# Quantifying air-surface exchange of elemental mercury vapor using enclosure and micrometeorological methods

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**Data Collection, Analysis and Application of Speciated Atmospheric Mercury**

3rd International Conference on Earth Science & Climate Change

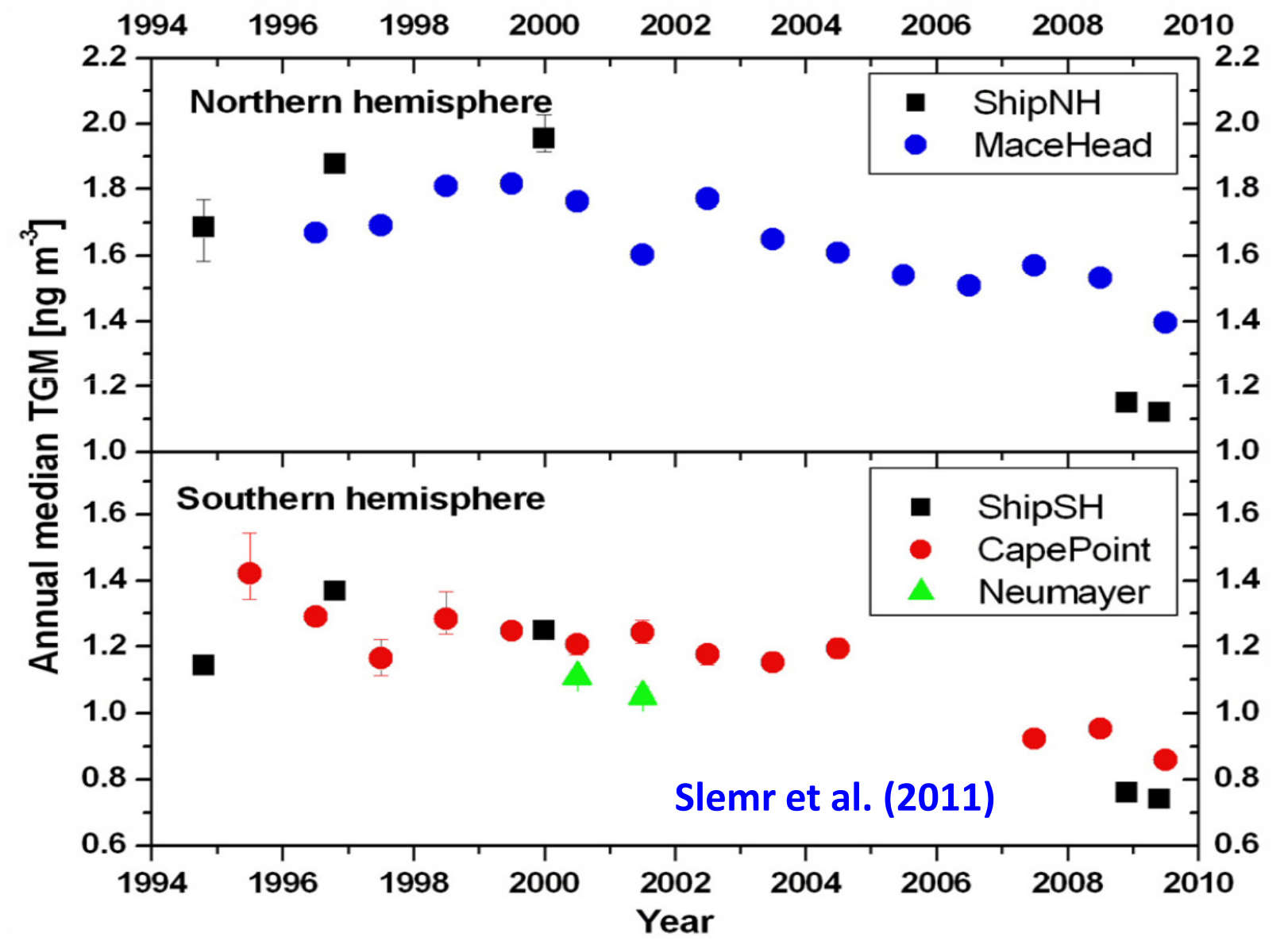
**July 29, 2014**

# Anthropogenic vs. Natural/Secondary

| Emissions (t/y) | Seigneur et al., 2004 | Mason et al., 1994 | Mason and Sheu, 2002 | Sunderland and Mason, 2007[c] | Selin et al., 2007 | Strode et al., 2007 | Selin et al., 2008 [b] |
|---|---|---|---|---|---|---|---|
| **Anthropogenic Emissions** | **2,143** | **4,000** | **2,400** | **2,260-3,380** | **2,200** | **2,180** | **3,400** |
| **Natural+Secondary Emissions** | **4,268** | **5,000** | **4,200** | **4,720** | **4,800** | **4,820** | **7,100** |
| **Natural Emissions** | **1,067** | **1,600** | **2,110** | **2,240** | **900** | **810** | **3,540** |
| from land | 625 | 1,000 | 810 | 880 | 500 | 500 | 1,500 |
| from Ocean | 442 | 600 | 1,300 | 1,360 | 400 | 310 | 2,040 |
| **Secondary Emissions** | **3,201** | **3,400** | **2,090** | **2,480** | **3,900** | **4,010** | **3,560** |
| from land | 1,665 | 2,000 | 790 | 1,220 | 1,500 | 1,500 | 600 |
| from ocean | 1,536 | 1,400 | 1,300 | 1,260 | 2,400 | 2,510 | 2,960 |
| **Total Emissions** | **6,411** | **9,000** | **6,600** | **7,020-7,650** | **7,000** | **7,000** | **10,500** |

| | Anthropogenic | Natural | Secondary |
|---|---|---|---|
| **Mean** | 2,735(787) | 1,752(972) | 3,234(714) |
| **Total** | **7,752(1653) t/y** | | |

# Background Hg Trend



# Objectives

- Review the micro-meteorological and enclosure methods for quantifying $Hg^0$ air-surface exchange
- Compare the characteristics of Hg exchange fluxes measured by different methods
- Evaluate the uncertainty of each flux quantification method

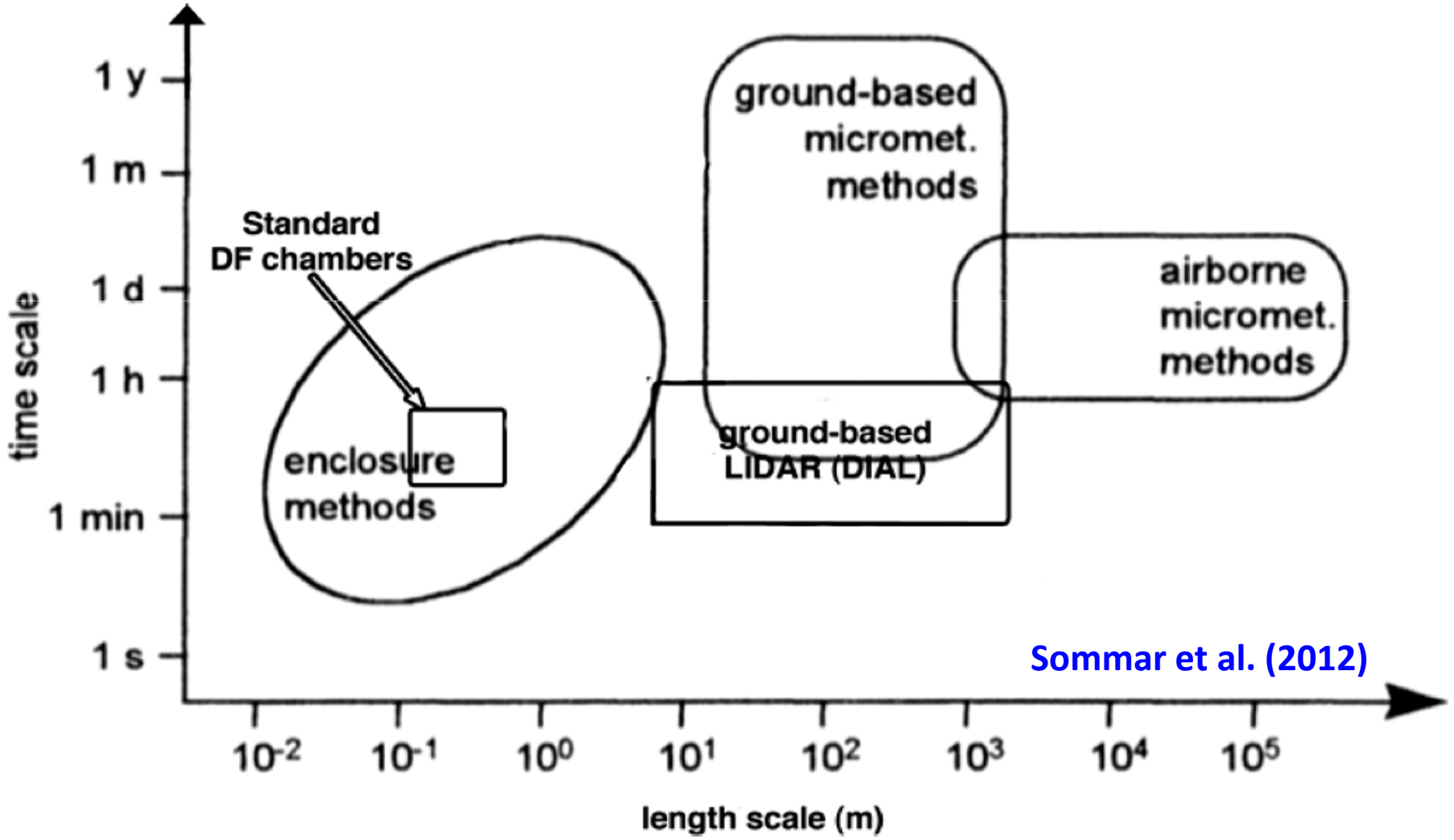
# Flux Measurement Approaches

- **Enclosure methods**
  - Static flux chamber
  - Flow-through (dynamic) flux chamber
- **Flux gradient methods**
  - Modified Bowen ratio
  - Aerodynamic gradient
- **Relaxed eddy accumulation (REA) method**
- **Differential absorption LIDAR**
- **Eddy covariance method (EC) ???**

# Quick Comparison

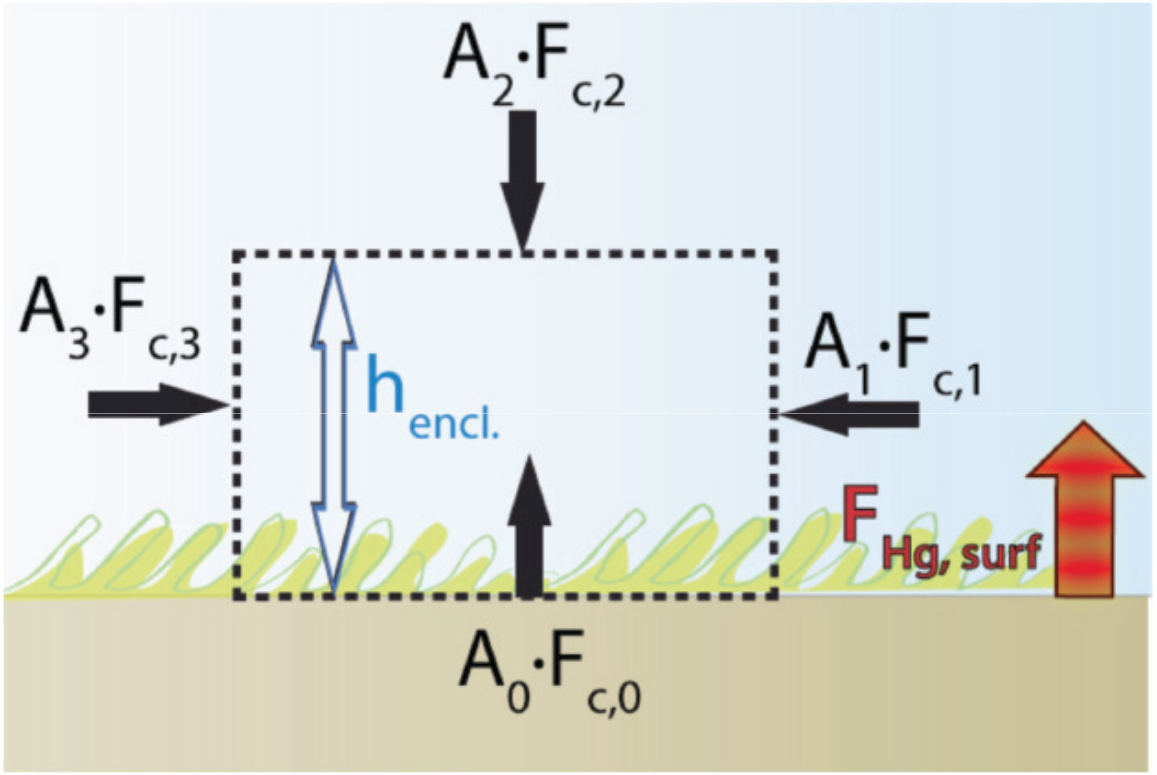
| | Enclosure methods | Flux-gradient methods | Relaxed eddy accumulation | Differential absorption LIDAR |
|---|---|---|---|---|
| **Sampling frequency** | Typically 5 min | 10–20 Hz | 10–20 Hz | 20 Hz |
| **Flux time resolution** | 10–20 min | 20–60 min | 10–30 min | ~ 60 min |
| **Requirements** | Tight seal to surface plot<br>Uniform flow over surface | Scalar similarity<br>Ratio of sampling heights | Constant sampling<br>Precise instrumental synchronization | Method sensitivity<br>Accurate measurement of vertical winds |
| **Restrictions in application** | Limited use for flux estimate of large area | Turbulent conditions<br>Difficult to apply on tall vegetation<br>Sufficient footprint area | Turbulent conditions<br>Sufficient footprint area<br>Scalar similarity | Restricted to point, line or small, well-defined strong areal sources |
| **Gas sampling & analytical system** | Chambers can potentially be operated using battery power | Analyzers need high precision, robust samples are required with sequential sampling at different heights to avoid the effect of tube dead volumes | Analyzers need high precision and high level of synchronization | Require high-power, narrow-bandwidth tunable lasers |
| **Weaknesses** | 1. Modification of microclimate.<br>2. Perturbations to gas concentration gradients and diffusion<br>3. Potential alteration to exchange process | 1. Relying on measurements of often small gradients<br>2. Different footprints for various sensor heights<br>3. Not applicable for low $u*$<br>4. Function of anemometer sensitive to rain | 1. Potential bias caused by low turbulence<br>2. Pressure/flow fluctu-ations in sampling system<br>3. Function of anemometer sensitive to rain | 1. Complex and bulky<br>2. Labor-intensive construction and operation<br>3. Interference from other trace gases |

# Time and Spatial Scales



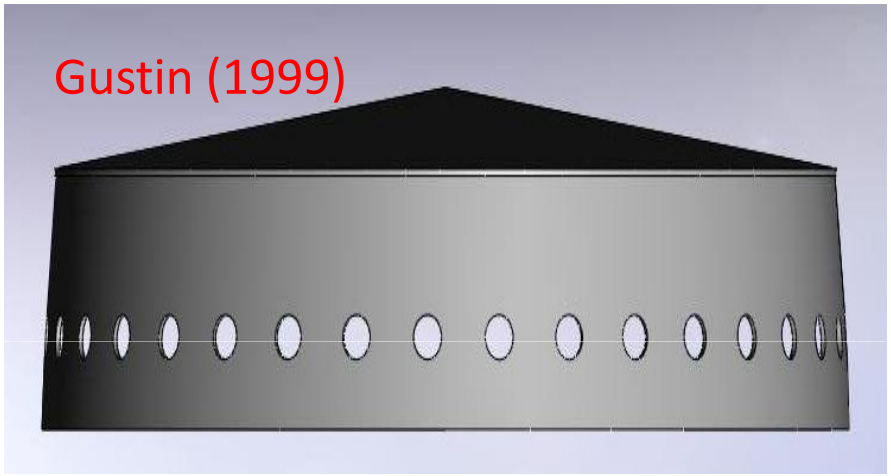

Sommar et al. (2012)

# Chamber Methods




$$V\frac{\partial}{\partial t}\langle C_{Hg}\rangle = \sum_{i=0}^{m} A_i \cdot F_{Hg,i}$$

# Dynamic Flux Chambers





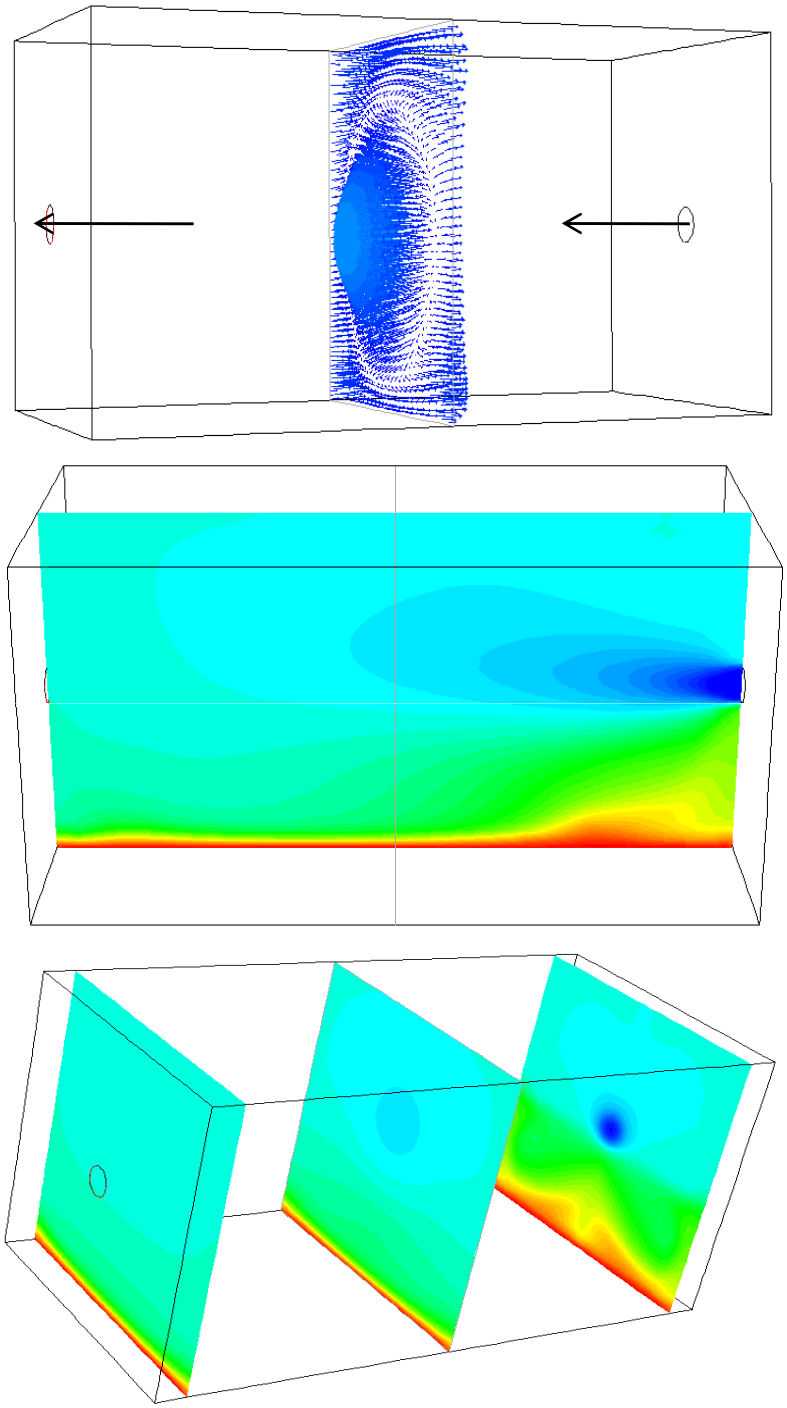


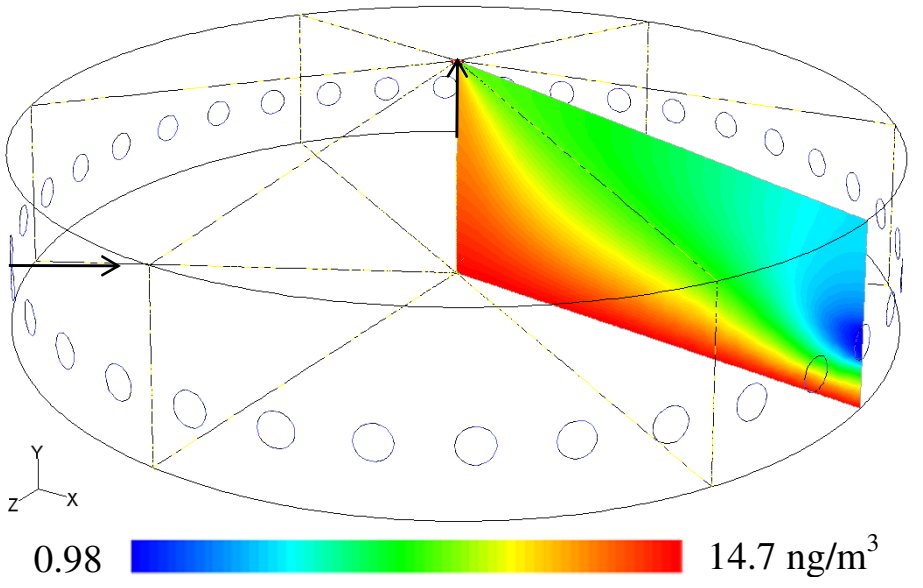
$$F_{Hg,\,surface} \cong \frac{Q}{A_0} \cdot \left(C_{Hg,out} - C_{Hg,in} - blank\right)$$

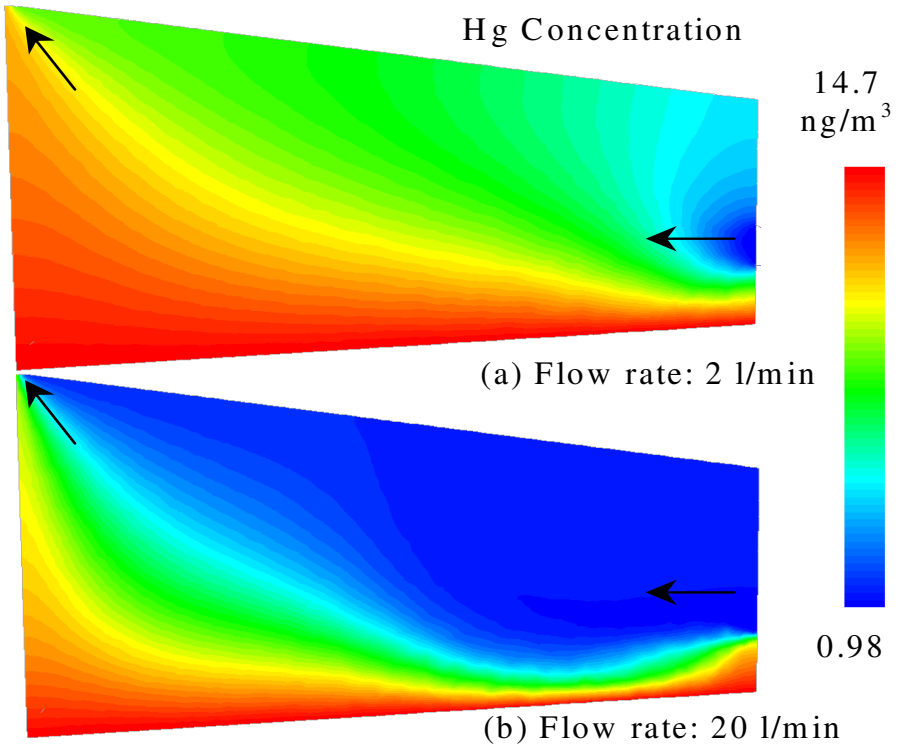
# Chamber Methods

| Area ($m^2$) | Volume (l) | Flow (l $min^{-1}$) (TOT—min) | Chamber material | Hg flux mean ± $\sigma$ (ng $m^{-2}$ $h^{-1}$) | Reference |
|---|---|---|---|---|---|
| 0.073 | 11.2 | 1.5 (7.5) | Polycarbonate | 0.4 ± 0.5 | Kuiken et al., 2008 |
| 0.13 | 10 | 1.5 (6.7) | Stainless steel/Teflon | 3.0 ± 2.2 | Poissant and Casimir, 1998 |
| 0.067 | 9.3 | 1.5 (6.2) | Polycarbonate | 5.69 ± 5.79 | Gabriel and Williamson, 2008 |
| 0.03 | 2.2 | 1.5 (1.5) | Teflon | Range: ~0–45[b] | Zhang et al., 2008 |
| 0.036 | 1.5 | 1.5 (1) | Polycarbonate | 2.1 | Ericksen and Gustin, 2006 |
| 0.13 | 25 | 1.8 (13.9) | Teflon | 200 ± 90 | He et al., 1998 |
| 0.16 | 32 | 2.0 (16) | Stainless steel | 1.4 ± 0.5[a] | Schroeder et al., 1989 |
| 0.063 | 3 | 2.31 (1.3) | Polycarbonate | Range: 0.7–35 | Eckley and Branfireun, 2008 |
| 0.12 | 24 | 3.2 (7.5) | Acrylic | 0.4 ± 0.4 | Magarelli and Fostier, 2005 |
| 0.12 | 24 | 5 (4.8) | Teflon | 2.7 ± 0.5 | Carpi and Lindberg, 1998 |
| 0.12 | 24 | 6 (4) | Plexiglass | 0.1–44.0 | Ferrara and Mazzolai, 1998 |
| 0.12 | 24 | 6 (4) | Teflon | 1.4 ± 1.4 | Zhang et al., 2001 |
| 0.031 | 1 | 6.5 (0.15) | Polycarbonate | 2.0 ± 4.1 | Nacht and Gustin, 2004 |
| NA | 2 | 6.7 (0.3) | Polycarbonate | Range: <1–70 | Gustin and Stamenkovic, 2005 |
| 0.031 | 1 | 10 (0.1) | Polycarbonate | Range: 0–27,600[c] | Engle et al., 2001 |
| 0.06 | 4.7 | 15 (0.31) | Quartz | 862 ± 807 | Wang et al., 2005 |

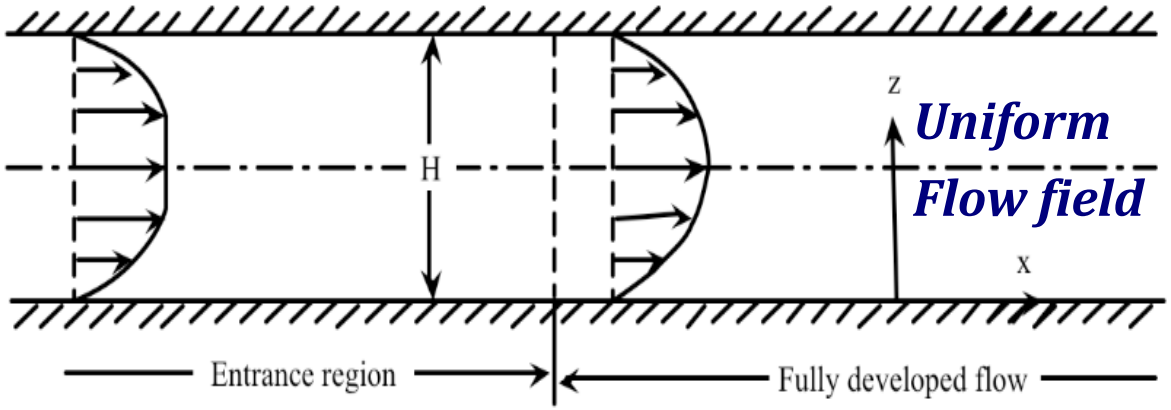
Eckley et al. (2010)




Y
Z
X
0.98
14.7 ng/m3


Hg Concentration
14.7
ng/m3
0.98
(a) Flow rate: 2 l/min
(b) Flow rate: 20 l/min

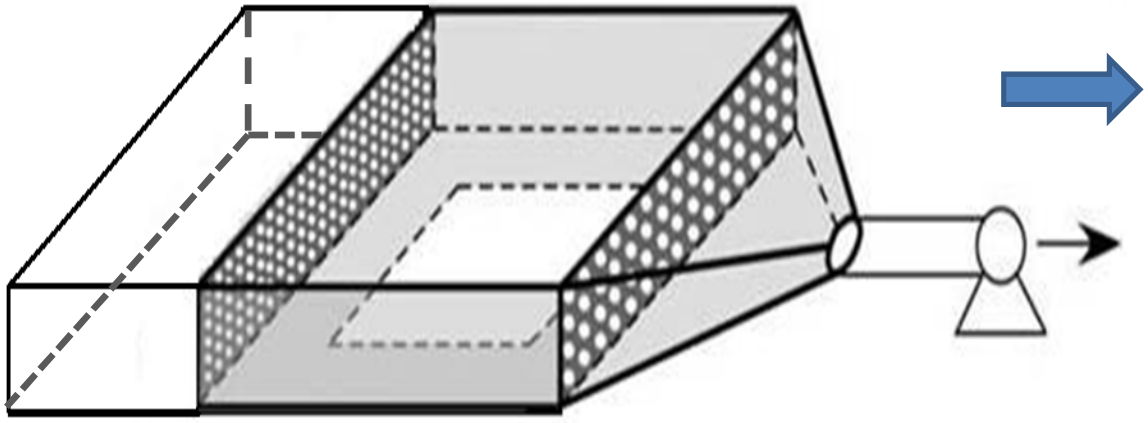
# DFC with Turbulence Correction

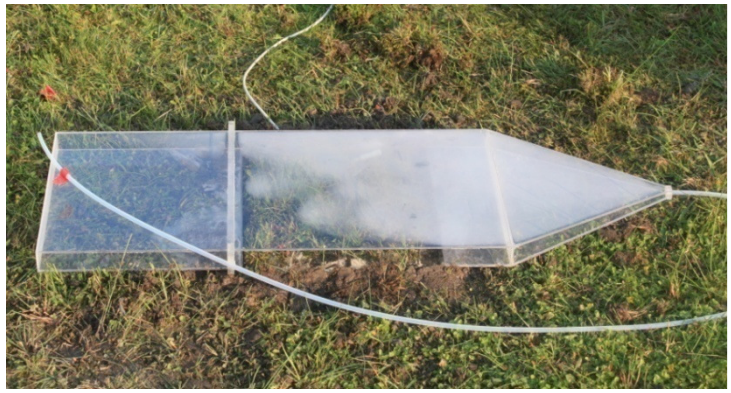



$$\frac{\partial}{\partial x_i}(\rho u_i) = 0 \qquad (1)$$

$$\frac{\partial}{\partial x_i}(\rho u_i u_j) = \rho \bar{g}_j - \frac{\partial P}{\partial x_j} + \frac{\partial}{\partial x_i}\left(\mu \frac{\partial u_j}{\partial x_i}\right) \qquad (2)$$

$$\frac{\partial}{\partial x_i}(\rho u_i C_j) = \frac{\partial}{\partial x_i}\left(\rho D_j \frac{\partial C_j}{\partial x_i}\right) \qquad (3)$$





$$F_a = F_m \frac{k_{mass\,(a)}}{k_{mass\,(m)}} = \frac{Q(\Delta C)}{A} \frac{k_{mass\,(a)}}{k_{mass\,(m)}}$$

Lin et al. (2012)

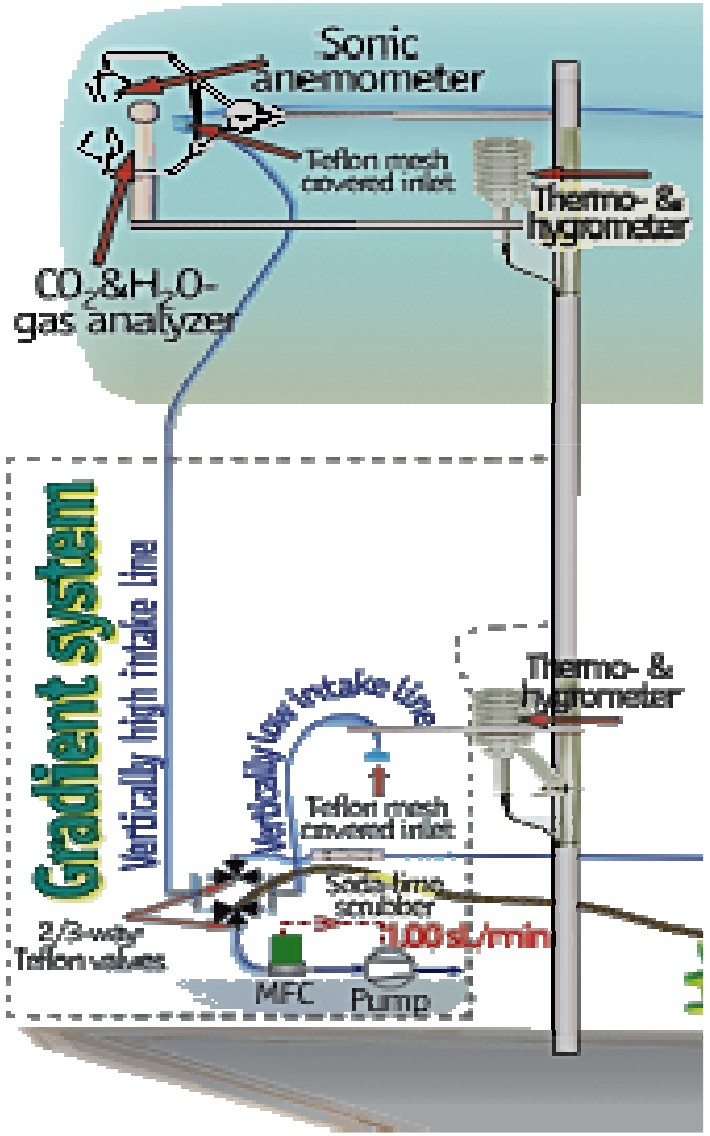
# Flux Gradient Methods

## Aerodynamic gradient (AGM) method

$$F = -K\frac{\partial C}{\partial z} \approx \frac{u_* \kappa \left(C_2 - C_1\right)}{\ln\left[\frac{z_2 - d}{z_1 - d}\right] - \Psi_{h2} + \Psi_{h1}}$$

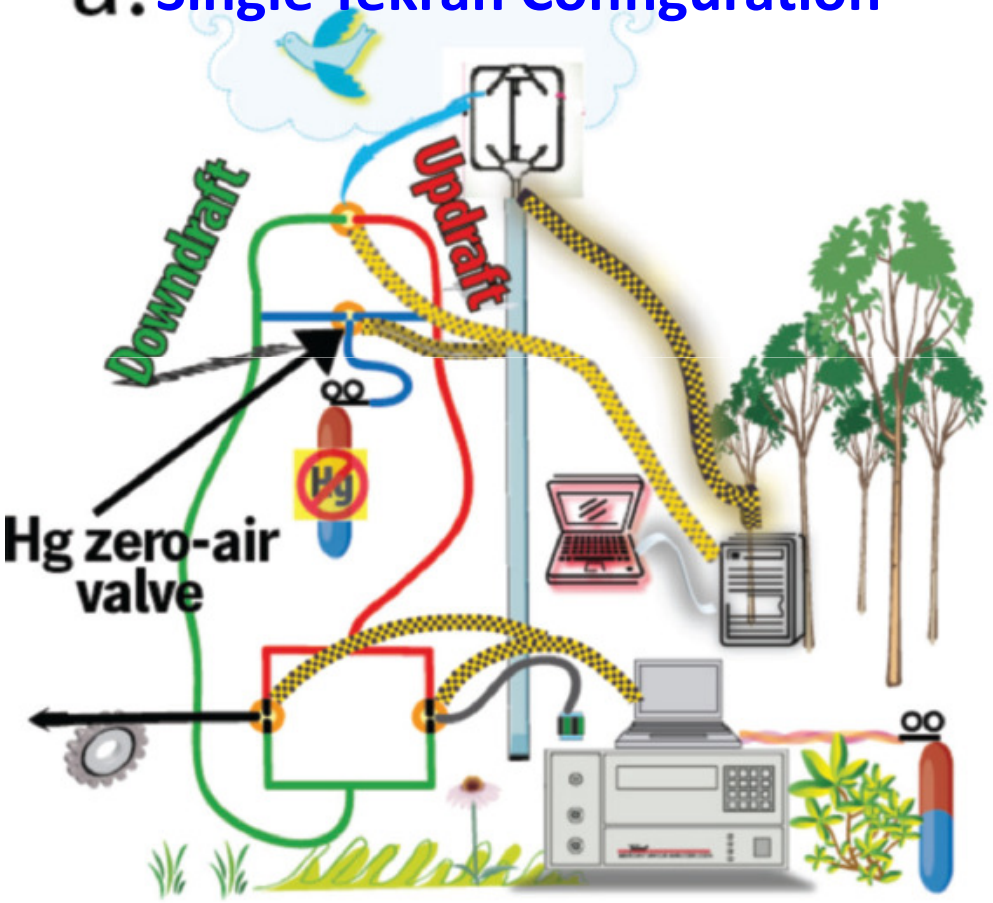
## Modified Bowen-ratio (MBR) method

$$F_{Hg} = \frac{\overline{w'\chi'}}{\Delta\bar{\chi}}\Delta\overline{C_{Hg}}$$

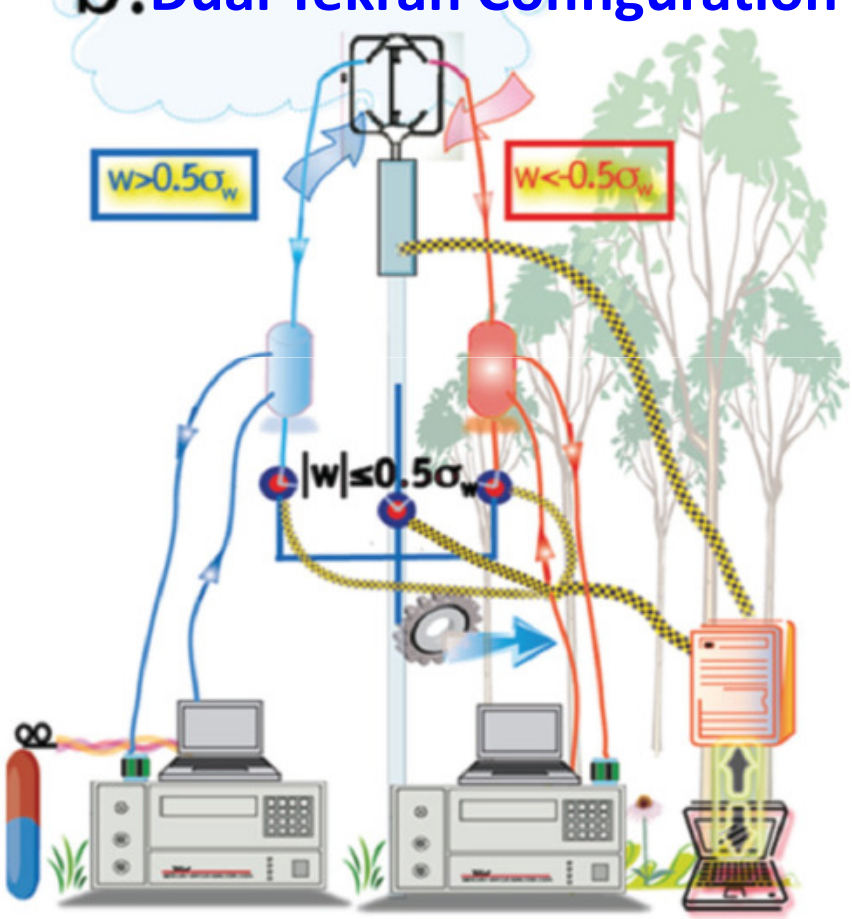


# Relaxed Eddy Accumulation Method

a. Single Tekran Configuration

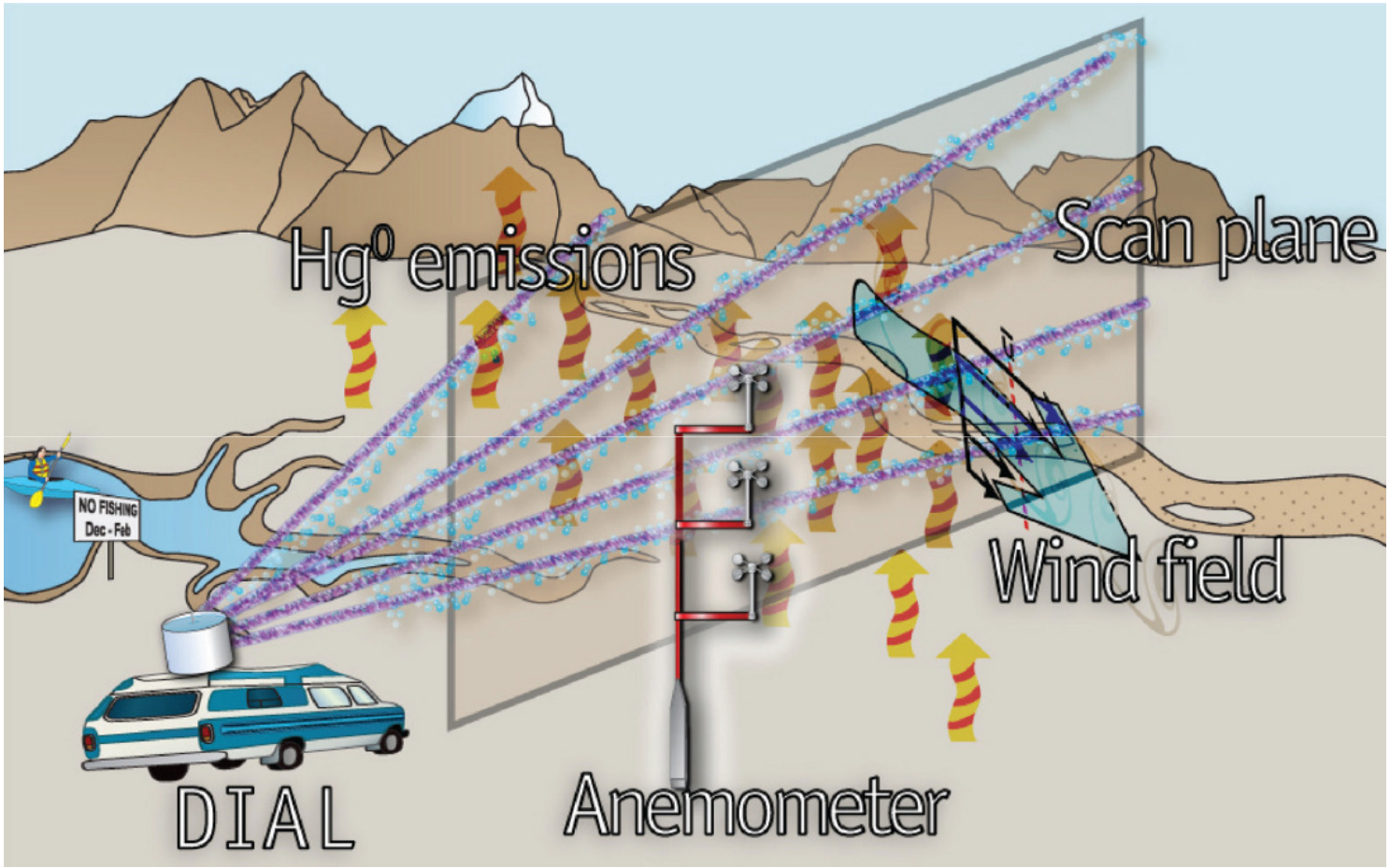



b. Dual Tekran Configuration



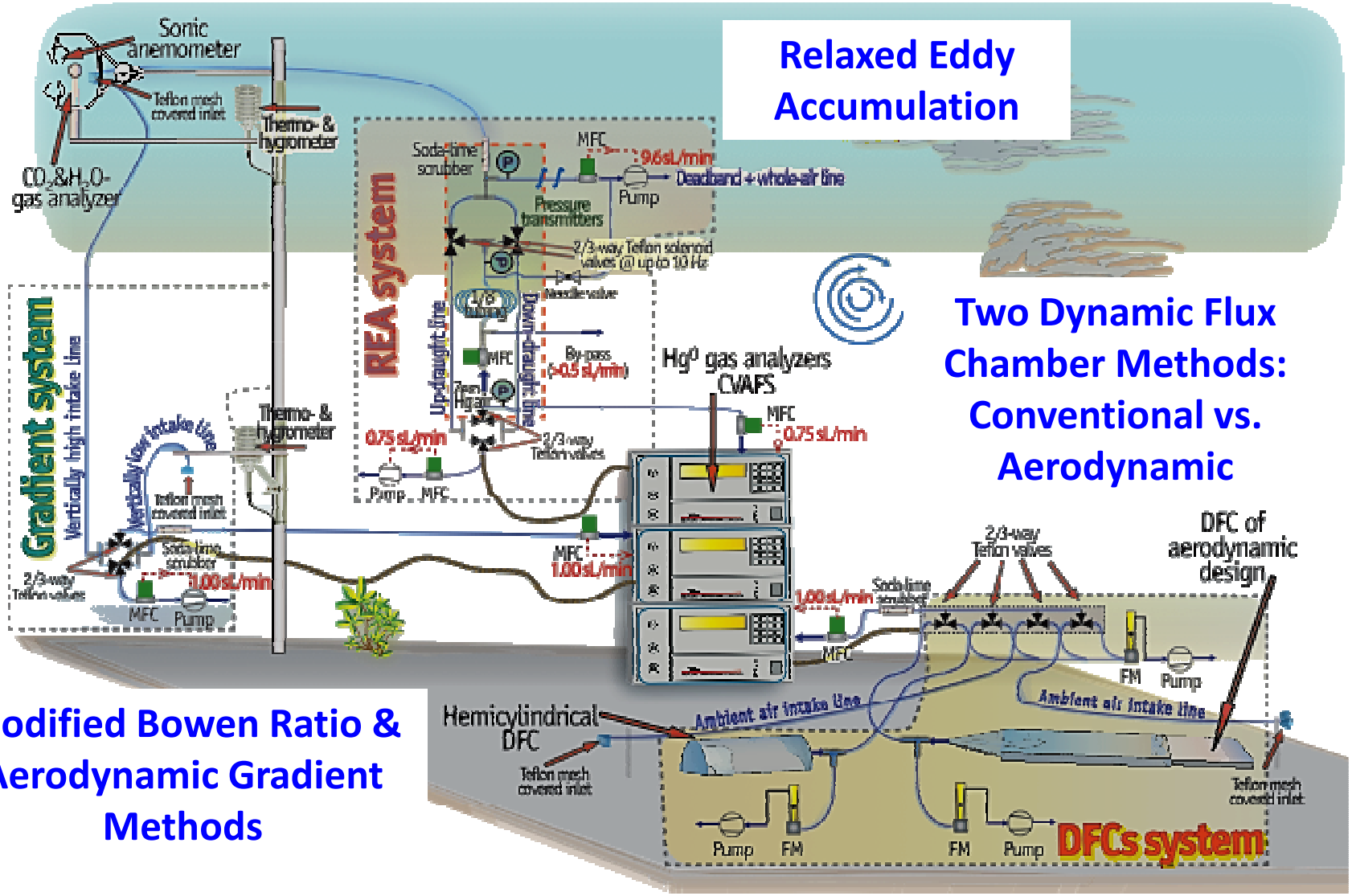

$$F_{GEM} = \beta_\chi \sigma_w \left( \overline{C\uparrow} - \overline{C\downarrow} \right)$$

# Differential LIDAR Method

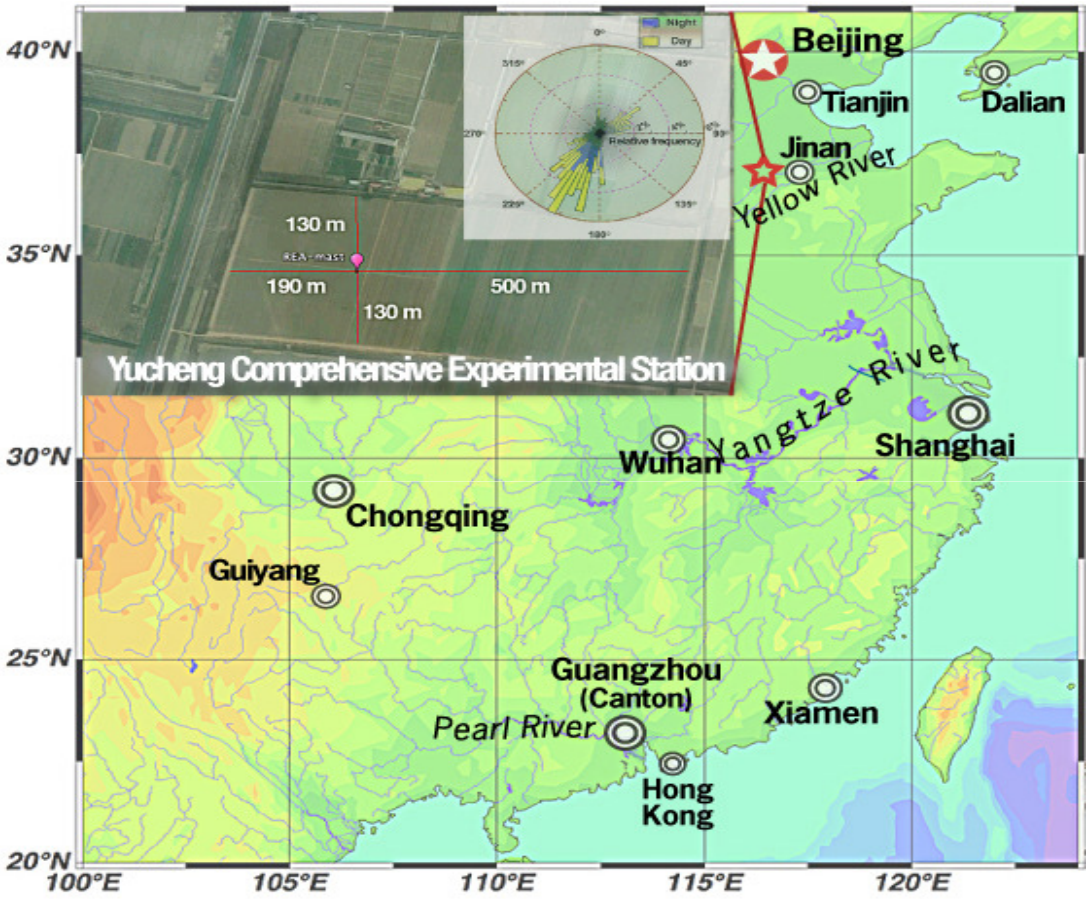



$$F_{Hg} = \frac{1}{\Delta t} \int_{\Delta t} w(t) C_{Hg}\, dt$$

# 5 Collocated Flux Measurements



# Field Measurement Site




- Wheat-corn agricultural field
- Flat surface
- Homogeneous soil THg

**Two Campaigns:**

- Autumn 2012 over bear soils
- Spring 2013 over canopy

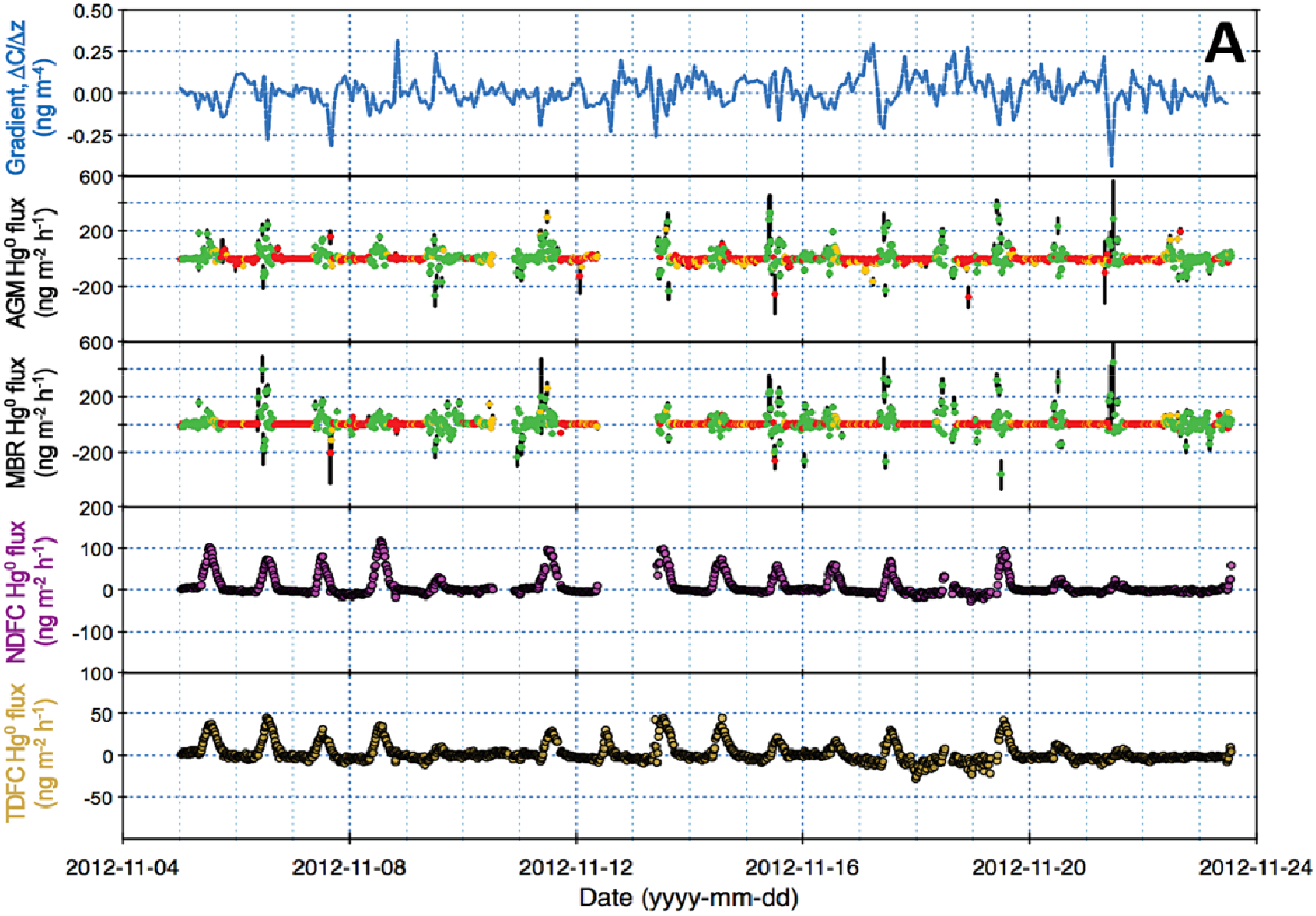
| Samples | Total mercury (HgT, μg $kg^{-1}$) | | | |
|---|---|---|---|---|
| | Minimum | Maximum | Mean | Std. dev |
| Surface soils (n=27) | 39 | 52 | 45 | 3.9 |

# Site Views

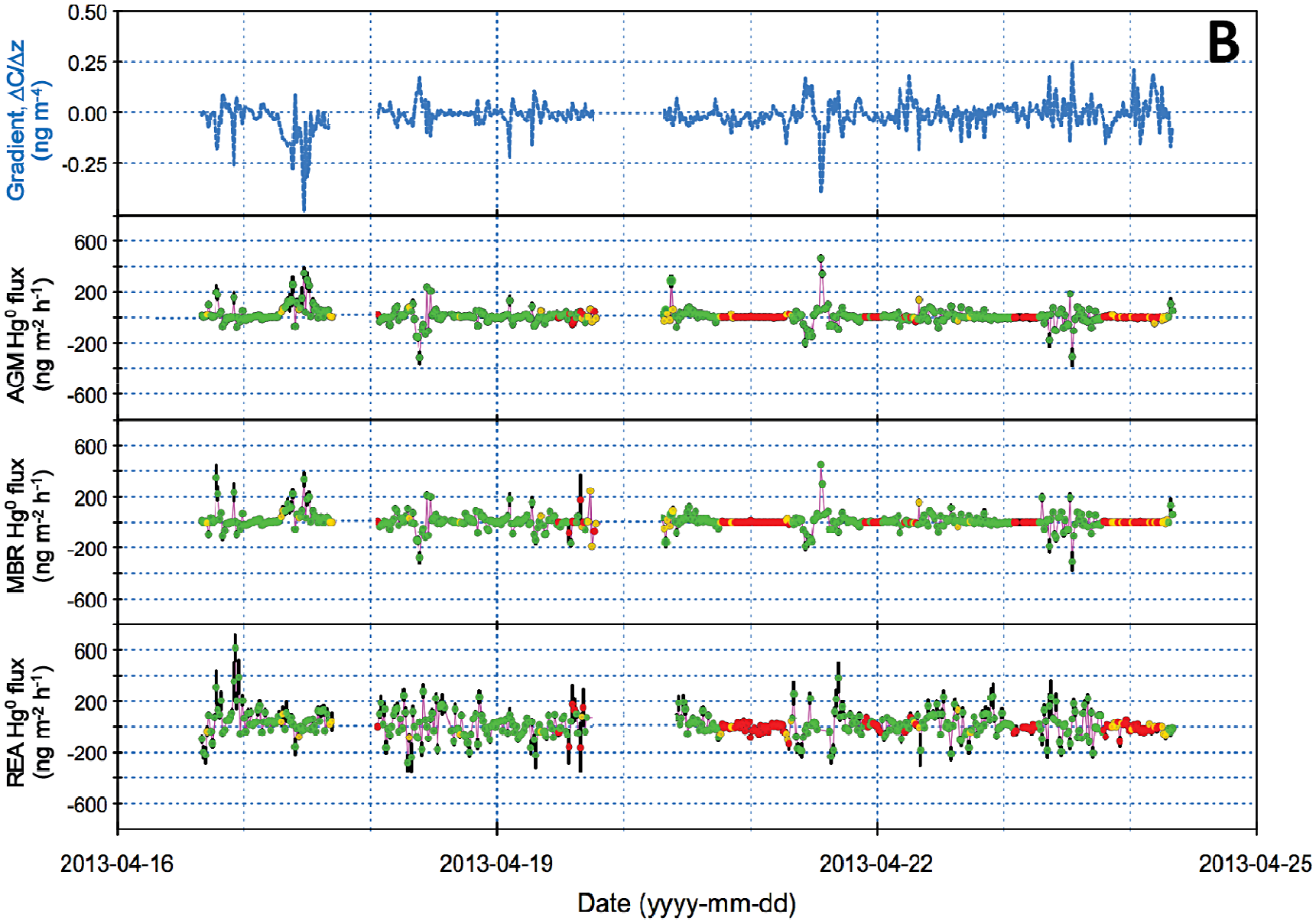




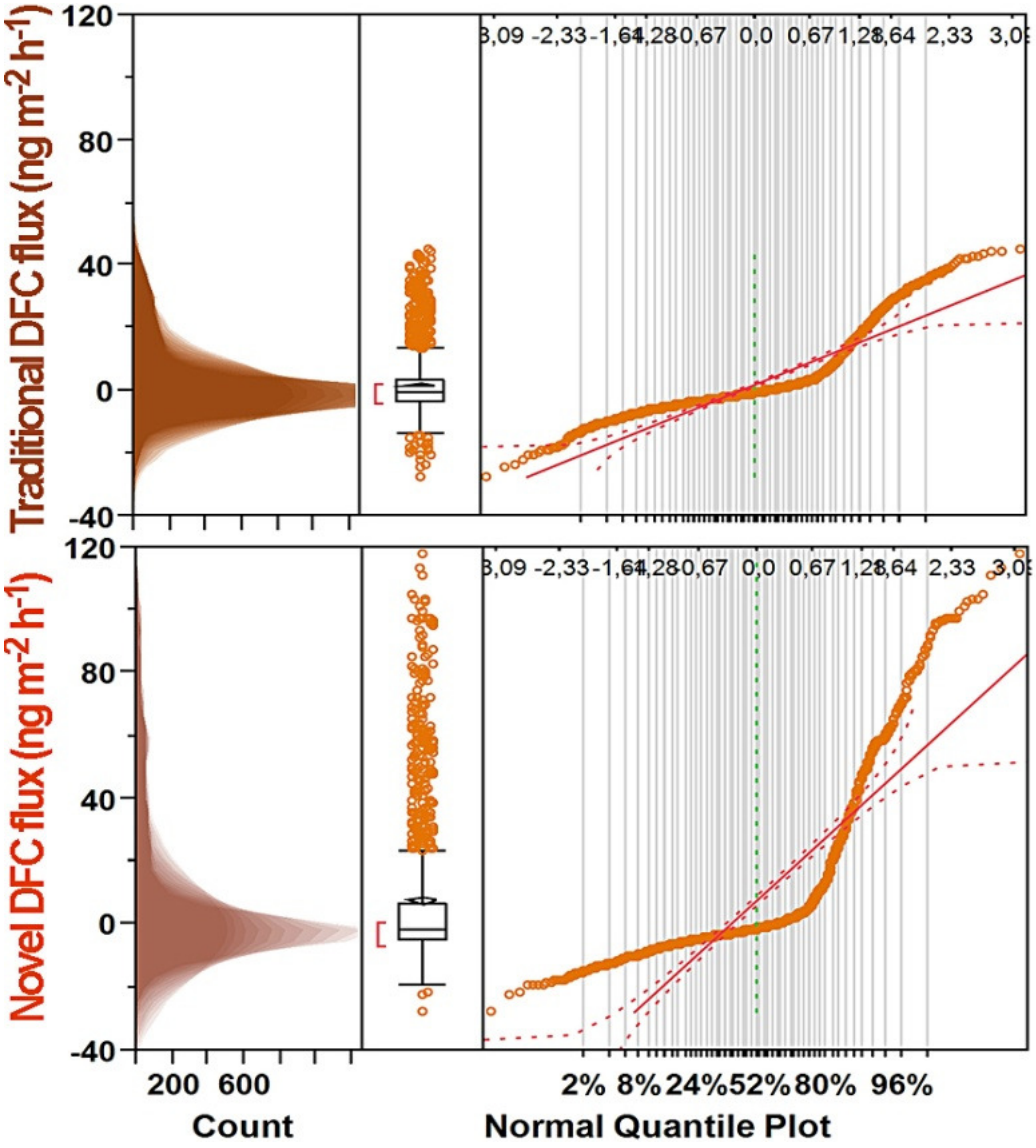
# Flux Over Soil

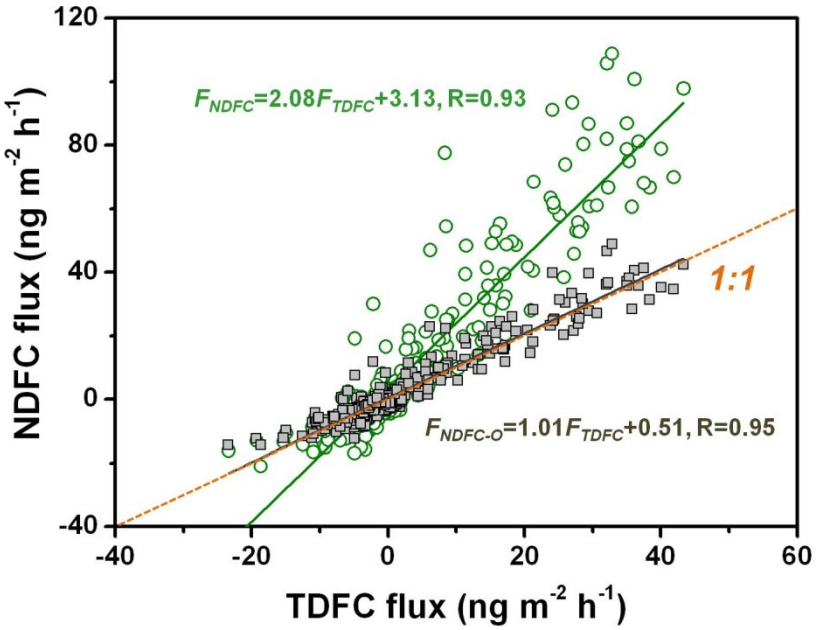


# Flux Over Wheat Canopy



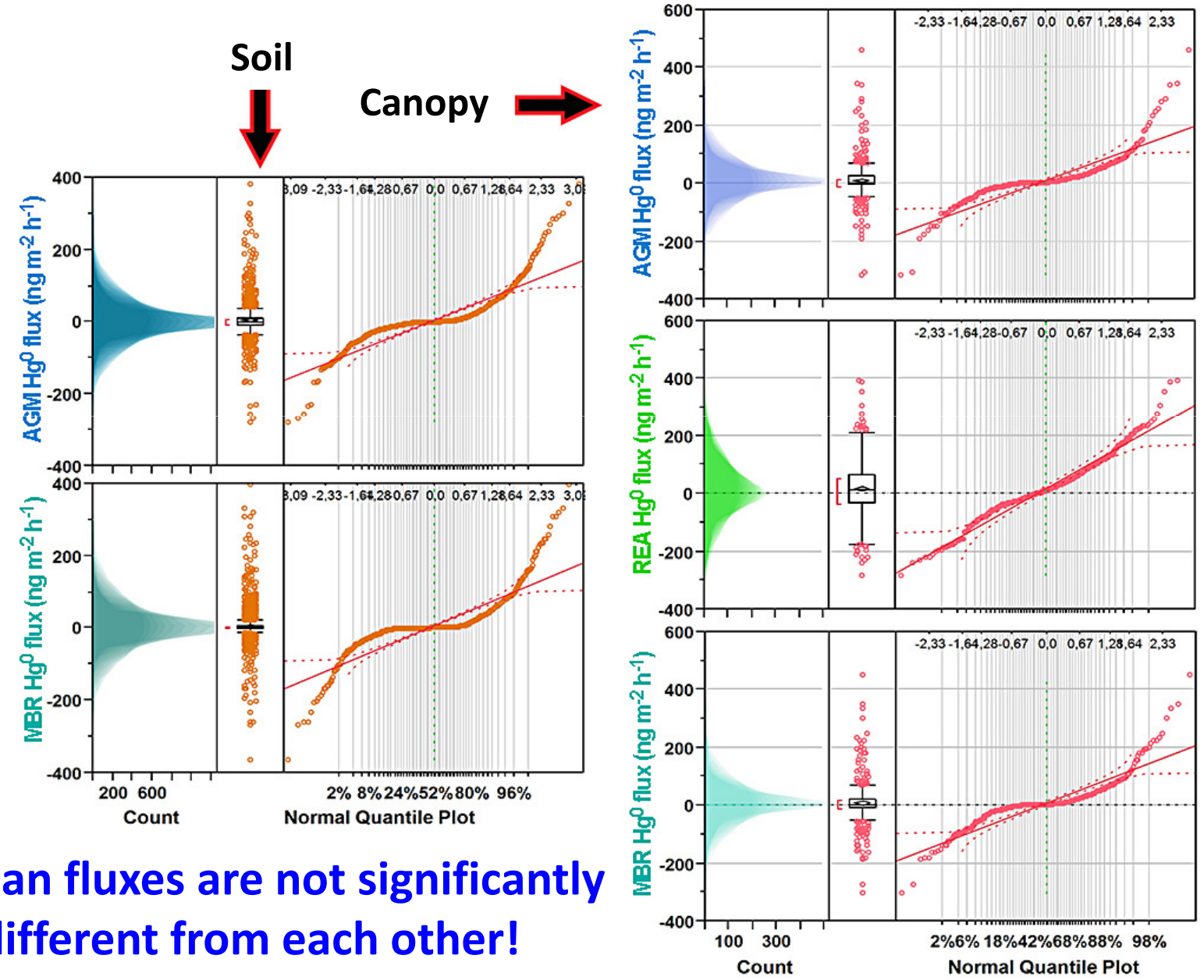
# Comparison of DFC Fluxes



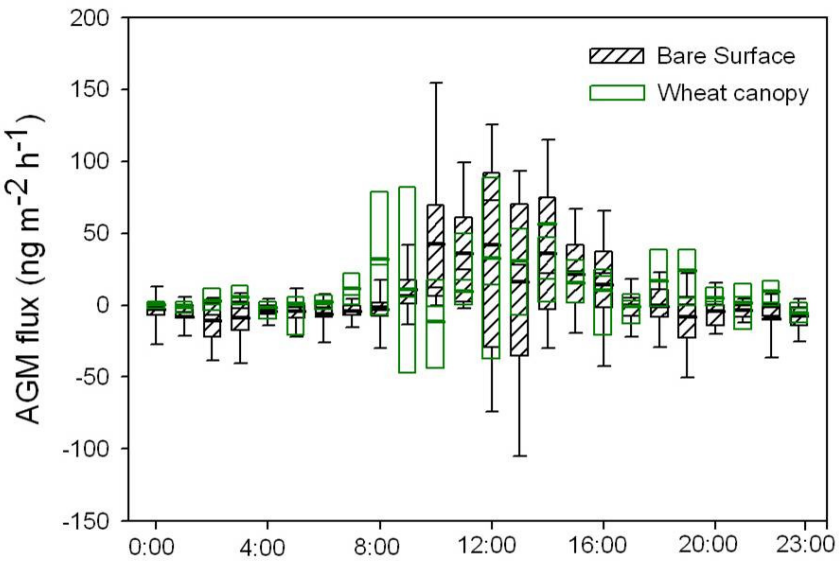

**Correction of mass transfer coefficient changes flux magnitude by 25-100% depending on friction velocity.**

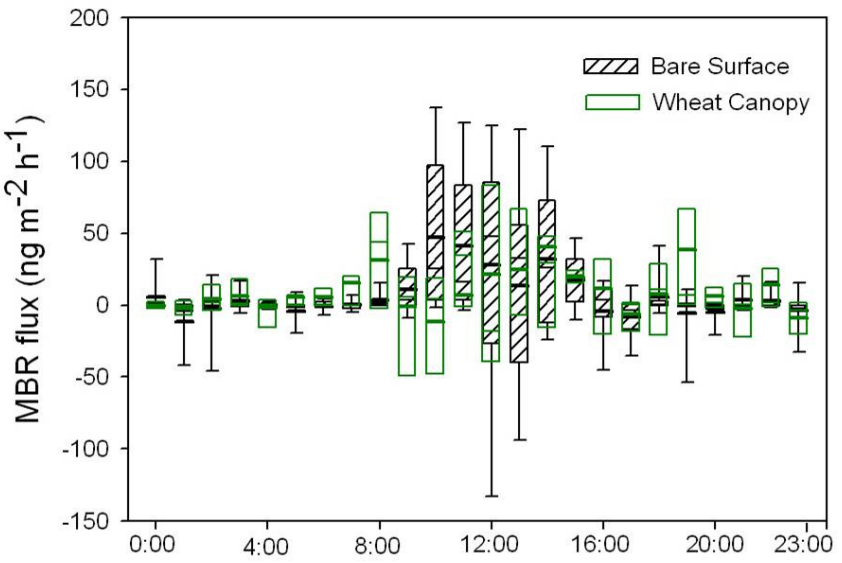
# Comparison of Micromet Fluxes

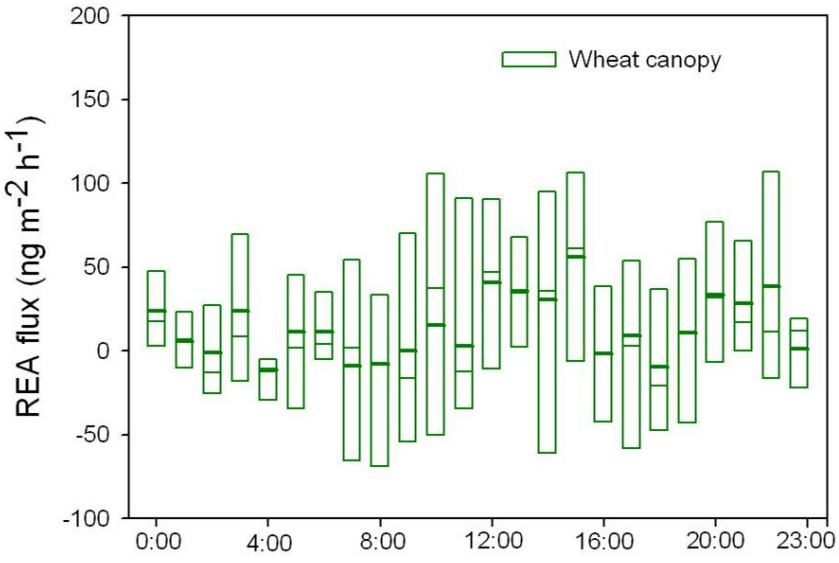


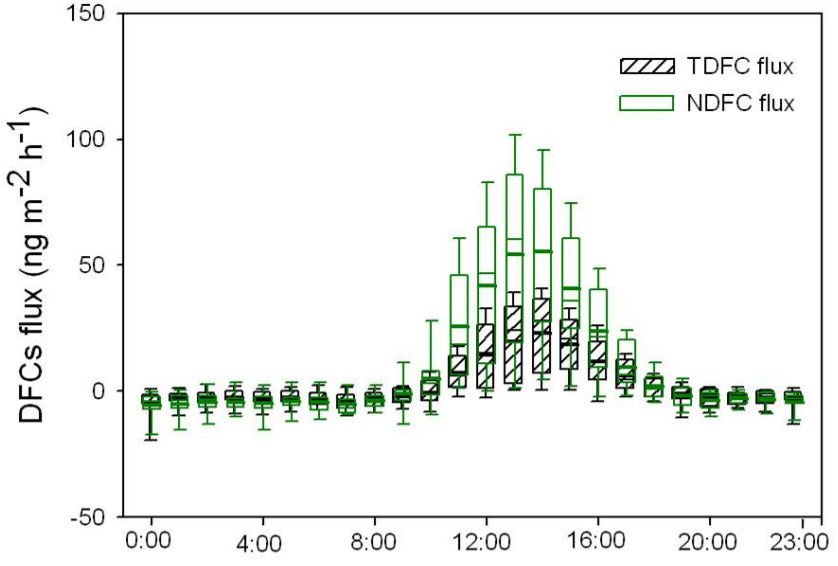

**Median fluxes are not significantly different from each other!**

# Flux Diurnal Variation

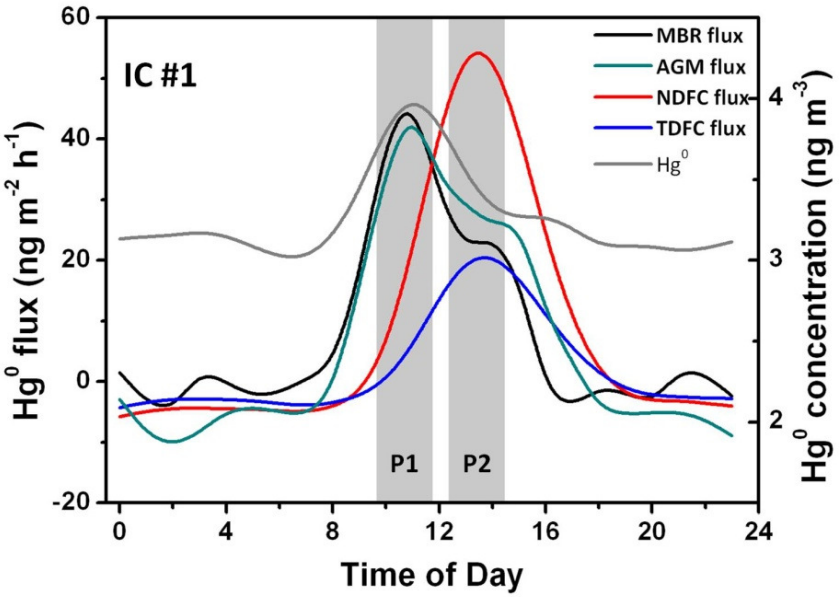


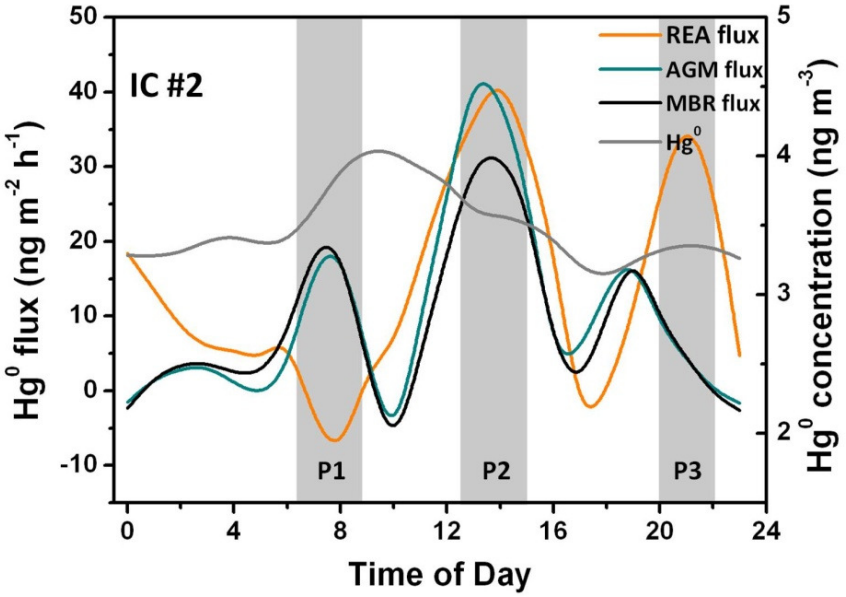



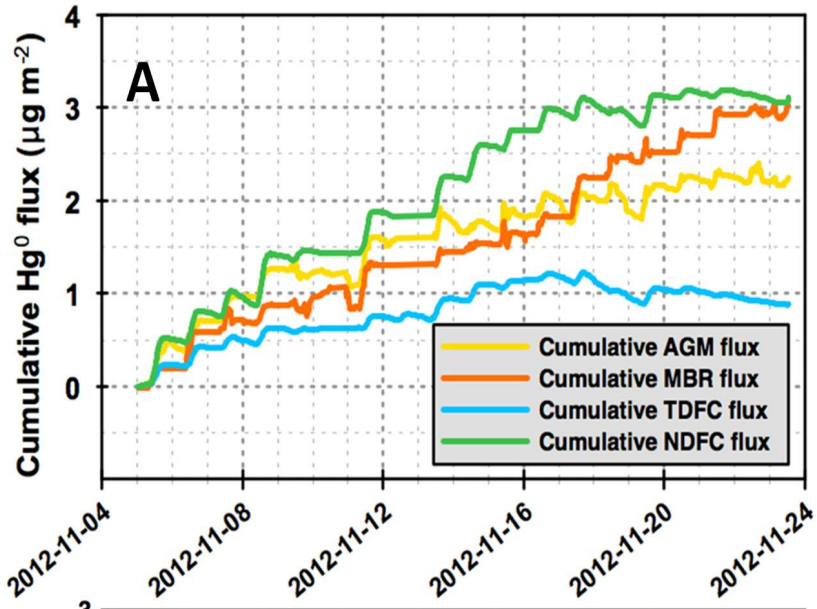



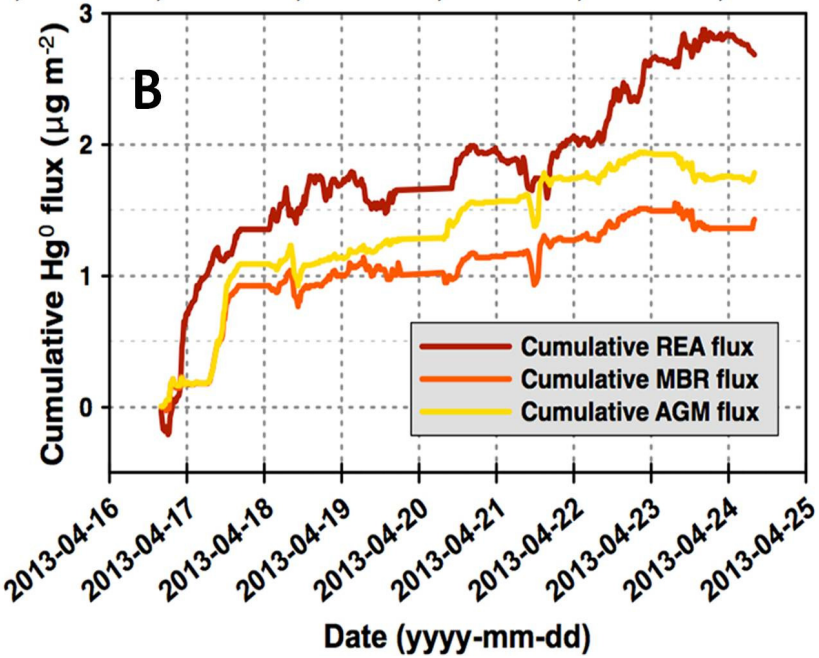



# Temporal Trend & Cumulative Flux

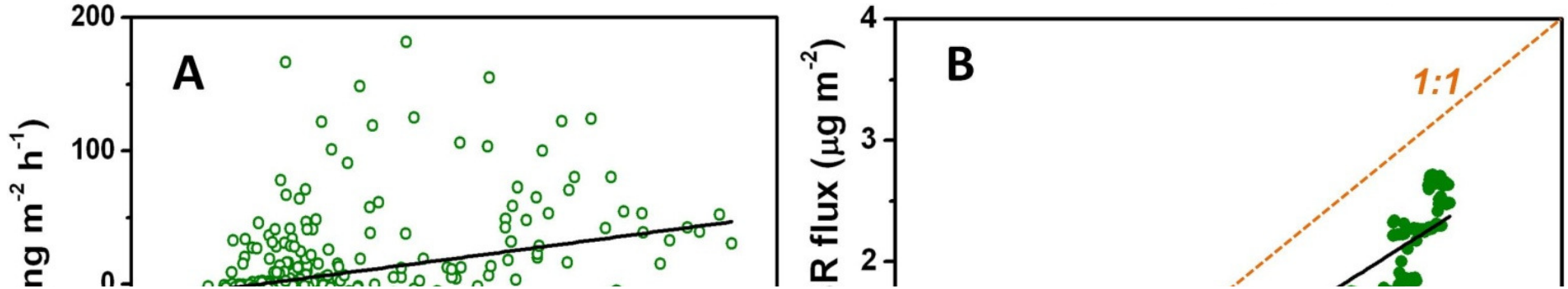


# Close Enough, But …



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