

Interactions of Iron, Manganese and Nitrogen in Muddy Sediments of the Bay of Biscay

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Bacterially-mediated oxidation of organic matter proceeds via a well-established sequence of primary redox reactions. These reactions result in the production of reduced by-products which participate in a wide diversity of secondary reactions. The secondary reactions affect the availability of oxidants and may therefore influence the relative importance of organic matter degradation pathways. Recent studies have highlighted novel secondary reactions coupling Fe, Mn and N. For example, manganese oxides may be reduced directly by ammonia (Aller et al., 1998; Hulth et al., 1999), while Mn^{2+} and Fe^{2+} may reduce nitrate to dinitrogen (Postma, 1990; Murray et al., 1995; Luther et al., 1997). In this paper, the interactions between iron, manganese and nitrogen are investigated in sediments of the Aquitaine margin of the Biscay Bay. Vertical distributions of dissolved manganese, iron, nitrate, and ammonia, as well as reactive solid Fe and Mn, total S, total C, organic C and radionuclides (^{210}Pb and ^{234}Th) were measured within the first decimeters of sediments collected at 150, 280, 550, 1000 and 2800 m water depths, across the slope of the Bay of Biscay in January 1999. The 5 sites can be separated into two groups. In the shallowest stations, located at depths above 300 m, sediments are highly bioturbated and organic carbon levels (2.5–3%) remain constant with depth. In the deeper stations, bioturbation is minimal (excess ^{210}Pb decreases exponentially), organic carbon levels are lower than 1% and decrease with depth. Based on the vertical concentration profiles, diffusive solute fluxes and, in non-bioturbated sediments, advective particulate fluxes were calculated. Profiles of reducible manganese oxides (extracted by ascorbate and 1N HCl) show subsurface maxima, which are attributed to detrital Mn-oxides and authigenic Mn-oxides precipitating from the oxidation of dissolved Mn^{2+} that diffuses from below. In the shallower stations, as a consequence of sediment mixing by bioturbation, measurable concentrations of Mn-oxides are found throughout the sediment. In contrast, at stations below 500 m water depth, concentrations decrease abruptly below the aerobic layer, reaching values close to zero, indicating complete reduction of the Mn-oxides. The concentrations of dissolved ammonia increase with depth and are highest in the shallower stations. Ammonia is oxidized at the bottom of the oxic layer where

manganese oxides represent a potential oxidizing agent. In the non-bioturbated stations, the flux calculations suggest that ammonia is almost entirely oxidized by Mn-oxides. Consequently, the reduction of manganese oxide by ammonia can compete with, or even short-circuit, the dissimilatory reduction of manganese oxides. In the shallower sediment we were unable to quantitatively assess the importance of the reduction of Mn-oxides by ammonia. Appreciable concentrations, between 50 and 100 $\mu\text{mol/g}$, of reactive iron (III) compounds extractable with ascorbate are present in the cores. Reactive Fe(III) decreases with depth in the deepest cores, whereas the profiles remain relatively constant in the bioturbated sediments. That is, extractable iron shows similar depth profiles as extractable manganese. Nitrate drops to concentrations close to zero below the oxic layer. In all the stations, nitrate profiles overlap with dissolved iron (II) profiles, suggesting that nitrate is a potential oxidant for reduced iron and helps to keep the iron redox cycle within the sediment. According to the flux calculations, between 4 and 39% of the downward nitrate fluxes are reduced by iron (II). The results of this study, including profile shapes, calculated fluxes, and reaction stoichiometries, suggest that reduction of Mn-oxide by ammonia and oxidation of dissolved iron by nitrate are important processes in the sediments of the Bay of Biscay. Those two secondary reactions reduce the availability of manganese oxides and nitrate for respiration of organic matter (dissimilatory manganese reduction and denitrification), hence making more organic matter available for iron oxide respiration and sulfate reduction.

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