### Division of Science, Research and Technology Research Project Summary

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# The Distribution of Chromium Species as a Function of Particle Size for Chromium Waste Laden Soils

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#### Abstract

Among the remediation criteria applied to COPR in Hudson County, New Jersey are those based on the cancer risk associated with inhalation of  $Cr^{+6}$ . For inhalation-based remediation criteria, the acceptable soil concentration is based on the concentration of  $Cr^{+6}$  on the respirable size particles. The default assumption is that the concentration of  $Cr^{+6}$  on the respirable size particles. The default assumption is that the concentration of  $Cr^{+6}$  on the same as the concentration in the bulk COPR soil material. To examine this assumption COPR soil from 8 locations was separated into size fractions. The concentration of  $Cr^{+6}$ , total Cr and  $Cr^{+3}$  was compared in the bulk soil and the individual size fractions including the respirable (<2.5 µm) material.  $Cr^{+6}$  was consistently enriched in the 2.5 µm fraction compared to the bulk COPR soil (mean enrichment = 63.7). In addition, the  $Cr^{+6}$  accounted for a larger percentage of the total Cr as the particle size decreased. In contrast total Cr and  $Cr^{+3}$  did not show a consistent enrichment in the 2.5 µm fraction. There was a strong relationship between  $Cr^{+6}$  concentration in the bulk material and in the 2.5 µm fraction that may allow analysis of  $Cr^{+6}$  in bulk COPR soil to be used as a surrogate analysis of the 2.5 µm fraction.

### Introduction

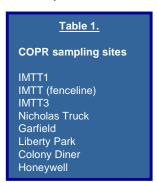
Chromate production waste (COPR), including the carcinogenic, hexavalent chromium, has been a concern in Hudson County and particularly in Jersey City, New Jersev since three large chromate production facilities that operated there for much of the twentieth century disposed of much of their waste on their own land as well as in numerous residential, commercial and industrial locations and on, then, vacant land. The New Jersey Department of Environmental Protection has developed soil remediation criteria based on exposure to Cr<sup>+6</sup> from various routes including inhalation of Cr<sup>+6</sup>containing particulates. The inhalation-based remediation criterion is derived by back-calculating the concentration of Cr<sup>+6</sup> in soil that will not result in exceeding the one-in-a-million lifetime inhalation cancer risk. This calculation is based on assumptions about the concentration of Cr<sup>+6</sup> as a function of the size of the soil particles that can become suspended in air. The current default approach assumes that Cr<sup>+6</sup> is distributed uniformly through the soil material, independent of the size of the soil particles. Using this assumption, the concentration of Cr<sup>+6</sup> in a bulk sample of soil will apply equally to the concentration in the smaller, respirable fraction of the soil. However, if the concentration of Cr<sup>+6</sup> in the respirable fraction of soil is either larger or smaller than the concentration in the bulk soil, the back-calculation of the acceptable concentration in soil will result in a soil remediation criterion that is either insufficiently protective (the former case) or unnecessarily restrictive

(the latter case). It is, therefore, important to determine how the concentration of  $Cr^{+6}$  varies as a function of soil particle size in chromate production waste in Jersey City.

#### Methods

Soil was collected from 8 COPR sites in Jersey City that had not yet undergone final remediation. These locations are shown in Table 1. Samples were collected at a depth of 1-6 inches at all sites. Additional samples were taken at a greater depth from the Honeywell site. Soil

was fractionated into size fractions of 250, 75, 38, <10, and <2.5  $\mu$ m diameter by elutriation. Each sample was analyzed for Cr<sup>+6</sup>, Cr<sup>+3</sup> and total Cr concentration at each size fraction. Cr<sup>+6</sup> and Cr<sup>+3</sup> were separated using an ion chromatographic procedure and Cr was quantified using inductivelycoupled mass spectrometry (ICPMS). Duplicate and



triplicate sample analysis were run to determine the analytical precision, and analytical accuracy was determined by analysis of two certified,Cr<sup>+6</sup>-containing, soil standards.

#### Results

Occurrence of respirable particles in COPR soils In the samples from the 5 of the 8 locations the distribution of the number of particles was determined across the various size fractions. For these samples, 70-90% of the soil particles were smaller than 2.5  $\mu$ m (i.e., within the range of particles with the ability to reach the alveolar portion of the lungs).

## Concentration of $Cr^{\pm 6}$ as a function of COPR soil particle size

For 7 of the 8 locations, the concentration of  $Cr^{+6}$  in the smallest size fraction of soil

(<2.5  $\mu$ m) was enriched compared to the bulk soil. This enrichment ranged from a factor of 2.8-318 (mean = 63.7, median = 41). The second smallest enrichment factor was 18. The enrichment data are summarized in Table 2.

### The Cr<sup>+6</sup>/total Cr ratio as a function of COPR soil particle size

Cr<sup>+6</sup> was also enriched relative to total Cr when comparing the bulk COPR soil to the 2.5  $\mu$ m fraction. Whereas Cr<sup>+6</sup> accounted for 0.2-27% (mean = 5.1%, median = 1.0%) of the total Cr in the bulk soil, Cr<sup>+6</sup> accounted for 5.7-38% (mean = 19.0%, median = 16.8%) of the total Cr in the 2.5  $\mu$ m fraction. These results are summarized in Table 3.

### Relationship between Cr<sup>±6</sup> in bulk COPR soil and Cr+6 in respirable particles

The concentration of  $Cr^{+6}$  in bulk COPR soil correlated strongly with the concentration of

Sampling Site

Cr<sup>+6</sup> in the 2.5  $\mu$ m fraction (r = 0.89; Cr<sub>2.5</sub> = 2.94 x Cr<sub>bulk</sub>). When two 2.5  $\mu$ m samples from the Honeywell site that were an order of magnitude higher concentration then those from the remainder of the sites were excluded, the strength of the correlation increased (r = 0.95; Cr<sub>2.5</sub> = 24.52 x Cr<sub>bulk</sub>).

Concentration of total Cr as a function of COPR soil particle size In contrast to Cr<sup>+6</sup>, total Cr was less clearly enriched in the 2.5 $\mu$ m fraction compared to the bulk COPR soil. At 6 of the 8 locations, the enrichment ranged from 0-5.3 (mean = 1.3, median = 0.5). At the two remaining locations, the total

Table 2.
Enrichment of Cr+6 as a function of COPR soil particle size

Sampling Site	Cr <sup>6+</sup> at each size/Cr <sup>6+</sup> in bulk portion						
	Bulk	250 µm	75 µm	38 µm	30-10 µm	10-2.5 µm	2.5 µm
IMTT1	1.0	2.1	2.4	1.8	14	17	61
IMTT Fenceline	1.0	2.8	4.8	5.1	2.8	36	48
IMTT3	1.0	15	16	23	133	164	318
Nicholas Truck	1.0	6.7	10.3	6.3	8.3	11	18
Garfield	1.0	1.7	2.2	2.2	4.6	9.6	27
Liberty Park	1.0	3.5	3.9	4.8	6.8	12	34
Colony Diner	1.0	1.1	0.5	1.4	1.1	0.9	1.1
Honeywell 0-6	1.0	1.0	1.7	2.6	1.5	6.2	2.8
Honeywell 6-12	1.0	1.1	1.9	4.2	2.7	4.8	3.0
Honeywell 1	1.0	1.2	2.0	3.1	NA	NA	NA
Honeywell 10 feet	1.0	1.6	1.9	1.1	NA	NA	NA

Cr in the 2.5  $\mu m$  fraction was enriched by a factor 10.0-46.7 compared to the bulk COPR soil.

### Concentration of Cr+3 as a function of COPR soil particle size

Not surprisingly, the pattern of  $Cr^{+3}$  enrichment in the 2.5  $\mu m$  fraction was very similar to that seen for total Cr.

### Conclusions

It is well known that Cr<sup>+6</sup> from COPR is mobile in the soil with the ability to move both vertically in the soil column resulting in "blooms" on the soil surface, and horizon-tally, resulting on deposition on interior walls. This mobility is a function of the solubility of most forms of Cr<sup>+6</sup> that has allowed it to be leached from sub-surface

<u>o                                    </u>	Ci <sup>+</sup> tii	at has allu		De leach		<b>D</b> -
	С	r+6 as a perc	Table cent of tota		rticle size	
1			Cr6+ in each	n size/Cr tota	l in each size (%	6)
	Bulk	250 µm	75 µm	38 µm	30-10 µm	5

	Bulk	250 µm	75 µm	38 µm	30-10 µm	10-2.5 µm	2.5 µm
IMTT1	5.6	2.6	2.1	1.2	2.9	2.6	7.3
IMTT Fenceline	1.2	2.8	2.4	2.1	2.8	4.2	5.7
IMTT3	0.5	3.2	2.7	4.0	20	23	28
Nicholas Truck	0.3	1.7	2.7	2.5	1.6	3.6	17.7
Garfield	0.8	0.9	1.6	1.4	5.1	6.7	15.8
Liberty Park	0.2	1.1	0.8	0.9	0.6	2.6	11.4
Colony Diner	27	29	13	32	27	23	28
Honeywell 0-6	5.2	6.8	11.9	20	11	45	38
Honeywell 6-12	3.5	4.8	8.0	15	20	48	49
Honeywell 1	7.5	10	19	31	NA	NA	NA
Honeywell 10 feet	NA	NA	NA	NA	NA	NA	NA

COPR over time. It is likely that this mobility is at least partly responsible for the concentration of Cr<sup>+6</sup> on the smallest size particles. This enrichment is enhanced by the greatly increased surface area provided by small particles compared to the larger bulk COPR material that may originally have contained the Cr<sup>+6</sup>. That this enrichment is a function of the movement of Cr<sup>+6</sup> from larger to smaller particles is supported by the observation that there is no consistent enrichment of total Cr or Cr<sup>+3</sup> on small particles. The enrichment found in this study has important implications for remediation criteria at COPR sites. However, the measurement of Cr<sup>+6</sup> on sized COPR particles is not likely to lend itself to routine analysis. The observation in this study that the concentration of Cr<sup>+6</sup> in bulk COPR soil is a good predictor of Cr<sup>+6</sup> in the 2.5  $\mu$ m fraction provides a means of predicting the Cr<sup>+6</sup> in the respirable fraction from the standard bulk Cr+6 analysis.

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### **RESEARCH PROJECT SUMMARY**

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