DIFFUSIVE GRADIENTS IN THIN FILMS AS A TOOL FOR ARSENIC SPECIATION IN THE ESTUARINE ENVIRONMENTS

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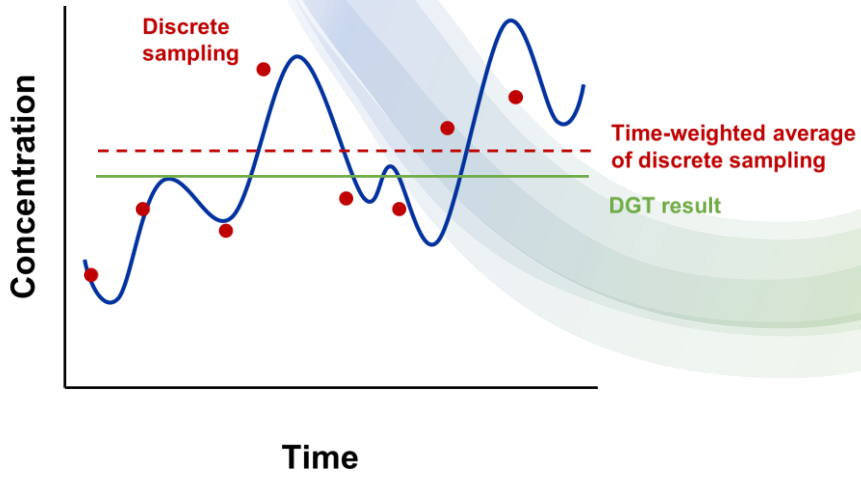
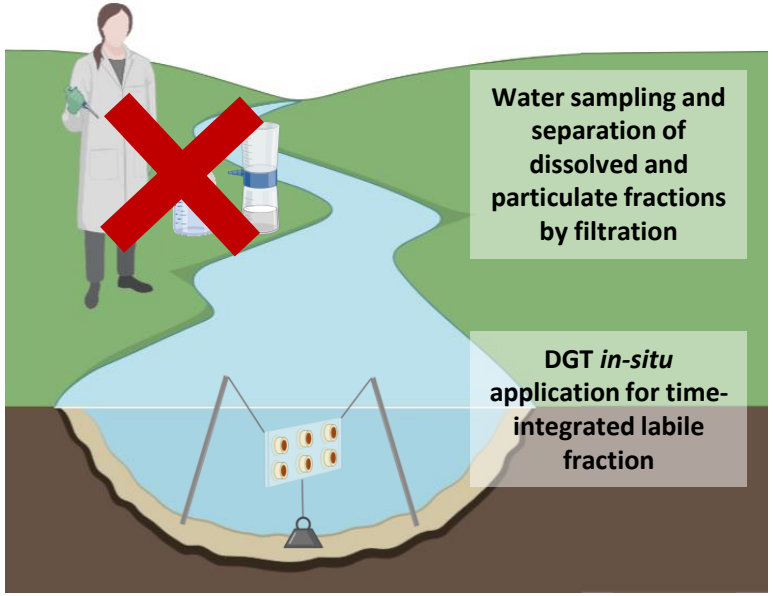
Active vs. passive sampling

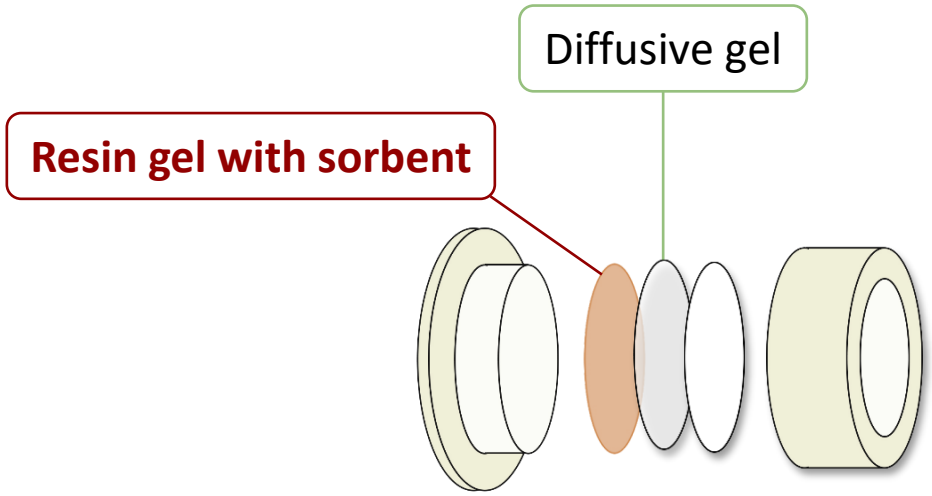
- **Conventional monitoring**
  - **particulate and dissolved fraction**,
  - may provide misleading results (e.g., in dynamic environments),
  - discrete sampling in time series.



- **Diffusive Gradients in Thin films (DGT)**
  - pre-concentration of analytes *in-situ*,
  - conservation of analytes,
  - **labile fraction** – provides information about element‘s bioavailability and speciation.



Arsenic DGT-speciation concept



As

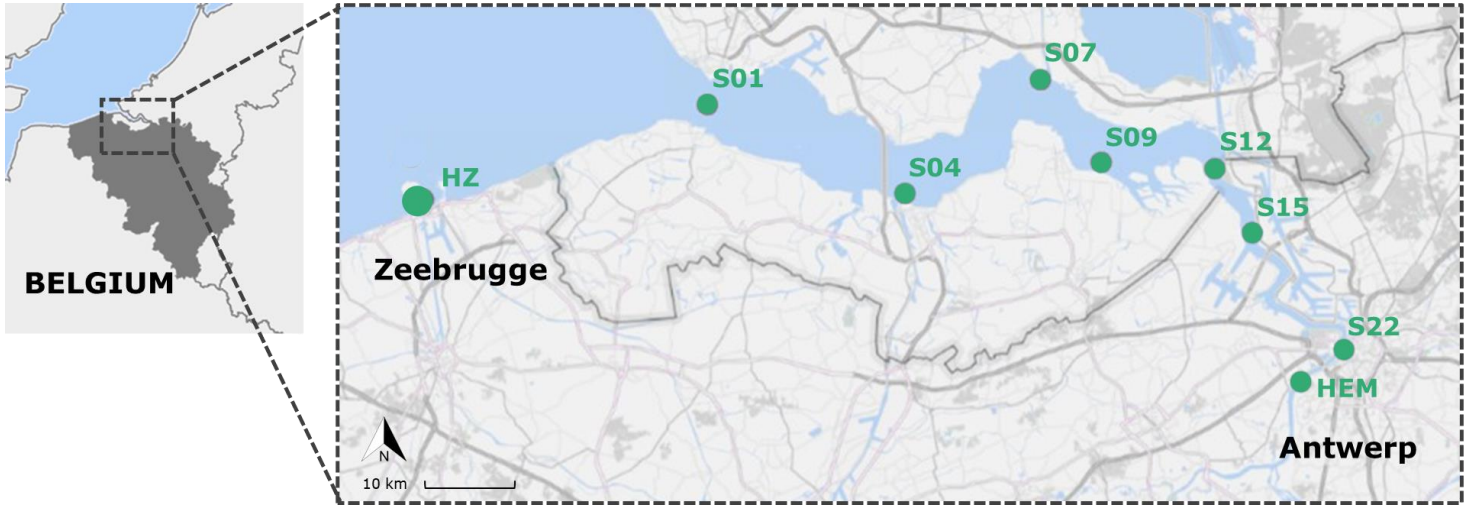
As^{III}, As^{V}

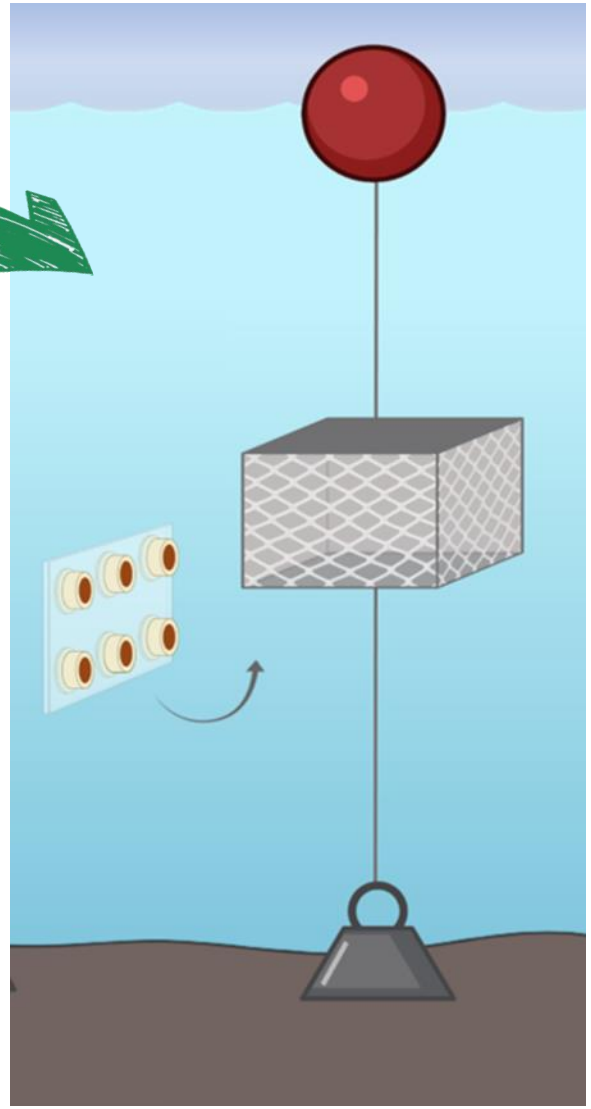
mono-/di-
methylated arsenic

- **DGT sorbents for As**
  - **Total As** – TiO_2, ZrO_2, FeO(OH), CeO_2 (used in their pure form or as commercial resins with these functional groups)
  - **As^{III}** – 3-mercaptopropyl functionalized silica (3MFS)
  - **As^{V}** – Amberlite IRA 910 (dimethyl ethanol amine) (Rolisola et al., 2014)

Scheldt estuary and Belgian coastal zone

- **RV Belgica campaigns**
  - March 2022 and 2023.
  - DGTs deployed in 6 replicates (per sorbent) for 12–24 hours.
  - Water samples collected at the begining and end of each DGT deployment time – filtration on 0.45 µm.
  - Physicochemical parameters (salinity, pH, dissolved O_2, temperature) and deployment times recorded.





Physichochemical parameters

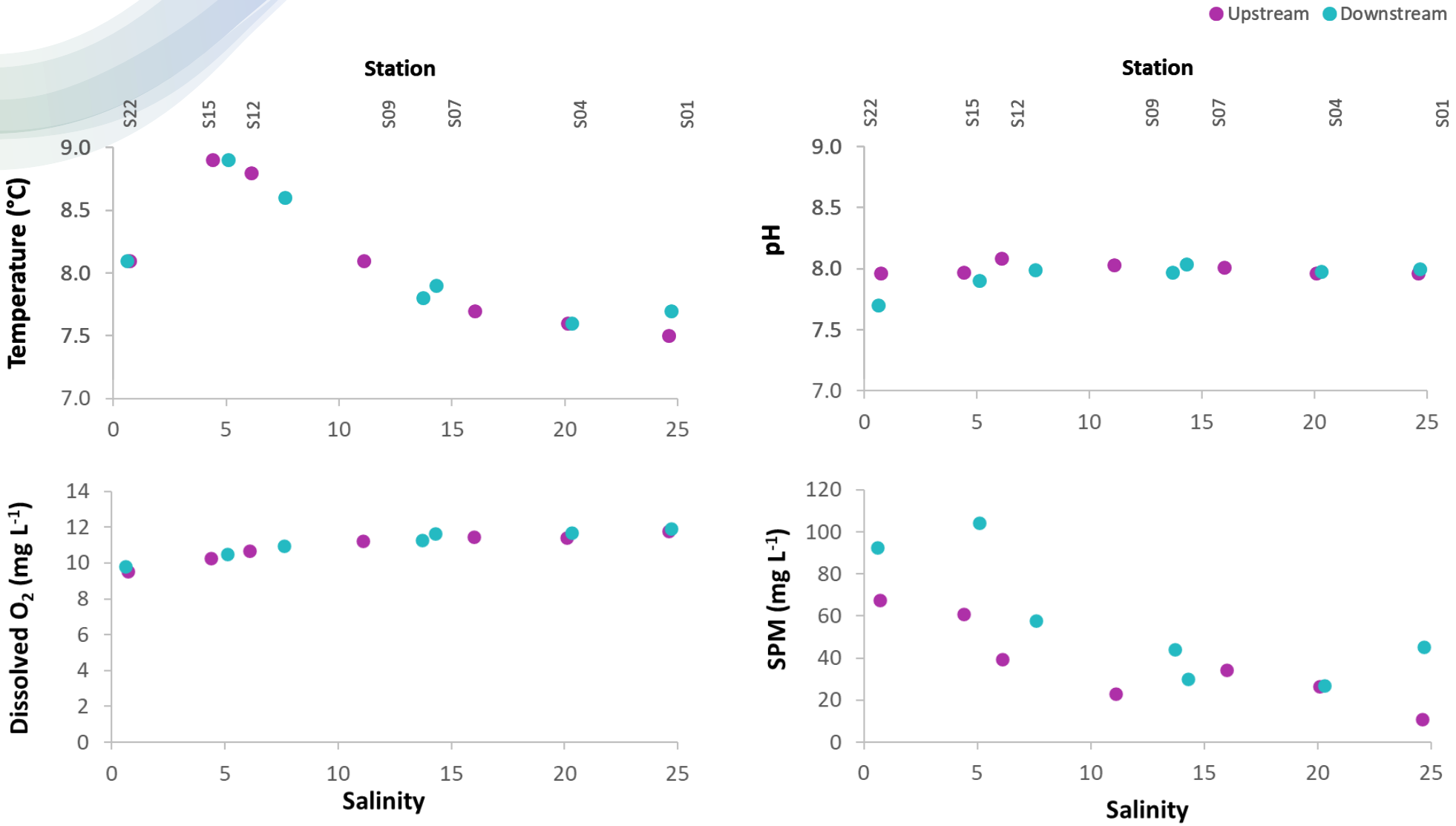


Fig. 1 Physicochemical parameters of water from stations S22–S01 during campaign in March 2022.

Arsenic dissolved and particulate fractions

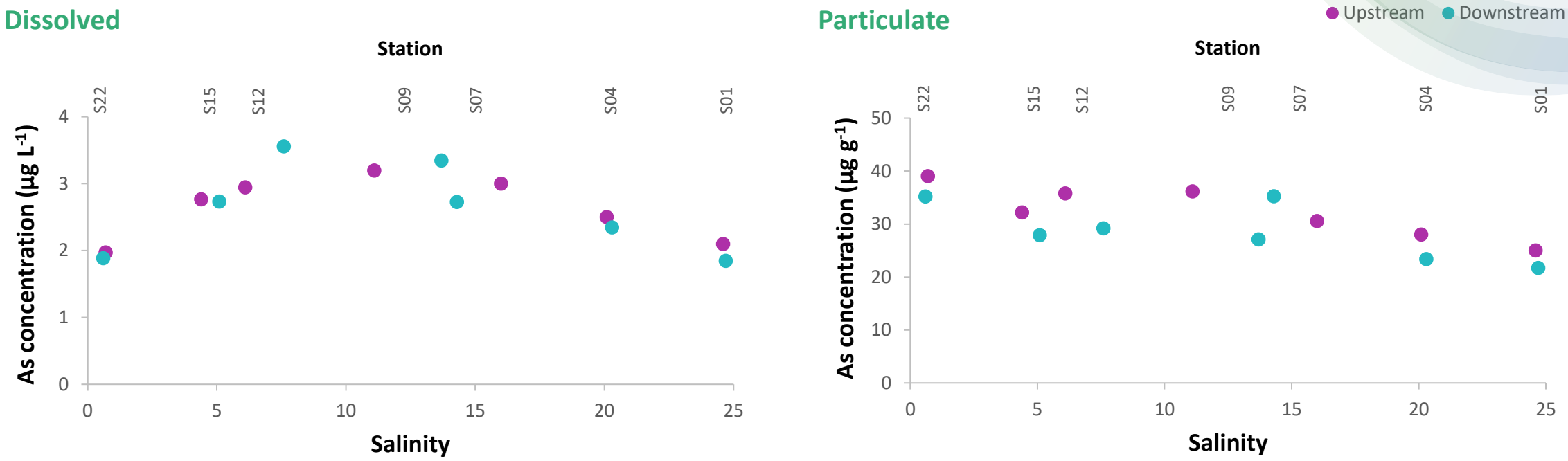


Fig. 2 Concentration profiles of dissolved and particulate As fractions along the salinity gradient in the Scheldt estuary recorded in March 2022.

- Dissolved As concentrations show typical non-conservative behaviour in the area (De Gieter et al. 2004).
- Particulate As concentrations decrease along the salinity gradient and represent 63–11% of As in the water column with incrasing salinity.

Arsenic DGT-determined fractions

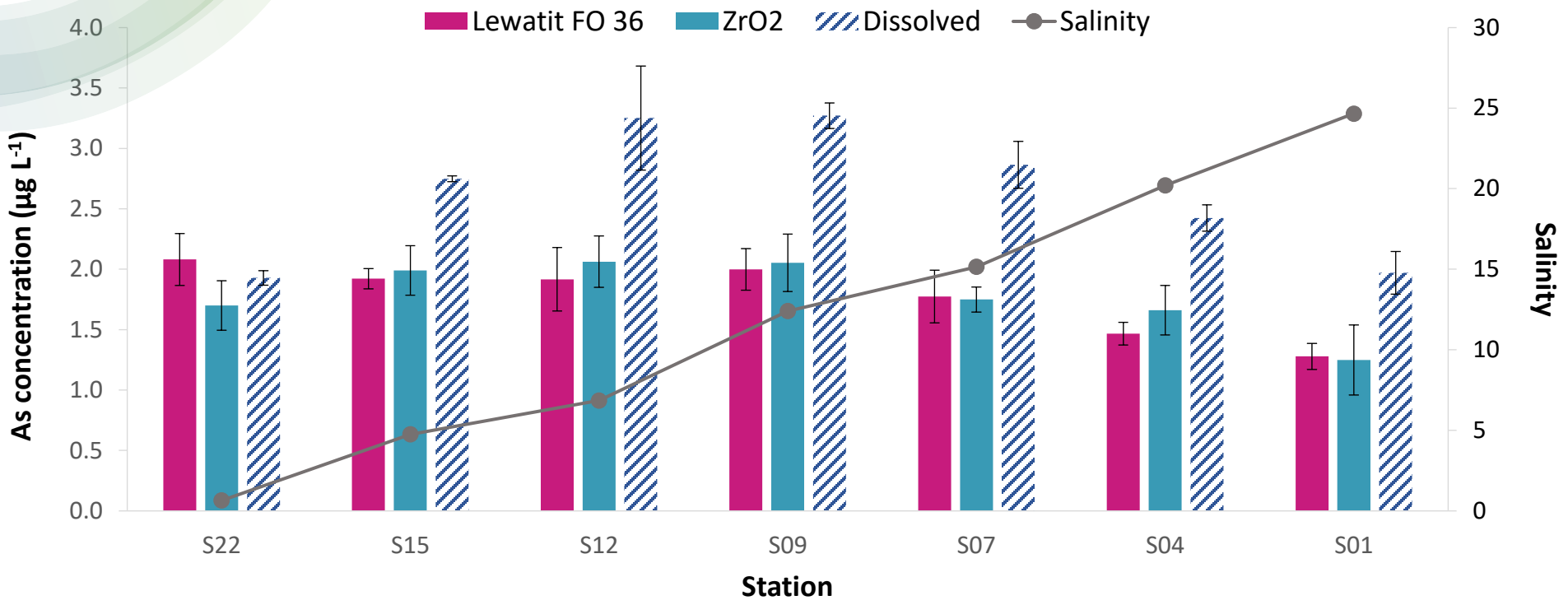


Fig. 3 Concentration profiles of dissolved and DGT-determined As concentrations in the function of the increasing salinity (grey line) along the Scheldt estuary during a campaign in March 2022 (n=6 for DGTs, n=2 for water samples).

- Total labile fraction of As determined by Lewatit FO 36 and ZrO_2 sorbents were in good agreement along the salinity gradient.
- The DGT-determined labile fraction of total As represents 98–64% → the observed decrease could be related to variations in time, presence of colloidal fraction or seawater matrix.

Arsenic DGT-speciation

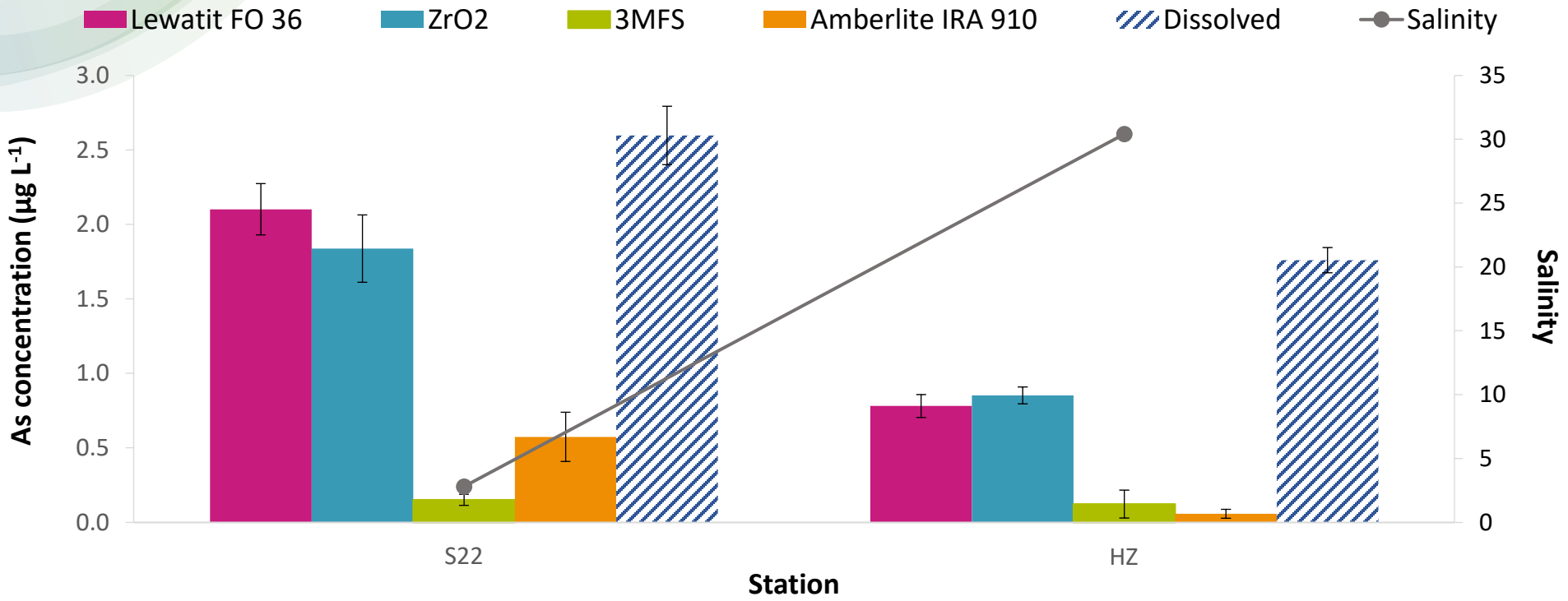


Fig. 3 Arsenic speciation of DGT-determined labile fractions using sorbents for total As (Lewatit FO 36, ZrO_2), As(III) (3MFS), and As(V) (Amberlite IRA 910) at station in Antwerp (S22) and in the Zeebrugge harbour (ZB) in March 2023 (n=6 for DGTs, n=2 for water samples).

- The labile As fraction is represented 7–11% of by As^{III} due to well oxidized environment.
- Labile As^{V} fraction is either not reliable due to the poor performance of Amberlite IRA 910, or it is actually very low and the majority of labile As is represented by methylated species.

Arsenic DGT-speciation

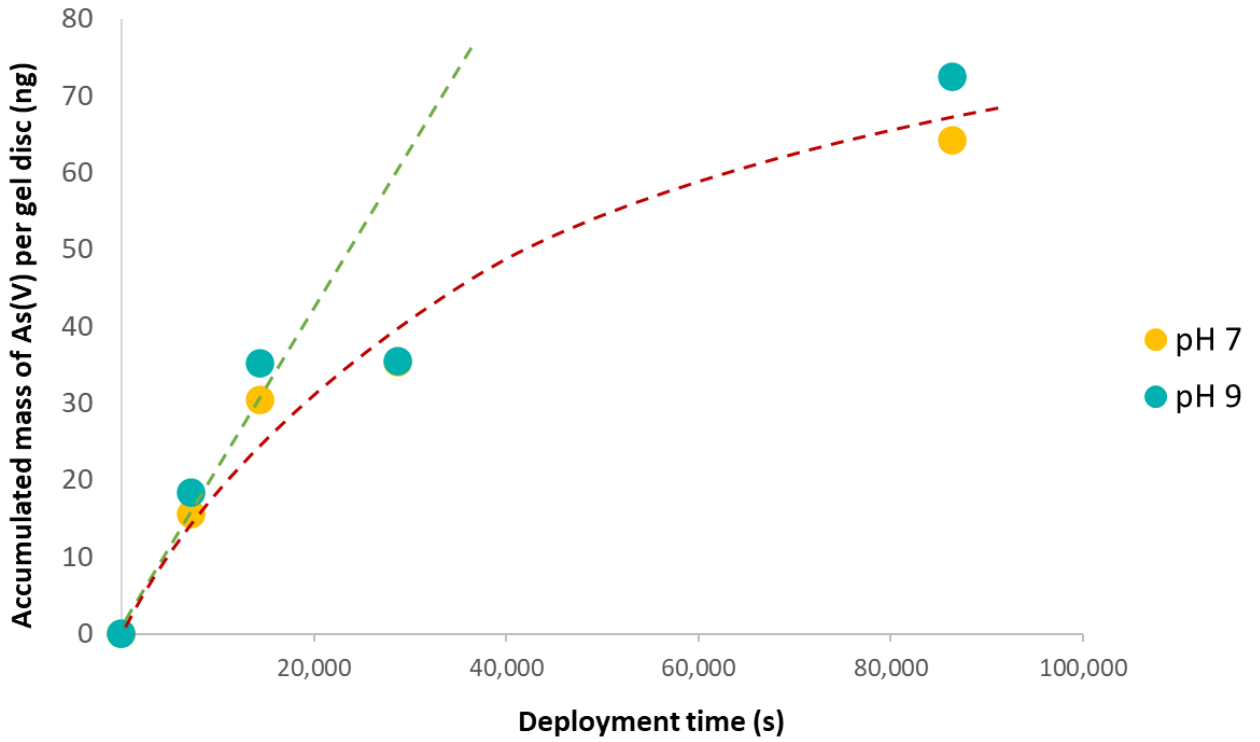


Fig. 4 Accumulation of As(V) by DGTs with Amberlite IRA 910 resin gels at pH 7 and 9 (deployment solution of 0.01 M $NaNO_3$, As(V) = 20 µg L^{-1}; n=2).

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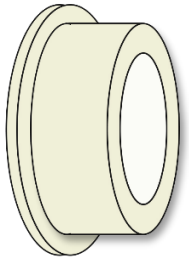
Conclusions and future perspectives

- The current state-of-the-art of the DGT technique is not sufficient for a thorough characterization of the As-labile fraction.
- It is necessary to find selective sorbents or investigate the possibility of coupling the DGTs with separation analytical techniques in order to obtain the speciation of the labile As fraction.



DGT

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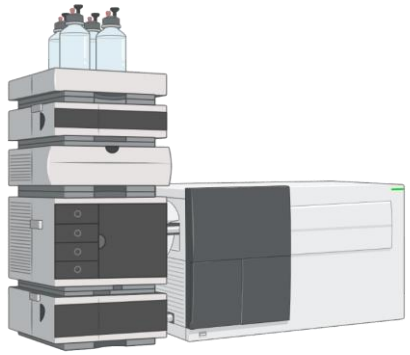

HPLC-ICP-QQQMS

= Speciation of labile As

Thank you for your attention

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