium concentrations were determined using an organic solvent (MIBK) extraction technique that recovers more than 95 percent of the hexavalent chromium and less than 5 percent of the trivalent chromium. Process blanks for the two procedures are up to 20 ppb and less than 1 ppb, respectively. Concentrations of total dissolved chromium were analyzed by direct injection into the graphite furnace of the atomic absorption spectrometer (both losses and blanks are insignificant for this technique, which has a sensitivity of less than 1 ppb).

The experimental results are presented in Table 1. One of the principal observations from these data is that approximately 90 percent of the dissolved chromium in the Hyperion effluent occurred in the trivalent form; the levels found (52 and 61 ppb) were in good agreement with the theoretical equilibrium level calculated for municipal wastewater in a collaborative effort with Prof. James Morgan of California Institute of Technology. Also, the sum of the trivalent and hexavalent values (62 ppb) was in good agreement with the quantity of total chromium measured (66 ppb). Relative to the average level (approximately 300 ppb) of chromium in unfiltered 5-mile effluent, the 6 ppb of hexavalent chromium measured in our samples represents only about 2 percent of the chromium being discharged from the outfall. This observation is consistent with the data produced by the Hyperion monitoring program.

The results from the spiking tests indicate that, at least at these relatively high levels, our analytical techniques for trivalent and hexavalent chromium are quite efficient and selective. The $\text{Fe}(\text{OH})_3$ method yielded approximately 90 percent of the chromium measured as total dissolved chromium following the trivalent chromium spike. Only 0.1 percent of this dissolved chromium was recovered using the MIBK procedure for hexavalent chromium. In contrast, when hexavalent chromium was added to the effluent, 99 percent of the total chromium measured in the subsequent filtrate was recovered by the MIBK procedure for the hexavalent form. Furthermore, less than about 5 percent of the hexavalent spike was recovered by the $\text{Fe}(\text{OH})_3$ method. It is important to note that almost 90 percent of the 10,000-ppb trivalent spike of the effluent was removed during filtration the following day, but there was no detectable removal of the 10,000-ppb spike of hexavalent chromium. This is consistent with the fact that hexavalent chromium is much more soluble than is trivalent chromium.

Results from the last two parts of this experiment indicate that the 100:1 seawater dilution did not immediately cause significant changes in the physical and chemical states of the trivalent and hexavalent chromium spikes in the effluent. Less than 0.2 percent of the diluted trivalent spike was found to be in the dissolved hexavalent form the next day. Also, it appears that less than 10 percent of the trivalent chromium that had become associated with the filterable particulates had gone back into solution 1 day after the seawater dilution. Finally, most of the hexavalent spike was recovered in the dissolved hexavalent form after the dilution.

The findings from this pilot experiment have given us considerable confidence in our analytical techniques for distinguishing between particulate, dissolved trivalent, and dissolved hexavalent chromium in municipal wastewaters. During the coming year, we hope to apply such procedures to all the major municipal effluents being discharged to the Bight so that we can better understand the forms and quantities of chromium introduced to the coastal marine ecosystem via this route.

Table 1. Concentrations (ppb) of total, trivalent, and hexavalent chromium in the dissolved fraction of Hyperion 5-mile effluent after various treatments. Samples were collected 24 November 1974; pH ranged from 7.7 to 7.9.

Sample	Total Cr	Cr ⁺³	Cr ⁺⁶
Filtered (0.45 micron) upon collection			
1a	65	52	6.8
1b	68	61	5.2
Spiked with 10,000 ppb Cr ⁺³ ; filtered on 2nd day			
2a	1,180	1,050	1.1
2b	1,140	1,000	1.3
Spiked with 10,000 ppb Cr ⁺⁶ ; filtered on 2nd day			
3a	10,500	510	10,000
3b	10,000	410	10,300
Spiked with 10,000 ppb Cr ⁺³ ; diluted with seawater 100:1 on 2nd day; filtered on 3rd day			
4a	11	8	<0.2
4b	21	7	<0.2
Spiked with 10,000 ppb Cr ⁺⁶ ; diluted with seawater 100:1 on 2nd day; filtered on 3rd day			
5a	105	4	88
5b	107	4	90