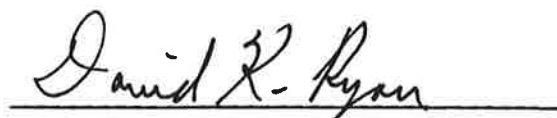


TRACE METAL SPECIATION STUDIES

Final Report and Data Synthesis

A handwritten signature in cursive script, reading "David K. Ryan", is positioned above a horizontal line.

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20 March 1986

Introduction

Of the priority pollutants surveyed in the SEDS Response to Contingencies Section 301(h) Waiver of Secondary Treatment Requirements (SESD, 1983), several metals had maximum concentrations above the EPA Water Quality Criteria (Fed. Reg., 1980). Two of these, chromium and antimony, were higher than the maximum values reported for EPA for 40 publicly-owned treatment works (U.S. EPA, 1982). This information combined with the known ability of both metals to be present in multiple forms (species) made them likely candidates for study.

Metal speciation has many important implications in transport, bioaccumulation and ultimate fate of metals in aquatic systems. Chromium speciation is known to be important with respect to its acute toxicity in biological systems. Antimony, by analogy of its behavior with that of arsenic, can also have different physicochemical and toxicological properties based on its chemical forms.

The work described here involves the speciation of chromium and analysis for antimony in samples from Salem Harbor and Salem Sound collected from September to November 1985. Chromium analyses were conducted for total chromium, free chromium and hexavalent chromium. This study is somewhat limited in that only a small number of samples were collected in a relatively short period of time. In addition, chromium and antimony inputs to this region have presumably decreased over the past few years, making ambient concentrations low or undetectable in many cases.

Materials and Methods

Samples were collected on October 8, 9 and 10, 1985, in 10-l GO-FLO samplers as described in the previous section. From a single 10-l hydrocast, several samples were taken. For this work two 1-l aliquot were taken for chromium speciation and two 500-ml aliquots were taken for total metal analysis and antimony speciation. Samples for chromium speciation were immediately stored on ice and later refrigerated at 4°C in the laboratory. One 500-ml aliquot for total antimony and total chromium analyses was acidified with 4 ml of Ultrex HCl and stored cold as above. The second 500 ml subsample for antimony speciation was "quick frozen" in a dry ice acetone bath immediately after sampling and stored frozen.

Additional samples for total chromium and chromium speciation were collected on 6 September 1985, 12 September 1985 and 20 November 1985. The stations included Station 1 and six new stations, designated A through F. Table 1 lists latitude and longitude for these new stations. Figure 1 is a chart of a section of Salem Sound with the stations marked. Station F is the site of the mussel cage for the bioaccumulation study.

The samples from these new stations were taken using an XRB sampler and polyethylene bottles prepared by acid leaching overnight. Sampling materials were taken to the site wrapped in plastic bags and opened immediately before use. Sampling was conducted over the side of a boat facing into the prevailing wind to reduce the possibility of contamination. Samples were put on ice for 2 to 3 hrs prior to refrigeration at 4°C. Chromium speciation by equilibrium dialysis was begun within 24 hrs.

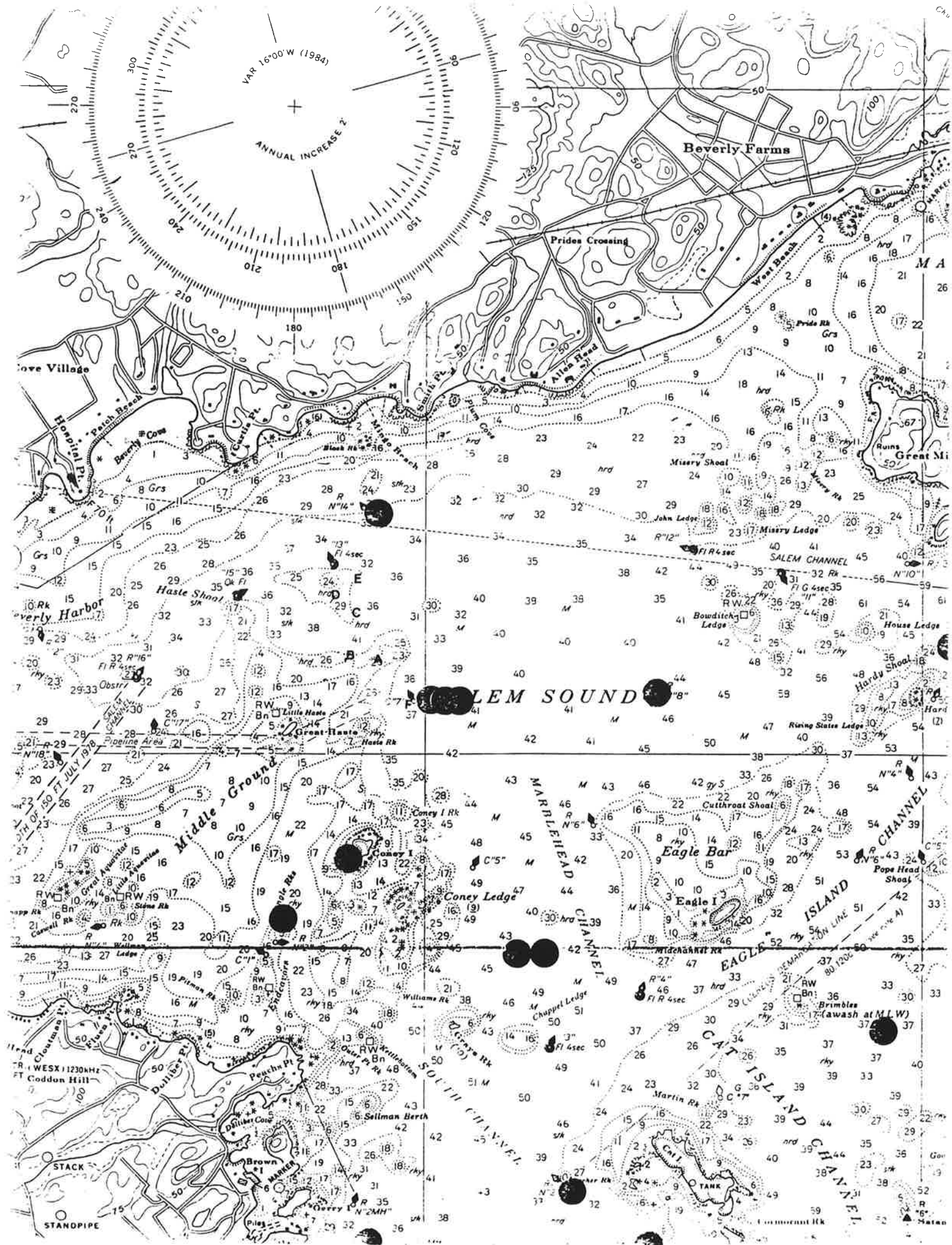
All sample manipulations and transfers in the laboratory took place in a Class 100 laminar-flow clean hood. Materials that came in contact with samples were acid leached overnight unless otherwise noted.

TABLE 1. Location of additional stations for chromium speciation studies.

<u>Station</u>	<u>Latitude</u>	<u>Longitude</u>
A	42°32.28'	70°50.20'
B	42°32.30'	70°50.30'
C	42°32.43'	70°50.27'
D	42°32.48'	70°50.37'
E	42°32.53'	70°50.27'
F	42°32.12'	70°50.13'

FIGURE 1

Chart of Salem Sound showing locations of additional stations
(A through F) for chromium speciation samples.



Total chromium analyses were conducted on subsamples of the HCl acidified seawater. A minimum of two determinations on each sample were performed by aspiration into a direct current argon plasma atomic emission spectrometer (DCP, Beckman). Standards from 1 to 100 ug/l and blanks were prepared from 0.45 um filtered seawater acidified with 1.25 ml Ultrex HCl per 100 ml. Samples were run in random order. Six replicate integrations of the emission intensity signal were recorded and averaged using a dedicated PDP 11/03 mini-computer (Charles River Data Systems).

Speciation of chromium into free inorganic forms and chromium complexes of large organic compounds was performed by equilibrium dialysis for samples with detectable total chromium. Duplicate 250 ml aliquots of a sample were dialyzed against 10 ml of 0.45 um filtered seawater using Spectra Por 7 membranes of 1000 molecular weight cut off (Spectrum Industries) for 48 hrs with gentle stirring (Ryan, 1986). At the end of this time period, aliquots were taken from both inside and outside the dialysis bags for chromium analysis.

Hexavalent chromium (Cr(VI)) was determined by a modification of EPA method 218.4 (US EPA, 1979). Samples of 100 or 200 ml were extracted with 1-pyrrolidine carbodithioic acid (PCDA) in chloroform. The pH of the samples was adjusted to 2.4 using Ultrex HCl starting from a bromophenol blue endpoint. After vigorous mixing for 3 min, the chloroform layer was drawn off and the extractions repeated twice more.

The combined PCDA-chloroform extracts were heated to near dryness and digested with 5 ml of redistilled HNO_3 . Digested samples were taken to volume in 25 ml volumetric flasks with a final HNO_3 concentration of 20%. Extraction blanks showed no detectable Cr(VI) at a calculated detection limit of 0.07 ug/l. Extractions of triplicate aliquots of a solution containing 10 ug/l Cr(VI) as $\text{K}_2\text{Cr}_2\text{O}_7$ gave an average recovery of 100.4% with a relative standard deviation of 2.1%.

Total inorganic antimony was determined by the method of Andreae et al. (1981) without cryogenic trapping. The Ultrex HCl acidified portion of each sample was reacted with KI and NaBH_4 to produce the volatile stibines. Analysis was by DCP with a 2σ detection limit of 0.6 ug/l.

Results

The results of total chromium and total antimony analyses are listed in Table 2, along with the sample depth and the date on which the samples were collected. In general, chromium is very low in the stations near the outfall and is not detectable in any of the outer station samples down to the 0.6 ug/l level. Inspection of the data with respect to depth seems to indicate generally higher Cr values in the samples taken closer to the surface.

Antimony, as total inorganic antimony, was not detected in any of the samples analyzed. Antimony standards prepared from potassium hexahydroxyantimonate (V), antimony potassium tartrate, methylstibonic acid and dimethylstibinic acid were used in the analyses and indicated that antimony could be readily detected to 0.6 ug/l in seawater samples.

Chromium speciation results are also listed in Table 2. The data represent two classes of chromium species, free chromium (i.e. small, inorganic forms) and hexavalent chromium. Since the total chromium levels were very low in the samples collected October 8 through 10, 1985, most of the speciation work was conducted on the additional samples collected on 20 November 1985.

In general, free Cr is no more than one-half of the total Cr concentration at a given station, with the possible exception of Station E. In two cases, stations C and D at 1 m, free Cr is approximately one-fourth the total Cr concentration.

TABLE 2. Analytical data for the analysis of antimony and the speciation of chromium in seawater and sewage effluent samples.

Date	Station	Depth (m)	Total Cr (ug/l)	Free Cr (ug/l)	Cr (VI) (ug/l)	Total Sb ^a (ug/l)
11/20/85	A	1	2.0±0.9	0.9±0.2	0.3±0.1	
	A	3	1.6±0.2	0.6±0.2	0.1±0.05	
	B	1	1.9±0.2	0.9±0.7	0.3±0.1	
	B	3	2.1±0.1	0.6±0.4	0.1±0.05	
	C	1	11.0±0.2	2.5±0.9	0.2±0.07	
	C	3	4.3±0.5	1.6±0.4	0.1±0.05	
	D	1	11.5±0.4	2.6±0.4	0.4±0.1	
	D	3	3 ±2	1.4±0.4	0.3±0.1	
	E	1	2.5±0.5	1.7±0.4	0.1±0.05	
	E	3	2 ±1	1.5±0.4	0.1±0.05	
	F	13	ND	ND	--	
9/12/85	1	0.5	34.8±0.7		6.8±0.2	ND
9/6/85	1	0.5	34.5±0.9		2.7±0.1	ND
10/10/85	1	3	1.5±0.6			ND
	1	9	1.2±0.9			ND
	2	3	1.0±1.7		0.4±0.1	ND
	2	11	1.6±0.3		0.4±0.1	ND
	3	4	0.5±0.2			ND
	3	8	ND			ND
10/9/85	4	4	ND			ND
	4	12	ND			ND
	4	20	ND			ND
	5	7	ND			ND
	5	16	ND			ND
	5	28	ND			ND
	6	5	ND			ND
	6	9	ND			ND
	6	19	ND			ND
	6	29	ND			ND
	6	39	ND			ND
10/8/85	7	32	ND			ND
	7	42	ND			ND
	8	8	ND			ND
	8	20	ND			ND
	8	28	ND			ND
9/25/85	Effluent		200±9		145±5 ^b	ND ^c
1/7-8/86	Effluent		193±9		22±1	ND ^c

ND = not detected (2 σ detection limit 0.6 ug/l)

a) Total inorganic antimony

b) Questionable value due to prolonged storage of sample prior to analysis

c) Detection limit 1.0 ug/l for these analyses

Hexavalent chromium values in Table 2 are quite low, ranging from 0.1 to 0.4 ug/l in all but two of the samples. The samples with the highest Cr(VI) are the samples collected nearest the surface at station 1. All of the samples from station 1 that were analyzed for Cr(VI) demonstrated high ratios of Cr(VI) to total chromium compared to the other stations.

In addition to the seawater samples analyzed for chromium and antimony, two sewage effluent samples were analyzed for total metal content and hexavalent chromium. The data for the ten metals determined in these samples is shown in Table 3. The standard deviation reported for each value gives an indication of the uncertainty of the value based on duplicate analyses and six replicate measurements of each sample. Only cadmium and antimony were undetected in these samples. Each of the other metals was present at nearly identical concentrations in the two samples, with the exception of manganese and lead.

Discussion

The results for total chromium and total inorganic antimony described above (Table 2) indicate much lower chromium and antimony inputs to Salem Harbor than expected based on the data presented in the 301(h) waiver document (SESD, 1983). The data for the total chromium and total antimony in the effluent samples allow a direct comparison. The grab sample taken on 25 September 1985 and the 24-hr composite from January 7 and 8, 1986, had very similar total chromium values of approximately 0.2 mg/l. Priority pollutant data for total chromium in the SESD effluent in the 301(h) document is as high as 1.24 mg/l (Table 3-1; SESD, 1983). The situation for antimony shows an even larger disparity. In this study, total inorganic antimony was below the detection limit of 0.001 mg/l for both effluent samples. However, the priority pollutant data for total antimony from 1982 showed 0.21 mg/l and 2.84 mg/l for dry and wet weather respectively (Table 3-1; SESD, 1983).

TABLE 3. Total concentrations of selected metals
in two sewage effluent sample

<u>Metals</u>	<u>Sample Concentration (mg/l)</u>	
	<u>9/25/85 1:15 p.m.</u>	<u>1/7-8/86 24 hr composite</u>
Al	2.0±0.3	1.8±0.3
Cd	<0.03	<0.03
Cr	0.200±0.009	0.193±0.009
Cu	0.058±0.007	0.050±0.007
Fe	0.67±0.02	0.65±0.02
Mn	0.22±0.01	0.14±0.01
Ni	0.031±0.004	0.030±0.004
Pb	0.28±0.04	0.18±0.04
Sb	<0.001	<0.001
Zn	0.10±0.02	0.10±0.02

Several possible factors may contribute to the large differences in effluent antimony and chromium values seen between 1982 and the present study. It is very likely that reduced metal loads in the effluent are a result of the District's Industrial Pretreatment Program, which was implemented in the time period between the 1982 priority pollutant analyses and this study.

Industrial and/or commercial enterprises are most certainly the source of pollutants such as chromium and antimony; therefore, improved waste treatment prior to discharge into the sewage system could be a very important factor.

Secondly, some of the polluters may have gone out of business. Information from the South Essex Sewerage District indicates that several potential chromium contributors to the sewerage system, such as tanneries and leather finishers, have gone out of business in the last few years. This factor combined with individual pretreatment could cause the noted effect.

Finally, it must be stated that the data presented is very limited and any conclusions drawn should reflect the overall uncertainty. Additional data on the total chromium content of the sewage effluent is available from SESD. Analyses conducted three times per month by the District agree to some extent with the data discussed above. Total chromium measured on the effluent in January 1986 showed a high of 0.21 mg/l, but was usually below the detection limit of 0.10 mg/l (personal communication, William Liss, SESD).

Some general observations can be made from the chromium data that was obtained. As mentioned previously, there seems to be a relationship between depth and total chromium concentrations. The samples at 0.5 m were by far the highest in chromium, with the 1 m samples having the next highest values, with some exceptions. Samples taken in deeper water are substantially lower in chromium, which decreases with distance from the outfall as expected.

A possible explanation for the higher chromium levels near the surface in the vicinity of the outfall is that the low salinity effluent (0 to 1 ‰) rises to the surface to some extent. This is partially substantiated by the lower salinities found for the 0.5 m samples collected on September 6 and 13, 1985 (27 and 22 ‰ respectively). The surfacing of the effluent may be expected strictly on the basis of the lack of a significant diffuser on the end of the effluent pipe, giving rise to the characteristic boil observed at station 1.

The chromium speciation results listed in Table 2 give some additional information about the behavior of this metal. Free chromium is all those chromium species not associated with particles or bound in large complexes with soluble organic compounds, such as those found in sewage effluent. Operationally free chromium is comprised of any chromium species that will diffuse through a 1000 molecular weight cut-off membrane and is generally restricted to inorganic forms of chromium including CrO_4^{2-} , $\text{Cr}(\text{OH})_2^{2+}$ in seawater, and possibly some small chromium organic matter complexes.

Free chromium is usually lower than total chromium in the samples analyzed by at least a factor of two. This indicates a substantial contribution of particulate chromium and/or dissolved complexes of chromium to the total chromium values. It may be that the surface samples with the highest total chromium have a large amount of particulate chromium present. Another view of the relationship between particulate and total metal can be obtained by comparing some of the particulate chromium data from the previous section on Trace Metal Studies (Gardner, Eganhouse and Wallace, 1986) with the data presented here. Table 4 gives the detectable chromium concentrations from Table 2 converted to nmol/l for direct comparison. The data for particulate Cr at stations 1, 2 and 3 (Gardner, Eganhouse and Wallace, 1986) can be compared to the corresponding total Cr values (Table 4) and subtracted to give

Table 4. Chromium Speciation Data in nmol/L Taken from Table 2.

Station	Depth (m)	Total Cr (nmol/L)	Free Cr (nmol/L)	Cr(VI) (nmol/L)
A	1.0	38.5	17.3	5.8
A	3.0	30.8	11.5	1.9
B	1.0	36.5	17.3	5.8
B	3.0	40.4	11.5	1.9
C	1.0	211.5	48.1	3.8
C	3.0	82.7	30.8	1.9
D	1.0	221.1	50.0	7.7
D	3.0	57.7	26.9	5.8
E	1.0	48.1	32.7	1.9
E	3.0	38.5	28.8	1.9
1	0.5	669.2		130.8
1	0.5	663.4		51.9
1	3.0	28.8		
1	9.0	23.1		
2	3.0	19.2		7.7
2	11.0	30.8		7.7
3	4.0	9.6		
Effluent		3846		2788a
Effluent		3711		423

a) Questionable value due to prolonged storage of sample.

dissolved Cr. Particulate chromium ranges from 35% to 67% of total Cr in the sample taken closer to the surface. The deeper samples exhibit less than one-quarter of the total as particulate chromium.

One of the chromium species that is part of the free chromium category is hexavalent chromium. The hexavalent chromium values shown in Table 2 (ug/l) and Table 4 (nmol/l) are only a small fraction of the chromium present. Many of the samples with the highest total chromium have high chromium (VI) concentrations, although this relationship does not hold throughout. In the case of the 0.5 m samples taken at station 1, the Cr(VI) concentrations are significantly different even though the total Cr concentrations are essentially identical. This can come about as a result of different initial loadings of Cr(VI) with respect to other chromium species or because the extent of reduction of Cr(VI) by other sewage components varies at different times depending on the composition of the sewage. Although a similar situation seems to be observed for the effluent samples, it should be noted that the value of 145 ug/l (2788 umol/l) of Cr(VI) in the effluent sample collected on 25 September 1985 is somewhat in question because the sample was not analyzed for several weeks after collection.

Chromium (VI) is of concern in the samples because it is the known toxic form of chromium. The levels present in these samples are not of major concern with regard to the Water Quality Criteria (Fed. Reg., 1980) or from an acute toxicity standpoint. However, Cr(VI) is present and the concentration may fluctuate to potentially problematic levels.

Chromium speciation in general should also be considered in terms of the potential for chromium bioaccumulation in marine organisms. Although no extensive or definitive studies have been conducted to clearly determine the forms of chromium that are available to marine organisms, it is generally

accepted for transition metals that the free forms have the greatest availability (Engel et al., 1981). For chromium it is probably the soluble inorganic forms (i.e. free Cr) that is most readily taken up (Carr et al., 1982). From the data presented in this study, it is clear that the amount of available or free chromium is low but significant. This, combined with the data from the bioaccumulation study also carried out as part of this project (Robinson et al., 1986), indicates that chromium may be a significant factor in the total metal body burden for marine organisms in the vicinity of the SESD sewage outfall. It is not clear what chromium species, hexavalent chromium, or other free or dissolved forms of chromium are the most important in the overall picture of chromium bioavailability.

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