Hydrobiologia **252**: 23–34, 1993.
H. L. Golterman (ed.), Sediment–Water Interaction 4.

Benthic nutrient fluxes in Cadiz Bay (SW Spain)

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Key words: benthic fluxes, oxygen demmand, benthic chambers, interstitial water, nutrients

Abstract

During summer and autumn 1988, benthic fluxes of nutrients and oxygen were measured in the Bay of Cadiz. The study was carried out using benthic chambers and in addition by determining gradients of nutrient concentration in interstitial water. Fluxes ranged between 13.5–24.3, 3.4–7.8, 6.1–28.4 and (−99.4)–(−188.5) mmol m^{-2} d^{-1}, for NH_4^+, o-P, SiO_2 and O_2 respectively. These values are far higher than those reported by other authors for locations at similar latitudes. The stoichiometry of O, N and P transference suggest that benthic degradation of principally allochthonous organic matter takes place mainly through anaerobic pathways.

Introduction

Nutrient regeneration is fundamental for the maintenance of primary productivity in coastal marine environments. Among other inputs, these areas receive a large quantity of labile organic matter which is liable of being mineralized swiftly. As a consequence, inorganic N and P compounds are released into the environment and can be utilized by phytoplankton or exported to nearby marine areas (Teal & Valiela, 1978). Due to the high surface-volume ratio of coastal ecosystems and the importance of bacterial colonization of the sea bottom (Dale, 1974), mineralization processes take place mainly in the sediment.

Several kinds of procedures for estimating benthic nutrient regeneration have been developed during the last two decades. While most of them remain inconvenient to use, benthic chambers provide the most accurate measurement of benthic metabolism (e.g.: Aller & Benninger, 1981; Callender & Hammond, 1982; Flint & Kamykowsky, 1984; Devol, 1987). '*In situ*' measuring has become more frequent in many marine environments since it was used for the first time by Rowe *et al.* (1975), and has been applied from intertidal zones (Asmus, 1986; Matsukama *et al.*, 1987) down to depths of over 6000 m (Smith *et al.*, 1983).

Direct measurements of nutrient fluxes through the sediment-water interface have been carried out in some European coastal zones, including several locations in the Baltic Sea (Hansen *et al.*, 1980; Kautsky & Wallentinus, 1980; Balzer *et al.*, 1983; Rutgers van der Loeff *et al.*, 1984; Anderson *et al.*, 1986; Sundby *et al.*, 1986; Pollehne, 1986; Asmus, 1986; Hall *et al.*, 1989) and the Mediterranean Sea (Giordani & Frignani, 1987; Vidal, 1988; Herndl *et al.*, 1989; Vidal *et al.*, 1989). Using other methods, such as incubating cores or determining interstitial water gradients, much more information has become available (e.g.: Henriksen *et al.*, 1980; Nedwell *et al.*, 1983; Blackburn & Henriksen, 1983; Kelderman, 1984;

Rutgers van der Loeff *et al.*, 1984; Jörgersen & Sörensen, 1985; Barbanti *et al.*, 1987). From the available literature, it can be inferred that benthic regeneration is a widely studied phenomenon whose dependence factors are known qualitatively. However, the great differences amongst fluxes from different locations denote that these factors affect the extent of the transference of chemicals across the water-sediment interface in a very complex way. Each coastal area thus requires specific study since data from other areas are not applicable to it. Moreover, each study of a new location extends the present body of data on benthic regeneration. This is of great interest for potential future modelling of this phenomenon in order to quantify it within nutrient cycles ocean-wide.

During the last few years, an estimation of nutrient regeneration potential capacity by means of ammonification, sulphate reduction, and phosphatase enzymatic activities has been carried out in Cadiz Bay (Blasco, 1985; Blasco *et al.*, 1986; Frutos *et al.*, 1988). Nevertheless, any information obtained by means of potential activities is only qualitative and cannot be used to define real regeneration values.

In this paper the results of the first investigations carried out in Cadiz Bay in order to determine '*in situ*' benthic fluxes of NH_4^+, NO_2^-, NO_3^-, o-P, SiO_2 and O_2 are presented. Measurements were made during summer and autumn 1988 at two selected stations. Additionally, 'in situ' fluxes were compared to diffusive fluxes, estimated by gradients of concentration of solutes in the interstitial water.

Material and methods

Description of sampling stations

Figure 1 shows the location of sampling stations. In choosing these locations, two factors were considered: (i) sediment composition, in terms of granulometry and organic matter input, and (ii) tidal current speed. Station 1 was situated near a sewage effluents outlet from the town of Puerto Real. This station is located in the intertidal zone, but is uncovered only during spring tides. Station 2 was situated at the northern end of the Sancti Petri sound. Its depth is 8.5 m below MSL and it is subjected to strong tidal currents, which sometimes exced 1.5 m s^{-1} at the surface. The sediment here is mainly clay.

Description of benthic chambers

Measurement of benthic nutrient fluxes was carried out '*in situ*' using opaque benthic chambers, provided with a stirring device (Fig. 2a). They were constructed of Plexiglass with a shape of spheroid (0.7 m in diameter). Their volumes ranged from 59.1 to 89.8 l. The use of chambers of different volumes depended upon the time of year when sampling was performed, since benthic fluxes had a pronounced seasonal component. Chambers thus had to be selected according to surface/volume ratios so that the variation in solute concentration inside during predetermined sampling period was high enough. Changing the chamber volume was preferred in this study, keeping a constant value for the area of sediment covered (0.385 m^2). Keeping a high area value provides better accuracy in the measurement of benthic fluxes, due to the reduction of variation arising from microheterogeneities existing in coastal sediments.

For deployment, chambers were arranged in a stainless steel pyramidal frame symmetrically ballasted at the base by weights totalling 30 kg (Fig. 2a). Each benthic chamber penetrated 3–10 cm into the sediment, according to the expected hardness of the sediment layer. A flange, attached above the basal opening, prevented the chamber from further penetrating into the sediment (Fig. 2b) in all instances.

A removable Plexiglass lid at the top of the chamber was used for supporting a recirculation pump, an oxygen sensor and a valve for evacuating air during chamber inmersion (Figs 2c and 2d). Its shape prevents the retention of air bubbles inside.

The recirculation pump prevents water inside

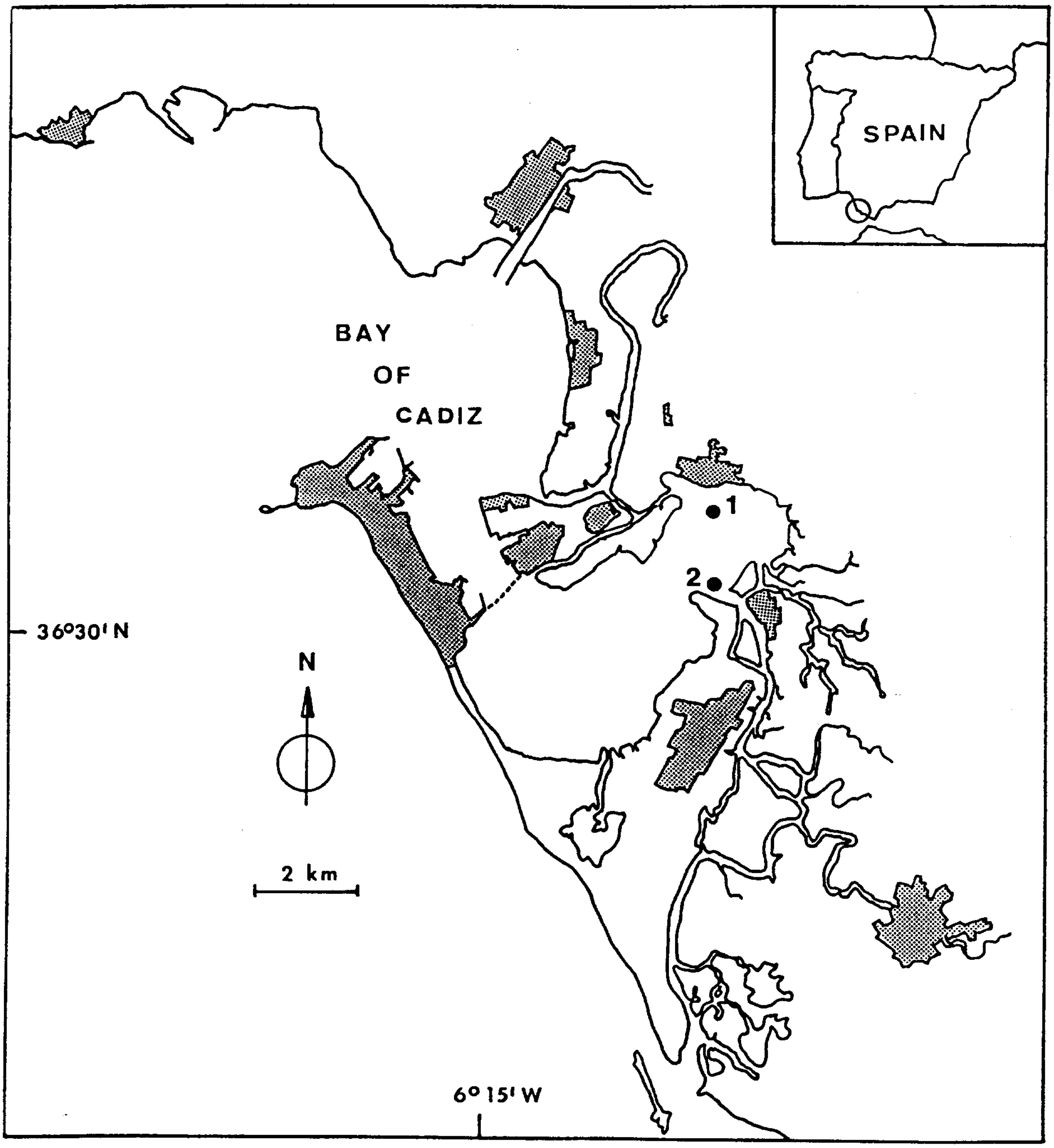

Fig. 1. Map of Cadiz Bay showing location of sampling sites.

the chamber from stratifying, so that samples obtained are representative of the whole volume; it also facilitates water circulation around the oxygen sensor membrane. Water flow can be controlled from the surface by means of a rheostat in order to simulate natural currents near the bottom. In the upper part of the pump a manifold for collecting samples from the surface is connected, and a small valve purges retained air in the recirculating system. Ambient seawater replaces sampled water through an opened inflow port.

One opaque and one transparent 2 l cylindrical

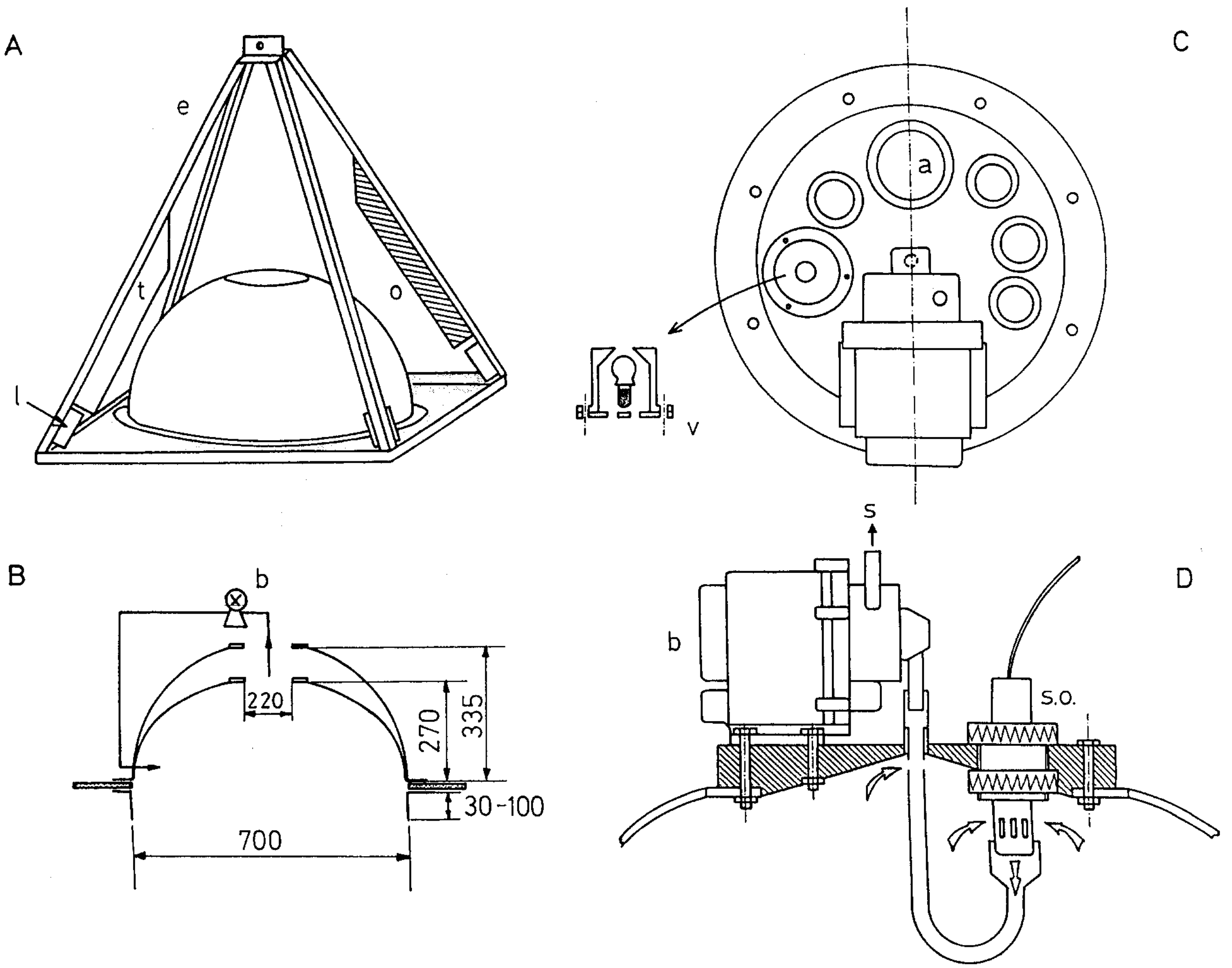

Fig. 2. Description of benthic chambers: (A) Pyramidal frame symmetrically ballasted for supporting benthic chambers, with transparent and opaque auxiliary bottles, (B) Dimensions (mm) of chambers and flanges utilized for benthic flux measurements, (C) Plexiglass lid used for placing recirculation pump, oxygen sensor and valve for evacuating air during chamber deployments, (D) Diagram of water circulation near to oxygen sensor.

bottle were attached to the structure in order to facilitate corrections due to processes taking place in the incubating water, unrelated to being in contact with the sediment. They were made of Plexiglass and provided with undirectional valves at their inlets to prevent mixing with outside water once the bottles had been filled (Fig. 2a).

Operating method

The main difficulty of using benthic chambers lies in installing them on the sea bottom while avoiding significant alteration of the sediment-water interface. In this study the amount of suspended solids inside the chamber has been taken as the criterion for evaluating installations. It was decided to reject all sampling operations in which densities of suspended solids inside the chamber, 3 to 5 min. after emplacement were 20% above the initial density of suspended solids at 10 cm above the sediment.

A YSI 5739 polarographic sensor was used for measuring oxygen concentration, at 5 minute intervals. It was calibrated following the Winkler method (Strickland & Parsons, 1968), just before being inserted into the chamber. During incubation, sampling was performed periodically (every 20–30 min) to determine nutrient concentration. Temperature was measured using the thermistor attached to the oxygen probe. Once sampling was finished, samples from the opaque bottle and the transparent bottle were collected for analysis of oxygen and nutrients.

Once collected, samples were kept in darkness at 4 °C and analyzed within 8 hours. Nutrient analyses were carried out using a TRAACS 800 Technicon autoanalyzer. Suspended solids were measured according to the method of APHA *et al.* (1985), by utilizing AP40 Millipore fibreglass filters (0.8 to 8 μm nominal pore size). Sulphate was determined gravimetrically.

Interstitial water samples were obtained from 40 mm i.d. cores by centrifugation at 24000 g. By following this procedure, and depending on granulometry, 74 to 83% of the total water contained in the sediment could be obtained. Org-C and N were determined in dry sediment at 110 °C. Org-C was determined according to the method of El Rayis (1985). Tot-N was measured by a Carlo Erba elemental analyzer (Mod. 1106). Results thus obtained differed by less than 12% from those for organic N. This concordance was empirically determined *a posteriori* from comparison with values from nine samples analyzed by the Kjeldhal method. This fact could be attributed to dissolved inorg-N being removed with interstitial water during centrifugation.

Results

Figure 3 shows concentrations of NH_3, o-P and SiO_2 inside the chamber during some of the sampling performed in summer. Unlike the findings of most published studies, concentrations in the chamber during sampling did not undergo linear variation with time in many cases. Similarly, Elderfield *et al.* (1981) noticed a curvature in the evolution of solute concentration during core incubation utilizing the flux method, as did Kautsky & Wallentinus (1980) and Devol (1987) with benthic chambers. This is due mainly to two reasons: (i) Whenever samples are taken for nutrient analysis, incubated water in the chamber becomes diluted with water from outside within which nutrient concentration is initially lower. (ii) Progressive increase of concentrations in incubated water decreases the gradient between the chamber and the interstitial water, thus decreasing flux through the water-sediment interface. This is a phenomenon which takes place whenever benthic chambers are used, since a concentration change of the species that is being diffused is an essential requirement for flux measuring. The former consideration allows of simple adjustment if sample volume collected from the chamber, and the temporal evolution of solute concentration outside, are known. The latter is more complex, since the way the gradient across the sediment-water interface inside the chamber changes, is not known. In any case, both phenomena have little effect at the beginning of the sampling period, although their influence on flux determination increases with time.

During operation, less than 3% of the chamber volume was withdrawn, and thus no correction for dilution was made. When using benthic chambers, fluxes through the sediment–water interface can be calculated using the equation:

$$J = \frac{1}{R}\frac{dC_i}{dt} - r_p + u_p,$$

where R is the surface-to-volume ratio in the chamber, C_i is the concentration of the studied species inside the chamber at time t, r_p is planktonic nutrient uptake and u_p is planktonic nutrient regeneration. Variations of concentration in the auxiliary bottles (transparent and opaque) during the incubation period in the chamber were not considered for flux calculation, since the variations were found to be very small in both cases. This finding is in agreement with that described by Fisher *et al.* (1982) indicating that nutrient planktonic regeneration (r_p) and consumption in the water column (u_p) tend to compensate each other, at least over short periods of time.

Most of the variation in C_i against t in the sampling performed in Cadiz Bay may be de-

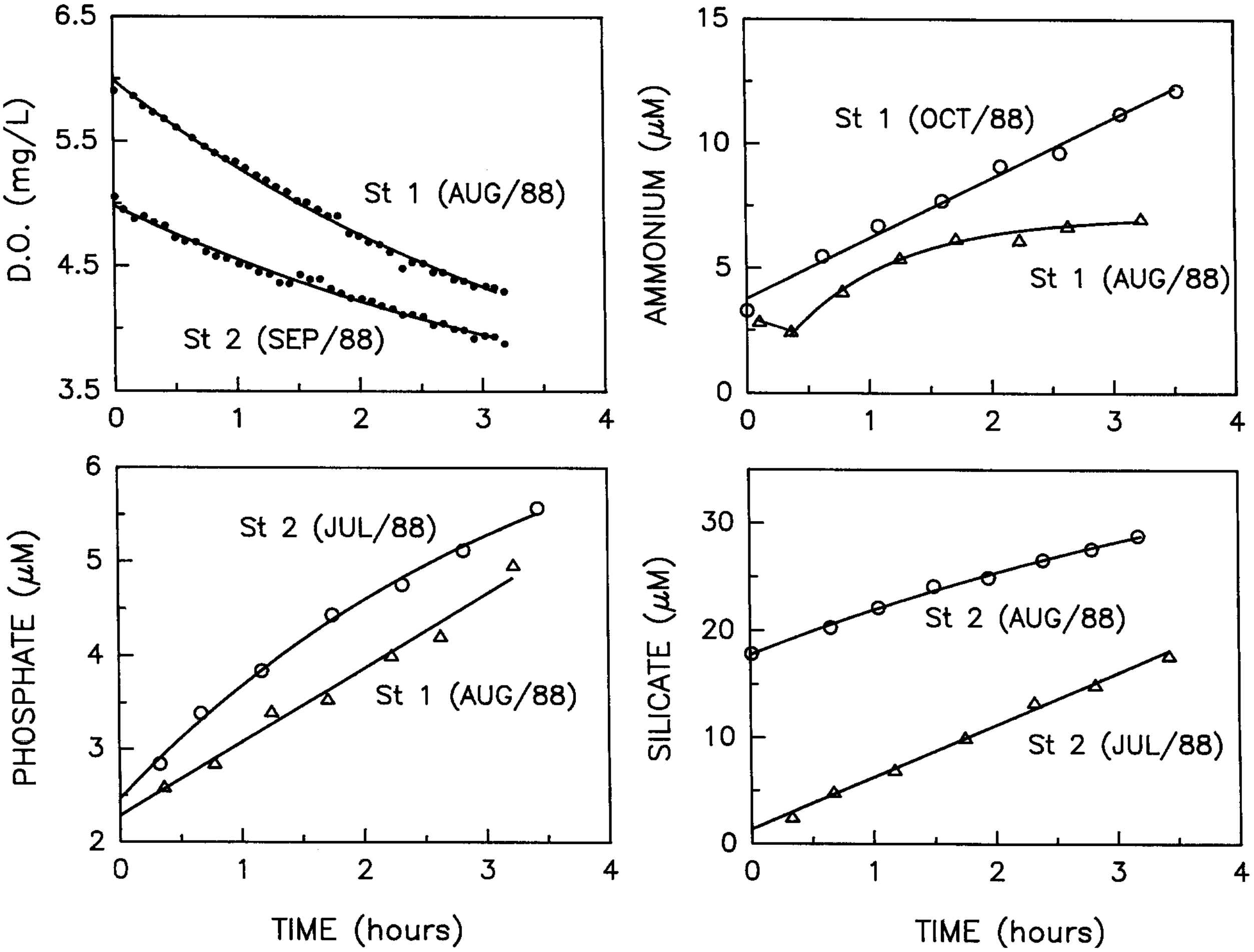

Fig. 3. Variation of O_2, NH_4^+, o-P and SiO_2 concentration inside the benthic chambers for some representative sampling occasions during summer and autumn 1988.

scribed by means of a linear equation of the type (Fig. 3; Table 1):

$$C_i = a + bt.$$

In this instance, flux through the interface is constant and can be obtained from the slope of the straight line, $J = b/R$.

Table 1. Type (EXP: Exponential, LIN: linear), fitted parameters and correlation coeficients of curves show in Fig. 3.

	Site (date)	Type	*a*	*b*	*k*	*r*
D.O. ($mg\,l^{-1}$)	St 1 (Aug/88)	EXP	2.139	− 3.824	0.187	0.996
NH_4^+ (μM)	St 1 (Oct/88)	LIN	3.776	2.407	–	0.995
o-P (μM)	St 2 (Jul/88)	EXP	7.390	4.926	0.281	0.996
SiO_2 (μM)	St 2 (Aug/88)	EXP	43.420	25.668	0.175	0.996
D.O. ($mg\,l^{-1}$)	St 2 (Sep/88)	EXP	3.000	− 1.987	0.244	0.989
NH_4^+ (μM)	St 1 (Aug/88)	EXP	7.066	6.148	0.942	0.970
o-P (μM)	St 1 (Aug/88)	LIN	2.285	0.788	–	0.991
SiO_2 (μM)	St 2 (Jul/88)	LIN	1.372	4.889	–	0.998

On some samplings occasions, variations in concentrations of O_2 and nutrients with time can be better described by an exponential fit (Fig. 3):

$$C_i = a - b\exp(-kt)$$

Table 1 shows fitted parameters of exponential variation shown in Fig. 3. This was mainly found in sampling during summer, suggesting that fluxes were not constant over the whole period of study. In these cases, fluxes were calculated replacing t by O in the firt derivative of the above equation (Forja, 1990), $J = bk/R$.

At the beginning of sampling, a decrease in the concentration of NH_3 inside the chamber was common (Fig. 3), increasing later in the way previously described. This pattern was particularly apparent in those samples where a clear alteration of the sediment-water interface was produced and which, as reported above, were therefore not used for the calculation of nutrient fluxes. A similar pattern was described by Hopkinson & Wetzel (1982). It may be initiated by an alteration of the water-sediment interface, due to a slight overpressure produced during the process of chamber deployment. This alteration would affect NH_3 fundamentally, due to its high mobility (Krom & Berner, 1980). In these cases, with the above-mentioned exceptions, flux calculation was carried out from the moment when concentration began to increase progressively.

Table 2 shows results obtained for nutrient and O_2 fluxes, together with salinity, temperature and pH (SWS scale) values at the time when sampling was carried out. In all cases, nitrite and nitrate fluxes were less than ± 0.1 mmol m^{-2} d^{-1}. For this reason, they are not considered for the calculations of fluxes of total inorg-N.

Flux values due to molecular diffusion through interstitial water were measured at Station 1. NH_3, o-P and SiO_2 profiles are shown in Fig. 4. In each of the 3 cases, it can be noticed that concentration increased along the whole of the analyzed core, but with higher variations in the superficial layer. At a depth 10 cm NH_3 and o-P values were over two orders of magnitude higher than those in the overlying water, while for SiO_2 they were only about twenty-fold higher. Profiles observed were relatively regular, especially for ammonia which shows no relationship with organic C evolution or with C/N ratio, for which considerable variations along the sediment column were noticed.

Diffusive flux (J_D) was calculated by means of Fick's law (Berner, 1976):

$$J_D = \phi D_s \left(\frac{\partial C}{\partial z}\right)_{z=0},$$

where C is the concentration in interstitial water, z is the depth within the sediment, ϕ is the porosity of the sediment surface layer, D_s is the diffusion coefficient of each ion, and $(\partial C/\partial z)_{z=0}$ is the concentration gradient across the water-sediment interface.

Porosity was measured as the loss of sediment weight at 110 °C (Ullman & Sandstron, 1987); its value was 0.682 ± 0.009 at the surface at Station 1. D_S was calculated by means of Li & Gregory's expression (1974):

$$D_s(i) = \phi^2 D^\circ(i),$$

Table 2. Average temperature, salinity, pH (SWS) and '*in situ*' fluxes of O_2, NH_4^+, o-P and SiO_2 from Cadiz Bay. Number following average is standard deviation for 3–4 deployments.

Station	Season	T (°C)	Fluxes (mmol m^{-2} d^{-1})					
			S (‰)	pH	D.O.	NH_4^+	o-P	SiO_2
1	Summer	25.4 ± 0.1	36.10 ± 0.11	8.13 ± 0.16	− 186.31 ± 49.46	24.34 ± 7.80	4.78 ± 0.37	19.99 ± 3.07
	Autumn	22.8 ± 2.7	36.50 ± 0.92	8.17 ± 0.09	− 105.06 − 14.26	13.47 ± 4.12	3.41 ± 0.86	6.10 ± 3.61
2	Summer	26.5 ± 0.6	37.07 ± 0.44	8.09 ± 0.14	− 188.50 ± 47.50	22.73 ± 1.46	7.80 ± 1.04	28.38 ± 5.04
	Autumn	18.5 ± 4.1	36.38 ± 0.87	8.15 ± 0.10	− 99.37 ± 16.76	18.28 ± 1.65	4.61 ± 0.51	18.48 ± 4.08

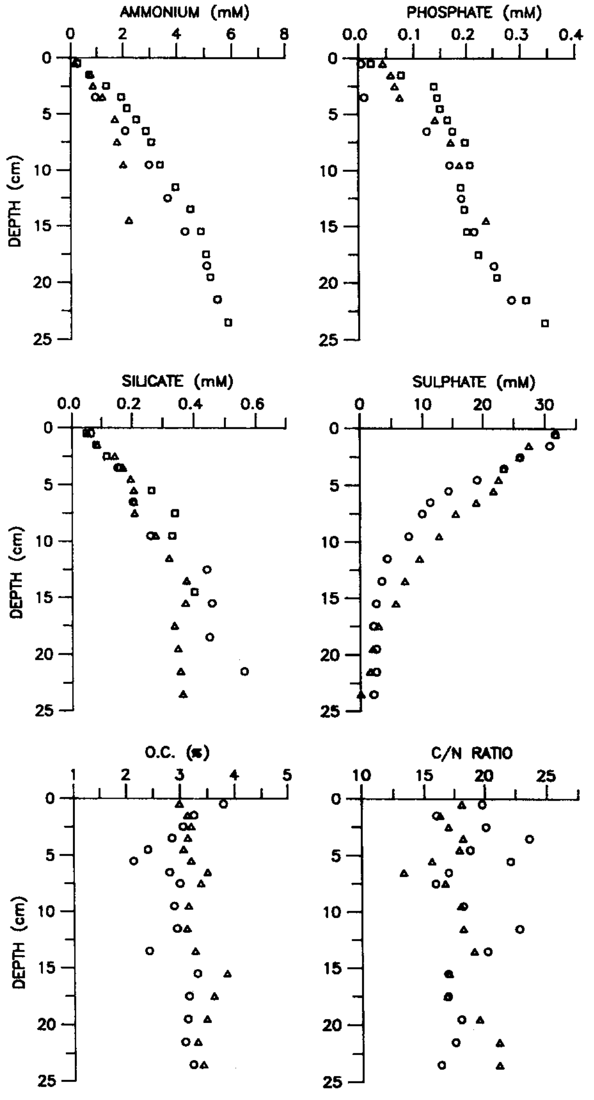

Fig. 4. Vertical profiles of NH_4^+, o-P, SiO_2 and SO_4^{2-} concentration in the interstitial water of sediments at Station 1 during summer and autumn 1988. Vertical variation of organic carbon content (O.C.) and the C/N ratio are also showed.

where D° (i) is the coefficient of diffusion in the overlying water. D° (i) for NH_3 and o-P were obtained by taking into account the dependence of diffusion on temperature (Krom & Berner, 1980). According to Lerman (1979, *op. cit.* in Callender & Hammond, 1982), a coefficient of diffusion corrected for the viscosity of sea water at infinite dilution has been utilized for SiO_2.

Calculation of $(\partial C/\partial z)_{z=0}$ was performed by means of exponential fitting of C against z for the superficial layer of the sediment (Krom & Berner, 1981; Rosenfeld, 1981). D_s and $(\partial C/\partial z)_{z=0}$ values utilized for calculating J_D, and the results for diffusive fluxes, are shown in Table 3.

Discussion

With respect to *in situ* fluxes, similar behaviour was observed at the two stations. Nevertheless, the highest o-P fluxes were detected at Station 2, which receives a less degraded organic matter input. SiO_2 fluxes were also higher at this station, as a consequence of a high SiO_2 content in the interstitial water of the sediments. Taking mean values, fluxes at both stations are very high in comparison to those from other coastal zones at similar latitudes (Table 4).

A decrease of benthic oxygen demand and of NH_4^+, o-P and SiO_2 fluxes was observed in the autumn, as compared to the summer, at both stations, due to the dependence of bacterial metabolism upon temperature. An average decrease of 32.1% in the flux of NH_3 and of 34.8% in the flux of o-P were attained when temperature decreased by only 5.3 °C. This is probably due to the temperatures recorded during the sampling period

Table 3. Mean values and standard deviations ($n = 3$) for diffusion coefficients, concentration gradients, correlation coefficients (r) and diffusive fluxes from Station 1 (Summer 1988).

	$D_s\ 10^6$ ($cm^2\ s^{-1}$)	$\lvert dC/dz \rvert_{z=0}$ ($mM\ m^{-1}$)	r	J_D ($mmol\ m^{-2}\ d^{-1}$)
NH_4^+	10.51 ± 0.25	0.524 ± 0.015	0.991 ± 0.005	3.26 ± 0.13
o-P	4.78 ± 0.07	0.050 ± 0.026	0.963 ± 0.001	0.14 ± 0.07
SiO_2	6.82 ± 0.09	0.038 ± 0.007	0.931 ± 0.025	0.16 ± 0.02

Table 4. Nutrient and oxygen benthic fluxes in some litoral zones of similar latitude of Cadiz Bay.

Site	*t* (°C)	Fluxes (mmol m^{-2} d^{-1})				References
		NH_4^+	o-P	SiO_2	D.O.	
South River Estuary (NC, USA)	22	5.3	0.4	–	- 56.2	Fisher *et al.* (1982)
Potomac Estuary (MD, USA)	–	8.1	0.8	10.1	- 67.0	Callender & Hammond (1982)
Long Island Sound (CT, USA)	22.1	5.2	–	4.8	–	Aller & Benninger (1981)
Texas Coast (TX, USA)	28	7.6	–	4.8	- 146.7	Flint & Kamykowski (1984)
NW Adriatic (Italy)	–	2.8	0.1	2.8	–	Giordani & Frigani (1987)
Narragansett Bay (RI, USA)	20	12.5	5.6	8.3	–	Elderfield *et al.* (1981)
Georgia Bay (GA, USA)	28	4.0	0.9	–	- 90.6	Hopkinson & Wetzel (1982)
Patuxent Estuary (MD, USA)	–	7.1	1.1	–	–	Boynton *et al.* (1980)
Cape Blanc (Western Sahara)	–	5.6	1.2	–	–	Rowe *et al.* (1975)
Cadiz Bay (Spain)	19–26	19.7	5.1	18.2	- 144.8	This study

falling within the range where Q_{10} values are high for ammonification and phosphatase activities in this zone (Frutos *et al.*, 1988).

Variations of similar magnitudes were found by Fisher *et al.* (1982) in several estuarine areas in North Carolina (USA). The fact that o-P flux variation is slightly greater than NH_3 flux variation is connected with the fact that its apparent energy activation for the diffusion process is also higher (Aller, 1980).

A different pattern of SiO_2 flux variation with temperature was obtained at the two Stations. At Station 2, a decrease from summer to automn was observed, its magnitude (34.9%) close to that described by Yamada & D'Elia (1984). These authors determined SiO_2 regeneration to be a consequence of biogenic SiO_2 dissolution depending on salinity and temperature. Nevertheless, if these two factors do not vary significantly, SiO_2 transference rate is directly proportional to the amount of biogenic SiO_2 available in the sediment. This fact suggest that Si flux variation at Station 1 depends largely on the settlement of dead cells of diatoms. As for other of phytoplankton in Cadiz Bay, diatoms show a great spatial variation (Lubián *et al.*, 1985).

Table 5. Stoichiometric ratio between '*in situ*' benthic fluxes at Cadiz Bay

Station	Season	N/P	N/Si	O/N
1	Summer	5.09	1.22	7.65
	Autumn	3.27	2.21	7.80
2	Summer	2.91	0.80	8.29
	Autumn	3.96	0.99	5.43

Table 5 shows ratios among N, P, Si and O_2 fluxes at the two locations studied. Concerning the stoichiometry of N and P emission from sediments, both Stations show similar values, with a mean N/P ratio of 4.8 at Station 1 and 3.4 at Station 2. In general, N/P flux ratios are very different to the value of 16 given by Redfield *et al.* (1963) for phytoplanktonic organic matter in the sea. Similar values to this study for the N/P flux ratio have been found by many authors at relatively unpolluted areas (e.g.: 4.6 by Hopkinson & Wetzel, 1982; 5.3 by Aller, 1980; 2.9 by Elderfield *et al.*, 1981). There are two possible explanations for the differences between these values and that of Redfield *et al.* (1963): (i) The studied areas are subject to a highly variable input of organic matter, (ii) There is no reason to suppose that the stoichiometry of benthic nutrient fluxes will be in accordance with the composition of organic matter entering the sediments, because several processes may co-occur (Golterman, 1984). In our case, the low N/P ratios obtained could arise from the expected preferential release of P relative to N during early stages of organic matter decomposition (Grill & Richards, 1964; Smetacek & Pollehne, 1986).

On the other hand, vertical profiles of the C/N ratio in the sediments (Fig. 4) suggest that microbial degradation is taking place with in a substrate whose origin is predominantly allochthonous.

Concerning the O/N ratio, values do not vary greatly at either of the stations, though they are quite different from the value of 17.2 given by Redfield *et al.* (*op. cit.*). Other authors have often obtained higher values, frequently attributed to the contribution of benthic meiofaunal and macrofaunal respiration to the aerobic degradation of organic matter. Such low values as those obtained in Cadiz Bay suggest that mineralization proceeds preferentially through anaerobic metabolic pathways. Available data for some potential enzymatic activities (Blasco, 1985) as well as for the SO_4^{2-} gradient in interstitial water (Fig. 4), show that sulphate reduction plays an important role in this zone. This is consistent with measurements of sulphate reduction measurements in several littoral ecosystems (e.g.: Jörgensen & Sörensen, 1985; Klump & Martens, 1989; Thode-Andersen & Jörgensen, 1989).

The diffusive fluxes, based upon concentration gradients in interstitial water, are considerably lower for the three nutrients than are the fluxes measured '*in situ*'. This is a common situation in most coastal system and it has been traditionally attributed to a bioturbation process by benthic macrofauna. This benthic macrofaunal density at this Station (Station 1) is about 1400 ± 130 individuals m^{-2}, 93% being Polychaeta which have a high irrigation capacity. The ratio between the '*in situ*' flux and the diffusive flux is 5.8 for NH_4^+. This value is frequently found in coastal areas (e.g.: Callender & Hammond, 1982; Hopkinson, 1987). The high value of 29.2 for the ratio between the '*in situ*' and the diffusive o-P flux could be related to the high Fe content of the sediments (approximately 3.3% on dry weight) at this station, Fe oxides having a high adsorption capacity for phosphate ions. The corresponding flux ratio for silicate is 81.5. This could be a consequence of the fact that biogenic silica regeneration takes place mostly at the sediment-water interface (Lerman, 1978).

Acknowledgements

We gratefully acknowledge the collaboration of María Francisca Osta in the fieldwork and analysis, and the assistance of Mr. Pablo Vidal during sampling. The work was supported by the Consejo Superior de Investigaciones Científicas through research grant 630/070-1988.

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