The influence of urban wastes on the interstitial water chemistry in coastal marine sediments of Cadiz Bay

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ABSTRACT

The authors determined, with visual profiles, the concentration of nutrients (i.e. ammonia, nitrate, phosphate and silica), inorganic carbon and sulphate in the interstitial water of Cadiz Bay, as well as organic carbon in sediment, using samples from three stations on Sancti Petri sound. These three stations suffer from different contamination levels due to untreated urban wastewater.

Our results show a degradation of the organic matter, principally in the first 30 cm of sediment. These concentration changes are important in the superficial water layer, indicating the efficiency of aerobic oxidation, the organic matter's principal mineralisation mechanism. Two stations, those nearest to the waste point, had the highest organic carbon concentrations in their sediment, as well as the highest vertical gradients of nutrient concentrations in their interstitial water. Sulphate reduction is the principal mechanism involved in the oxidation of organic matter. On the other hand, at the other station studied, with lower organic carbon levels, the gradients were smoother.

Key words: Coastal ecosystem, benthic regeneration, diffusive fluxes, organic matter, nutrients, inorganic carbon.

RESUMEN

Influencia de los vertidos urbanos sobre la química del agua intersticial de sedimentos marinos costeros en la bahía de Cádiz

Se han caracterizado los perfiles verticales en el agua intersticial de las concentraciones de nutrientes (amonio, nitrato, fosfato y silicato), carbono inorgánico y sulfato, así como de carbono orgánico en el sedimento en tres estaciones del caño de Sancti Petri, sujetas a distinto grado de contaminación por vertidos urbanos sin depurar.

Analizando globalmente las variaciones con la profundidad de las concentraciones de las distintas especies estudiadas, se puede afirmar que existe una degradación continuada de la materia orgánica, al menos, en los primeros 30 cm del sedimento. Esta hipótesis se encuentra reforzada por la propia disminución de la concentración de carbono orgánico en el sedimento con la profundidad. Estos cambios de concentración son especialmente acusados en la lámina de agua más superficial, poniendo de manifiesto la eficiencia de la oxidación aeróbica como mecanismo de mineralización de la materia orgánica.

Las dos estaciones más próximas al vertido, que poseen concentraciones de carbono orgánico más elevadas en el sedimento, presentan también mayores gradientes verticales de concentración de nutrientes en el agua intersticial, y la sulfatorreducción adquiere una mayor importancia relativa como vía de oxidación de la materia orgánica. Por el contrario, en la estación situada en el extremo sur del caño, menos afectada por los aportes de materia orgánica, se observan gradientes más suaves.

Palabras clave: Ecosistema costero, regeneración béntica, flujos difusivos, materia orgánica, nutrientes, carbón inorgánico.

INTRODUCTION

The regeneration benthic nutrients is a result of several physical, chemical and biological processes which lead to organic matter's mineralisation and then to the diffusion of several chemical species into the water column. These processes are controlled by the availability of labile organic matter of terrestrial, littoral, pelagic and occasionally autochthonous origin present on the sediment surface, resulting in different degradation levels (Hartwing, 1978).

Benthic regeneration in the littoral ecosystems is the main factor controlling the nutrient cycle, and is associated with high values of primary production detected in those zones (Berner, 1977; Hopkinson and Wetzel, 1982; Flint and Kamikowski, 1984; Balzer, Von Bodungen and Pollehen, 1985; Flint, 1985; Herndl, Peduzzi and Fanuko, 1989). Berner (1978) considers that the benthic-pelagic interactions in coastal zones occur on a shorter time scale compared with oceanic areas, due to higher and more complex inputs of organic matter to sediments, as well as highly fluctuating physical conditions.

Benthic systems show high levels of metabolism and efficiency near the sediment surface, so that only a low proportion of this organic matter is degraded at deeper levels (Balzer, Von Bodungen and Pollehen, 1985). In general, the contents of organic carbon, nitrogen and phosphorous decrease exponentially with depth, being higher in the surface area (Balzer, 1984). The result of benthic regeneration is an increase of C:N and C:P ratios of organic matter, because in the first phase of their decomposition N and P are mobilised preferentially (Aller and Yingst, 1980). Therefore, these ratios can be used as an index of the intensity of diagenetic processes.

The relative intensity of regeneration processes in littoral ecosystems is closely related to sediment porosity, as well to the availability and to the characteristic of the organic matter. The relationship between grain size and organic matter adsorption is inverse (Dale, 1974). The matter fluxes across the water-sediment interface can be assisted by different mechanisms, e.g. macrofauna irrigation (Aller, 1980), water dynamics (Hammond, Simpson and Mathieu, 1977) and tides (Pollehne, 1986; Whiting and Childers, 1989) near the bottom.

The present study's objectives were:

a) characterise the effects associated with anthropogenic inputs of organic matter on diagenetic processes in Sancti Petri sound
b) establish the relationship between the benthic nutrient levels and carbon fluxes with organic carbon concentration in sediment

MATERIALS AND METHODS

The study was carried out in a salt-marsh area to the south of Cadiz Bay (southwest Spain). The samples were taken from stations along an 18-km channel, Sancti Petri sound (figure 1). Tidal flows from the Atlantic Ocean and from within the bay enter by both entrances of the channel and meet close to the position of station B. Untreated urban effluents from the city of San Fernando (population 100 000) are dumped into the channel. The three sampling stations were selected in order to characterise the impact of this urban wastewater on different sedimentary environments (Gómez-Parra, Establier and Escolar, 1984; González-Mazo *et al.*, 1997; Del Valls *et al.*, 1997, Del Valls, Forja and Gómez-Parra, 1998).

Station A is located at the south of the sound, 3 km from the Atlantic Ocean entrance. It is characterised by having mainly sandy sediment, and is not significantly affected by anthropogenic activity. Station B is in the centre of the sound, 14 km from the southern end, close to the discharge point of raw sewage from the city of San Fernando (pop. 100 000). Sediments at this site are fundamentally clayey and have a high organic matter content. Station C is located 18 km from the sound's southern entrance, near inner Cadiz Bay. The mainly clayey sediments in this area are affected by strong tidal currents and sewage discharges from San Fernando.

At each station, 10 sediment cores were collected using a gravity corer of Ø45 mm. They were sliced at 1-cm intervals and the sections thus obtained were centrifuged at 39 200 g for 30 min. This procedure allows the recovery of 79 % to 85 % of water contained in the sediment. Handling of sediment cores and subsequent analysis of interstitial waters were performed in an inert atmosphere. Sediment porosity was calculated by determining the weight loss after evaporation during 48 h at 85 °C.

Figure 1. Map of Cadiz Bay and location of sampling stations along Sancti Petri sound. The wastewater discharge point of San Fernando is indicated by the white arrows
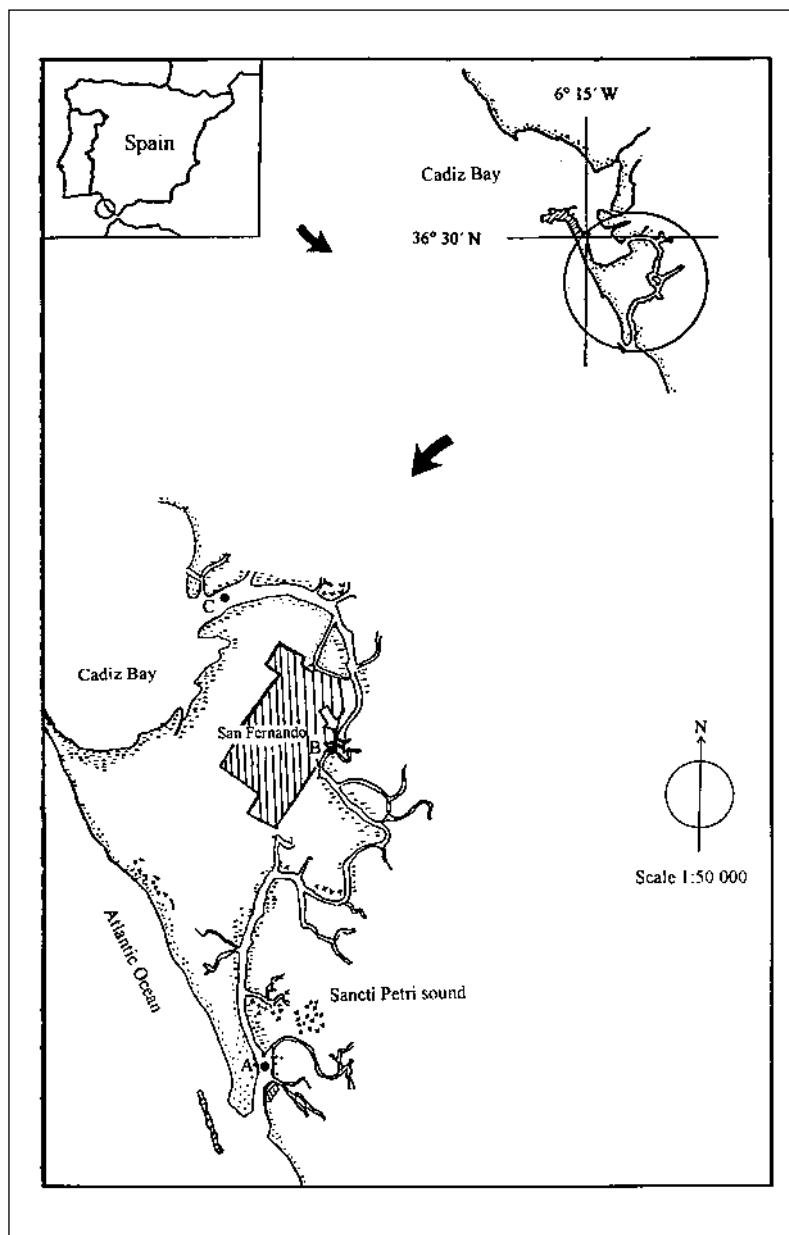
Organic carbon content was determined in sediment samples according to the method of El Rayis (1985), and elemental analysis was carried out with a Carlo Erba CHN analyser (Model 1106).

Nutrient analyses (ammonia, phosphate, nitrate and silicate) in interstitial water were carried out in a Traccs800 Bran-Luebbe autoanalyser. Sulphate concentration was gravimetrically measured in 2-ml aliquots, using a version of modified Forja's method (1991).

Inorganic carbon concentration was determined by potentiometric titration (Methrom 670 Titroprocessor). Total alkalinity and inorganic carbon

speciation were determined by applying Gran functions, which consider the existence of the main acid-base equilibriums found in interstitial water (Ortega, 1996).

RESULTS AND DISCUSSION

The vertical profiles of ammonia and inorganic carbon concentrations in interstitial water are shown for each sampling station in figure 2. The gradients are smoother at the sediment surface, probably because of homogenisation and nutrient
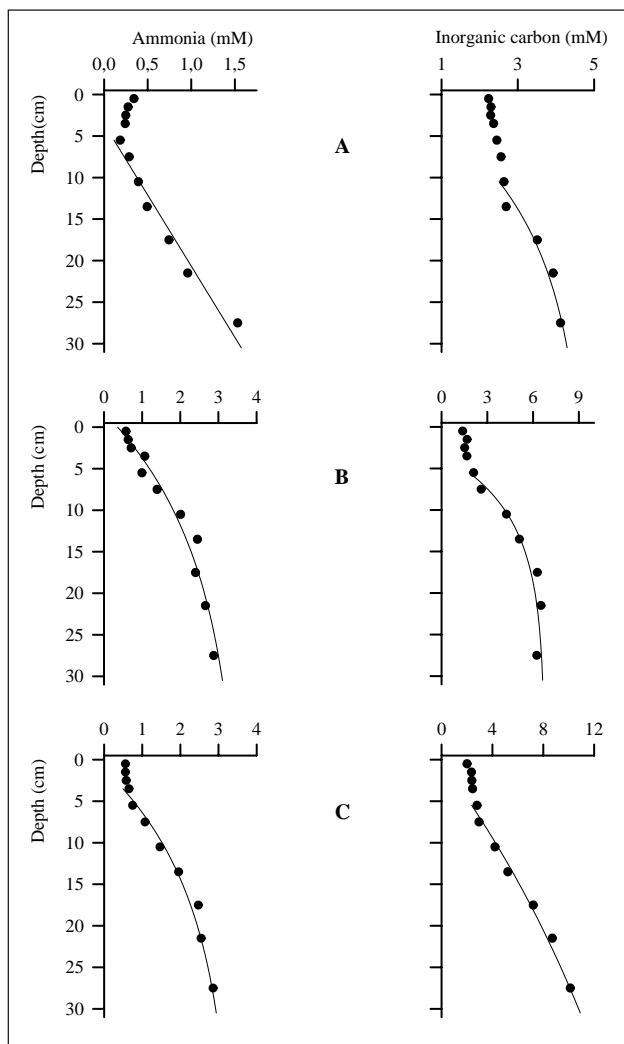
Figure 2. Profiles of ammonia and inorganic carbon in the porewater from the three sampling stations

irrigation due to bioturbation by benthic macrofauna (Aller, 1980; Forja, 1991).

Station A had a high density of benthic macrofauna, which produced a bioturbation area to the depth of approximately 6 cm. At stations B and C, bioturbation was narrower (4 cm) than at station A.

Below this superficial irrigation area, an increase of nutrients and inorganic carbon concentrations appeared with depth, being clearer at stations B and C. The best linear correlation functions are shown in figure 2, in which the main transport mechanism is molecular diffusion.

The importance of the irrigation due to macrofauna is related to the increase in the molecular diffusive processes between interstitial water and overlaying water, and the consequent increase in oxygenation of the superficial sediment layer.

Hence, the irrigation also affects the oxic layer depth in sediments. The position of the maximum nitrate concentration can be used to estimate the size of this layer, because it is a consequence of the coupling of nitrate reduction and nitrification, as well as to estimate the depth at which the decrease in the sulphate concentration begins, due to sulphate reduction process (figure 3). The oxic layer depth determined by the nitrate and sulphate vertical profiles at station C is similar to the one estimated for the three stations using the ammonia and inorganic carbon vertical profiles.
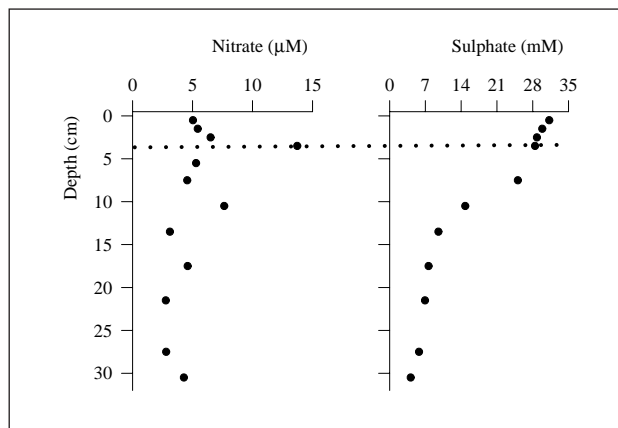

Figure 3. Profiles of nitrate and sulphate at station C. Discontinuous lines indicate the lower limit of the oxic layer

As to organic carbon levels in the sediment, figure 4 shows a decreasing trend with depth for the three stations, stronger at stations B and C, and weaker at station A. This is related to the high organic matter inputs in these areas, which are not matched by the bacterial degradation. Although the high efficiency of the aerobic oxidation in the superficial layers, the high organic matter levels measured at the two stations produce a degradation of this matter at higher depths due to less mechanism such as those anaerobics (sulphate reduction). As may be inferred from table I, these C/N ratios show an aloctone origin for the organic matter. This ratio increases with depth, and is related to the relative weakness of the C-N links. Because station A is far from the discharge point, its organic matter is more degraded than at B and C, so its C:N ratio is higher, too.

To calculate the diffusive fluxes across the water-sediment interface, we used the vertical gradients
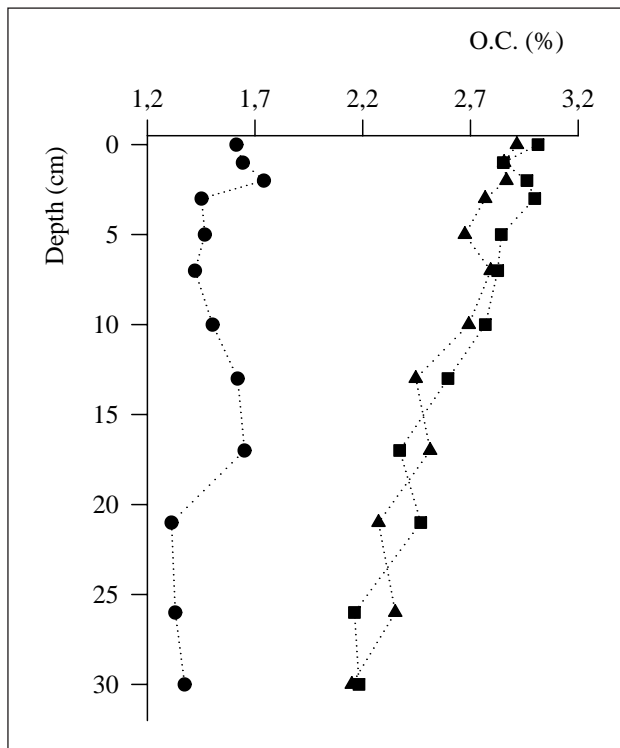
Figure 4. Variation of organic carbon content (%) in sediment at the three sampling stations. (•): Station A; (■): Station B; (▲): Station C

Table I. C/N ratio values for superficial sediment at different depths

Depth (cm)	Station A	Station B	Station C
0.5	66.68	24.57	22.95
1.5	70.53	39.16	24.15
2.5	186.22	44.47	25.18
3.5	156.11	52.51	27.19
5.5	159.44	103.96	39.53
7.5	99.72	141.69	32.65

measured in the interstitial water and the first law of Fick.

We adjusted the porosity variations with the depth to an exponential expression such as (Morse, 1974; Lerman, 1976; Murray, Grundmains and Smethie, 1978):

$$J = \pm \phi \, D_s \left[\frac{\partial C}{\partial z} \right]_{z=0} \qquad [1]$$

$$\phi = \phi_z + (\phi_0 - \phi z)\, e^{-az} \qquad [2]$$

in which ϕ_z is the porosity asintote and ϕ_0 its value at z = 0.

The diffusion coefficient DS in the superficial layers has been calculated using that expression re-

ported by Sweerts, Baer-Gilissen and Cornelese (1991):

$$D_S = D^0 \, (-0.73\phi + 2.17)^{-1} \qquad [3]$$

The value of the diffusion coefficient at infinite dilution (D^0) used for each species is detailed in table II. The inorganic carbon was considered be equal to bicarbonate, which is the predominant species in interstitial water.

Table II. Values of trace-diffusion coefficient in water for those species analysed

Species	$D^0 \cdot 10^{-6}$ (cm² s⁻¹)	References
NH_4^+	$(0.4T + 9.8)$	Li and Gregory, 1974
HPO_4^{2-}	7.0 ± 0.5 (20 °C)	Krom and Berner, 1980
SiO_2	10.0 ± 0.5 (25 °C)	Wollast and Garrels, 1971
SO_4^{2-}	$(0.228T + 5.00)$	Li and Gregory, 1974
I.C.	$(0.257T + 5.39)$	Li and Gregory, 1974

Figure 5 shows the relationship between the diffusive fluxes of nutrients and inorganic carbon and the contents of organic matter in the topmost portion of sediment at the three stations. The highest fluxes were measured at stations B and C, which are highly influenced by the sewage discharge source. The same applies to the ammonia and inorganic carbon fluxes. The highest inorganic carbon flux is due to the fact that carbon is the main element freed during organic matter's remineralisation. The highest ammonia fluxes are due to the high diffusion coefficient for this specie.

Sulphate reduction is relatively important for each area, as shown in figure 6. At station B, both the highest sulphate flux and the thinnest oxic layer were found. This indicates that the anaerobic mechanism is the principal one involved in organic matter regeneration. The sulphate flux decreases at stations C and A as much as organic matter does at the sediment surface, increasing the oxic layer size. In these cases, the regeneration of anaerobic organic matter has a lower contribution than at station B.
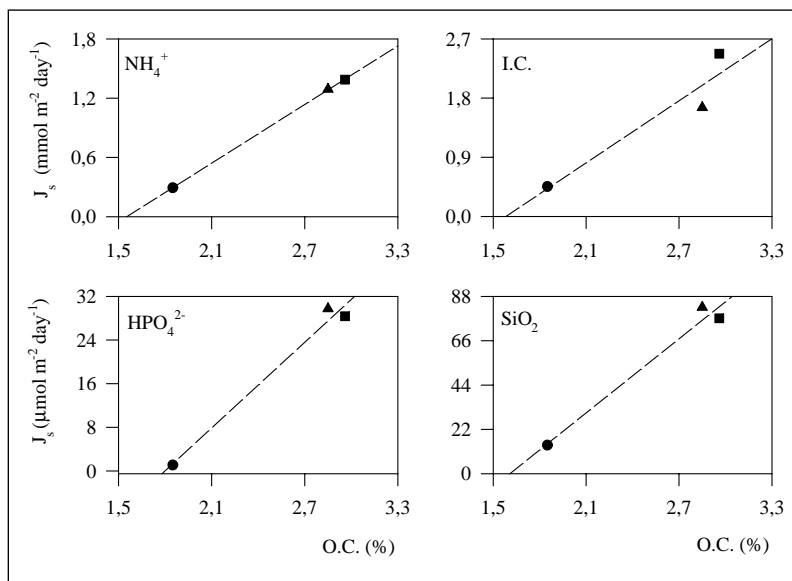
ACKNOWLEDGEMENTS

Figure 5. Relationship between ammonia, inorganic carbon, phosphate and silicate diffusive fluxes with organic carbon content in sediment (%) at the three sampling stations. (•): Station A; (■): Station B; (▲): Station C
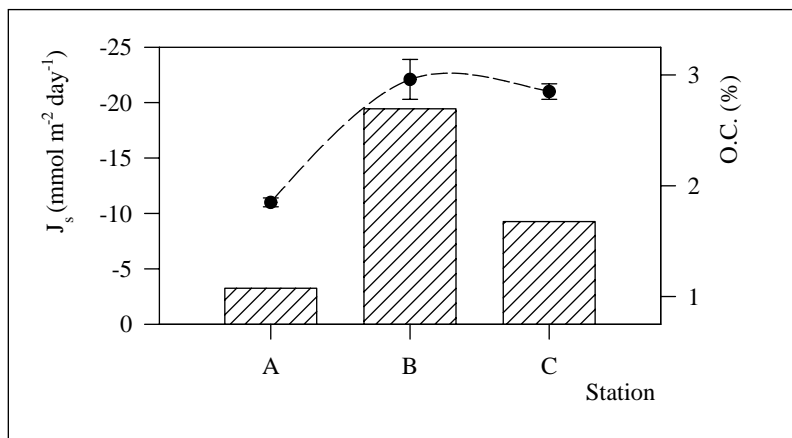

Figure 6. Sulphate diffusive fluxes (dotted line) and organic carbon (vertical bars) in sediments at the three sampling stations

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