Trace Gas Concentration and Micrometeorological Flux Measurement

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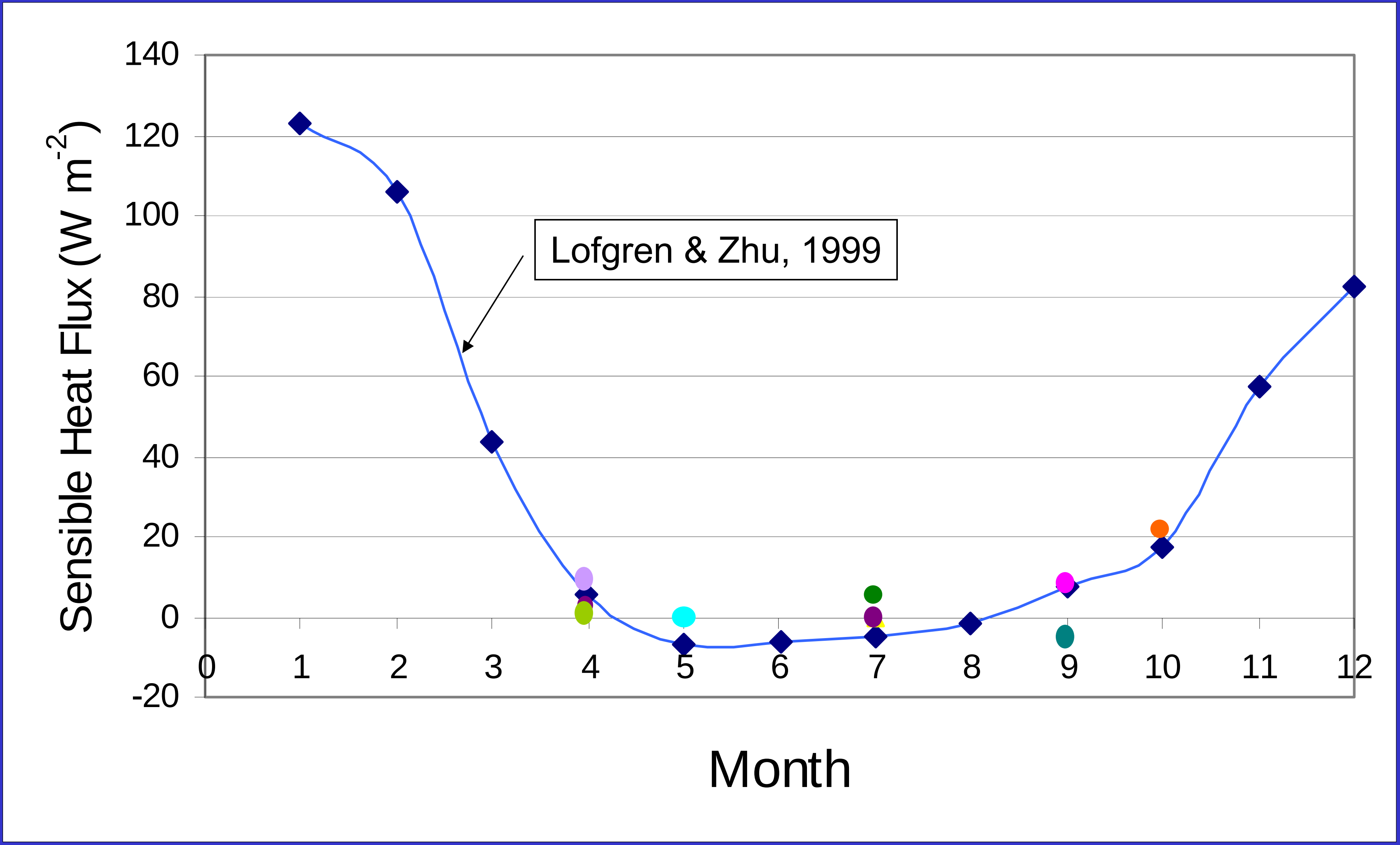
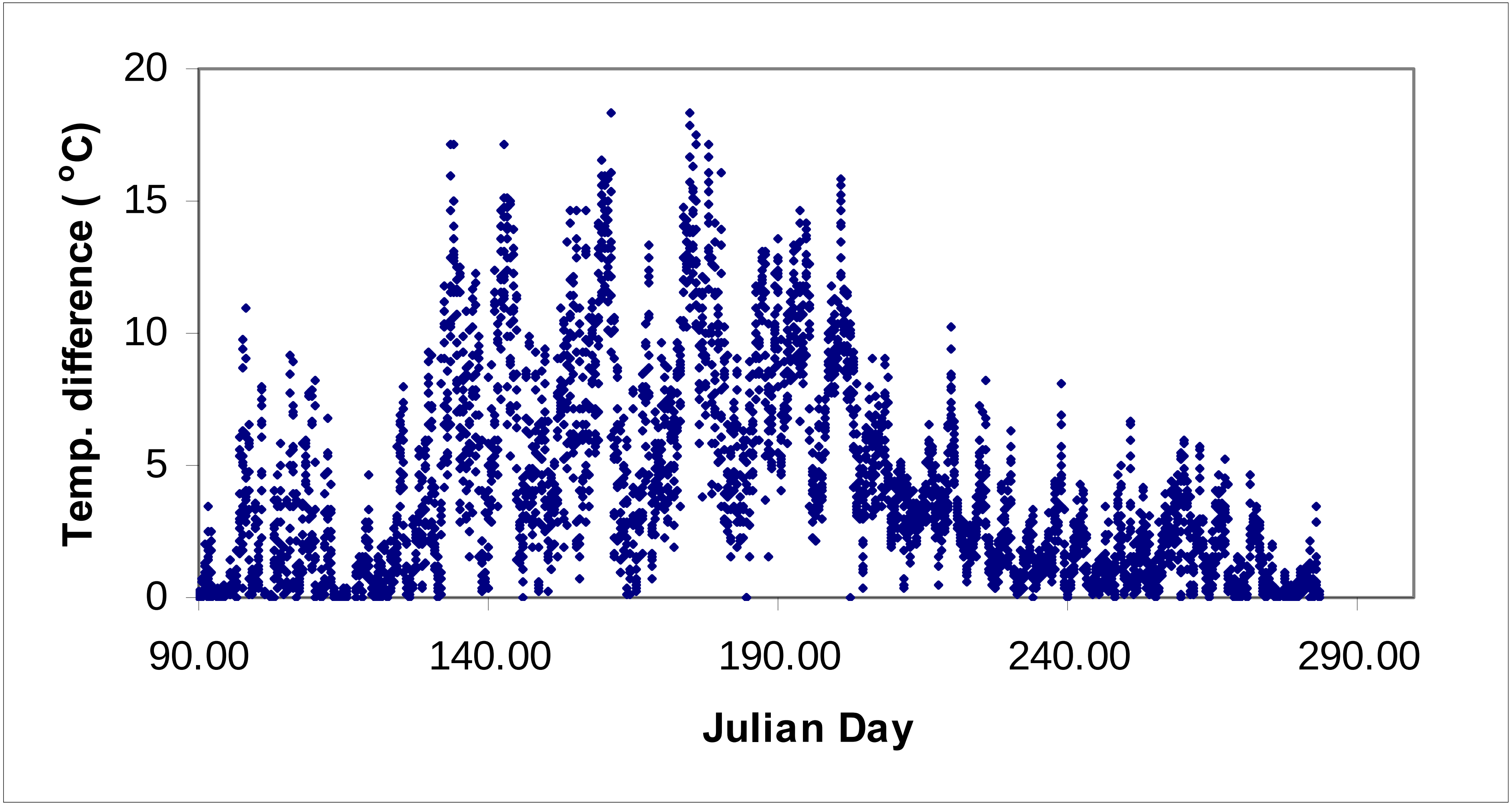
Present Need for Trace Gas Flux Measurement in the Great Lakes Region

- Water (and heat) budget closure, e.g., for hydrodynamic modeling
- Measurement of GLWQA-mandated anthropogenic trace gas fluxes/loadings (e.g., organics and Hg)
- Study of the process of trace gas air-water exchange in coastal ecosystems
- Quantification of the contribution of CO_2 flux to the regional terrestrial CO_2 flux and to in-lake C cycling
- Study of secondary organic aerosol formation and its influence on climate forcing

Comparison of Estimated and Measured H Values for Lake Superior



T(35 m) – T(1 m)
Lake Superior, 2001



Sources of Bias in IADN PBT Loading Estimation Method

- on-land vs. over-water atmospheric stability differences
- transfer velocity parameterizations are inaccurate
- Henry’s law constants are sensitive to temperature and temperature correction factors are unknown or uncertain
- undocumented actual variation in gaseous and aqueous concentrations

Technological Developments Enabling Trace Gas Micrometeorological Flux Measurement

- Fast-response (10 Hz or greater) sensors of heat and some trace gases (e.g., H_2O, CO_2) have been developed
- Computer processor speed and memory increases

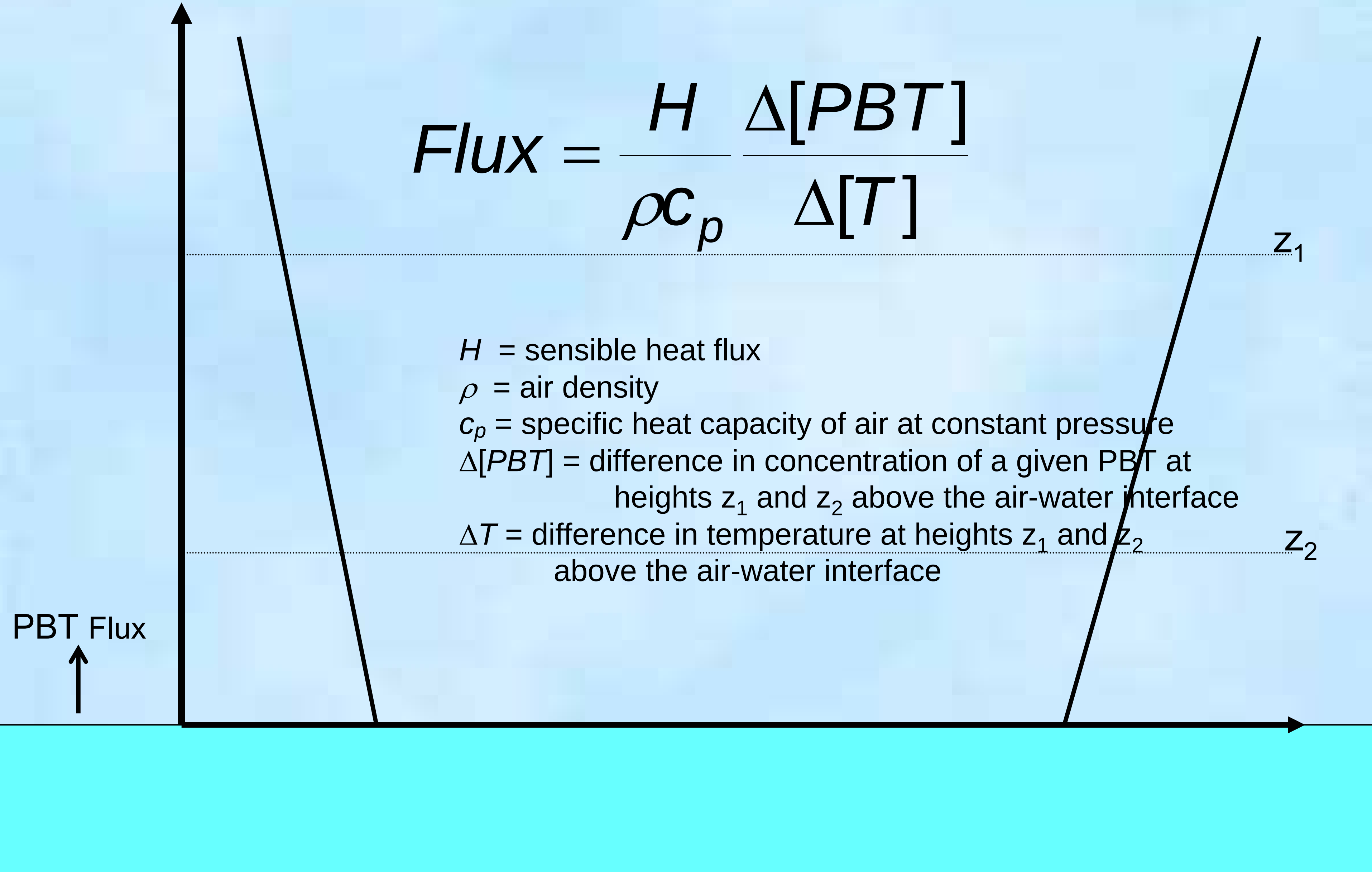
Micrometeorological Flux Measurements

- Direct Covariance – feasible if a fast sensor for the gas of interest is available
- Gradient Approaches
  - modified Bowen ratio
- Eddy Accumulation
  - relaxed eddy accumulation
  - disjunct eddy accumulation
  - hyperbolic eddy accumulation

Modified Bowen Ratio

$$Flux = \frac{H}{\rho c_p} \frac{\Delta[PBT]}{\Delta[T]}$$

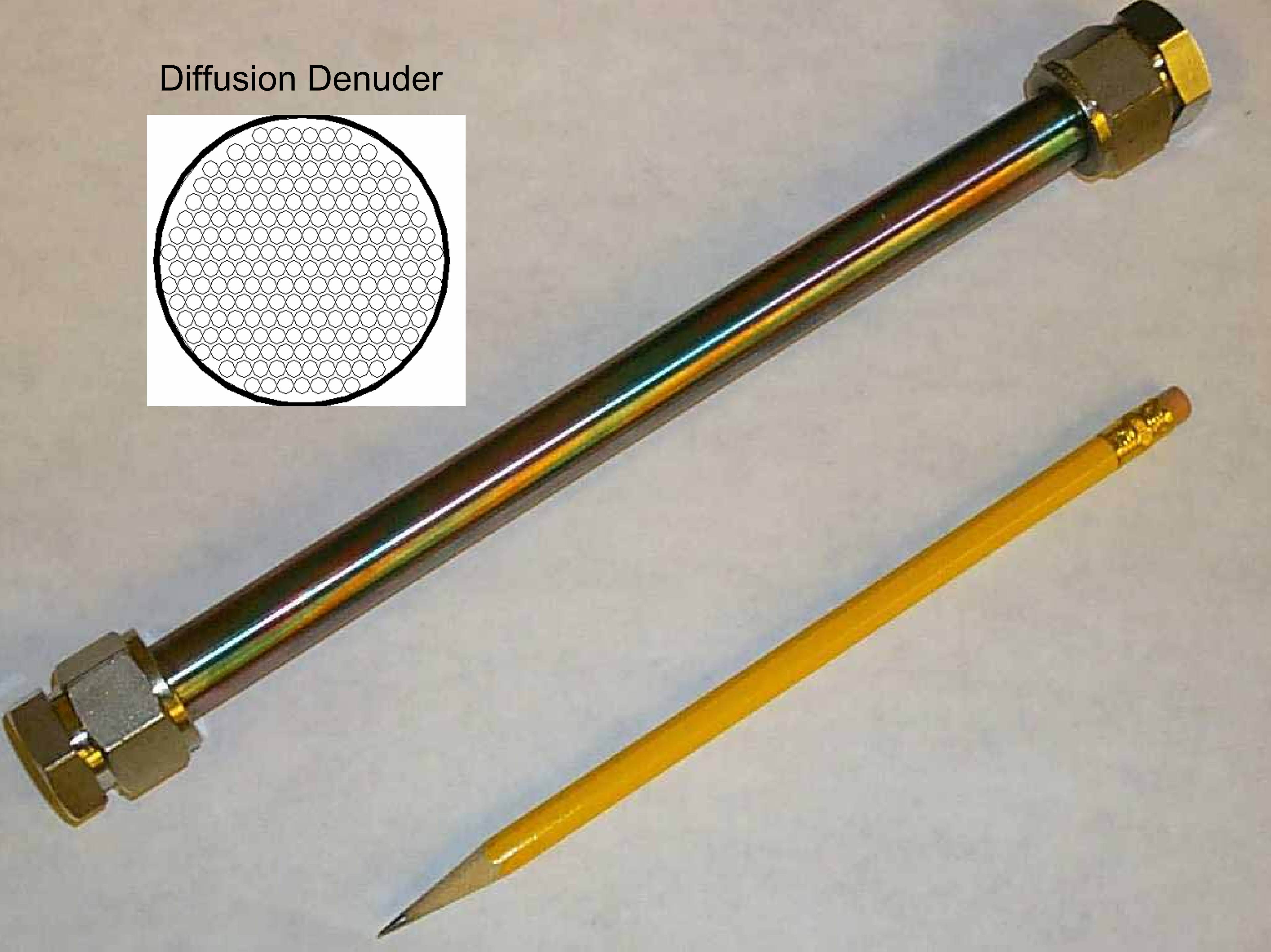
H = sensible heat flux
ρ = air density
c_p = specific heat capacity of air at constant pressure
$\Delta[PBT]$ = difference in concentration of a given PBT at heights z_1 and z_2 above the air-water interface
ΔT = difference in temperature at heights z_1 and z_2 above the air-water interface



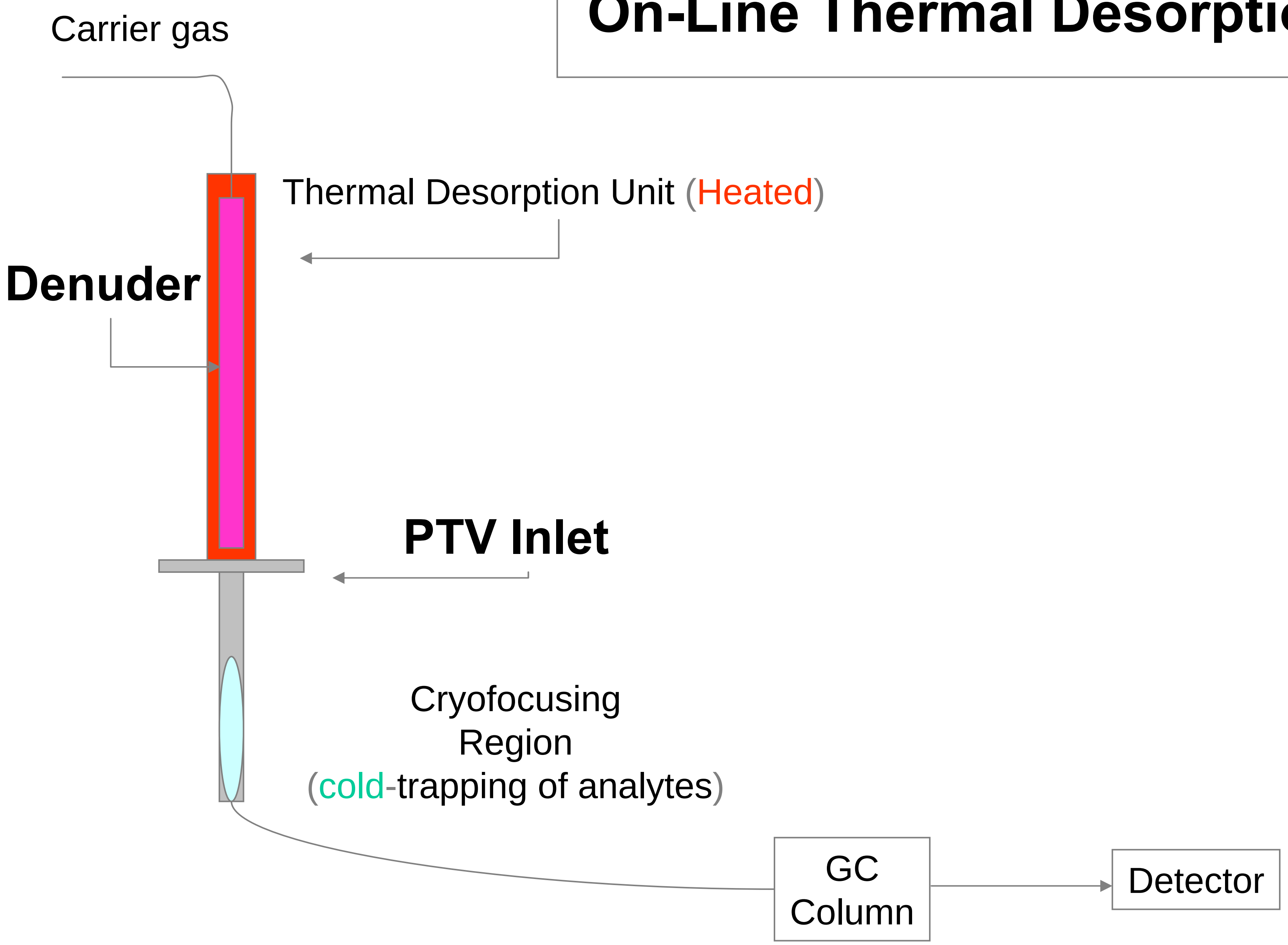

8/18/2001


R/V AGASSIZ

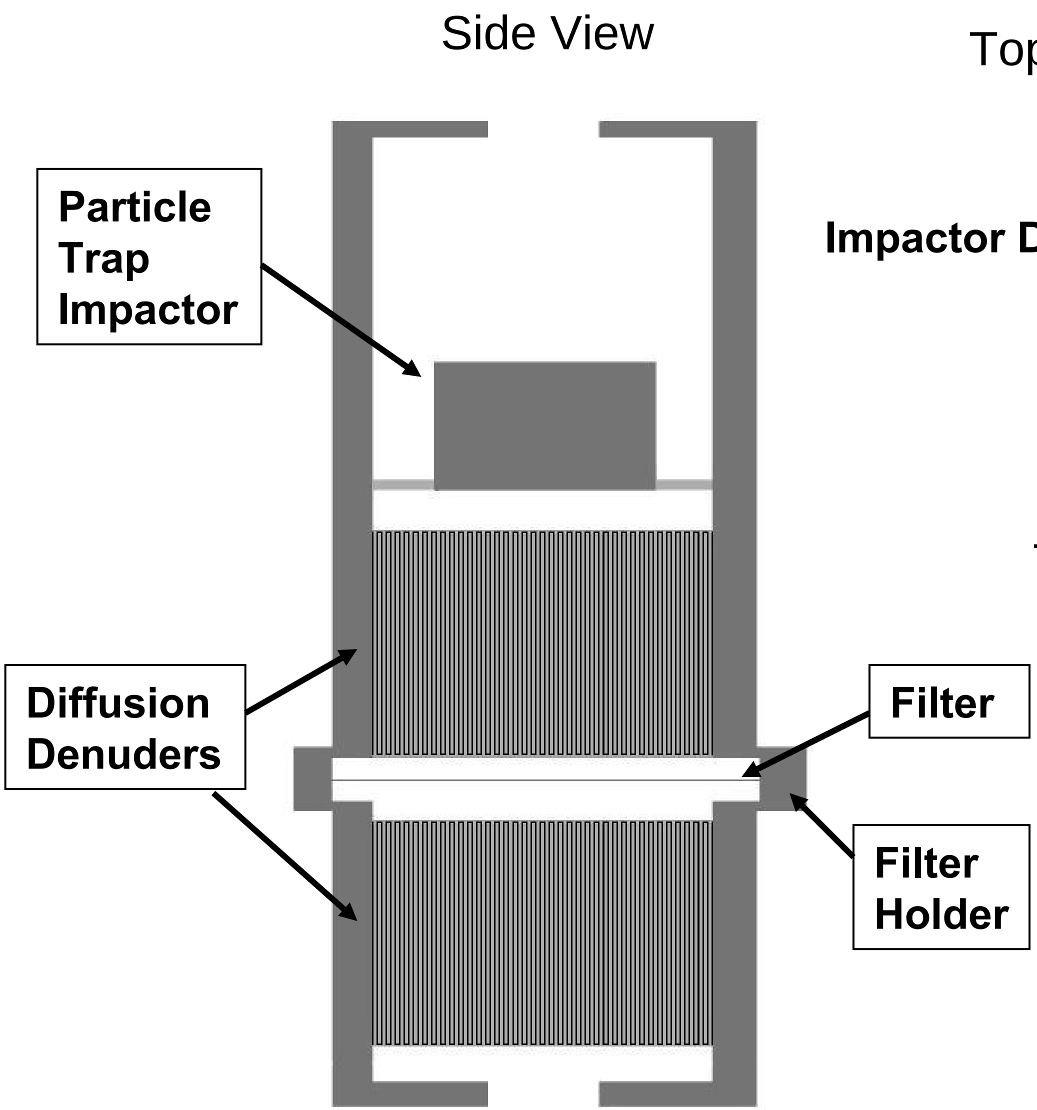
Diffusion Denuder

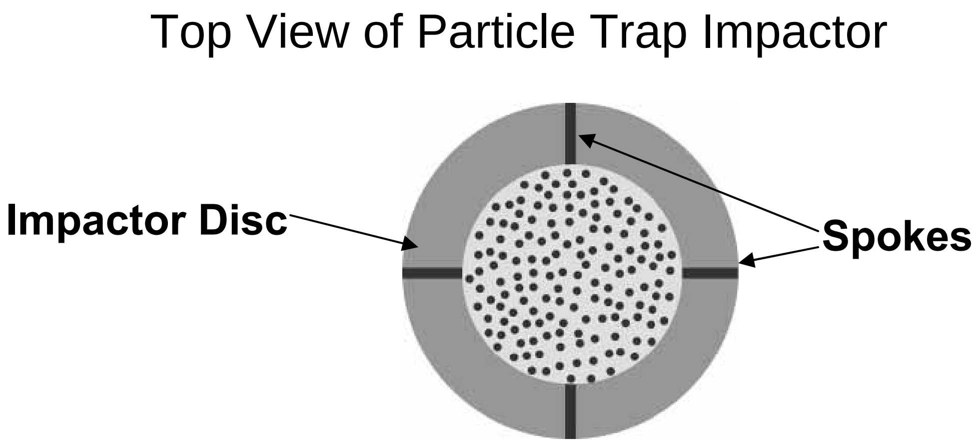


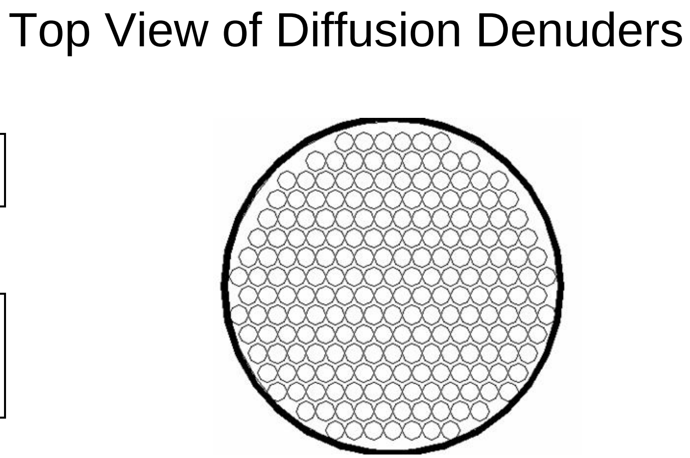
On-Line Thermal Desorption



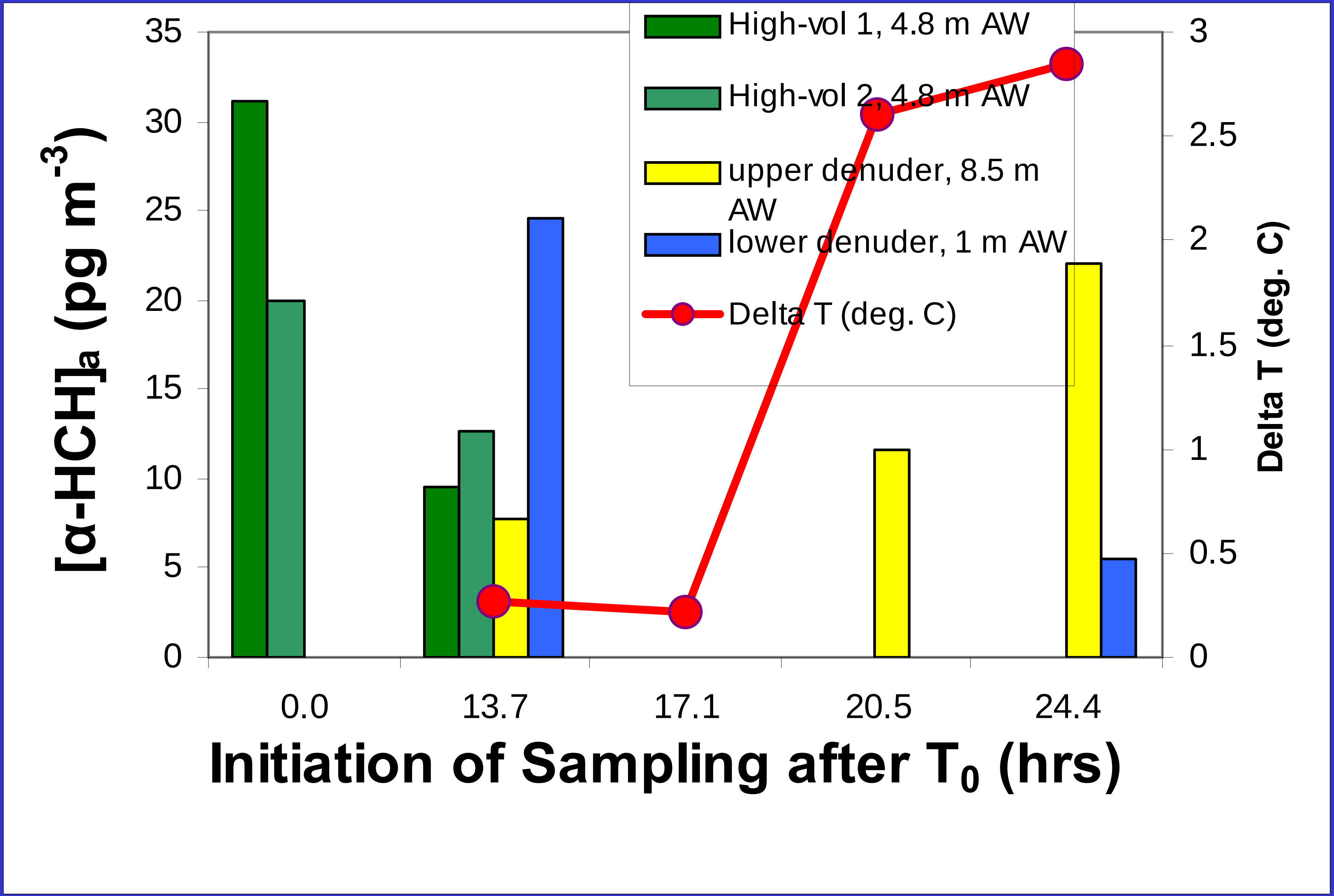
Multi-Capillary Collection Device



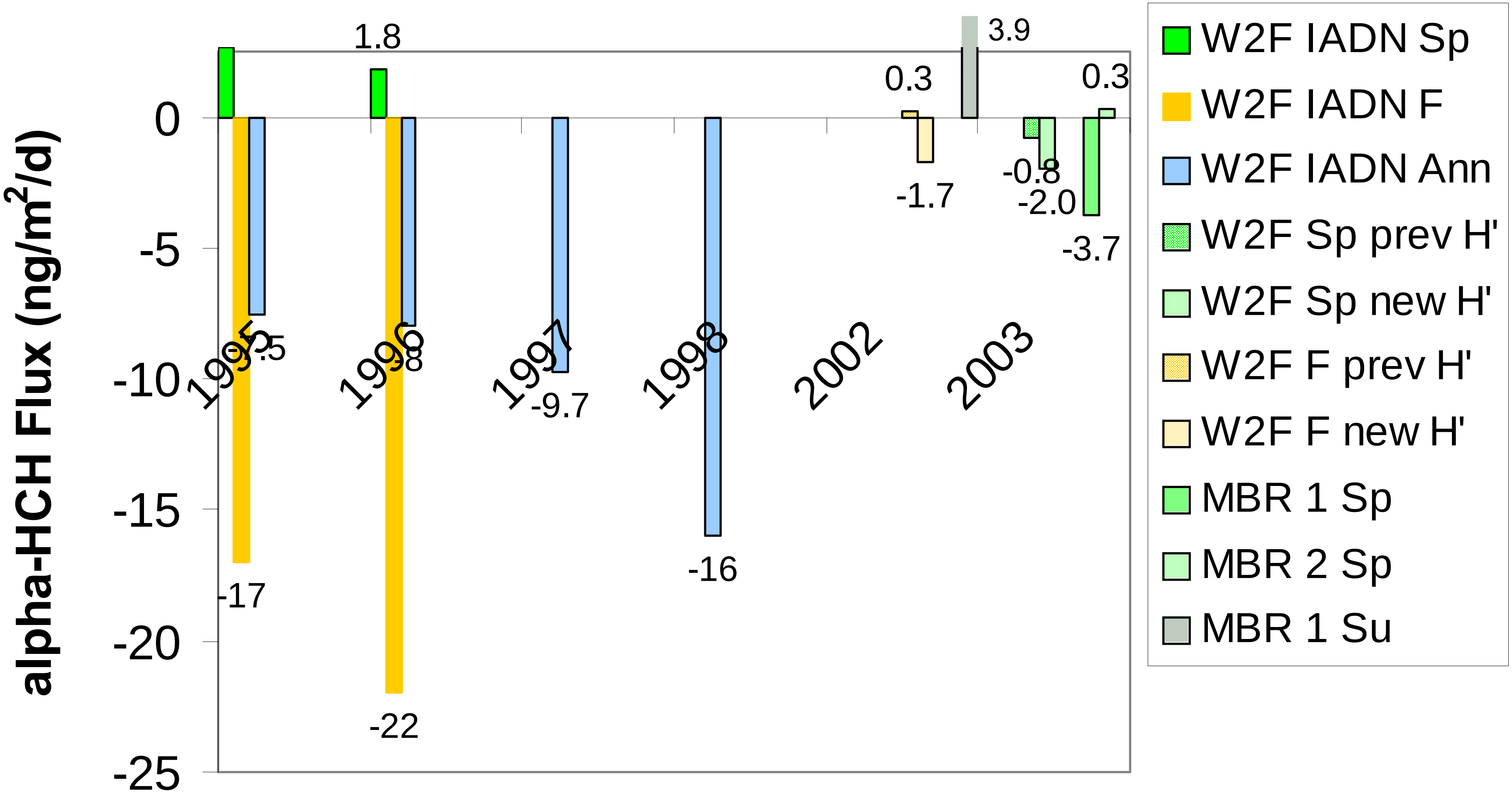




[α-HCH]$_a$, *R/V Lake Guardian* Sampling, 4/25/03 – 4/27/03



Flux of α-HCH out of Lake Superior



Flux data from 1995 to 1998 are from the IADN Project.

Advantages of PBT Concentration Measurement Method

1. Particles are collected after gaseous PBT collection.
   - Particulate and gaseous phase PBT conc's. are differentiated (impossible using passive sampling).
   - Re-partitioning of PBTs between particulate and gas phases can be minimized.

2. Significantly less sample processing is required as compared to XAD/PUF sample processing.
   - Fewer artifacts/losses can occur.
   - No XAD/PUF pre-cleaning, extraction, clean-up, or concentration is required.
   - Little solvent is required; no XAD or PUF is required.
   - Significantly less analytical time (5 vs. 20 hours) and cost (estimate 75 % savings) per sample are required.

Advantages of Micrometeorological PBT Flux Measurement Method

1. Approaches account for all resistances to mass transfer.

2. Higher spatiotemporal resolution in sampling is possible (with current method sampling time is 1 to 3 hours vs. 1 to 42 days in L. Superior).

3. Measurements provide a means to assess accuracy based on one assumption. Uncertainty (accuracy and precision; 10 to 300 %) is less than the reported imprecision of Whitman two-film flux estimates (50 to 7400%).

Possible Uses of Methods to Supplement Current IADN Project

1. measure gas/particulate phase PBT concentrations using MCCDs at IADN stations – reduce project cost
2. study air-water exchange processes in-lake – optimize sampling protocol
3. measure and/or estimate dry deposition in-lake utilizing buoys, research/passenger vessels, lighthouses, and/or towers as platforms

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