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Ryan R. Roseburrough

Dauphin Island Sea Lab; Spring Hill College, ryan.roseburrough@email.shc.edu

Xiangli Wang

Dauphin Island Sea Lab; University of South Alabama, xwang@southalabama.edu

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SHORT COMMUNICATION

CHROMIUM DISTRIBUTION IN WATER AND SEDIMENTS IN THE MOBILE RIVER AND BAY, ALABAMA[§]

Ryan Roseburrough^{1,2} and Xiangli Wang^{1,3*}

¹Dauphin Island Sea Lab, University Programs, 101 Bienville Boulevard, Dauphin Island, AL USA 36528; ²Spring Hill College, 4000 Dauphin Street, Mobile, AL, USA; ³University of South Alabama, Department of Marine Sciences, Mobile, AL, USA 36688;

*Corresponding author, email: xwang@southalabama.edu

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INTRODUCTION

Industrial activities have led to wide-spread heavy metal contamination in the environment (Gambrell 1994). Chromium (Cr) is widely used for anti-corrosion and tanning industries and can cause severe groundwater contaminations (e.g., Ball and Izbicki 2004). Chromium mainly exists in 2 valence states, trivalent Cr (III) and hexavalent Cr (VI). Cr (III) is insoluble at circumneutral pH and is a bioessential micronutrient (Rai et al. 1987). In contrast, Cr (VI) is carcinogenic and soluble, and thus can cause wide-spread pollution (Dayan and Paine 2001).

Chromium distribution is poorly studied in the Mobile-Tensaw river estuary system in Alabama. Two main potential point sources of Cr exist in the lower reach of the Mobile-Tensaw river: Alabama Power's Plant Barry and the Industrial Park in downtown Mobile, Alabama. Plant Barry is a coal burning power plant with a risk of allowing heavy metals that were once trapped in coal ash to leak into the river system from the unlined, on-site ash pond that sits on the bank of the Mobile River (Callaway et al. 2018). Although Cr in coal ash is mostly (>95%) non-toxic Cr(III) (Huffman et al. 1994), Cr(III) contained in large amounts of coal ash can be oxidized to the harmful Cr(VI), thus posing long-term risks to the environment. A limited number of sediment and groundwater samples taken at the plant showed detectable dissolved Cr in groundwater and higher Cr in sediments near the plant compared to background sediments (Callaway et al. 2018). Therefore, it is necessary to take more sediment samples as well as surface water samples in the vicinity of the plant to address potential effects on surrounding surface environments. The Industrial Park contains large quantities of ship building and manufacturing plants, which may release Cr into the Mobile Bay system. The goal of this study is to quantify understudied Cr concentrations in the sediments and surface water throughout the Mobile Bay estuarine system, and to test the hypothesis that Cr concentrations will be higher adjacent to areas of land with heavy urban and industrial uses.

MATERIALS AND METHODS

Labware cleaning

All HCl and HNO₃ used were distilled using Savillex DST-1000 acid distills. Before use, all plastics were acid washed in 10% HCl, either in an acid bath for a minimum of 3 days or refluxed overnight at 50°C, and all Teflon beakers were washed in a 50% HNO₃ bath heated for at least 6 h at 90°C. After acid washing, all plastics and Teflon beakers were rinsed twice with Milli-Q (MQ) water with 18.2 MΩ resistivity. Plastic pipette tips were cleaned with 6N HCl and MQ water.

Sampling

All samples were collected on 17 June 2019 from the Mobile River and Mobile Bay (Figure 1). Sample 1 was taken for approximate upstream background levels, while samples 3 and 4, the Ash Pond and Outflow of Plant Barry respectively, and 14–16, the Industrial Park, were taken in areas with heavy industrial uses. All other samples were taken from areas not as heavily influenced by urbanization. Water samples were collected at the surface in 1 L plastic bottles. All sediment samples, except for sample 2, were collected from the riverbed channel using a Peterson grab, and only fresh sediments from the core of the grab were collected in acid-washed plastic 50 mL centrifuge tubes for analysis. Sample 2 was taken from the exposed river bank rock above the water. Samples were placed in a cooler with ice packs until returning to the lab where they were put into a refrigerator (4°C). Water samples were then vacuum filtered two days later through 0.45 μm filters (Advantec® membrane filter) and returned to the refrigerator overnight. The next day, filtered water samples were acidified to pH < 2 with 2 mL of 6N HCl to reduce Cr(VI) to Cr(III) and to purify Cr from sample matrices. Acidified water samples were then stored at room temperature for 2 weeks to allow reduction to take place.

Digestion of Sediment Samples

After being refrigerated for one day, wet sediment samples were transferred to 15 mL centrifuge tubes to be freeze

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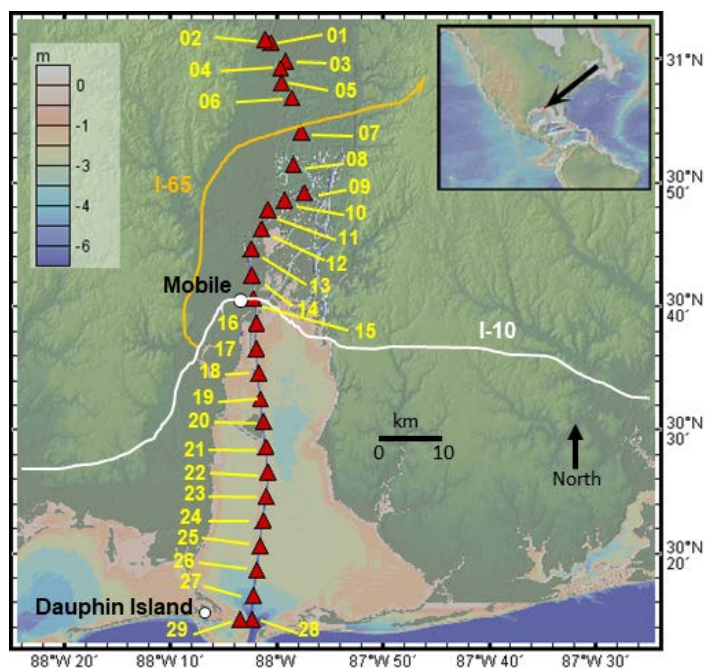


FIGURE 1. A map of sampling locations. The color scale is for water depths. At location 2, one sediment sample from the dry, exposed bank was taken, but no water was collected. At all other locations, both sediments from the bottom of the channel and surface water samples were collected. Samples 3-4, the Ash Pond and Outflow of Plant Barry respectively, and 14-16, the Industrial Park, were taken from areas of higher industrialization. Other samples were taken around these areas of heavy industrialization and were likely less impacted. The total distance between locations 1 and 29 is 104 km.

dried for about 48 h. Once dried, about 1 g of each sample was ground into a fine powder with an agate mortar and pestle and transferred to small, clean plastic bags for storage at room temperature for five days. Samples (0.05 g) were weighed in ceramic crucibles, which were precleaned in a 6N HCl bath at room temperature overnight. Samples, in covered crucibles, were ashed at 500°C for 6 h in an oven to remove organic matter. After ashing, the powders were transferred to 15 mL Teflon beakers to be dissolved by mineral acids.

To dissolve the powders, 1 mL of concentrated, trace metal grade hydrofluoric acid (HF) was added to the sample, followed by 0.2 mL of concentrated, distilled HNO₃. To prevent rapid degassing and sample loss, these acids were added very slowly to the powders. The uncapped solutions were heated at 100°C for 1 h before being tightly capped and heated for an additional 24 h at 130°C. After the 24 h, the solutions were dried to incipient dryness on a hotplate at 100°C, 1.5 mL of 6N HCl was added, and the solution was completely dried on the hotplate at 100°C. The 6N HCl addition step was repeated until the solution was clear of fluorides, e.g., when no solid, white particulate matter remained floating around the beaker. The dried final solid was dissolved in 4 mL of 2N HCl and stored in 8 mL plastic bottles prior to analysis.

Extracting Cr from water

Chromium in water samples was extracted with an iron coprecipitation method (Cranston and Murray 1978). The Cr concentration was measured with an isotope dilution method (Jeandel and Minster 1984). A 50 mL aliquot of each acidified water sample was mixed with a ⁵⁰Cr–⁵⁴Cr double-spike tracer solution. These samples were then shaken overnight on an orbital shaker table at 100 rpm to allow sample-spike equilibration. Water samples were adjusted to a pH of ~10 using concentrated NH₄OH before 0.4 mL of a 0.1M Fe(OH)₂ suspension was added. The Fe(OH)₂ suspension was made by dissolving 0.0588 g Iron (II) Ammonium Sulfate Hexahydrate in 15 mL of MQ water and adding 0.3 mL of 1N NH₄OH to the solution. Once the suspension was added, the samples were shaken for 1 h and left to settle overnight. The Fe(OH)₂ quickly oxidizes to Fe(OH)₃. Because Cr (III) is very particle-reactive, the formation of Fe(OH)₃ scavenges Cr (III) very efficiently. The Fe(OH)₃ precipitate was separated by centrifugation at 4000 RPM for 5 min and then dissolved in 2 mL of 6N HCl.

Before measuring Cr concentration, Fe was removed by anion exchange resin AG1-X8 (100–200 mesh), since Fe forms anionic FeCl₄⁻ that binds to the resin in 6N HCl, while Cr is in cationic forms that passes through the resin. The columns, charged with 0.3 mL of resin, were cleaned 2 times with 1 mL of 6N HCl. Samples were then loaded onto the columns, and Cr was collected in clean Teflon beakers. Residual Cr was pushed down with another 1 mL of 6N HCl and combined with the first collection. The collected solution was dried on a hotplate at 100°C. One drop of concentrated HNO₃ was added to each sample at 130°C to remove organics that can interfere with spectrometer measurements. Once dried again, the samples were redissolved in 5% HNO₃ for measurement.

Mass spectrometry sample analyses

Water samples were analyzed on a Thermo Scientific Neptune MC-ICP-MS housed at the Dauphin Island Sea Lab (DISL), AL. The instrument was operated in the high-resolution mode to avoid polyatomic interferences. Masses of 49 (Ti), 50 (Ti, Cr, V), 51 (V), 52 (Cr), 53 (Cr), 54 (Cr, Fe), and 56 (Fe) were simultaneously measured on Faraday Cups connected to 10¹¹ Ω amplifiers. Interferences of 50Ti and 50V on 50Cr and 54Fe on 54Cr were corrected for based on measured 49Ti and 54V intensities and standard 49Ti/50Ti, 51V/50V, and 54Fe/56Fe ratios. Each measurement consisted of 20 cycles, each with 4.19 s integration time. The long-term precision of Cr concentration using this method is <5%. Sediment Cr and Ti concentrations were measured on an Agilent 7700 ICP-MS at DISL using the He gas mode, with a long-term precision of ~10%. Modern ICP-MS instruments can routinely achieve these precisions.

TABLE 1. Location, salinity and chromium (Cr) concentration data of samples collected from the Mobile Bay, AL estuary on 17 June 2019. Sample locations shown in Figure 1. Ti = Titanium

Sample	Location #	Latitude	Longitude	Salinity (PSU)	Total dissolved Cr (ng/mL)	Sediment Cr ($\mu\text{g/mL}$)	Sediment Cr/Ti
MB 01	1	31° 01.340'	-88° 00.550'	0.1	0.13	2.19	0.011
MB 02*	2	31° 02.680'	-88° 01.818'			20.26	0.008
MB 03	3	30° 59.840'	-87° 59.179'	0.2	0.12	103.13	0.017
MB 04	4	30° 59.268'	-87° 59.633'	0.1	0.13	50.00	0.015
MB 05	5	30° 58.159'	-87° 59.540'	0.1	0.11	1.62	0.009
MB 06	6	30° 56.884'	-87° 58.585'	0.2	0.10	7.56	0.004
MB 07	7	30° 54.122'	-87° 57.700'	0.1	0.10	1.77	0.013
MB 08	8	30° 51.550'	-87° 58.470'	0.1	0.10	2.19	0.010
MB 09	9	30° 49.241'	-87° 57.409'	0.4	0.09	94.74	0.018
MB 10	10	30° 48.648'	-87° 59.270'	0.8	0.08	5.69	0.008
MB 11	11	30° 47.885'	-88° 00.828'	1.9	0.15		
MB 12	12	30° 46.313'	-88° 01.437'	2.8	0.18	17.30	0.014
MB 13	13	30° 44.730'	-88° 02.422'	4.8	0.11	4.80	0.011
MB 14	14	30° 42.612'	-88° 02.346'	3.7	0.06	116.85	0.023
MB 15	15	30° 40.711'	-88° 02.174'	3.2	0.07	112.11	
MB 16	16	30° 38.708'	-88° 01.909'	3.9	0.07	106.17	0.023
MB 17	17	30° 36.654'	-88° 01.921'	5.8	0.14	93.41	
MB 18	18	30° 34.686'	-88° 01.672'	7.4	0.04	99.34	
MB 19	19	30° 32.549'	-88° 01.530'	7.1	0.07	100.64	0.022
MB 20	20	30° 30.768'	-88° 01.247'	7.8	0.09	98.28	
MB 21	21	30° 28.693'	-88° 01.036'	9.4	0.04	97.97	
MB 22	22	30° 26.676'	-88° 00.838'	10.9	0.07	100.94	0.022
MB 23	23	30° 24.680'	-88° 00.973'	11.0	0.05	106.32	
MB 24	24	30° 22.723'	-88° 01.292'	11.0	0.04	92.39	
MB 25	25	30° 20.699'	-88° 01.567'	16.2	0.06	100.94	0.024
MB 26	26	30° 18.721'	-88° 01.845'	13.5	0.04	94.13	
MB 27	27	30° 16.656'	-88° 02.198'	17.6	0.05	29.87	
MB 28	28	30° 14.719'	-88° 02.296'	15.5	0.05	96.31	0.028
MB 29	29	30° 14.708'	-88° 03.484'	17.0	0.05	2.84	

*Soil sample taken on the river bank

RESULTS AND DISCUSSION

Sediments

Chromium concentrations in sediments varied greatly (~2–117 $\mu\text{g/g}$) among sampling locations (Table 1; Figure 2A). Samples in the Industrial Park and its downstream areas mostly show high Cr concentrations (~92–117 $\mu\text{g/g}$) except for 2 samples at locations 26 and 29. Samples 1–13, the Mobile River samples, except for 3, 4, and 9, have lower concentrations (~2–20 $\mu\text{g/g}$) than the exposed river bank sediment, sample 2.

However, absolute Cr concentration alone cannot reliably show enrichment due to natural or anthropogenic contribution because it can be influenced by the types of sediments (e.g., sands have much lower Cr content than mud). Normalizing Cr to an immobile element, such as Al or Ti, can more clearly reveal Cr enrichment (Reinhard et al. 2014; Tribovillard et al. 2006). The Cr/Ti ratios for samples 1–13, except for sample 6 (Figure 2B), are between the ratios for the river bank sediment (0.0083) and the mean upper continental crust, UCC (0.0240; Rudnick and Gao 2003), the latter being derived from shales. In contrast, samples at locations south of location 14 were similar to the UCC value (Figure 2B). This shift in Cr/Ti was consistent with the shift from

sandy/silty to muddy sediments. The shift of sediment components from the upper to lower stream can be attributed to water energy; faster upstream water allowed coarser grains to settle to the riverbed first, leaving finer clays to settle to the bottom when the water slowed down when entering low energy environments. The fact that the fluctuating Cr/Ti of samples 1–13 generally lied between river bank sediment and UCC suggests that Cr in these samples were a result of mixing of variable proportions of sands/silts and clays.

Gauging whether there is anthropogenic Cr contribution to sediment samples 1–13 has uncertainties due to variable sediment components. Since the absolute Cr concentrations of samples 1–13 were mostly below the river bank sediment (Figure 2A), however, we favored the hypothesis of simple mixing of different sediment types over anthropogenic input. Two additional observations appeared to support this hypothesis: 1) samples away from the ash pond and outflow (samples 1 and 5–8) had similar Cr/Ti (Figure 2B); and 2) samples at locations 5, 6 and 10 showed very low Cr/Ti, indicating that the transport of pollutants to downstream locations can be ruled out. Because the mud samples from the Industrial Park had similar Cr/Ti ratios as the shale-based mean Cr/Ti, anthropogenic input appeared to be insignifi-

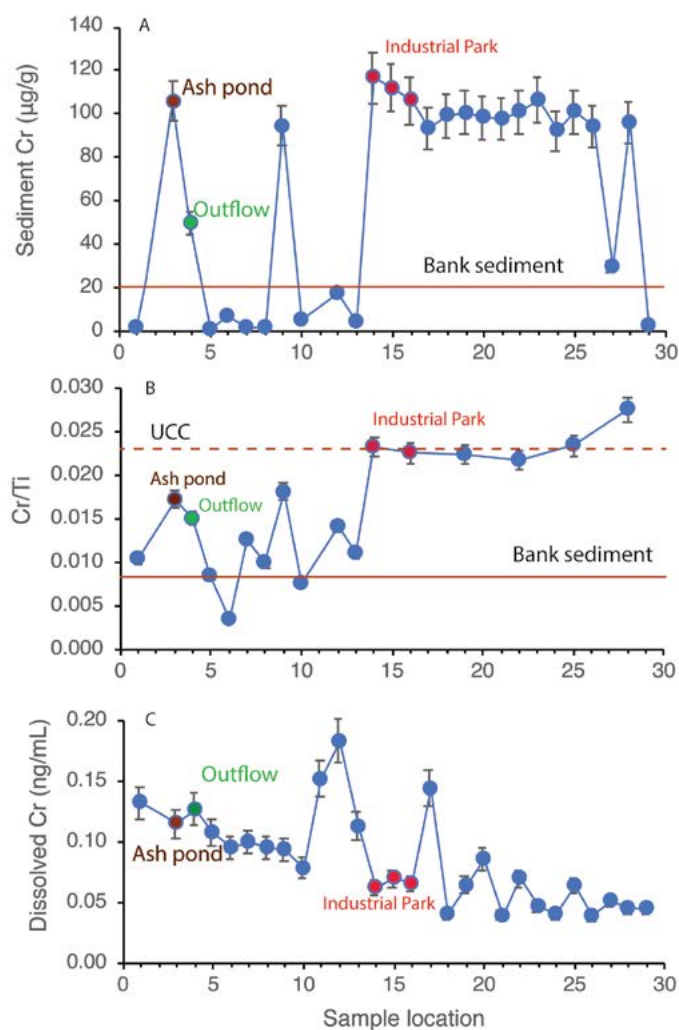


FIGURE 2. Chromium concentrations in water and sediments from 29 sites in the Mobile Bay estuary. A. Total chromium (Cr) in sediments ($\mu\text{g/g}$). B. Chromium/Titanium (Cr/Ti) ratios in sediments. C. Total dissolved chromium (Cr) in water (ng/mL). Sample locations illustrated in Figure 1. In panel B, the red solid line indicates the mean ratio of bank sediments, and the red dashed line indicates the mean ratio in the upper continental crust (0.0240, from Rudnick and Gao 2003).

cant to these sediments. However, given the limited number of samples in a single sampling event and uncertainties regarding whether global average shale Cr/Ti can be taken as the local background, a more definite conclusion regarding the possibility of anthropogenic Cr contribution to the sediments in the Mobile Bay requires more spatially resolved sediment samples and a better constraint on the Cr/Ti in the background sediments.

Surface Water

The measured total dissolved Cr concentrations fell between 0.04 and 0.18 ng/mL in surface waters (Figure 2C), which are all below the regulated maximum contamination level of 50 ng/mL in drinking water (Baral et al. 2002). Near the cooling water outflow of Plant Barry, dissolved Cr was slightly elevated compared to adjacent samples 5–9. However, the difference was very small, and dissolved Cr quickly

returned to spatial background levels. Within the Industrial Park (samples 14–16) dissolved Cr was the same as the background level, whereas those samples surrounding the Industrial Park (samples 12–13 and 17), were relatively elevated (Figure 2C). This pattern can be explained by a highly heterogeneous Cr distribution due to mixing. The salinity at locations 10–20 increased from near 0 to 10 (Table 1), indicating intense mixing of different water bodies. However, because both Gulf of Mexico seawater, found in samples 17–29 as this water flows into the Mobile Bay, and Mobile River water (samples 1–10) have lower dissolved Cr compared to the water near the Industrial Park, simple mixing of these two water masses cannot explain the relatively high Cr in waters near the Industrial Park. Possible additional Cr sources could include sediment pore water and industrial input. Although we did not measure pore water dissolved Cr concentrations, previous studies reported that porewater typically has less dissolved Cr than the overlying seawater (e.g., Ciceri et al. 1992), which is consistent with the conventional view that marine sediments are a net sink of Cr from seawater (Reinhard et al. 2013). Therefore, we suggest that the relatively elevated total dissolved Cr near the Industrial Park was due to the manufacturing activities in this area, and the highly dynamic range of Cr concentration can be explained by intensive tidal mixing.

CONCLUSIONS

Our data suggest that there were increases in total dissolved Cr concentrations around areas with heavy industrial influences, such as Plant Barry and Industrial Park. However, these industrial inputs do not seem to represent a major influx of Cr into the estuarine system, and their effects are limited to a confined spatial range, based on these 3 key observations: 1) a lack of definite evidence of Cr enrichment in sediments, suggesting that small inputs of dissolved Cr did not contribute significant Cr flux to sediments; 2) locations closest to Industrial Park have background-level total dissolved Cr levels; 3) elevated total dissolved Cr only occurs in this mixing region of Mobile Bay water and Mobile River water, from about samples 11–17. The range of total dissolved Cr concentrations in the water can be explained by the tidal mixing of different water bodies and anthropogenic input. The range of Cr concentrations in sediments can be explained by varying proportions of low-Cr sand/silt and high-Cr mud. We acknowledge that these conclusions have uncertainties because they are based on a single sampling event, with a limited number of samples. However, given that these areas of heavy industrialization are very close to sea level and that hurricane risks in this region are generally elevated, conservative preventative strategies and continued monitoring should be carried out to ensure these areas do not contribute to potential Cr pollution of the Mobile Bay estuarine system.

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