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Bacterial activities driving arsenic speciation and solubility in marine sediments

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Harbour and marina sediments represent particular environments, with high concentrations in organic carbon and pollutants. Over 50 million m3 of marine sediments are dredged every year in French maritime and commercial ports, to maintain the water depth suitable for navigation, and the most part of them is discharged in deeper sea zones. The present study aimed to elucidate, using a range of complementary approaches, the influence of bacterial activity on arsenic speciation and mobility in marina sediments. Two sites were considered: L'Estaque, impacted by metallurgical activities and by the commercial port of Marseille, and St-Mandrier, less polluted, affected by classical chemical pollutants associated to professional and recreational boating. Arsenic concentration was noticeably higher in l'Estaque sediment (200-350 mg/kg) than in St-Mandrier sediment (15-50 mg/kg). In the solid phases, As(III) was the dominant species in L'Estaque sediment, whereas As(V) was the main form in St Mandrier sediment. At both sites, arsenic was the major trace element detected in interstitial water. Free sulfide and thio-arsenic complexes were detected in the interstitial water of l'Estaque sediment, suggesting a role of sulfate-reduction bacterial activity on arsenic solubility. Anaerobic microcosm experiments confirmed this hypothesis, as stimulation of sulfate-reduction induced a dramatic increase of arsenic concentration in the liquid phase, linked to the formation of soluble thio-arsenic complexes. Nevertheless, microcosms performed in aerobic conditions showed that bacterial activity globally decreased the transfer of arsenic from the sediment toward the overlying water. A red-brown fine layer developed at the sediment-water interface. Altogether, these results suggest that the sediment-water interface zone and the close transition area between aerobic and anaerobic conditions host intense biogeochemical reactions involving As, Fe and S species. These reactions most probably include dissolution of FeS (which confers to the muddy sediment its deep dark color), oxidation of Fe(II) to Fe(III), oxidation of As(III) to As(V), oxidation of S(-II) to S°, S(VI) and maybe other intermediate species, adsorption of As(V) onto fresh iron oxides. Bacterial activity tests applied to the crude sediments indicated that As(III)-oxidizing and As(V)-reducing micro-organisms have the potential to be active at both sites. Detection of aoxB and arrA genes, respectively specific to As(III)-oxidation and respiratory As(V)-reduction, revealed the presence of diverse bacterial communities able to contribute to As transformation in both St-Mandrier and l'Estaque marina sediments. As(III)-oxidizing bacteria probably contribute to the biogeochemical stabilization of arsenic, wherever electron acceptors are available. Whereas reducing conditions prevail in organic carbon-rich marina sediment, bacteria able to oxidize As(III) are present and can be rapidly active as soon as electron acceptors are available. The present study showed that arsenic, which inorganic forms As(III) and As(V) are particularly toxic, is one of the most mobile pollutants in polluted marina sediments. The biogeochemical reactions governing its mobility should thus be considered in the management of sediment dredging operations.

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