

# Monthly variation of trace metals in the North Sea sediments. From experimental data to modelling calculations

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**Introduction:** The Belgian Continental Plate (BCP), located in the Southern part of the North Sea, is 65 km (length of the coastline) x 31 km (offshore). This work was carried out in the framework of the MICROMET, with sediments from the station 130 (51°16.25 N - 02°54.30 E; depth: ±11 m), one of the most metal-contaminated subtidal stations of the BCP [1,2]. The main objective was the study of trace metal monthly variations in pore waters of the station 130. Several physico-chemical parameters such as pH, temperature, sulfide and organic matter contents were also measured in order to estimate the role and influence they have in the speciation of trace metals.

**Methods:** Sediments were collected using a Reineck corer onboard the “Zeeleeuw” research vessel. Truly dissolved metal concentrations in overlying water and porewater were determined by using DGT pistons and High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICPMS) after elution of the DGT in 1 mL of HNO<sub>3</sub> 1 M solution [2]. Sulfide concentrations were determined by using DGT-AgI probe [2,3]. DOC concentrations were measured by a Dohrman Apollo 9000 total organic carbon analyser. The software VisualMinteq was used for calculation of metal speciation in the liquid phase.

**Results:** The concentration of dissolved sulfides in autumn, winter and spring is < 1 μmol L<sup>-1</sup> in the 6 first cm. Below 6 cm, sulfide contents increased to reach variable maxima up to 100 μmol L<sup>-1</sup>. In June and July, profiles exhibit high maxima at around 3-5 cm depth, with dissolved sulfide values that raised about 400 μmol.L<sup>-1</sup> in pore waters.

Trace metal profiles assessed by DGT showed, in most of the cases, a typical behavior bound to the redox properties of the sediments. Mn had the highest concentrations in the subsurface sediments, and the lowest values in deep layers. No clear monthly tendency was found for this metal. Fe shows similar redox behavior, with minimal values in the deeper layers and maximal values in the first centimeter depth. Average concentration of Fe for the first 10 cm showed clearly the highest values in winter and

the lowest in summer. Co profiles showed maximal values at about 0-4 cm depth, but these maxima were less significant in summer. Cd concentrations decreased at the interface, as well with lowest values in summer. Pb and Cu present very low values, with several sharp peaks at different depths and without clear seasonal effects. Seasonal effects clearly impacted Ni concentrations with lowest values in summer.

**Discussion:** Because of the high affinity of Fe, Co, Ni and Cd with sulfides to form precipitates, the high production of sulfides during the summer results in the scavenging of these trace metals at this season. Cu and Pb behaviour was found to be less influenced by sulfides, since they are also strongly associated to organic matter according to our calculations. Overall, the whole set of results clearly indicated that most of the metal speciation in these sediments are controlled by the production of sulfides via the sulfato reduction process, and the recycling of OM in the surface sediments. As the free metal cations are generally considered as the most toxic species for the organisms, it appears that surface sediments may be more toxic during the winter period than during the summer.

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**References:** [1] Gillan and Pernet (2007) *Biofouling* **23**:1-13, [2] Gao et al. (2009) *Mar. Chem.* **117**:88-96; [3] DeVries and Wang (2003) *Environ. Sci. Technol.* **37**:792-797.