# Modelling post-inflow trace metal partitioning in the Gotland Deep, Baltic Sea

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The Baltic Sea is one of the largest brackish sea areas in the world, well structured into a series of basins and deeps separated by sills. Water balance is affected by freshwater surplus which causes a large-scale estuarine circulation and maintains a stable stratification in the central Baltic deeps by local convective mixing. The only effective mechanism of bottom water renewal is episodic advective inflow of larger amounts (e.g. 300 km$^3$) of saline and oxygen-rich water from the North Sea through the Belt Sea into the Arcona basin, the Bornholm basin and, last in the row, over the Stolpe sill into the Gotland Deep. However, such major inflow events are highly intermittend and may occur only once in a decade. We will report here on such an inflow event, which led to precipitation of about 150,000 tons of particulate oxihydroxides within a few weeks upon oxygenation of the dissolved Fe and Mn pool (Brügmann et al., 1997), and its impact on the trace metal geochemistry in the Gotland Deep.

Sampling was performed in October 1995 (i.e. nearly two years after a major inflow event) at the HELCOM-BMP station BY15 (57°18.30'N/ 20°04.60'E, water depth 249 m). Analysis was performed for all relevant oceanographic chemistry parameters and major as well as trace components including dissolved (< 0.4 μm) and particulate metals. In addition, automated electron microprobe X-ray analysis was used to characterize the particles from the suspended matter, which revealed that at depths below 100 m (i.e. below the halocline) Mn-rich particles are the dominating particle fraction (i.e. pure Mn oxihydroxides or Mn-coated detritus, with up to 4 μM Mn near the bottom). Unexpectedly low particulate Zn, Cu, Ni, and Cd in the order of 5−10 % of the total concentrations have been found at these depths, albeit significant scavenging effects have been suggested to occur upon the precipitation event (Brügmann et al., 1997). Modelling of the trace metal geochemistry was performed to resolve this enigma.

For a strictly thermodynamic model of the seawater geochemistry, the less common Gibbs energy minimisation (GEM) approach was used as implemented in the Selektor-A code (see abstract by Kulik). The thermodynamic data file is based on the latest SPRONS data for aqueous species (Shock et al., 1997), extended to account for aqueous trace metal complexes and surface species by means of (quasi)isocoulombic extrapolations. The HKF/EOS-based ion-association model of normative seawater was fine-tuned against known carbonate system parameters by adjusting $G_{298}^0$ values of $MgHCO_3^+$, $NaBO_2^0$, $NaCO_3^-$, and $NaHCO_3^0$ complexes within $\pm 1.14$ kJ mol$^{-1}$, or 0.2 pK units, to correctly reproduce measured pH values both in activity (pH$_{NBS}$ scale) and total H$^+$ (pH$_{TRIS}$ scale) in a wide range of $T$, $P$, and salinity. Bulk composition of the brackish waters has been reproduced by a conservative mixing model between the normative seawater and normative Baltic tributary river water end-members (Millero, 1978). Actual compositions of water layers in stratified Gotland Deep water column were calculated assuming conservative mixing between a 'Baltic surface water' of 7 PSU and a 'Belt Sea inflow water' of 20 PSU, both equilibrated to large excess of dry model atmosphere. Both end-member waters were then closed and mixed according to the measured salinity, $T$, and $P$ to produce a 'model blank profile' representing the 'pre-formed' concentrations of dissolved nutrients and $O_2$. Apparent $O_2$, N, and P utilisation parameters (AOU, AON, AOP) were calculated by subtracting the model blank from field-measured concentrations. Chemical changes in the water column were then modelled by addition of Redfield-like composition of re-mineralised C$_{org}$, modified to account for the local Baltic characteristics and verified using measured pH and DIC profiles. Aqueous and solid Fe and Mn species were added to follow distribution of these elements in the AOU-driven profile.

The solubility of γ- and δ-modifications of natural

non-stoichiometric Mn oxides ($MnO_x$, with $1.5 < x < 2$) in response to pH and Eh variations was reproduced by a binary $(MnO_2)_{2n-3}$-$(MnOOH)_{4-2n}$ solid solution model suggested by Gramm-Osipov (1997), where $1.5 < n < 2.0$ is the average Mn oxidation number. Although Gibbs energies of formation $G^0_f$ of the two end-members are known only for synthetic $\gamma$-$MnO_x$ but not for natural $\delta$-$MnO_x$ (birnessite/buserite), they can be fitted from the field data to reproduce the dissolved Mn profile at the suboxic conditions encountered at depth. The resulting values of $G^0_{298}(MnO_2) = -459.7 \pm 3$ kJ $mol^{-1}$ and $G^0_{298}(MnOOH) = -567.1 \pm 3$ kJ $mol^{-1}$ were used in this study as end-members of the non-stoichiometric $\delta$-$MnO_x$ sorbent, with a specific surface area $A = 290$ $m^2 g^{-1}$ and a specific surface free energy in water $\sigma = 0.59$ J $m^{-2}$. Finally, dissolved, solid and adsorbed trace metal species were introduced to follow partitioning and speciation in Gotland Deep water column (details on the TLM sorption model see abstract by Kulik and Kersten).

The modelling results show, that at an euphotic zone pH above 8, the sorbent concentration would lead to an efficient scavenging of the trace metals, but not at the ambient pH of as low as 7.2 induced by organic matter mineralisation below the halocline. The effect of this pH decrease of about one unit is a significantly decreased scavenging efficiency, except for Pb where the adsorption edge lies at a much lower pH value than for the other metals. Moreover, the trace metal partitioning coefficients exhibit a strong particle concentration effect which can be related to the dissolved $Mn^{2+}$ concentrations rather than the particulate Mn increasing concurrently with depth due to the increasingly suboxic conditions near the bottom. Free $Mn^{2+}$ ions probably compete with the other metals for sorption sites on the Mn-oxyhydroxides. They were thus considered in the TLM calculations as an additional background electrolyte cation together with $Ca^{2+}$ and $Mg^{2+}$, but forming innersphere rather than outersphere complexes. Upon accounting for this competitive sorption process, the model could explain the near-bottom indentation in the particulate metal profiles. The adsorption model then matches perfectly the field observations on metal partitioning between dissolved and particulate forms at least below the halocline. Above that the basic assumption that the particulate trace metal portion is solely adsorbed to $MnO_x$ is no more valid, because at depths above 100 m that adsorbent is no more dominating the suspended particle population. Other sorbents like organic matter with a higher sorption efficiency may become more important in the euphotic zone, but no suitable data are yet available to account for these even more complex sorbents.

## References

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