



Development of Passive Air Samplers (PAS) for Persistent Bioaccumulative and Toxic (PBTs) Chemicals

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Acknowledgements

- Tom Harner – Environment Canada
- Co-PI Suresh Dhaniyala
- Students - Justin Thomas, Paul Ashman, Jiaoyan Huang
- Great Lakes Commission - GLAD (Jon Dettling Project Officer).

Outline

- Advantages and disadvantages of passive samplers
- Types of passive samplers
- Computable fluid dynamic model: FLUENT
- Wind tunnel and field experiments
- Conclusions
- Future work

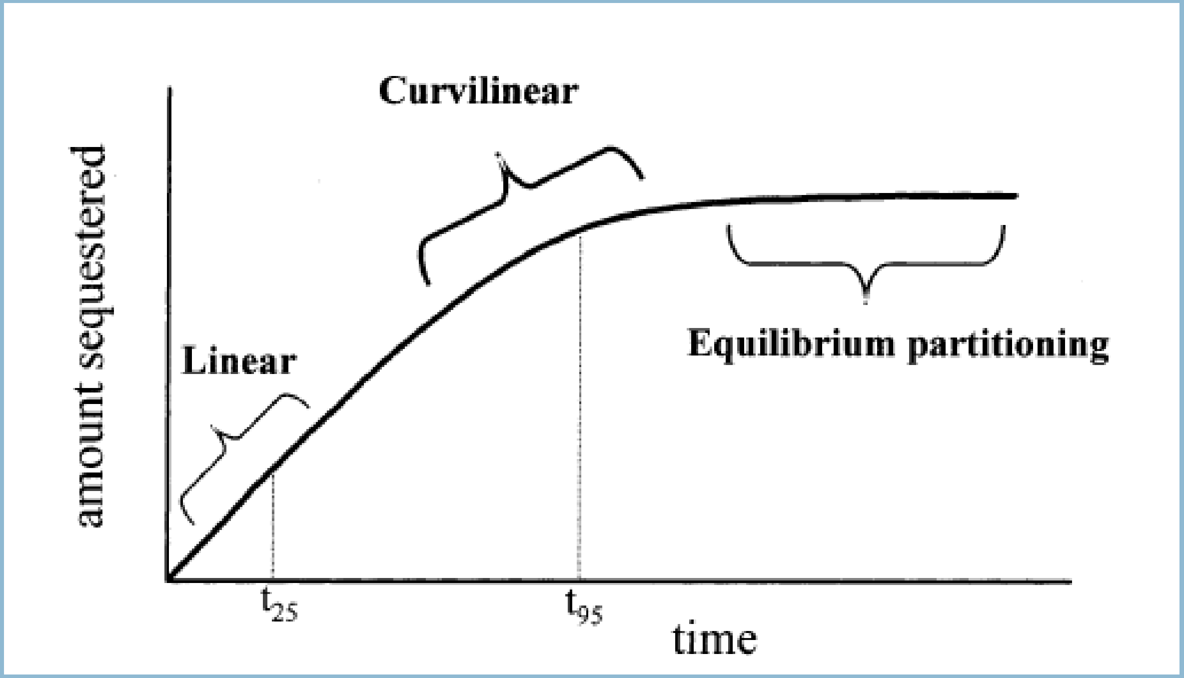
Introduction

- Passive air sampler – a sampler that can be used to "measure" air concentrations without power
- Advantages – simple, generally cheap, do not require specialized sampling platforms, can have long exposure times, measure average concentrations.
- Disadvantages – can require long exposure times, measure average concentrations (events can be missed), generate few data points, sampling volumes are unknown.

Passive samplers

- Collection media
  - Semipermeable membrane
  - Polymer-coated glass
  - XAD-2 resin
  - Polyurethane foam disk (PUF)
- Housing
  - Flow-through samplers
  - Flying saucer samplers

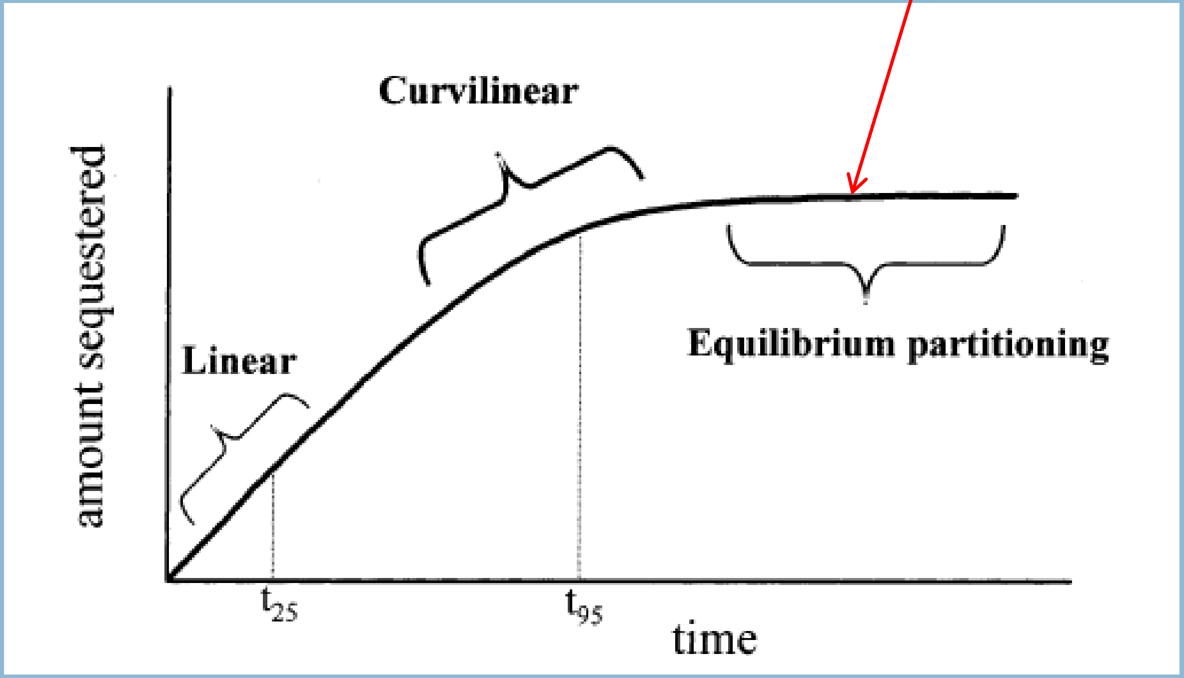
Chemical Uptake by Media



Shoeib, M., Harner, T. 2002. *Environ. Sci. Technol.* 36, 4142-4151.

Chemical Uptake by Media

Equilibrium samplers



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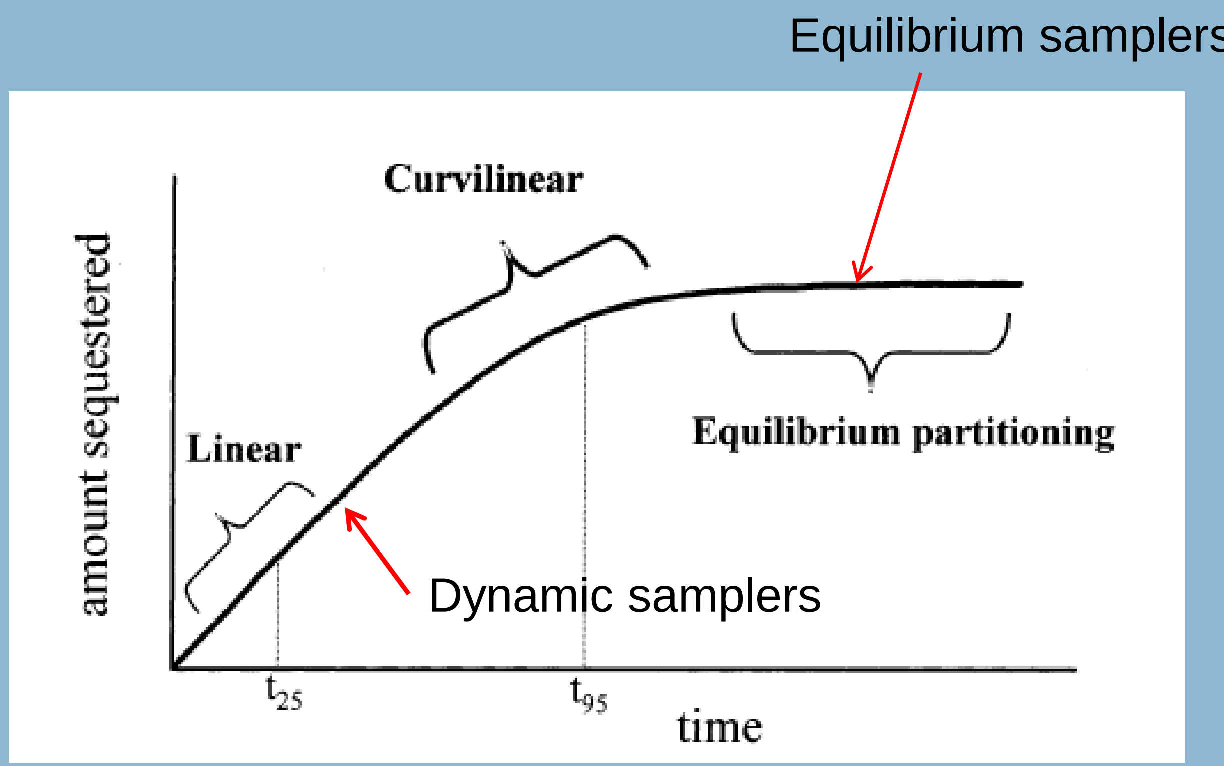
Chemical Uptake by Media



Shoeib, M., Harner, T. 2002. *Environ. Sci. Technol.* 36, 4142-4151.

Equilibrium Sampler

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- To determine air concentration the media-air partition coefficient (K_{am}) is needed

$$C_A = \frac{c_m}{K_{am}}$$

C_a – air concentration

C_m – mass on the media

POG

- POlymer-coated Glass (POG) samplers
- Coating of ethylene vinyl acetate (EVA) less than 1 μm thick coated on to glass.
- Time to equilibrium varies between a few hours to approx. 20 d for PCB-18 and PCB-138, respectively.

- Farrar et al Environ. Sci. Technol. **2005**, 39, 261-267

Dynamic Sampler

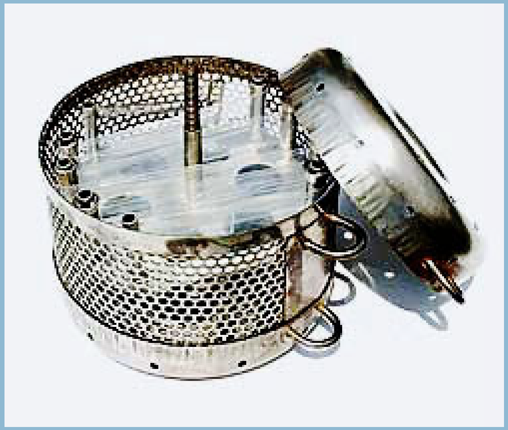
- To determine air concentration a sampling rate (SR) is needed (m^3/day)

$$C_A = \frac{c_m}{SR * time}$$

C_a – air concentration

C_m – mass on the media

Semipermeable Membrane Device (SPMD)

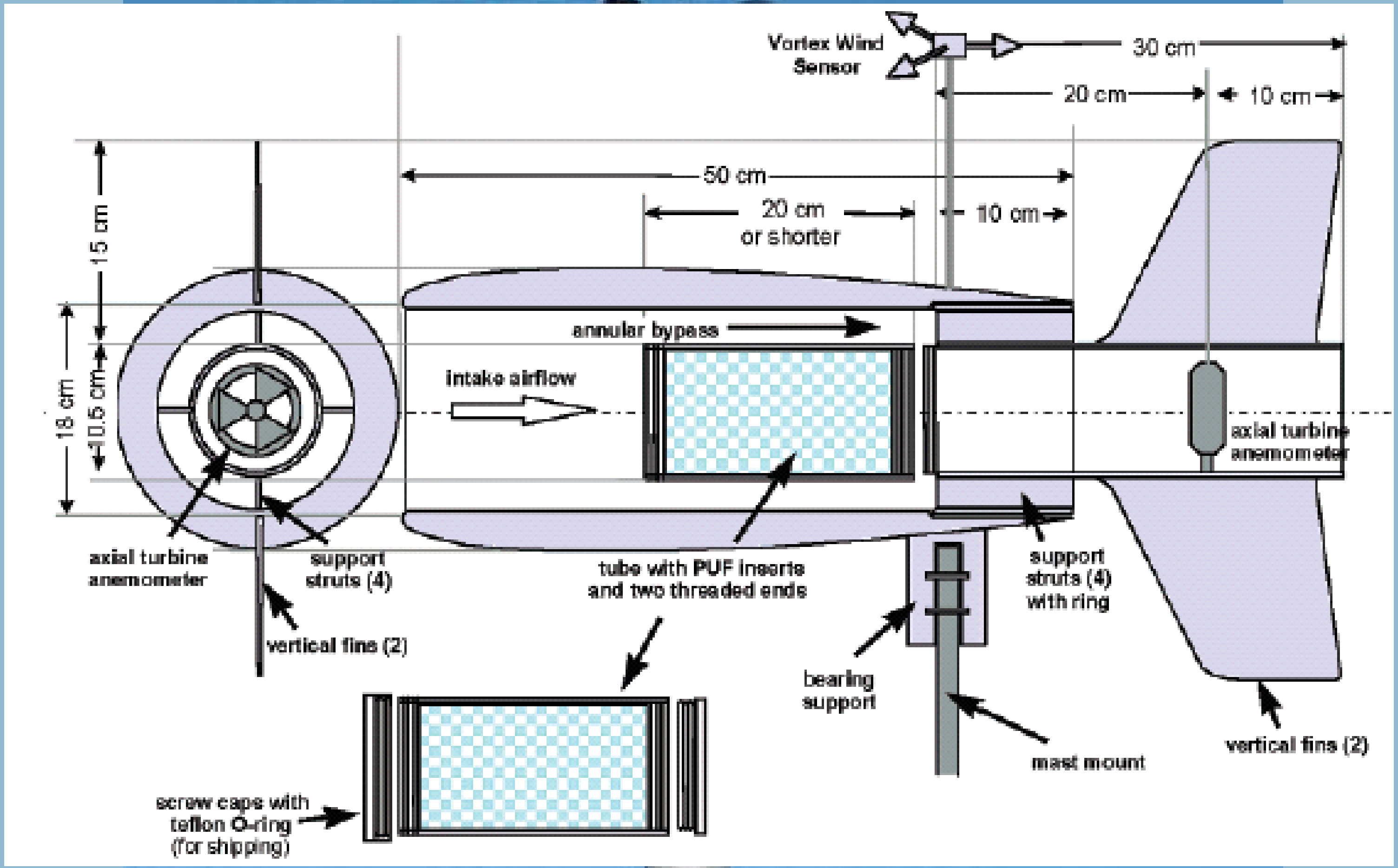


Tubing: lay flat low density polyethylene
Triolein: 99% purity

Sampling rates range between 0.6 and 6.1 $m^3\ d^{-1}$ for PAHs – sampling time was 32 days (Bartkow et al. Atmos Env 38 (2004) 5983-5990).

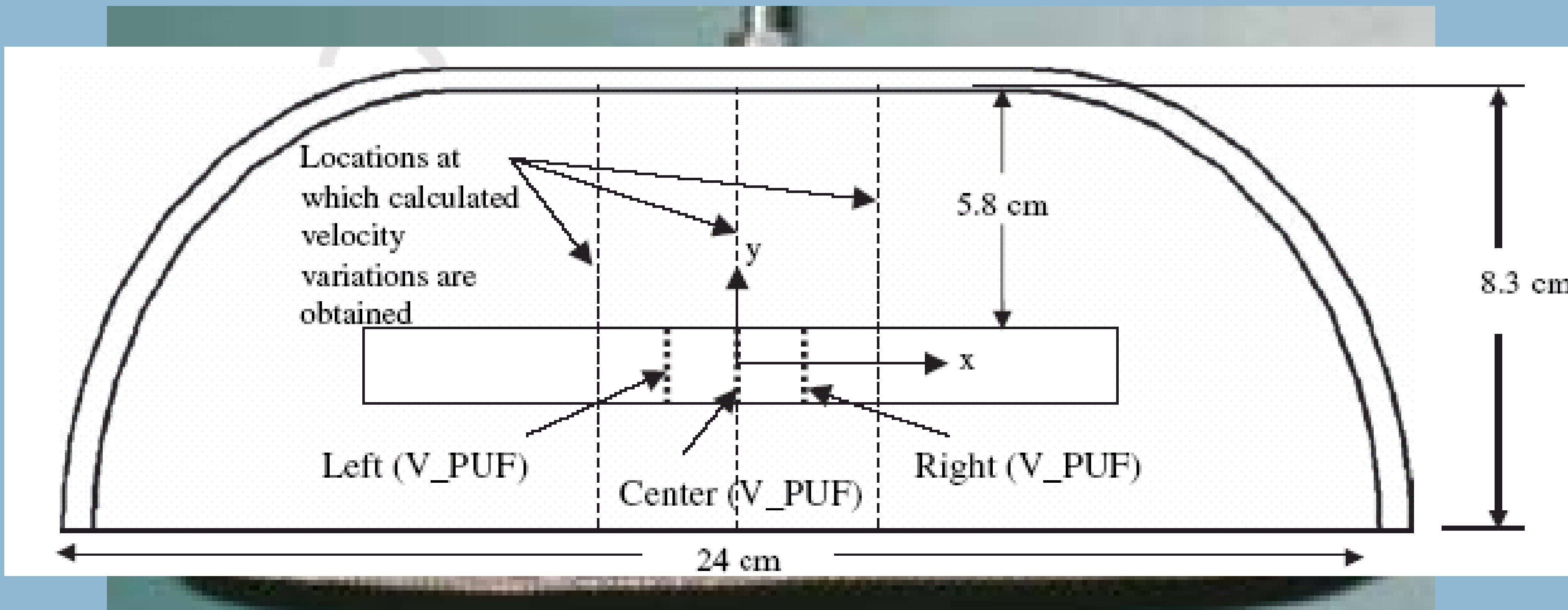
http://www.est-lab.com/spmd.php

Flow-through sampler



Sampling rate 15 up to 100 m^3/d – seasonal or monthly samples
Wania et al., 2007

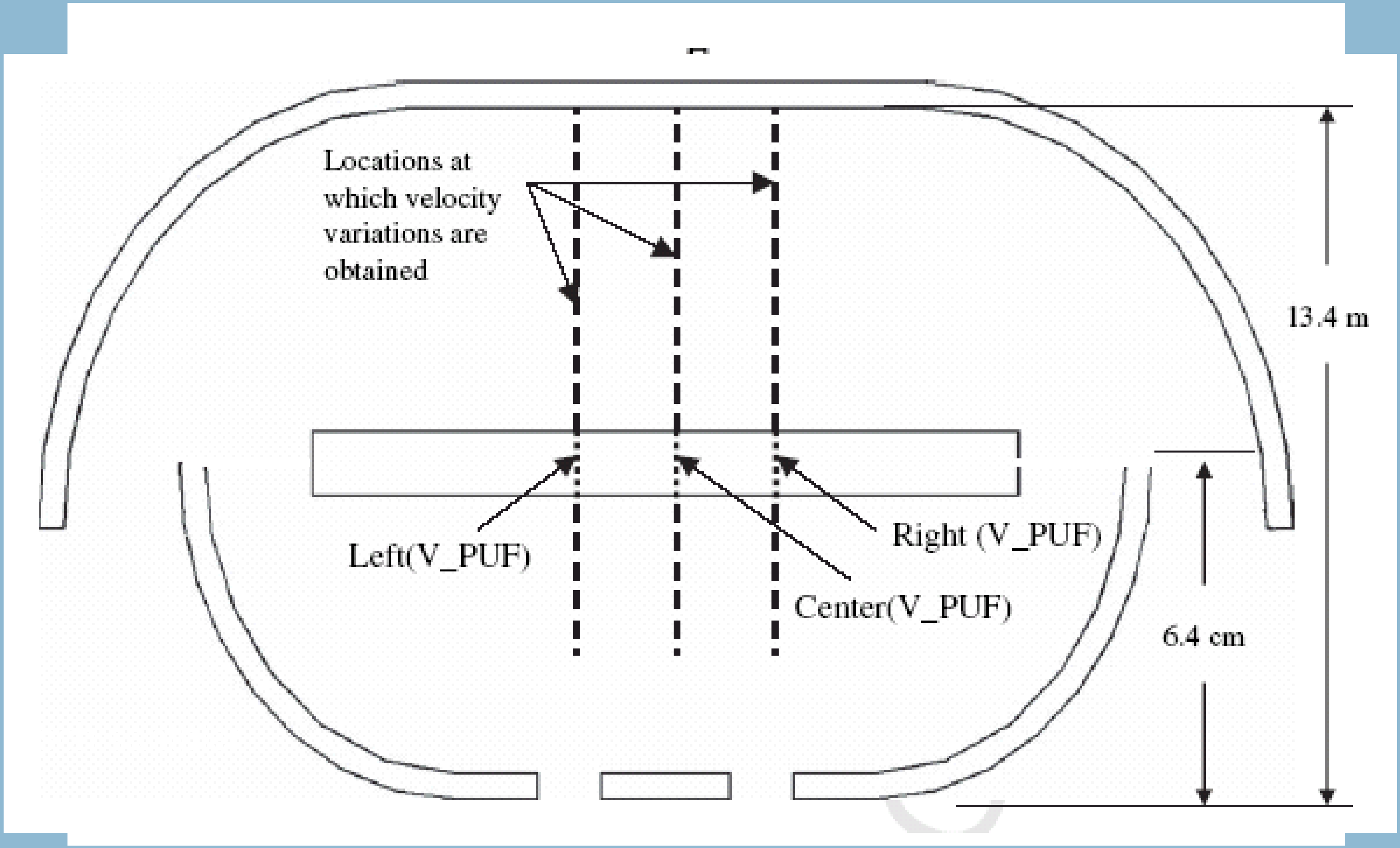
Single bowl sampler



Sampling rate 8 – 15m^3/d; Thomas et al., 2006

XAD-samplers

PUF-Disk sampler



Harner et al., 2006; Thomas et al., 2006

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Air

GAPS

Global Atmospheric Passive Sampling (GAPS) Network Research Publications and Conference Presentations

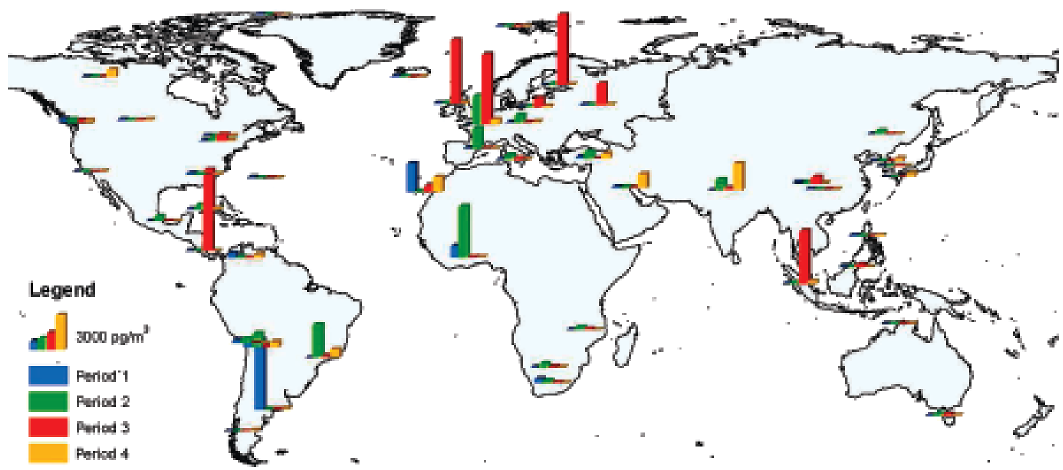


FIGURE 3. Concentrations in air (pg·m^{-3}) for endosulfans (sum of isomers: endosulfan 1 + endosulfan 2 +endosulfan sulfate) over four sampling periods during December 2004 to December 2005. Endosulfan, a currently used pesticide shows strong variability spatially and among seasons at sites impacted by its use. See Table S1 for sampling dates.

Seasonally Resolved Concentrations of Persistent Organic Pollutants in the Global Atmosphere from the First Year of the GAPS Study Karla Pozo, Tom Harner, Sum Chi Lee, Frank Wania, Derek C. G. Muir and Kevin C. Jones *Environ. Sci. Technol.*, **2009**, *43* (3), pp 796–803

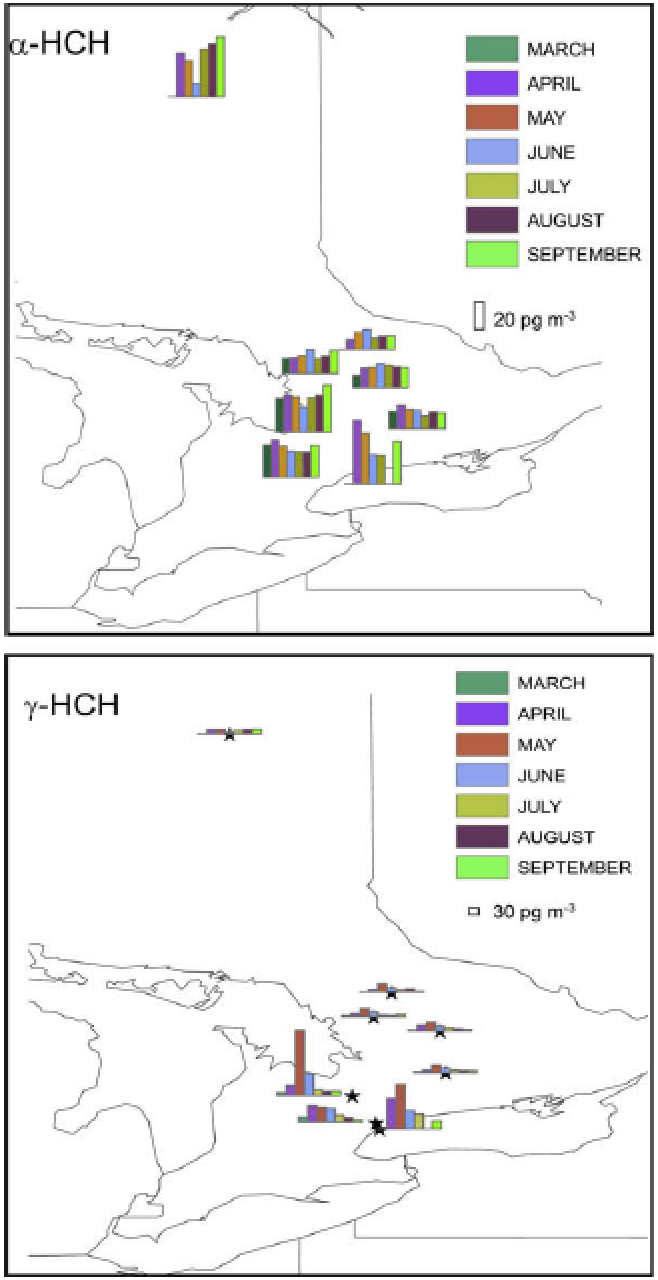
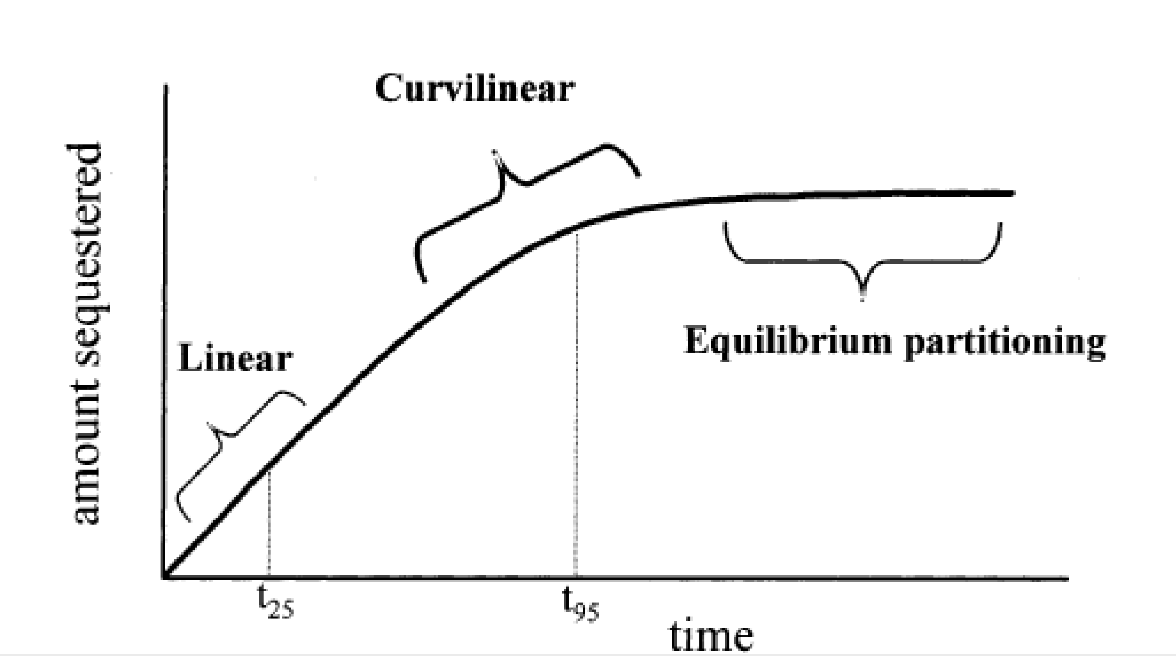


Fig. 3. Estimated monthly air concentration for α-HCH and γ-HCH during the growing season of 2003 at each of the passive air sampling sites in Ontario, based on an air sampling rate of 3.5 $m^3 d^{-1}$.

- Atmospheric concentrations of current-use pesticides across south-central Ontario using monthly-resolved passive air samplers
- T. Gouin, M. Shoeib, T. Harner
- Atmospheric Environment 42 (2008) 8096–8104

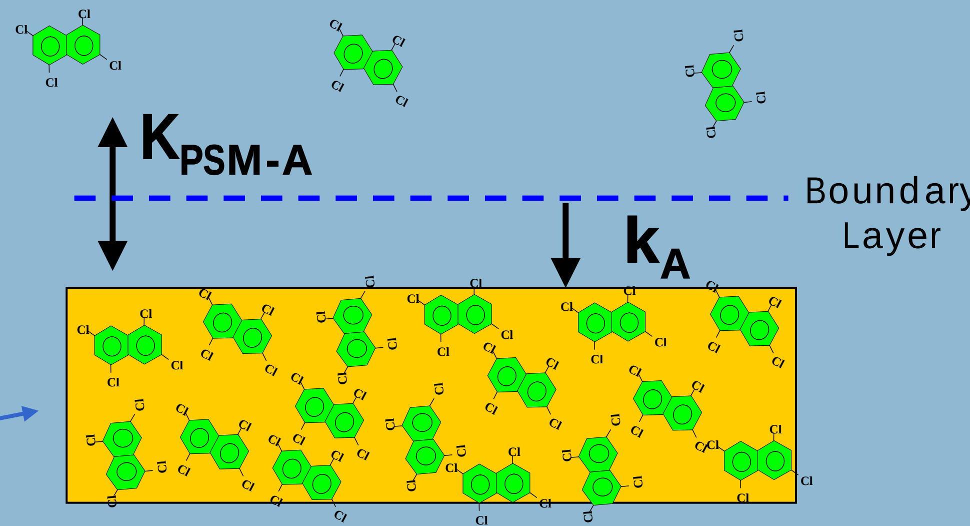
Dynamic Sampler Theory

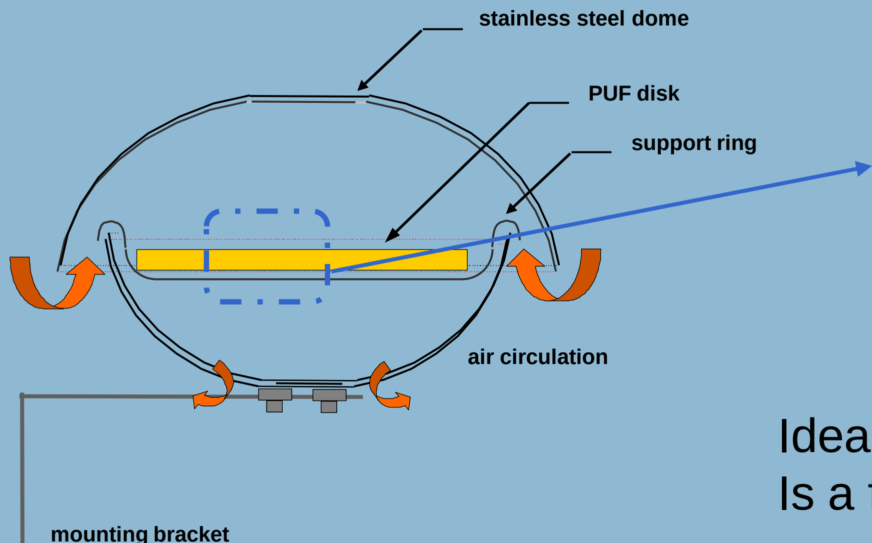


$$V_{PSM}\,(dC_{PSM}/dt) = k_A\,A_{PSM}\,(C_A - C_{PSM}/K_{PSM\text{-}A})$$

Linear region governed by $\mathbf{k_A}$, air-side mass transfer coefficient (MTC)

Equilibrium determined by $\mathbf{K_{PSM\text{-}A}}$, the passive sampling medium-air partition coefficient





Ideally k_A is independent of sampling conditions
Is a function of chemical properties (D_A)

Uptake Parameters:

- **K_{PSM-A}**, passive sampling medium-air partition coefficient

  (K_{PSM-A} is similar to K_{OA}, the octanol-air coefficient)

- **k_A**, air-side MTC (approx. D_A/boundary layer thickness

Determining sampling rates (SR)

- Compare active and passive samplers side-by-side
- Add depuration compounds (dc) to media before sampling (loss of dc is a measure of uptake rate)
- Perform controlled experiments

SR variability

SRs are a function of:

k_A (MTC)

- Sampler design
- Wind speed
- Temperature
- External flow fields
- Sampler orientation

$K_{psm\text{-}A}$(partition coefficient)

Wind tunnel experiments

Wind tunnel experiments

SRs calculated from wind tunnel measurements

Water evaporation

$$SR = \frac{P_a M_a}{\left(1 - \frac{RH}{100}\right)\rho_a P_{sat}(T) M_w} \frac{\Delta m}{\Delta t}$$

$$SR_{PCB} = SR_{H_2O}\left[\frac{D_{a,PCB}}{D_{a,H_2O}}\right]^{\alpha}$$

$\alpha = 0.5$ or 0.67

Mercury uptake

$$SR = \frac{\Delta m / \Delta t}{C_{Freestream}}$$

Measured by Tekran 2537

SRs calculated from computational fluid dynamic modeling

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$$J = D \times \frac{dC}{dL}$$

$$SR = \frac{J \times A}{C_{freestream}}$$

D: diffusivity

dC/dL: concentration gradient (C_0 was assumed to be 0)

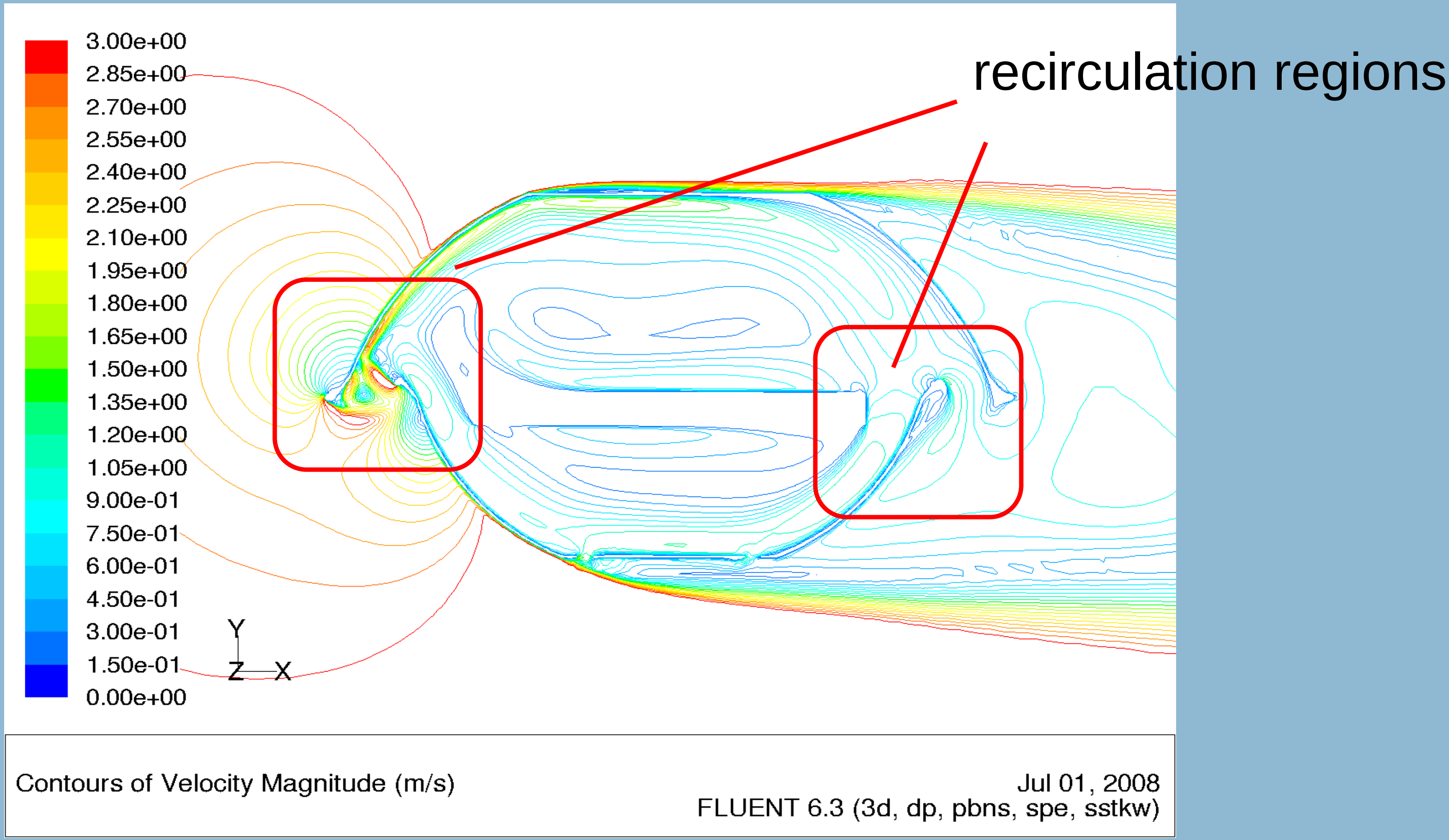
A: surface area of PUF

$C_{freestream}$: concentrations in free stream

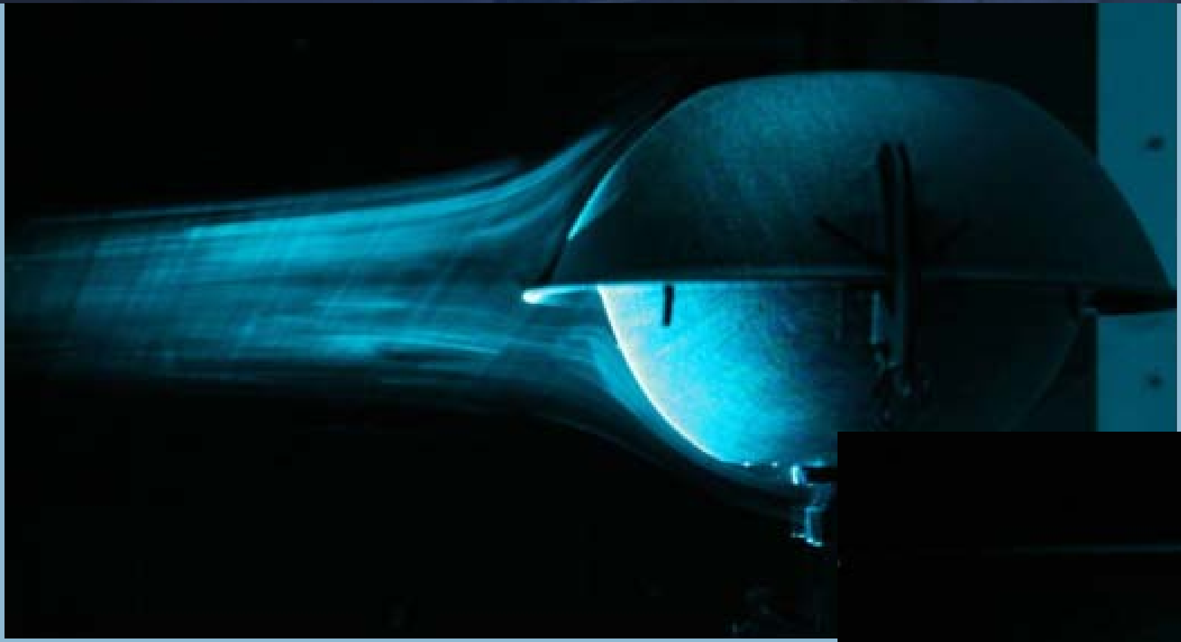
Numerical values are collected using “rakes”. These rakes consist of a specific number of points oriented in a line perpendicular to the surface of the sampling medium (PUF).

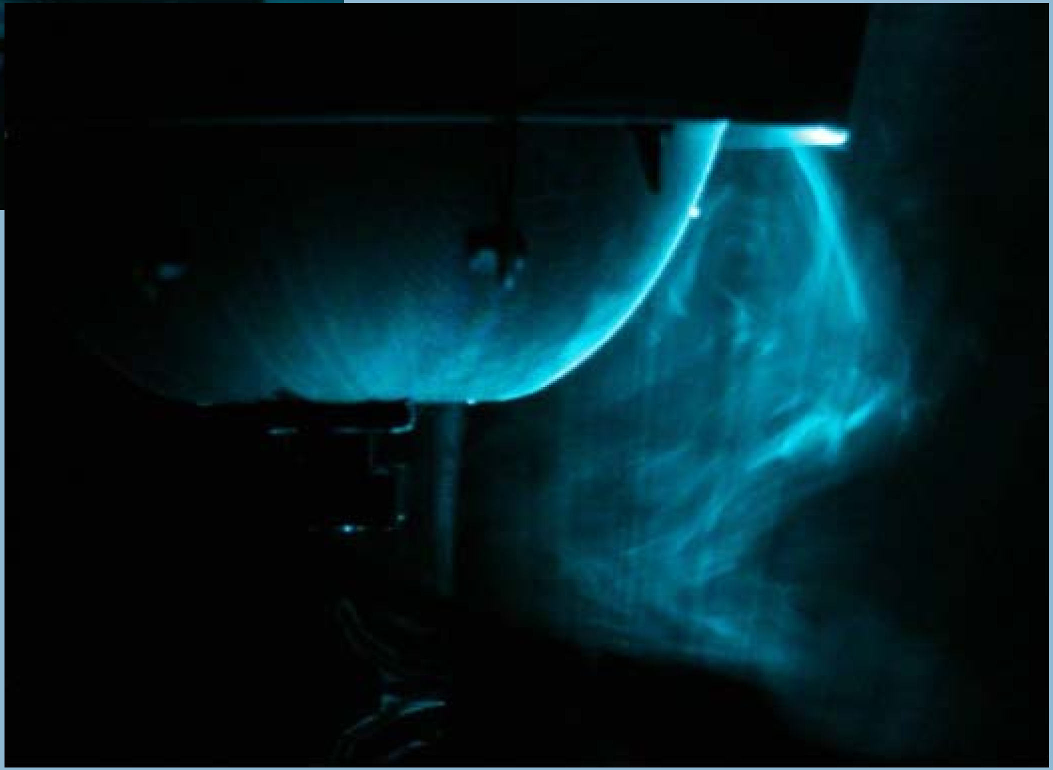
The first point above PUF on mesh line was used to calculated dC/dL.

Velocity contour results from 3D CFD

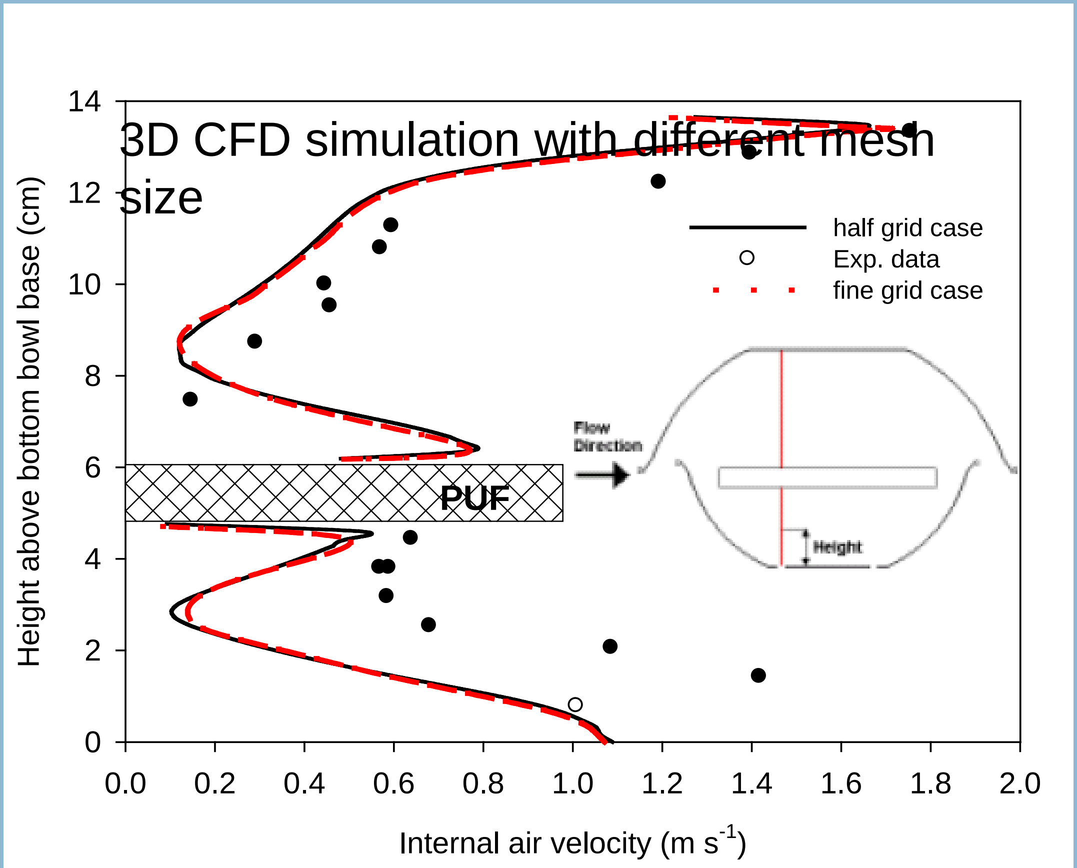


Wind Tunnel Measurements

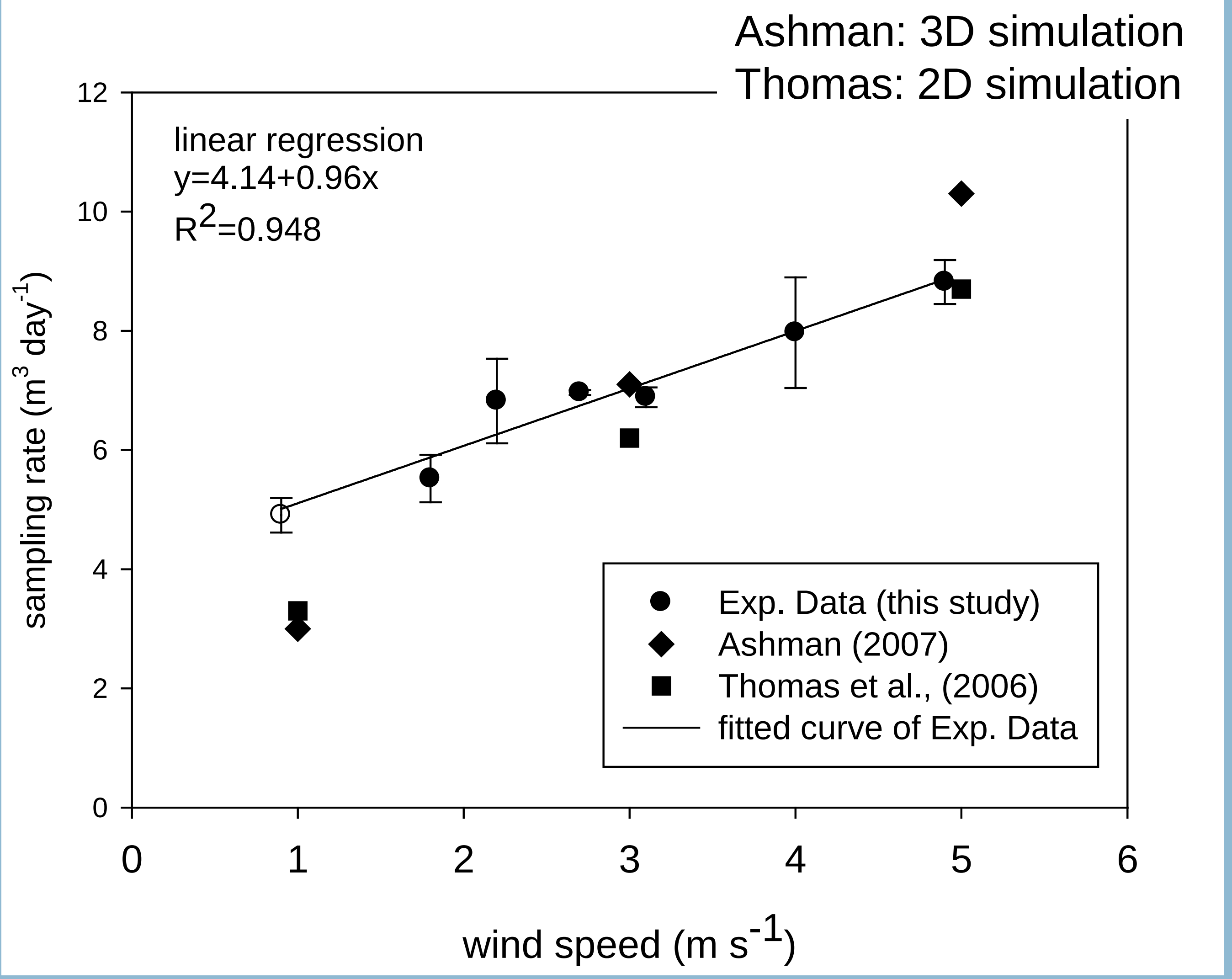




Internal wind speed distribution at 3 m s^{-1} external wind speed



PCBs SR converted from water evaporation and CFD simulations



Sampling Rates (SR) for PCBs

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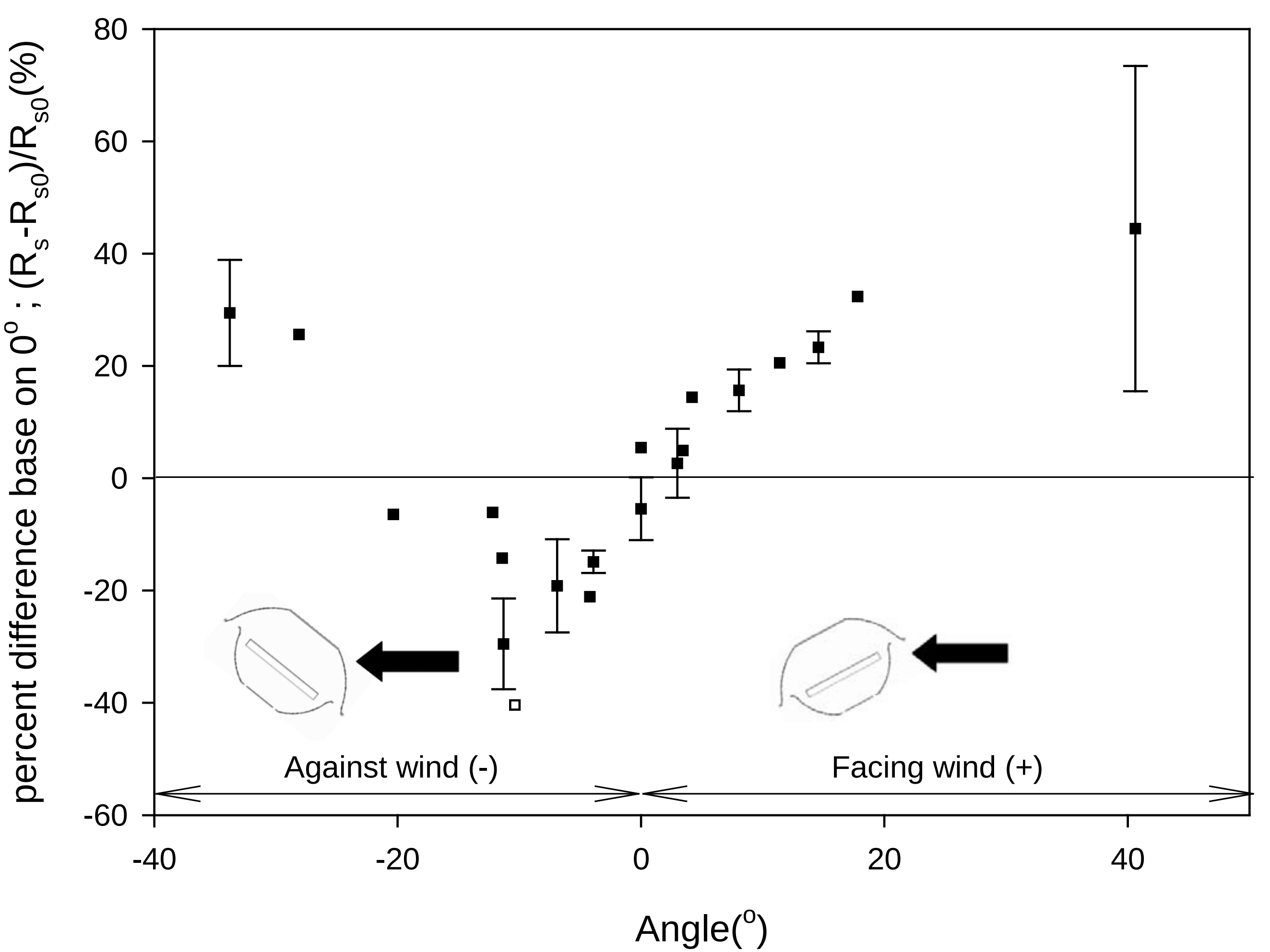
PUF disk sampler			
Source	Sampling rate: $U_o = 1\ m\ s^{-1}$	Sampling rate: $U_o = 3\ m\ s^{-1}$	Sampling rate: $U_o = 5\ m\ s^{-1}$
Thomas et al. (2006)	3.3	6.2	8.7
Ashman et al (2007)	3.8	6.8	10.3
	Mean ($m^3\ day^{-1}$)	Minimum ($m^3\ day^{-1}$)	Maximum ($m^3\ day^{-1}$)
Gouin et al. (2005)	3.1	1.5	5.7
Mari et al. (2008)	3.8	1.6	4.9
Chaemfa et al. (2008)	4.9	2.9	7.3

Thomas et al., 2006 – 2-D CFD modeling
Ashman et al., (2010) – 3-D CFD modeling
Mari et al., 2008; Chaemfa et al., 2008 – uptake experiments
Gouin et al., 2005 – depuration

Variation of water evaporation with different orientations at 3 m s^{-1}

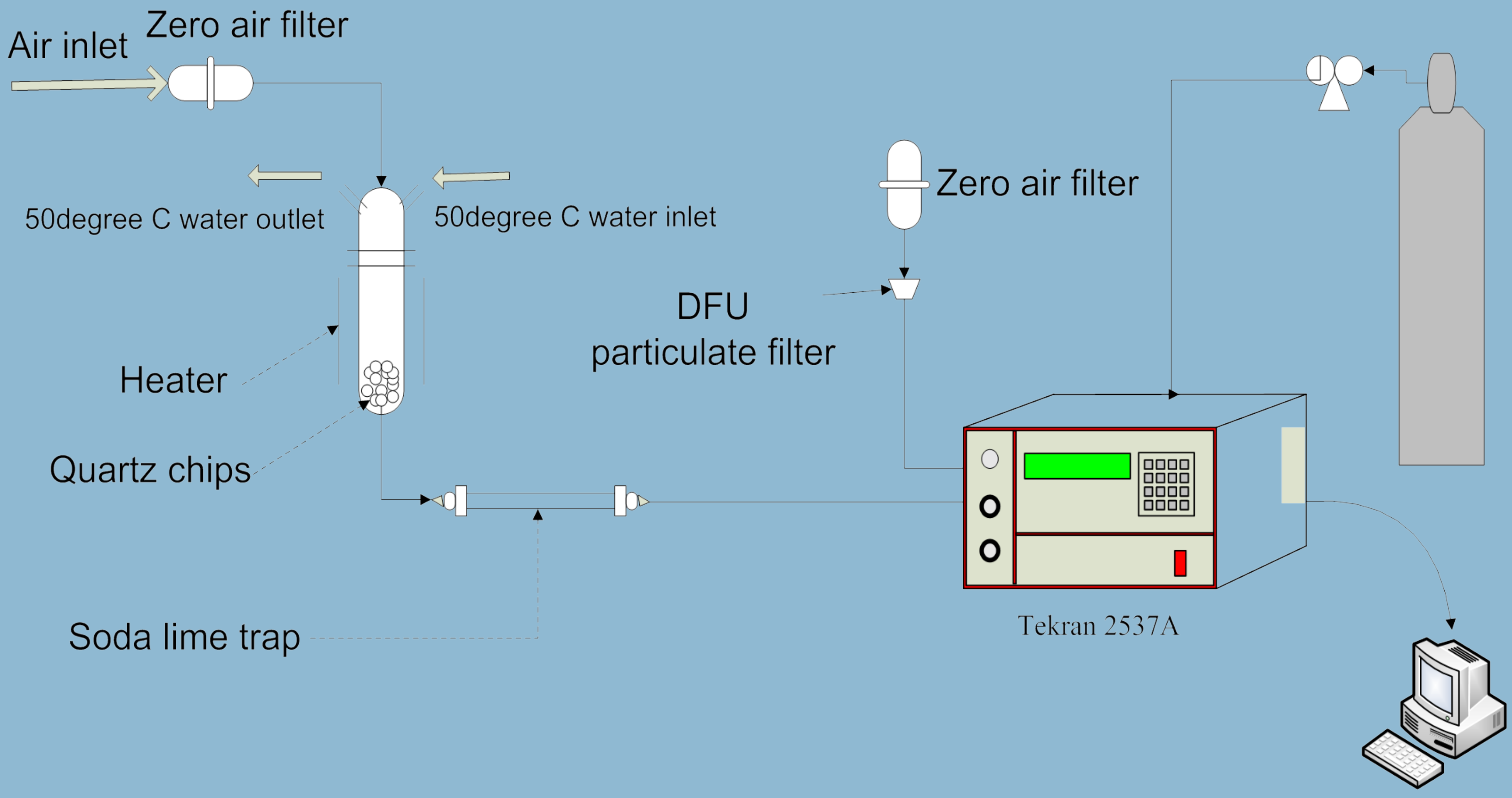


Mercury Passive Sampler

PUF disk and holder replaced with filter holder
Four upward facing and four downward facing filters

Gold-coated filter for Hg°
Ion-exchange membrane for GOM (RGM)

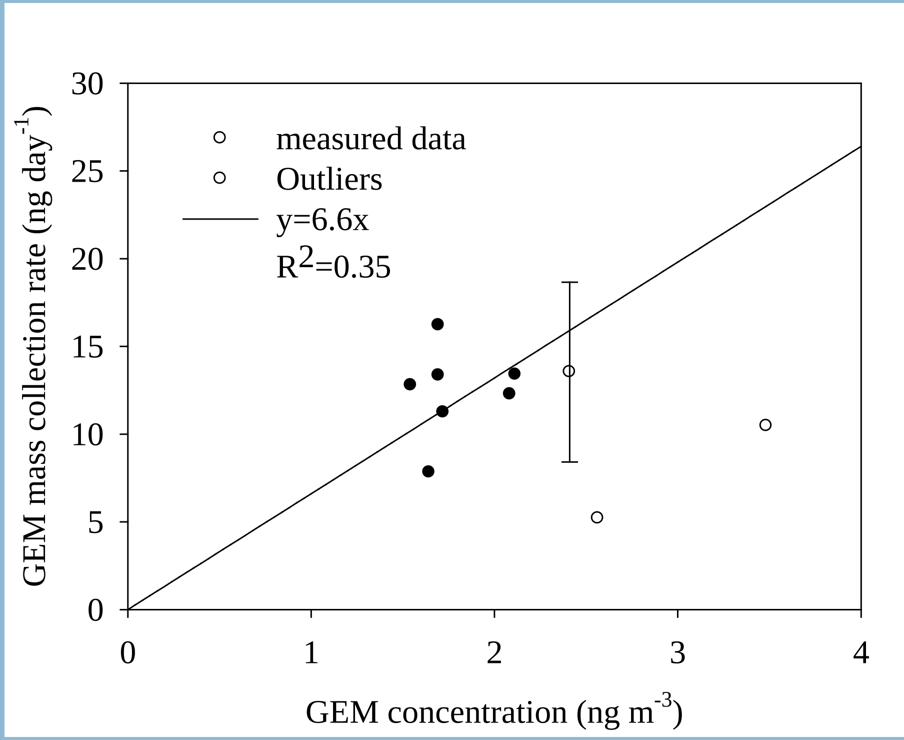
Gold-coated QFF analytical method – thermal desorption



Hg° sampling rates

at 3 m/s

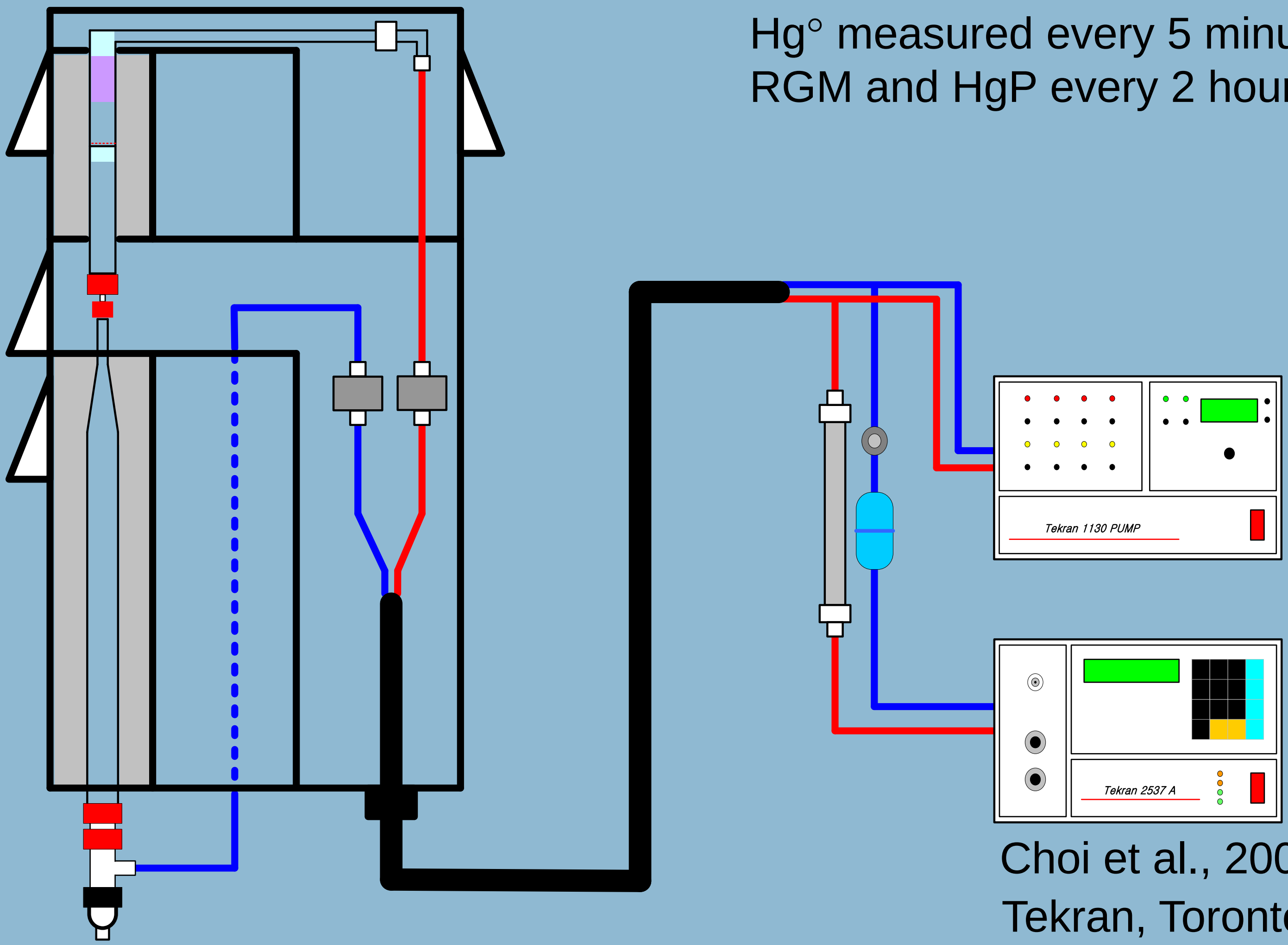
- Wind tunnel measured Hg° SR : 10.2 ± 0.2 m^3 day^{-1}
- CFD Simulated Hg° SR: 9.9 m^3 day^{-1}



Field – 6.6 m^3/d

Tekran Automated Hg Speciation System

Hg° measured every 5 minutes
RGM and HgP every 2 hours



Choi et al., 2009
Tekran, Toronto, CA

GOM mass collection rate

- Ion-exchange membrane was used to measure captured RGM
- Analytical method: EPA 1631 E

Gaseous oxidized Hg (GOM or RGM)

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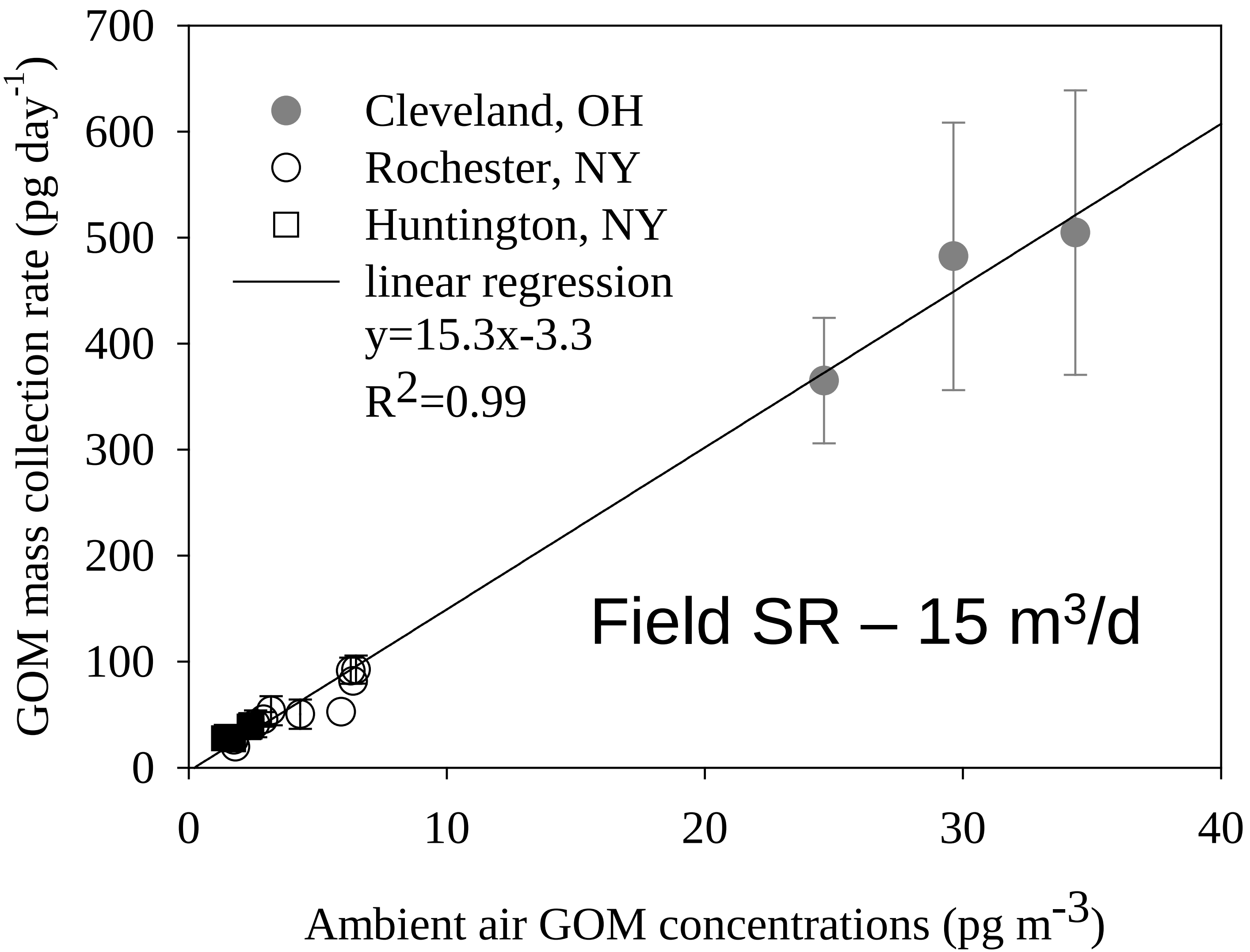
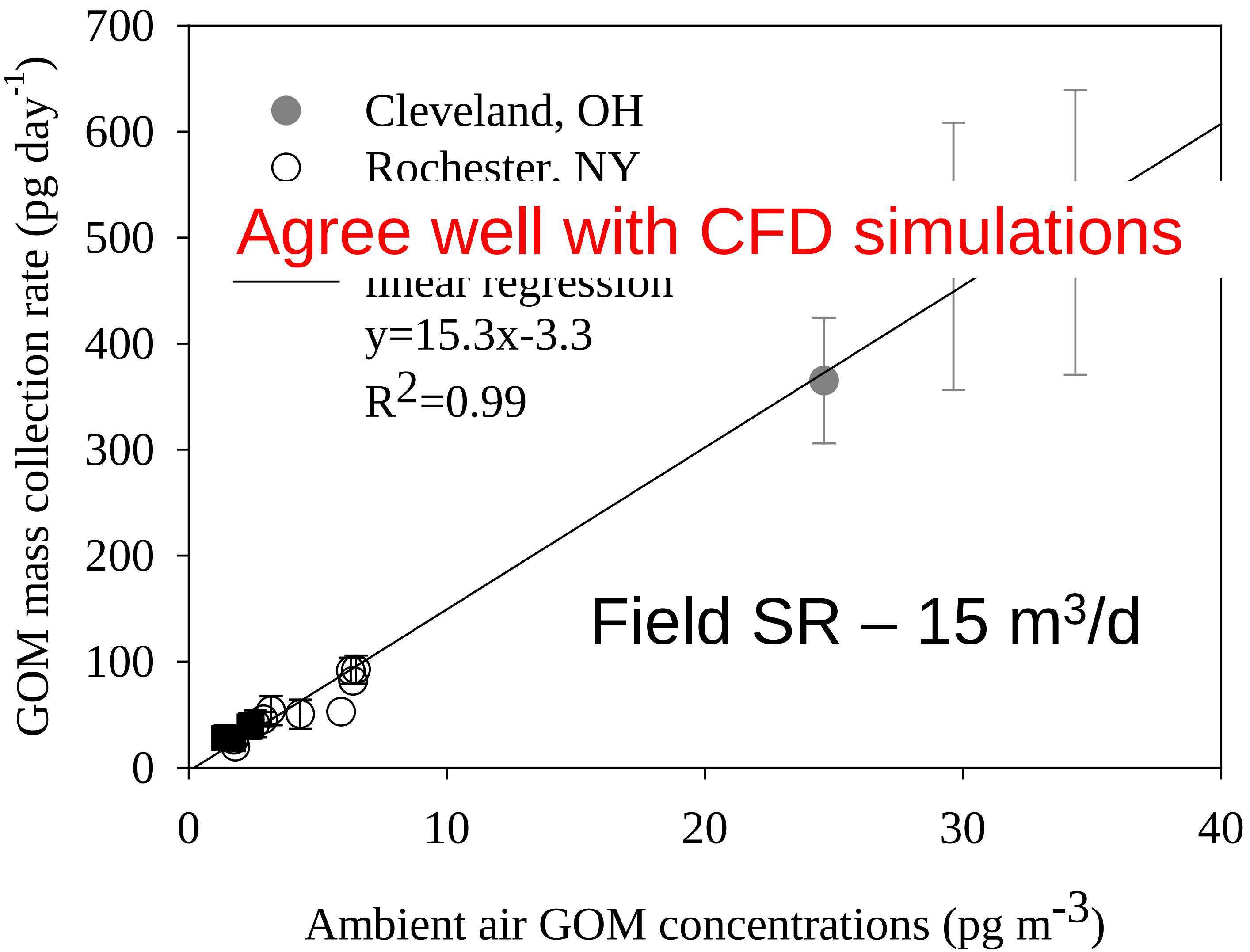


Gaseous oxidized Hg (GOM or RGM)



Agree well with CFD simulations

Field SR – 15 m^3/d

Multiple Screen PAS

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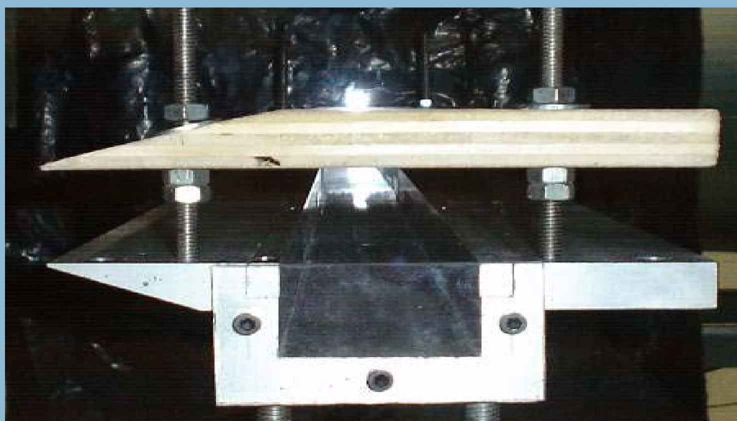
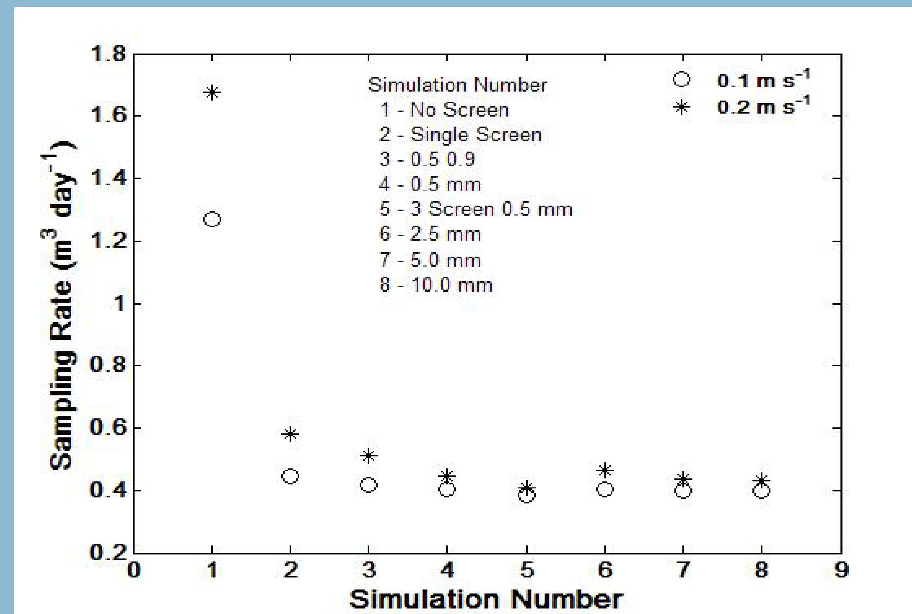
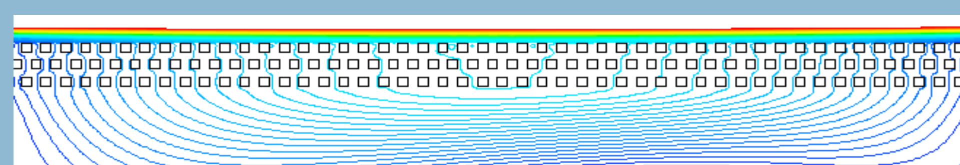
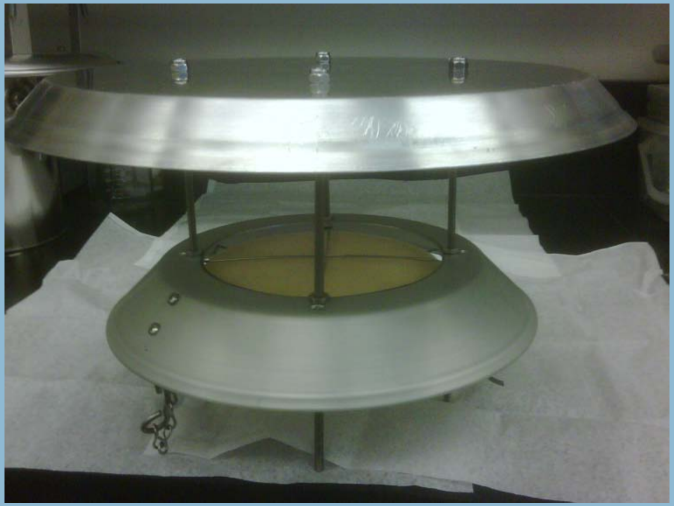


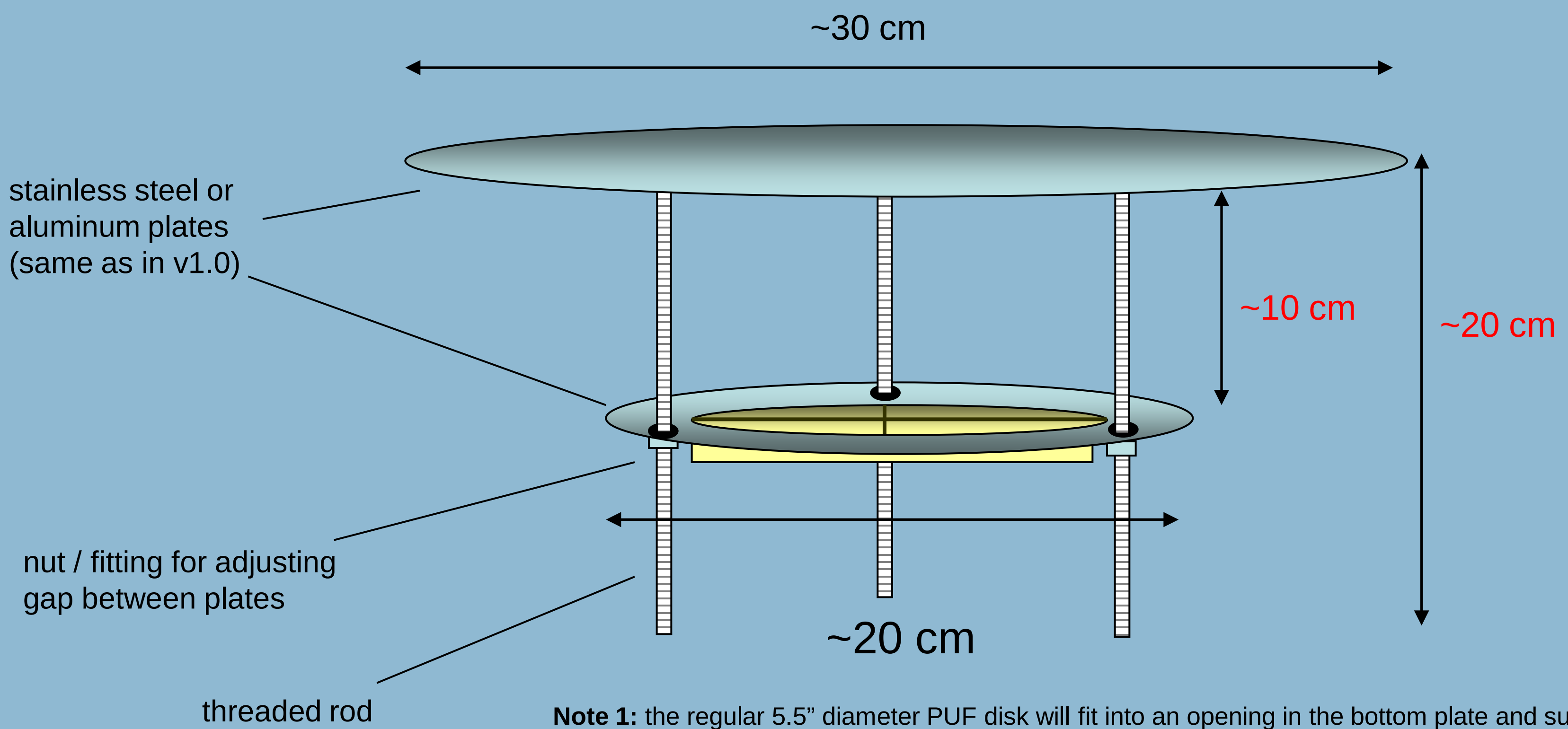




Passive Aerosol Collector - v.2.0

October 1, 2010
Tom Harner





Note 1: the regular 5.5" diameter PUF disk will fit into an opening in the bottom plate and supported by a wire support with '+' pattern on the top and bottom. The top of the surface of the PUF disk should sit Recessed about ¼" below the surface of the plate. The wire support should not protrude above the top surface of the plate.
Note 2: the unit should be mounted from the top plate

Conclusions

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- Passive air samplers (PAS) are an effective way to measure average concentrations
- Wind tunnel measurements and CFD simulations improve our understanding of PAS
- Modifying existing samplers may improve their performance

Future work

- To improve our understanding of factors influencing sampling rates of Hg in the field, such as O_3 concentrations and RH.
- To improve our understanding of particle capture.
- Improve on existing PAS designs

Acknowledgements

- Great Lakes Commission (Jon Dettling Project Officer).

Thanks for your attention!

Questions?