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STABLE CARBON ISOTOPES IN PORE WATERS OF COASTAL MARINE SEDIMENTS (THE GULF OF TRIESTE, N ADRIATIC)†

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Abstract

The sources of dissolved inorganic carbon (DIC) were determined in pore waters of coastal marine sediments in the Gulf of Trieste, Northern Adriatic Sea, using stable carbon isotopes. The negative correlation between concentration and isotopic composition of DIC indicates that the oxidation of organic carbon, C_{org}, is an important process in the CO_2 formation. A diffusion-reaction-exchange model that accurately described the profiles of DIC concentrations at this site could not be used to reproduce the observed isotopic profiles. The values of $\delta^{13}C_{DIC}$ added to the sediment pore waters calculated using a mixing model for non-methanogenic sediments were between –3.8 and –13.7‰, significantly greater than $\delta^{13}C$ of C_{org} (–21‰). Dissolution of $CaCO_3$ was estimated to contribute 35-57% to DIC in winter and late spring and 14% in late summer when the degradation of organic matter was the highest. Another source of ^{13}C-enriched carbon in pore waters might be diffusion of bottom-water CO_3^{2-} ion into the sediments, or the diffusion of ^{13}C-depleted $H_2CO_3^*$ from pore waters to bottom water.

Introduction

The carbon cycle plays a dominant role in controlling many biological and chemical processes in the marine environment. With relevance to the global cycling of carbon and the processes, which act to control levels of atmospheric CO_2 numerous studies have focused on the remineralization of organic carbon in sediments, specially in coastal zone. Oxidation of organic carbon during early diagenesis effects nutrient balance in coastal system, the residence of pollutants in sediments and the nature of the sediments themselves. In shallow coastal waters, like the Gulf of Trieste (northern Adriatic Sea) where the euphothic zone is present down to the sediment-water interface, oxygen and sulfate appear to be the quantitatively important electron acceptors. Moreover, the majority of O_2 seems to be consumed in the oxidation of reduced species.[1]

The concentration of dissolved inorganic carbon (DIC) in marine sediments interstitial solutions reflects the remineralization of sedimented and sedimentary organic C to CO_2 and the dissolution and precipitation of carbonates. Because the O_2 consumption integrates benthic respiration and oxidation of reduced chemical species in these sediments, it is almost impossible to calculate the actual contribution of benthic O_2 respiration to carbon decomposition. Measuring benthic DIC fluxes could solve this problem since DIC in pore waters is the result of degradation of labile sedimentary organic carbon via various decomposition pathways, if the dissolution and precipitation of carbonates are known.[2] Stable ^{13}C isotopic composition of DIC ($\delta^{13}C_{DIC}$)‡ can be used to investigate the complex processes affecting the production of DIC in coastal sediments.[3-5] Processes that have major effect on pore water DIC are the oxidation of organic carbon, exchange with bottom water and the dissolution and precipitation of carbonates. The isotopic composition of DIC is a sensitive tracer of the oxidation of organic matter within sediments because the $\delta^{13}C$ value of sedimentary organic matter (≈ −20.0‰) is much less than that of bottom–water DIC (≈ 0.0‰) and $CaCO_3$ (≈ 1.0‰). Recent studies showed that $\delta^{13}C_{DIC}$ values in sediment pore waters decrease with depth and DIC added to the pore waters was ^{13}C enriched with respect to the sedimentary organic matter, even considering $CaCO_3$ dissolution.[6,7] Additionally, diagenetic models have been also applied to DIC and dissolved Ca data from deep-sea sediments[8-12] and near shore sediments[7] as well as to stable carbon isotope data,[5,13] to provide quantitative estimates of the oxidation rates and construction of carbon budgets.

In this study we coupled an investigation of the $\delta^{13}C_{DIC}$ in pore water with a comprehensive pore water chemistry and sediment environment at a coastal site in order to define the sources of DIC to pore water. The model accounting for diffusion, irrigation, and the remineralization of organic carbon was used to better understand the observed variations in concentration and isotopic composition of DIC.

Materials and methods

Study area – The Gulf of Trieste is a small (approx. 500 m^2) and relatively shallow marine basin in the northernmost part of the Adriatic Sea. The salinity of the waters in the Gulf ranges between 33 and 38.5 and bottom water temperatures from 8 (February) to 22 °C (September). Vertical temperature and salinity gradients in late summer often result in bottom water hypoxia (occasionally anoxia). The marine geology was described elsewhere.[14] The study site, station F1 (13° 33’ E, 45° 32.298’ N) is located in the central part of the Gulf of Trieste at the depth of 21 m. The sediment her is composed of silty sand that is high in biogenic carbonate and is inhabited by a surface population of brittle stars, sponges and tunicates. The composition of the sediment vertical profile is practically uniform; the $\delta^{13}C$ values of the bulk carbonate averaged +1.13 ± 0.18‰ throughout the upper 20 cm of the sediment core, while the average $\delta^{13}C$ values of sedimentary C_{org} was determined to be –21.3 ± 0.7‰,[15] a value typical of surficial sediments in the central part of the Gulf of Trieste.[16] The organic C and total N contents in the surficial layer averaged 0.7% and 0.15%, respectively, decreasing with depth. The C/N ratios (atomic) were low and varied between 4 and 8 throughout the sediment core, also indicating that the sedimentary organic matter is labile, originates from marine sources and is probably protected by sorption.[16] The ^{210}Pb accumulation rates are 1.2 mm yr^{-1}.[17] The surficial sediments are bioturbated mostly by polychaetes and bivalves.

Sampling **-** Virtually undisturbed sediment cores were obtained to a depth of 30 cm in June and September 1995, and January 1996 by SCUBA diving, inserting a Plexiglas tube (6 cm i.d.) directly into the sediment. The sediment was extruded and divided into 1, 2 and 4 cm intervals in a N_2-filled glove bag. Pore waters were extracted from sediments under a N_2 pressure of 0.4 MPa using a nylon squeezer containing a 0.45 μm Millipore HA membrane filter.[18] In pore waters pH, total alkalinity (TA), $\delta^{13}C_{DIC}$, sulfide and sulfate were analyzed immediately. Pore water samples for Ca determinations were acidified using “ultrapure” HNO_3.

Analyses **-** The pH of pore waters was measured inside the glove bag using an UniFET microelectrode. TA was determined by Gran titration.[19] DIC was calculated from carbonate alkalinity (CA), *in situ* temperature-corrected pH and salinity using the apparent dissociation constants reported by Hansson and Jagner (1973).[20] For comparison, DIC was determined also using a Dohrmann TOC analyzer after acidification of samples with 1M HCl; a good correlation was observed between calculated and measured DIC ($DIC_{cal} = 0.97 \times DIC_{meas} + 0.18$; $r^2 = 0.96$; n = 20). Ca was determined by flame AAS. Sulfide was analyzed colorimetrically[21] and sulfate tubidimetrically.[22]

Pore water samples for determination of $\delta^{13}C_{DIC}$ values were analyzed on CO_2 liberated from 5 mL of water after acidification with 100% H_3PO_4. The stable isotopic composition of the CO_2 produced was determined with an Isotope Ratio Mass Spectrometer – IRMS Europa 20-20 with ANCA-TG preparation module for trace gas samples. Pore water samples (15-25 mL) for analysis of the isotopic composition of dissolved organic carbon, $\delta^{13}C_{DOC}$, were determined according to the procedure described by Fry et al., 1993.[23] Briefly, samples were first filtered through 0.2 μm Millipore filter to remove particulate matter. Then they were freeze dried and treated with 1M HCl. The remaining material was then combusted and the CO_2 produced was determined using Europa Scientific 20-20 IRMS with ANCA-SL preparation module for solid and liquid samples. Stable isotopic results are reported with δ-values as deviations in ‰ from the V-PDB standard.

The precisions, based on replicate analyses, were ±5% for S^{2-} and SO_4^{2-} ions, ±3% for O_2, ±1% for TA, ±2% for directly measured DIC and ±2% for Ca. The precision of pH measurements was ±0.01, while the estimated probable error in the calculated DIC using pH-CA was ±3.8%. The precision of the analyses of $\delta^{13}C_{DIC}$ and $\delta^{13}C_{DOC}$ values based on replicate measurements was ±0.2‰.

Results and discussion

Vertical pore water profiles of TA, DIC, $\delta^{13}C_{DIC}$ and Ca for each sampling period are presented in Figure 1.

The concentrations of TA in overlying water were always higher than those in pore water, and decreased with sediment depth. The vertical decrease of TA indicates the consumption of alkalinity probably due to metabolic acid production during oxidation of reduced species in this bioturbated sediment as reported for other surficial anoxic near-shore marine sediments.[7,24] The concentrations of DIC along the vertical profile show an initial increase followed by a decrease, except in January 1996 when DIC concentrations increased at lower depths. In September 1995, a high concentration of DIC was observed in the overlying water due to oxidation of the highly reactive component of organic matter at the sediment-water interface. Concentrations of Ca, increased in June 1995 but decreased in September 1995 and January 1996 to a nearly constant level less than the subsurficial maximum observed at depths of 2 to 4 cm. Large differences existed in

$\delta^{13}C_{DIC}$ values between the three sampling periods even at greater depths. The $\delta^{13}C_{DIC}$ values decreased along the depth profile in January 1996 but increased in June and September 1995 (Figure 1). The depletion of $\delta^{13}C_{DIC}$ in pore waters was more pronounced in January 1996 when the values of $\delta^{13}C_{DIC}$ ranged from –6.7 to –9.8‰. The $\delta^{13}C_{DOC}$ values (not present), measured only in June 1995, were low, ranging between -24 and -26‰. The concentrations of dissolved sulfide (not presented), measured to correct total alkalinity to carbonate alkalinity, were less than 10 µM while sulfate (not presented) was approximately constant, ranging between 25-30 mM, throughout the pore water profiles.

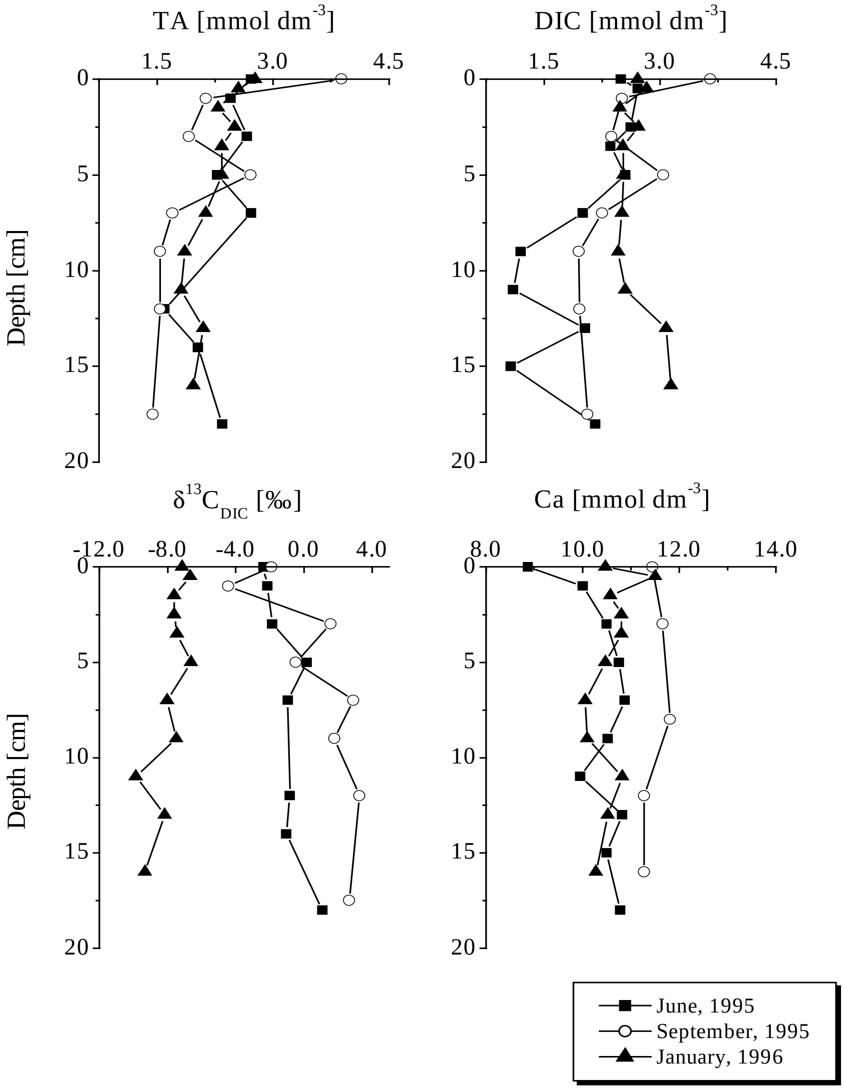

Figure 1. Depth profiles of pore water total alkalinity (TA), DIC concentrations, $\delta^{13}C_{DIC}$ values and dissolved Ca concentrations at sampling station F1 in the Gulf of Trieste on June 1995, September 1995, and January 1996.

The calculated saturation index (Ω; Figure 2) in pore water, using the solubility products (K_{sp}) of calcite and aragonite of Mucci[25] showed that the pore waters were consistently undersaturated with respect to $CaCO_3$ and thus, the conditions for $CaCO_3$ dissolution in these surficial sediments were favorable. On the other hand, the overlying waters were clearly supersaturated with respect to calcite.

The primary source of the pore water DIC can be determined from the plot of DIC concentration as a function of its ^{13}C isotopic composition (Figure 3). The negative correlation observed indicates that the oxidation of C_{org}, using various electron acceptors, is an important process in CO_2 formation in these pore waters.[5]

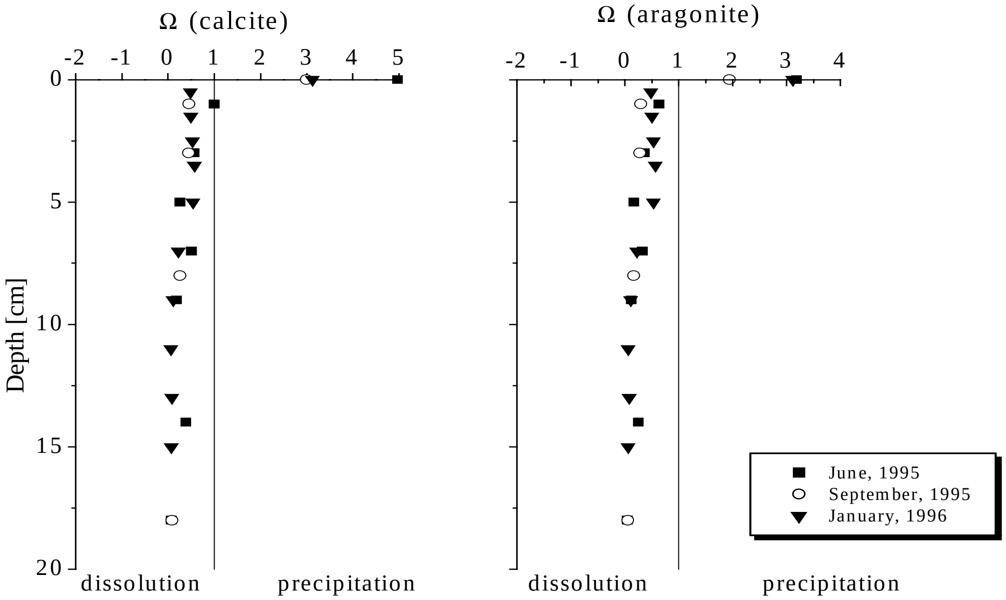

Figure 2. The calculated saturation index (Ω) for aragonite and calcite in pore waters from sampling station F1 in the Gulf of Trieste. The straight vertical lines represent an equilibrium value for calcite and aragonite.[25]

Methanogenesis is considered to be negligible in these sediments since dissolved sulfate is present in these pore waters throughout the core and sulfate reduction is the most important oxidation pathway.[1] Applying a »mixing curve«, proposed by Claypool and Kaplan (1974)[26] for non-methanogenic sediments to observed data, the possible sources of organic carbon in this region can be calculated.[27] The simple situation can be described with the Eq. 1:

$$\delta^{13}C_{DIC} = \delta^{13}C(f) + B'/C_{DIC} \tag{1}$$

where the possible source of organic carbon is defined as $\delta^{13}C_{org}$

$$\delta^{13}C(f) = \delta^{13}C_{org} \tag{2}$$

and

$$B' = [\delta^{13}C_{DIC,i} - \delta^{13}C_{org}] \cdot C_{DIC,i} \tag{3}$$

$C_{DIC,i}$ and $\delta^{13}C_{DIC,i}$ represent the initial concentration of DIC and its isotopic composition, respectively. The calculated values of $\delta^{13}C_{org}$ from the resulting best fit equations (Figure 3) were –3.8‰, –4.1‰ and –13.7‰ for June 1995, September 1995 and January 1996, respectively, indicating an enrichment in ^{13}C with respect to C_{org} ($\delta^{13}C_{org} = -21$‰) probably due to carbonate dissolution.

To better understand the observed data it was necessary to construct a model describing the main processes affecting the pore water concentration of DIC and its isotopic composition in coastal sediment. Stoichiometric models (organic matter with Redfield stoichiometry) have been applied to DIC and dissolved Ca data[8-12] as well as to stable C isotope data[13] from deep-sea sediments. However, their application to near shore sediments is questionable. These sediments exhibit higher biological mixing intensities while a shallow water column and increased productivity provide a greater supply of highly labile organic matter to the sediment-water interface.

Hence, the model developed by McNichol *et al.* (1988)[7] was used in order to define the sources of DIC to pore waters and verify the above statement. The model considers major processes affecting DIC in near shore waters: diffusion, irrigation, remineralization of organic carbon and dissolution and precipitation of $CaCO_3$, and requires no stoichiometric assumption.

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) [mol dm^{-3} s^{-1}]. Rc(z) is assumed to decrease exponentially with depth and it is described by two exponential functions. This assumption considers that organic matter is composed of two reactive fractions of different reactivities, and a non-degradable fraction.[28] Thus, Rc(z) is defined by

$$Rc = R_0 \exp(-\beta_1 z) \qquad \text{from 0 to } z_b \qquad (4)$$

$$Rc = R_{zb} \exp[-\beta_2 (z - z_b)] \qquad \text{from } z_b \text{ to } \infty \qquad (5)$$

where R_0 is the production of DIC at the sediment-water interface, β_1 and β_2 are the depth attenuation coefficients [cm^{-1}], and z_b [cm] is the depth at which the rapidly degradable material is exhausted and $R_{zb} = R_0 \exp(-\beta_1 z_b)$.

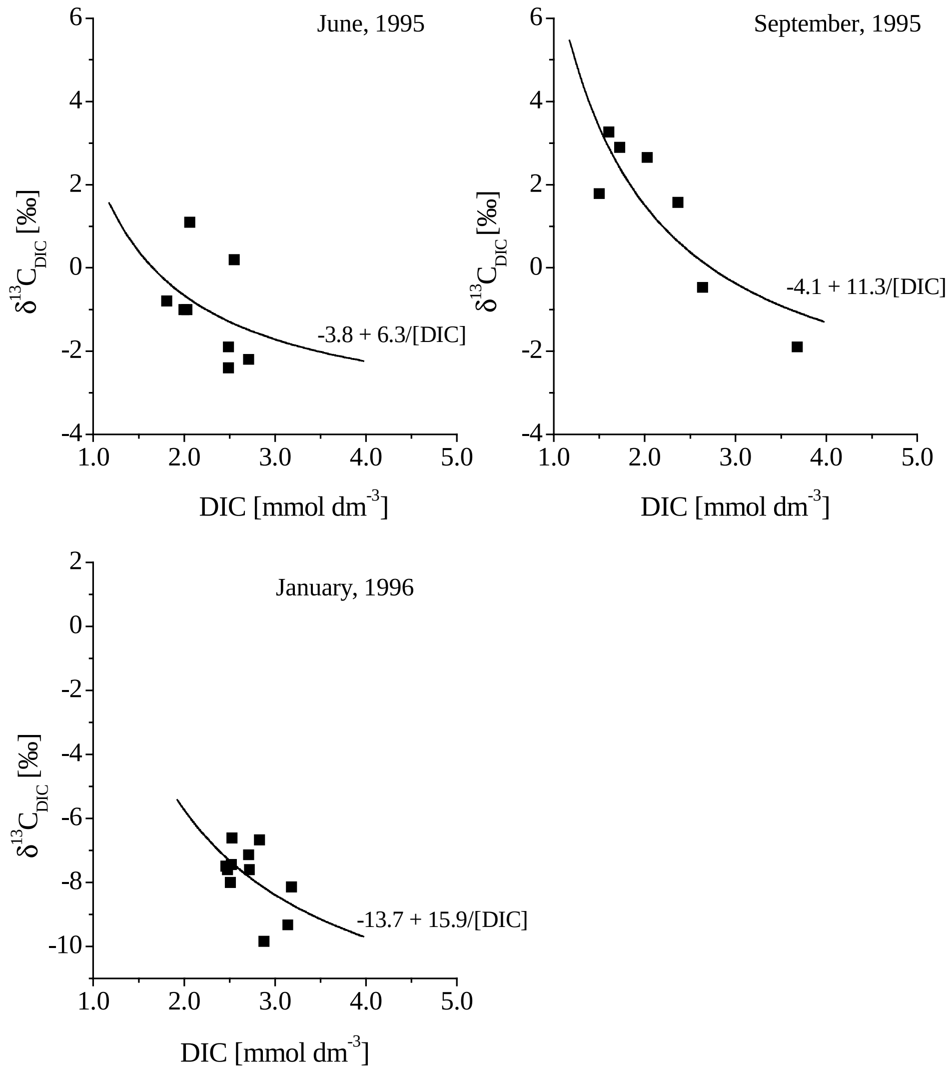

Figure 3. Relationships between $\delta^{13}C_{DIC}$ values and DIC concentrations in pore waters from sampling station F1 in the Gulf of Trieste from June 1995, September 1995, and January 1996. The lines shown are best-fit lines calculated from Eq. 1.

Physical disturbance such as mixing by tides and waves or biological activity (mostly by polychaetes and bivalves in our sediments) can enhance the exchange between pore water and the overlaying water. The transport of DIC due to mixing and irrigation is described using a non-local source model.[29] The intensity of water flushing is represented by an irrigation exchange coefficient α [s^{-1}]. The rate of addition or removal of DIC at depth z in the sediment, due to flushing of overlaying bottom water, is given by

$$S = \alpha (C_{DIC,0} - C_{DIC,z}) \tag{6}$$

where $C_{DIC,0}$ and $C_{DIC,z}$ [mmol dm^{-3}] are the concentrations of DIC at the sediment-water interface at z=0 and at a depth z, respectively. Thus, the general equation describing the changes of DIC with time and depth is

$$\frac{\partial C_{DIC}}{\partial t} = D_{HCO_3^-}\left(\frac{\partial^2 C_{DIC}}{\partial z^2}\right) - \alpha(C_{DIC,z} - C_{DIC,0}) + Rc(z) \qquad (7).$$

In Eq. 7 t is time [s], z is depth [cm], $D_{HCO_3^-}$ [$cm^2\ s^{-1}$] is the sediment diffusion coefficient for HCO_3^-, corrected for temperature and porosity ($\phi = 0.65$),[30] calculated from the diffusion coefficient of Li and Gregory (1974)[31]. The sediment diffusion coefficient ($D_{HCO_3^-}$) was assumed to be constant with depth. Values of $D_{HCO_3^-}$ calculated for each study period are listed in Table 1.

Eq. 7 was solved assuming steady-state conditions, i.e. $\partial C_{DIC}/\partial t = 0$. Since the rates of respiration and other processes vary significantly in response to seasonal changes the validity of steady-state conditions should be discussed. Aller (1980)[32] found in his study in Long Island Sound that short diffusion distance from sediment to burrow channel in the radial diffusion model coupled with the rapid reaction rates observed in near shore sediments led to the rapid establishment of steady-state. The above statement is valid also for the model presented here since the non-local source model used in our calculation is analogous to the radial diffusion model.[33] Also, all evidences show that the seasonal variations occurring within a single year are annually reproducible.[17,30] Therefore, biogeochemical processes at this site approach steady-state conditions on an annual basis.

In order to use the model to calculate Rc(z), the irrigation parameter α, should be known independently. Unfortunately, there are no data available on the magnitude of irrigation at this location. First, Eq. 7 was solved numerically to estimate the value α, using a single exponential function for Rc(z). The calculated results are presented in Table 1. Similar values for α were obtained in other studies by Emerson et al. (1984)[29] (α ranged from 1×10^{-7} to 20×10^{-7} s^{-1}) and Hammond et al. (1985)[34] (α between 2×10^{-7} and 20×10^{-7} s^{-1}). A rather high α indicates that irrigation is an important transport mechanism for DIC in the warmer months in the sediments of the Gulf of Trieste.

Then the data were fit by applying the obtained values for α and by subsequently varying Rc(z) to optimize the fit to the data using four adjustable parameters R_0, β_1, β_2 and z_b. The fits obtained for each period are shown in Figure 4 and the model-calculated values of adjustable parameters are listed in Table 1. The model-calculated values of the CO_2-production rate at the sediment-water interface, R_0, range from a low value 1.6×10^{-9} mol dm^{-3} s^{-1} in January 1996 to a high of 3.5×10^{-9} mol dm^{-3} s^{-1} in June 1995. In general, the data are well fit using this model. However, the measured DIC concentrations at the sediment-water interface were greater than predicted by the model especially in September 1995 (Figure 4). If the data are real they suggest that there was an extremely active zone of mineralization and the CO_2-production rate was much greater than that calculated from the remainder of the sediment column. It is also possible that the data were an artifact of the sampling procedure since sampling handling may increase the CO_2-production rate by an uncertain amount especially at the bottom water.

Results from previous studies indicate that in September usually a highly reactive portion of organic matter derived from benthic microalgae and deposited phytoplankton reaches the sediments.[17]

Table 1. Parameters used to fit the observed dissolved inorganic carbon (DIC) profiles at station F1 with the calculated sediment diffusion coefficients for HCO_3^-. The model fits are shown in Figure 4.

Period	T [°C]	R_0 ($\times10^9$) [mol dm^{-3} s^{-1}]	Rc(z) β_1 [cm^{-1}]	β_2 [cm^{-1}]	z_b [cm]	α [s^{-1}]	$D_{HCO_3^-}$ [cm^2 s^{-1}]
June, 1995	17	3.5	0.23	0.98	5.0	1.5×10^{-6}	3.7×10^{-6}
September, 1995	19.5	2.9	0.18	0.60	2.8	1.0×10^{-6}	4.2×10^{-6}
January, 1996	12	1.6	0.31	0.63	0.7	4.1×10^{-7}	3.5×10^{-6}

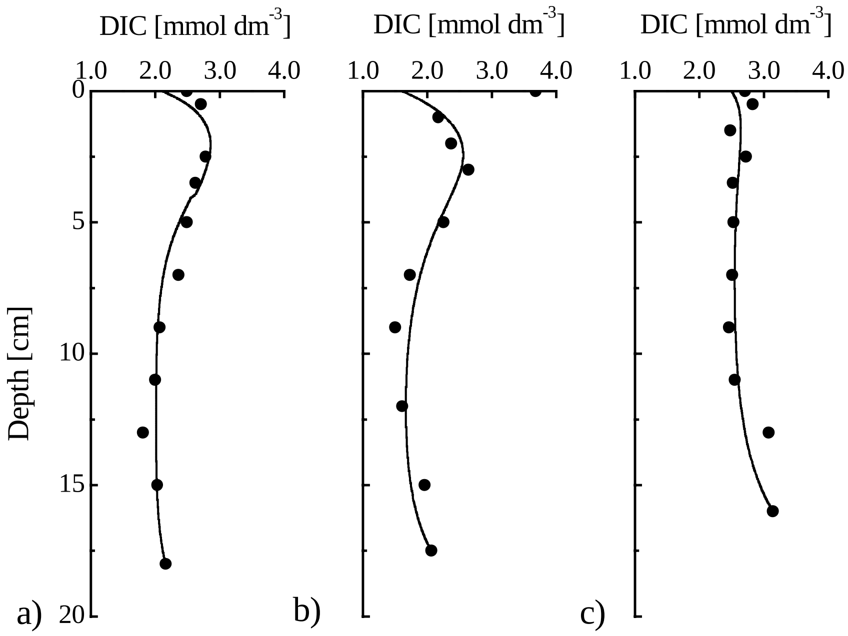

Figure 4. Model best-fits to dissolved inorganic carbon (DIC) data; a) June 1995, b) September 1995, c) January 1996; the parameters used to fit data are listed in Table 1.

The released DIC could be the product of this "fresher" organic matter oxidized at the sediment water interface. In case that model was forced to go through the bottom water value the calculated value of the R_0 would be negative in September 1995 indicating a consumption of CO_2 in sediment column. This is not plausible since all other results showed more pronounced decomposition of organic matter in this period. Therefore, the starting value $C_{DIC,0}$ was defined by solving Eq. 7 numerically with the estimated value for α and using a single exponential function for Rc(z). Then Rc(z) was described using two exponential functions. The calculated functions indicate that there is a more reactive form of organic matter present in the sediments between 0 and 5 cm.

In general, the profiles indicate that, based on DIC profiles, the production of CO_2 is most rapid at the sediment water interface decrease rapidly to very low values by approximately 10 cm.[35]

We also used this model to describe the profiles of ^{13}C isotopic composition of DIC ($\delta^{13}C_{DIC}$). In this case Eq. 7 should be written for ^{13}C and ^{12}C and solved at steady-state conditions $\partial^{a}C_{DIC}/\partial t = 0$, where the superscript a denotes the ^{12}C and ^{13}C isotopes, respectively.[5] In this calculation we used the parameters listed in Table 1. The only parameter necessary to define is a value for $\delta^{13}C$ of the carbon added to the pore water during early diagenesis. We generated pore water profiles of $\delta^{13}C_{DIC}$ using values of $\delta^{13}C$ added of –20.0‰ and –10.0‰ representing organic carbon and 1:1 mixture of organic and inorganic carbon, respectively.[5,36] It was found that this model does not reproduce the observed data in both situations. However, using the value of –10.0‰ for $\delta^{13}C$ added generates profile that more closely approximate the observed data in January 1996, while in other two months the model was not able to reproduce the observed profiles (Figure 5). These findings lead us to suppose that not all the processes affecting DIC in pore waters are taken into account. Thus, data from all the cores indicate that the inorganic carbon added to pore water during early diagenesis is enriched in ^{13}C with respect to C_{org}. The possibilities, which could be responsible for this enrichment are examined below.

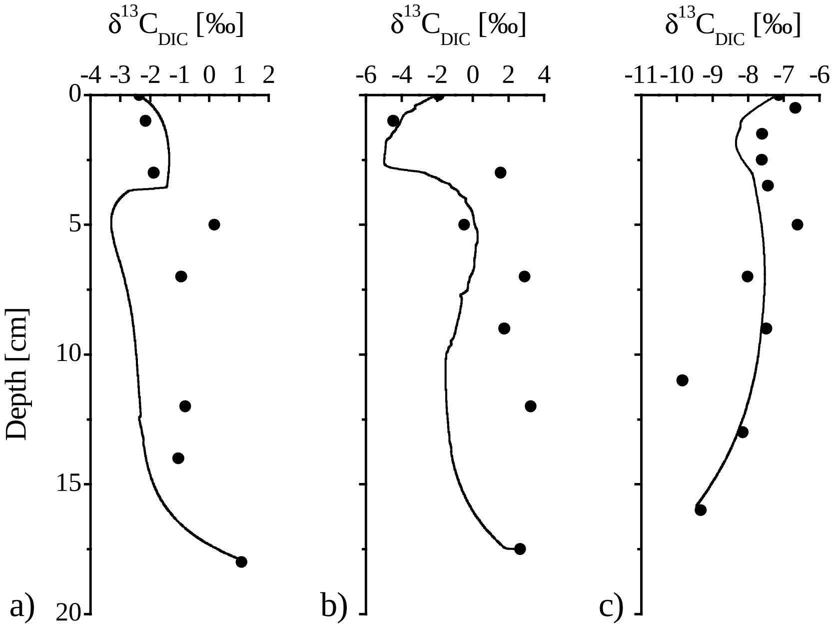

Figure 5: The model fit found using $\delta^{13}C_{add}$ = –10‰ for profiles of $\delta^{13}C_{DIC}$ for a)June 1995, b)September 1995 and c)January 1996.

$CaCO_3$ in sediments

The contribution of calcite dissolution to DIC was estimated in two ways: using the C isotope mass balance equation and using the calculated value of Rc(z). As defined above, Rc(z) includes the net production of inorganic carbon from the oxidation of organic carbon and dissolution or precipitation of $CaCO_3$.

First, we calculated the fractions of the DIC flux (J_{DIC}) derived from organic C oxidation and carbonate dissolution from the measured $\delta^{13}C_{DIC}$ values and various C sources using the mass balance equations in the form:[6]

$$\delta^{13}C_{J\text{-}DIC} * J_{DIC} = \delta^{13}C_{org} * J_{org} + \delta^{13}C_{ca} * J_{ca} \qquad (8)$$

$$J_{DIC} = J_{ca} + J_{org} \qquad (9)$$

J_{org} is the flux derived from organic C oxidation, J_{ca} the flux derived from carbonate dissolution or precipitation and $\delta^{13}C_{org}$ and $\delta^{13}C_{Ca}$ are the mean $\delta^{13}C$ values of sedimentary organic C and the bulk sedimentary carbonates, respectively ($\delta^{13}C_{org}$ = -21‰; $\delta^{13}C_{ca}$= +1.1‰). $\delta^{13}C_{J\text{-}DIC}$ is the isotopic composition of the DIC flux and was calculated from the slope of the regression line of $(C_{DIC,z}/C_{DIC,0})–1$ vs $\delta^{13}C_{DIC}*(C_{DIC,z}/C_{DIC,0})$,[6] where the subscripcts 0 and z represent the concentration of DIC at depth z=0 and z, respectively. The $\delta^{13}C_{J\text{-}DIC}$ values were –4.3‰ in June 1995, –5.5‰ in September 1995 and –13.9‰ in January 1996. Applying these data to Eqs. (8) and (9) it appears that the contribution of calcite dissolution in June and September 1995 would be about 76% and 70%, respectively, and about 32% in January 1996.

An independent estimation of calcite dissolution was performed from the calculated DIC production rate, Rc(z). First the amount of DIC produced, ΣC_{DIC}, was calculated from the Eq. 10

$$\sum C_{DIC} = \phi \int_0^\infty Rc(z)dz \qquad (10)$$

where ϕ is porosity, given a value of 0.65[30] and assumed to be constant with depth. ΣC_{DIC} corresponds primarily to carbon produced from the oxidation of C_{org}. A curve-fitting routine was used to calculate a polynomial function that describes the vertical profiles of Ca concentrations.[7] Assuming steady-state conditions, the net amount of CO_3^{2-} added due to dissolution can be calculated from

$$\sum C_{Ca} = \int_{z1}^{z2} R_{Ca} dz = \int_{z1}^{z2} [D_{Ca} \frac{d^2 C_{Ca}}{dz^2} - \alpha(C_{Ca,z} - C_{Ca,0})]dz \qquad (11)$$

In Eq. 11 D_{ca} [$cm^2\ s^{-1}$] is the sediment diffusion coefficient for Ca^{2+} ions corrected for temperature and porosity from the diffusion coefficient of Li and Gregory (1974),[31] z is depth, $C_{ca,z}$ and $C_{ca,0}$ are the concentrations of Ca^{2+} at the depth z and at z=0, respectively, and α is the irrigation exchange coefficient. The calculated amount of DIC produced and CO_3^{2-} added due to dissolution of $CaCO_3$ is listed in Table 2 together with the sediment diffusion coefficients for Ca^{2+} used in our calculations. In June 1995, 57% of DIC fluxes would be derived from carbonate dissolution, in September 1995 the contribution of $CaCO_3$ dissolution would be only 14% and in January 1996 about 35%.

Dissolution of carbonates in these sediments thus appears to be controlled by seasonal processes[7] while precipitation of carbonates does not seem to be important. This is in accordance with the general unsaturation of pore waters with respect to $CaCO_3$ in these surficial sediments (Figure 2), indicating that the conditions are favorable for carbonate dissolution even in sediments overlying by supersaturated bottom waters.[37] Organic matter decay results in an increase in pore water acidity, which leads to a decrease in the saturation state of pore water with respect to calcite and may cause the dissolution of $CaCO_3$.[6,38,39] The production of acid was evident also from the pH decrease through the depth profile in all periods (from pH = 8.0 at the sediment water interface to a pH = 6.3 at the depth of 20 cm – data not presented). In addition, dissolved Ca concentrations provide direct evidence that dissolution of $CaCO_3$ is the major source of dissolved Ca to the pore water. The concentrations were always grater than those in the bottom water indicating that there is dissolution of $CaCO_3$ in the sediment column.

Table 2. The calculated amount of DIC (ΣC_{DIC}), the amount of CO_3^{2-} added due to dissolution of $CaCO_3$ (ΣC_{Ca}), calculated sediment diffusion coefficients for Ca^{2+} (D_{Ca}), and calculated values of the isotopic composition of DIC, ($\delta^{13}C_{J\text{-}DIC}$) at the sediment-water interface at station F1.

Period	ΣC_{DIC} [mmol m^{-2} d^{-1}]	ΣC_{Ca} [mmol m^{-2} d^{-1}]	D_{Ca} [cm^2 s^{-1}]	$\delta^{13}C_{J\text{-}DIC}$ [‰]
June, 1995	6.38	3.64	2.5×10^{-6}	–4.3
September, 1995	5.28	0.72	2.9×10^{-6}	–5.5
January, 1996	1.81	0.64	2.4×10^{-6}	–13.9

Other sources of ^{13}C–enriched carbon in pore waters

There was a good agreement between estimates of the contribution of calcite dissolution to DIC fluxes using the isotopic data, and those calculated from Rc(z) only in January 1996. Thus, other processes must be enriching ^{13}C in pore waters. One source could be carbonate ion from bottom water. The measured values of pH, TA and PO_4^{3-}

were used to calculate concentrations of CO_3^{2-}, HCO_3^- and $H_2CO_3^*$.[25] The concentration of CO_3^{2-} was much higher in supernatant (215 μM) than in pore waters (5 μM). Most of the carbonate ion would become protonated in pore water since the pH ranges between 6.5 and 7.0 and would be transferred back to the interface. Since this transport is more pronounced in heavily bioturbated areas could be also possible in our sediments. This flux, J_{bw}, is considered in the general isotope mass balance:

$$\delta^{13}C_{J\text{-}DIC} * J_{DIC} = \delta^{13}C_{org} * J_{org} + \delta^{13}C_{ca} * J_{ca} + \delta^{13}C_{bw} * J_{bw} \qquad (12)$$

$$J_{DIC} = J_{ca} + J_{org} + J_{bw} \qquad (13)$$

In this calculation the fractionation between CO_3^{2-} and HCO_3^- was also included. Based on theoretical calculations, the $\delta^{13}C$ of CO_3^{2-} was approximately 2.5‰ less than the $\delta^{13}C$ of HCO_3^- for the temperature range between 5 and 25 °C.[40] The calculations indicate that in June 1995 about 26% of the DIC flux would be derived from diffusion of CO_3^{2-} into pore water. Data from September 1995 were not used in this calculation because the isotopic values are much heavier than could be obtained by any of the processes described so far.

Not all fluxes were included in the budget. For example, the role of dissolved organic carbon (DOC) in fractionation was not determined. DOC is composed of a variety of compounds, such as lipids and amino acids, which are not well characterized. These compounds have very different reactivity, $\delta^{13}C$ signatures, and also different mobility in pore water. Some preliminary isotopic studies of DOC in the ocean indicate that the $\delta^{13}C$ of DOC in pore water is either the same as or greater than that of C_{org}.[41,42] In the pore waters of reducing sediments, the $\delta^{13}C$ of DOC was found to be the same or less than that of C_{org}.[23] Our preliminary measurements of $\delta^{13}C_{DOC}$ in these pore waters showed more negative $\delta^{13}C$ values ranging between –24 and –26‰ compared to the $\delta^{13}C_{org}$ values of sedimentary organic C, suggesting that the pore water DOC is refractory[43] with an allochthonous imprint. Little is known about the rate of transfer of DOC from pore water to overlaying water. It was found that only about 2% of the DOC escapes remineralization in sediments by transport across the sediment water interface.[44] Therefore, in our situation their contribution to the $\delta^{13}C_{J\text{-}DIC}$ could be estimated to about 0.5‰. However, the actual effects of the early diagenetic reactions on the structure of organic matter in sediments and dissolved in pore water are not well known. The reactivity of DOC is also questionable. It is well known that pore water DOC is stabilized by adsorption on mineral surfaces[45] and it is uncertain how they react with the remaining DOC. It is difficult to predict the effect of DOC in sedimentary carbon cycle without a better understanding of these processes.

The probable explanation for the discrepancy observed in September 1995 lies in the unidentified sources of ^{13}C-enriched C in pore waters.[5] In this context the diffusion of ^{13}C-depleted $H_2CO_3^*$ from pore waters could play a role in ^{13}C enrichment of DIC in pore waters. Higher alkalinities observed at the sediment-water interface than in pore waters (Figure 1) suggest that the oxidation of sulfides is an important process in these sediments.[1] The resulting production of strong acid may explain our data. At pH=6.5-7.0, as observed in our pore water samples, the flux of $H_2CO_3^*$ comprised a significant percentage, about 40%,[46] of the total DIC flux. The ^{13}C fractionation between $H_2CO_3^*$ and HCO_3^- is approx. 8‰ with $H_2CO_3^*$ enriched in ^{12}C.[47] It is possible, then, that diffusion of $H_2CO_3^*$ from the sediments preferentially removes ^{12}C from sediments. The addition of the $H_2CO_3^*$-HCO_3^- fractionation of about –8‰ to the δ^{13}C value of oxidized organic C in pore waters of –13.3‰ would yield a value close to that of sedimentary organic C. This assumption was also supported by the higher δ^{13}C values obtained in pore waters than in supernatant water in the laboratory incubated flux chamber in September 1996.[48] It was found that the pore water $\delta^{13}C_{DIC}$ value was –2.2‰, about 5‰ higher than in the overlying water ($\delta^{13}C_{DIC}$= –7.1‰) in September 1996. However, this enrichment was not observed in March 1996; after 45 days of incubation the $\delta^{13}C_{DIC}$ value in pore water was –6.6‰, while in the overlying water it was –7.3‰.[48] Enrichment of ^{13}C in pore water DIC by the loss of ^{13}C-depleted $H_2CO_3^*$ by enhanced bioirrigation in summer could explain this discrepancy.

Conclusions

The negative correlation observed between $\delta^{13}C_{DIC}$ and DIC concentrations in pore waters in the carbonate-rich surficial sediments of the Gulf of Trieste (northern Adriatic) suggested the importance of degradation of sedimentary organic matter while the carbonate dissolution in DIC formation is of minor importance. The calculated $\delta^{13}C_{J\text{-}DIC}$ values and modeled DIC and Ca fluxes, derived from pore water profiles, revealed temporal variations and different sources of DIC fluxes at the sediment-water interface.

The highest contribution of carbonate dissolution appeared in late spring (57%) while in winter it was lower. The discrepancy observed between the origin of the DIC fluxes determined from the $\delta^{13}C_{J\text{-}DIC}$ values and those from the DIC and Ca fluxes observed in late spring can be most likely explained by the presence of the diffusion of bottom-water CO_3^{2-} ion into the sediments, which would neutralized the acid produced during the oxidation of organic matter. The discrepancy observed in late summer probably originates from the enhanced diffusion of ^{13}C-depleted $H_2CO_3^*$ from pore waters to bottom water, resulting from the oxidation of sulfides and production of strong acid, due to intense bioirrigation in that period.

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References and Notes

‡ Carbon isotopic composition is reported as $\delta^{13}C$ value in ‰, where $\delta^{13}C = [(R_{sample})/(R_{std})-1] \times 1000$, $R = {}^{13}C/{}^{12}C$ and $R_{std} = 0.0112372$.

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Povzetek

V pričujočem delu smo s pomočjo izotopskih analiz ogljika določili izvore raztopljenega anorganskega ogljika (DIC) v pornih vodah morskega sedimenta v Tržaškem zalivu. Iz negativne odvisnosti izotopske sestave $\delta^{13}C_{DIC}$ od koncentracije DIC smo ugotovili, da ima razgradnja organske snovi pomembno vlogo pri nastanku CO_2 v porni vodi. Reakcijsko-difuzijski-izmenjalni model, s katerim smo uspešno opisali spremembe koncentracij DIC, ne moremo uporabiti pri opisu globinskih profilov izotopske sestave $\delta^{13}C_{DIC}$. Z uporabo modela mešanja, ki se uporablja za področja, kjer ni metanogeneze, smo določili izotopsko sestavo ogljika, ki se sprošča v porni vodi med diagenezo. Izračunane vrednosti so se gibale med –3.8 in –13.7‰, kar pomeni, da prihaja med diagenetskimi procesi do obogatitve z izotopom ^{13}C glede na organski ogljik v sedimentu (–21‰). Ocenili smo, da je prispevek raztapljanja $CaCO_3$ največji pozno pomladi (57%), najmanjši pa pozno poleti (14%), ko je najbolj izrazita razgradnja organske snovi. Obogatitev porne vode s težjim izotopom ogljika, ^{13}C, lahko dodatno razložimo z intenzivno izmenjavo DIC v vodi na dnu s porno vodo oziroma z difuzijo z izotopom ^{13}C osiromašeno $H_2CO_3^*$ iz porne vode v vodni stolpec.