Biogeochemical cycle of Mercury (Hg) in sediment of the Scheldt Estuary and the Belgian Part of the North Sea (BPNS)

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Introduction

- **Principal forms:** Hg^{0}, Hg^{2+}, Monomethylmercury (MMHg) and Dimethylmercury (DMHg) → the Hg cycle
- **Natural sources:** volcanoes, vegetation and water
- **Anthropogenic sources:** Cinnabar, fossil fuels, industrial processes
- **Hazardous environmental pollutant:** Neurotoxic → Minamata disease (1956)
- **Human exposure:** seafood consumption → bioaccumulation & biomagnification (MMHg is the main concern)

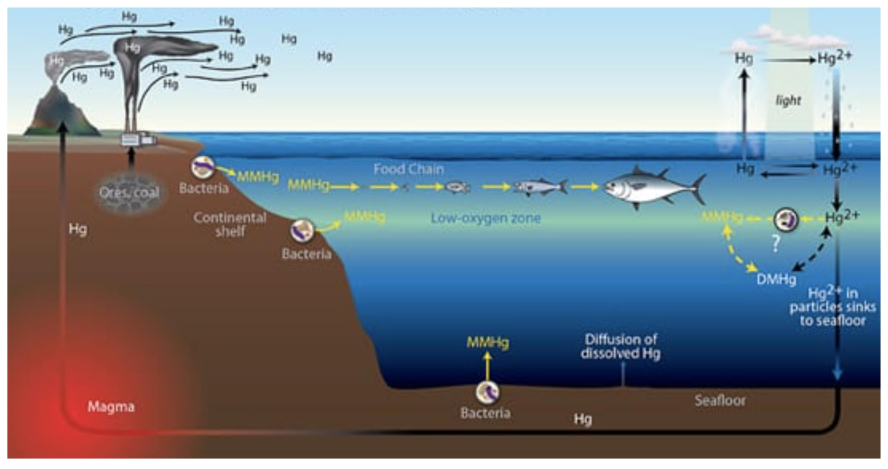

Figure 1. The Hg cycle [1]

Objectives

- **Assess the Hg contamination levels in sediment of the Scheldt estuary and the Belgian Part of the North Sea (BPNS) since the sediment is the place that methylation of mercury occurs.**

Material and methods

Sediment porewater

- **Concentration level:** ng/L
- **Classic sampling with Rhizon:** porewater conc. of Hg and MMHg
- **Passive sampling with DGT** (Diffusive Gradients in Thin-films (DGT)) [2]**:** labile Hg
  - 3-Mercaptopropyl Functionalized Silica (3-MFS):Thiol-group based binding resin
  - $C = \frac{M \times \Delta g}{D \times A \times t}$
    - C: Concentration of Hg in the solution (ng mL^{-1})
    - M: Accumulated Mass on the binding gel (ng)
    - Δg: The total thickness of the diffusive gel and filter (cm)
    - D: The diffusion coefficient of Hg in the diffusive gel (cm^2 s^{-1})
    - A: Exposed area (cm^2)
    - t: Deployed time (s)

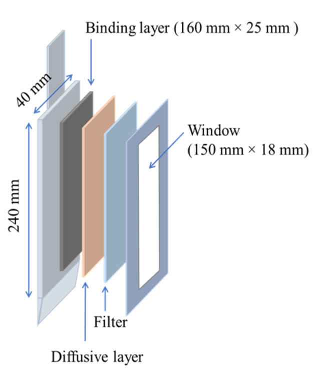

Figure 2. Schematic framework of a DGT Probe

Sediment solid phase

- **Sediment slicing (2 cm)**
  - Porewater extracted with Rhizon
  - Sediment solid phase (freeze-drying)
- **Loss On Ignition (LOI)**
  - 0.5 – 2 g of sample placed in oven at 530 °C for 5 hours (m1)
  - Cool down and weigh the sample again (m2)
  - **OM (%)** = $\frac{m1 - m2}{THg}$ **x 100**
- **Apparatus**
  - Advanced Mercury Analyser (AAS AMA-254) [3] → THg in resin gel and solid sediment
  - Cold Vapor-Atomic Fluorescence Spectrometer (CV-AFS PSA) → THg in porewater
  - Gas Chromatography-Atomic Fluorescence Spectrometer (GC-AFS TEKRAN® 2700) → MMHg in porewater and solid sediment

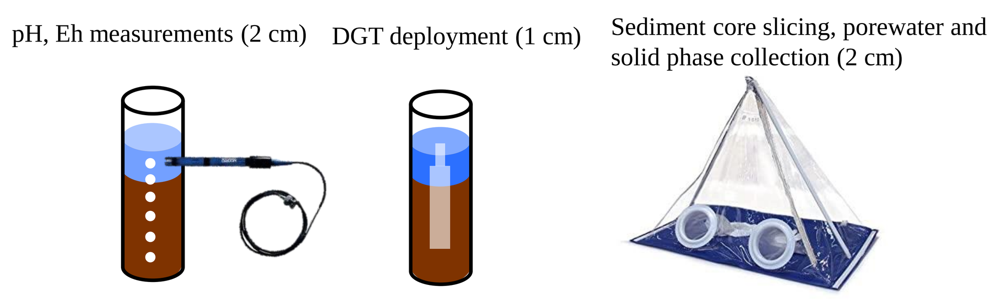

Figure 3. Sediment treatment

Sampling sites

- **Belgica campaign in March 2020 & 2021**
- **Scheldt estuary and Belgian Part of the North Sea (BPNS)**
- **Sediment sampling stations:** S15 and ZB

Figure 4. Map of sampling sites

Results and discussions

Sediment features

- **ZB:** mud
- **S15:** mixture of mud, sand and clay

pH and Eh profiles

- **pH:** small variations in ZB and S15
- **Anoxic conditions** under Sediment Water Interface (SWI)

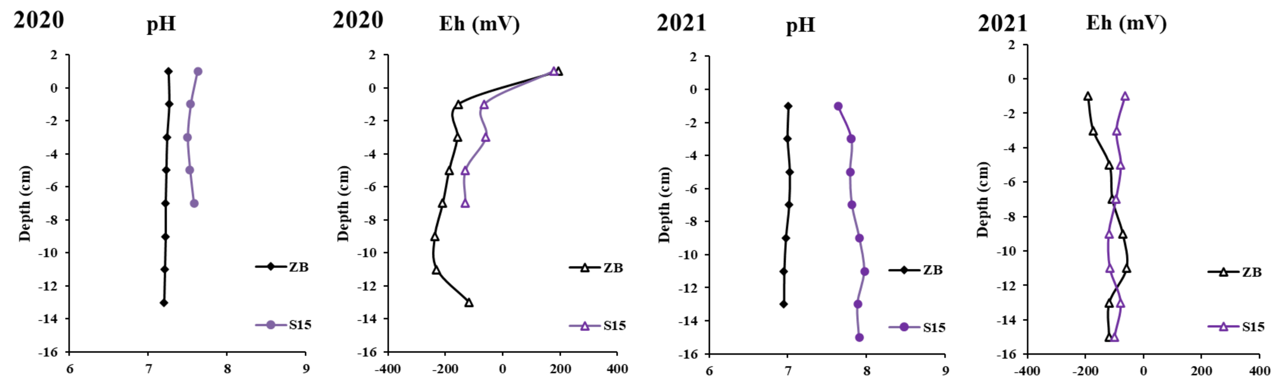

Figure 5. Profiles of pH and redox potentials (Eh) in sediment

Hg and MMHg in sediment solid phase

- **[Hg]:** S15 > ZB both in 2020 and 2021
- **[Hg] in ZB:** sediment was dredged 4 days before sampling in 2021 which may cause the trend of Hg in sediment was different from 2020
- **[Hg] in S15:** was contaminated by Hg historically from Hg-based chlor-alkali industry. The Hg cell process has been phased out in Europe since 2017 (Regulation EU 2017/852).
  - [Hg] (AUG, 1990) [4] >> [Hg] (MAR, 2021) > [Hg] (MAR, 2020)
  - [MMHg] (AUG, 1990) >> [Hg] (MAR, 2021)
- Small ratio of MMHg to THg for both stations (below 1.5%)

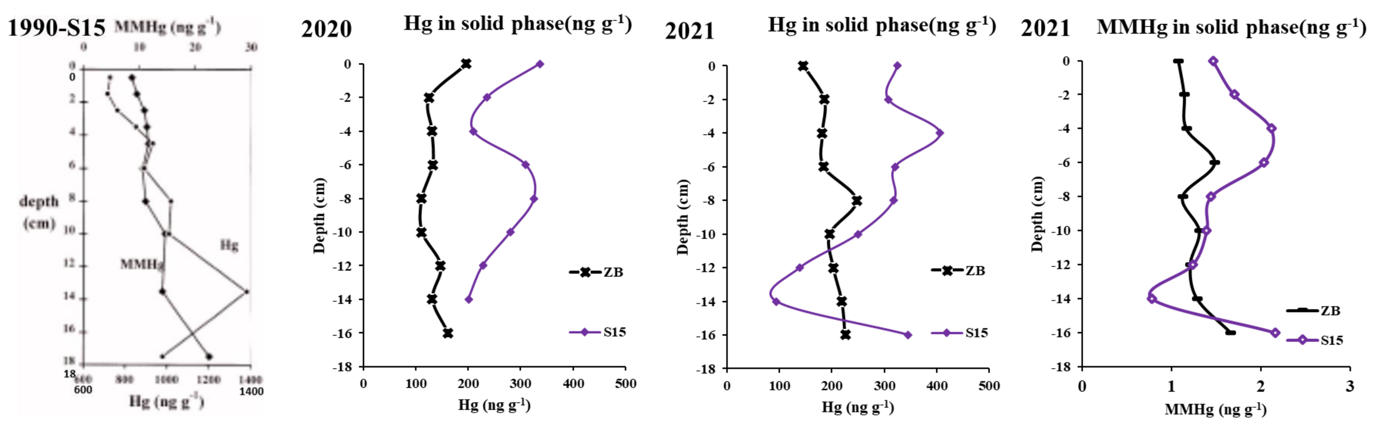

Figure 6. Hg distributions in sediment solid phase

- **THg – MMHg correlations**
  - S15: Significantly positive correlation (R^2 = 0.6625, p = 0.004<0.05) MMHg level increases with increasing THg
  - ZB: No correlation between MMHg and THg (R^2 = 0.1181, p>0.05) MMHg concentration is not always influenced by THg variations
- **MMHg - % OM correlations**
  - Positive correlation between [MMHg] and % OM (S15)
  - No correlation between MMHg and % OM in ZB

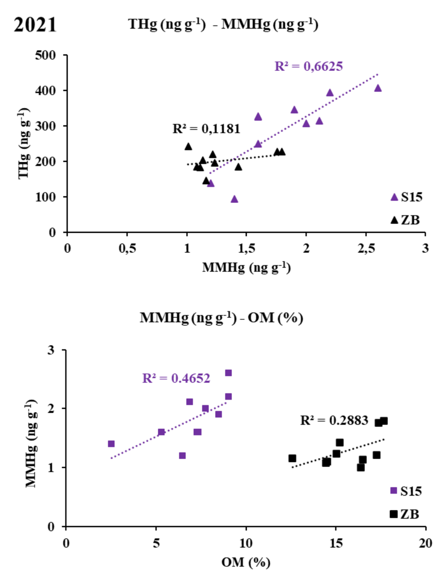

Figure 7. MMHg correlations with Hg and % OM in sediment solid phase

THg and MMHg in sediment porewater

- **2020**
  - [THg] increased towards the bottom, sediment could be a source of Hg to water column
  - ZB: labile Hg fluctuated under SWI
  - S15: [Labile Hg] > [THg] under SWI (technical problem)
- **2021**
  - Anthropogenic activities in ZB: dredge event may cause low [THg] and [labile Hg] in 2021
  - ZB: sharp peak of THg and MMHg at -10 cm
  - S15: Higher [THg] in porewater
  - S15: inverse trend of labile Hg was found

    Dredging/dumping operation(s) between the two sampling campaigns in 2020 and 2021
  - Similar to sediment solid phase, small ratio of MMHg to THg for both stations were found as well

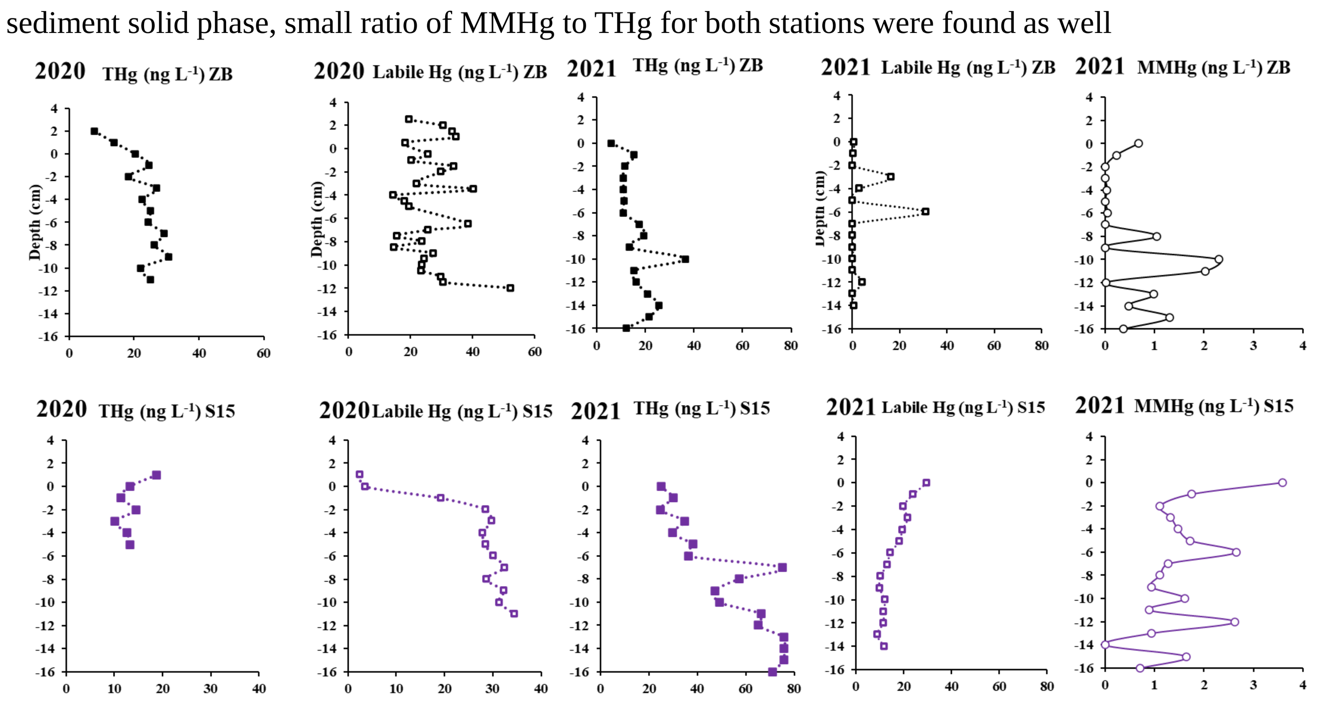

Figure 8. Hg distributions in porewater

Conclusions

- **S15: Highest Hg concentrations both in sediment porewater and solid phase. However, lower Hg and MMHg concentrations were found in sediment solid phase in comparison to the 90s which indicates the reduce of impact from the chlor-alkali industry.**
- **Small percentage of MMHg to THg in sediment porewater and solid phase.**
- **Anthropogenic activities in the estuary and coastal area significantly effect Hg levels and distributions in sediment.**
- **Dynamic supply of Hg from solid phase to porewater is important.**

Perspectives

- ❑ **To improve the study of MMHg in sediment**
  - Optimization of porewater analysis
  - Assess labile MMHg with DGT
- ❑ **Sequential extractions to identify the Hg binding phases in sediment**

References

[1] Mercury Cycle. Woods Hole Oceanographic Institution. https://www.whoi.edu/multimedia/mercury-cycle/. (2020, May 6).

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Acknowledgements

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https://researchportal.be/en/project/be-mermaid-bioavailable-mercury-methylation-adriatic-sea

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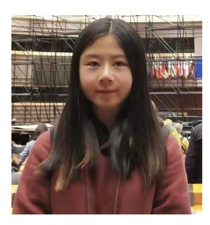

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