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# Dynamics of zero-valent sulfur species, including polysulfides, in Wadden Sea tidal flat pools

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Zero-valent sulfur (ZVS) species (rhombic elemental sulfur, colloidal elemental sulfur, inorganic polysulfides ($S_n^{2-}$) and polythionates ($S_nO_6^{2-}$)) play an important role in a variety of environmentally, geochemically and biogeochemically important processes. Polysulfides are known to decompose halogenated pollutants by reductive dehalogenation pathway. They are the important reactants in pyrite formation and sulfurization of sedimentary organic matter during early diagenesis. ZVS compounds are also important bacterial substrates. In natural aquatic systems ZVS species can be produced by microbial as well as by chemical pathways.

ZVS species dynamics in tidal flat pools of Wadden Sea (North Sea) was studied. Concentrations of solid sulfur, colloidal sulfur and distribution of inorganic polysulfide species were detected in different pools as a function of time after detachment of the pool from the sea.

Every sample was analysed by the protocol that consists of 4 procedures: 1) detection of individual inorganic polysulfides by rapid single-phase derivatization with methyl trifluoromethanesulfonate followed by HPLC-UV detection of dimethylpolysulfanes [1]; 2) detection of colloidal elemental sulfur, polysulfide and polythionate ZVS by reaction with hydrogen cyanide followed by HPLC-UV detection of thiocyanate; 3) pre-treatment with zinc chloride solution followed by chloroform extraction and HPLC-UV detection of elemental sulfur; 4) analysis of individual polythionates by HPLC-UV. Detection limit of each procedure was ≤2 µM.

Maximum sulfide concentration detected in the pools was 273 µM. During the initial 2 hours of pool detachment from the sea the main ZVS pools were colloidal sulfur and polysulfides. Despersed solid sulfur concentrations reached significant values only 5 hours after pool detachment. Maximum concentration of colloidal sulfur detected in the pools was 73 µM and total ZVS >100 µM. Polythionates with n=4-6 were not observed in any of the analysed samples.

Individual polysulfides with chain lengths of 4-6 sulfur atoms were quanitatively detected for the first time in marine waters. Polysulfides concentrations were found to be lower than the predicted ones by calculations based on thermodynamic values. Maximum detected sum of $S_4^{2-}$, $S_5^{2-}$ and $S_6^{2-}$ concentrations was 5.9 µM.

**References**

[1] Kamyshny A., Jr. et *al.* (2006) *Anal. Chem.* **78**, 2631-2639.