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BENTHIC FLUXES AND PORE WATER PROFILES IN THE TIGULLIO GULF

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Diffusive fluxes of elements (NO_2^- , NO_3^- , NH_4^+ , SiO_2 , PO_4^{3-} , Cl^- , SO_4^{2-} , Fe, Mn) have been measured by applying the Fick's first law in two stations of the Tigullio Gulf: the first one characterized by sandy sediments rich in vegetal detritus and the second one, located to within the tourist harbour, characterized by a silty-clay sediments.

Benthic fluxes were measured only in the second station by means of benthic chamber experiments. Although the significant presence of dissolved oxygen in the surface sediments, and the evidence of processes usually occurring in oxidised sediments such as nitrification, both stations also presented characteristics of anoxic sediments such as high oxygen consumption rate and high pore water concentrations of ion, manganese and N-ammonia and reactive orthophosphate.

In both stations, sediments seemed to represent a potential source for most of the chemical species studied, although fluxes were not confirmed for ion, manganese and reactive orthophosphate in benthic chamber experiments.

Diffusive fluxes presented a general agreement for both stations, with higher fluxes of N-nitrate and N-nitrite at the first station were oxidative processes of N-ammonia in the upper layer of the sediments seemed to be more active. The comparison between diffusive and benthic fluxes showed a possible contribution of bioturbation.

Keywords: Benthic fluxes; benthic chamber; pore water profiles

1. INTRODUCTION

Nutrient elements, silica, iron and manganese play a very important role for life in marine environments being the constituents of proteins and nucleic acids. Their concentration in marine coastal waters depends on many factors such as land transport, waste water discharges, local biomass productivity and structure, hydrodynamics

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and water-sediment exchanges. Organic matter regeneration in near shore sediments takes place through different diagenetic reactions most of them biologically assisted and depends on various factors such as sediment composition, sedimentation rate, bioturbation and irrigation (Price, 1976; Emerson *et al.*, 1984).

Diagenesis in surface sediments leads to a great increase of pore water concentration of basic constituents of the organic matter and to a depletion of dissolved oxygen and nitrate (Bernier, 1980). The latter produces benthic fluxes at the sediment-water interface which may become of great extent in coastal areas with high nutrient and sedimentable particulate matter input. Sediment contribution in the nutrient balance of a coastal area has been dealt in the literature with computing diffusive fluxes at the sediment-water interface by applying the Fick's first law (Lermann and Brunskill, 1971; Schink *et al.*, 1975; Ulman and Aller, 1982), through the estimation of nutrient concentration gradient and calculating the "true" diffusion coefficient according to sediment tortuosity and pore water salinity (Bear, 1972; Bernier, 1980) as well as pore water nutrient speciation (Van Klump and Martens, 1981).

More recently, the use of benthic chambers (Hall, 1984; Ciceri *et al.*, 1992; Cambiaghi *et al.*, 1993) allowed the direct measurements of benthic fluxes by taking into account the effect of bioturbation.

The design of benthic chambers was improved during the recent years to reduce some experimental artefacts such as the decrease of pH and dissolved oxygen concentration with time in the water inside the benthic chamber (Hammond *et al.*, 1985; Sumbay *et al.*, 1986), due to the effect of sediment oxidation processes and their products. Furthermore, attention has been paid in simulating the effect of bottom currents inside the benthic chamber which may affect the rate of sediment-water exchanges.

In this paper, the diffusive fluxes measured in two stations characterized by a different sediment grain size and benthos structure as well as different water hydrodynamics has been compared with the aim of evaluating the effect of these parameters on the fluxes. In one of the two stations, benthic and diffusive fluxes have been compared with the aim of evaluating the importance of the bioturbation and to provide evidence of the removal of some chemical species at the sediment-water interface.

2. BENTHIC CHAMBER EXPERIMENTS

2.1. Materials and Methods

Experiments were carried out in two stations within the Tigullio Gulf (Ligurian Sea). The first one (Prelo) had a 5 m water depth and was characterized by the presence of *Posidonia oceanica* on a vegetal detritus-rich sandy sediments. The second station, located inside the tourist harbour of Rapallo, had a 5 m water depth with silty-clay sediments and was characterized by a heavy tourist boat traffic inducing sediment resuspension.

During the first week of October 1996, a Plexiglas benthic chamber (Fig. 1) of about 70 cm i.d., 45 cm height, 120 l capacity, was manually inserted by a diver for about 15 cm depth in the sediments, with a minimum perturbation, at the Rapallo station.

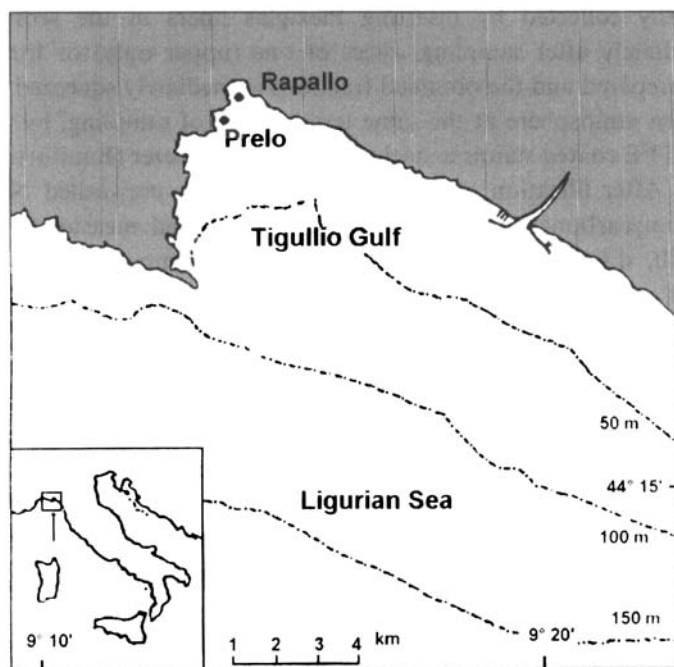


FIGURE 1 Location of sampling stations.

An automatic control device and a continuous stirring system (30 cm in length, 6–7 r.p.m.), with an induced magnetic movement, was installed in the chamber in order to restore dissolved oxygen consumption and to simulate the effect of currents on the sea floor without producing sediment resuspension (Barbanti *et al.*, 1992a; Tenberg *et al.*, 1998).

Sampling of water from the benthic chambers was carried out by divers by using 400 ml precleaned Plexiglas syringes, just after the location and 8 times following the period of 71 hours after positioning.

Water quality (pH, Eh, dissolved O₂, conductivity, salinity and temperature) was measured in the field using a multiparametric probe (Idronaut, Ocean Seven 501).

Nine water samples were collected by a diver as near as possible to the sea floor using 1 l precleaned polyethylene bottle, just before the collection of each benthic chamber sample.

For both stations, before chamber deployment, fifteen undisturbed sediment cores (15–20 cm in length and 5.5 cm diameter) were manually collected by inserting Plexiglas liners in the sediments. Immediately after sampling, slices of one (upper only) or three cm were prepared and the obtained fractions immediately squeezed under nitrogen atmosphere at the same temperature of sampling, by means of a PTFE coated stainless steel low pressure squeezer (Boniforti *et al.*, 1986). After filtration under nitrogen on 47 mm prewashed Nucleopore polycarbonate membrane filters (0.4 µm) and measurements of pH, Eh, dissolved oxygen, conductivity and temperature by using proper probes, both overlaying water and pore water were frozen at –18°C and then analysed for the determination of N-nitrite, N-ammonium nitrate, silica and reactive P-phosphate, by means of an automatic colorimetric analyser (Lachat Quickchem AE multichannel Flow Injection Analyser). Sulphate and chloride were determined by ion chromatography (Dionex 2000 i). Sulphide was determined by bromatometric titration on a subsample treated with 0.5 M zinc acetate immediately after collection and filtration under pressure through a cellulose acetate Millipore Millex membrane filter (0.45 µm prewashed and nitrogen conditioned).

Iron and manganese were determined by ICP-OES on aliquots acidified with subboiled purified nitric acid at pH < 4 just after filtration. Sediment porosity was determined according to Ciceri and

Martinotti (1988), while the resistivity formation factor was obtained as the ratio of sediment specific resistivity to that of the enclosed pore solution (Archie, 1942).

2.2. Computing Benthic Fluxes

Diffusive fluxes at the sediment-water interface were computed applying the first Fick's law in the following form (Lermann and Brunskill, 1971; Ciceri *et al.*, 1992):

$$J_d = (C_{p.w.} - C_{s.w.}) * D_o * \Delta x^{-1} * F^{-1} \Phi^{-1},$$

where $C_{p.w.}$ and $C_{s.w.}$ are the concentrations of the considered ion in pore water extracted from the first centimetre of sediment and in the water collected in the water layer just near the sediments, D_o is the diffusion coefficient; Δx is the thickness of sediments across which diffusion takes place; F is the resistivity formation factor and Φ is the porosity of the first centimetre of sediments. Literature data of D_o (Li and Gregory, 1974) were corrected for temperature and salinity effects and, for orthophosphate, for ion pair effect (Van Klump and Martens, 1981).

Benthic fluxes (J_s) were computed by measuring the variation in concentration of the studied species with time inside the benthic chambers, using the following equation, which considers negligible the fraction of ion sorbed by the suspended matter inside the benthic chamber after diffusion:

$$J_s = (C_{t1} - C_{t0}) * h * \Delta t^{-1}, \quad (1)$$

where C_{t0} is the concentration in the water at the beginning of the experiment; C_{t1} the concentration Δt hours later; h the height of the water column inside the benthic chamber. When concentration profiles of the studied species in the water inside the benthic chamber were linear with time over many days, single values for each experiment were interpolated and the term $(C_{t1} - C_{t0})/\Delta t$ of Eq. (1) was obtained from the curve slope; when profiles were not linear over many days (the case of silica), this term was obtained taking into account only the linear part of the curve.

3. RESULTS AND DISCUSSION

3.1. Benthic Chamber Experiments

Temperature variation inside the benthic chamber was about 0.5°C , due to the weather condition with vertical mixing of water and a freshwater supply from land.

Figure 2 reports dissolved oxygen and pH profiles inside the benthic chamber: the characteristic oxygen profile is the consequence of the restoring system; pH decreasing is due to the effect of carbon dioxide produced during organic matter degradation in sediments.

From the amount of the injected oxygen was possible to estimate the average oxygen sediment uptake at the Rapallo station which resulted $1320 \text{ mg m}^{-2} \text{ g}^{-1}$, of the same order of magnitude than those measured in lagoon systems (Ciceri *et al.*, 1998).

Table I reports the concentration of the studied species with time inside and outside the benthic chamber. Some of these profiles are displayed in Figure 3. Each one reports the linear regression line which interpolates experimental data, its algebraic form and the value of the

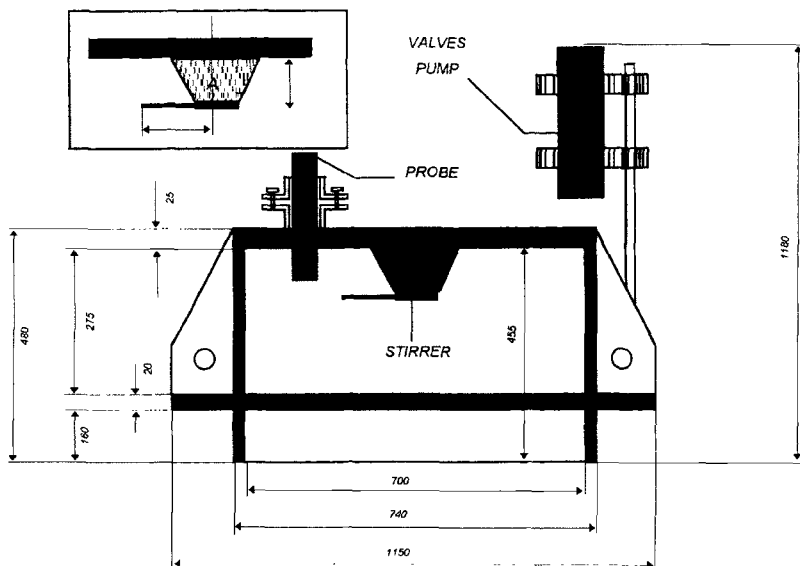


FIGURE 2 Scheme of the benthic chamber.

TABLE I Concentration of the studied species inside and outside the benthic chamber (Rapallo station)

	Time (hours)									
	0	7	14	23	30	37	47	54	61	71
<i>Inside</i>										
SiO ₂ (µgSi/L)	60	71	114	122	138	151	177	192	171	156
NH ₄ ⁺ (µgN/L)	21	44	39	48	59	69	83	87	104	113
NO ₃ ⁻ (µgN/L)	6	9	10	13	21	15	24	25	36	37
NO ₂ ⁻ (µgN/L)	2	2	2	4	6	5	7	12	11	13
Cl ⁻ (g/L)	21	21	21	21	21	22	21	22	22	21
SO ₄ ²⁻ (g/L)	2.5	2.5	2.6	2.5	2.6	2.7	3	2.7	2.7	2.6
Fe (µg/L)	1	3	6	3	1	9	7	3	1	2
Mn (µg/L)	< 6	< 6	< 6	< 6	< 6	< 6	< 6	9	< 6	< 6
P(ort.) (µg/L)	10	12	11	9	10	10	12	11	10	14
HS ⁻ (µg/L)	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50
O ₂ (mg/L)	7.31	6.51	6.38	7.27	7.41	6.95	6.72	6.87	6.74	6.83
pH (unit)	8.24	8.24	8.20	8.16	8.12	8.07	8.03	7.99	7.96	7.92
<i>Outside</i>										
SiO ₂ (µgSi/L)	99	94	116	82	48	128	119	135	123	115
NH ₄ ⁺ (µgN/L)	14	20	28	23	44	36	37	18	28	13
NO ₃ ⁻ (µgN/L)	7	14	12	10	6	20	23	5	7	22
NO ₂ ⁻ (µgN/L)	3	4	4	1	9	5	4	3	4	3
Cl ⁻ (g/L)	20	22	20	21	21	21	21	21	20	21
SO ₄ ²⁻ (g/L)	2.6	2.7	2.4	2.4	2.7	2.5	2.5	2.6	2.5	2.5
Fe (µg/L)	1	2	11	7	5	1	13	3	6	2
Mn (µg/L)	< 6	< 6	< 6	< 6	< 6	< 6	< 6	< 6	< 6	< 6
P(ort.) (µg/L)	8	8	9	8	8	8	9	8	9	8
HS ⁻ (µg/L)	< 50	-	-	-	< 50	-	< 50	-	-	-
O ₂ (µg/L)	7.8	-	7.5	-	-	7.6	-	-	-	7.4
pH (unit)	8	-	8.1	-	-	8	-	-	-	8

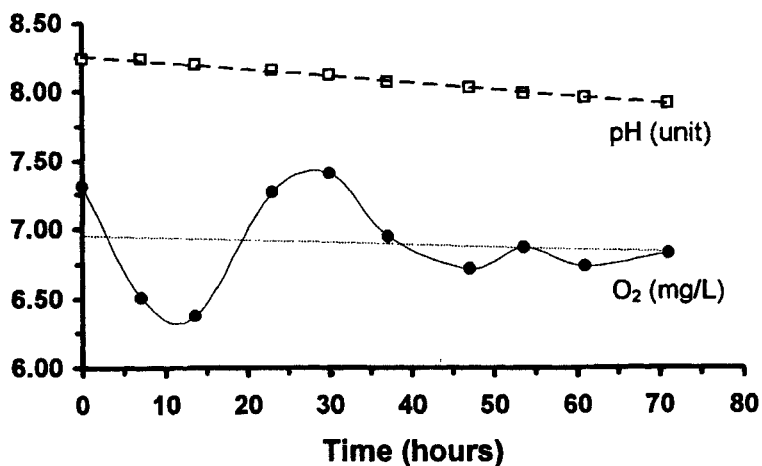


FIGURE 3 pH and dissolved O₂ profiles inside the benthic chamber (Rapallo station).

correlation coefficient (R^2). For silica, experimental and used profiles for the linear regression are reported.

The soluble fraction of reactive orthophosphate, sulphide, iron and manganese did not show significant variability with time and their benthic fluxes can be assumed to be equal to zero. However, it is likely that some of these benthic fluxes may be a significant difference from zero (mainly from iron and phosphorus) but not detectable using our experimental set-up. Iron diffusing from sediment (where it is present as Fe(II)) is quickly oxidised to Fe(III) by the dissolved oxygen in the overlying water and it becomes insoluble as iron hydroxide which may be removed at the sediment-water interface or on the membrane filter during filtration. Reactive orthophosphate may follow the same fate being coprecipitated with the iron hydroxide and/or adsorbed on clay mineral present at the sediment-water interface (Chen, 1972), or precipitated after formation of insoluble minerals (Barbanti *et al.*, 1992b; Van Cappelen and Berner, 1989; Jahnke, 1984). As regards manganese it is likely that no flux was really occurring being the oxidation rate of Mn(II) (soluble), which diffuses from sediments, to Mn(IV) (insoluble) low enough to be compared to the time necessary for sample collection and treatment. It is likely that manganese is removed at the sediment-water interface.

Benthic fluxes of sulphide (mainly present in sea water as HS), cannot be quantified since its pore water concentration is below the detection limit in the upper layer of sediments (Rapallo) or very close to the detection limit (Prelo). Furthermore, pore waters were oxygenated in the upper layer of the sediments with a possible removal by oxidation.

N-ammonia concentration inside the benthic chamber (Fig. 3) constantly increased with time up to 5 times the starting value, indicating a positive flux (from sediment to overlying water). N-ammonia concentration outside the benthic chamber (Tab. I) presented a significant variability with time, but it was always below the concentrations measured inside the benthic chamber and with no significant trend.

N-nitrate concentration inside the benthic chamber (Fig. 4) constantly increased with time due to either a benthic flux from sediment to overlaying water or to the nitrification of the N-ammonia coming from sediments. Since N-nitrate pore water concentration

higher than in water column (Tab. I), it is likely that a real flux of nitrate occurred from sediments. However, we can suppose that the increase of nitrate concentration inside the benthic chamber is also produced by nitrification which is likely to be active considering the presence of an intermediate product of this reaction (N-nitrite). Nitrification seemed to take place both in the water column and in the upper part of the sediments where nitrite is significantly more concentrated than in the overlying water. Then, the trend showed in Figure 4, would represent (like nitrate) the effect of the sum of two processes: benthic flux from sediments and nitrification. N-nitrate pore water concentration outside the benthic chamber (Tab. I) presented a variability with time but it was always below the concentration measured inside the benthic chamber and with no significant trend.

Silica profile inside the benthic chamber (Fig. 4) showed a maximum 55 hours after the chamber positioning followed by a drop of the concentration probably due to the polymerisation process that turned it into chemical forms which are not detectable by the used analytical method. The silica benthic flux from sediment to overlaying water is in agreement with the concentration gradient at the sediment-water interface. Although outside the benthic chamber, silica presented a slight increment with time; this trend was not regular and probably due to the weather conditions during the experiment with freshwater income from land. Figure 4 reports sulphate and chloride profiles inside the benthic chamber. These species showed an increment in concentration with time, but their concentration outside the benthic chamber resulted, affected by a variability comparable to this increment (Tab. I), so that no conclusion can be drawn about whether or not a benthic flux would really exist.

3.2. Pore Water Profiles

Concentration profiles of some of the studied species for both the studied stations are reported in Figures 5 and 6. The other data are displayed in Table II.

In both stations sediments are oxygenated; nevertheless, pH profiles and concentration gradients at the sediment-water interface (Fig. 5) indicate that diagenetic reactions are active in the upper layer of sediments, at least at Prelo station. This is confirmed by the iron

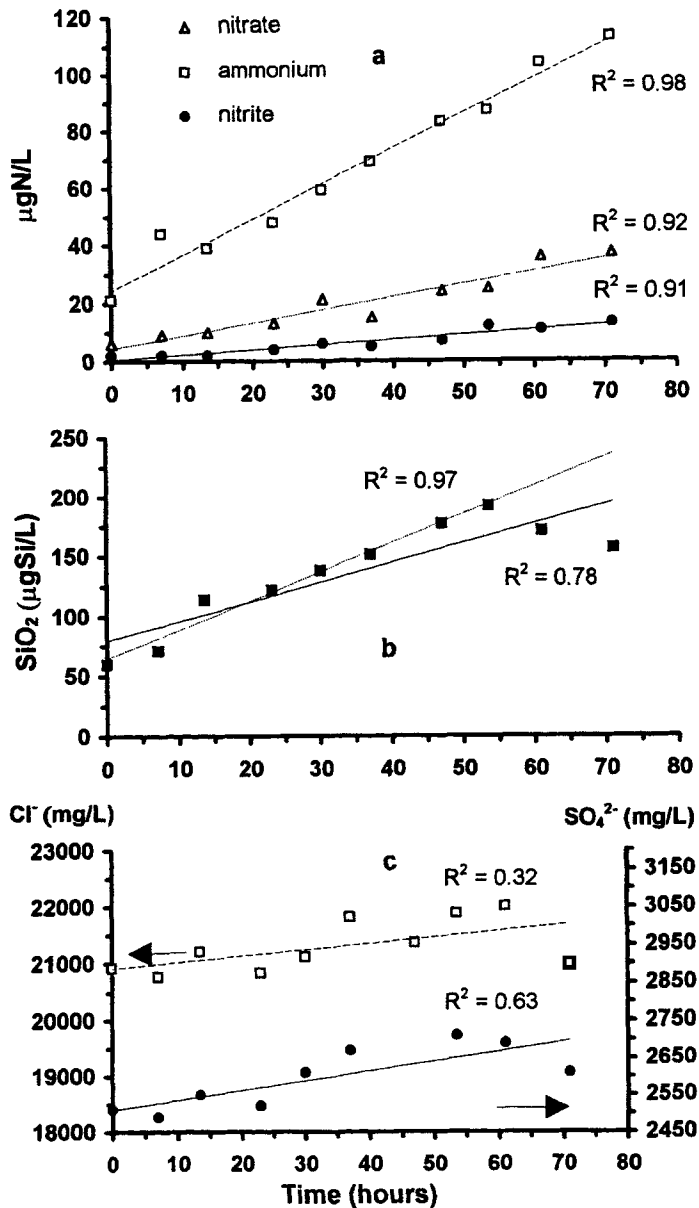


FIGURE 4 Example of benthic chamber profiles and linear regression parameters (Rapallo station).

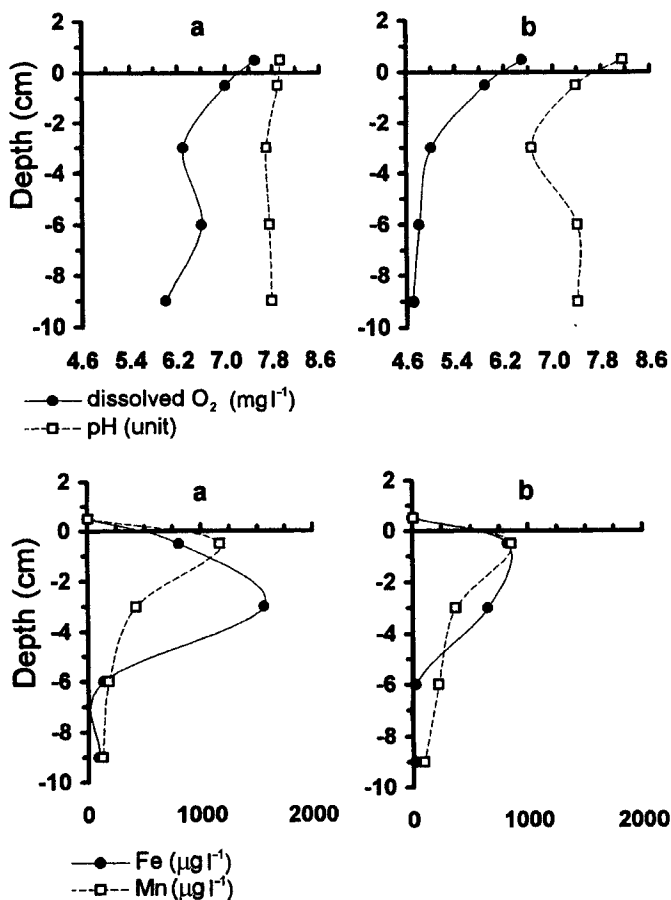


FIGURE 5 Dissolved oxygen, pH, iron and manganese profiles in pore waters: (a) Rapallo station; (b) Prelo station.

profile (Fig. 5) which reaches the maximum concentration just at the sediment-water interface at Prelo station, while for Rapallo station, where pH profile was quite constant with depth, the maximum concentration of iron was registered within the sediments. Manganese profiles (Fig. 5) resulted in very similar changes in the two stations because manganese hydroxides are those easily reducible than the iron ones. What happens in practice, once the organic matter has reached the sea floor, is its oxidative demolition to carbon dioxide with

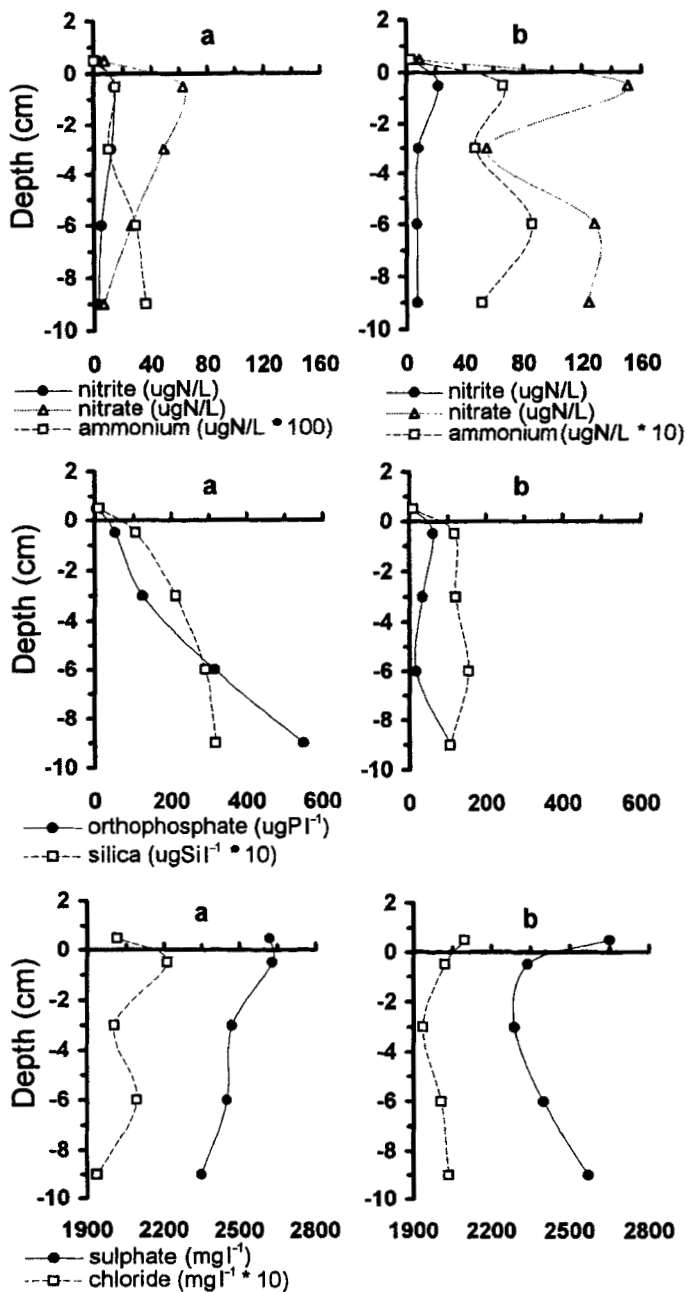


FIGURE 6 Nutrient elements ($N - NO_2^-$, $N - NO_3^-$, $N - NH_4^+$, $Si - SiO_2$, $P - PO_4^{3-}$, Cl^- , SO_4^{2-}) in pore water profiles: (a) Rapallo station; (b) Prelo station.

TABLE II Water quality parameters and concentration of sulphide in the water column and in pore water at Prelo and Rapallo stations

Parameter		HS^- ($mg\ l^{-1}$)	T ($^{\circ}C$)	Salinity	Conductivity ($mS\ cm^{-1}$)	Eh ($mg\ V.l$)	
Water Column	Rapallo	< 3	21.4	37.0	53.1	106	
	Prelo	6.5	n.d.	21.3	n.d.	277	
Pore waters (slice)	0–1 cm	Rapallo	< 3	20.1	31.9	44.0	100
		Prelo	5.9	n.d.	20.1	n.d.	210
	2–4 cm	Rapallo	< 3	19.4	31.9	43.2	87
		Prelo	5.0	n.d.	20.4	n.d.	179
	5–7 cm	Rapallo	0.35	21.2	32.7	46.2	112
		Prelo	4.8	n.d.	21.2	n.d.	30
	8–10 cm	Rapallo	0.55	21.2	31.7	44.7	125
		Prelo	4.7	n.d.	21.9	n.d.	–290

local decreasing of pH and dissolved oxygen depletion in pore waters. Once the dissolved oxygen concentration falls below $0.5\ mg\ l^{-1}$, other electron acceptors are used for the oxidation of organic matter: at first nitrate (Devol, 1975), with molecular nitrogen production (denitrification), then manganese and iron hydroxides, and at last sulphate which is converted into sulphide.

Furthermore, the proteolysis of the organic matter produces amino acids which are subsequently degraded with accumulation of ammonium and phosphates in pore water and generation of concentration gradients at the sediment-water interface.

In the case studied, probably due to the surface sediment resuspension (Rapallo) or to the sediment grain size (Prelo), we observed the effect of diagenetic reactions usually occurring in anoxic sediments (high concentrations of iron, manganese, ammonia phosphate, Fig. 5), with the parallel effect of processes like nitrification in the upper layer of the sediments, which usually takes place at the sediment-water interface or in the water near the sediments; this requires the availability of dissolved oxygen. Nitrification produced at first nitrite, and then nitrate, which appeared in the pore waters as shown in Figure 6.

Reactive orthophosphate profiles in pore water are characterised by opposite trend for the two stations (Fig. 6). This may be ascribed to the different removal mechanism of this species inside the sediments which depends on the composition of the pore water (Claypool and Kaplan, 1974; Stumm and Morgan, 1981).

Silica profiles in pore waters (Fig. 6) showed a great concentration gradients at the sediment-water interface.

Pore water concentration profiles of sulphate (Fig. 6) indicated that they are removed in the sediments: this may take place directly (as gypsum) or as insoluble metallic sulphides after reduction.

Pore water concentration profiles of chloride (Fig. 6) resulted, with a very high variability so that no conclusion can be drawn from the analysis of the experimental data.

In conclusion for all the studied species, with the exception of sulphide and chloride at the Prelo station, pore water concentrations in the upper layer of sediments were higher than in overlaying water indicating the sediments of both stations as a potential source, with expected fluxes towards the water column.

3.3. Benthic and Diffusive Fluxes

Table III reports the data used for computing diffusive fluxes according to the application of the Fick's first law. Diffusion coefficients were taken from literature and corrected for temperature and salinity effect (Wollast and Garrels, 1971; Li and Gregory, 1974) and, in case of phosphorus, for ion pair effect (Van Klump and Martens, 1981). Porosity values are reflecting the different sediment structure and grain size at the two stations. For both stations, the value of " Δx " was taken as 0.5 cm, which corresponds to the half of the thickness of the first slice of sampled sediments used for pore water extraction.

Computed benthic (J_s) and diffusive fluxes (J_d) are reported in Table IV. In agreement with their concentration gradients, most of the studied species presented positive diffusive fluxes (from sediment to overlaying water) with the exception of sulphate and chloride at the Prelo station.

Positive diffusive fluxes were decreasing in the order at Rapallo station: $\text{Cl}^- > \text{N} - \text{NH}_4^+ > \text{SO}_4^{2-} > \text{SiO}_2 > \text{Mn} > \text{Fe} > \text{N} - \text{NO}_3^- > \text{P} > \text{N} - \text{NO}_2^-$ and at Prelo $\text{N} - \text{NH}_4^+ > \text{SiO}_2 > \text{N} - \text{NO}_3^- > \text{Mn} > \text{Fe} > \text{N} - \text{NO}_2^- > \text{P}$. Limited to Prelo station, negative diffusive fluxes were decreasing in the order $\text{Cl}^- > \text{SO}_4^{2-}$. Benthic fluxes at Rapallo station (positive) were decreasing in the order:

$\text{Cl}^- > \text{SO}_4^{2-} > \text{N} - \text{NH}_4^+ > \text{SiO}_2 > \text{N} - \text{NO}_3^- > \text{N} - \text{NO}_2^- > \text{P}, \text{Mn}, \text{Fe}$.

TABLE III Data used for computing diffusive fluxes

Station	Parameter	Si-SiO ₂	N-NH ₄ ⁺	N-NO ₃ ⁻	N-NO ₂ ⁻	Chemical species			P (ort.)	Fe	Mn
						Cl ⁻	SO ₄ ²⁻				
Rapallo	Δx	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
	$D_o^*(10^{-6})$	9.87	16.5	15.8	15.5	16.9	8.85	10.1	5.87	5.70	5.70
	Porosity	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67
Prelo	Δx	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
	$D_o^*(10^{-6})$	9.87	16.4	15.8	15.4	16.8	8.80	10.1	5.84	5.67	5.67
	Porosity	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43

The Parameter F was taken as 1.56 and 3.44 for Rapallo and Prelo station.

Salinity was 36.7 and 38.1 for Rapallo and Prelo station.

Temperature was taken 21.4°C and 21.3°C for Rapallo and Prelo station.

TABLE IV Benthic (J_s) and diffusive (J_d) fluxes

	Flux ($\text{mole m}^{-2} \text{d}^{-1}$)		
	Rapallo		Prelo
	J_d	J_s	J_d
Si - SiO ₂	5.61E - 04	6.04E - 04	4.53E - 04
N - NH ₄ ⁺	2.96E - 03	6.21E - 04	8.73E - 04
N - NO ₃ ⁻	1.05E - 04	2.21E - 04	1.87E - 04
N - NO ₂ ⁻	2.02E - 05	8.54E - 05	2.32E - 05
Cl ⁻	1.56E + 00	2.17E + 00	- 4.15E - 01
SO ₄ ²⁻	1.52E - 03	1.93E - 01	- 3.32E - 02
P (ort.)	2.59E - 05	n.f.	2.02E - 05
Fe	1.41E - 04	n.f.	1.01E - 04
Mn	1.99E - 04	n.f.	1.02E - 04

n.f: no flux.

The expected diffusive fluxes for iron, manganese and phosphorus at the Rapallo station were not shown in the benthic chamber experiments, so that they are only potential fluxes.

Diffusive fluxes for chloride and sulphate presented some discordance in sign at Rapallo and Prelo stations, but they are probably incorrect due to the high variability of the water and pore water concentration profiles: thus, the agreement between the diffusive and the benthic fluxes at the Rapallo station has to be considered as casual.

Difference between benthic and diffusive fluxes for sulphate at Rapallo station resulted in about two order of magnitude, in accordance with similar results in lagoon systems (Ciceri *et al.*, 1998). For all the other studied species minor differences between diffusive and benthic fluxes were observed: higher fluxes of silica and N-ammonia were registered at Rapallo (to a factor of 3), probably due to the higher organic matter sedimentation rate in the harbour area. Diffusive fluxes for reactive orthophosphate, iron and manganese resulted in higher levels at Rapallo station, but they were only potential fluxes according to the results of the benthic chamber experiments. Only for N-nitric and N-nitrate diffusive fluxes were higher at Prelo than at Rapallo station, indicating that at Prelo nitrification inside the sediments is more active.

Benthic fluxes of silica and nitrogen species at Rapallo station were higher than the correspondent diffusive fluxes indicating a role of bio-turbation in their exchange at the sediment-water interface.

4. CONCLUSIONS

Sediments of Rapallo and Prelo stations, although with some differences due to their structure and grain-size, as well as limitation in water circulation and possibility of sediment resuspension at Rapallo station, showed the characteristics usually occurring in anoxic marine sediments with high oxygen uptake and high pore water concentration of iron manganese ammonia and reactive orthophosphate.

The presence of dissolved oxygen in sediments of both stations, probably to be ascribed to their specific peculiarity, and led to the concomitant activity of oxygen dependent processes like nitrification of N-ammonium, which usually occur at the sediment-water interface or in the water layer just above the sediments.

Pore water concentrations of the studied species were higher than in the overlaying water (with the only exception of chloride and sulphate at the Prelo station), indicating a possible source effect of sediments. However, some of these expected fluxes (iron, manganese and reactive orthophosphate) were only potential, according to the results of the benthic chamber experiments, probably due to the removal at the sediment-water interface (Mn) and/or in the water layer just above the sediments by oxidation and precipitation (Fe) or coprecipitation/adsorption or insoluble minerals generation (P).

Diffusive fluxes are in general comparable at the two stations (usually higher at Rapallo station), apart for chloride and sulphate, although they seemed not to have realistic values due to the high variability of pore water concentrations compared to the respective concentration gradients at the sediment-water interface. Only for N-nitrite and N-nitrate diffusive fluxes were higher at Prelo than at Rapallo station where nitrogen oxidative processes seemed to be of less importance.

Benthic fluxes of silica and nitrogen species at Rapallo station were higher than the correspondent diffusive fluxes indicating that in this station, bioturbation plays a more important role.

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