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Biogeochemical processes in sediments of the Manfredonia Gulf (Southern Adriatic Sea): early diagenesis of carbon and nutrient and benthic exchange

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Abstract

In order to understand the mechanisms responsible of the recycle of carbon and nutrients at the sediment-water interface and to understand the role of sediments in nutrients mass balance in coastal water, cores were collected (pore waters and solid phases) and benthic fluxes (oxygen, dissolved nutrients, dissolved iron and manganese, alkalinity and TCO₂) were measured in two stations in the Gulf of Manfredonia (Southern Adriatic Sea). Stations were chosen to include a site, in the offshore part of the gulf, under the influence of western Adriatic current and another site, in the inner part of the gulf, under influence of gyres occurring inside the gulf. Both stations were placed in areas characterized by high sedimentation rate. Fluxes at sediment water interface show higher values in S2 site during the summer. Bio-irrigation seems to be the main transport mechanism characterizing both sites, with more evident effects during summer in S1 site.

1 Introduction

The sediment-water interface is a site of intense chemical, physical, and biological reactions, which can lead both to the formation of new phases and alteration of existing minerals and to changes in the composition of waters themselves. The reactions involving the oxidation of organic matter are carried out largely by bacteria using a series of electron acceptors which operate at decreasing redox potentials at increasing depth in the sediment. It is well known that different available terminal acceptors are used by the microbial community in the order of decreasing free energy production per mole of organic carbon oxidized (Froelich et al., 1979; Berner, 1980). These reactions are controlled by external factors, such as temperature, sedimentation rate, organic matter inputs, sea bottom water chemistry and hydrodynamics (Berner, 1980), bioturbation and irrigation. In coastal marine environments with shallow waters and fine sediments, early diagenetic processes play a predominant role in the biogeochemical cycling of

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nutrients, i.e. they determine the amount of nutrients buried versus the amount of nutrients recycled to the water column as benthic fluxes (Aller, 1980; Giordani and Hammond, 1985; Degobbis et al., 1986; Hammond et al., 1985). Such benthic fluxes can represent an internal input comparable to or higher than external inputs from terrestrial sources (Hammond et al., 1984). Hence, nutrient input and consequently the primary productivity in a shallow coastal ecosystem can be closely associated with sea-floor biogeochemical processes (Cloern, 1996).

The study focuses on the processes that influence the early diagenesis in a shallow basin in southern Adriatic Sea (Gulf of Manfredonia – Fig. 1), where seasonal variation of nutrient inputs and coexistence of multiple nutrient sources (e.g. nearby rivers or by North Adriatic Currents), can produce seasonal variations of diagenetic processes, and influence quality and quantity of decomposing material.

2 Study area

The Gulf of Manfredonia is situated in the western part of Southern Adriatic Sea (Fig. 1). To the North it is delimited by the Gargano Peninsula which morphologically marks the northern border of the Southern Adriatic.

The Gulf is characterized by limited circulation and high sedimentation rate (Damiani et al., 1988; Bianchi and Zurlini, 1984). It represents a transition zone between the Middle Adriatic circulation and the Southern circulation which presents Ionian Sea characteristics, such as oligotrophic waters (Damiani et al., 1988). Recent investigations about surface circulation and current measurements in the Adriatic Sea confirmed a cyclonic circulation in the Southern sub-basin (Poulain, 2001; Kovacevic et al., 1999) characterized by seasonal variability (Poulain, 1999; Artegiani et al., 1997). A cyclonic gyre is often observed in the Gulf of Manfredonia, but may reverse depending on wind direction (Signell, pers. comm.): cyclonic and anticyclonic gyres are respectively generated by N-NW and S-SE winds (Simeoni et al., 1992).

Biogeochemical properties of the Gulf of Manfredonia are affected by the southward

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coastal current enriched in nutrients (Western Adriatic Current, WAC) flowing along the Western coast of the Adriatic basin. The WAC connects the northern and southern ecosystem and affect of the biogeochemical properties of the whole weastern Adriatic basin. In the Southern Adriatic open waters, however, show clearly oligotrophic characteristics (Vilicic et al., 1989) and the nutrient supply to the euphotic zone depends strongly on the vertical stratification/mixing processes.

Based on grain size analyses in surface sediments 3 sediment types can be recognized: silt sandy, silt and clay. The distribution of these sediment types is essentially the result of wave influence: grain-size in fact decrease with increasing water depth and distance from shore (Brondi et al., 1976; Colantoni et al., 1975). Silt sandy sediments are common in zones adjacent to the shoreline between depth 2–4 m where wave currents are lower. Silty and clay sediments are found in the central part of the Gulf (>8 m of depth) and in the deeper zones. Bioclastic fragments are found in some coastal sites (>6 m of depth) due to breaking coral reef (Simeoni, 1992).

The average water temperature difference between winter and summer months is approximately 11–20°C. Water column productivity has been shown to be higher in summer months (Spagnoli et al., 2004a).

3 Methods

During two oceanographic cruises carried out in late summer (October 2002) and late winter (March 2003) gravity cores were collected in two stations (Fig. 1) in which high sedimentation rate occur using a SW-104 corer, a device which assures the collection of the undisturbed sediment-water interface. Cores recovered shipboard were sectioned and centrifuged for pore water and solid phase analyses. The water overlying the cores was generally clear, suggesting minimal disturbance, although the sediment surface was often uneven. Each core was sectioned in a nitrogen-filled glove box on board, and punch in pH and Eh measurements were made during the sectioning. In order to extract pore waters, the mud was transferred into plastic tubes and

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centrifuged for about 15 min at 5500 rpm in a refrigerated centrifuge at near in situ temperatures. Pore waters were filtered under a nitrogen atmosphere through Nucleopore filters (0.4 μm) in plastic holders. Four splits were saved unacidified for alkalinity, TCO_2 , DOC and nutrients measurements, and another was acidified (to about pH 1.5) and used to analyse dissolved Fe and Mn. Pore water extraction and filtration was generally completed within 6 hours from core collection. The centrifuged mud was recovered, frozen and subsequently dried at room temperature for analysis of solid phases (organic and total C, total N). In the first cruise replicate cores were collected to estimate sedimentation rates and bioturbation coefficients by ^{210}Pb excess, ^{137}Cs , ^{234}Th measurements. The excess activities of ^{210}Pb were calculated from ^{226}Ra supported ^{210}Pb deduced from the activities of ^{214}Pb and ^{214}Bi . Radionuclides were counted using a HPGe (30–60% relative efficiency, 2 KeV of resolution). In the second cruise replicate cores were collected to measure dissolved oxygen penetration by microelectrode profiler. Sampling and instrumental difficulties prevented us from collecting complete data sets in both surveys.

In situ benthic flux chambers were deployed in each sites. Two chambers were displayed in each site one by side to replicate measurements. Benthic chambers capture approximately 39 l of water in contact with 0.25 m^2 of sea bed. Each chamber was sampled six times during deployments of about 24 h. The incubation period of 24 h was sufficient to generate measurable changes in concentration, but not long enough to produce significant changes in fluxes.

A CsCl spike was injected in the incubation soon after the first sampling and the observed dilution of this spike in subsequent sample draws was used to calculate chamber volume and was used as tracer for chamber water exchange with pore water. Chambers were stirred by a rotating paddle such that the diffusive boundary layer thickness within the chamber was unaffected.

Porosity was calculated after drying each sample at 60°C, total and organic carbon and total nitrogen (all expressed as weight %) were measured by CHN elemental analyzer (Carlo Erba) after removal of the inorganic carbon with HCl (Froelich et al., 1979).

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Organic nitrogen was assumed to equal total nitrogen (Giordani and Angiolini 1983). Dissolved phosphate, ammonia, nitrite, nitrate and silicate were measured on pore waters and benthic chamber samples by colorimetric autoanalyser technique. Alkalinity was determined by Gran titration (Gieskes and Rogers, 1973) and TCO_2 was determined from alkalinity, pH, salinity and temperature. Additionally, in the second cruise, an aliquot of 5 ml was collected for the analyses of TCO_2 by manometric measurements (McCorkle et al., 1985). Fe, Mn and Cs were determined on the acidified aliquots by Flame-AAS. Ca, Mg and other dissolved cations were determined by HPLC. For each parameters analysed benthic fluxes were calculated as the product of the slope of concentration vs. incubation time and chamber height, without including bottom water data in the calculation. Benthic flux calculations were determined only from the linear portion of the concentration vs. time plots (Berelson et al., 1998) and no flux was reported if we had fewer than 4 data points.

Using two deployment, fluxes were averaged and the uncertainty in the mean was calculated in two ways; (a) as the standard error of the mean; or (b) as the square root of the sum of the variance of each flux value, divided by the number of flux measurements. We report the larger of these two uncertainties, following the procedure described by Hammond et al. (1996).

4 Results and discussion

4.1 Solid phase measurements

Down-core changes in porosity, ^{210}Pb activity and organic C were measured on cores collected. In the study sites surficial sediments have a porosity 0.75–0.8 and this value decreases to 0.60–0.65 at 25–30 cm (Fig. 2).

The excess activity of ^{210}Pb ($t_{1/2}=22.3\text{y}$) (Fig. 3a), decreasing exponentially below the interface in both stations, may be used to estimate the rates of sediment accumulation (Koide et al., 1972). Applying Constant Flux-Constant Supply (CF-CS) model to

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the $^{210}\text{Pb}_{\text{ex}}$ profiles (Lalou, 1982), sedimentation rates (w) from each stations were estimated to be $0.35 \text{ cm}^2 \text{ y}^{-1}$ in station S1 and $0.43 \text{ cm}^2 \text{ y}^{-1}$ in station S2. These values are similar to those calculated by Giordani et al. (1992) and by Hammond et al. (1999) in the Northern Adriatic sea. In order to check sedimentation rates the vertical profile of ^{137}Cs (Fig. 2b) is used. It is well known that a significant input of this radionuclide in the environment occurred in the 1963 related to atmospheric weapon tests. Hence maxima concentrations in cesium vertical profiles correspond to sediments buried in this age (Cochran, 1985), supporting the dating calculated by $^{210}\text{Pb}_{\text{ex}}$.

Thorium activities were also measured as useful tracer of sediment mixing. The mixing of the upper 10 cm of sediment caused by macrofauna is referred to as bioturbation, it can alter the physical and chemical properties of sediment affecting both particle and solute transport (Schink and Guinasco, 1977; Rhoads, 1974; Aller, 1980; Aller and Aller, 1986). In order to calculate bioturbation coefficients (D_b) the relation calculated by Pope et al. (1996) was applied to ^{234}Th exponential profile (S2 station) and D_b was estimated to be $0.20 \text{ cm}^2 \text{ y}^{-1}$. This value falls on the low end of a compilation by Tromp et al. (1995) relating D_b to w for similar environments, perhaps because of the episodic presence of low oxygen bottom water. The profiles of ^{234}Th in station S1 is constant from sediment water interface down to 5 cm, suggesting a bioturbated layer too.

Organic carbon concentrations in all the cores (Fig. 2) rapidly decrease from the sediment-water interface to 5–7 cm, deeper it reaches a low constant value and exhibits a regular trend interrupted only by relatively high values at about 20 cm in both sites. Total N concentrations also show a down-core decreasing trend. Continental margin sediments are a mixture of terrestrial and marine components so to identify the source of the organic matter undergoing diagenesis the C/N ratio might be used (Froelich et al., 1979). The Redfield ratio of C:N:P in marine sediments, 106:16:1 (C/N~7), might be representative of settled marine phytoplankton, whereas higher values may reflect the breakdown of terrestrial derived particulate organic carbon (POC). The C/N average ratios range from 5 ± 2 to 7 ± 2 in winter and in summer cruise respectively, with higher values shown by surface sediments collected in summer, and similar those calculated

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in north Adriatic by Hammond et al. (1999). Therefore, the origin of organic matter should be marine.

4.2 Pore water profiles

In continental slope and rise sediments underlying well-oxygenated bottom waters, O_2 is the most important electron acceptor for organic matter decomposition. In continental margins sediments anoxic conditions occur in few centimeters of depth due to high sedimentation rates and high organic matter inputs. Thus, the sedimentary O_2 consumption rate is a good first-order indicator of organic matter oxidation rates in many locations. In the sampled sites dissolved oxygen exponentially decreases below the sediment-water interface and at depth greater than 1 cm suboxic conditions occur in both sites (Fig. 4). Higher oxygen concentration at the sediment water interface and sharper gradient are displayed at S2 station.

Pore water NO_3^- profiles (Fig. 5) show the effects of nitrification in the oxic zone of the sediments and of denitrification immediately below the oxic zone. At sites where we have both O_2 and NO_3^- concentrations, the depth at which denitrification begins is just above or within the depth range over which O_2 concentrations reach zero. The NO_3^- reaches 0 values depth at about 20 cm. The low, constant, non-zero values observed below 20 cm at S2 site are most likely non-zero because of a calibration problem.

Suboxic diagenesis is indicated by the pore water profiles of dissolved manganese and iron (Fig. 6) according to the well-established depth sequence of diagenetic reactions, governed by the preferential use of Mn and Fe oxide phases as electron acceptors, that yields the highest amount of free energy for the bacterially mediated oxidation of organic matter (Froelich et al., 1979). Dissolved manganese profiles exhibit, in both stations, near surface peaks, just below the oxygen penetration depth. A secondary peak in Mn^{2+} pore water profile is observed in S2 site at 13 cm in summer, deeper the trend continues quite constant. The dissolved Fe shows, in all profiles, a sharp increase just below the depth range in which Mn concentrations reach maxima values, At higher depth dissolved iron concentrations decrease quickly down to 10–20 cm and then in-

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crease in both summer cores and in the S2 winter core. The increase of dissolved Fe with depth seems to suggest a complexation with dissolved refractory organic matter, hence any reaction occur with reduced sulphur to form FeS, thermodynamically preferred, or with carbonate, as siderite (Postma, 1982). This is a working hypothesis that needs of further study. The peaks of dissolved Mn and Fe are attributed to the production of these metals in anaerobic condition by dissimilatory reduction of oxy-hydroxide manganese and iron by bacteria activity: oxide phases may be used as terminal electron acceptors in bacterial oxidation of organic carbon. About the pore water SO_4 profiles, the trends are rather constant displaying higher concentrations in the summer profiles in S2 station, hence sulphate reduction does not seem to take place.

The decomposition of organic matter, using Mn and Fe oxy-hydroxides as electron acceptors below the denitrification layer, results in the release of NH_4^+ and TCO_2 into the pore waters. Pore water data (Fig. 5) reflect this process, as they show monotonically increasing $[\text{NH}_4^+]$ and TCO_2 below the denitrification layer. From the sediment-water interface to 10 cm of depth, the distribution of both organic matter degradation products (TCO_2 and ammonia) is scattered, suggesting bio-mixing and irrigation processes. Activity of macrofauna may deepen and channelize the penetration depth of oxygen and improve solute fluxes across the sediment-water interface. We have not available data on the activities of macrofauna, hence this hypothesis needs further study. The NH_4^+ released to the pore waters by anoxic diagenesis diffuses upwards in the sediment column, where most of it is apparently oxidized before it reaches the sediment-water interface.

The dissolved PO_4^{3-} in pore waters in all cores has a similar trend: a rapid and irregular increase in a layer near surface (about 3 cm depth), a second relative peak is displayed at about 17 cm, at higher depth the profiles approach the analytical detection limit. The higher value are shown in S1 cores. The irregular trend is due to the complexity of P cycle: the low concentrations at the sediment water interface are due to the precipitation with Fe oxy-hydroxides, from the sub-surface to 20 cm the PO_4^{3-} concentration increase as a result of release by organic decomposition and dissolution

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of Fe-oxhydroxides and then it decreases because of removal to a sedimentary phase.

As a summary, the pore water profiles display a marked seasonality, with degradative processes more intense in the summer period due to higher temperature and higher input of fresh organic matter.

4.3 Chamber data

Benthic chamber experiments were successful for the determination of ammonium, nitrate, nitrite, phosphate, silicate, alkalinity, TCO_2 , manganese, iron, cesium and oxygen fluxes in both sites (Stations S1, S2). As the incubation time increases, there is the possibility that chamber chemistry or other artifacts will produce non-constant fluxes.

This is recognizable in some data, so flux calculations were determined only from the linear portion of the concentration vs. time plots and no flux was reported if we had fewer than 4 data points (Berelson et al., 1998).

In Fig. 6 a comparison of benthic fluxes in both seasons is presented. Greatest oxygen uptake occurred in winter in S1 while in S2 oxygen uptake was pretty similar throughout the year. Nitrate flux was always into sediment in S1 site and out of sediment in S2, greatest variability is evident in S2. Dissolved manganese and iron show positive fluxes, stronger seasonality is shown at S1 site. Ammonia fluxes were always out of sediment, with lowest fluxes occurring in winter, and so behave TCO_2 and phosphate. Measured benthic fluxes of degradative organic matter products are significantly higher during the summer in both station, with more significant differences in S2 station.

Actually data on primary productivity are not available, so we are not able to define the seasonal productivity pattern in the Gulf of Manfredonia, however the seasonal variations in benthic chamber fluxes for silicate, nitrate and TCO_2 suggest that higher inputs of fresh organic matter occurred during summer. The variations are stronger in station S2, where also a different source of organic matter might be present, as suggested by inorganic geochemistry of surface sediments, associated to the material

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transported by the WAC (Spagnoli et al., 2004b).

5 Conclusions

Pore water profiles of different electron acceptors for organic carbon oxidation indicate that in the Gulf of Manfredonia diagenesis of organic matter progresses through oxygen respiration, denitrification, manganese and iron reduction, while sulphate reduction and methanogenesis do not take place. The depth-dependent characteristics of profiles were similar in both sites and seasons. Degradative processes of a prevalently marine organic matter are more intense during summer, as testified by the pore-water profiles and by the increased benthic fluxes of nutrients at the sediment-water interface. The processes of oxidation of organic matter might be influenced by bioturbation and bioirrigation, that are particularly active in the uppermost 10 cm of the sediment.

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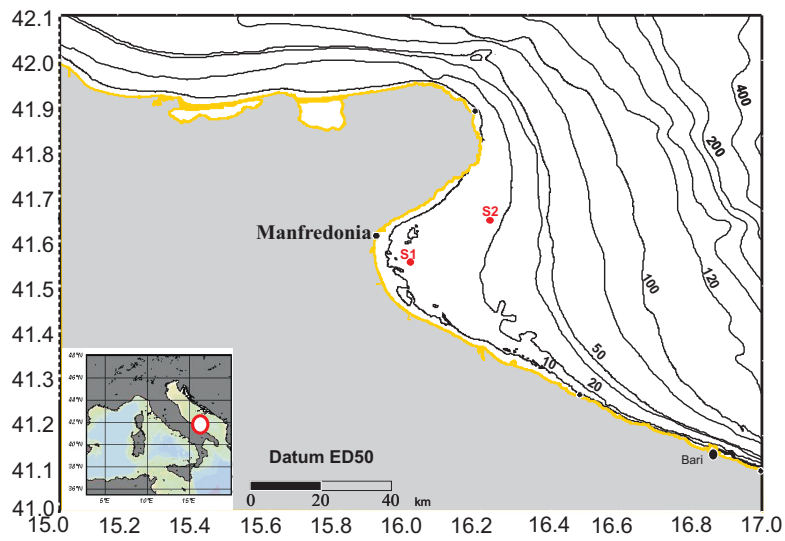


Fig. 1. Site map an stations location.

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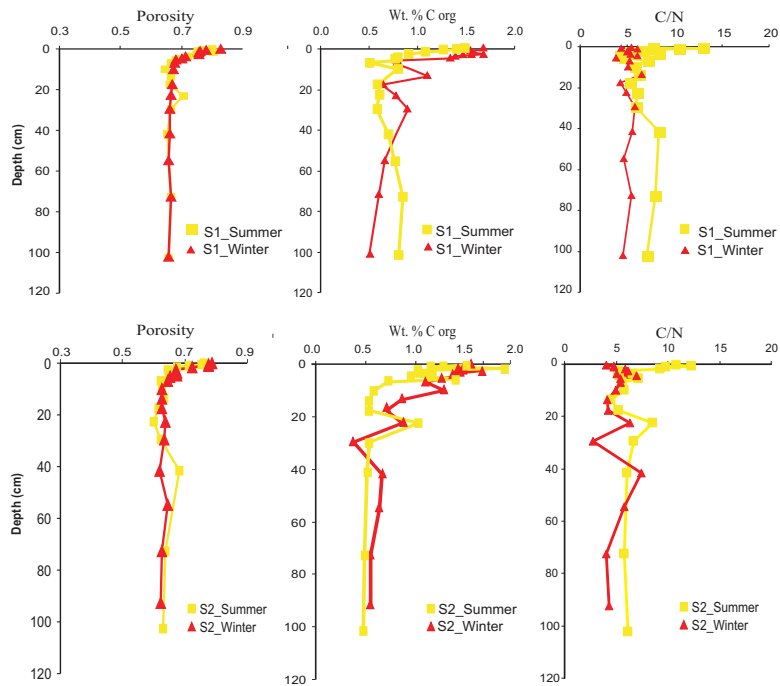


Fig. 2. Sediment profiles of porosity, wt.% C_{org} and C_{org} vs. N total from cores collected in Gulf of Manfredonia. Depth intervals were 0.5 cm for the first four points, 1cm for the next 4 points, 3 and 5 for the subsequent point, data are plotted at the mid-point of the interval.

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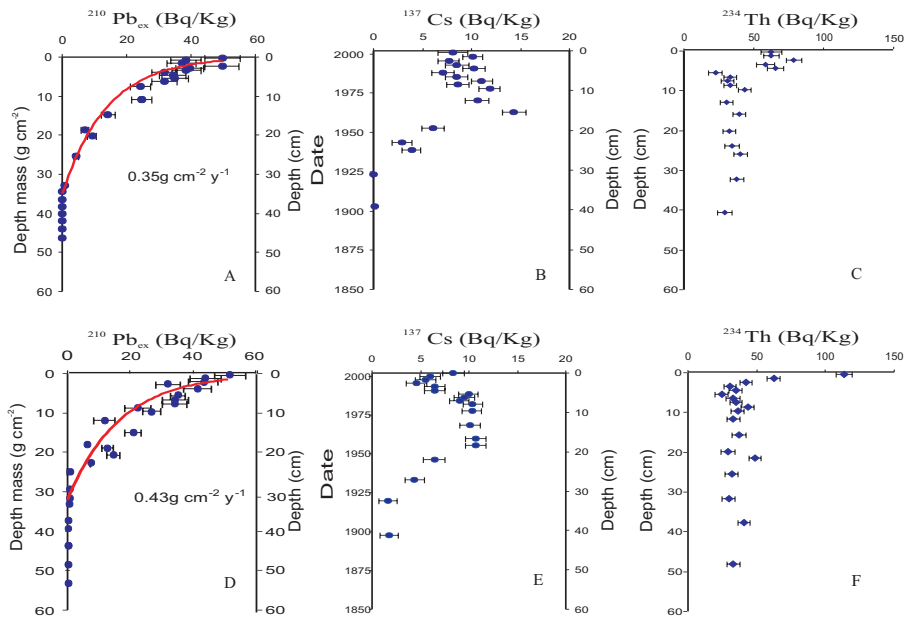


Fig. 3. Profiles of solid phase constituents at representative inshore (Sta. S1 (a), (b), (c)) and offshore (Sta. S2 (d), (e), (f)) stations. The solid red line shows the fit of an exponential function to excess Pb-210 vs. mass depth.

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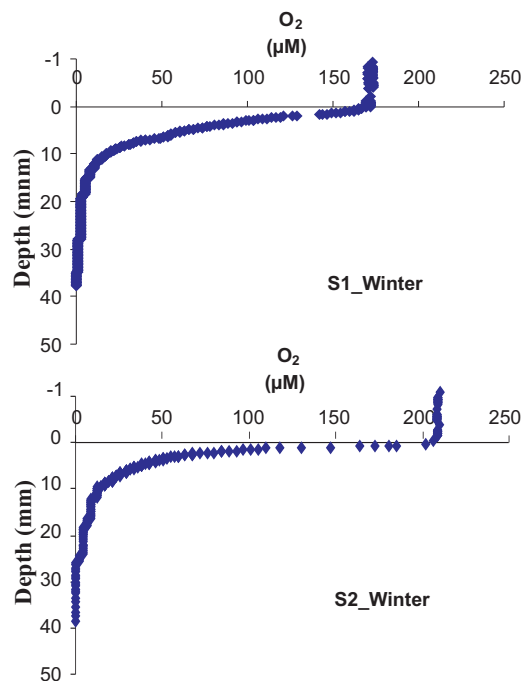


Fig. 4. Dissolved oxygen profiles in cores collected in winter cruise.

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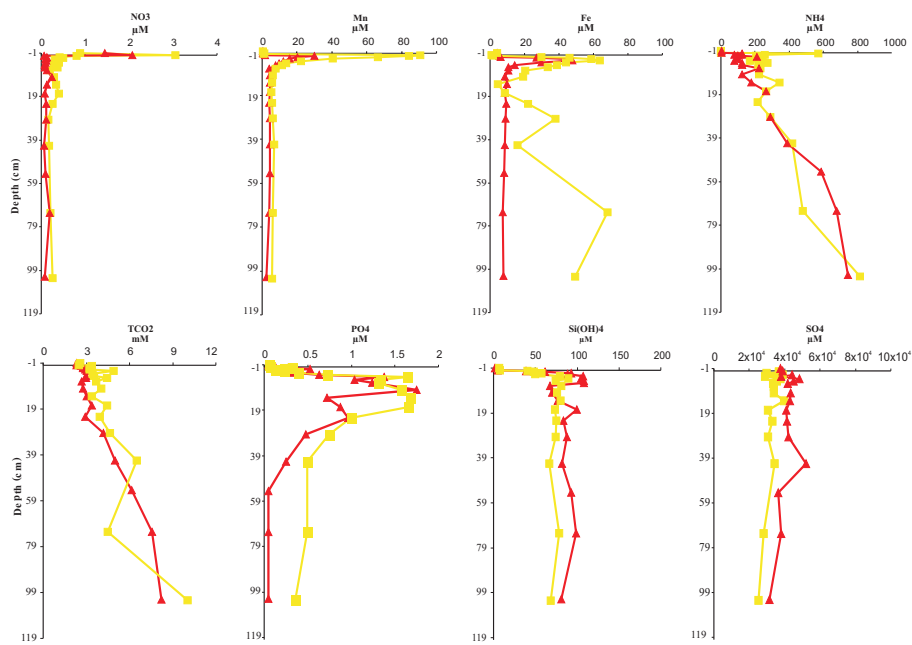


Fig. 5. (a) Pore water profiles of nutrients and TCO_2 from cores collected in Gulf of Manfredonia in S1 station. Depth intervals were 0.5 cm for the first four points, 1 cm for the next 4 points, 3 and 5 for the subsequent point, data are plotted at the mid-point of the interval. Two season are identified by the different symbols (red triangle = Winter, yellow square = Summer). Points at -1 depth indicate bottom water values.

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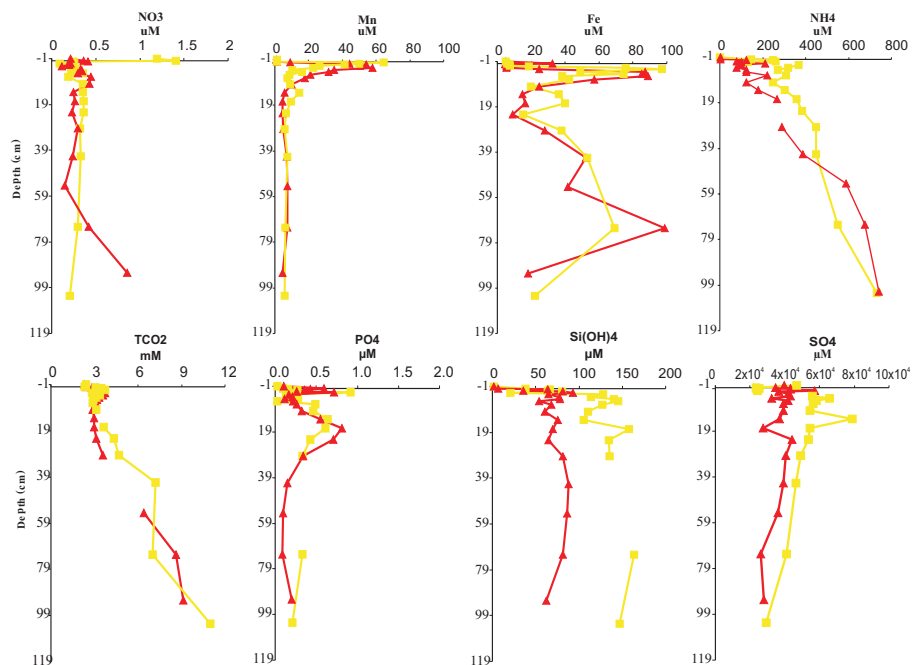


Fig. 5. (b) Pore water profiles of nutrients and TCO_2 from cores collected in Gulf of Manfredonia in S2 station. Depth intervals were 0.5 cm for the first four points, 1 cm for the next 4 points, 3 and 5 for the subsequent point, data are plotted at the mid-point of the interval. Two season are identified by the different symbols (red triangle = Winter, yellow square = Summer). Points at -1 depth indicate bottom water values.

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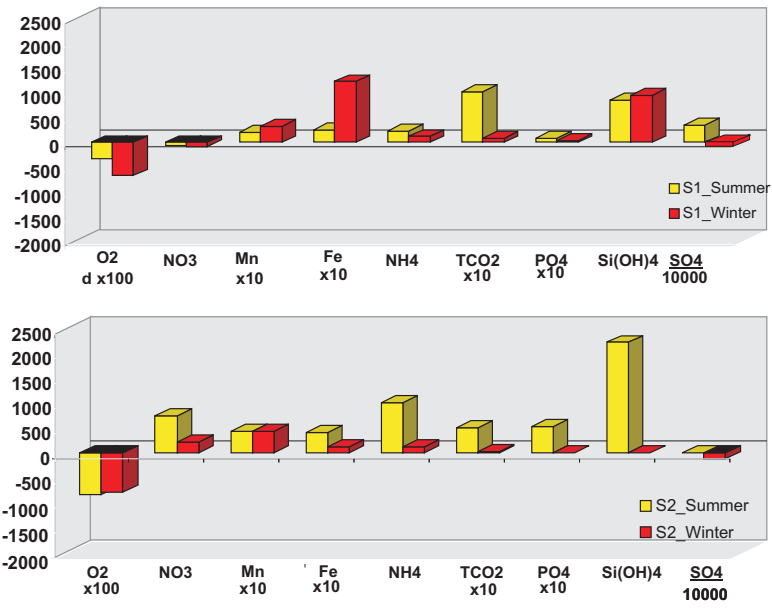


Fig. 6. Benthic fluxes of nutrients and TCO₂ from deployments used in Gulf of Manfredonia in S1 and S2 station. Units are $\mu\text{mol m}^{-2} \text{d}$ for nutrients and $\text{mmol m}^{-2} \text{d}$ for O₂ and TCO₂.