Development of a Sampling and Analysis Method for the Measurement of Hexavalent Chromium in Ambient Air

Zhihua (Tina) Fan, Ph.D.

Environmental and Occupational Health Sciences Institute
UMDNJ and Rutgers University

Presentation at NESCAUM Annual Meeting, Mystic, CT
October 17-18, 2007

Background

- Hexavalent chromium [Cr(VI)] is recognized as a pulmonary carcinogen. Cr(VI) compounds have been enlisted as one of the 18 core HAPs by the USEPA.
- It is difficult to measure Cr(VI) because of its instability.
  - Cr(VI) $\leftrightarrow$ Cr(III)
- There was no standard method available for the measurement of Cr(VI) in air.

EPA Method for Cr(VI) Measurement in Air

- Developed by Eastern Research Group (ERG)
  - IC-UV method
    - $NaHCO_3$ pre-treated cellulose filter for collection
    - IC separation
    - post-column derivatization with diphenylcarbohydrazide
    - UV detection at 540 nm
  - MDL: 0.0074 ng/m^3

Limitations of the EPA Method

- Can't monitor Cr(VI) ↔ Cr(III) inter-conversion.
- Stability of Cr(VI) during sampling and analysis has not been thoroughly evaluated.

Objectives

Develop a reliable, sensitive sampling and analytical method to measure hexavalent chromium [Cr(VI)] in ambient air.

- **Optimize the Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry (IC/ICPMS) method for Cr(VI) analysis and lower the detection limit.**
- **Investigate the optimal extraction condition for Cr(VI) air samples.**
- **Investigate the stability of Cr(VI) during sampling, sample processing and sample storage after sampling.**
- **Quantify Cr(VI) and Cr(III) interconversion using the EPA 6800 method (Speciated isotope-dilution mass spectrometry method)**

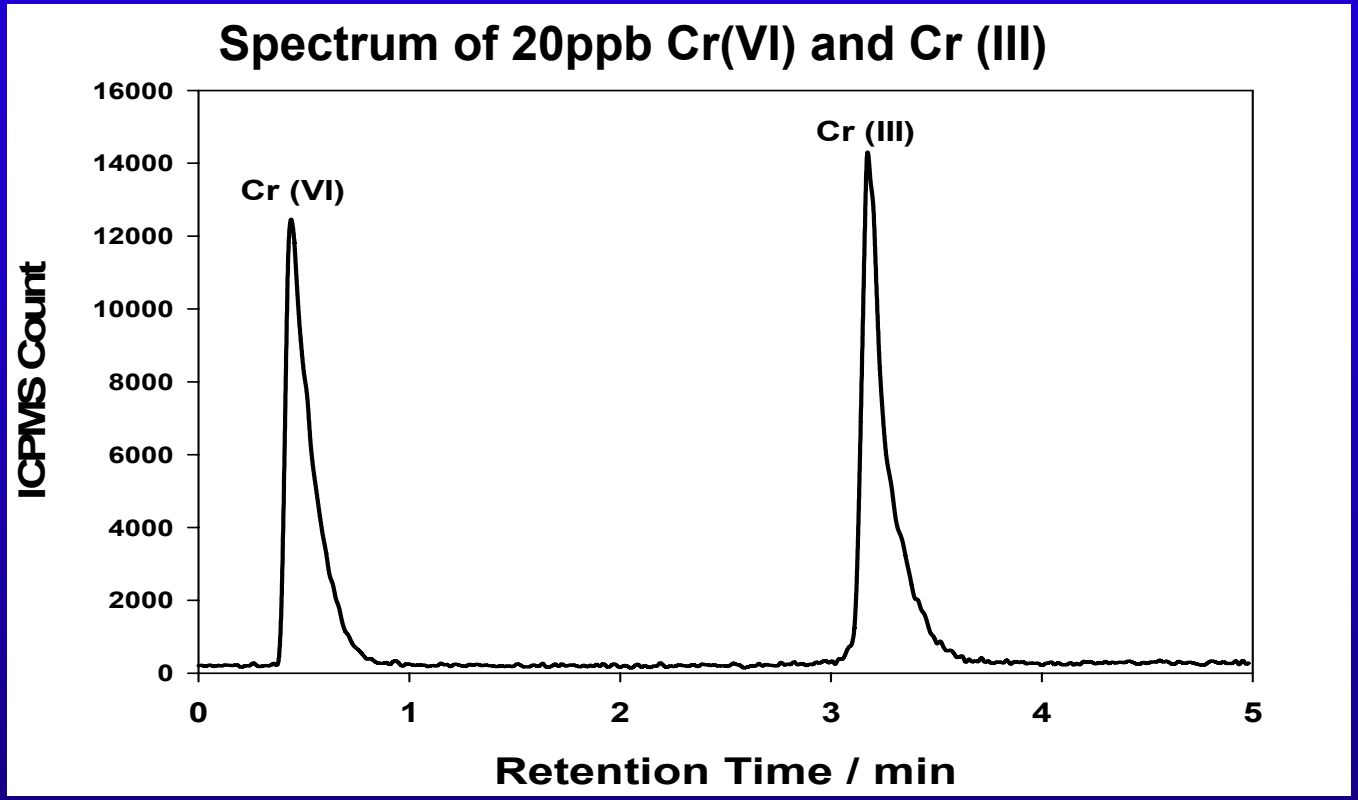
Flow Chart for Cr(VI) Measurement

Air Sampling
(Sampling Artifact)

→ Sample storage
(Stability)

→ Extraction
(Stability and Efficiency)

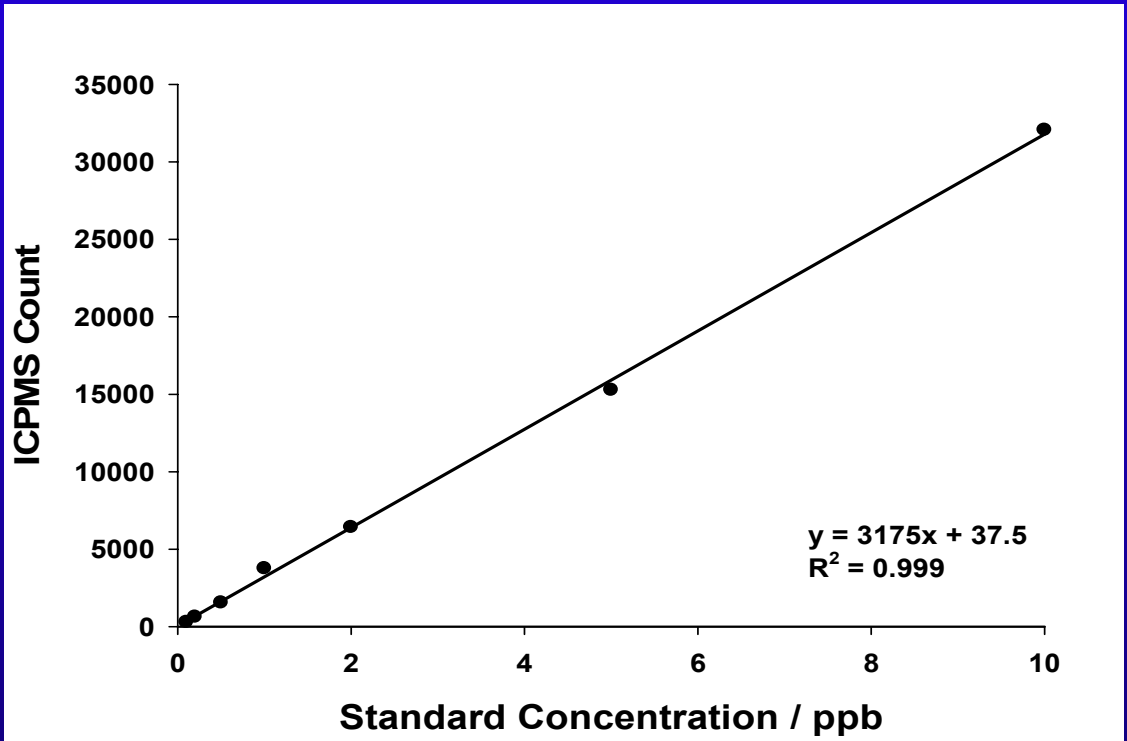
→ Ion Chromatography/Inductively Coupled Plasma Mass Spectrometry (IC/ICPMS)
(Optimal separation condition for IC; Optimal detection condition for ICPMS)



- Separation Condition:
- CG5A cation exchange column
- HNO_3 as mobile phase with flow rate of 1.25 mL/min
- IC program:
- Injection volume: 100 µL/min

  60% 1M HNO_3 and 40% DI H_2O

Instrument Tuning and Detection Limit



Tuning Solution	Analytical Detection Limit	Equivalent to Air Conc.(24 m^3)
10 ppb Indium	0.12 ppb	0.050 ng/m^3
10 ppb ^{52}Cr	0.32 ppb	0.13 ng/m^3
10 ppb ^{53}Cr	0.25 ppb	0.10 ng/m^3

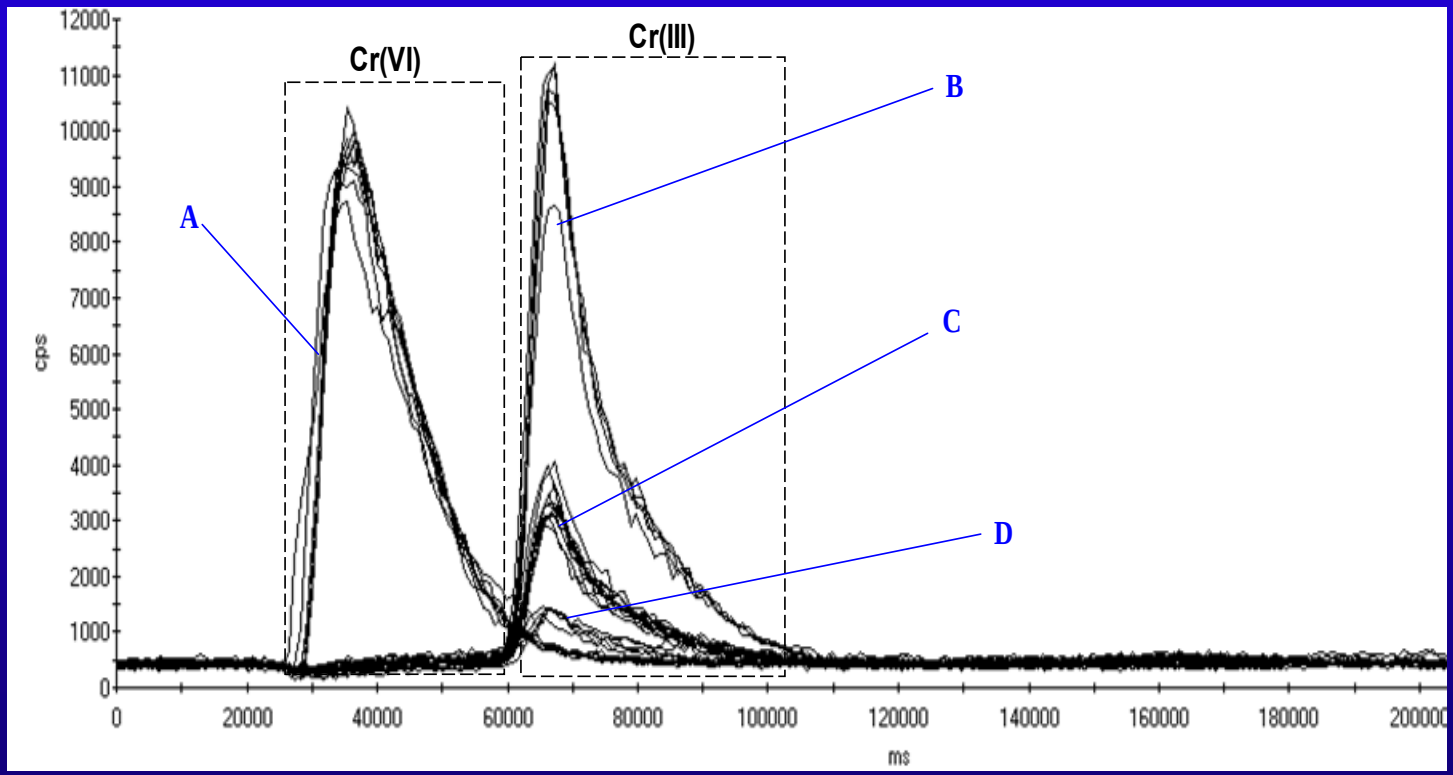
Optimal Extraction Method

- No Interferences
- High extraction efficiency
- Cr(VI) is stable during extraction
- Minimum interconversion between Cr(VI) and Cr(III)

Extraction Solution

- Extraction solutions tested:
  - H_2O
  - $NaHCO_3/Na_2CO_3$
  - $NaOH$
  - NH_4OH
  - K_2HPO_4/KH_2PO_4
  - $NH_4H_2PO_4/(NH_4)_2HPO_4$
  - HNO_3
- Sample tested: NIST 1648 particulate matter + Cr(VI) + Cr(III) + Teflon or $NaHCO_3$ pretreated cellulose filter.

Chromatogram of Cr(VI) and Cr(III)

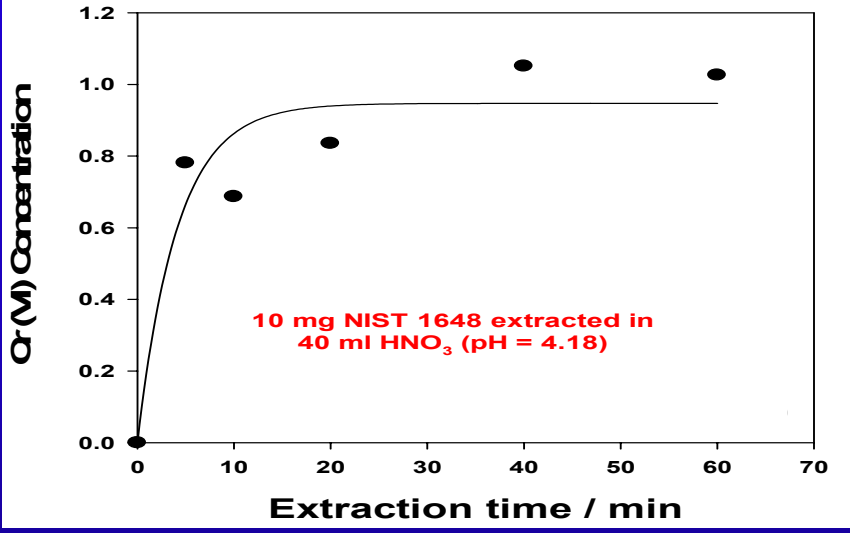


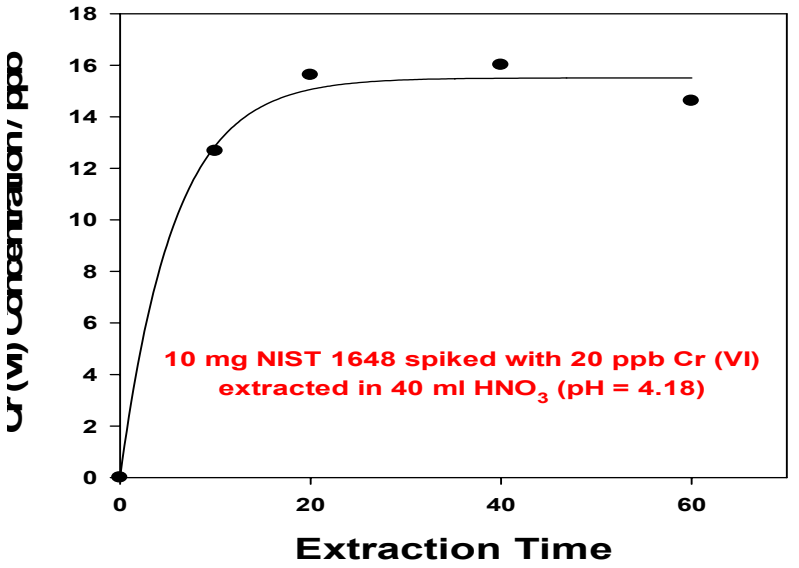
Group A: Cr(VI) under neutral, acidic and basic conditions
Group B: Cr (III) under neutral and acidic conditions.
Group C: Cr (III) at pH=8.5 in NH_4OH, pH=10-14 in NH_4OH-NaOH and then acidified by HNO_3 to pH=1-2.
Group D: Cr (III) at pH=10-12 in NH_4OH-NaOH, then acidified by HNO_3 to pH=2-4.

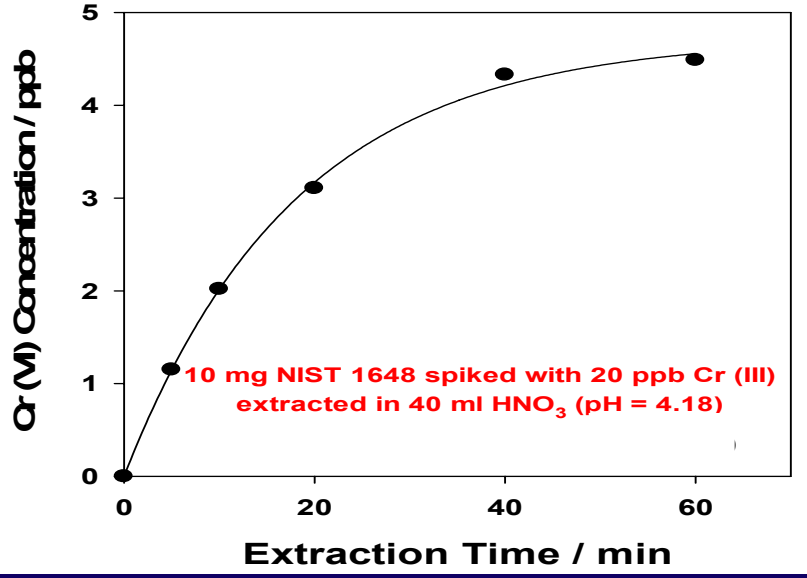
Extraction Temperature and Time

- Extract time:
  - 5, 10, 20, 40, 60 minutes
- Extraction temperature
  - 0°C, room temperature, 60°C
- Sample: NIST 1648 particulate matter +Cr(VI)+Cr(III)+ Teflon or $NaHCO_3$ pretreated cellulose filter.

Extraction Time and Cr(VI) Stability







- Optimal extraction time is 40 min.
- No significant conversion was observed from Cr(VI)[53] to Cr (III)[50], but Cr (III)[50] is not stable during extraction.

Note: Isotopes were spiked on the a filter coated with 1648 particles and then processed.

Field Evaluation during UCAMPP

- Precision – duplicate samples of both 52Cr(VI) (nature abundant) and 53Cr(VI) (isotope)
- Inter-conversion rate
- Recovery

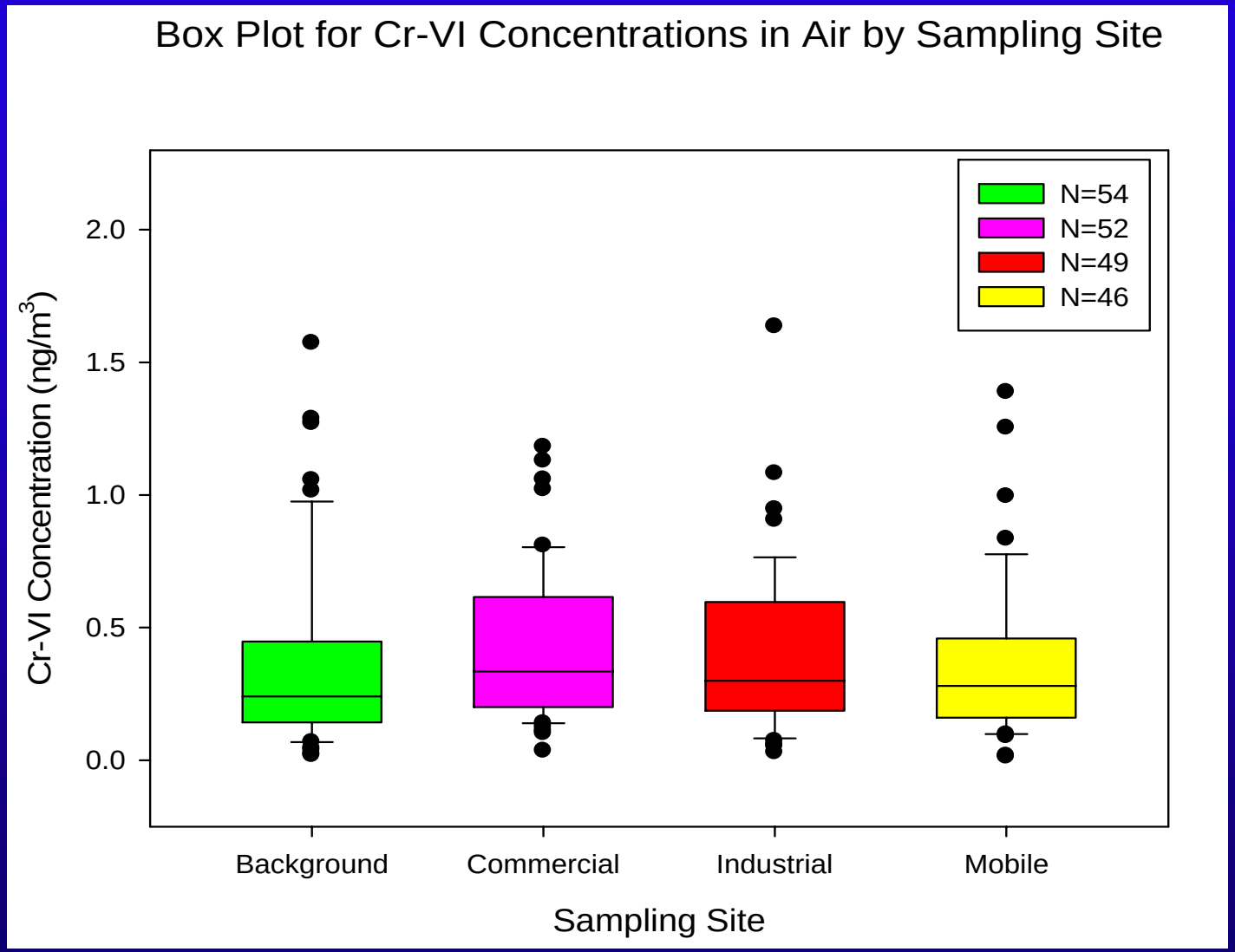
Relative Abs. Percent Difference [Cr(VI)]

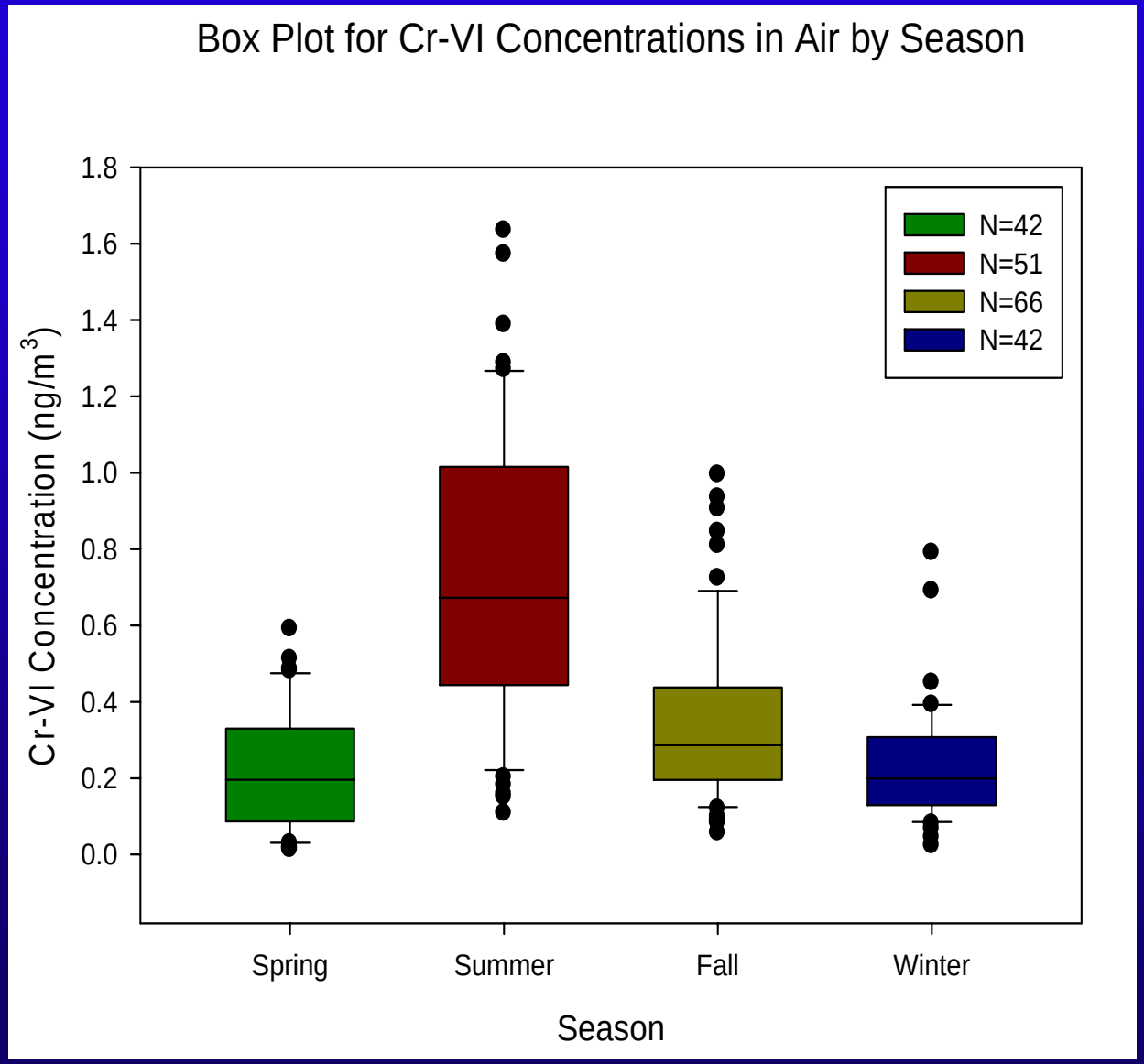
	N	mean	std	median
52Cr(VI)	21	16%	15%	15%
53Cr(VI)	23	12%	16%	7%

MDL: 0.18 ng/m^3 (0.86 ng/mL)

Inter-conversion and Recovery Rate [^{53}Cr(VI) and ^{50}Cr(III)]

	N	mean	std	median
Interconversion Rate				
Cr(VI) ->Cr(III)	77	8%	6%	8%
Cr(III)->Cr(VI)	30	18%	24%	11%
Recovery				
53Cr(VI)	49	73%	22%	78%
50Cr(III)	49	43%	33%	33%


Box Plot for Cr-VI Concentrations in Air by Sampling Site
N=54
N=52
N=49
N=46
2.0
1.5
1.0
0.5
0.0
Cr-VI Concentration (ng/m3)
Background
Commercial
Industrial
Mobile
Sampling Site


Box Plot for Cr-VI Concentrations in Air by Season
Cr-VI Concentration (ng/m3)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
N=42
N=51
N=66
N=42
Spring
Summer
Fall
Winter
Season

Summary of the Cr(VI) Measurement Procedures

Air Sampling
(Cellulose filter soaked by 2M NaHCO3)

↓

→ Sample storage at -15˚C → Extraction
(HNO_3 pH = 4.2; ultra-sonication at 60° for 40 min)

→ Ion Chromatography/Inductively Coupled Plasma Mass Spectrometry (IC/ICPMS)
(Separation with 60% 1M HNO_3 and 40% DI water, ICPMS is tuned by In)

Future work

- Reduce field blank Cr(VI) levels.
- Reduce/finalize inter-conversation rate between Cr(VI) and Cr(III).
- Investigate the impact of different environmental factors (O_3, UV, temperature, aerosol type, etc.) on Cr(VI) measurement.
- Inter-laboratory comparison of sampling and analytical methods.

Acknowledgments

- Dr. Linda Bonanno and other scientists at the NJ DEP
- Colleagues at EOHSI: B. Buckley, L. Lin, C.-H. Yu, K. Black, M. Hernandez, J. Kwon, Q. Meng (EPA), X. Zhu, R. Stiles
- This study is supported by the USEPA, the NJDEP, NIEHS Center at EOHSI