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Insights into elemental mercury air-sea exchange from long-term ground-based observations

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Motivation

Role of Hg^0 air-sea exchange in the Hg biogeochemical cycle:

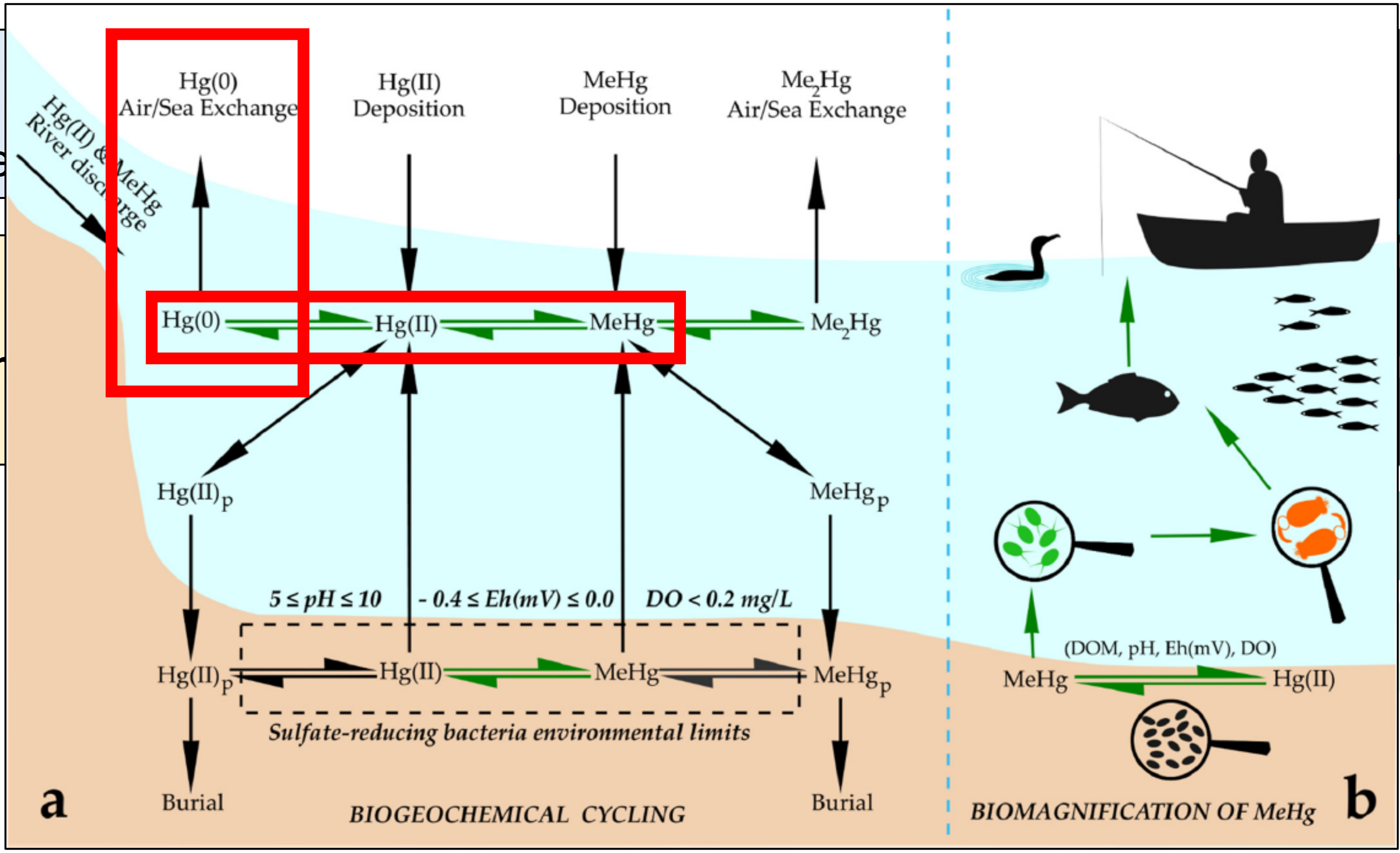
- Influences distribution of dissolved Hg in the ocean.
- Reduces the pool of available Hg^{II} for methylation.

Challenges:

- Sparsity in direct measurements in the air-sea inte

Main goal:

- Study Hg^0 air-sea exchange using **long-term, atm based monitoring sites.**

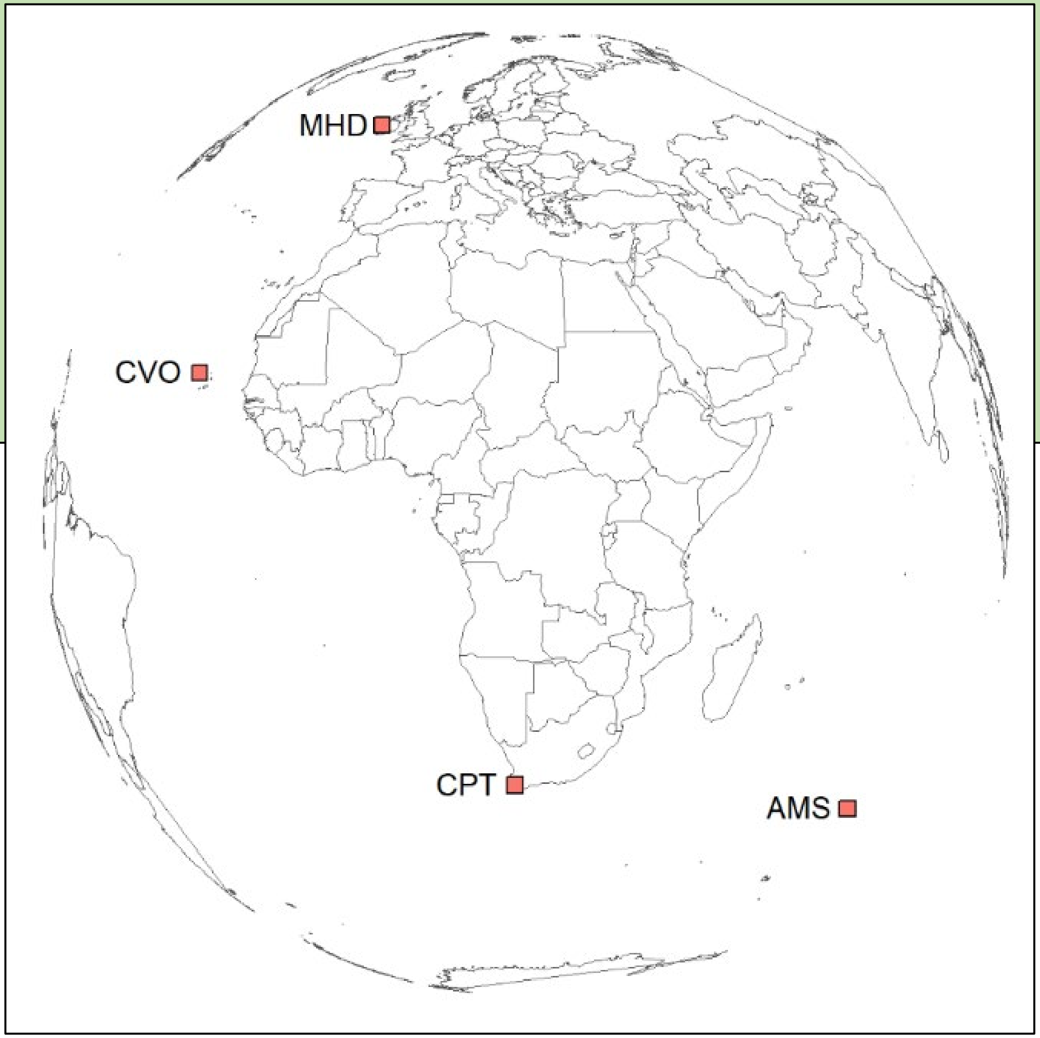


Adapted from Gojkovic et al. (2022)

Long-term, ground-based Hg^0_{air}* measurements

Hourly Hg^0_{air} measurements at:

- Mace Head (MHD): 1996 – 2020
- Cape Verde Observatory (CVO): 2011 – 2015
- Cape Point (CPT): 2007 – 2017
- Amsterdam Island (AMS): 2012 – 2020



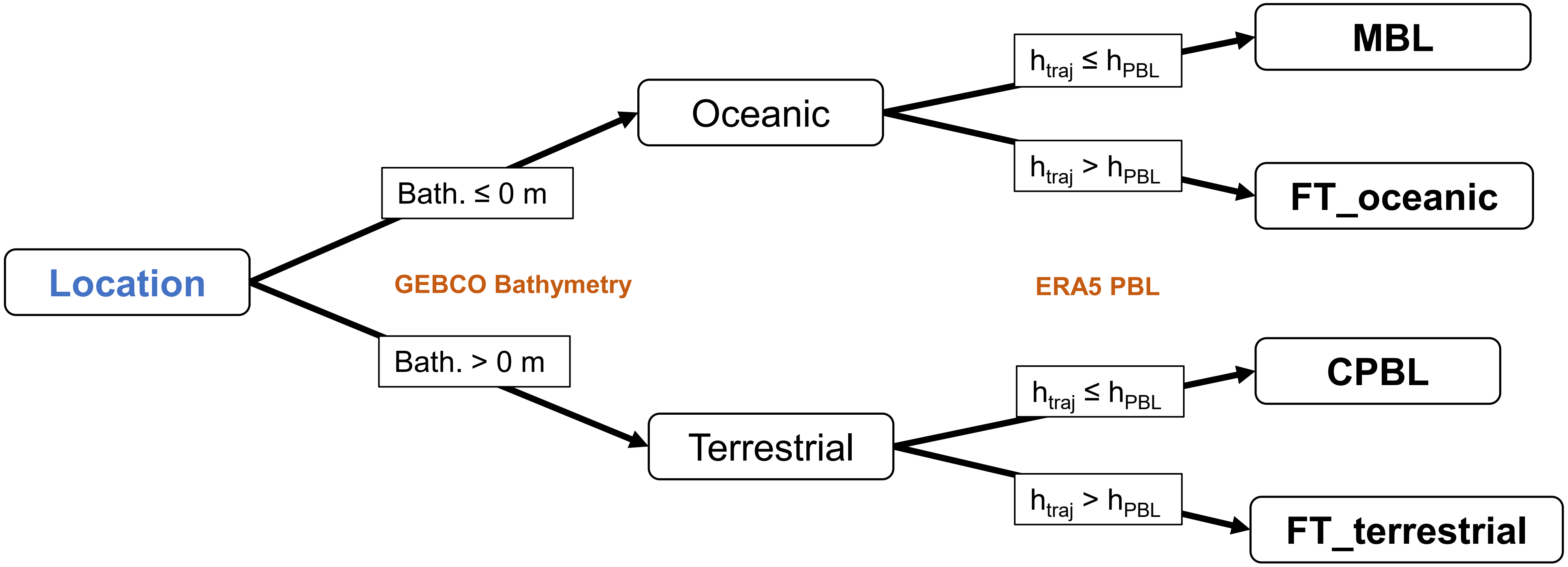
Methodological framework

Hourly Hg^0_{air} measurements at:

- Mace Head (MHD): 1996 – 2020
- Cape Verde Observatory (CVO): 2011 – 2015
- Cape Point (CPT): 2007 – 2017
- Amsterdam Island (AMS): 2012 – 2020

HYSPLIT back trajectories:

- 144-hour (6-day) back trajectory for every Hg^0_{air} observation
- Assign **location** of each trajectory segment



h_{traj} = height of trajectory segment

h_{PBL} = planetary boundary layer height

Hg^0_{air} cycling in the MBL

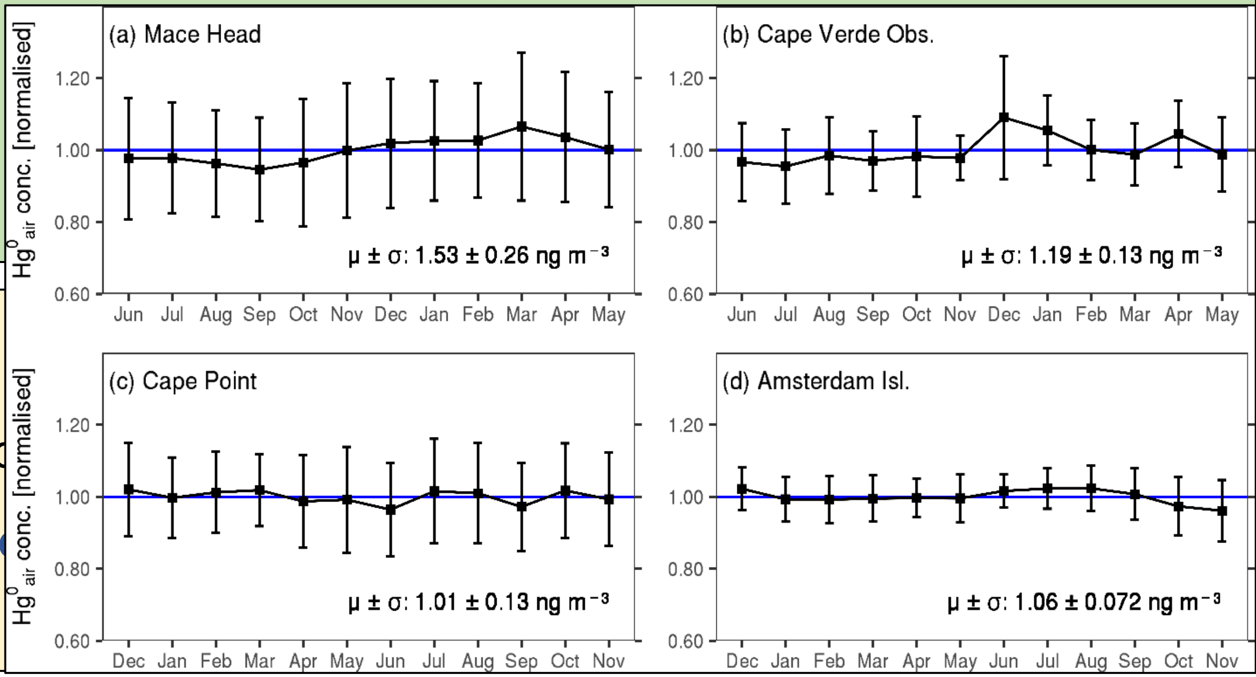
What we found:

I. Sites measure largely MBL air masses…

II. But seasonal and diurnal variation **weak.**

What the literature says:

- Hg^0 air-sea exchange a major process driving concentratio
- Exchange driven by surface ocean-atmosphere Hg^0 **conce**
- … and **wind speed** and **solar radiation**



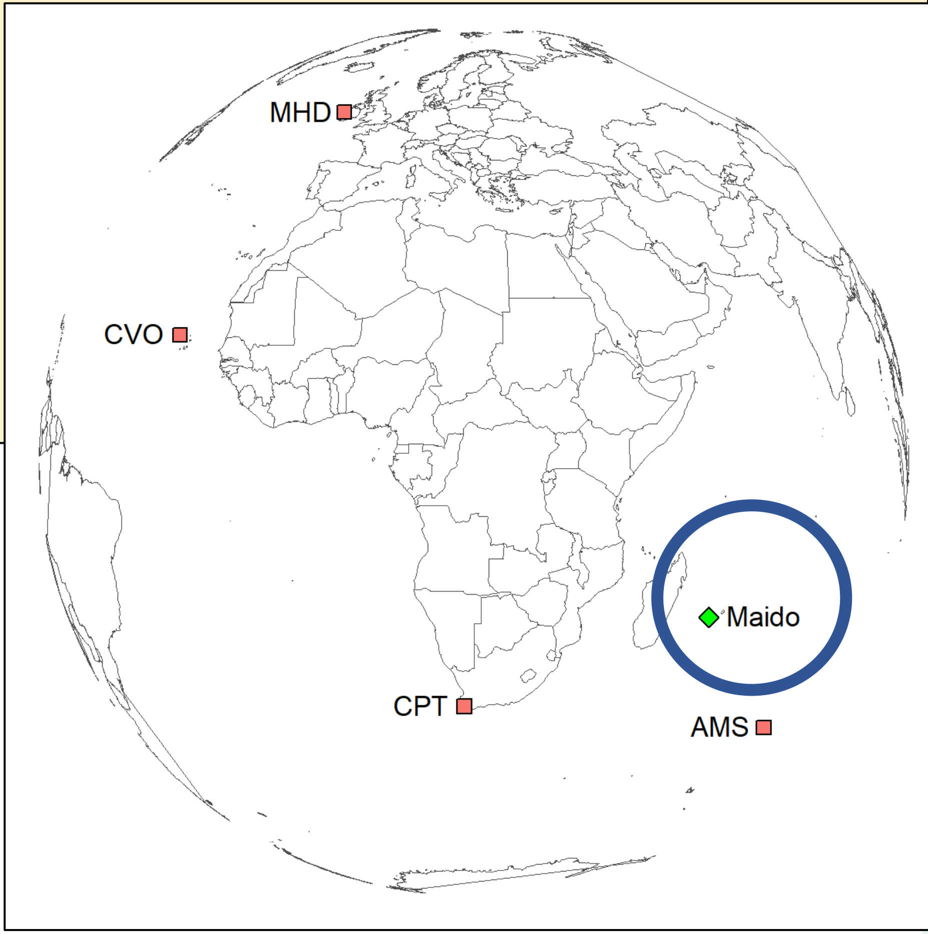
Why seasonal and diurnal variability weak??

Hg^0_{air} cycling in the MBL

More from the literature…:

- (L)FT Hg^0_{air} concentrations:
  - **0.73 ng m^{-3}** at Maïdo (Koenig et al., 2023).
  - **1.3 ng m^{-3}** over central Europe (Weigelt et al., 2016).

Site	MBL* Hg^0 concentration [ng m^{-3}]
MHD	1.53 ± 0.26
CVO	1.19 ± 0.11
CPT	1.01 ± 0.12
AMS	1.06 ± 0.07



MBL concentration: ≥ 90 % of traj. segments assigned as MBL

Hg^0_{air} cycling in the MBL

More from the literature…:

- (L)FT Hg^0_{air} concentrations:
  - ❖ **0.73 ng m^{-3}** at Maïdo (Koenig et al., 2023).
  - ❖ **1.3 ng m^{-3}** over central Europe (Weigelt et al., 2016).
- Most Hg^0_{aq} in the ocean produced by dark reduction (Lamborg et al., 2021).

Hypothesis:

- Air masses entering the MBL from the LFT carry a signature Hg^0 concentration of this environment.
- In the MBL, they exchange Hg^0 with surface ocean.
- Surface ocean supersaturated in Hg^0 → net emission to the atmosphere → gradual increase in the Hg^0 concentration of the air mass.

❖ **Air masses that have recently spent more time in the MBL have higher Hg^0_{air} concentration.**

Hg^0_{air} conc. vs air mass recent MBL time

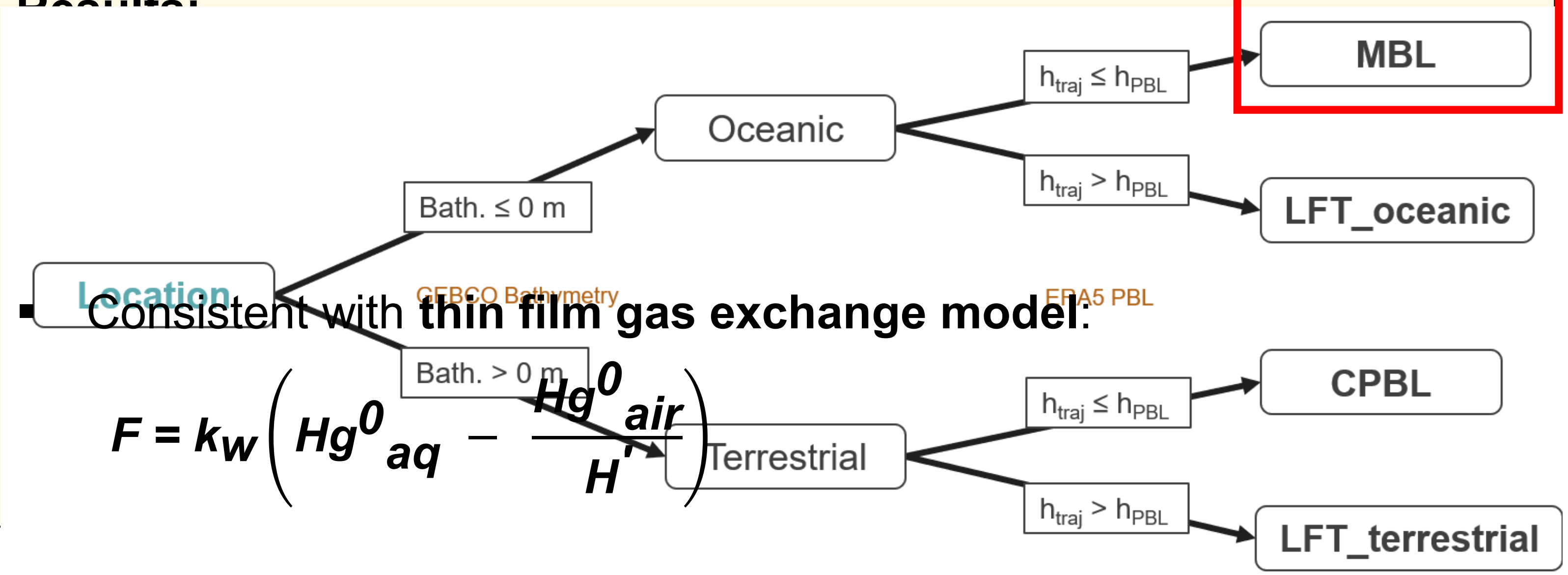
Hypothesis:

- …air masses that have recently spent more time in the MBL have higher Hg^0_{air} concentration.

How to test?

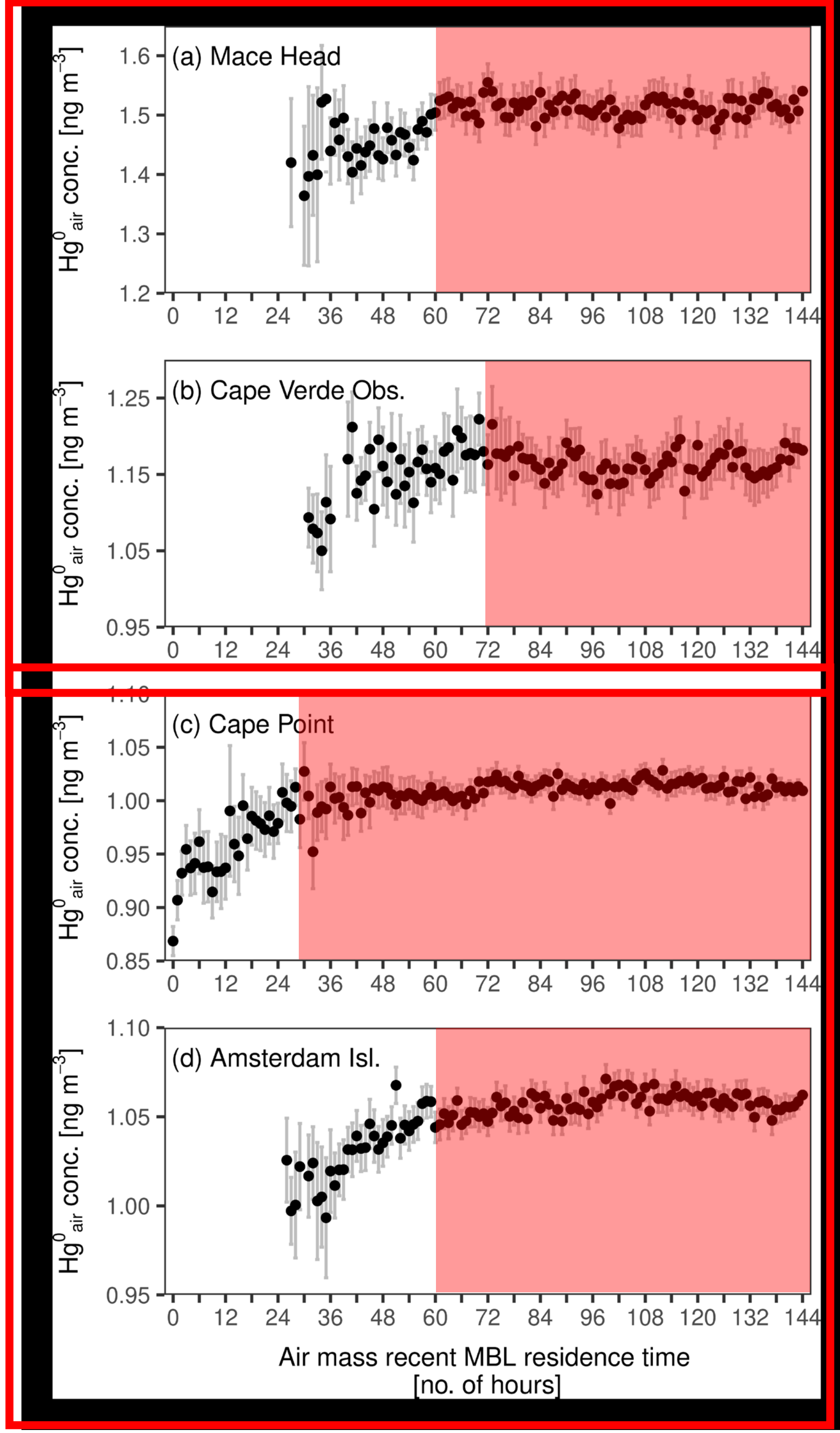
- Group Hg^0_{air} observations by air mass recent* MBL residence time.

Results:



- Consistent with **thin film gas exchange model**:

$$F = k_w\left(Hg^0_{aq} - \frac{Hg^0_{air}}{H'}\right)$$

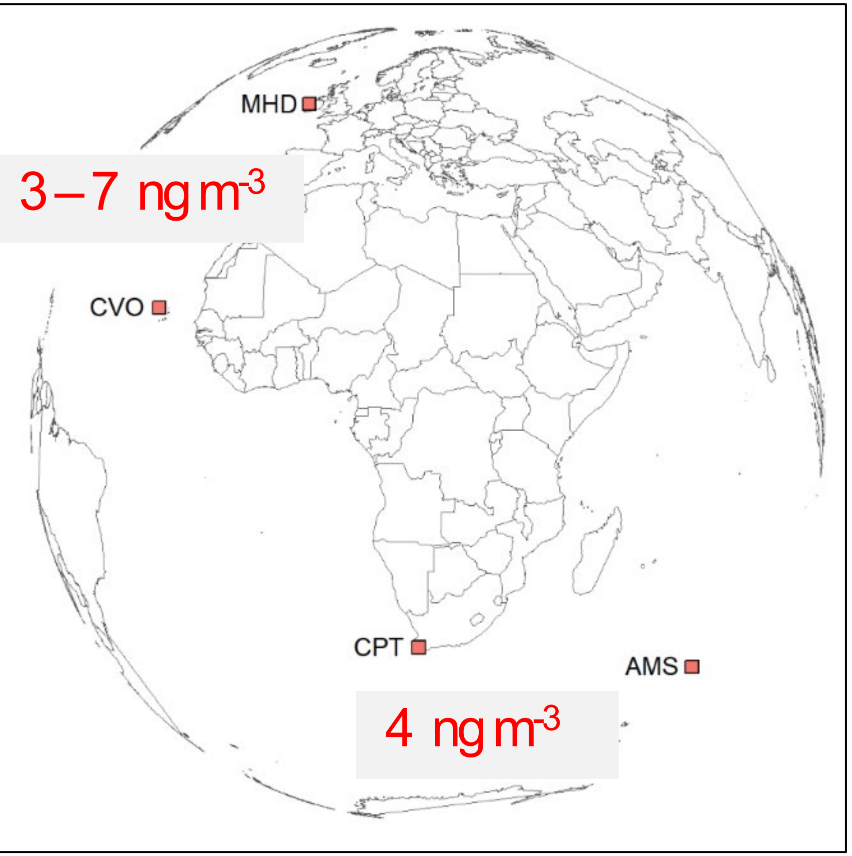


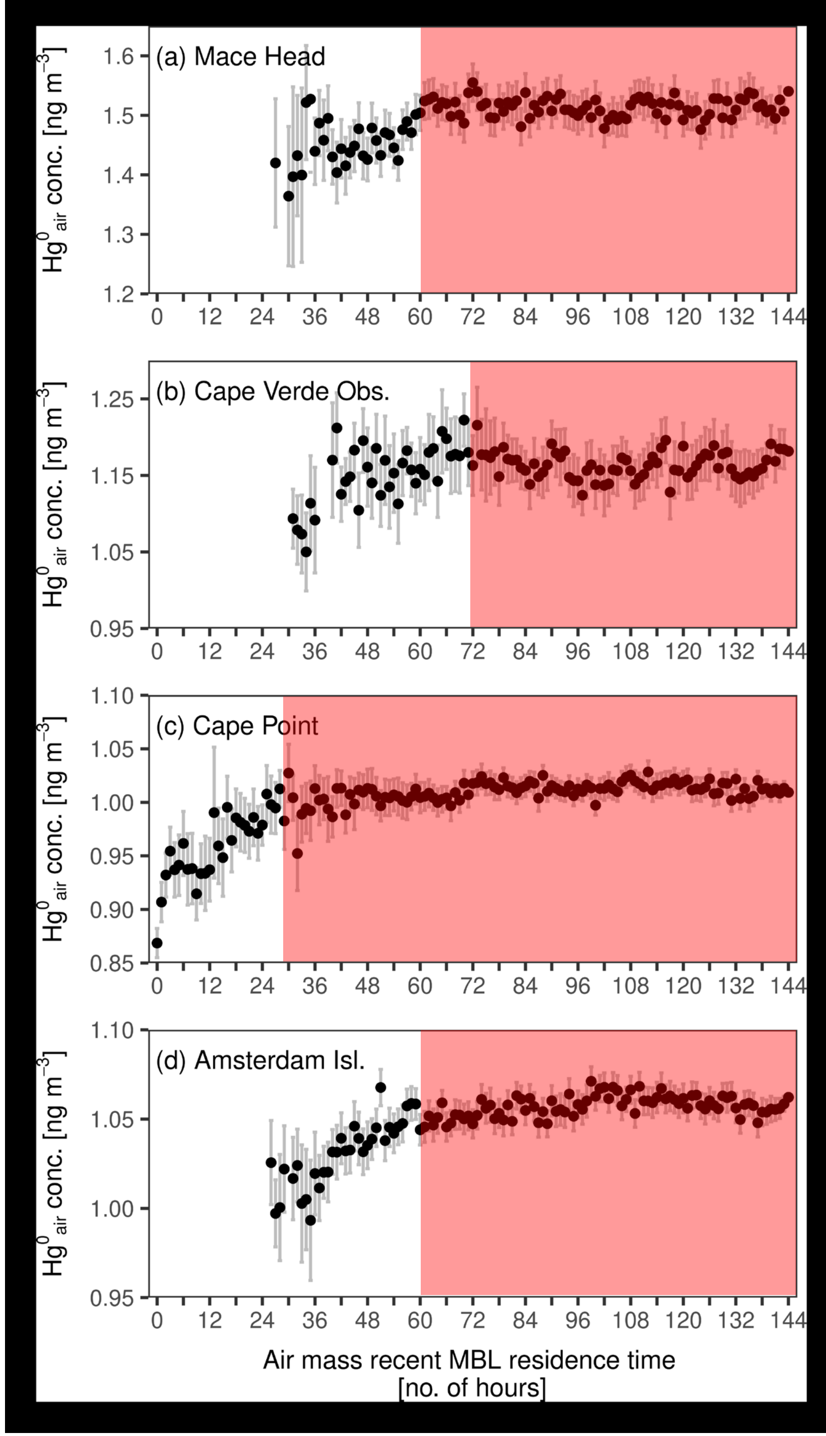
*Recent = in the **last 144 hours** before arrival at the sampling site

Hg^0_{aq} concentrations

thin film gas exchange model:

$$F = k_w\left(Hg^0_{aq} - \frac{Hg^0_{air}}{H'}\right) \rightarrow Hg^0_{aq} = \frac{Hg^0_{air(ss)}}{H'}$$



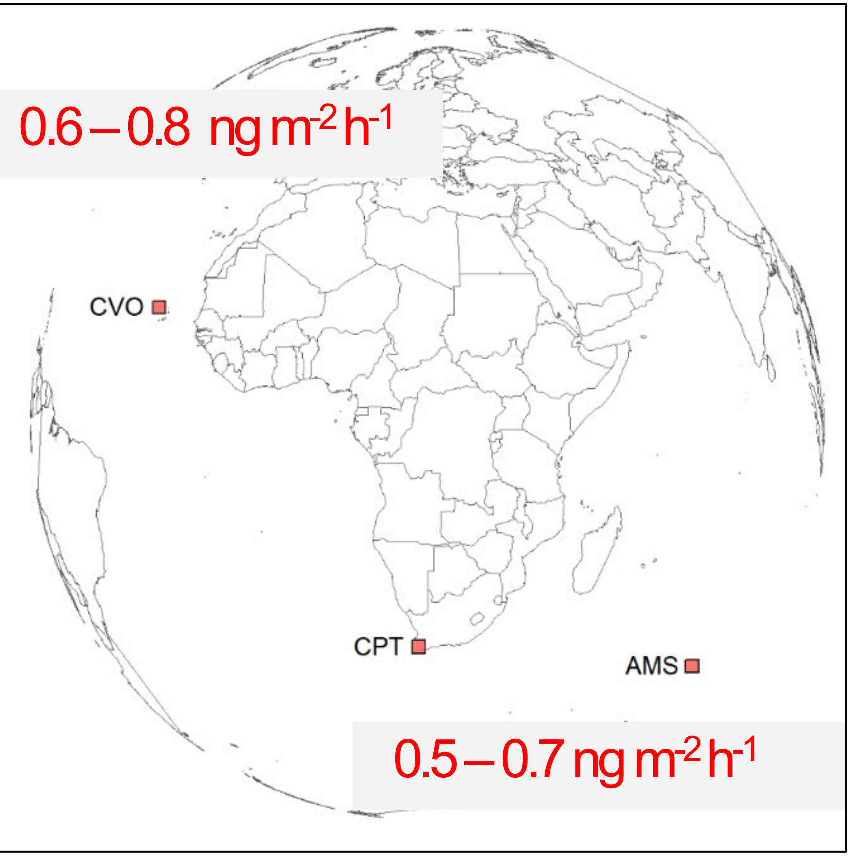


Ocean Hg^0 evasion fluxes

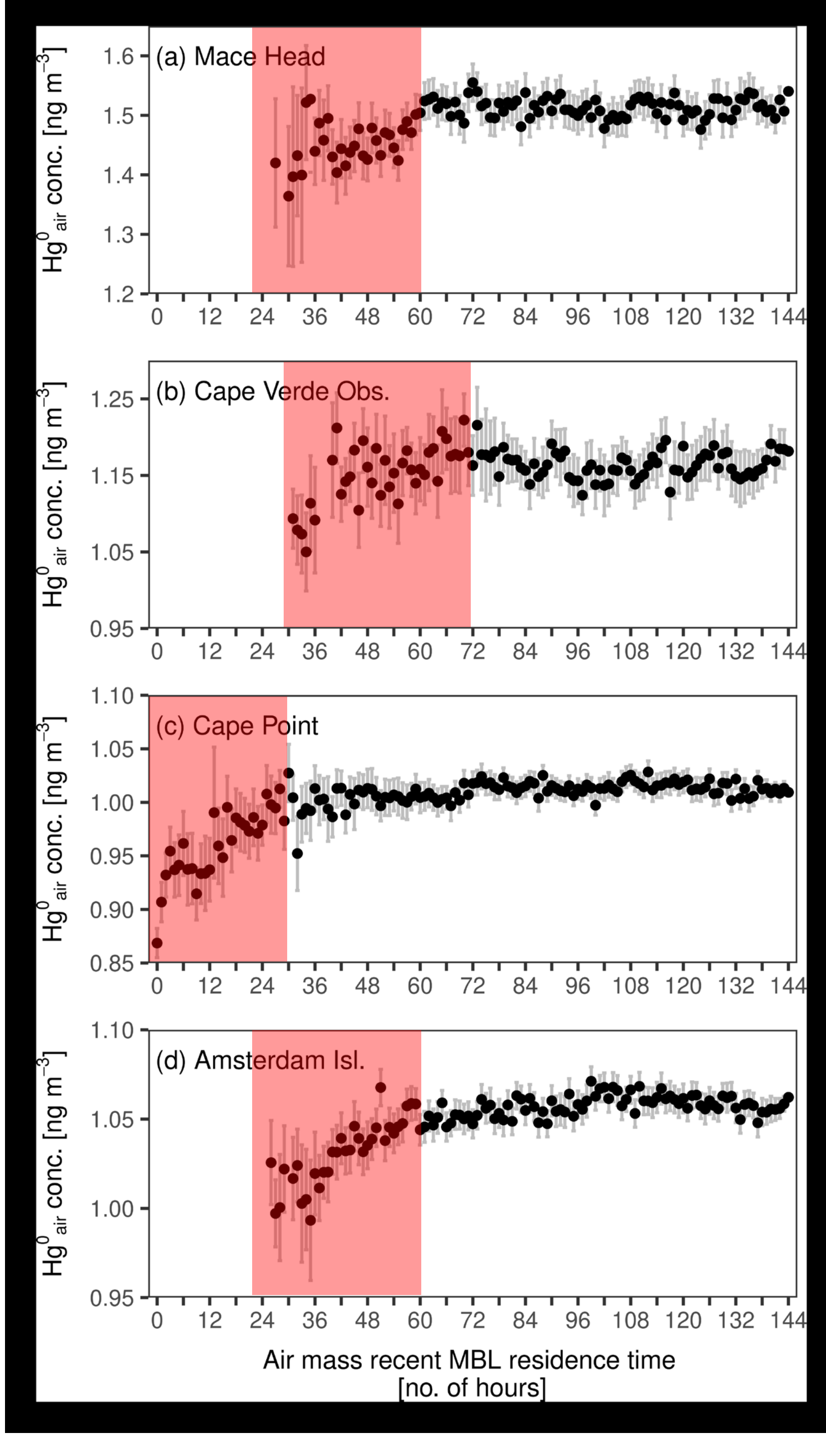
Change in Hg^0 mixing ratio along a trajectory[1]:

$$\frac{d\mu}{dt} = \frac{1}{\rho_a}\frac{F}{h_{PBL}}$$

[1]Brasseur and Jacob (2017)

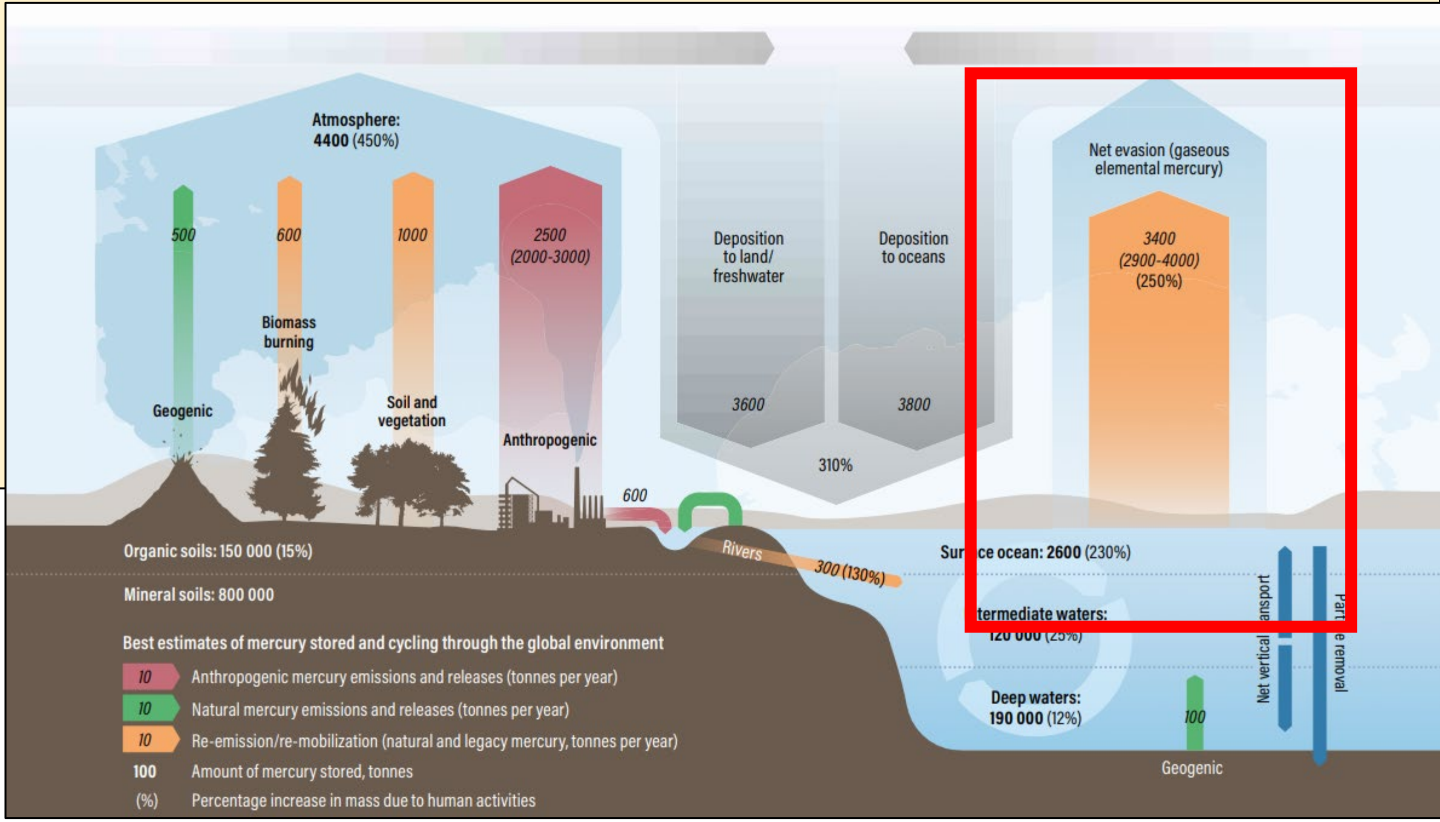


Global flux: 1900 t y-1 (1200 – 2600 t y-1)



Ocean Hg^0 evasion fluxes

- **Our estimate: 1900 t y^{-1} (1200 – 2600 t y^{-1})**
- **Current estimates: 2800 – 4000 t y^{-1}** (Horowitz et al., 2017; AMAP/UNEP, 2018; Shah et al., 2021; Zhang et al., 2023)
- **Emerging research:**
  - ❖ **Johannes Bieser (*ICMGP*): 1800 ty^{-1}**
  - ❖ **Hui Zhang (*ICMGP*): < 1200 t y^{-1}**



Adapted from AMAP/UNEP, 2018

Take home messages

- Hg^0 air-sea exchange evident from ground-based, **coastal monitoring observations**.
- Ground-based Hg^0_{air} observations a **useful tool** for studying Hg^0 air-sea exchange +
- …can be applied to constrain Hg^0_{aq} concentrations as well ocean evasion fluxes.

Thank you!

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Estimating global flux

Global_flux = (oceanA_area * oceanA_flux + oceanB_area * oceanB + oceanB_area * oceanB) / oceanGlobal_area #ng m-2 h-1

Global_flux = Global_flux * 365 * 24 #ng m-2 y-1

Global_flux = Global_flux * 10^-15 #t m-2 y-1

Global_flux = Global_flux * oceanGlobal_area #t y-1

Note:
oceanGlobal_area = oceanA_area + oceanB_area + oceanB_area