REMINERALIZATION RATES OF ORGANIC CARBON IN THE SEDIMENTS IN THE GULF OF TRIESTE (N ADRIATIC)

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Abstract

Remineralization rates of organic matter were calculated in high carbonate coastal marine sediments of the Gulf of Trieste, northern Adriatic, using a non-local exchange, vertical diffusion-reaction model of the dissolved inorganic carbon (DIC) depth profiles. It appears that there is a reactive portion of organic matter which is oxidized at the sediment water interface. Examination of the dissolved Ca^{2+} profiles indicated that there was significant production of acid which dissolved $CaCO_3$ in the sediment in winter and late spring. The calculated remineralization rates varied seasonally with the highest observed in September 1995. During this period the dissolution of $CaCO_3$ accounted for only 9% of DIC produced.

Key-words: carbon, sediments, Adriatic Sea

Introduction

Sediment biogeochemistry plays an active role in the regulation of carbon cycling in aquatic environments. Processes in sediments are coupled to the microbially-mediated degradation of organic matter deposited from the overlying water. The electron and mass balances in sediments are coupled to each other and are determined primarily by the microbial oxidation of organic matter. The concentration of dissolved inorganic carbon in marine sediment interstitial solution reflects the remineralization of organic carbon to CO_2 in marine sediments. In coastal environments other factors influencing the dissolved inorganic carbon (DIC) in pore water are dissolution or precipitation of carbonates, and mixing with dissolved inorganic carbon from the overlaying water column [1, 2]. In order to investigate the complex mechanisms that regulate the remineralization of organic carbon, pore water and solid profile measurements are made [3] and combined with benthic flux measurements [4, 5, 6], or laboratory experiments [4, 7]. Additionally, mathematical models may be used to provide quantitative estimates of the remineralization of organic carbon in sediments [8, 9]. Most commonly applied are stoichiometric models assuming that organic matter with Redfield stoichiometry (C:N:P = 106:16:1) is oxidized to CO_2 using O_2, NO_3^-, MnO_2, Fe_2O_3, SO_4^{2-}, CO_2 as electron acceptors. Changes in DIC with depth are predicted considering equilibrium with calcite, the stoichiometry of oxidation, the diffusion of solutes through pore water, and assumed rates of oxidation of organic matter [8, 9]. This approach has been useful in understanding processes in deep-sea sediments, but its application in nearshore sediments is more uncertain. The active benthic community in coastal sediments enhances solute transport through mixing and irrigation [1, 2].

In this paper the amount of organic carbon oxidized to CO_2 was estimated by applying a simple non-local - diffusion - reaction model to the DIC depth profiles. This study shows that in high carbonate surficial sediments of coastal marine environments, the degradation of organic carbon is the principal source of DIC in pore water during all seasons. However, the contribution of calcite dissolution should be taken into account, especially in the colder months when the rate of degradation of organic matter is slower.

Methods and site description

Site description. Sediment samples were collected in the central part of Gulf of Trieste in the northern Adriatic. The sampling site is at a depth of 21 m. Vertical temperature and salinity gradients in late summer often result in bottom water hypoxia (occasionally anoxia). The sediment is composed of silty sand with up to 80% carbonate. Carbonate minerals are mostly composed of low-magnesium calcite. The sediment contains approximately 0.7 wt % C of dry sediment as organic carbon. The composition of the sediment in profile is practically uniform. Sedimentation rates, based on ^{210}Pb distributions, are approx. 1-2 mm yr^{-1} in the central part of the gulf [10]. The surficial sediments are bioturbated mostly by polychaetes and bivalves.

Sampling methods. Sediment samples were taken in June and September in 1995 and in January 1996 by SCUBA divers inserting a plexiglass tube (6 cm i.d.) directly into the sediment (approx. 30 cm). Undisturbed sediment cores were transported immediately to the laboratory. In a N_2-filled glove bag, cores were cut into 1, 2 or 4 cm

segments. Pore water was squeezed from the sediment under 0.4 MPa nitrogen through a $0.45\,\mu m$ membrane filter. The pH electrode was inside the glove bag and pH was measured immediately after collecting the sample. Subsequent samples were collected for alkalinity. Ca^{2+}, Mg^{2+}, dissolved Fe and Mn, PO_4^{3-}, NO_3^-, NH_4^+ and SO_4^{2-}. Samples for metal analysis were acidified with ultrapure HNO_3. A portion of the sediment solid phase was freeze-dried and ground to a fine powder for analysis of organic C and total N.

Chemical analysis. Standard analytical methods were used. Alkalinity was determined by the Gran titration method; the precision of the analysis was ± 1% [11]. DIC was calculated from alkalinity, pH and salinity data using the apparent dissociation constants of Mehrbach *et al.* (using the fitting functions given by Dickson and Millero [12]), and the boric acid acidity constant of Lyman [12]. Concentrations of metal cations were determined by flame AAS. Phosphate, nitrate, ammonia, and sulphide were analyzed using standard colorimetrical methods [13]. Analysis of organic C and total N in sediment samples were performed using a Carlo Erba elemental analyzer (mod. EA 1108) after acidification with 1M HCl [14].

Results and discussion

The data collected in this study were used to calculate seasonal rates of mineralization of organic carbon to CO_2. The rate of oxidation of organic carbon was determined by modeling the seasonal profiles of DIC in the central part of the Gulf of Trieste. The major processes affecting the pore water concentration of DIC described in the model are diffusion, irrigation, oxidation of organic carbon and dissolution or precipitation of $CaCO_3$. Changes in the concentration of DIC by oxidation of organic matter or equilibration with $CaCO_3$ are described by the CO_2-production rate, $Rc(z)$. $Rc(z)$ is assumed to decrease exponentially with depth and in our model it is described by two exponential functions. This assumption was based on a study by Westrich and Berner [15], which showed that organic matter was composed of two reactive fractions of different reactivities, and a non-degradable fraction. Thus the functions describing $Rc(z)$ are [1]:

$$Rc = R_0 \exp(-\beta_1 z) \qquad \text{from 0 to } z_b \qquad (1)$$

$$Rc = R_{zb} \exp[-\beta_2 (z-z_b)] \qquad \text{from } z_b \text{ to } \infty \qquad (2)$$

where R_0 is the production of DIC at the sediment-water interface, β_1 and β_2 are the so-called depth attenuation coefficients, and z_b is the depth at which the rapidly degradable material is exhausted and $R_{zb} = R_0 \exp(-\beta_1 z_b)$. The transport of DIC due to biological irrigation was described using the non-local source model of Emerson *et al.* [16]. Given the above assumptions, the equation defining the change of DIC with time and depth is:

$$\frac{\partial C}{\partial t} = D_{HCO_3} \left(\frac{\partial^2 C}{\partial z^2} \right) - \alpha \left(C_z - C_0 \right) + Rc(z) \qquad (3)$$

In the equation C_z and C_0 [mM] are the concentration of DIC at the depth z and at the sediment-water interface at z=0, respectively, t is time [sec], D_{HCO_3} is the sediment diffusion coefficient for HCO_3^- corrected for temperature and tortuosity from the diffusion coefficient of Li and Gregory [17] [cm^2 sec^{-1}], and α is the irrigation parameter [sec^{-1}]. Eqn. (3) was solved assuming steady-state conditions, *i.e.* $\partial C/\partial t = 0$. To use the model to calculate $Rc(z)$, the irrigation parameter, α must