AMBIENT AIR CONCENTRATION OF HEXAVALENT CHROMIUM IN DISTRICT OF COLUMBIA: ANY HEALTH CONCERN?

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Disclaimer

This presentation and the analysis therein, do not necessarily represent or express the opinion of the Department of the Environment or the District of Columbia Government.
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• ERG: Julie Swift, Ray Merraill & Jaime Hauser
• EPA: Michael Jones and Joanne Rice
Overview

• Cr(VI) Monitoring Program
• Ambient Cr(VI) Data Analysis
• Risk analysis
• Discussion and Remarks
Chromium Types (video)

- Chromium element in rocks, animals, plants, soil and volcanic dust and gases
- Common forms:
  - elemental chromium Cr
  - trivalent or Cr(III)
  - hexavalent or Cr(VI)
- Cr(III) is an essential nutrient
- Cr and Cr(VI) are product of human activities
Chromium Sources

• Primary sources
• Minor sources
• Other sources: chromium based automotive catalytic converters and tobacco smoke (ATSDR, 2008)
• In the District of Columbia, automobiles may be the primary sources.
District Cr(VI) Monitoring

• Start Date: March 2005
• Sampling is 1-in-6 schedule
• Co-Lo every 8 to 10 weeks
Monitoring Method

• Cr(VI) ambient air TSP (STP)
  – sodium bicarbonate impregnated cellulose filter
• Sampling flow rate: 15 liters per minute
• Sample duration is 24 hours per sampling period
• Exposed filters analyzed by ERG at RTP lab
• EPA Compendium Method IO-3.5 inductively coupled plasma/mass spectrometry (ICP/MS) for metals (Jones, 2009; EPA, 2007; Rice, 2003)
Sampler

921 ERG CHROMIUM VI SAMPLER

Primary
Project Data Quality Objectives Ambient Cr(VI) in DC

• Cr(VI) data for 2006-2008 period considered
• Cr(VI) AQS Code 12115 (TSP-STP)
• Method Detection Limit (MDL) availability a major factor in use of this method
• Minimum of 85% data completeness
• Data checks and comparisons with other Cr(VI) monitoring sites
2007 Sampled Concentration vs MDL

Concentration (ng/m³) vs Time

- Blue line: Cr IV Conc
- Red line: MDL
Raw Data Averages by Season

July 4th 0.64 value excluded
Mean = 0.026370 ng/m³
NATTS Sites - 2006

<table>
<thead>
<tr>
<th>Urban Sites</th>
<th>Rural Sites</th>
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</thead>
<tbody>
<tr>
<td>Providence, RI</td>
<td>Underhill, VT</td>
</tr>
<tr>
<td>Boston ( Roxbury ), MA</td>
<td>Hazard, KY</td>
</tr>
<tr>
<td>New York, NY</td>
<td>Chesterfield, SC</td>
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<tr>
<td>Rochester, NY</td>
<td>Mayville, WI</td>
</tr>
<tr>
<td>Washington, DC</td>
<td>Grand Junction, CO</td>
</tr>
<tr>
<td>Decatur, GA</td>
<td>La Grande, OR</td>
</tr>
<tr>
<td>Tampa, FL</td>
<td>Harrison County, TX</td>
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<tr>
<td>Detroit, MI</td>
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<tr>
<td>Chicago, IL</td>
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<tr>
<td>Houston (Deer Park), TX</td>
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<td>St. Louis, MO</td>
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<tr>
<td>Roanoke, UT</td>
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<td>San Jose, CA</td>
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<tr>
<td>Phoenix, AZ</td>
<td></td>
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<tr>
<td>Seattle WA</td>
<td></td>
</tr>
</tbody>
</table>

Source: Dennis A. Miller
EPA–OAQPS–AQAD
CrVI 12115 All Sites

July 4th
11-DC=0.645
26-MI=0.496
29-MO=0.422
22-LA=0.367
44-RI=0.192
August 20, 2005
Outlier
Unknown issue

2005 did not have 85% DC
Health Concerns

• Typical routes of exposure ingestion, inhalation and absorption.
• As mentioned earlier, chromium has different forms, depending on the oxidation state, which ranges from -2 to +6 valence (ATSDR, 2008)
• Its health effect is a function of its valency.
• Elemental, trivalent and Hexavalent states have been noted to be most stable
Health Concerns

• Mutagenic DNA lesions results from Cr(VI) reduction to Cr(III)
• Epidemiological results among Cr exposed workers show Cr to be carcinogenic via inhalation route of exposure.
• Animal data further supports human data and implicates Cr(VI), against total Cr, as the carcinogen.

Source: EPA, 1998a
Health Concerns cont.

Weight-of-Evidence Narrative


• Carcinogenicity by the oral route of exposure cannot be determined and is classified as Group D (EPA 1998a & b).
Risk Analysis Assumptions

• Sample collection/analysis is devoid of significant errors
• Total ambient concentrations are captured and accounted for in analysis
• District population is exposed to total ambient concentration
• Population respond equally to ambient concentration of the pollutant
• No significant confounding factors in overall analysis
• Focus here is health risk from population exposure via inhalation only
Analysis Method

• 50% of yearly data below MDL, except 2006 (48% below)

• 2 treatment types:
  – ND (non detect) = MDL/2
  – ND = MDL

• Other treatments of interest
  – Maximum Likelihood Estimate or Cohen’s Distribution considered better (Helsel, 2005; Gilbert, 1987)
  
  *Is 1-in-6-sampling sufficient for calculating annual statistics using this technique?*
  – Robust Regression Order Statistics (ROS)
  – Kaplan Meier (KM)
Ref Conc. & Unit Risk

- Reference Concentration (RfC)
  $= 1 \times 10^{-4}$ mg/m$^3$ Cr(VI) particulates
- Inhalation Unit Risk
  $= 1.2 \times 10^{-2}$ per mg/m$^3$

Inhalation conc. @specified risk levels:
1 in 1,000,000 is $8 \times 10^{-5}$ µ/m$^3$

(IRIS-USEPA, 1998)
Risk Estimates

Cancer Risk

• 2 comparisons:
  – Inhalation Unit Risk (IUR)*Annual Mean Conc.
  – Annual mean compared with Regional Screening Levels (2.9E-05) Region III
Risk Estimates

Non-cancer risk or Margin of Exposure (MOE)

\[
\text{MOE} = \frac{\text{Cr(VI) average concentration}}{\text{RfC}}
\]

Example: 2006

\[\text{ND} = \text{MDL}/2: \frac{2.98E-05 \mu g/m^3}{(1X10^{-1} \mu g/m^3)} = 0.000298\]

\[\text{ND} = \text{MDL}: \frac{3.21034E-05 \mu g/m^3}{(1X10^{-1} \mu g/m^3)} = 0.000321034\]

MOE is less than 1
Risk Estimates: Cancer

Cancer Risk

\[(\text{Inhalation Unit Risk}) \times (\text{annual Cr(VI) Mean})\]

Example 2006

ND=MDL/2: \(1.2 \times 10^{-2}\) per \(\mu g/m^3\)\(\times 0.0000298 \mu g/m^3\)
\[=3.57E-07\]

ND=MDL: \(1.2 \times 10^{-2}\) per \(\mu g/m^3\)\(\times 0.0000321 \mu g/m^3\)
\[=3.85241E-07\]
Exposure Risk Estimate

<table>
<thead>
<tr>
<th>YEAR</th>
<th>Non-Cancer Risk (MOE)</th>
<th>Cancer Risk</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>ND=MDL</td>
<td>ND=MDL</td>
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<tr>
<td></td>
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<tr>
<td>2006</td>
<td>0.0003</td>
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<tr>
<td>2007</td>
<td>0.0001</td>
<td>1E-7</td>
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<tr>
<td>2008</td>
<td>0.0001</td>
<td>1E-7</td>
</tr>
</tbody>
</table>
Risk Based Concentration Comparison 2006

Date

Concentration ng/m³

0 0.02 0.04 0.06 0.08 0.1 0.12 0.14 0.16 0.18 0.2

20060105 20060107 20060109 20060110 20060112 20060114 20060116 20060118 20060120 20060122 20060124 20060126 20060128 20060130 20060201 20060203 20060205 20060207 20060209 20060211 20060213 20060215 20060217 20060219 20060221 20060223

20060301 20060303 20060305 20060307 20060309 20060311 20060313 20060315 20060317 20060319 20060321 20060323 20060325 20060327 20060329 20060401 20060403 20060405 20060407 20060409 20060411 20060413 20060415 20060417 20060419 20060421 20060423 20060425 20060427 20060429

20060501 20060503 20060505 20060507 20060509 20060511 20060513 20060515 20060517 20060519 20060521 20060523 20060525 20060527 20060529 20060601 20060603 20060605 20060607 20060609 20060611 20060613 20060615 20060617 20060619 20060621 20060623 20060625 20060627 20060629

20060701 20060703 20060705 20060707 20060709 20060711 20060713 20060715 20060717 20060719 20060721 20060723 20060725 20060727 20060729 20060801 20060803 20060805 20060807 20060809 20060811 20060813 20060815 20060817 20060819 20060821 20060823 20060825 20060827 20060829

20060901 20060903 20060905 20060907 20060909 20060911 20060913 20060915 20060917 20060919 20060921 20060923 20060925 20060927 20060929 20061001 20061003 20061005 20061007 20061009 20061011 20061013 20061015 20061017 20061019 20061021 20061023 20061025 20061027 20061029

20061101 20061103 20061105 20061107 20061109 20061111 20061113 20061115 20061117 20061119 20061121 20061123 20061125 20061127 20061129 20061201 20061203 20061205 20061207 20061209 20061211 20061213 20061215 20061217 20061219 20061221 20061223 20061225 20061227 20061229
Risk Based Concentration Comparison 2008

Date

Concentration ng/m³

MDL/2
ND=MDL
Risk Based Concentration (RBC)
Discussions

• Substituting non-detect with MDL is very conservative; (EPA, 2009).

• The MDL/2 does not give a true estimate of ambient concentration and the subsequent exposure measure either, as it tends to give a measure that is considered higher than the true ambient concentration (EPA, 2009; Helsel, 2005; Warren and Nussbaum, 2009).

• The true statistical reflection of ambient concentration is considered to be maximum likelihood estimation (MLE), (ibid). Doubts however, have been casted on this approach, with regards to 1-in-6 samples.
Discussions

• Acceptable cancer risk level is $1E-06$ or 1 in 1,000,000 (EPA 1998b).

• Current estimate using the conservative non-detect=MDL or MDL/2 still shows an estimate below the acceptable level.

• Indoor concentration is worth noting too, as build up, resulting from proximity to road ways, and/or smoking may raise level to several fold higher than the ambient concentration.
Limitations

• Errors from using new sampling method
• MDL and MDL/2 are too conservative to give a true reflection of ambient air concentration and subsequent exposure analysis
• Cohen method suggested need to be looked at even though sampling is 1-in-6.
Conclusions

• Cr(VI) concentration in the District’s ambient air is generally well below levels considered harmful.
• Occasional spikes of short duration observed
• High percentage of non-detect needs to be accounted for
References


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