MEASUREMENT OF BACKGROUND LEVELS OF Cr(VI) IN NJ SOILS

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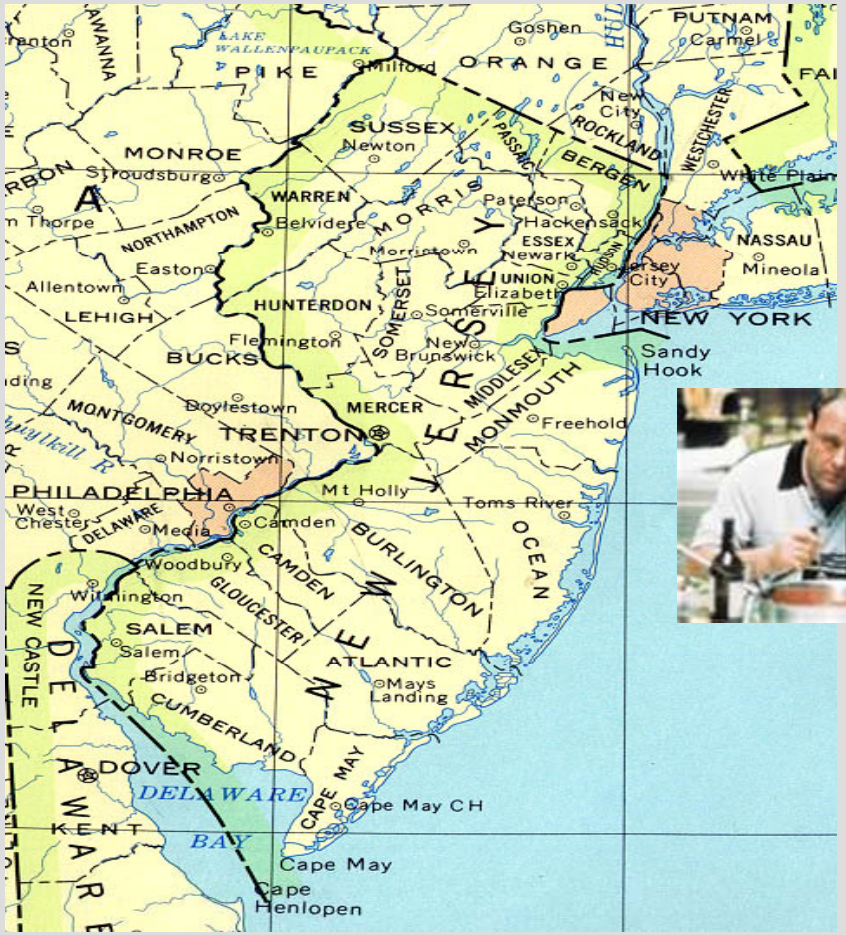
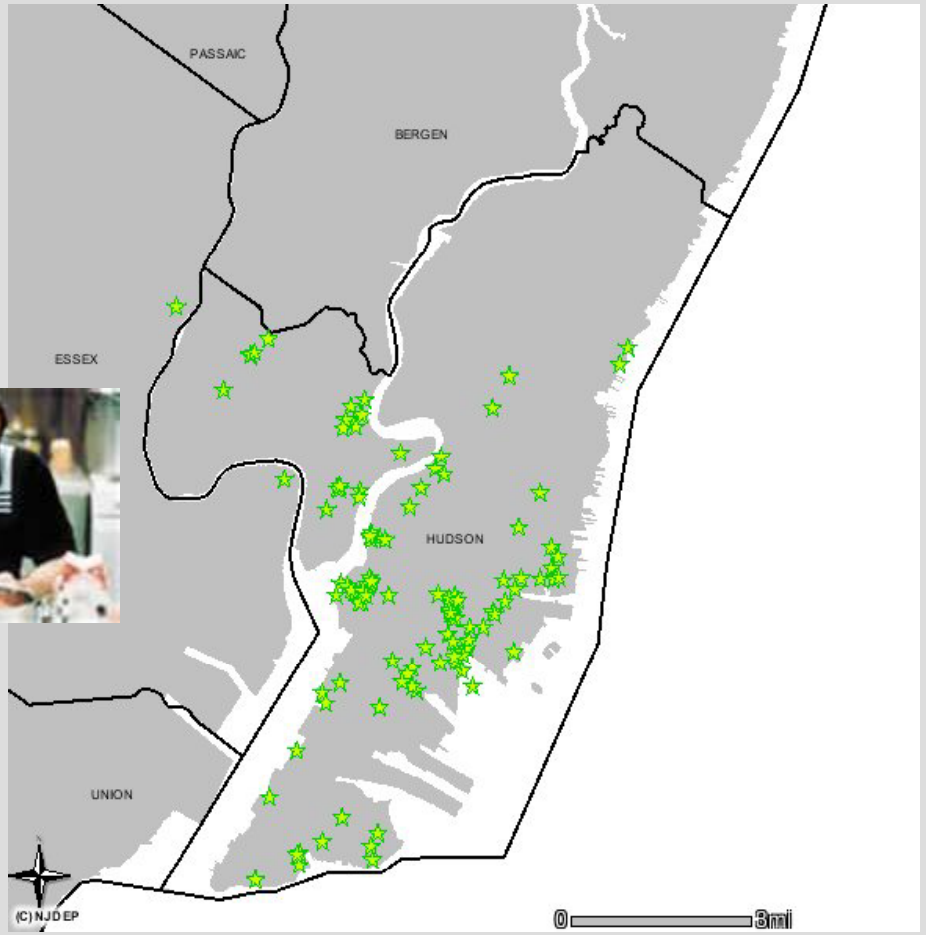
NJ Cr(VI) CONTAMINATED SITES





185 Sites ID'd; 72 Remediated

Cr(VI) IN NJ - HISTORICAL

- In the first half of the 20th century, millions of tons of chromite ore processing residue (COPR) were deposited in northern NJ by major chemical companies
- Studies have reported excess lung cancers in those living in close proximity to COPR sites; also possible GI cancer correlation
- Remedial decisions involve complex technical, economic, legal and political issues
- Current process uses EPA methods pair (3060A and 7190) to a 20 ppm. residential clean-up std.; in 2006, NJDEP study proposed modifying the protocols used to analyze soils containing COPR using a tiered analytical approach, but this has yet to be implemented

Cr(VI) IN NJ - CURRENT

- A 2009 NJDEP risk assessment study proposes lowering the residential clean-up level for Cr(VI) in soils to 1 ppm

- Before this policy option can be considered, several essential technical issues must be addressed:
  - What is the level of Cr(VI) in NJ soils that are believed to be free from anthropogenic impact?
  - Using method pair 3060A/7199, how well can we measure Cr(VI) at 1 ppm in soil digests?
    - Accuracy
    - Sensitivity

ANALYSIS OF Cr(VI) IN SOILS

- Two steps needed:
  - Extraction (Method 3060A)
  - Determination
    - ☒3 method options:
      - **7196A**
      - **7199**
      - **SIDMS (6800)**

OVERVIEW OF NJ BACKGROUND SOIL STUDY FOR Cr(VI): LOGISTICAL

- 2 previous NJDEP studies of ambient concentrations of metals were used as a basis for developing our sampling strategy
- Public sites (parks, ballfields…) in urban areas were selected, avoiding paved areas & sites near transportation or agriculture
- Predominant type of soil in each locale was targeted
- 370 samples at 185 sites were collected from 14 NJ counties (more samples were collected than could be analyzed)

OVERVIEW OF NJ BACKGROUND SOIL STUDY FOR Cr(VI): TECHNICAL

- 258 samples analyzed by Method 7199; 58 samples analyzed by Method 6800. All preceded by digestion by Method 3060A
- Only samples with measurable Cr(VI) by Method 7199 were submitted for analysis by Method 6800
- NIST SRMs were used as additional project QC
- Ancillary parameters (% moisture, ORP, pH, total Cr, Mn, TOC) also measured
- NJDEP performed data review and report preparation

USE OF NIST SRMs TO EVALUATE Cr(VI) DATA

	7196A	7199	6800
NIST SRM 2700	**10.2 ± 1.9**	**10.1 ± 1.0**	**14.9 ± 0.7**
NIST SRM 2701	**384 ± 74**	**388 ± 72**	**551 ± 35**
	-----Information-----		**Certified**

Method 7199 at Section 5.4 requires use of RMs

Options Include:

- Use 2700 as batch QC (LCS) when Cr(VI) sample concentrations are expected to be low
- Use 2700 or 2701 as source material for performing matrix spikes

METHOD 7199 DATA SUMMARY

- Approximately 36% of the background soil samples had quantifiable levels of hexavalent chromium (64% of the data were non-detect values).
- The results indicate the following percentiles of Cr(VI) in mg/kg for urban soils in NJ using Method 7199:

Median	75th Pctl	90th Pctl	95th Pctl	99th Pctl	Maximum
<1.00*	1.40	1.90	2.50	5.50	7.70

- *Because of the high % of NDs, the estimate of the median concentration is uncertain and estimates of concentrations corresponding to lower percentiles is unreliable.
- **The expectation going into the study was that no measurable Cr(VI) would be found in any sample.**

METHOD 7199 vs. METHOD 6800

2 additional QA tools were used:

- 1/100 dilution of NIST SRM 2701 was run as a LCS
- 25 mg. of NIST SRM 2701 to 2.5 g. of soil was used as a matrix spike

Targeted value of [Cr(VI)] ~5 ppm

	7199	6800
LCS (1/100 dil. of SRM 2701 w/glass beads)	92.5%	109.1%
Matrix Spike (25 mg. of SRM 2701 to 2.5 g. soil)	59.0%	105.0%

For samples where analyses by both Methods 7199 and 6800 are available, the absolute % difference is 82.7% ± 84.2%,

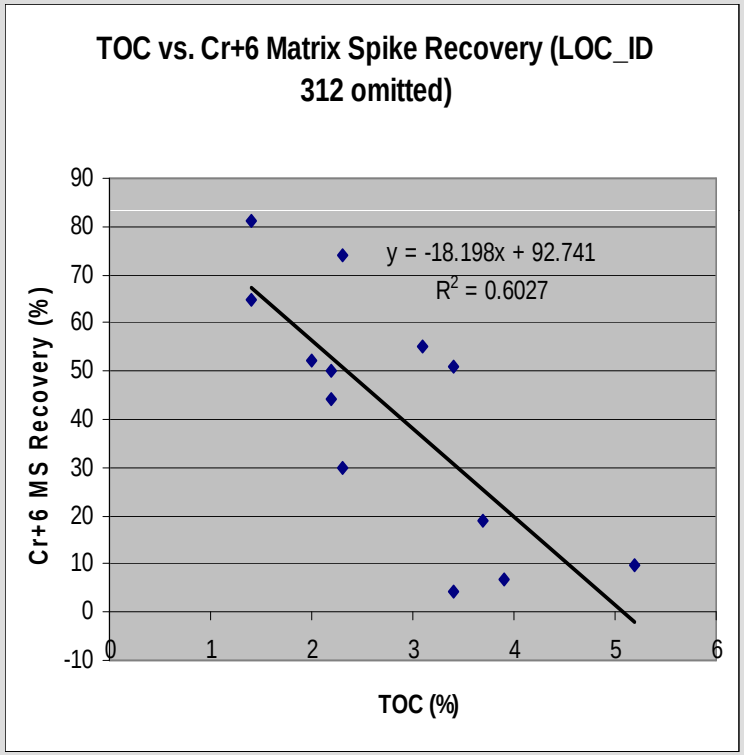
with the Method 6800 data being higher

Cr(VI) IN MO TANNERY WASTE

MO DNR used NIST SRM 2701 as a matrix spike for their soil contamination study

Analyses were performed by IC/MS

Lower than expected recoveries consistent with the reducing nature of these contaminated soils



Data courtesy of Julieann Warren and Michael Stroh, MO DNR

CAN WE ACCURATELY MEASURE Cr(VI) BY METHOD 7199 AT 1 PPM?

1. Dilute candidate NIST SRM 2700 anticipated [Cr(VI) ~10 mg/kg] w/w with clean quartz sand that is provided as follows:
   - Sample A: Weigh 0.125 g. of NIST SRM 2700 and add enough clean quartz sand to make the total sample weight 2.5 g.
   - Sample B: Weigh 0.250 g. of NIST SRM 2700 and add enough clean quartz sand to make the total sample weight 5.0 g.
   - Sample C: Weigh 2.5 g. of clean quartz sand
2. Digest Samples A, B and C by USEPA Method 3060A.
3. Analyze all digests by USEPA Method 7199.
4. Report the measured [Cr(VI)] in the samples.

True Value of Dilution using NIST SRM: 0.52 mg/kg

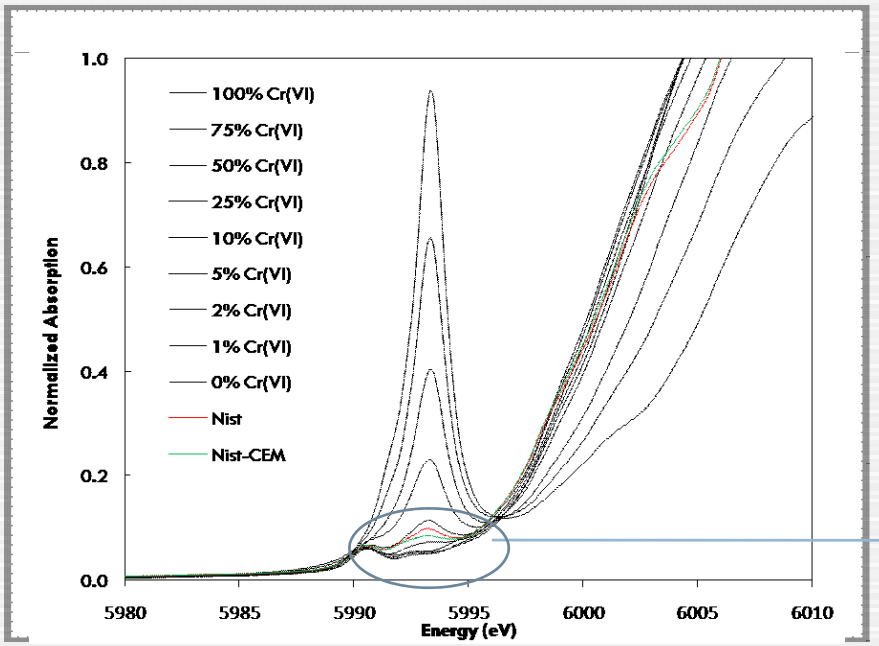
Lab.	Measured [Cr(VI)] in mg/kg	% Difference
A	0.55	+ 5.7
B	0.50	- 3.8
C	0.58	+ 11.5

XANES Analysis of NIST SRM 2701

Malherbe, J. et. al., NEMC 2010

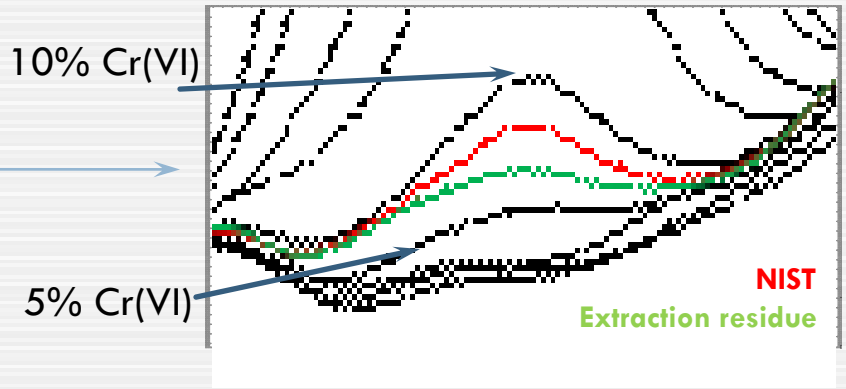
- **Certified values using EPA 3060A and 6800:** Cr(VI)= 551.2 ppm; Cr tot= 4.26%, hence Cr(VI) represents 1.3% of the total chromium

XANES quantification



- SRM 2701 clearly appears to have a Cr(VI) content is around 9% of Cr tot. Hence Cr(VI) should be around 3700 ppm

Only ~15% of the Cr(VI) in NIST SRM is removed by Method 3060A



CONCLUSIONS

- Use of the 3060A/7199 method pair can measure Cr(VI) in soil digests at or below 1 mg/kg.
- Measurements by the 3060A/7199 method pair can significantly under-report the amount of Cr(VI) in the digest
- Use of NIST SRMs for method QC can provide greater certainty about the quality of the results and decisions that are based upon them
- These concerns are most relevant at concentrations that are close to a regulatory limit.
- **BUT … IF WE ARE NOT MEASURING ALL Cr(VI) IN SOME SOILS, AND THE AMOUNT OF Cr(VI) REMOVED BY METHOD 3060A VARY BY SOIL TYPE, WHAT DOES ANY OF THE ABOVE MATTER???**

ACKNOWLEDGEMENTS

- Those @ the NJDEP who endorsed this project and allowed me to contribute

- EPA, USGS and NIST, for recognizing the need to develop speciated reference materials

- All labs. who volunteered their resources to provide the data for the SRM and sensitivity studies

- My colleagues in the Office of Science who co-authored the NJ Cr(VI) background soils report

GAIL CARTER: 1957-2010