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

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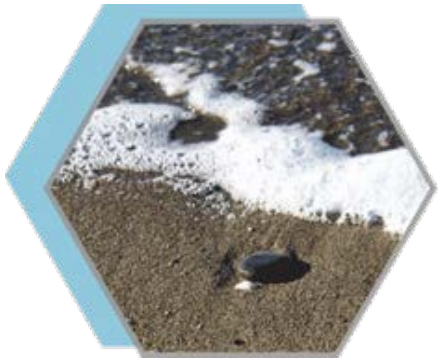


Outline

- 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!

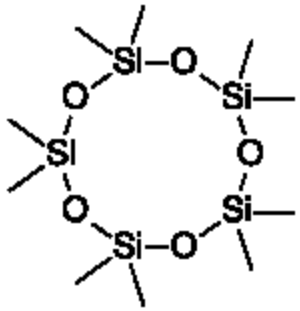
Siloxanes

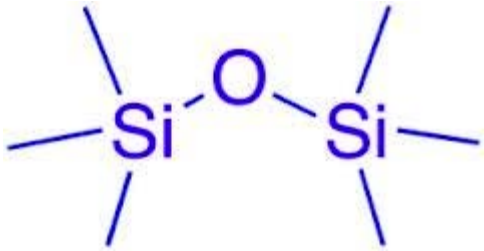
- **Anthropogenic chemicals having a multitude of applications in the production of household, automotive, construction, and personal care products.**
- **Intermediates in the production of silicon polymers.**
- **Beneficial Properties**
- **Invented by DOW**

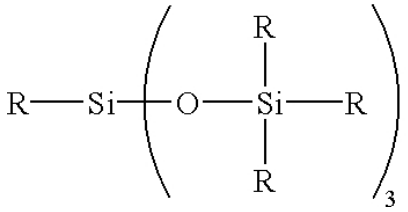
Siloxanes

- **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







Name	Formula	AKA
Hexamethylcyclotrisiloxane	$C_{12}H_{18}O_3Si_3$	D3
Octamethylcyclotetrasiloxane	$C_8H_{24}O_4Si_4$	D4
Decamethylcyclopentasiloxane	$C_{10}H_{30}O_5Si_5$	D5
Dodecamethylcyclohexasiloxane	$C_{12}H_{36}O_6Si_6$	D6
Hexamethyldisiloxane	$C_6H_{18}Si_2O$	L2
Octamethyltrisiloxane	$C_8H_{24}Si_3O_2$	L3
Decamethyltetrasiloxane	$C_{10}H_{30}Si_4O_3$	L4
Dodecamethylpentasiloxane	$C_{12}H_{36}Si_5O_4$	L5

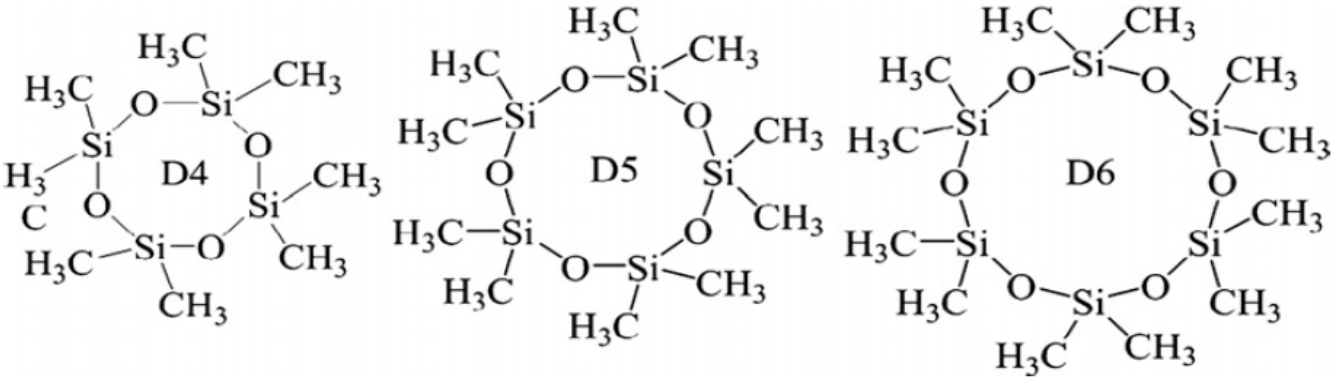
Solubility in Water

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

Siloxane	Solubility (ug/L)
D4	56
D5	17
D6	5

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

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).

Environment Canada

Legislation

- 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.

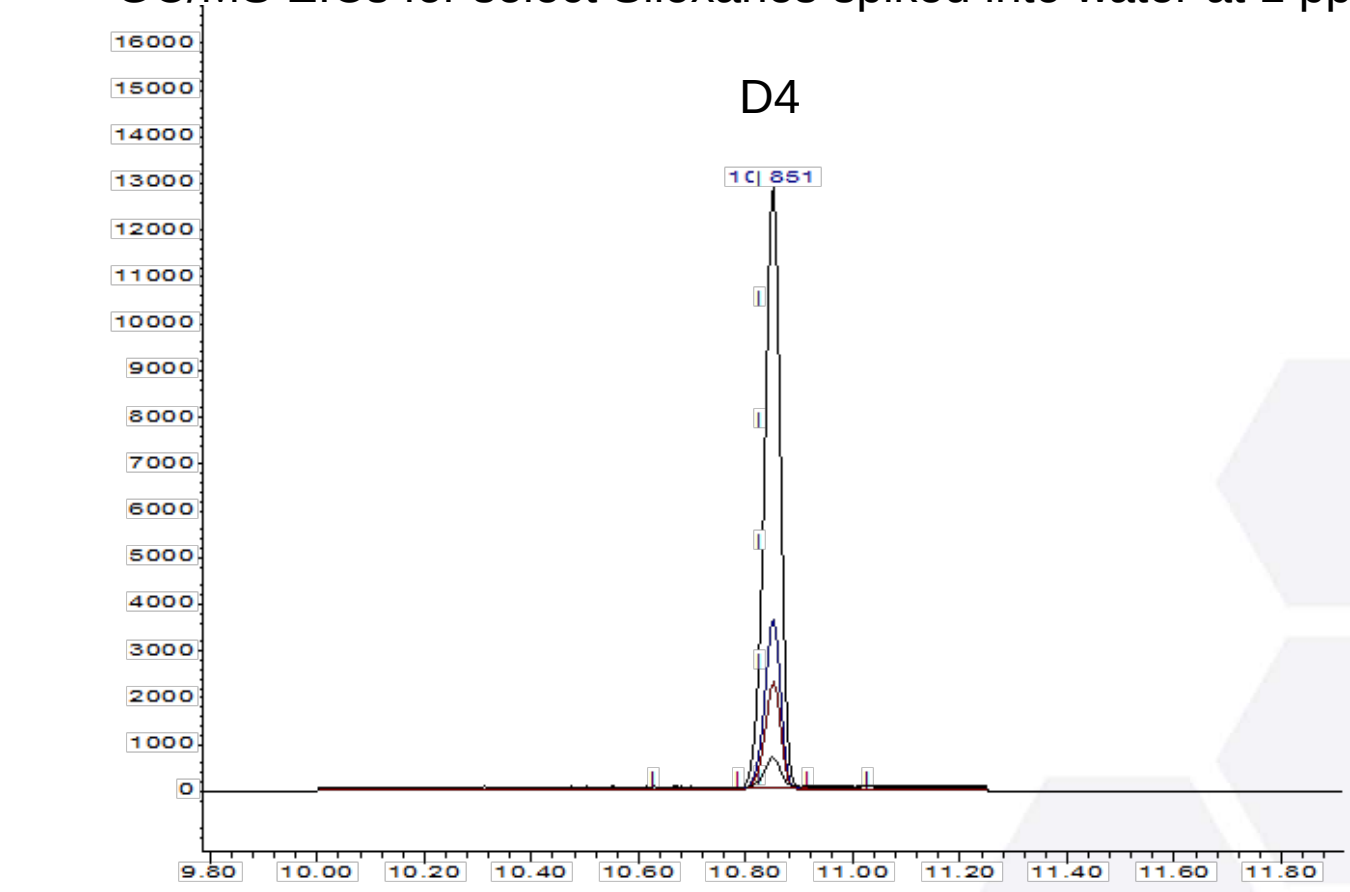
Siloxanes in Water

Siloxane	MDL (ug/L)	Precision (%)	Accuracy (%)
L2	0.19	2.9	109
L3	0.13	2.6	110
D4	0.98	7.3	127
D5	0.49	4.3	110

Response in Water

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 ug/L for D4 was easily achieved.

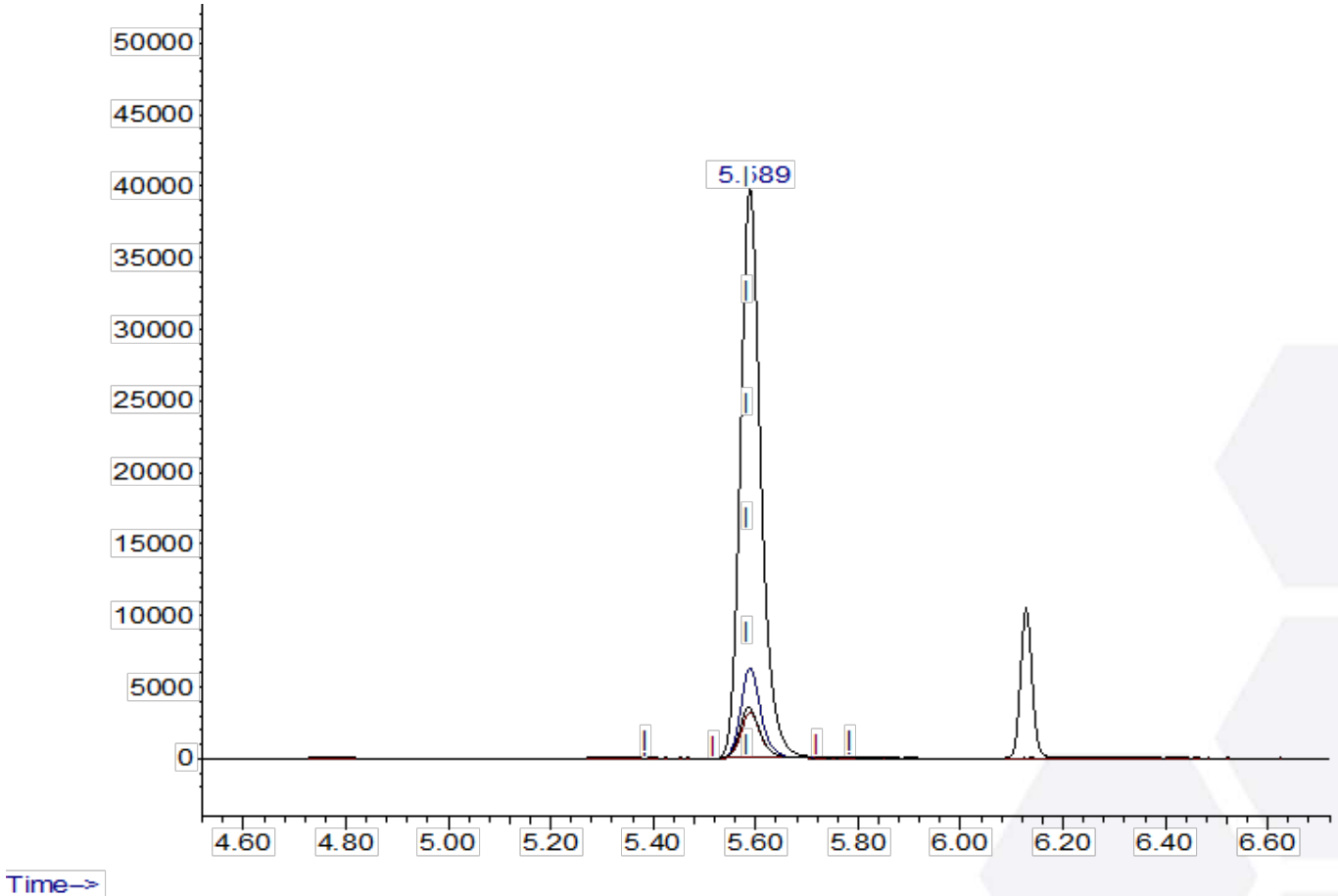
GC/MS EICs for select Siloxanes spiked into water at 1 ppb



Response in Water

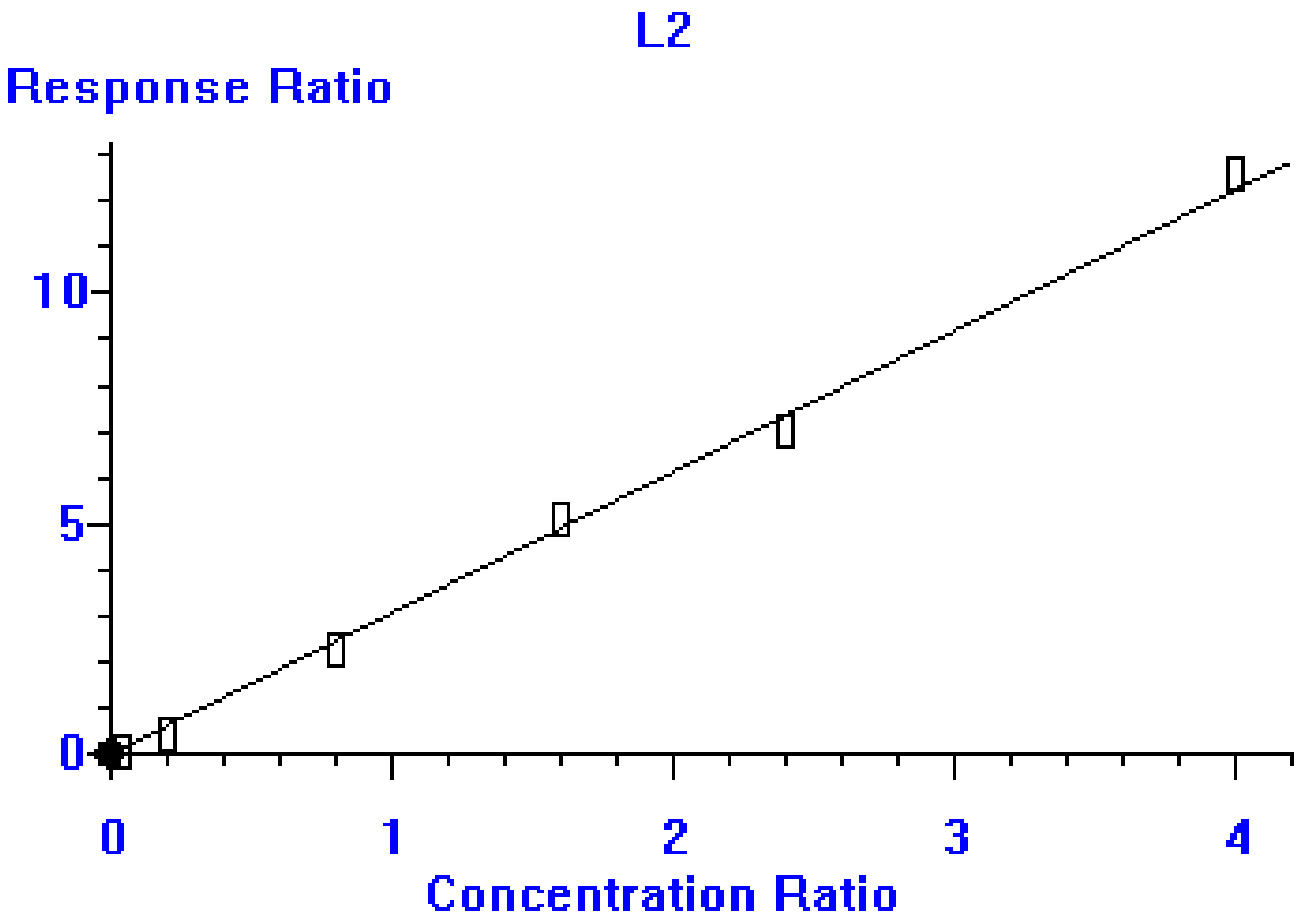
GC/MS EICs for select Siloxanes spiked into water at 1 ppb

L2



Siloxanes in Water

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



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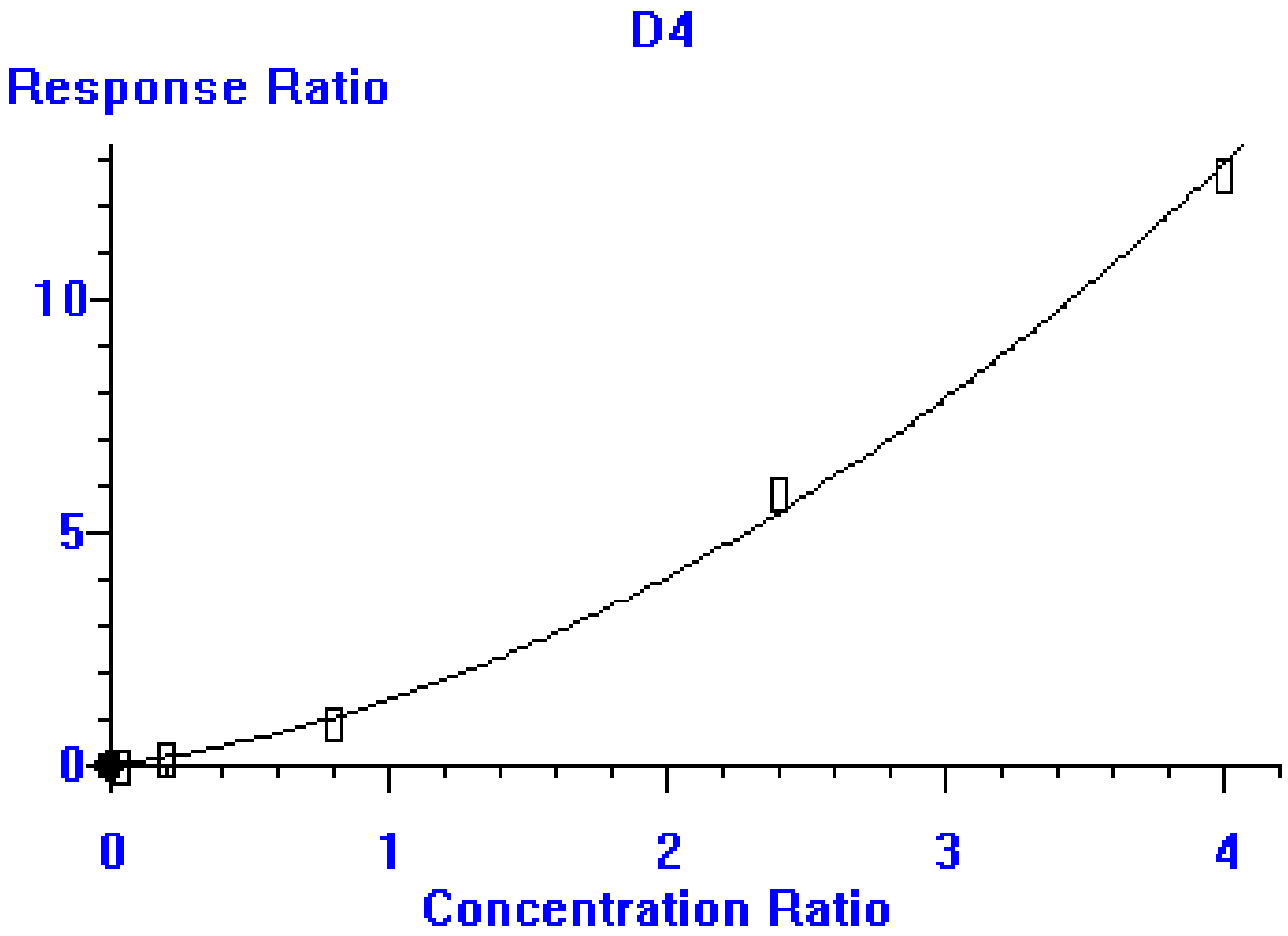


Siloxanes in Water

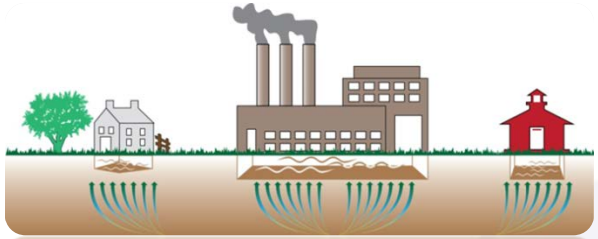
- **Analytes of Interest**
  - Hexamethyldisiloxane (L2),
  - Octamethyltrisiloxane (L3),
  - Octamethylcyclotetrasiloxane (D4),
  - Decamethylcyclopentasiloxane (D5),
- 90%+ QC Recoveries
- Similar To Volatiles Methodology
- Short Hold Time
- No Headspace Samples
- Neutral pH Stability
- Glass Vials
- 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 ,
  - Hexamethylcyclotrisiloxane (D3)
  - Octamethylcyclotrisiloxane
- 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?

Siloxanes QC

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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