Trace metals in estuarine and coastal waters: dynamics, speciation and bioavailability under various environmental conditions

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Along with a worldwide growth of the human population, aquatic environments are facing an ever-increasing chemical input. With the aim of regulating chemical use and protecting both humans and the environment, several regulatory frameworks have been introduced at the European scale. Yet, these regulations only focus on a limited list of priority pollutants. Moreover, and regarding hazardous elements such as trace metals, the EQS-directive of 2013 (2013/39/EU) which defines environmental quality standards (EQS) only takes into account dissolved or particulate concentrations of trace metals, or concentrations in the biota. Thus, no appropriate EQS exists for bioavailable concentrations (i.e. the fraction which is likely to be assimilated by an organism). In addition, the behavior, transport, and fate of these concerning elements in the environment remains poorly understood. To partly address this analytical gap, new ways of monitoring trace metals along our coasts and seas were investigated. More precisely, this research work, which was carried out in the framework of the NewSTHEPS project (funded by the Belgian Science Policy Office BRAIN-be), focused on the development and use of alternative sampling techniques like passive samplers (Diffusive Gradients in Thin-films, DGT) and sediment traps, which were combined with classic analytical tools, to eventually better quantify trace metals and extend the study of their biogeochemistry and bioavailability in aquatic environments. This was combined with stable isotope analysis of Suspended Particulate Matter (SPM) to trace the SPM towards its origin, alongside with the measurements of various physico-chemical parameters inherent to the environments of study.

This unique approach was applied and evaluated in the Belgian Part of the North Sea (BPNS), in the Scheldt estuary as well as in the Baltic Sea, which are three regions of great ecological, economic, even touristic values and places of intense human and industrial activities. To make an assessment of the BPNS and its estuary was essential as an almost 10-years monitoring gap exists for trace metals (total dissolved and particulate phases), and allowed to highlight new insights into the presence, transport, exposure and ecological effects of harmful metals in the shallow coastal areas and estuaries of the Southern Bight of the North Sea.

In addition, the passive sampling technique of DGT was for the first time applied in the BPNS and in the Scheldt estuary, and a first database about labile metal concentrations was therefore obtained in these areas. Key results were obtained in conjunction with existing methods and laboratory experiments at various locations, revealing traces of historical and present contamination in the areas of study.

We focused our attention on the dynamic and speciation of trace metals from the Scheldt estuary to the coastal zone: they seem to be strongly affected by environmental features and gradients (salinity, water oxygenation, tides, shape of the estuarine/seabed), while several temporal and local variabilities were highlighted (seasonally, monthly, year after year by comparisons with literature data). Concurrently, the role of SPM in trapping and storing trace metals was also observed, which certainly decreases the direct impact of dissolved metals on marine organisms. However, this big reservoir may also become a source of pollution when trace metal resuspension and solubilization happen. Finally, the combination of field and analytical techniques allowed to generate a unique set of knowledge and data, supplying the most recent information for the policy makers, and challenging new European assessment criteria for the marine environment under the Water Framework Directive.

In the future, the use of DGT for evaluating the bioavailability of trace metals in fresh and marine waters should be recommended considering its unique features. Additionally, a detailed focus on SPM with the measurements of carbon and nitrogen stable isotopes has shown a good interest for tracing the origin of SPM, giving us supplementary information on trace metal sources and SPM organic composition. This

research ultimately contributes to the development of a toolbox to evaluate anthropogenic pressures on estuarine and coastal ecosystems, regarding trace metals. Thus, this extensive approach has the potential to be part of a new standard and legal framework for future environmental monitoring.