Siloxanes: Quantifying a New Emergent Pollutant in Water, Air and Soil

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Outline

• Who is CARO?
• What are Siloxanes?
• Concerns
• Legislation
• Water Air and Soil Methodology
• Summary and Credits
Who is CARO?

- Western Canadian full service environmental lab:
  - Edmonton, Alberta
  - Vancouver, British Columbia (Head Office)
  - Kelowna, British Columbia
  - Whitehorse, Yukon

- Vision: CARING ABOUT RESULTS
  - Technical Leadership
  - Client Collaboration
  - Developed & Motivated Staff

- Capabilities:
  - Contaminated Sites: Hydrocarbons, SVOCs, VOCs, Metals
  - Water Quality: Physical Parameters, Nutrients, Anions, Metals
  - Microbiology and Toxicology
  - Award Winning - Soil Vapour Capabilities!
Siloxanes

• Anthropogenic chemicals having a multitude of applications in the production of household, automotive, construction, and personal care products.

• Intermediates in the production of silicon polymers.

• Beneficial Properties

• Invented by DOW

better living through chemistry
Siloxanes

- Emerging organic contaminants in the environment over the past two decades.
- D4 and D5 in one out of every seven of the 41,000 different personal care products
- Lipstick, body lotions, French fries, water repellents, and lubricants, amongst other things.
# Structure

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>AKA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexamethylcyclotrisiloxane</td>
<td>C_{12}H_{18}O_{3}Si_{3}</td>
<td>D3</td>
</tr>
<tr>
<td>Octamethylcyclotetrasiloxane</td>
<td>C_{8}H_{24}O_{4}Si_{4}</td>
<td>D4</td>
</tr>
<tr>
<td>Decamethylcyclopentasiloxane</td>
<td>C_{10}H_{30}O_{5}Si_{6}</td>
<td>D5</td>
</tr>
<tr>
<td>Dodecamethylcyclohexasiloxane</td>
<td>C_{12}H_{36}O_{6}Si_{6}</td>
<td>D6</td>
</tr>
<tr>
<td>Hexamethyldisiloxane</td>
<td>C_{6}H_{16}Si_{2}O</td>
<td>L2</td>
</tr>
<tr>
<td>Octamethyltrisiloxane</td>
<td>C_{8}H_{24}Si_{3}O_{2}</td>
<td>L3</td>
</tr>
<tr>
<td>Decamethylderasiloxane</td>
<td>C_{10}H_{30}Si_{4}O_{3}</td>
<td>L4</td>
</tr>
<tr>
<td>Dodecamethyldipentasiloxane</td>
<td>C_{12}H_{36}Si_{5}O_{4}</td>
<td>L5</td>
</tr>
</tbody>
</table>
Solubility in Water

- Relatively Low Solubility in Water
- Generally Decreasing Solubility with Size

<table>
<thead>
<tr>
<th>Siloxane</th>
<th>Solubility (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D4</td>
<td>56</td>
</tr>
<tr>
<td>D5</td>
<td>17</td>
</tr>
<tr>
<td>D6</td>
<td>5</td>
</tr>
</tbody>
</table>
Concerns

• Primary concerns
  – toxicity
  – destructive impact they have on biogas combustion equipment.
  – Prevalence in consumer products combined with their high volatility, bioaccumulation and relatively long half-lives in air.
  – These characteristics give way to concern about long range transport and bioaccumulation
  – Cyclic Siloxanes Octamethylcyclotetrasiloxane (D4), Decamethylcyclopentasiloxane (D5), and Dodecamethylcyclohexasiloxane (D6), shown below.
LOADING AND DISTRIBUTION

- Landfill sites
- Wastewater treatment plants and their surrounding areas
- Detecting the cyclic Siloxane D5 in indoor and outdoor air in various residential and commercial settings.
- Proving to be ubiquitous environmental contaminants, being detected at trace levels in even the most remote locations.
Legislation

- Environment Canada has recently published a notice announcing the requirement for preparation and implementation of pollution prevention plans in respect to D4 in industrial effluents. 17.3 ug/L

- D4 has been identified by Environment Canada and Health Canada as potentially having “long-term harmful effects on the environment or its biological diversity”, and as meeting the criteria of a persistent chemical in the environment (Environment Canada, 2012).
• Additionally, D4 was recently added to a list of chemicals for further review by the U.S. EPA for 2013-2014, which could lead to regulations under the Toxic Substances Control Act.
<table>
<thead>
<tr>
<th>Siloxane</th>
<th>MDL (ug/L)</th>
<th>Precision (%)</th>
<th>Accuracy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L2</td>
<td>0.19</td>
<td>2.9</td>
<td>109</td>
</tr>
<tr>
<td>L3</td>
<td>0.13</td>
<td>2.6</td>
<td>110</td>
</tr>
<tr>
<td>D4</td>
<td>0.98</td>
<td>7.3</td>
<td>127</td>
</tr>
<tr>
<td>D5</td>
<td>0.49</td>
<td>4.3</td>
<td>110</td>
</tr>
</tbody>
</table>
CARO’s GC/MS method for the analysis of Siloxanes in water is for the quantitation of L2, L3, D4, and D5. The chromatographic sensitivity required for the anticipated regulatory limit of 17.3 μg/L for D4 was easily achieved.

GC/MS EICs for select Siloxanes spiked into water at 1 ppb
Response in Water

GC/MS EICs for select Siloxanes spiked into water at 1 ppb
Siloxanes in Water

Siloxane in Water Calibration Curves (range is 0-100 ug/L)
Siloxanes in Water

Siloxane in Water Calibration Curves (range is 0-100 ug/L)
Siloxanes in Water

- **Analytes of Interest**
  - Hexamethyldisiloxane (L2),
  - Octamethyltrisiloxane (L3),
  - Octamethylcyclotetrasiloxane (D4),
  - Decamethylcyclopentasiloxane (D5),
- 90%+ QC Recoveries
- Similar To Volatiles Methodology
- Short Hold Time
- No Headspace Samples
- Neutral pH Stability
- Glass Vials
- Reported Detection Limit 2 ug/L
Siloxanes in Air

- Turbo Matrix instrumentation:
  - First lab in western Canada (2008)
  - First lab with redundancy (2012)

- Accreditation - Fall 2008
  - First BC lab (Canadian Association for Laboratory Accreditation)

- Methods 2008/2009
  - BC Ministry of Environment
  - BC Environmental Laboratory Technical Advisory Committee
  - Authored VOC by TD-GCMS & VHv Methods
  - Fractionation: Aromatics and Non-Aromatics (Aliphatics)

- Method Development and SR&ED
Siloxanes in Air

- SR&ED Client Project – Siloxanes in Air
  - 1,1,3,3-Tetramethyltrisiloxane,
  - Pentamethyldisiloxane,
  - Hexamethyldisiloxane (L2),
  - Octamethyldisiloxane ,
  - Hexamethyldicyclotrisiloxane (D3)
  - Octamethyldicyclotrisiloxane
- 90% + recoveries for QC
- Reported Detection Limit 0.01 ug
- VPHv quantitation
Siloxanes in Soil

- **Analytes of Interest**
  - Hexamethyldisiloxane (L2),
  - Octamethyltrisiloxane (L3),
  - Octamethylcyclotetrasiloxane (D4),
  - Decamethylcyclopentasiloxane (D5),
- 90%+ QC Recoveries
- Similar To Volatiles Methodology
- Short Hold Time
- No Headspace Samples
- Reported Detection Limit 1ug/g
- Methanol Field Preservation?
Internal Standard and Surrogates

- Fluorobenzene: Neat, Internal Standard.
- Chlorobenzene-d5: Neat, Internal Standard.
- Toluene-d8: Neat, Surrogate.
- 4-Bromofluorobenzene: Neat, Surrogate.
- 1,4-Dichlorobenzene-d4: Neat, Surrogate.

Quality Control Samples

- **Surrogate Standards**: Added to each sample and standard solution, and used to monitor the method performance on a sample-to-sample basis.
- **Method Blanks**: The laboratory blank consists of organic-free (P&T) water. Blanks should be below the reported detection limits.
- **Method (Blank) Spikes**: *This is equivalent to the Siloxane Calibration Verification Standard.*
- **Duplicates**: Duplicate sample analysis in batch to check reproducibility.
Future Developments

• Field Considerations
  • Sample Collection
    • Long term monitoring of sites
    • Seasonal variations
    • Site specific conditions

• Specialized Testing & Method Development
  • Siloxanes
    • Other Siloxanes
    • Degradation Products
    • Precursors
  • Others related potential contaminants of concerns
    • Hormones
    • Hormone mimickers
    • Drugs
    • Low Level Pesticides
Summary

- Siloxanes Are A Proven Potential Contaminant of Concern
- Predominantly Found in Landfill and Wastewater, but Not Well Understood in Other Areas – Human Exposure?
- Regulatory Environment Continuing to Identify New PCOCs Like Siloxanes
- Methodology for Water, Air & Soil Exists to Meet Future Regulations
- Continuous Advancements Adapting to Client and Market Forces
Acknowledgements

CARING ABOUT RESULTS

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Our Clients

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