Measurement Techniques and Modeling of PBT Transport in the Lake Superior Basin

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- Collaborators: Chris Fairall, Noel Urban, Paul Doskey
- Captains and crews of the R/V Lake Guardian and R/V Agassiz

Outline

- Background
- Atmospheric concentration measurement
- Air-water exchange flux measurement
- Internal boundary layer transport-exchange (IBLTE) model
- Case study
- Summary and Conclusions

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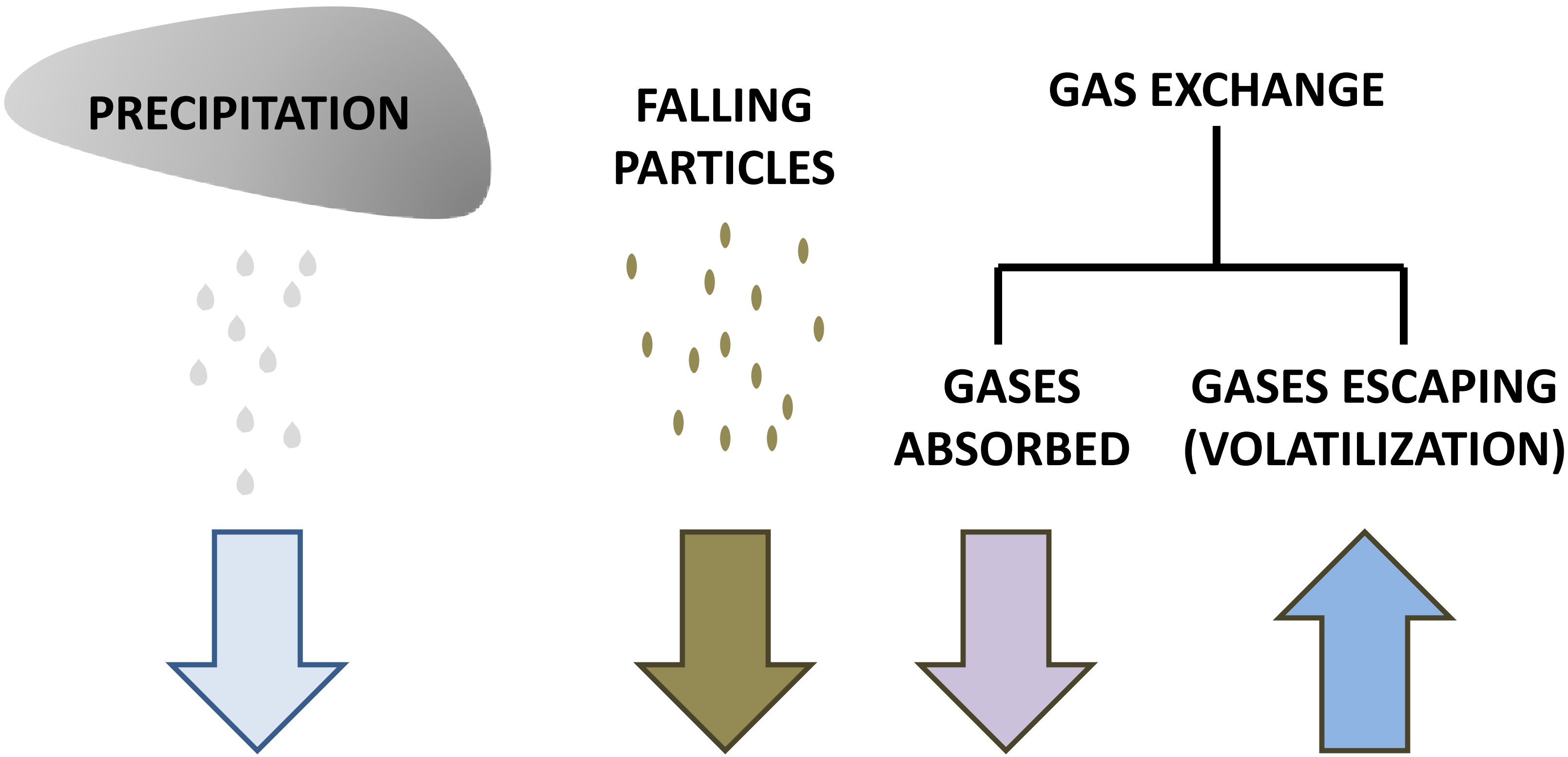
Houghton, Michigan
CANADA
Lake Superior
Duluth
216 miles
Minneapolis
352 miles
Green Bay
215 miles
Lake Michigan
Traverse City
400 miles
Lake Huron
Grand Rapids
514 miles
Detroit
550 miles
Lake Erie
Des Moines
597 miles
Chicago
421 miles
Cleveland
722 miles
Indianapolis
606 miles

Atmospheric Deposition of PBTs to Lakes

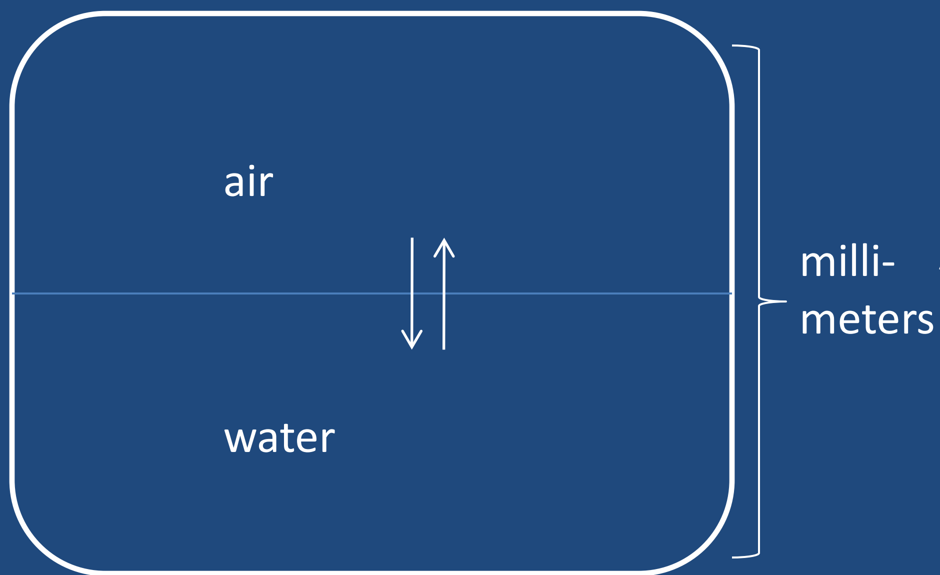


TOTAL AMOUNT THAT ENTERS LAKE TIME^{-1} = RAIN/SNOW LOADING + PARTICLE LOADING + ABSORPTION LOADING + VOLATILIZATION LOADING

Loading = Flux ·Surface Area

$(M\cdot T^{-1}) = (M \cdot L^{-2} \cdot T^{-1}) \cdot (L^{2})$

Two-film Model Parameterization of Gas Transfer (Whitman, 1923)



$$\text{Flux} = k_{ol}(C_\text{a}(K_\text{aw})^{-1} - C_\text{w})$$

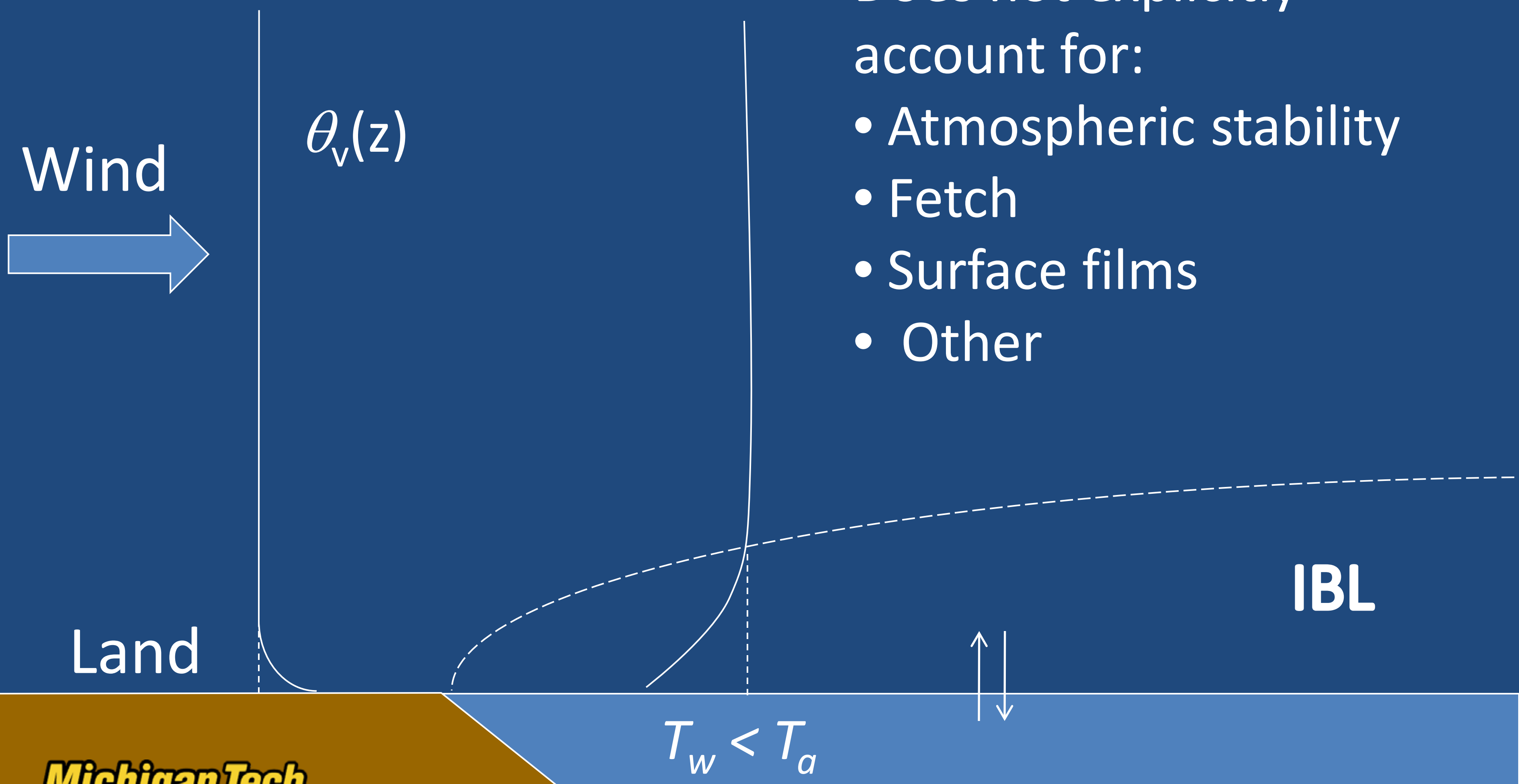
$$k_{ol} = \left[\frac{1}{k_w} + \frac{1}{K_{aw}k_a}\right]^{-1}$$

$$k_\text{a}, k_\text{w} = f(D_\text{i}, U_\text{ref})$$

Potential Shortcomings of Two-film Model

Does not explicitly account for:

- Atmospheric stability
- Fetch
- Surface films
- Other



Fetch: the length of water over which a given wind has blown

Atmospheric Boundary Layer

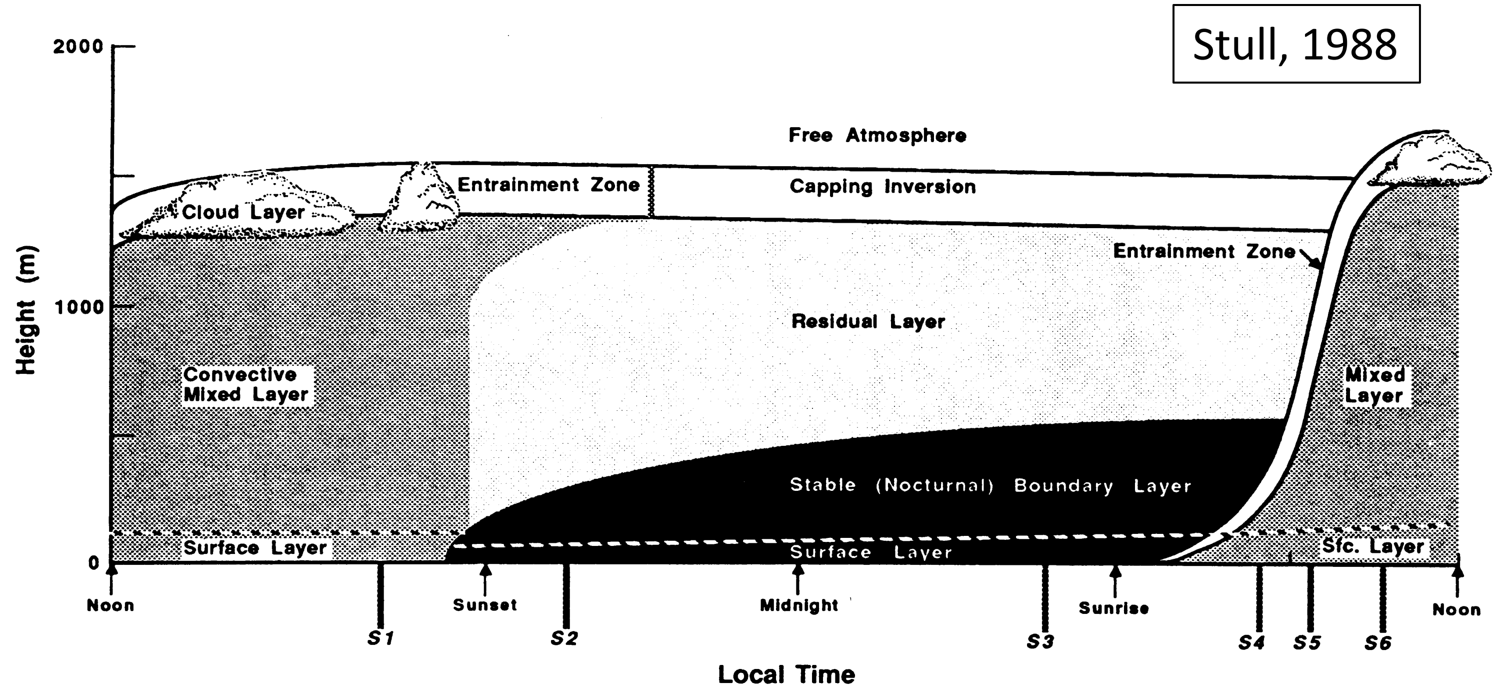


Fig. 1.7 The boundary layer in high pressure regions over land consists of three major parts: a very turbulent mixed layer; a less-turbulent residual layer containing former mixed-layer air; and a nocturnal stable boundary layer of sporadic turbulence. The mixed layer can be subdivided into a cloud layer and a subcloud layer. Time markers indicated by S1-S6 will be used in Fig. 1.12.

Micrometeorology ≡ the study of turbulence on spatial scales less than 3 km and with time scales shorter than ~ 1 hour.

Overall Project Objectives

- Develop and utilize micrometeorological methods to measure atmospheric concentration and air-water exchange flux of PBTs
- Develop and utilize a model for air-water exchange that accounts for effects of atmospheric stability and fetch

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Atmospheric PBT Sampling Technologies

- High-volume (active)
- Passive
- Multicapillary collection device (active)

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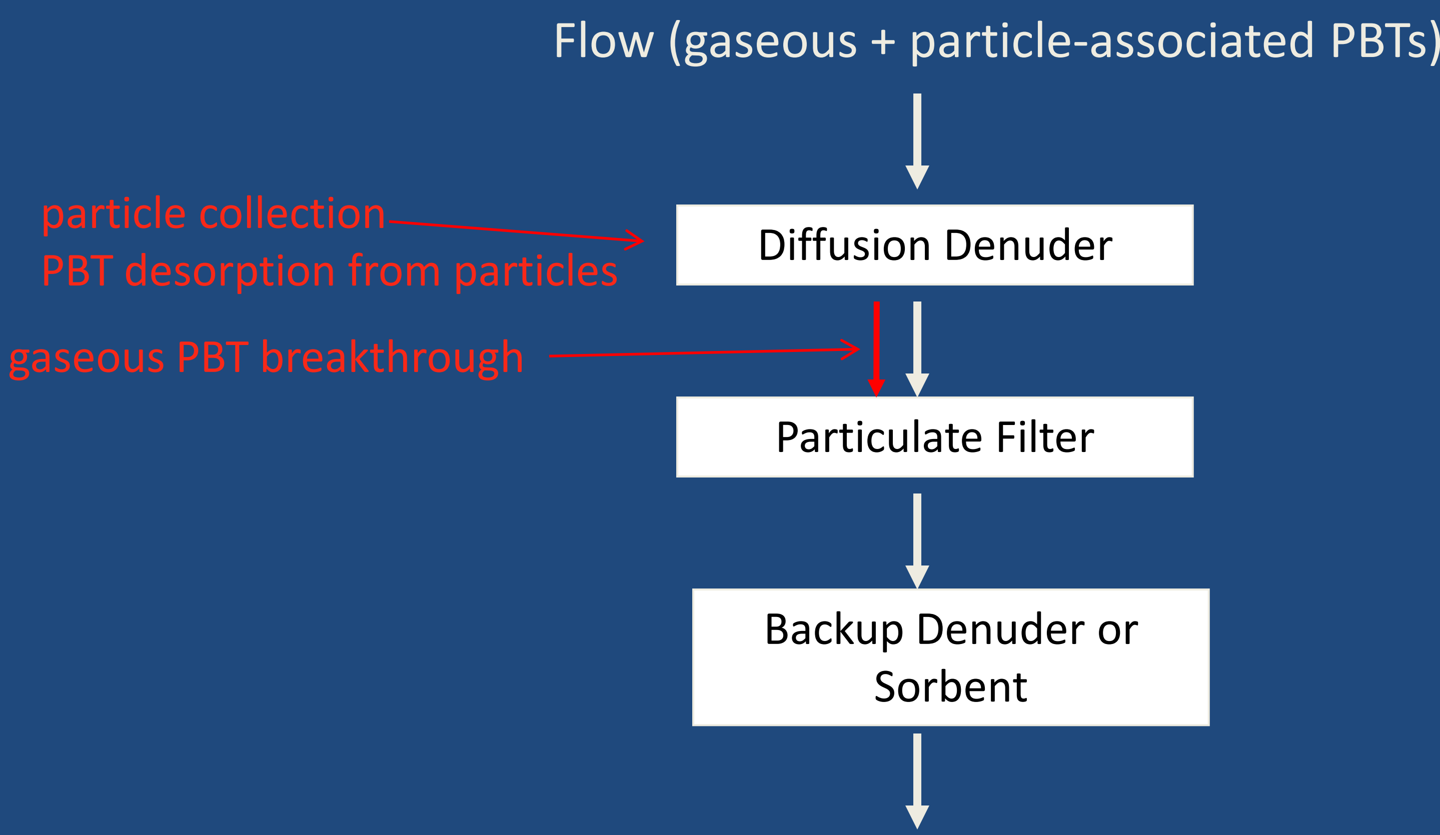
MCCD PBT Collection

and Potential Artifacts



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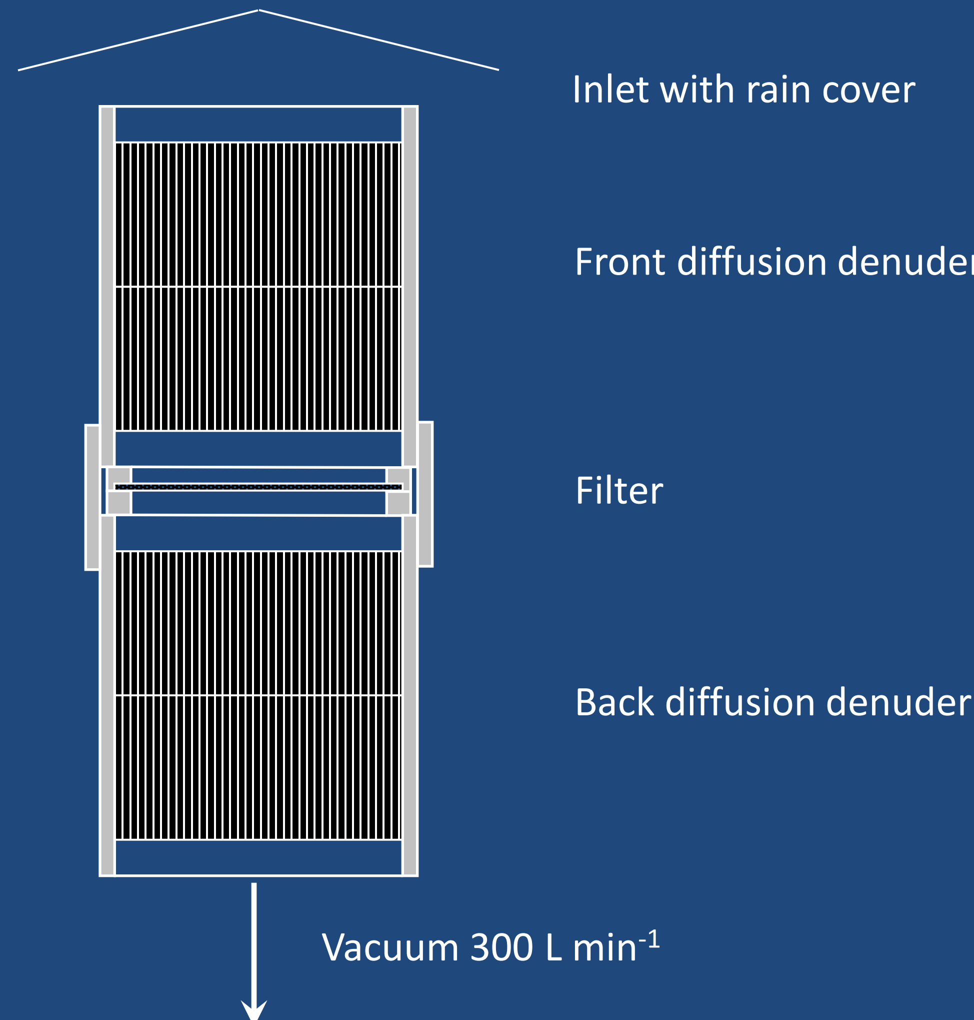
Low-flow Multicapillary Diffusion Denuder Sampling/Analysis

- 90 min. sample, 1.3 – 1.7 m^3
- Clean up of sample by thermal elution through silica gel
- Thermally desorb cleaned up sample into the GC
- GC-ECD analysis
  - HCB, octachlorostyrene
  - PBDE 47, 99
  - 144 PCB congeners

25 cm

Tobias, DE, Morrow, PS, Doskey, PV, Perram, DL, and Perlinger, JA, 2007, J. Chromatogr. A, 1140, 1-12
Rowe, MD, and Perlinger, JA, 2009, J. Chromatogr. A., 1216, 5940-5948

High-flow Multicapillary Collection Device Cross-section



High-flow Multicapillary Collection Device (**300 L min^{-1}**)

Rowe and Perlinger, 2010, Environ. Sci. Technol., 44, 2098-2104

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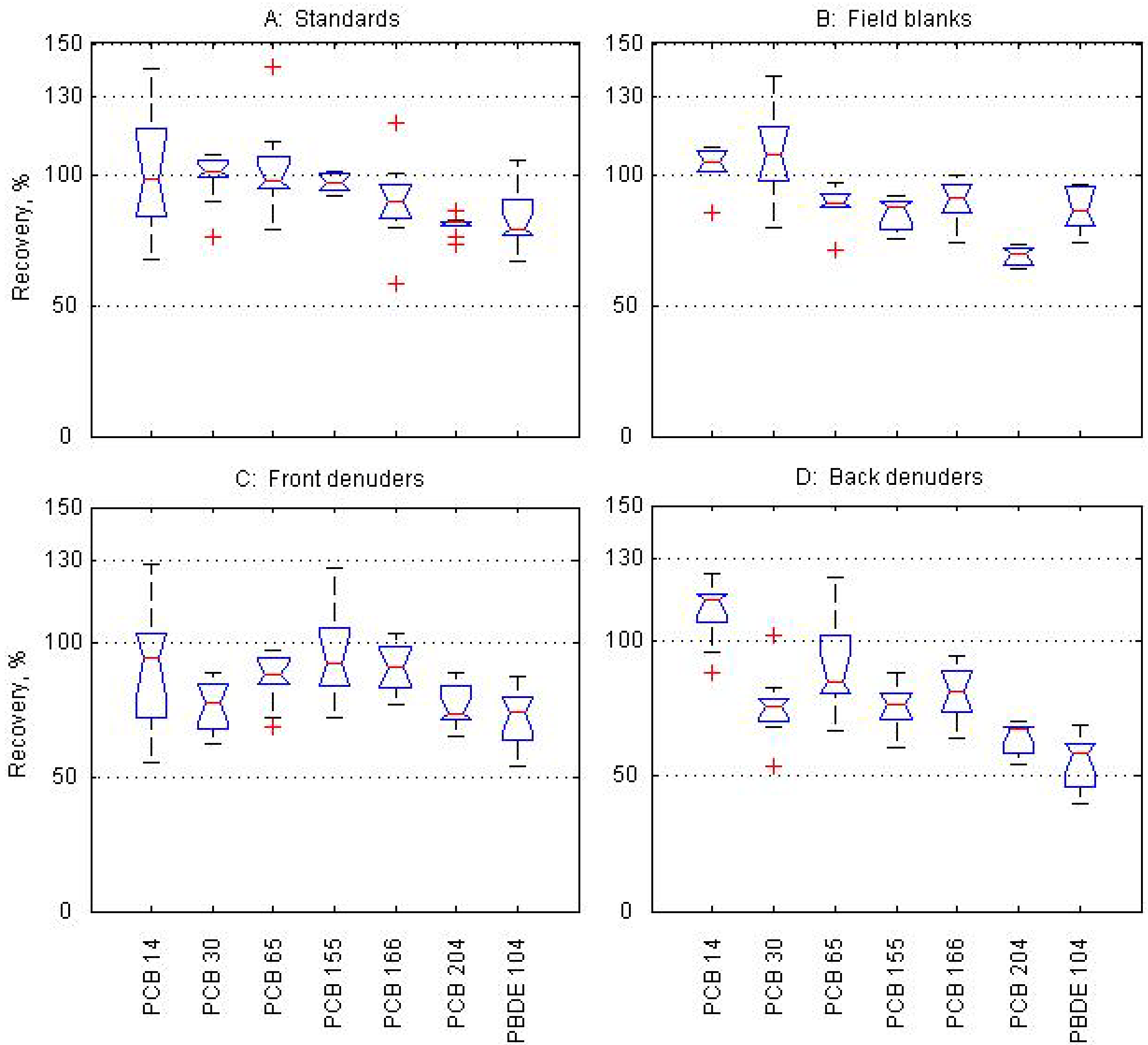
Recovery of Spiked Standards



Comparison of High-flow to Hi-vol Sampling

	Units	High flow - high volume	High flow - high flow	High volume - high volume
No. of paired samples	--	5	3	17
No. of paired measurements	--	70	67	532
Median concentration	pg m^{-3}	1.6	0.7	0.5
Median difference	pg m^{-3}	-0.39	0.02	0.00
Relative difference	%	-25.1	3.5	-0.7
Sign test [a]	*P* value	< 0.001	0.050	0.208
MMAD	pg m^{-3}	1.5	0.1	0.1
CoV	%	97.0	16.4	21.0

Rowe and Perlinger, 2010, Environ. Sci. Technol., 44, 2098-2104

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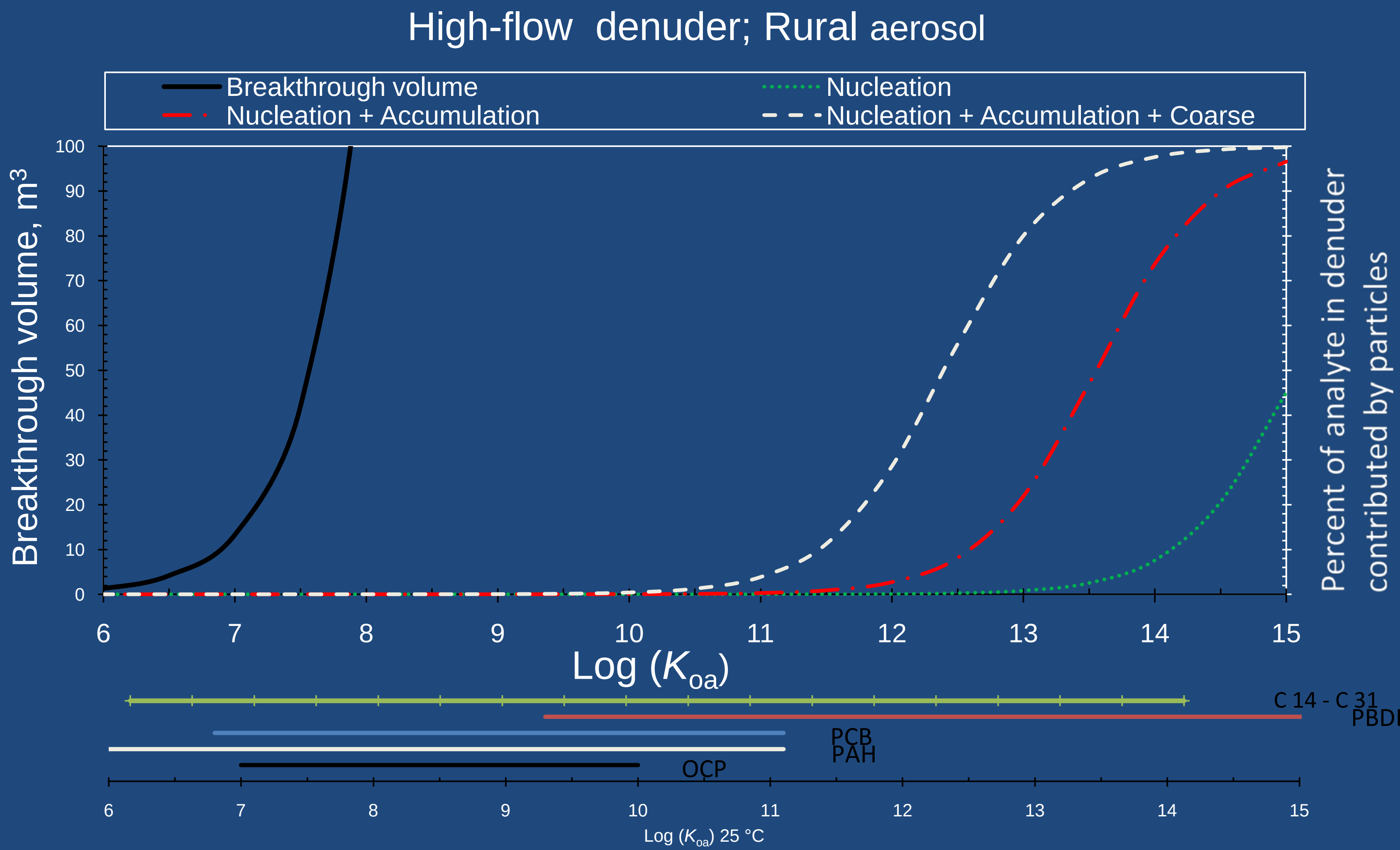
Predicted Gaseous PBT Breakthrough Volume and Particulate PBT Retention



Rowe, MD, and Perlinger, JA, 2010, J. Chromatogr. A, 1217, 256-263;
Collection Efficiency Model for Mass Determination (CEMOMD) Visual Basic Program

Advantages of MCCD Sampling

- Low headloss ⟶ lower pump power requirements, quieter
- Samplers are reusable
- Low-flow sampler is light-weight
- Separation of gaseous and particle-associated PBTs achieved
- Short sampling times can be achieved, dependent on target analyte, concentration, and temperature (minutes – hours *vs*. days (hi-vol) – weeks/months (passive))
- Re-partitioning between gaseous and particle-associated phases in the sampler during (and after) sample collection can be avoided
- Solvent extraction can be avoided

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Advantages of Thermal Extraction

- Solventless ⟶ environmentally-friendly
- Complete or fractional analyte transfer into analytic instrument can be used
- No PUF/XAD solvent pre-cleaning, extraction, cleanup, or concentration required
- As compared to Soxhlet extraction, significantly less time and expense involved in sample preparation for GC analysis
  - 5 *vs*. 20 person-hours
  - ca. $5 vs. $500 consumables per sample
- Less sample handling required
  - Fewer losses/artifacts

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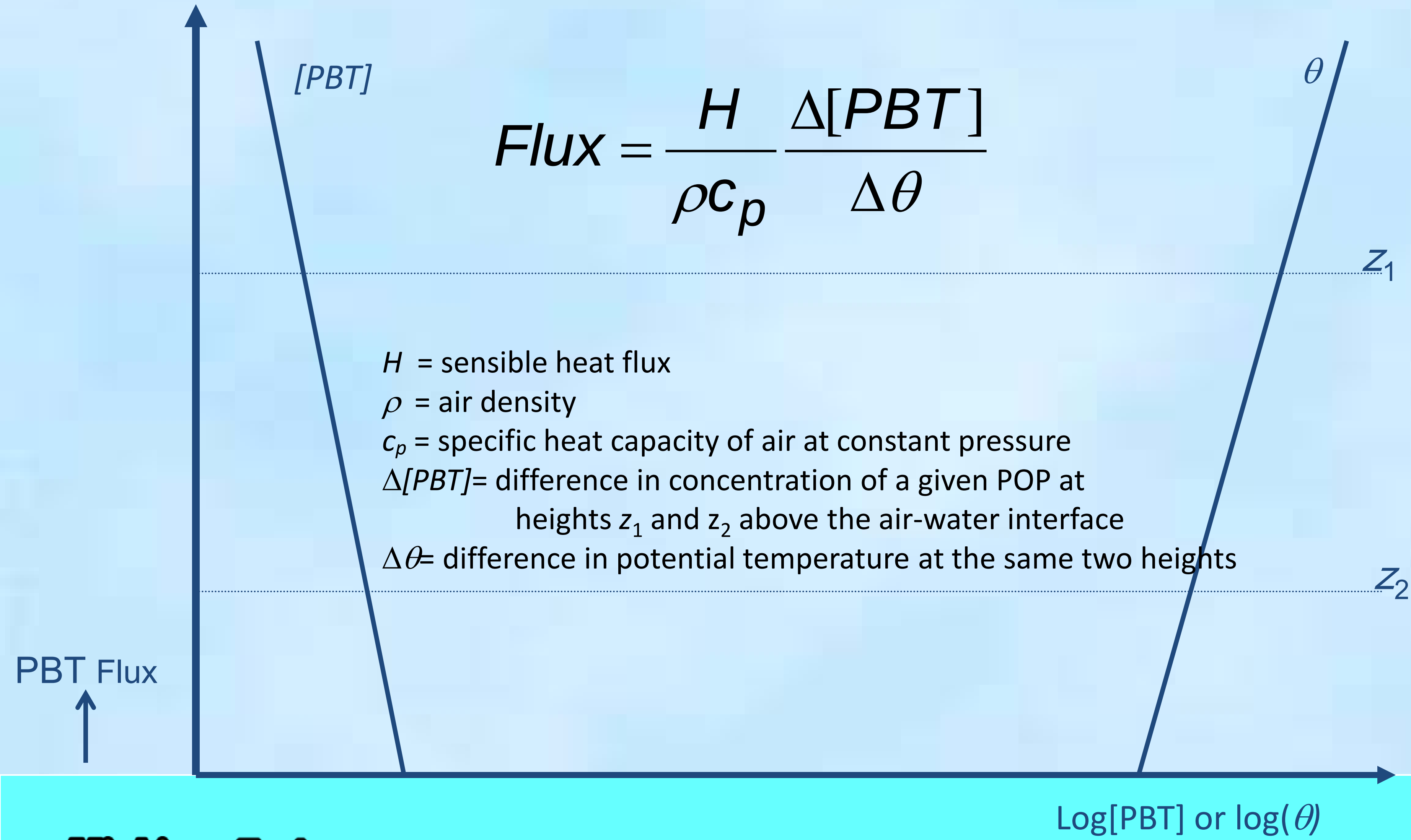
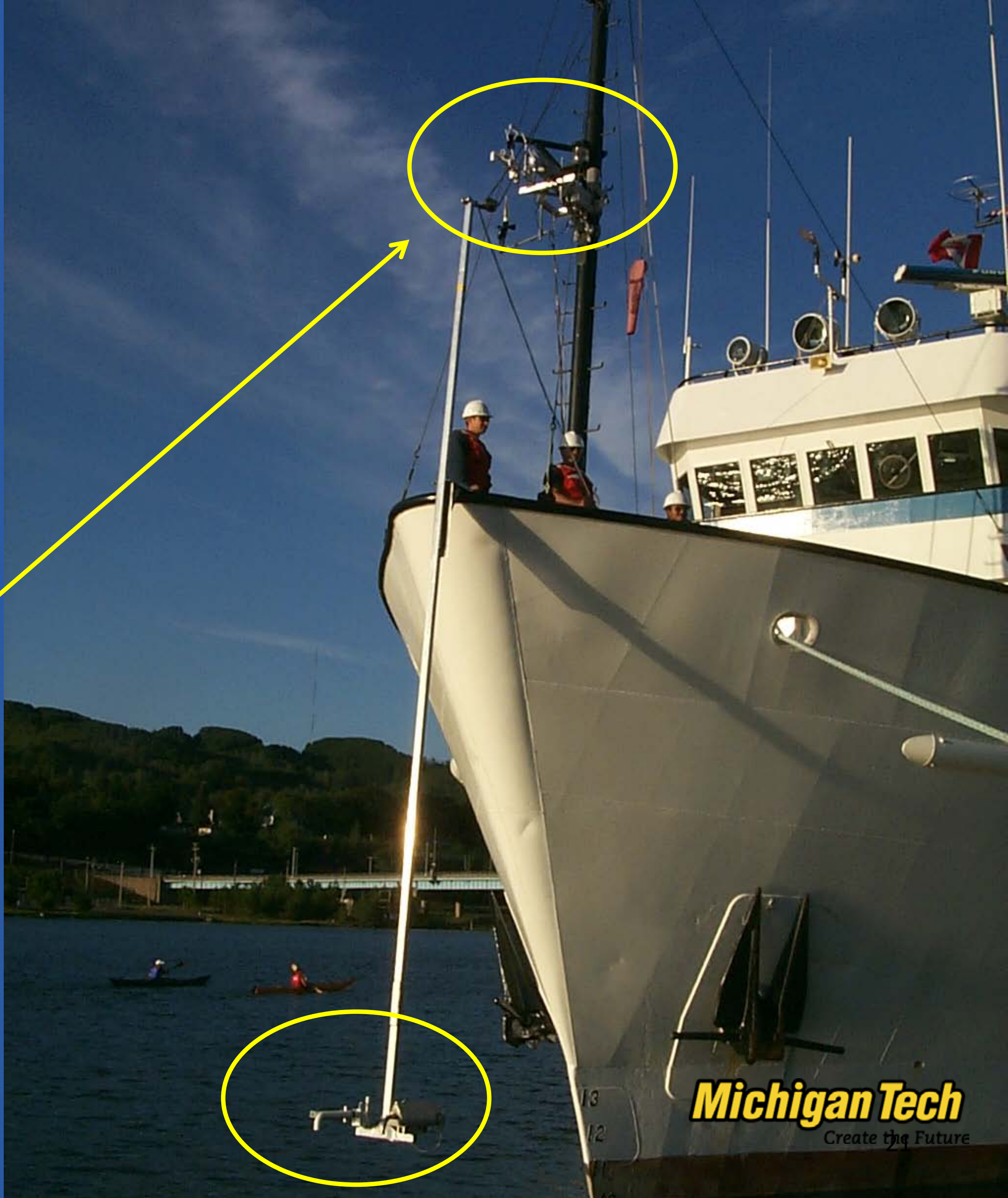
Modified Bowen Ratio



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

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

Modified Bowen ratio flux-gradient sampling platforms on the U.S. EPA *R/V Lake Guardian*



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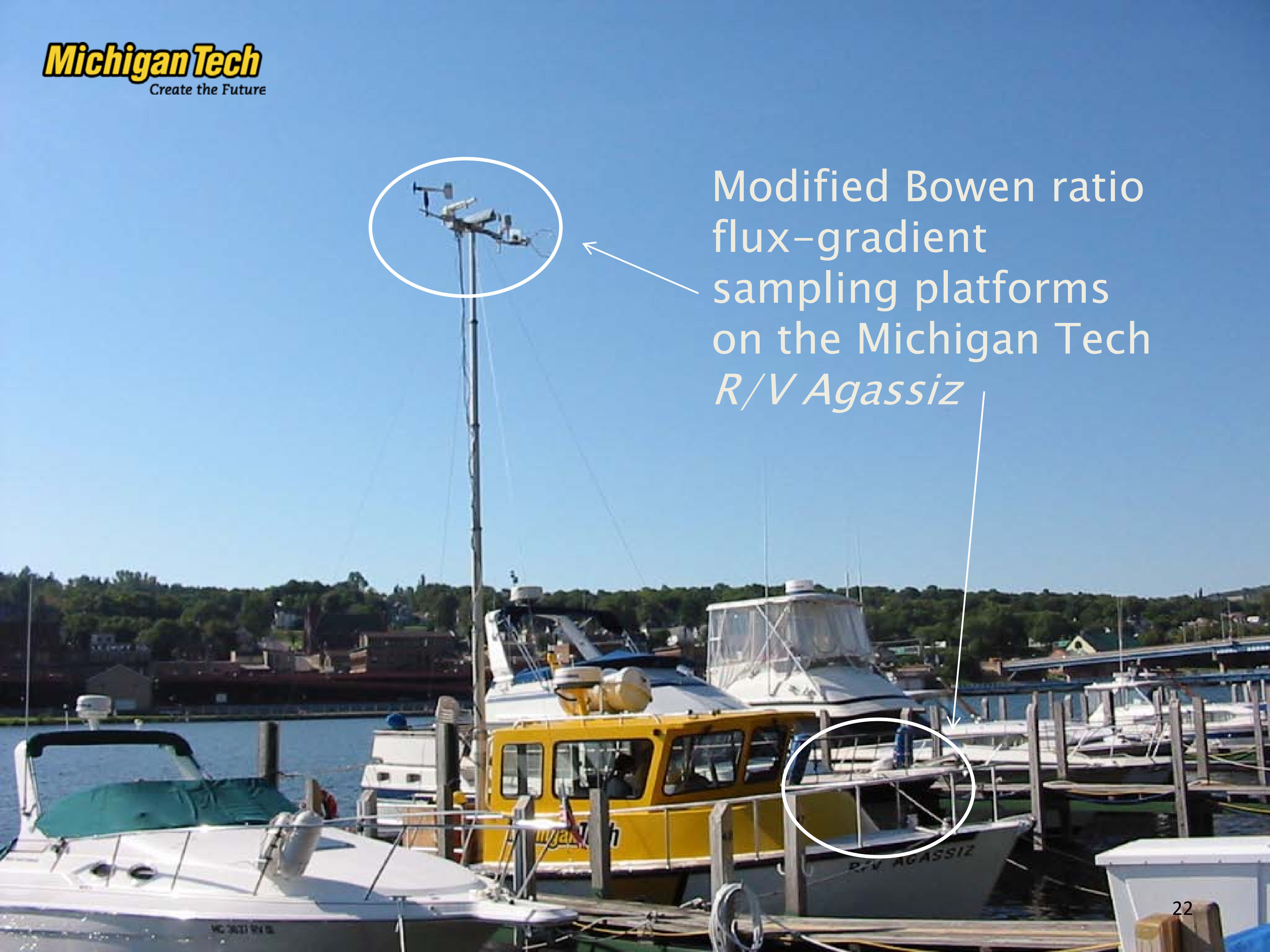
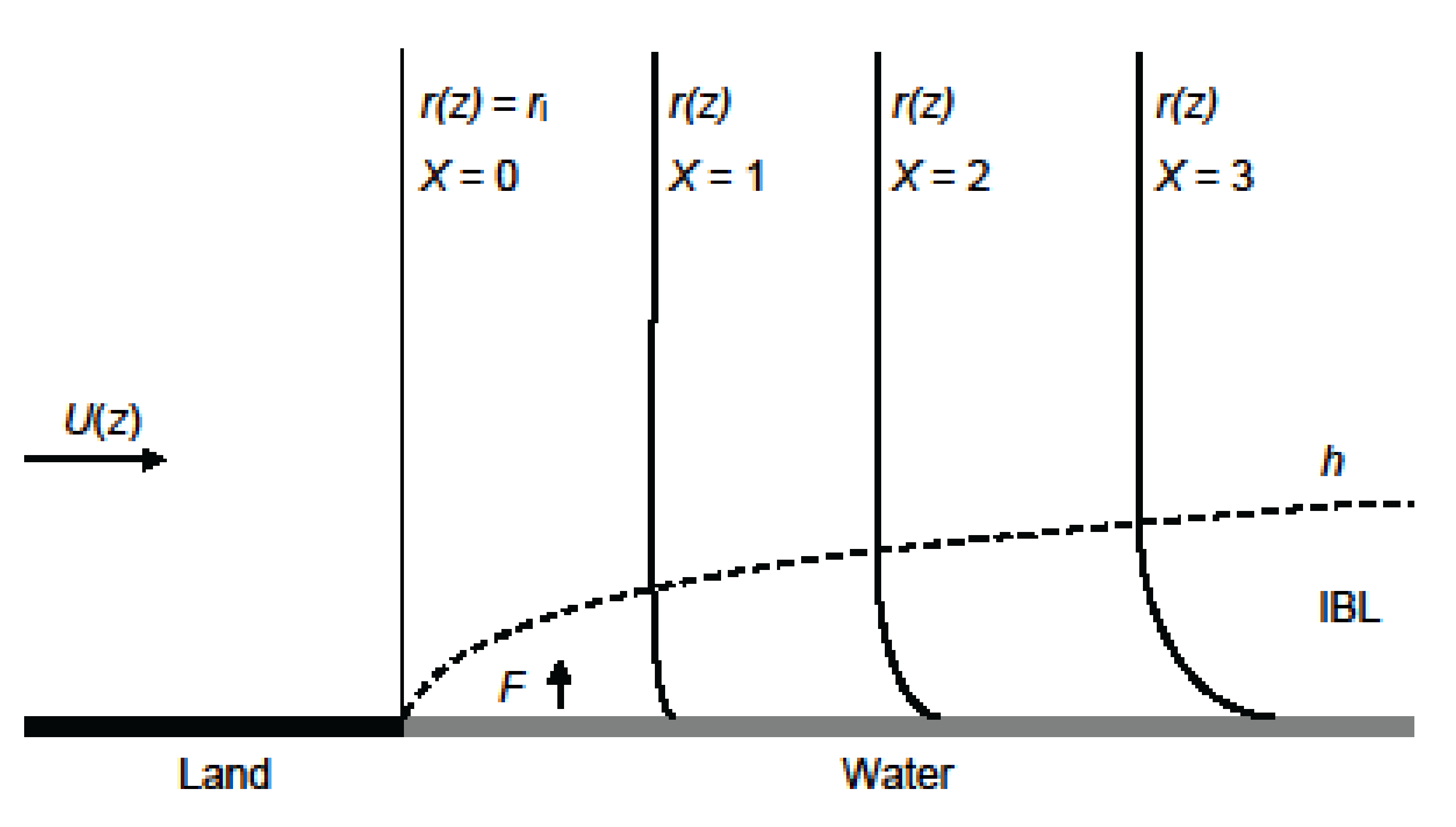


Modified Bowen ratio flux-gradient sampling platforms on the Michigan Tech *R/V Agassiz*

Concentration Profile, *r*(*z*), Modification with Fetch, *X*



Rowe, MD, Perlinger, JA, and Fairall, CW, Boundary-Layer Meteorol., *in review*

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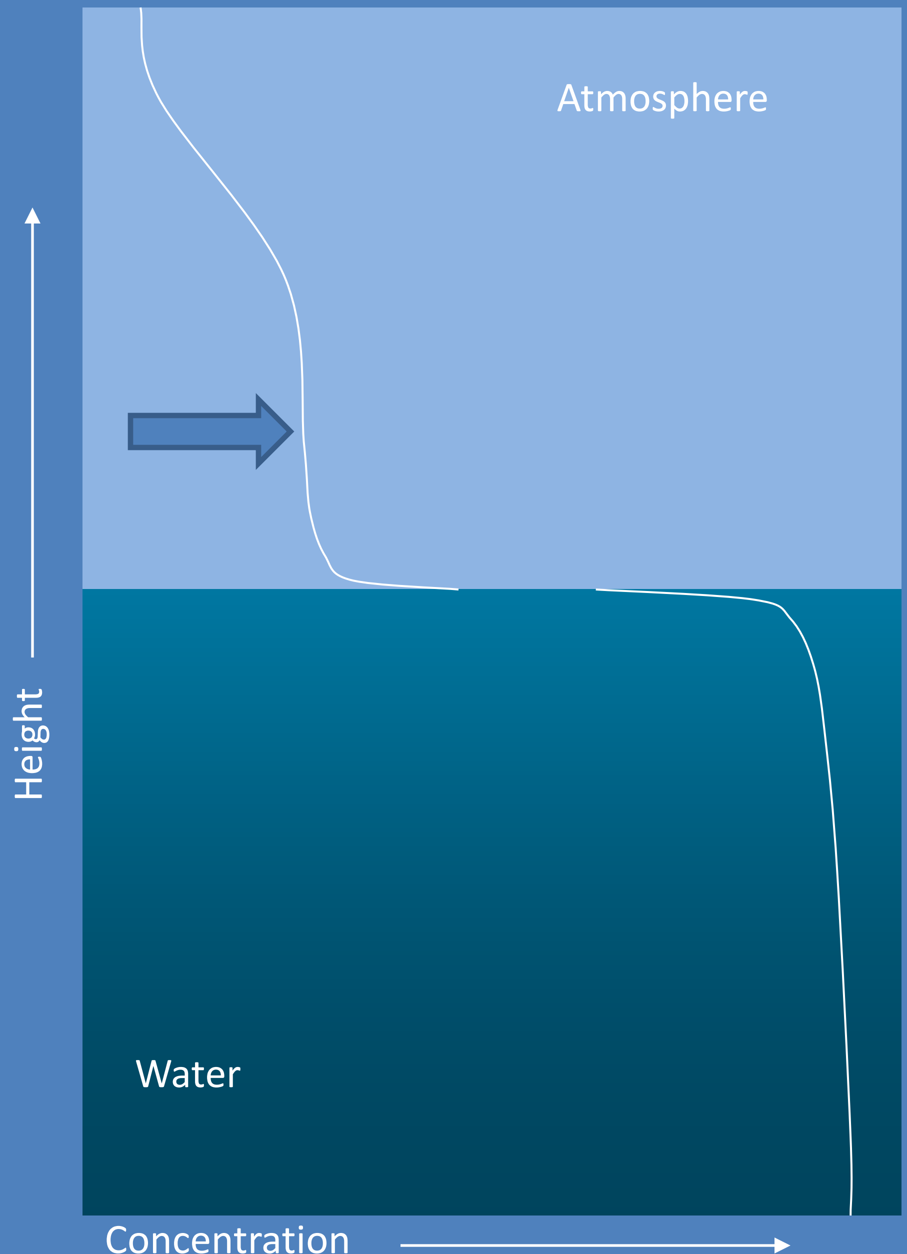
Gas Transfer Models



Internal Boundary Layer Transport-Exchange Model

NOAA COARE Model

Bulk flux algorithm

gas transfer model

Two-film Model

$$\text{Flux} = k(C_a(K_{a/w})^{-1} - C_w)$$

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NOAA COARE Gas Transfer Model

Air-side transfer coefficient

$$k_a = \frac{u_*}{[13.3S_{ca}^{1/2} + \kappa^{-1}[\ln(z/z_o) - \psi_t(z/L)] - 5 + \ln(S_{ca})/(2\kappa)]}$$

Water – non-bubble transfer coefficient

$$k_{wnb} = \frac{u_*}{\sqrt{\rho_w/\rho_a}[\frac{13.3}{A\varphi}S_{cw}^{1/2} + \kappa^{-1}\ln(z_{wr}/\delta_{uw})]}$$

Water - bubble transfer coefficient

$$k_{wb} = 0.0068BK_{aw}U_{10}^{3.41}\left[1+\left(\frac{14S_{cw}^{1/2}}{K_{aw}}\right)^{\frac{-1}{1.2}}\right]^{-1.2}$$

- Parameterization (Fairall et al. 2000, Soloviev and Schluessel 1994, Woolf 1997)
- Calibration to eddy-covariance CO_2 fluxes
  - GasEx 1998, 2001 (Hare et al. 2004)
- Comparison to eddy-covariance dimethylsulfide fluxes (Blomquist et al. 2006)

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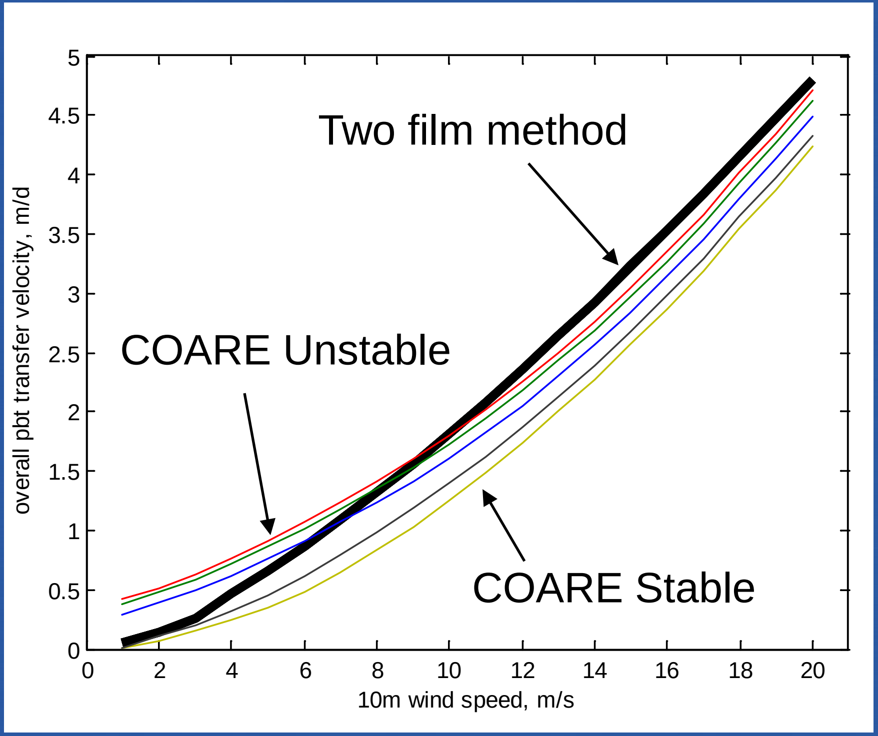
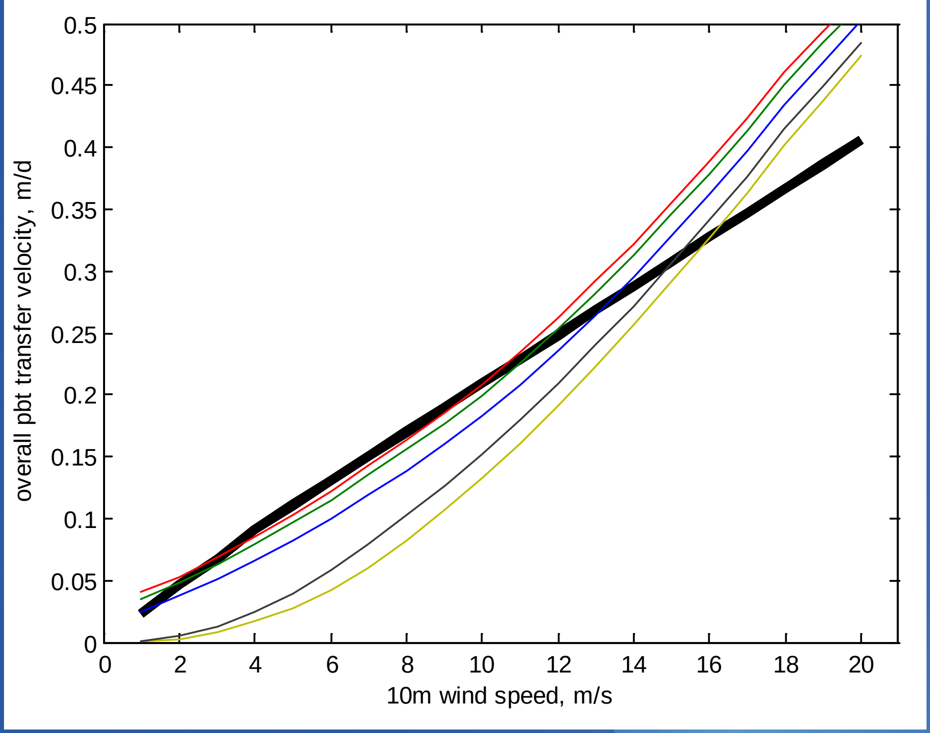
Comparison of NOAA COARE vs. Two-Film PBT Overall Transfer Velocity, m/d

triCB



PBDE 47



Water T = 20 °C

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Internal Boundary Layer Transport-Exchange (IBLTE) Model

- Inputs
  - Over-land meteorology and concentration
  - Water temperature, K_{aw}, aqueous concentration

- Output
  - Flux and concentration modification with fetch
  - Vertical concentration profiles

- How the model works
  - Surface fluxes from NOAA COARE gas transfer model
  - Mass balance over IBL, Lagrangian perspective
  - IBL growth rate calibration
    - 6926 paired land-lake measurements of T and T_d modification
    - IFYGL 1973 network of data buoys in Lake Ontario, 12-month coverage*

*Phillips and Irbe. 1978. Atmospheric Environment Service, Environment Canada.

Rowe, MD, Perlinger, JA, and Fairall, CW, Boundary-Layer Meteorol., *in review*

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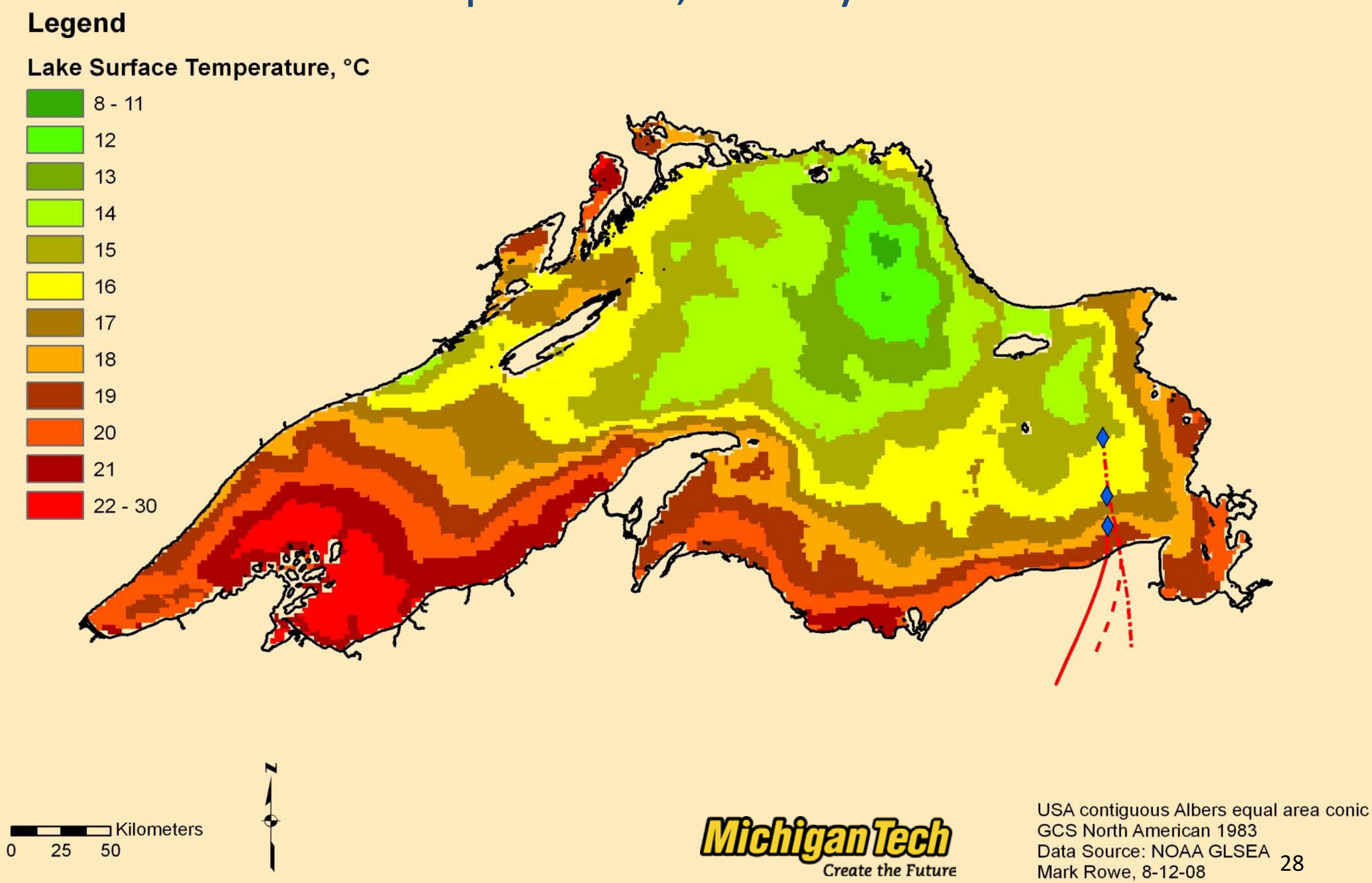
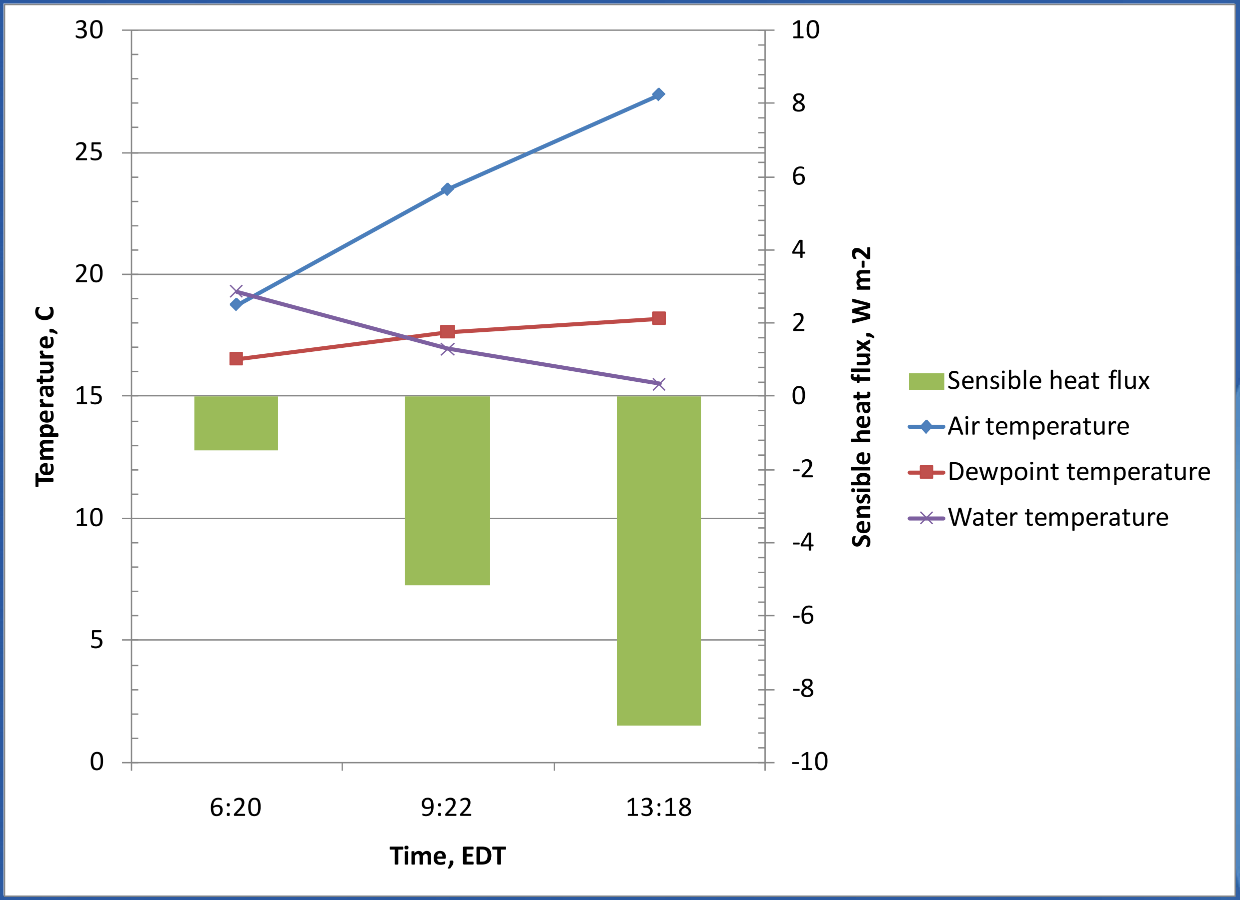
Concentration and Gas Transfer Measurement Experiment, 14 July 2006

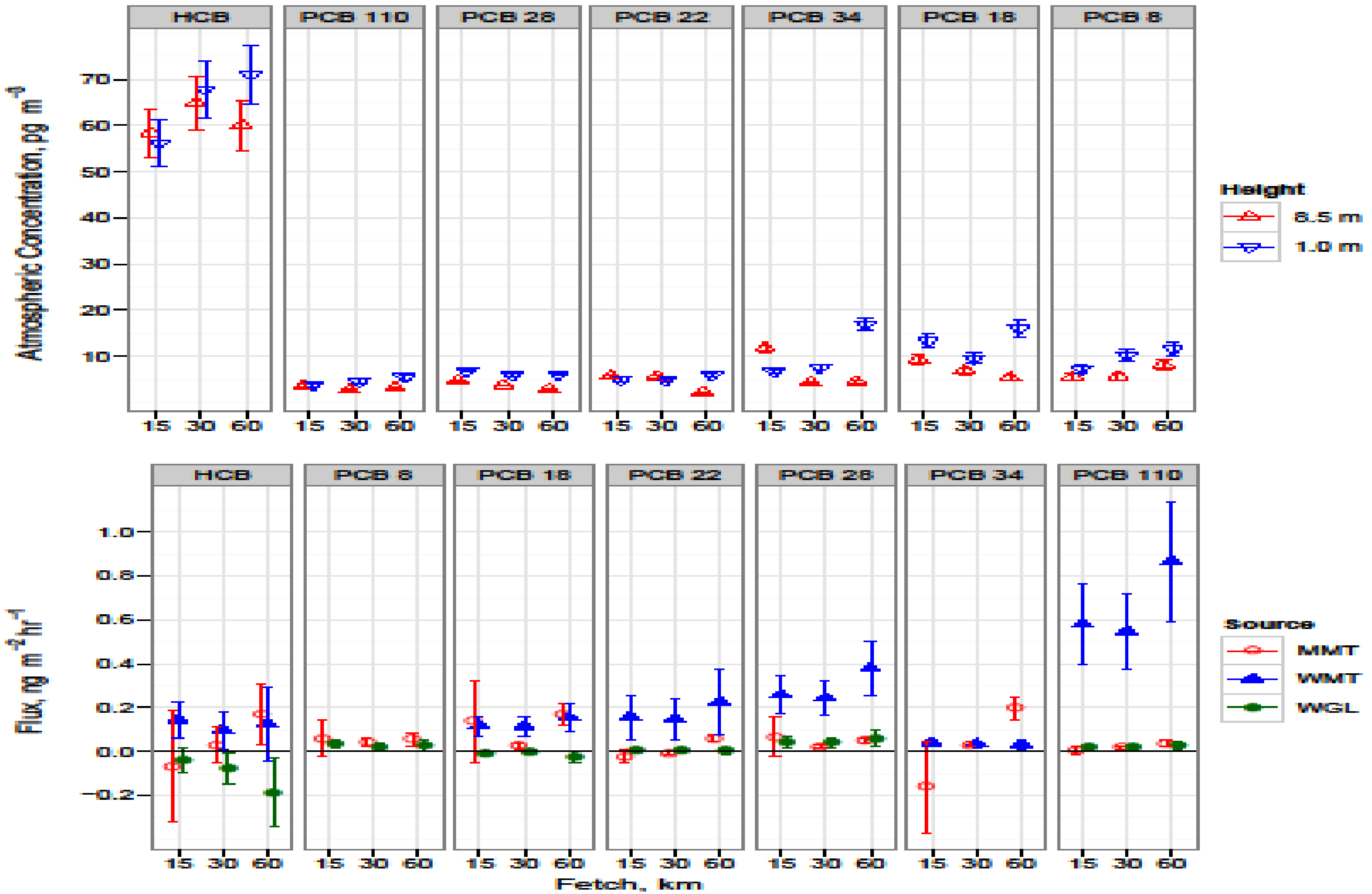


Meteorological Conditions

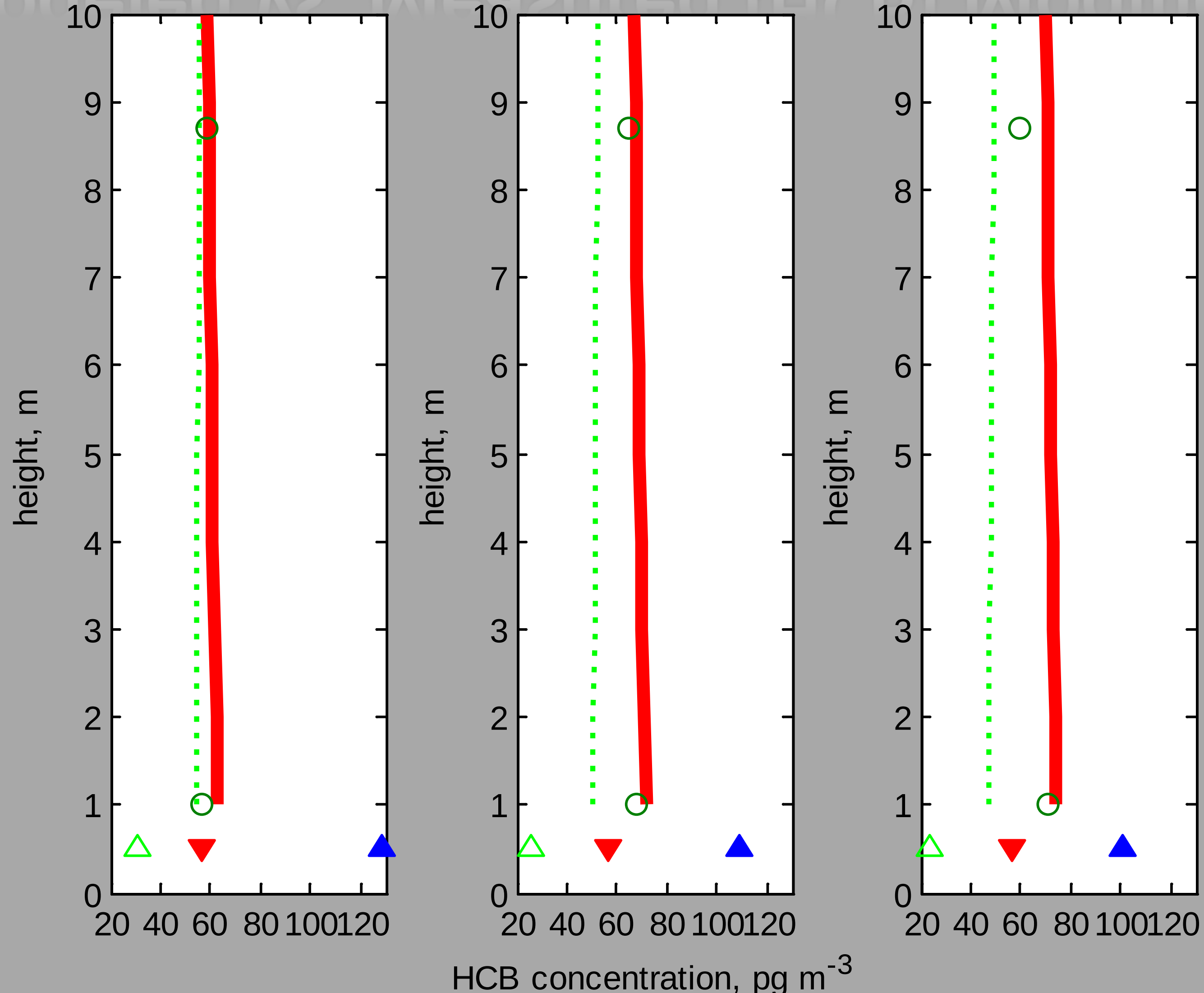


- strong increase in over-land temperature during the day
- decreasing water temperature with fetch
- neutral, stable, and very stable conditions at 15.7-, 28.3-, and 58.8-km stations, respectively

Concentrations and Fluxes



Modeled *vs.* Measured [HCB] Modification



[HCB] modification with fetch is consistent with flux predicted by K_{aw} and Michigan Tech C_w.

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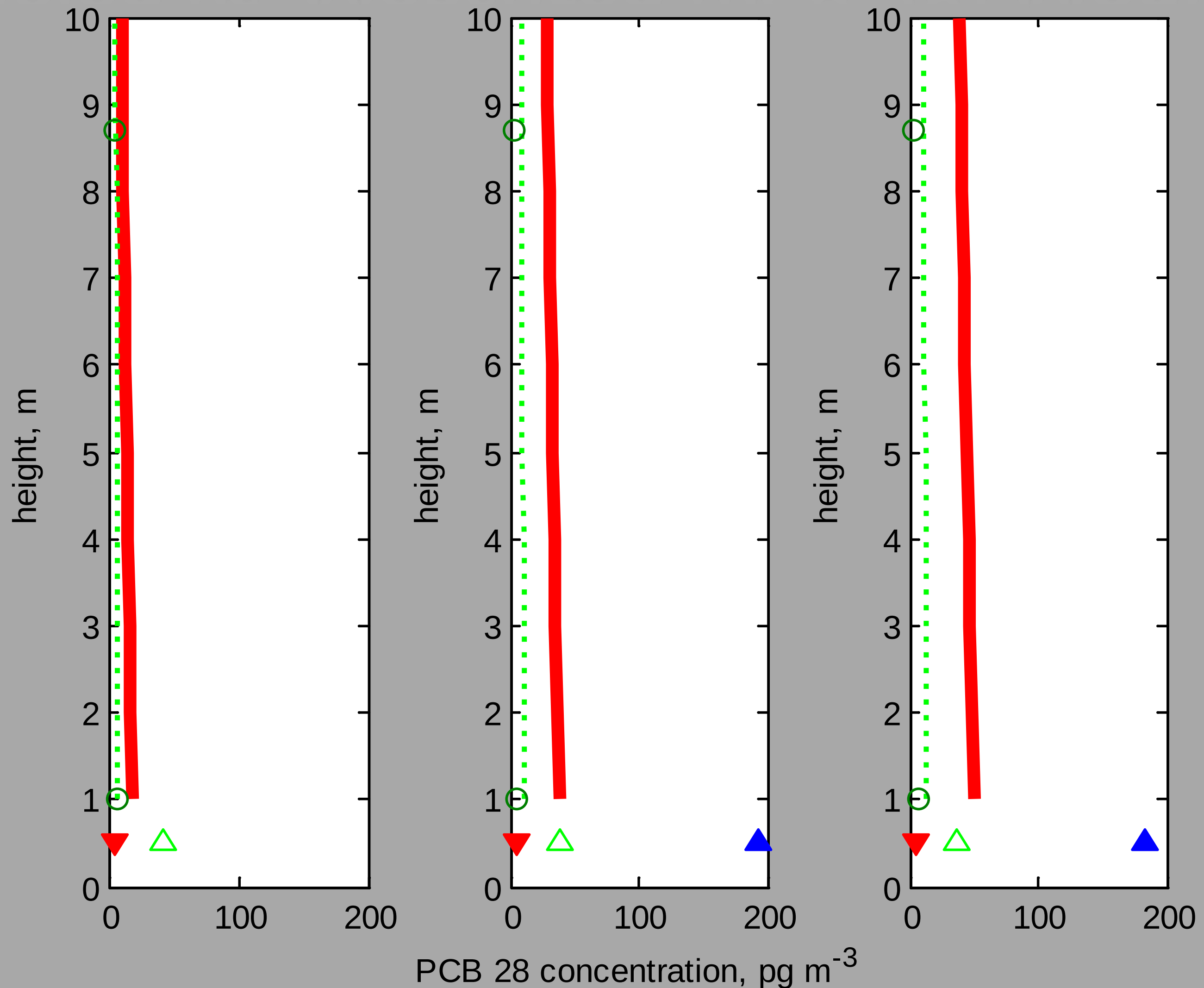
Modeled *vs.* Measured [PCB 28] Modification



[PCB 28] modification with fetch is more consistent with flux predicted by K_{aw} and GLACS C_w.

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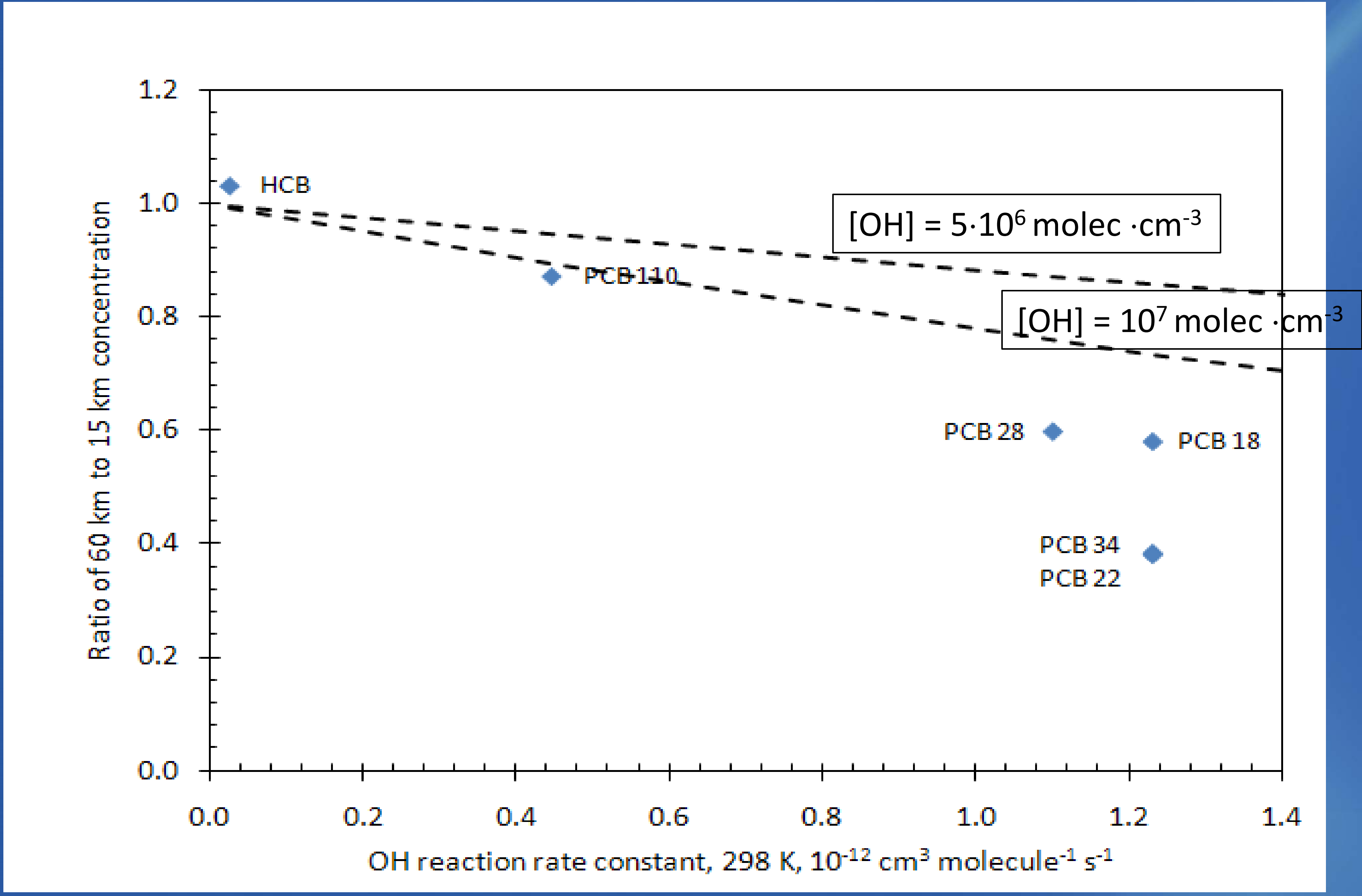
Ratio of 60-km to 15-km Conc *vs.* OH Radical Reaction Rate Constant



Rate constants: Anderson and Hites, 1996. Environ. Sci. Technol. 30(5) 1756-1763; Brubaker and Hites, 1998. Environ. Sci. Technol. 32(6):766-769.

Summary

- MCCDs were designed, built, characterized, and used to quickly and inexpensively measure PBT concentrations in built and natural environments
- The modified Bowen ratio micrometeorological method proved to be a feasible means to measure air-water exchange fluxes of PBTs at timescales comparable to relevant PBT transport and transformation processes of ~1 hour
- The IBLTE model provided means to study processes that determine PBT concentration and air-water exchange flux

Conclusions from Case Study

- The flux measurements were consistent with existing models for air-water exchange.
- More detailed micrometeorological measurements could allow for a more critical examination of air-water exchange models.
- PCBs have traditionally been treated as non-reactive. These measurements support more recent work indicating that PCBs can be destroyed by ambient OH radical on relatively short time scales.

References

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*Request the Collection Efficiency Model for Mass Determination (CEMOMD) Microsoft Excel Visual Basic Program from J. Perlinger, jperl@mtu.edu

Thank You!