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Coastal sediments under the influence of multiple organic enrichment sources: An evaluation using carbon and nitrogen stable isotopes

Leandro Sampaio [a], Rosa Freitas [a], Cristina Máguas [b], Ana Rodrigues [a], Victor Quintino [a,*]

[a] CESAM (Centro de Estudos do Ambiente e Mar), Departamento de Biologia, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
[b] CBA (Centro de Biologia Ambiental), Faculdade de Ciências da Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

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ABSTRACT

Sediment descriptors (grain size, total volatile solids, redox potential) and stable carbon and nitrogen isotopes were used to trace the origin of organic matter in a coastal area under multiple organic enrichment sources (urban outfall and a major estuary). The sediments fines content and total volatile solids were similar to outfall pre-operation period (1994), but the incorporation of terrestrial organic matter within the sediments located closer to the outfall was diagnosed by depleted ^{13}C values (−24.2 ± 0.38‰) and ^{15}N values (2.4 ± 0.93‰). Data also indicated depleted nitrogen signature at larger distances from the outfall than the carbon signature, due to confounding sediment grain size properties. Analysis in the bivalve *Abra alba* gave the same results for both isotopes and thus allowed a coherent interpretation of the spatial extent of the organic enrichment, highlighting the importance of bringing a biological element into the environmental assessment.

1. Introduction

Organic enrichment and contaminant inputs from urban and industrial sewage effluent discharges, aquaculture waste, storm water and agriculture runoff, have become common stressors to the marine environment, and in particular to the sedimentary habitat and biotopes (Pearson and Rosenberg, 1978; Sweeney et al., 1980; McClelland and Valiela, 1998; Kauppila et al., 2005; Tewfik et al., 2005; Vizzini and Mazzola, 2006).

The extent and dispersal of anthropogenic inputs depend namely on the quantity and type of waste, local hydrography, hydrodynamic regime and other environmental features of the disposal area (Sarà et al., 2006; Vizzini and Mazzola, 2006). Organic matter concentrations in sediments, in particular, may depend on the deposition rate, the nature of organic sources and their flux rates, their preservation potential during transport and burial, mineralization and degradation (Owen and Lee, 2004; Ogrinc et al., 2005; Gao et al., 2008). The sedimentary organic matter is a heterogeneous and complex mixture of organic compounds with different chemical characteristics, originating from different sources (Tesi et al., 2007). Stable isotopes techniques can help to identify the origin of organic matter by discriminating between terrestrial and marine sources (Deegan and Garritt, 1997; Vizzini and Mazzola, 2003; Ogrinc et al., 2005; Vizzini et al., 2005; Usui et al., 2006; Tesi et al., 2007; Gao et al., 2008). The stable isotope approach considers the existence of differences among natural abundances of carbon and nitrogen stable isotopes and C/N elemental ratios in organic matter from terrigenous and marine origin (Liu et al., 2006). This approach relies on the assumption that isotopic and C/N ratios from sedimentary organic matter are conservative and that their natural distribution reflects the mixing of material from distinct end-member sources (Machás et al., 2003; Liu et al., 2006). In general, terrestrial organic matter has depleted $\delta^{13}C$ and $\delta^{15}N$ values when compared to marine organic matter (Vizzini et al., 2005). As such, a typical sewage effluent may present $\delta^{13}C$ values in the range of −22.4‰ to −26.5‰ and $\delta^{15}N$ values between +1.8‰ and +3.8‰ (Sweeney et al., 1980; Spies et al., 1989; Gearing et al., 1991; Van Dover et al., 1992; Rogers, 1999; Conlan et al., 2006) whereas marine organic matter presents $\delta^{13}C$ values in the range of −18‰ to −24‰ and $\delta^{15}N$ values between +4‰ and +9‰ (Fry and Sherr, 1984; Tucker et al., 1999).

The different isotopic composition of organic matter in sewage waste, relative to the marine autochthonous organic matter, may help to trace the extension of sewage waste in coastal areas. In fact, stable isotopes studies have supplied evidence of sewage particulates accumulation in sediments and subsequent incorporation in marine food webs (Van Dover et al., 1992). Consequently, this method has been successfully used to indicate sediment recovery to background values after cessation of sewage discharges (Tucker et al., 1999). Nevertheless, some studies have reported no signs of sewage impact on the sediments while detected on the biota (Waldron et al., 2001). Also, when looking for carbon and nitrogen signatures to trace the origin of organic sources to the coastal

* Corresponding author. Tel.: +351 234370769; fax: +351 234372587.
E-mail address: victor.quintino@ua.pt (V. Quintino).

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sedimentary environment, few studies include data on baseline variables, such as grain size or total volatile solids, nor discuss their potential confounding role. Gao et al. (2008) namely found a linear correlation in uncontaminated estuarine and coastal sediments between carbon and nitrogen stable isotopes and mean sediment grain size and considered this factor to be of influence to the isotopic distributions.

In this study, carbon and nitrogen stable isotopes were used to trace organic sources to sediments in a coastal shelf area off Lisbon subject to organic matter inputs from an urban wastewater marine outfall serving a population around 800,000, the largest in Portugal, from the Tagus River, the largest in the Iberian Peninsula, and from autochthon primary production (Silva et al., 2004). At the moment of conducting this study, the effluent from the wastewater marine outfall only received a preliminary treatment mainly consisting in the screening and removal of grit and non-degradable materials. Before released into the coastal area, the effluent passes through a series of sand retention and sieving systems, the last of which corresponds to a rotating drum equipped with a 5 mm sieve. This situation will soon be altered as an enhanced primary treatment coupled to a disinfection system is about to enter into operation. Previous studies have shown no organic matter accumulation near the outfall discharge area or a relevant alteration of sediment properties and contaminants concentrations, with the exception of a proximate redox potential decrease when compared to the reference situation (Quintino et al., 2001), denoting the dispersive rather than accumulative characteristics of this coastal area. Also, although the outfall diffusers are located in an area of fine sand with less than 5% fines content, with increasing depth or towards the Tagus Estuary this sediment gradually shifts to very fine sand with larger fines content and to mud with fines up to 80% of the total sediment (Freitas et al., 2006). The potentially confounding role of such heterogeneous seabed seascape in the patterns of the stable isotopes is addressed in this study.

2. Methodology

2.1. Study area and sampling

The study area is located in the coastal shelf off Lisbon at water depth ranging from 30 to 90 m. A marine sewage outfall is placed about 15 km west of the mouth of the Tagus estuary and the effluents are discharged in the final 400 m of a double branch system, approximately between 2350 and 2750 m offshore at an average depth of 40 m. A baseline characterization of the sediments in the study area prior to the operation of the outfall was undertaken in 1994 and is reported namely in Quintino et al. (2001) and Silva et al. (2004). All 20 sampling sites described in those studies were revisited in this study, which also includes samples taken in extra 10 sites (21–30), 1 replicate per site, positioned according to Fig. 1. The sediment baseline characterization included grain size, total volatile solids and on board measurement of redox potential. These samples were used to describe the overall seabed seascape in the study area and to assist the decision of where to take replicate samples for the subsequent sediment analysis including the isotopic composition. An additional 60 sediment samples were then taken, in 15 sites arranged in 5 areas placed at increasing distance from the outfall, 3 sites per area and 4 replicates per site (cf. Fig. 1). Sediment grain size, total volatile solids, redox potential and carbon and nitrogen isotopes were determined in these 60 samples. For the isotopic analysis and the total volatile solids determination, sediment samples were collected from the upper 5 cm layer and stored in Whirl-Pak bags and frozen on board at −20 °C. The remaining sediment was washed on board over a 2 mm-mesh sieve in order to collect a representative species of the resident macrofauna community, also for the analysis of carbon and nitrogen isotopes. All sediment samples were collected using a 0.1 m^2 Smith-McIntyre grab. The macrofauna sample was stored in Whirl-Pak bags and immediately frozen at −20 °C. The

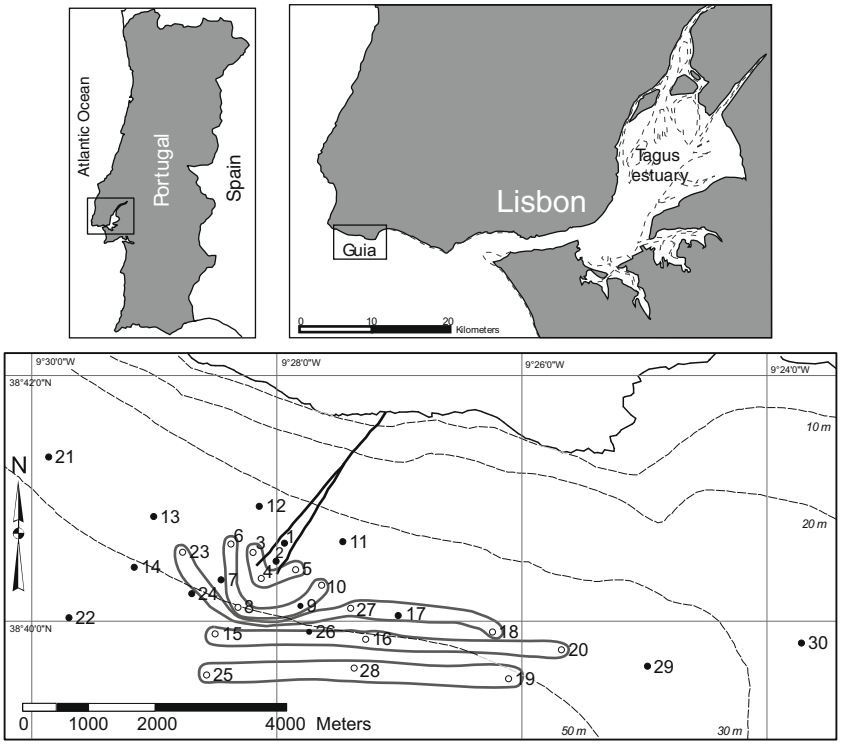

Fig. 1. Study area showing the positioning of the double branch marine outfall and the 30 sampling sites, indicating the 5 areas (A1 to A5) and the 15 sites (white circles), at which 4 replicate samples were taken for the study of the sediment isotopic composition. A1 = sites 3, 4 and 5; A2 = sites 6, 8 and 10; A3 = sites 18, 23 and 27; A4 = sites 15, 16 and 20; A5 = sites 19, 25 and 28.