



Partitioning of reduced-S forms and stability of trace metals in anoxic sediments of a shallow eutrophic Mediterranean lagoon

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In coastal marine sediments, the cycling of sulfur is controlled by the bacterial sulfate respiration. Sulfate-reducing bacteria produce sulfide by using sea water sulfate as the terminal electron acceptor in the degradation of organic matter. The sulfide produced (H_2S , HS^- , S^{2-}) is mobile unless it reacts chemically with various metals. In many marine ecosystems iron is quantitatively the most important metal. Ferrous iron (Fe^{2+}) can react with sulfide resulting in the formation of amorphous FeS and/or crystallized FeS forms (such as mackinawite and greigite), which are precursors to pyrite generation. During this sulfidation process, trace metals can adsorb onto or coprecipitate with FeS minerals or precipitate directly as discrete sulfides. As a result, the partitioning of trace metals (e.g. Zn, Pb, Cu, Cd, etc..) in anoxic sediments is mostly dominated by their presence as sulfide phases. In the presence of oxygen, sulfide can be oxidized and may result in the formation of sulfate and/or partly reduced intermediates (elemental sulfur, sulfite...) and in the removal of associated trace metals. Thus, the stability of the reduced-S solid phases in sediments governs the sink of the trace metal contaminants in anoxic environments.

In Thau lagoon sediments, where the sulfate respiration is the dominant process in the mineralization of the organic matter, the formation of FeS and FeS_2 can be considered as a temporal sink for sulfide and trace metal elements. Two sampling stations were selected in contrasted areas of this Mediterranean shallow coastal lagoon. The first one was located in a shellfish farming zone (Station C5) while the second was outside,

in the centre of the lagoon (Station C4). In Thau lagoon sediments, the solid-S phase distribution show an upper monosulfide-rich layer (AVS-rich layer) and an underlying pyrite-rich layer (Pyrite-S -rich layer). In the oyster production zone (Station C5), the AVS (Acid Volatil Sulfides) concentrations in the upper layer (3.5-5 mg.g⁻¹) were twice order of magnitude much important than in the centre of the lagoon (Station C4: 1.6-2.1 mg.g⁻¹) due to high sedimentation and organic matter mineralization rates that limit the AVS oxidation. In the underlying layer, Pyrite-S concentrations increased with depth, with 9.5 mg.g⁻¹ at Station C5 and 7.8 mg.g⁻¹ at Station C4. In the both stations, the Degree of Pyritization was generally less than 40% and increased with the Degree of Sulfidisation with sediment depth, indicating that the availability of reactive iron was not a limiting factor to the formation of iron sulfide minerals. The high AVS contents and their large excess to trace metal contents (Cd, Cu, Pb and Zn) in Thau sediments suggest that trace metals are likely to be bound as sulfide minerals. The decrease of AVS to pyrite-S ratios and HCl-trace metal extractability with increasing depth reflect the replacement of AVS by pyrite and simultaneously the sequestration of trace elements by pyrite. This efficient conversion to pyrite in the oyster production zone sediments (Station C5) provide a long-term sink for trace metals. Conversely, in the centre of the lagoon, where the amount of trace metals is 1.5 to 2 order of magnitude less important than in Station C5 and the pyritization rate is low, sediments are a less efficient trace element sink. Trace metals are mainly associated with AVS representing a temporary sink that can potentially release these elements during oxidation stages (bioturbation, resuspension of anoxic sediments ...).