

## Spatial and Seasonal Variation of *In Situ* Benthic Fluxes in the Bay of Cadiz (South-west Spain)

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Spatial and seasonal variation in benthic fluxes of nutrients, oxygen and alkalinity were measured in the Bay of Cadiz, a temperate semi-confined shallow water ecosystem. Oxygen, alkalinity, ammonia, phosphate and silicate fluxes averaged (mean  $\pm$  SD)  $137.5 \pm 48.1$ ,  $376.3 \pm 177.3$ ,  $17.7 \pm 7.5$ ,  $4.4 \pm 2.5$  and  $14.8 \pm 8.8$  mmol m<sup>-2</sup> day<sup>-1</sup>, respectively. These values are high in comparison to those previously reported for other coastal locations in similar latitudes. Benthic fluxes clearly changed seasonally and an exponential relationship with temperature was found. Apparent flux activation energies ranged between 10.7 kcal mol<sup>-1</sup> for phosphate and 18.1 kcal mol<sup>-1</sup> for silicate. Seasonal variation in the stoichiometry of nutrient, oxygen and alkalinity fluxes revealed an intensification in the anaerobic decomposition pathways of organic matter during the summer. Spatial variation, oxygen and alkalinity fluxes were found to be linearly correlated with the organic matter content of the sediment (measured as organic carbon). Also, ammonia and phosphate fluxes increased as the C/N ratio of the incorporated organic matter in the sediment decreased.

### Introduction

Since the initial work of Rowe *et al.* (1977), studies of *in situ* benthic fluxes of nutrients and oxygen have been performed in many locations, from intertidal zones (e.g. Asmus, 1986; Matsukawa *et al.*, 1987) to deep waters close to 6000 m in depth (Smith, 1987).

Most studies have been carried out in coastal ecosystems where the contribution of *benthic regeneration to sustaining local productivity at each location* has been estimated (e.g. Billen, 1978; Callender & Hammond, 1982; Fisher *et al.*, 1982; Florek & Rowe, 1983; Flint, 1985; Hopkinson, 1987). In addition, such studies have usually addressed the seasonal evolution of fluxes and their spatial variation, paying particular attention to dependence upon salinity, organic matter content of the sediment, and benthic macrofaunal density.

Concerning temporal variation, Elderfield *et al.* (1981) found a marked seasonal evolution of phosphate, ammonia and silicate fluxes in Narragansett Bay. Similar

variation was detected by Boynton and Kemp (1985) in Chesapeake Bay for benthic oxygen demand and *in situ* ammonia fluxes. In Cape Lookout Bay, Klump and Martens (1981) found ammonia and phosphate fluxes to increase by one order of magnitude between February (water temperature 5.5 °C) and July (22.0 °C). Seasonal evolution of silicate fluxes on the west coast of Sweden has been described by Rutgers van der Loeff *et al.* (1984). Temporal variation of benthic oxygen demand has also been frequently reported in the literature, both for coastal systems (Chanton & Martens, 1987) and for oceanic systems (Smith, 1987).

From the available literature, it can be inferred that benthic regeneration is a widely studied phenomenon whose dependence on certain factors is known qualitatively. However, the great differences between fluxes at different locations denote that these factors affect the extent of the transfer of chemicals across the water-sediment interface in a complex way. Each coastal zone requires specific study since data from other areas are not applicable to it. Moreover, each study of 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.

Until recently, no such study had been attempted in the Bay of Cadiz. Indirect information available on potential enzymatic activities (sulphate reduction, ammonification and phosphatase) suggested a high level on benthic nutrient regeneration, in agreement with the high level of exploitation of the local biological resources by man.

The present study concentrated on determining spatial and temporal variation in benthic oxygen demand, *in situ* nutrient fluxes (ammonia, phosphate and silicate) and alkalinity fluxes. Additional information was sought on their apparent activation energies as well as the stoichiometry of their production, the latter in an attempt to identify the relative contribution of the principal bacterial metabolic pathways involved in the decomposition of organic matter in the sediment.

## Material and methods

### *Study area*

The Bay of Cadiz is a temperate shallow water coastal ecosystem. The present study was carried out in the inner part of the bay, which has a surface area of 36.6 km<sup>2</sup> and an average depth of 4 m. This zone (Figure 1) is bounded on the south and east by 60 km<sup>2</sup> of salt ponds. Productivity is supported by high irradiation (3244 h year<sup>-1</sup>), temperature (18.4 ± 6.8 °C) (Guillemot, 1986), and anthropogenic inputs of organic matter (Blasco *et al.*, 1987). This situation has permitted exploitation of the biomass by means of different types of aquaculture.

Sampling stations were located as shown in Figure 1. The study of seasonal variation in benthic fluxes was performed during 1988–89 at stations LC and PR. Station LC is located at the northern aperture of the main channel draining the marsh (Sancti Petri Sound). This channel is 8.5 m deep and affected by strong tidal currents. The bottom is largely of clay. Station PR is close to the town of Puerto Real, and was affected by urban sewage up to the beginning of 1989; the bottom is compacted clay. During this study, in February 1989, the zone where this station is situated was dredged, increasing its depth from 0.5 to 2 m. This dredging was performed within a period of a few days, but blocked access to the site for a month.

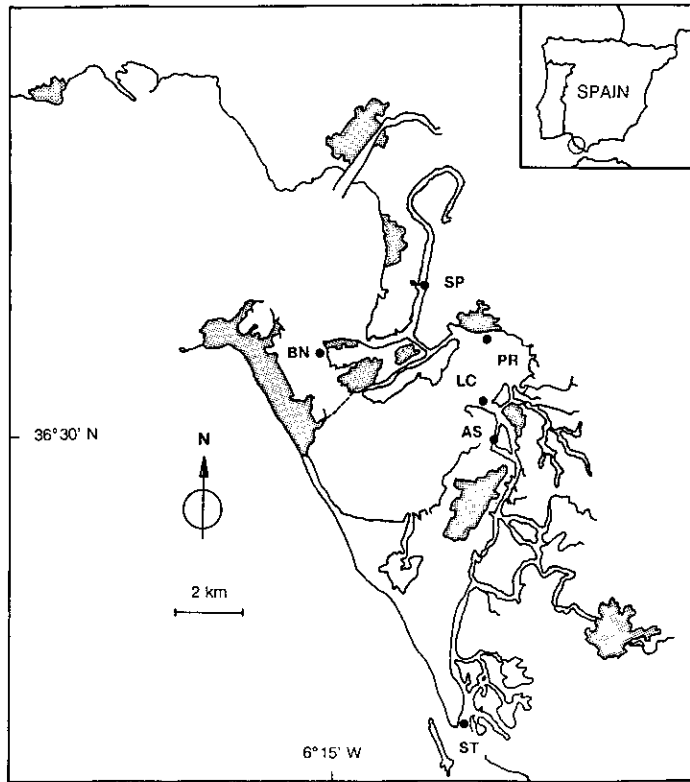


Figure 1. Map of Cadiz Bay and location of the sampling stations.

Sampling to establish the spatial distribution of benthic fluxes was performed in summer 1989. Six sampling stations were selected to include a variety of sedimentary environments in terms of organic matter inputs and granulometry.

#### *In situ flux measurements*

Fluxes through the sediment–water interface were measured using Plexiglass opaque benthic chambers constructed with a semi-ellipsoid shape of circular section measuring  $0.385 \text{ m}^2$ . The surface/volume ratio of the chambers varied from  $4.3$  to  $6.5 \text{ m}^{-1}$  depending on the expected fluxes. The chambers were provided with a variable-speed recirculation pump in order to stimulate current speeds approximating those found in the proximity of the sediment in this zone ( $5\text{--}15 \text{ cm s}^{-1}$ ). According to Gundersen and Jorgensen (1990), these speeds do not give rise to any important alteration of the water–sediment interface structure.

Chambers remained on the sea bottom for 4–5 h, and samples for the determination of nutrients, alkalinity, dissolved oxygen, salinity and suspended solids content were collected every 30 min. These samples were removed by means of a device that would not cause degasification (Gómez-Parra *et al.*, 1987) operated from on-board ship or piers. The water volume removed was replaced by ambient bottom water entering the chamber via a one-way valve. Temperature and oxygen concentration were continuously

TABLE 1. Mean values ( $n=22$ ), range and standard deviation ( $\sigma$ ) of benthic fluxes in the Bay of Cadiz

	Mean ( $\text{mmol m}^{-2} \text{ day}^{-1}$ )	Maximum ( $\text{mmol m}^2 \text{ day}^{-1}$ )	Minimum ( $\text{mmol m}^{-2} \text{ day}^{-1}$ )	$\sigma$
Oxygen	-137.5	-235.8	-69.1	48.1
Alkalinity	376.3	655.1	131.7	177.3
Ammonia	17.7	36.6	6.2	7.5
Phosphate	4.4	9.1	0.5	2.5
Silicate	14.8	35.5	6.2	8.8

recorded by means of a polarographic probe and a thermistor (YSI Model 5776). Samples were kept at 4 °C and analysed within 8 h of collection.

Nutrient determinations were performed in a Technicon Traacs 800 Autoanalyser. Alkalinity was measured by a modification of the method of Van der Berg and Rogers (1987). Deviations of the oxygen probe, attributable mainly to high water turbidity in the area, were corrected every 30 min by analysing the samples using the Winkler method (Grasshoff *et al.*, 1983). Suspended solids were gravimetrically measured using Millipore AP40 filters. Salinity was measured using a salinometer (Beckman RS10).

Data on concentrations obtained from chamber samples were corrected for the dilution due to sampling, which in some instances may lead to errors approximating 5% (Forja *et al.*, 1990). For this reason, the evolution of alkalinity, nutrient concentration and dissolved oxygen in the outside of the chamber was followed during the entire incubation period. Fluxes through the interface were calculated by empirical linear or exponential fitting of concentration against time. In the case of exponential fitting, fluxes were derived from the slope at time zero.

#### *Sediment measurements*

Sediment sampling was carried out using a 4 cm internal diameter gravity core. Interstitial water was obtained from slices of 1 cm thickness after centrifugation at 24 000 *g*. By following this procedure, and depending on granulometry, 74–83% of the total water contained in the sediment could be obtained. Core transportation and further treatment were performed under a nitrogen atmosphere. Organic carbon content was determined in sediment samples using the El Rayis (1985) modification. Elemental analysis was carried out with a CHN Carlo Erba (Model 1106). Assuming that a high proportion of the inorganic nitrogen is removed with the interstitial water during centrifuging, total nitrogen values should not differ significantly from organic nitrogen in the sediment, especially if porosity is high. Results thus obtained differed by less than 12% from those for organic nitrogen. This concordance was empirically determined *a posteriori* from comparison with values from nine samples analysed by the Kjeldhal method.

### **Results and discussion**

Table 1 shows the mean values of benthic oxygen, alkalinity and nutrient fluxes from all *in situ* chamber measurements performed in the Bay of Cadiz. The high standard deviations denote the considerable influence of temperature and the nature of the

sediment on benthic fluxes. Values obtained are generally high in comparison to those obtained by other authors working in similar latitudes (Table 2).

The high values of benthic fluxes in Cadiz Bay are related to the high sedimentation rate in this area together with the nature of the sediments, which are predominantly clay. These factors give rise to a high organic matter content within the sediment ( $2.16 \pm 0.78\%$ ), and under these conditions the mineralization process would be very rapid. In addition, two other factors could contribute to the increase of benthic fluxes within the area: (1) high macrofaunal density is known to be one of the principal factors enhancing benthic fluxes (e.g. Aller, 1980; Klump & Martens, 1989), and (2) due to the shallowness of the area, considerable currents occur near the sediment-water interface and consequently the transfer of chemical species across this interface is intensified (e.g. Pollehne, 1986; Whiting & Childers, 1989).

Taking into account the dimensions of study area (surface and mean depth), the C:N:P Redfield ratios, and primary productivity inside of bay ( $12.8 \text{ mg C m}^{-3} \text{ h}^{-1}$ ) (Gómez-Parra & Forja, 1992), it can be concluded that benthic regeneration of nitrogen and phosphorus exceeds, on average by 127 and 380%, respectively, the requirements established for phytoplankton in the area.

No appreciable fluxes of nitrite or nitrate were recorded in any instance, values always being lower than  $0.1 \text{ mmol m}^{-2} \text{ day}^{-1}$ . According to Smethie (1987), this could be due to the existence of a coupling effect between nitrification and denitrification processes at the 'oxic limit' of the sediment by which the production of these species would compensate for their consumption.

#### *Spatial variation of fluxes*

Benthic fluxes at the six sampling stations, as well as organic carbon content and the C/N ratio in the superficial sediments, are shown in Table 3. Appreciable differences of up to nearly an order of magnitude exist amongst fluxes from one place to another, especially for  $\text{HPO}_4^{2-}$  and  $\text{SiO}_2$ .

Highest benthic fluxes were detected at those stations (LC and PR) that received important input of anthropogenic organic matter. Maximum benthic macrofaunal densities of 1960 and 1540 individuals  $\text{m}^{-2}$ , respectively, were also found at these stations.

With the exception of station AS, both alkalinity and oxygen fluxes appear to have a linear relationship with the organic carbon content of the sediment [Figure 2(a,b);  $r^2=0.90$  and  $r^2=0.92$ , respectively]. In this regard, many authors have stated that organic matter degradation in marine sediments, which is the main process responsible for oxygen and  $\text{CO}_2$  fluxes through the water-sediment interface, follows first-order kinetics with respect to the organic matter content (e.g. Lasaga & Holland, 1976; Grundmanis & Murray, 1982; Martens & Klump, 1984; Klump & Martens, 1987, 1989).

Station AS, however, exhibits anomalous behaviour [Figure 2(a,b)]. In spite of the high organic carbon concentration (2.65%), alkalinity and oxygen fluxes are low, suggesting that at this station organic matter degradation may occur through the aerobic pathway. This is supported by two facts: (a) a low ratio between alkalinity and oxygen fluxes (1.34), which is relatively close to the theoretical value that would be obtained if a stoichiometric equation of organic matter oxidation is adopted, and (b) poorly marked  $\text{SO}_4^{2-}$  gradients through the interstitial water, indicating a low level of sulphate reduction at this station. At all other stations the ratios between alkalinity and oxygen fluxes are higher (up to 2.9 at stations LC and PR) while sulphate, sulphide and

TABLE 2. Nutrient and oxygen benthic fluxes in some littoral zones

Site	Oxygen (mmol m <sup>-2</sup> day <sup>-1</sup> )	Ammonia (mmol m <sup>-2</sup> day <sup>-1</sup> )	Phosphate (mmol m <sup>-2</sup> day <sup>-1</sup> )	Silicate (mmol m <sup>-2</sup> day <sup>-1</sup> )	Reference
Potomac Estuary (MD, U.S.A.)	-67.0 ± 1.5	8.1 ± 0.3	0.78 ± 0.05	10.1 ± 0.4	Callender and Hammond (1982)
Georgia Bay (GA, U.S.A.)	-118.8	1.38	0.54	—	Hopkinson (1987)
Narragansett Bay (RI, U.S.A.)	—	13.7	1.6	—	Hopkinson <i>et al.</i> (1991)
Texas coast (TX, U.S.A.)	—	12.5	5.6	8.3	Elderfield <i>et al.</i> (1981)
Long Island Sound (CT, U.S.A.)	-146.7	7.6	—	4.8	Flint and Kamykowski (1984)
North-west Adriatic (Italy)	—	5.2	—	4.8	Aller and Benninger (1981)
South River Estuary (NC, U.S.A.)	-36.2 ± 6.2	2.8	0.1	2.8	Giordani and Frignani (1987)
Great Bay (NH, U.S.A.)	—	5.38 ± 1.22	0.34 ± 0.14	—	Fisher <i>et al.</i> (1982)
Tomales Bay (CA, U.S.A.)	-9.37 ± 12.55	2.35	0.28	3.17	Lyons <i>et al.</i> (1982)
Cadiz Bay (Spain)	-137.5 ± 48.1	17.7 ± 7.5	4.4 ± 2.5	14.8 ± 8.8	Dollar <i>et al.</i> (1991) This study

TABLE 3. Spatial distribution of benthic fluxes at Cadiz Bay. Organic carbon content and organic carbon/nitrogen ratios are derived from sediments of depth ≤ 1 cm. Samples were taken on 5-7 July 1989, with the exception of station PR which was sampled 18 July 1988, prior to dredging

Station	Temperature (°C)	Salinity	Oxygen (mmol m <sup>-2</sup> day <sup>-1</sup> )	Alkalinity (mmol m <sup>-2</sup> day <sup>-1</sup> )	Ammonia (mmol m <sup>-2</sup> day <sup>-1</sup> )	Phosphate (mmol m <sup>-2</sup> day <sup>-1</sup> )	Silicate (mmol m <sup>-2</sup> day <sup>-1</sup> )	Organic carbon	C/N ratio
LC	25.9	37.56	-209.3	613.2	20.8	7.8	24.5	2.95	15.9
PR	25.3	36.21	-235.8	402.5	32.1	5.2	23.1	2.86	14.7
BN	24.7	36.54	-161.0	374.5	15.1	0.6	10.0	2.02	22.4
SP	25.8	36.93	-122.2	223.1	11.1	2.5	23.6	1.14	24.8
AS	25.3	37.80	-115.1	154.6	20.1	2.7	8.0	2.65	16.6
ST	25.5	37.25	-164.6	233.0	10.6	0.9	4.5	1.37	22.8

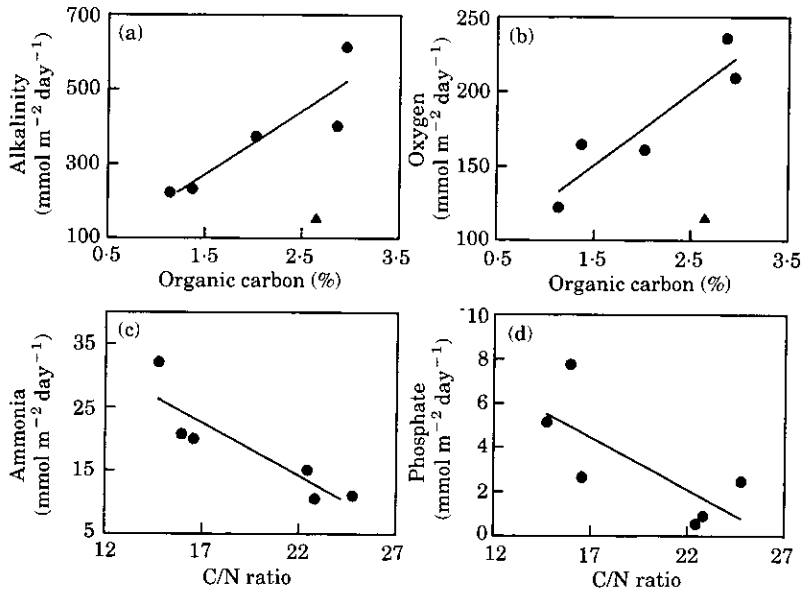


Figure 2. Variation of (a) alkalinity and (b) oxygen fluxes with organic carbon content, and variation of (c) ammonia and (d) phosphate fluxes with organic carbon/nitrogen ratio at Cadiz Bay. The station LC (▲) was not used for regression fits in (a) and (b).

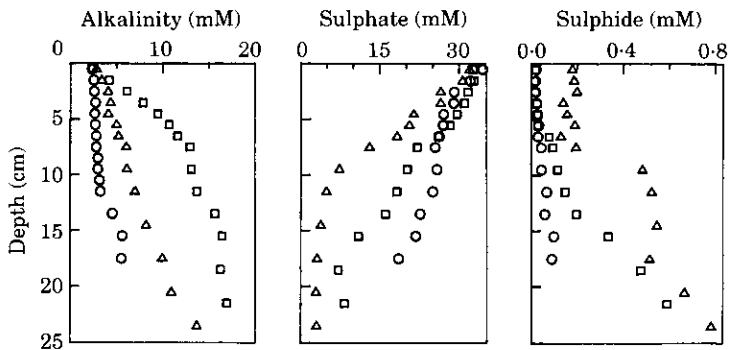


Figure 3. Vertical profiles of alkalinity, and sulphate and sulphide concentrations in interstitial waters of stations AS (O), PR (□) and LC (Δ).

alkalinity vertical profiles in interstitial waters are more marked (Figure 3), showing an important contribution of sulphate reduction to organic matter decomposition. This is in accordance with the high potential sulphate reduction activity found by Blasco (1985) at these locations.

There is a negative correlation ( $r^2=0.89$ ) between ammonia fluxes and the C/N ratio in the sediment [Figure 2(c)]. Although the correlation is lower ( $r^2=0.74$ ), this relation also exists for phosphate fluxes [Figure 2(d)], revealing a dependence of nutrient benthic regeneration on the degree of decomposition of the organic matter in the sediment. From a different viewpoint, this result confirms the C/N ratio as a reliable index of organic matter lability in this zone. On the other hand, the C/N ratio of organic matter in the first

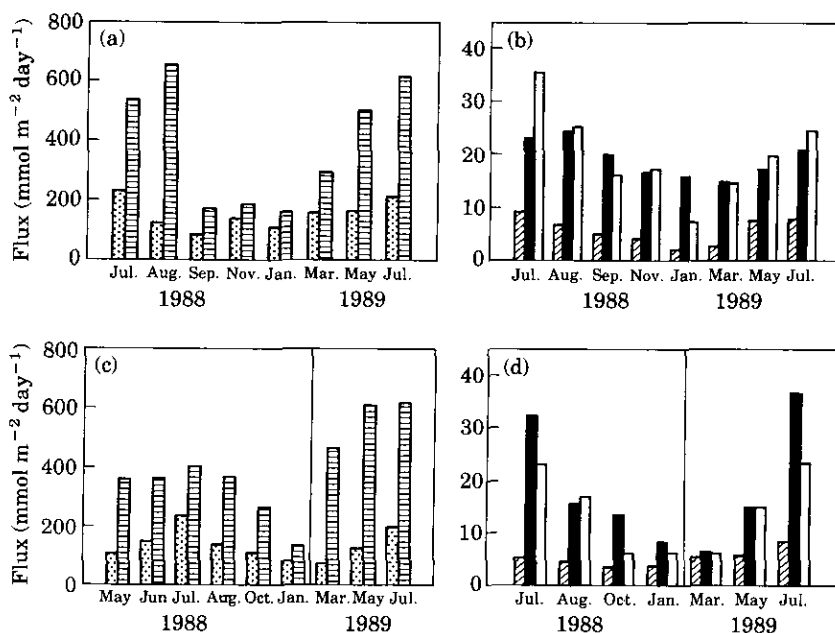


Figure 4. Seasonal variation of benthic fluxes at stations (a,b) LC and (c,d) PR. Vertical lines in (c) and (d) denote the date when the zone was dredged. □, Oxygen; ▨, alkalinity; ▩, phosphate; ■, ammonia; □, silicate.

cm of the sediment is high at all stations when compared to values proposed by Redfield *et al.* (1963) for the average composition of marine plankton. Although Redfield ratios may exhibit significant local variations, the present results ( $19.6 \pm 4.3$ ) suggest a prevalently allochthonous origin for the superficial organic matter in the Bay of Cadiz.

Silicate benthic fluxes are related to biogenic silica availability in the sediments (Hurd & Birdwhistell, 1983; Emerson *et al.*, 1984) since amorphous silica shows a high solubility in seawater (Kamatani & Riley, 1979). In view of the constancy over all stations sampled of temperature and salinity (Table 3), these being the main factors responsible for SiO<sub>2</sub> solubility (Yamada & D'Elia, 1984), the magnitude of spatial variation found in this study might be related to irregular diatom patches in the area. Small-scale spatial variations in diatom density have been detected in Cadiz Bay (Lubian *et al.*, 1985).

#### Seasonal variations of benthic fluxes

Figure 4 shows temporal variations of oxygen, alkalinity and nutrient fluxes at stations LC and PR. Vertical lines in Figure 4(c,d), corresponding to station PR, denote the date when the zone was dredged. As can be seen, fluxes of all species analysed follow a marked seasonal evolution at both stations, although fluxes at station LC are noticeably higher all year round. The largest amount of variation was found for the alkalinity flux, which ranged from 655 to 153 mmol m<sup>-2</sup> day<sup>-1</sup> at station LC, and 402 to 131 mmol m<sup>-2</sup> day<sup>-1</sup> at station PR. Fluxes are high all year, but differences between maximum and minimum values are, in relative terms, similar to those found in other coastal areas.



TABLE 4. Apparent activation energy ( $E_a$ ) of benthic fluxes of oxygen, alkalinity and nutrients in the Bay of Cadiz. Correlation coefficients and sample size for calculating  $E_a$  after linearization of Arrhenius equation at stations PR and LC are included

	$E_a$ (kcal mol <sup>-1</sup> )	$r^2$ (n)	
		LC	PR
Oxygen	11.29 ± 2.43	0.93 (7)	0.81 (9)
Alkalinity	17.71 ± 1.01	0.99 (7)	0.81 (6)
Ammonia	13.27 ± 4.41	0.85 (8)	0.79 (7)
Phosphate	10.78 ± 4.76	0.89 (8)	0.63 (4)
Silicate	18.09 ± 2.25	0.86 (8)	0.90 (7)

Benthic fluxes are generally dependent on temperature for all species studied. This dependence has often been described by linear (e.g. Pamatmat & Banse, 1969; Boynton *et al.*, 1980; Fisher *et al.*, 1982; D'Elia *et al.*, 1983) or exponential relations assuming the Arrhenius equation (e.g. Aller, 1980; Aller & Benninger, 1981; Rutgers van der Loeff *et al.*, 1984; Doering *et al.*, 1987). This latter procedure enables calculation of the apparent activation energy of benthic fluxes. Seasonal variations of benthic fluxes in the Bay of Cadiz are better fitted to an exponential model of variation.

Table 4 shows apparent activation energies of oxygen, alkalinity and nutrient fluxes obtained through a linear regression of the Arrhenius equation. Data on alkalinity and phosphate fluxes after dredging were excluded from calculations relating to station PR. In addition, the application of initial statistical screening to data from station LC led to the elimination from the data set of oxygen and alkalinity fluxes in September 1988. Differences between activation energies at both stations are high for ammonia and phosphate fluxes (8.81 and 9.56 kcal mol<sup>-1</sup>, respectively). This is caused by the narrow range of seasonal variation of ammonia fluxes at station LC, and phosphate fluxes at station PR [Figure 4(b,d)]. This fact makes the average apparent activation energies of ammonia and phosphate fluxes slightly lower than those described in the literature (Aller, 1980; Elderfield *et al.*, 1981; Crill & Martens, 1987). The activation energies of silicate fluxes are close to values given by Aller (1980), Elderfield *et al.* (1981) and Rutgers van der Loeff *et al.* (1984).

Dredging of the zone where station PR was located had a clear effect only on oxygen and alkalinity fluxes. A general decrease in oxygen with respect to the previous year is related to the almost complete elimination of the benthic fauna. Alkalinity fluxes rose markedly after dredging, causing the summer maximum of 1989 to be 50% higher than that of the previous year.

The influence of dredging on temporal evolution of ammonia and silicate fluxes is undetectable. This is normal in the case of SiO<sub>2</sub> since its regeneration responds basically to a physicochemical process (Yamada & D'Elia, 1984). Thus, the benthic SiO<sub>2</sub> flux in this zone is controlled by the fixation of biogenic silica from the water column into the sediment. Nevertheless, an increasing of *in situ* benthic fluxes were not detected in March (after a month of dredging). This fact suggests that the mobilization of nutrients and alkalinity was produced in a short time period.

The evolution of fluxes in the dredged area can be better understood if modifications illustrated by vertical profiles of alkalinity and nutrients in the interstitial water are taken into account. Figure 5 shows these profiles before dredging (January 1989) and after

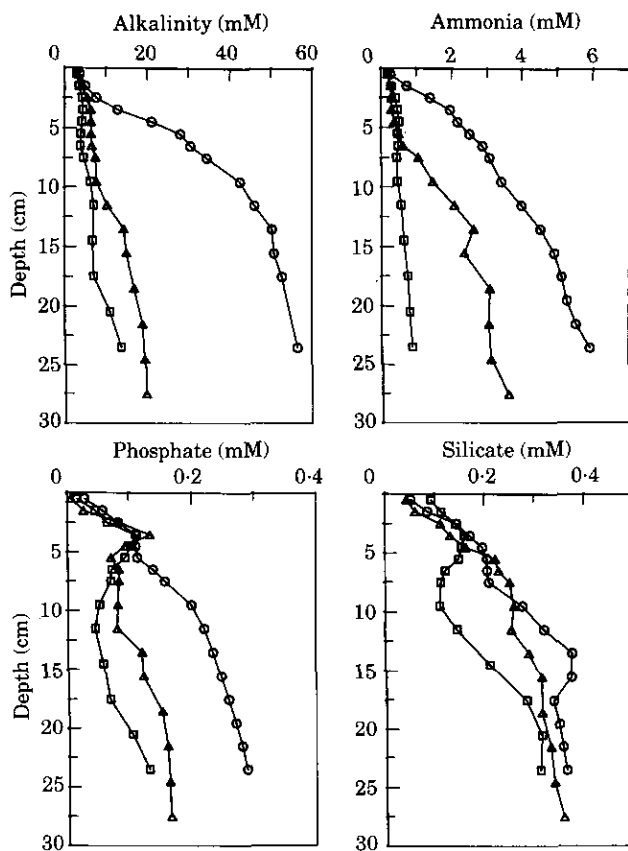


Figure 5. Vertical profiles of alkalinity, ammonia, phosphate and silicate at station PR before and after dredging. ○—○, January 1989; △—△, April 1989; □—□, August 1989.

dredging (April and August 1989). The mean values of the examined cores (over a depth *c.* 25 cm) show how the concentration of all species analysed is lower 2 months following dredging, which took place in February 1989.

Taking into account that dredging places together overlying water with the new superficial sediment much higher in nutrients and alkalinity by as much as one order of magnitude, it is obvious that an important transfer of species occurred from the sediments towards the water column. This is due to an intensification in diffusive processes, as a consequence of a higher gradient of concentration generated on both sides of the water–sediment interface.

After dredging a concentration decrease of all species in the interstitial water of the sediment was registered. This is due to the fact that the new superficial sediment was previously 2 m deep. In this way, the diffusive fluxes cannot be compensated by nutrient production from the sediment, due to the nutrient regeneration rate exponential decrease with depth (Klump & Martens, 1989).

The continued lowering of nutrient concentration and alkalinity in the sediment 6 months after dredging [August 1989, Figure 4(a)] indicates that benthic fluxes are

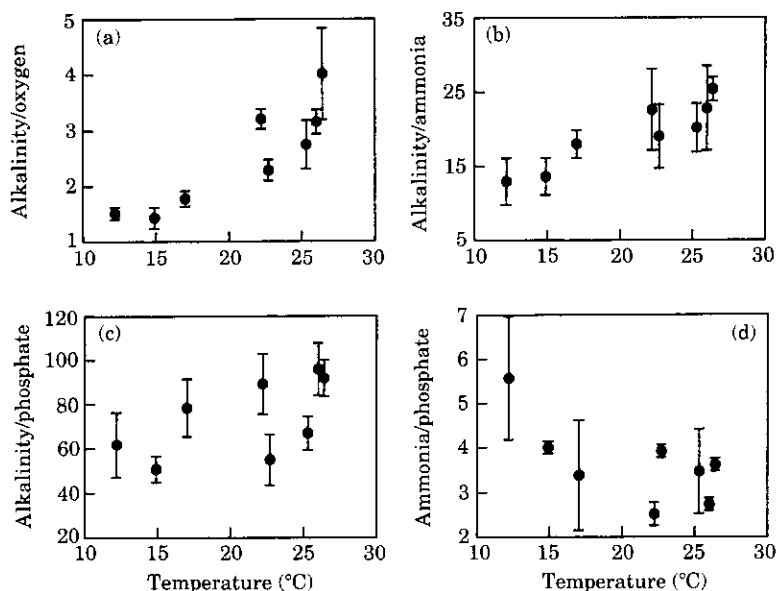


Figure 6. Variation of (a) alkalinity/oxygen (b) alkalinity/ammonia (c) alkalinity/phosphate and (d) ammonia/phosphate flux ratios with temperature. (Bars indicate standard deviations.)

maintained due to the stock of nutrients contained in the sediment, and that a return to the original conditions prior to dredging requires a lot of time.

The marked increase of *in situ* alkalinity fluxes during the months subsequent to dredging [Figure 4(c)] does not correspond to the profiles found in the interstitial water. This increase could be caused by an apparent contribution to alkalinity fluxes of  $\text{CaCO}_3$  from the more superficial sediments where its concentration is very high after dredging. In this regard it should be noted that the rate of  $\text{CaCO}_3$  precipitation in the interstitial water varies exponentially with depth (Boudreau & Canfield, 1988). On the other hand, Lerman (1978) has estimated that almost 60% of  $\text{CaCO}_3$  passing to the ocean comes from dissolution at the water-sediment interface.

#### *Flux stoichiometry*

The temperature dependence of stoichiometric flux ratios is shown in Figure 6. The ratio between alkalinity and oxygen fluxes ranges from 1.4 to 4.0, and increases exponentially with temperature [ $r^2=0.92$ , Figure 6(a)], suggesting that in winter organic matter decomposition is basically aerobic. Since oxygen penetration into clay sediments is to only a very few mm (Revsbech *et al.*, 1983; Plante *et al.*, 1989; Witt *et al.*, 1989), decomposition will take place mainly at the surface.

In contrast, high alkalinity/oxygen flux ratios in summer suggest an important contribution of anaerobic pathways to organic matter oxidation during this season. This is also suggested by a marked seasonal change in sulphate reduction in coastal ecosystems (Jorgensen & Sorensen, 1985; Klump & Martens, 1987; King, 1988). The ratio between alkalinity and ammonia fluxes also shows an exponential increase with temperature [ $r^2=0.79$ , Figure 6(b)]. Since no significant exchange occurs amongst other inorganic nitrogen species, ammonia may be equated with inorganic nitrogen fluxes.

This ratio ranged from 12.9 in winter to 22.7 in summer, and in all instances was higher than the C/N ratio of Redfield. Variations of the alkalinity/ammonia flux ratio may not be attributable to seasonal variation in the amount or composition of organic matter in the sediment, since vertical profiles of organic carbon and the C/N ratio remain relatively constant all the year around. Instead, as temperature rises the higher metabolic activity of microorganisms speeds up organic matter decomposition. There also exists an increase of the alkalinity/phosphate flux ratio with temperature, although observed values are more dispersed in this case [ $r^2=0.56$ , Figure 6(c)], ranging from 50.8 to 95.8 which is markedly lower than Redfield ratios. Similar results have been reported by other authors (e.g. Berner, 1977), and this has been generally related to a more rapid release of phosphorus from organic matter during the initial steps of its degradation (Smetacek & Pollehne, 1986). This fact can be more clearly appreciated by looking at the variations of the ammonia/phosphate flux ratio with temperature [ $r^2=0.65$ , Figure 6(d)]. The ratio varies between 5.6 and 2.5, similar to values obtained by Elderfield *et al.* (1981). In this case, values are higher in winter and the ratio decreases with temperature as decomposition affects the less labile organic matter.

### Conclusions

We have found high benthic fluxes throughout the Bay of Cadiz. There are several reasons for it: (i) the large input of allochthonous organic matter entering the Bay, (ii) the shallowness and clayish nature of the bottom, and (iii) the climatic conditions, especially the high annual mean temperature.

Benthic fluxes of nutrients depend largely on the temperature, showing an apparent activation energy close to values pointed out in other coastal ecosystems. On the other hand, the oxygen/alkalinity flux ratios provide a good indicator for estimating the contribution of both aerobic and anaerobic pathways to the degradation of organic matter, at least from a qualitative viewpoint.

Besides other effects derived from the resuspension of sediments, dredging of coastal sites generates a sharp gradient of alkalinity and nutrients through the sediment-water interface. This produces a remarkable intensification of diffusive processes in the sediment. The information attained in this work suggest that the large-scale releasing of nutrients is produced in a very fast way.

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