

Spatial variability of organic matter quality and metal reactivity in the port of Rotterdam sediments

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Introduction: Each year, 10-15 million m³ of sediment are dredged from the waterways in the port of Rotterdam, one of the world's largest harbors [1]. The fine-grained and often organic-rich sediment is either relocated at sea or, when contaminated, disposed in a confined facility. In light of the poorly understood environmental impact – in particular, greenhouse gas and metal emissions – of dredged material and considering the growing interest in sediment reuse for 'building with nature', it is of great interest to understand the chemical composition and biogeochemical behavior of dredged harbor sediment, particularly the organic matter (OM) quality and metal mobility.

Methods: Bulk sediments throughout the harbor were collected during a sampling campaign in 2021. Total elemental composition of porewater and solid phase (after total digestion) were analyzed with ICP-MS. We employed C/N with isotope analysis and flash pyrolysis GC-MS to characterize the bulk OM and the isolated macromolecular organic matter (MOM). To further understand the metal speciation and mobility, different metal extractions were performed with extraction strengths from ion exchange in salt solutions to dissolution of stable minerals in concentrated oxidizing acids. Additionally, heavy metal release under different pH was quantified for two contrasting sites through pH-static leaching experiments and geochemical modelling.

Results: OM content was high at all sites except several sandy sediments mainly located in the river channel. A general west-to-east gradient of marine influence was presented throughout the harbor, which coincided with the changes of carbon and nitrogen content and their isotope abundance. The MOM was of a mixture of terrestrial, marine, and potential anthropogenic origins, and particularly the abundance

of terrestrial biomolecules (guaiacol, phenol and syringols) decreased as deposition setting became marine influence dominated. Trace metals (Cd, Ni, Cu, Zn) were enriched in finer and less marine influenced sediments, while grain size and the extent of marine influence were poorly correlated with the highly reactive metal fractions. Additionally, the highly reactive fraction among trace elements were different, with Zn and Cd (>85%) significantly larger than Ni (33%) and Cu (55%). Such mobility variance among elements was also reflected in the pH-static leaching experiment and modelling results, where mobility was lower at neutral condition while higher at acid or alkaline conditions.

Discussion: Our results suggest depositional environment plays an important role in sedimental geochemistry. Grain size significantly affects Al/Fe content, TOC preservation, and S sequestration [2]. Salinity at the depositional environment affects metal behaviors, in particular Fe, through sulfur cycling [3]. The variance of OM quality between marine and river sediments might influence the early diagenesis and greenhouse gas generation. The strongly reducing nature and high content of (reactive) organic matter suggest these sediments likely respond strongly to oxidation during dredging and disposal. The implications of our findings within the context of sediment reuse and present future plans therefore offer theoretical explanations for estimating greenhouse gases and metals release under different disposal scenarios.

References: [1] Kirichek (2018) *Rostocker Baggertseminar*; [2] Kraal et al. (2013) *Geochimica et Cosmochimica Acta* **122**:75-88 ; [3] Du Laing et al. (2009) *Sci. of Total Environment* **407**:3972-3985.