

Isotopes and the Elements:

Isotopic Geochemistry of Air and Water

Kavita Hardy
Swarthmore College
GCEP Fellow, Summer 2007
University of Illinois, Chicago

AIR

(and FIRE)

MILAGRO

- Characterize carbon aerosols in Mexico City; determine sources of carbon pollution
- Several labs participating in effort

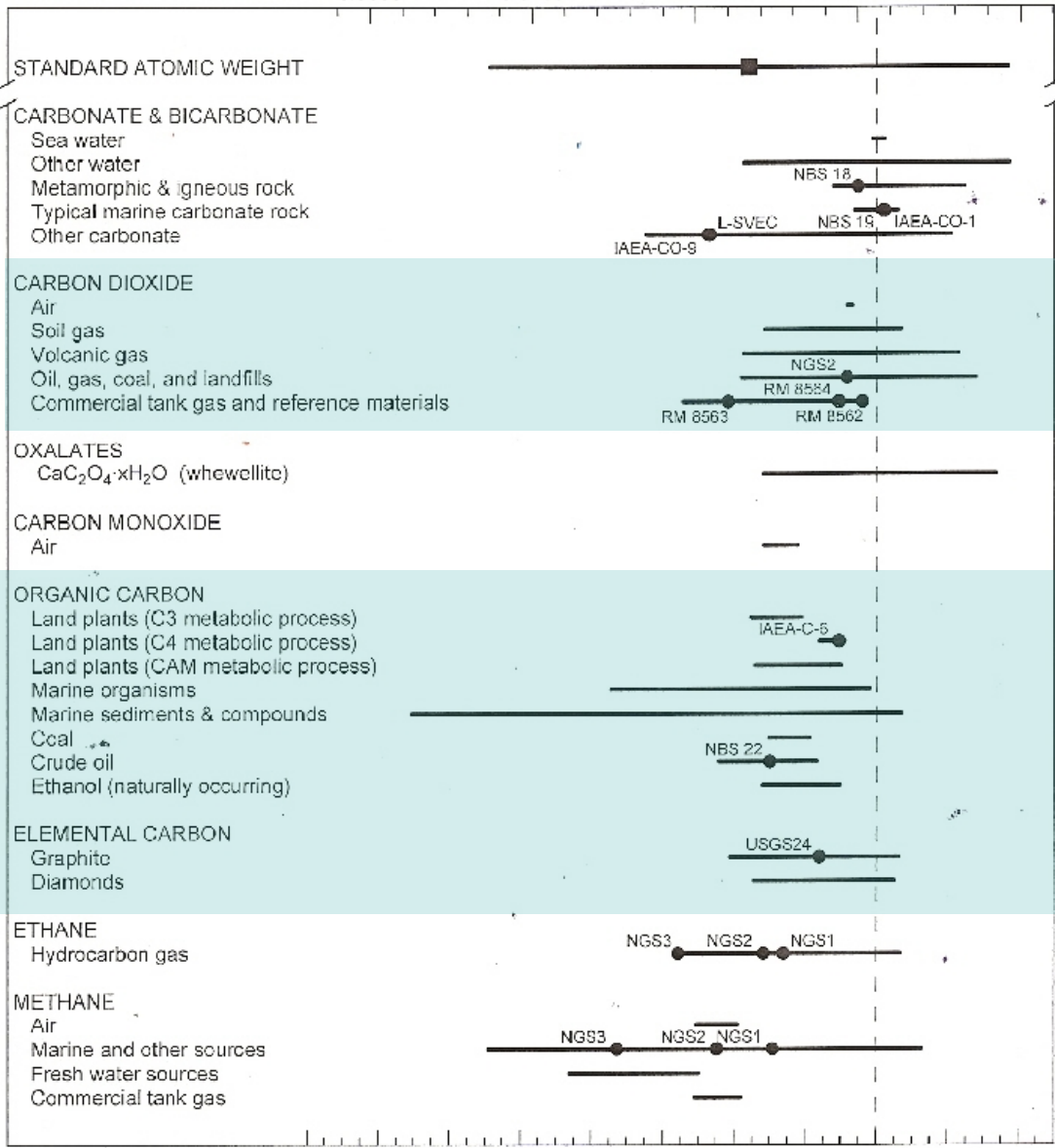
Isotopic Characterization

- $^{13}\text{C}/^{12}\text{C}$
 - Ratio measured by mass spectrometer, compared to a standard
 - Ratio a “signature of source”
- ^{14}C (Carbon dating)
 - Measure concentration of ^{14}C
 - Extrapolate data to determine age of sample

12.0095 12.0100 12.0105 12.0110 12.0115

Mole Fraction of ¹³C

0.0095 0.0100 0.0105 0.0110 0.0115



Combustion

CO_2

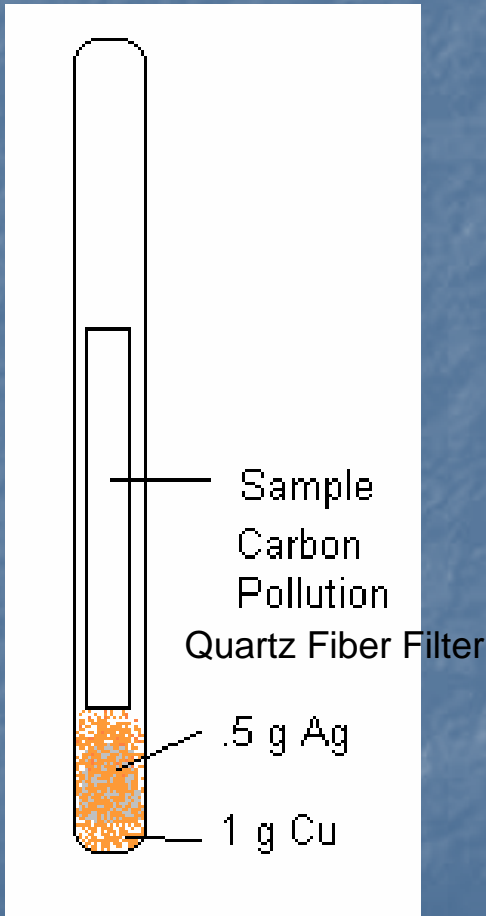
H_2O

Cu^{2+} , CuO

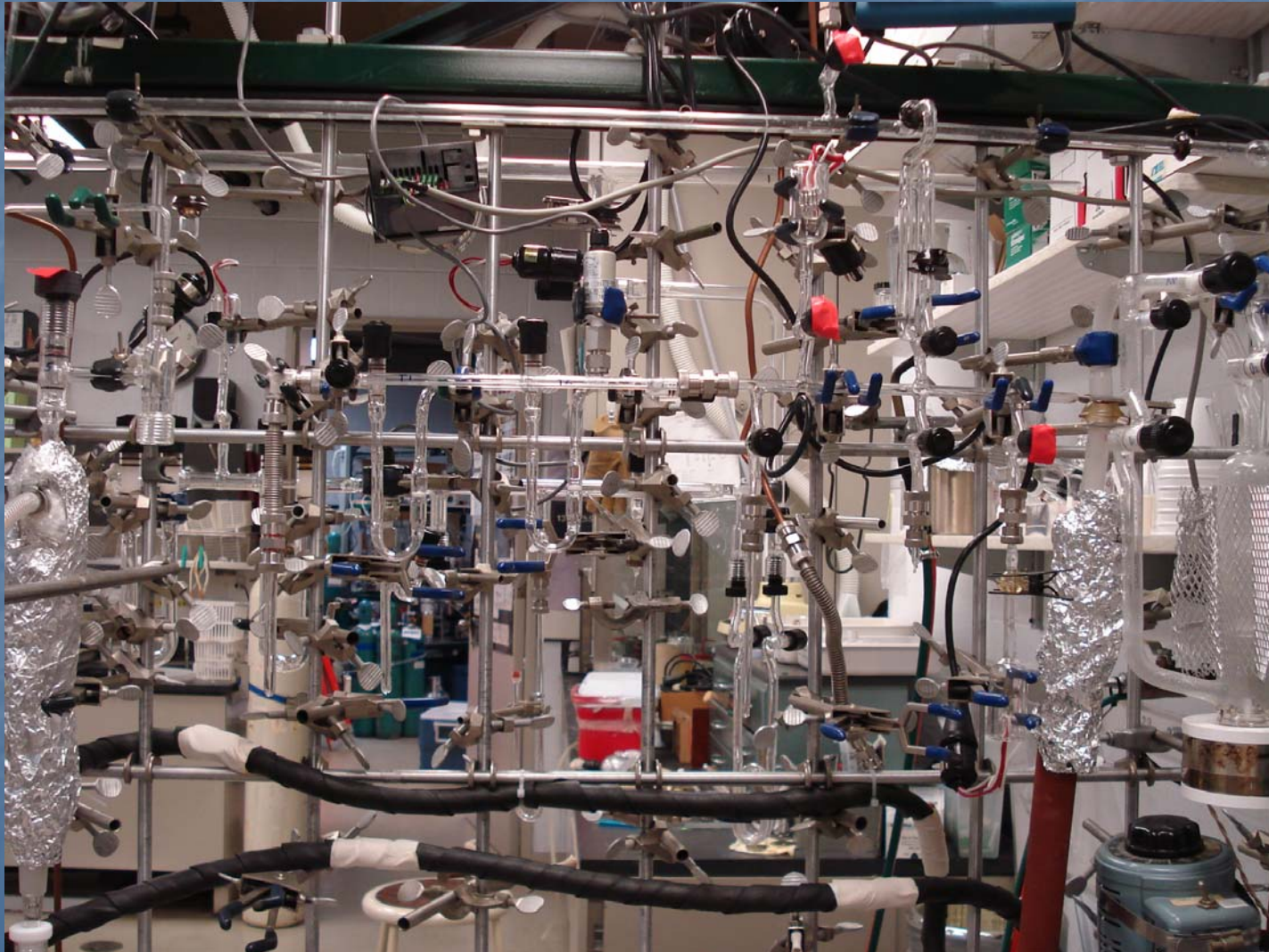
Trace gases

850°C

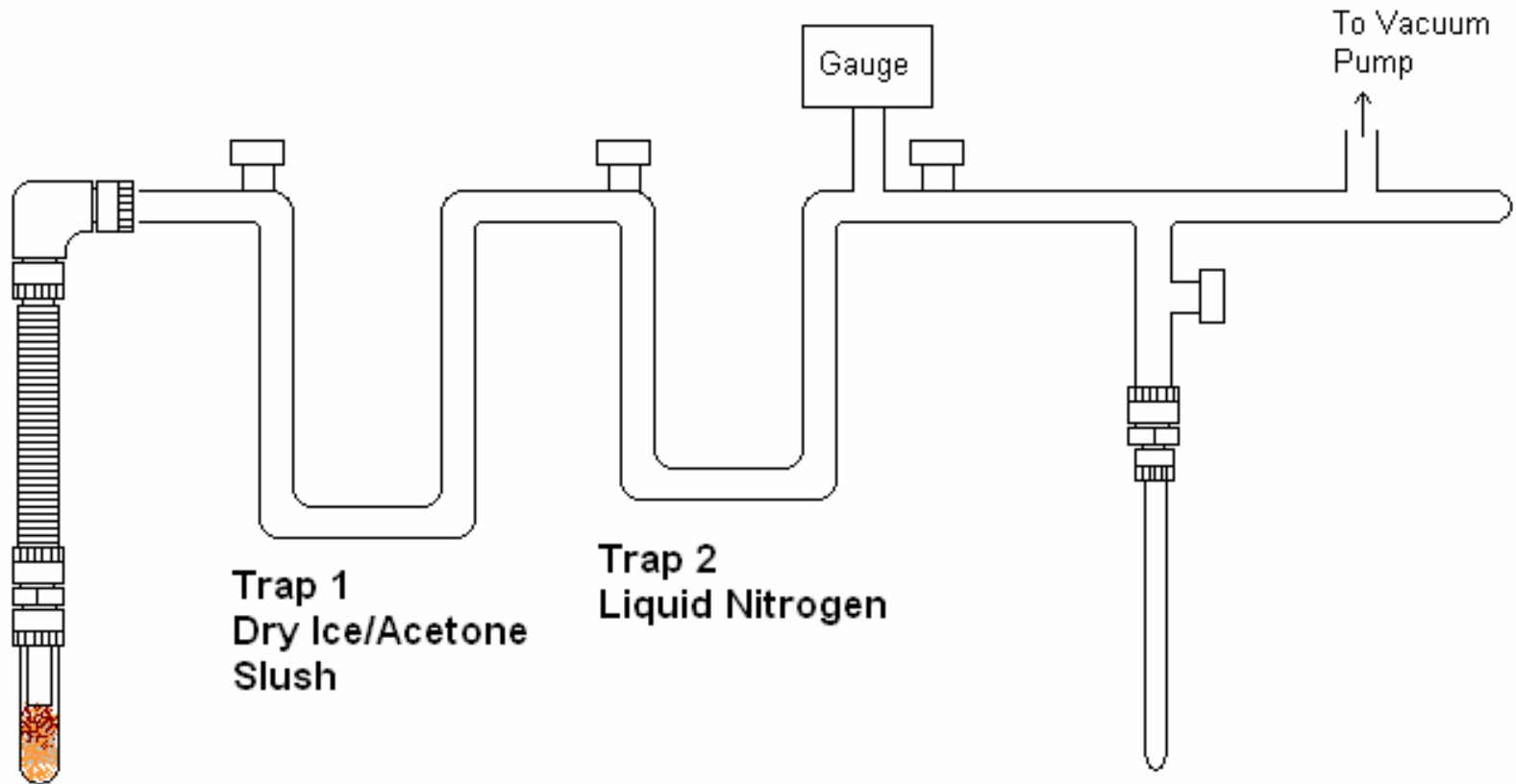
4 hrs



Cryogenic Separation of CO₂



Cryogenic Separation of CO₂



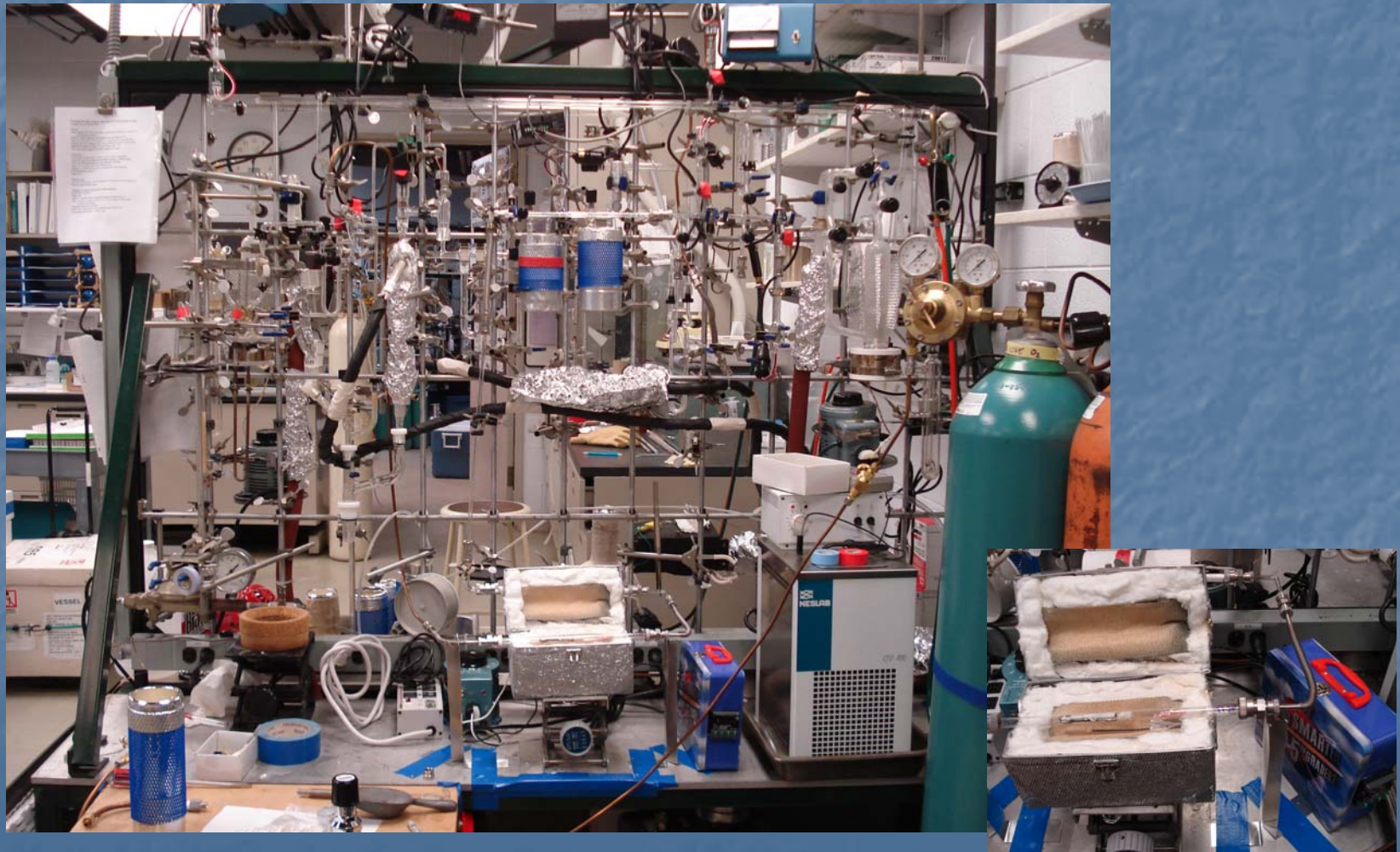
Thermal Evolution of Organic and Elemental Carbon

Organic-volatizable carbon

Elemental-fully reduced carbon, like soot or graphitic carbon

- Thermal evolution to separate organic from elemental carbon; can compare isotopic ratio of both components
 - With other types of data (chemical composition, optical properties), can further differentiate sources of pollution.

Thermal Evolution of Organic and Elemental CO₂, cont.



Preliminary Results (Bulk Carbon)

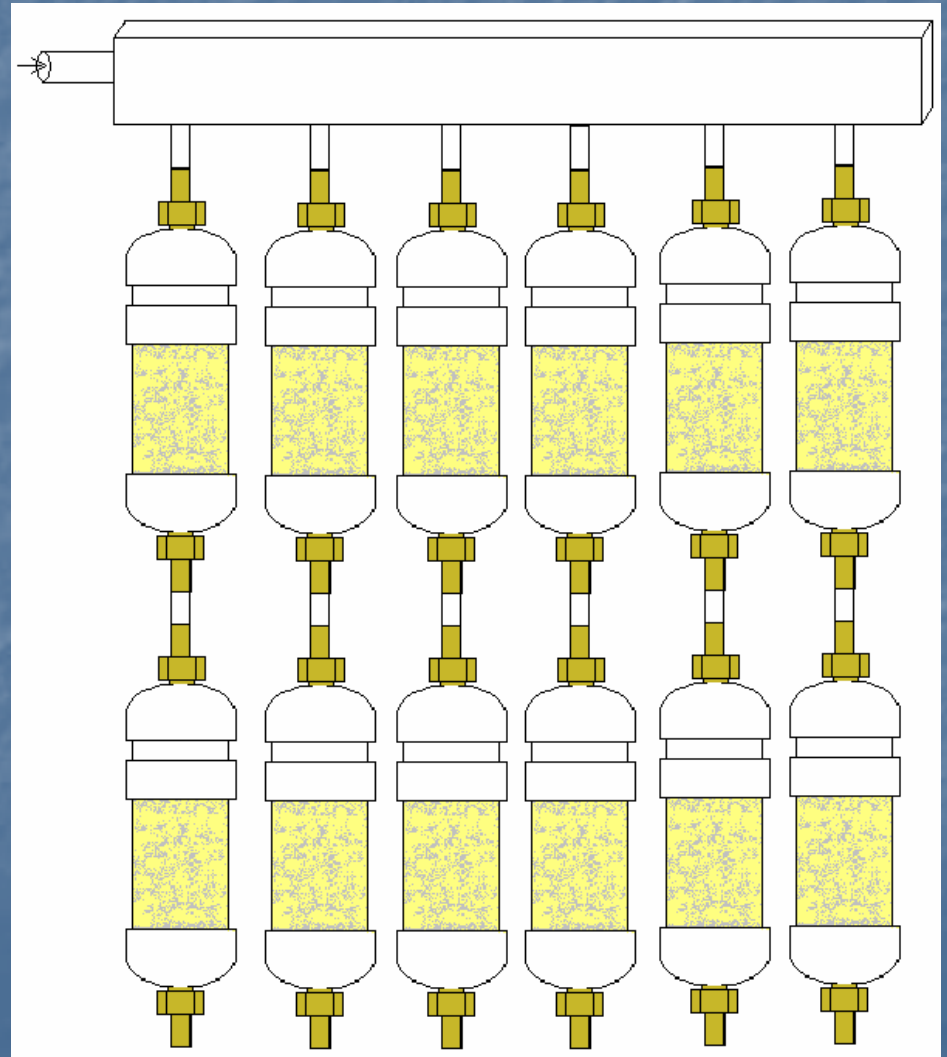
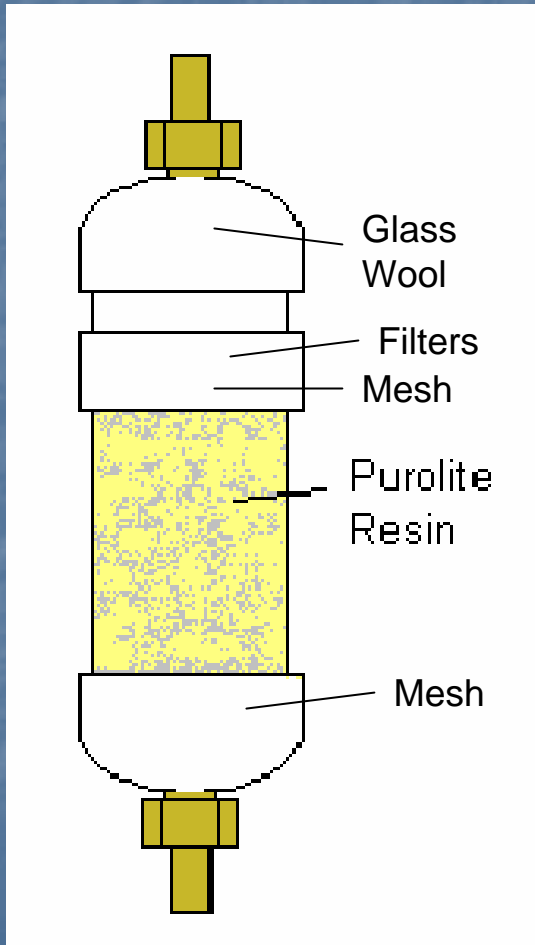
- ^{13}C measurements:
 - Enriched in ^{13}C with more negative values, especially at T1 site
 - Suggests burning of C4 plants and other types of biomass
- ^{14}C measurements:
 - Enriched in ^{14}C
 - T0: 50-60% recent carbon
 - T1: 70-80% recent carbon
- Preliminary conclusions: Biomass is a dominant source of regional and even city carbon aerosols

WATER

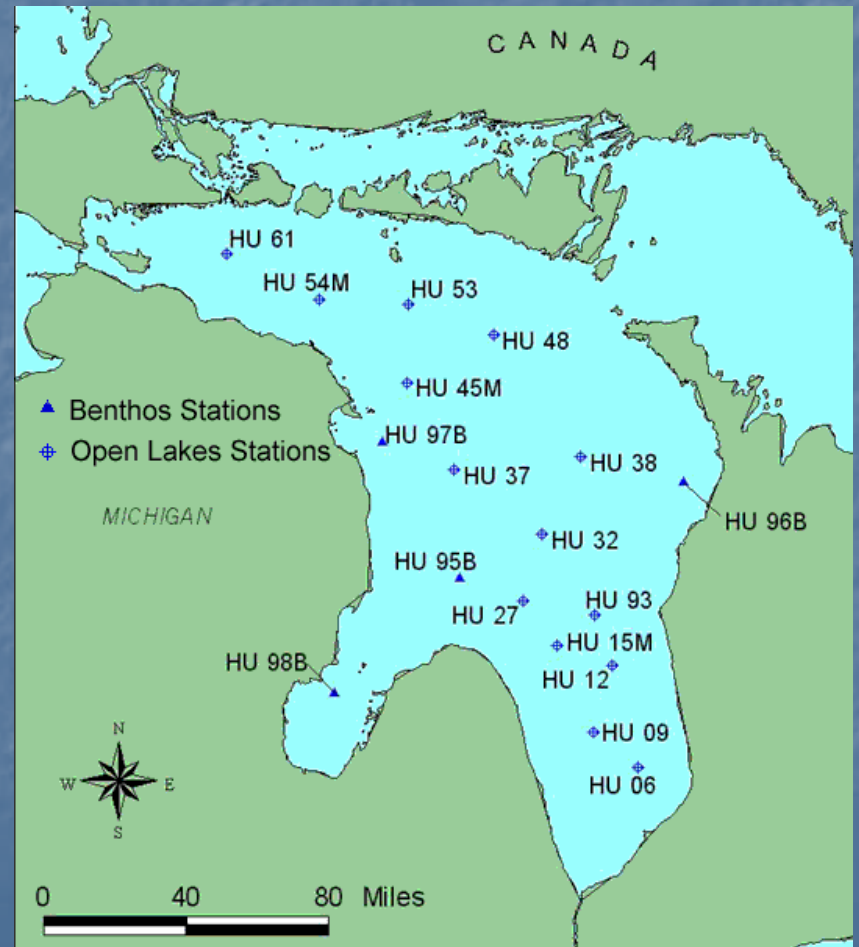
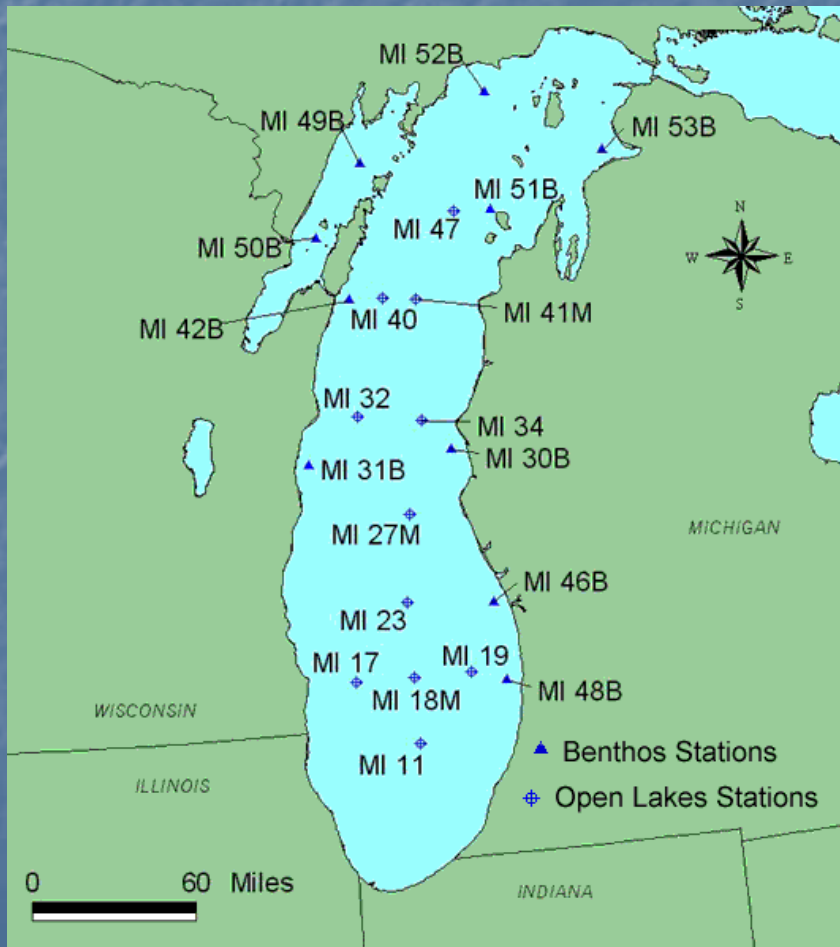
Perchlorates in the Great Lakes

- Widespread contamination of Perchlorate (ClO_4^-) in waterways
 - Natural sources: Evaporate deposits, ex. Chile.
 - Anthropogenic sources: used in rockets and missiles, fireworks, munitions, highway flares, air bags, matches.
 - Past disposal practice to burn perchlorate-containing materials and then discharge wastewater
- Conventional water treatment technologies not effective in removing perchlorate: non-volatile, common salts are highly soluble in water, chemically stable in aqueous solution.
- Suspected carcinogen
- Conducting a base-line study of presence and character in Great Lakes

Sample Collection: Purolite Resin Columns



Sample Sites



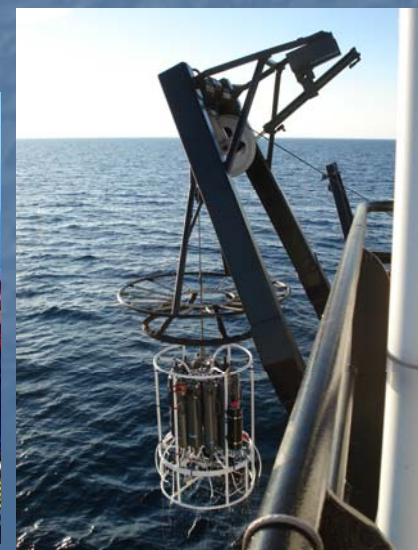


The *Lake Guardian*



The Rosette sampler collects water samples at depths corresponding to layers within the lake. These samples are then be analyzed for a variety of nutrients, chemicals, and conditions.

This multipurpose lab became our lab-away-from-lab. We ran over 30,000 L of lakewater through these tanks and our two columns to trap just a couple milligrams of perchlorate.



Analysis

- Concentration
- Isotopic:
 - Release and purify perchlorate, then conduct further reactions to combust oxygen from chlorine.
 - Analyze by mass spectrometer:
 - $^{18}\text{O}/^{16}\text{O}$
 - $^{37}\text{Cl}/^{35}\text{Cl}$ – as methyl chloride (CH_3Cl).

Acknowledgements

- GCEP: Dr. Jeff Gaffney, Dr. Milton Constantin, Dr. Nancy Marley
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Lab Improvements

