DEVELOPMENT OF COMPLEMENTARY CE-MS METHODS FOR SPECIATION ANALYSIS OF METAL-BASED ANTIFOULING BIOCIDES IN SURFACE WATER

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All underwater surfaces are subjected to biofouling, which causes substantial encroachments e.g. for shipping. On the one hand, global shipping traffic can lead to spreading of invasive species, on the other hand biofouling causes a higher flow resistance of ships and thereby increased fuel consumption and greenhouse gas emissions.

Until 2008, tin based antifouling compounds (TBT) were applied, but because of their persistence and severe toxicity on non-target organisms these were banned nearly worldwide. Today, frequently used paints are based on Cu and Zn with addition of booster biocides for enhanced efficiency. These are organic pesticides, which can be analyzed rather easily, or certain metal based complexes like Cu and Zn pyrithione[1]. Some toxic effects of pyrithione complexes on non-target organisms, e.g. blue mussels (Zn pyrithione LD_{50} = 2.5 µg/L[2]) and annelids (Cu pyrithione LD_{50} = 0.06 mg/L[3]), as well as possible bioaccumulation[4] were already reported.

Through transmetalation or biotic and abiotic degradation processes of the mentioned metal-complexes in the environment, cations from sediments can be made bioavailable again and species/transformation products showing altered environmental properties (e.g. enhanced bioaccumulation) can be formed. However, suitable analytical methods for investigating the environmental behavior of initial metal-based biocides and different species are missing.

This work presents a new method for speciation analysis based on capillary electrophoresis coupled to mass spectrometry (CE-MS), which allows investigations of the environmental behavior of metal-pyrithione complexes in surface water. Employing CE/ESI-ToF-MS, emerging species could be successfully identified and quantified. In the case of unavailability of species-specific standards as well as investigations regarding transmetalation, complementary CE/ICP-MS enables a species-unspecific quantification and closing of mass balances. Release and degradation of zinc pyrithione from biocide containing antifouling paints in real matrices (surface water) were investigated successfully with these methods.

[1] Antifouling-Produktliste 2017, LimnoMar.
[2] J. Bellas et al. *Mar. Pollut. Bull.* **2005**, 50, 1382-1385.
[3] K. Mochida et al. *Chemosphere* **2011**, *82*, 390- 397.
[4] M. Marcheselli et al. *Aquat. Toxicol.* **2011**, *102*, 39-47.