Seasonal Variations in Sediment Sulfur Cycling in the Ballastplaat Mudflat, Belgium

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ABSTRACT: Sulfate reduction rate (SRR) and pools of reduced inorganic sulfur, acid volatile sulfide (AVS), chromium reducible sulfur (CRS), and elemental sulfur (S0), were studied from June 1990 till March 1992 at two locations on the Ballastplaat mudflat in the Scheldt estuary. The sediment composition at station A was mainly sand with low organic content whereas sediments at station B were dominated by silt and clay with high organic content. SRR was positively related to temperature; more pronounced at station B (Ea = 190 kJ mol-1) than at station A (Ea = 110 kJ mol-1). The maximum SRR values observed equalled 14 μmol cm-3 d-1 at station B and 1 μmol cm-3 d-1 at station A. AVS was the dominant radiolabelled end product of the sulfate reduction reaction, except in surface sediments where pyrite and S0 were more dominant. However, CRS was the predominant reduced inorganic sulfur pool in the sediments. Both AVS and CRS pools showed temporal variations out of phase with SRR. SRR peaked in summer, while the concentrations of AVS and CRS were highest in fall. The accumulation of AVS and CRS started late summer after depletion of oxidants, which had accumulated during winter and spring. The estimated annual SRR and thus sulfide production in the upper 15 cm of station B was of the order of 100 mol m-2 yr-1, and at station A of the order of 12 mol m-2 yr-1. The sulfur mass balance shows that only a very small fraction, if any, of the produced sulfide is retained as reduced inorganic sulfur in the sediment.

Introduction

Sulfate is the dominant electron acceptor for oxidation of organic carbon via dissimilatory sulfate reduction in oxygen depleted marine environments (Goldhaber and Kaplan 1974; Postgate 1979). Aquatic sediments are largely anaerobic beneath a shallow, oxic layer, which is usually only a few millimeters deep (Revsbech et al. 1980). Decomposition of organic matter in marine sediments is therefore a function of aerobic metabolism in this narrow surface layer together with anaerobic decomposition which proceeds below the oxic layer. Anaerobic decomposition relies upon the interactions of a complex community of anaerobic bacteria, each of which brings about partial oxidation of the organic substrates leading to simpler organic molecules, acetate being the most important. In the terminal stages the sulphate respiring bacteria are responsible for the ultimate conversion of organic carbon to carbon dioxide (Abram and Nedwell 1978; Nedwell 1984). The reason for their importance is that seawater contains approximately 26 mM sulphate, providing abundant electron acceptors for this group of bacteria. In Long Island Sound, about 11% of the net primary production in the top 10 cm of the sediment is broken down by sulfate reducers (Aller and Yingst 1980). It has been demonstrated that in coastal marine sediments 10% to 50% of the organic matter mineralization is driven by sulphate respiration with the balance due to aerobic metabolism (Jørgensen 1982). Mackin and Swider (1989) reported that 65% to 85% of organic carbon in coastal marine sediments is decomposed by sulfate reduction. In the muddy sediments of the Ballastplaat (the sampling area in this study), Elskens et al. (1991) found that less than 20% of the electron flux involved in the anaerobic degradation of the organic matter relates to Fe(III) reduction, the remaining and major part resulting from sulfate reduction. Skyring (1987) reviewed the sulfate reduction rates and noted that they vary seasonally and between sediment types. High sulfate reduction rates are usually found in sediments containing a high amount of organic matter.

The H2S produced from the organic matter oxidation process is partially lost through atmospheric emission or reoxidation into sulfate in oxidized environments (King 1988; Luther et al. 1991), while the other part reacts with reactive metals in anaerobic environments to form insoluble metal sulfides (Salomons and Forstner 1984; Morse 1994). Iron monosulfide (FeS) and pyrite (FeS2)
generally represent the major reduced inorganic sulfur pools in marine sediments (Berner 1984; King et al. 1985; Thamdrup et al. 1994). The retention of freshly produced sulfide varies from one system to another. Jørgensen et al. (1990) estimated that only about 10% of the produced sulfide is buried in coastal marine sediments, while Chanton et al. (1987) found that up to 77% is retained in rapidly accumulating sediments. The role of benthic bioturbation as a loss process for sulfide and pyrite was reported by Berner and Westrich (1985).

During a study on the geochemical behavior of heavy metals in sediments of the Ballastplaat mudflat (Fig. 1), it became clear that reduced inorganic sulfur (RIS) pools played an important role on the mobility of the metals in these sediments (Panutrakul and Baeyens 1991). Therefore, more information about the sulfur cycle and the seasonal variations in RIS-pools in these mudflat sediments was needed.

Sampling Area

The Ballastplaat, a 250 hectares mudflat, is located in the Scheldt estuary near the Belgium-Dutch border, about 60 km from the river mouth. Details about the physical and hydrodynamical characteristics of the Scheldt, which is one of the most polluted estuaries in Europe, can be found elsewhere (Baeyens et al. 1998). It is, however, worthwhile to note that the dissolved oxygen content in the Scheldt estuary near the Belgium-Dutch border varies seasonally from close to zero in summer to almost saturated in winter (Somville and De Pauw 1982; Baeyens et al. 1998). Two sampling stations (stations A and B) representing a sandy and a muddy type of sediment were chosen according to their sediment characteristics. Sediments at station A consist of about 85% sand (grain size > 63 μm), while sediments at station B contain about 85% silt and clay (grain size < 63 μm). Results from a preliminary study on the geochemical behavior of Fe, Mn, Cd, and Pb in the sediments of the Ballastplaat are reported by Baeyens et al. (1991). In addition, redox profiles at stations A and B were shown: at the sediment surface at station A the redox potential equals 350 mV, smoothly decreases to 250 mV at 5 cm depth and then rapidly falls down to −100 mV at 10 cm depth, while at the sediment surface at station B the redox potential equals 80 mV and then rapidly falls down to −200 mV at 2.5 cm depth.

Microbial Description of the Sampling Stations

In the upper layer of the sandy sediment (station A), oxygen is apparently the terminal electron acceptor. Substantial numbers of aerobic chemoheterotrophic bacteria (most of which were gram-negative) have been enumerated by a classical plate count method (Elskens et al. 1991). As oxygen is consumed, conditions become locally anaerobic and fermentative organisms develop. The products of fermentation then diffuse to regions in which oxygen is still present or they may be oxidized anaerobically by organisms able to reduce nitrates, sulfates, or carbonates. Reduction of iron and sulfate was already detected close to the subsurface of the sediment. The FeS (+FeS₂) profile increased slowly with depth below the upper 1-cm slice, but most of the iron remained in the ferric form. Small concentrations of reduced sulfur were detected in the interstitial water (Panutrakul 1993).