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Biogeochemical dynamics in sediments of a coastal fresh water lake

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In this study, we examine a data set of pore water and solid phase concentrations of the major redox-reactive species in sediments with a reaction-transport model. Use of the model allows for determination of carbon mineralization rates and the rates of secondary redox reactions. The model can also be used as a predictive tool to simulate the response of the sediment to changing conditions in the overlying water.

The Haringvliet is a fresh water lake in the southwestern Netherlands. The lake was formerly a brackish, tidal estuary but was closed from the North Sea by a dam in 1970. Since closure, the Haringvliet has accumulated contaminated sediment carried by its source waters, the Rhine and Meuse rivers. Pore water and sediment samples were collected during three research cruises between 2001-2003. Plans for the possible restoration of estuarine conditions have prompted this study of biogeochemical processes in the sediment.

The Biogeochemical Reaction Network Simulator (BRNS) was used to conduct the modeling study [1]. This modular modeling framework allows for flexibility when constructing the multicomponent reaction network and transport conditions. The model includes 26 species and 31 reaction pathways. Model parameters were estimated from site data or from previous modeling studies [2].

Dissolved O_2 and NO_3^- are rapidly consumed in the pore water (penetration depths less than 5 mm). The majority of carbon mineralization below this depth is the result of methanogenesis. The oxidation of CH_4 and NH_4^+ are significant secondary redox reactions occurring near the sediment water interface. Simulation of estuarine restoration predict increased sulfate reduction, sulfide precipitation, and dissolution of Fe(III) minerals, on the one hand, and decreased methanogenesis and methane oxidation, on the other.

References
[1] Regnier P.A.G., Jourabchi P., and Slomp C.P. (2003) *Neth. J. Geosci.* **82,** 5-18.
[2] Van Cappellen P., and Wang Y. (1996) *Amer. J. Sci* **296,** 197-243.

4.3.47

Biogeochemical process identification in aquatic sediments: A model approach

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We apply a reactive transport model to quantify the depth distribution of redox processes in deep sea sediments. Since most of these processes influence the proton balance, pH is used as a diagnostic indicator of their relative intensities provided that the buffering effect of calcite dissolution induced by redox chemistry is also taken into account.

The one-dimensional model is mainly driven by inputs of organic and inorganic carbon. The reaction network consists of organic carbon oxidation pathways (primary redox reactions), secondary redox reactions among inorganic species, mineral dissolution / precipitation reactions, and acid-base chemistry. The reaction formulations are combined with the transport processes: sedimentation, bioturbation, and molecular diffusion. The resulting set of equations for all species concentrations is solved at steady state. Published pH profiles from various sites with distinct bottom water compositions and particulate depositional fluxes show common features that are successfully reproduced by the model.

The rates of proton production / consumption are calculated a posteriori from the resulting profiles of species concentrations and process rates. This computational scheme allows for the identification of the main processes affecting pH. The pH profile can be divided into two zones, each of which contains an extreme value in pH. The first zone identified by a pH minimum and the depth at which the minimum occurs are related to oxic respiration and calcite dissolution. The pH drop in the zone of oxic respiration is limited by the buffering effect of calcite dissolution. In the second deeper zone, the maximum value of pH and its corresponding depth are related to metal oxide reduction and secondary redox reactions. Specifically, most secondary redox reactions limit the increase in pH caused by dissimilatory manganese oxide and iron (hydr)oxide reduction. Our systematic analysis provides a theoretical framework for the quantitative interpretation of high resolution porewater pH profiles. This interpretation can then be used to unravel the interplay of the major processes involved in redox and carbonate geochemistry of deep sea sediments.