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Biogeochemistry of hydrogen sulfide and methane in sediments of the Namibian upwelling system and their relationship to water column anoxia and nutrient levels (NAMIBGAS)

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Free water column hydrogen sulfide in the Namibian coastal upwelling system is an extreme result of oxygen deficiency and has been implicated as a major player in causing massive fish kills, particularly of juvenile stages in protected near-shore habitats. The goal of the BMBF Geotechnologien funded project NAMIBGAS is to understand the physical, biological, and chemical processes that control the episodic rise and disappearance of water column hydrogen sulfide and its effects on living resources. Extremely high anaerobic carbon degradation rates in the diatomaceous muds of this upwelling system fuel hydrogen sulfide and methane production. Direct radiotracer measurements indicate that water column hydrogen sulfide derives predominantly from the underlying sediments from which it is transported by diffusion and by gas-driven advection.

Strong temporal variations exist in the supply of dissolved oxygen and nitrate to the bottom waters. These compounds are important electron acceptors for the bacterial oxidation of hydrogen sulfide. ^{15}N-incubations and high-resolution microsensor profiles of dissolved sulfide, oxygen, and pH across the sediment water interface suggest that hydrogen sulfide is oxidized even in the absence of dissolved oxygen using nitrate as electron acceptor. At the sediment-water interface, the large nitrate- and sulfur-storing

bacteria *Beggiatoa* and *Thiomargarita* sp. catalyze bacterial sulfide oxidation. Temporal variations in the supply of nitrate to the upwelling system have a profound influence on the development of sulfidic bottom waters. The biomass of the large sulfur bacteria *Beggiatoa* sp. increased after a brief period of mild bottom water oxygenation, which was coincident with bottom water nitrate replenishment. These conditions effectively minimized the flux of hydrogen sulfide across the sediment surface. N_2 gas was the dominant product of nitrate reduction and indicated that bacterial sulfide oxidation catalyzed an important nutrient loss pathway in these sediments.

Local hotspots in methane accumulation coincided with areas where the diatomaceous muds are the thickest supporting the *in-situ* production of methane. Substantial accumulation of methane just below the sediment surface episodically exceeds the hydrostatic pressure and the shear strength of the sediment, which results in gas ebullition and associated advective hydrogen sulfide transport. The total area of gas-saturated sediment is about 1350 km^2, which is less than two percent of the Namibian continental shelf. Strong abrupt temporal variations in methane concentration occur simultaneously in the top 10 cm of sediment at stations more 100 km apart. Brief episodic methane spikes were also detected with moored sensors in the overlying water column. During these periods, the net flux of hydrogen sulfide to the sediment surface is enhanced several fold. These events are unrelated to changes in rates of sedimentary bacterial sulfate reduction and methanogenesis. Instead, they suggest episodically enhanced methane transport by currently poorly understood physical processes that change the pressure balance between the sediment and the overlying water column.