Total organic carbon measurements reveal large gaps in emissions monitoring and reporting

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Introduction

Government monitoring of gaseous organic emissions has traditionally relied upon measurements of lighter volatile organic compounds (VOCs).

In reality, carbon emissions from most anthropogenic sources span a wide range of molecular sizes and functionalities. This is particularly relevant for the **oil and gas sector**, where emitted hydrocarbons from extraction and processing include heavier intermediate-volatility and semi-volatile organic compounds **(IVOCs and SVOCs**, C_{12+}) that form secondary air pollution.

Source: Wikipedia

Specifically, the Athabasca oil sands (OS) region in Canada, which currently produces ~3 million barrels of crude bitumen per day, provides a major opportunity to examine air pollutant reporting uncertainties.

Problem

- The global transition to unconventional petroleum resources and the associated shift in the volatility of emissions present challenges for traditional organic carbon monitoring and reporting.
- Limited reported emissions of individual carbon species from Canadian oil sands regions cannot be reconciled with incomplete existing emissions measurements.

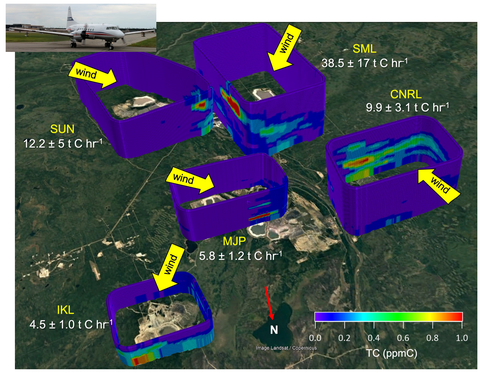
Purpose & Objectives

We use **airborne real-time measurements of total gaseous organic carbon (TC)** to compare top-down emissions from oil sands mining operations to industry-reported bottom-up estimates.

- Chemically speciate organic carbon emissions to highlight reporting discrepancies
- Compare the magnitude of emissions from oil sands operations to other Canadian sources
- Capture the full range of organic air pollutants and demonstrate the need to improve routine emissions reporting and monitoring beyond VOCs

Methods

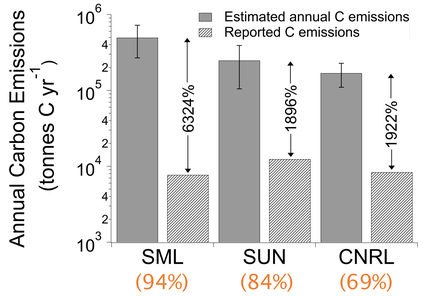
- First application of sampling on a plane with offline high resolution mass spectrometry
- Research aircraft flew in box patterns and straight-line tracks to **sample airborne measurements above oil sands facilities** in summer 2018



- Online instruments: real-time measurements for total gaseous organic carbon & NOy
- Offline instruments: adsorbent tube sample collection of I/SVOCs, analyzed via GC-MS

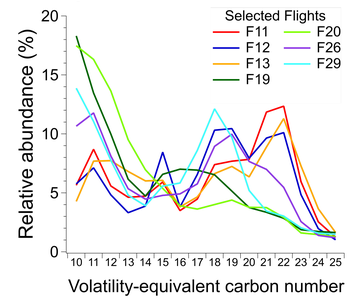
Results

1. Total observed emissions greatly exceed reported emissions

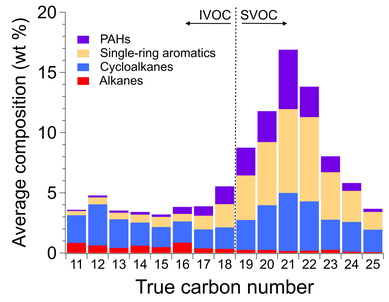


*For major facilities, a significant amount of carbon mass heavier than VOCs is **missing**, highlighting the importance of accounting for I/SVOCs.*

2. Abundant complex I/SVOC mixtures near OS operations

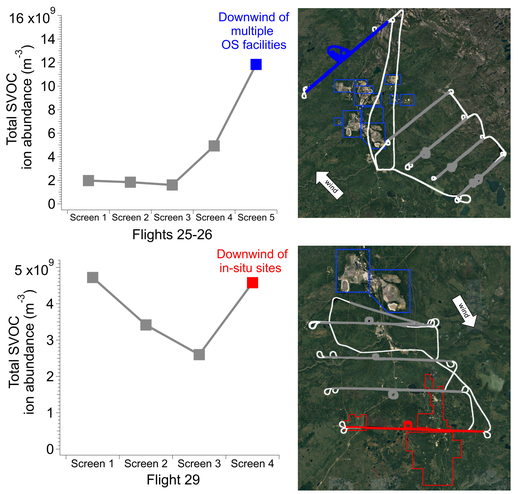


Volatility distribution of hydrocarbons.

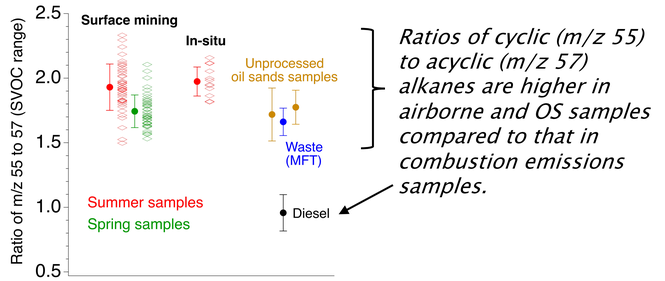


Average chemical breakdown of I/SVOCs.

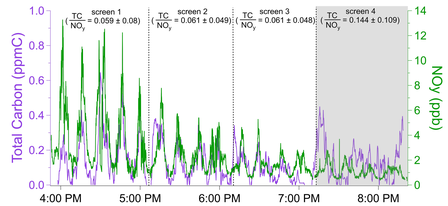
3. Carbon enhancements downwind of OS



4. An important role for non-combustion emissions

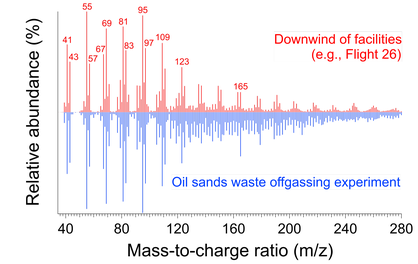


Ratios of cyclic (m/z 55) to acyclic (m/z 57) alkanes are higher in airborne and OS samples compared to that in combustion emissions samples.



Total carbon increases in last screen (greyed) relative to NOy, a combustion tracer.

5. Potential non-combustion emission pathways



Similarity of mass spectra (m/z) between airborne samples and waste product off-gassing emissions samples.

Conclusions

- The magnitude of emissions from OS facilities far exceeds industry reports
  - Underlying pathways are OS-derived
- Adequate reporting requires complete coverage of a wider volatility range of emissions (I/SVOCs)
- The total carbon approach here is a valuable tool to capture a broader range of chemical species and identify previously unknown organic carbon
- Demonstrates the importance of accounting for lifecycle-wide emissions across petrochemical and many other anthropogenic sources

Acknowledgement: Environment and Climate Change Canada