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Origin of sedimentary organic matter in the north-western Adriatic Sea

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ABSTRACT

In order to evaluate the origin and the transformation of organic matter on the shallow shelf of the NW Adriatic Sea, organic carbon, total nitrogen and stable isotope ratios of organic carbon were analysed in riverine suspended matter and sediments as well as in marine suspended and sedimentary organic matter, in marine phytoplankton and zooplankton.

The deposition of organic matter is influenced by fine sediment concentration. Surface sediments were characterised by highly variable biogeochemical conditions on the sea floor, whereas sub-surface sediments showed a more homogeneous hypoxic/anoxic environment.

Low C_{org}/N ratio and high organic carbon and nitrogen concentrations in riverine suspended organic matter indicate an important contribution of freshwater phytoplankton within rivers, particularly during low flow regimes, which adds to the marine phyto- and zooplankton at shelf locations.

In order to evaluate the importance of terrestrial, riverine and marine sources of OM in shelf sediments, a three end-member mixing model was applied to shelf surface sediments using $^{13}C/^{12}C$ values for organic matter and N/C ratios. The model showed an elevated contribution of terrestrial organic substances at intermediate depths (10–15 m), mostly corresponding to an area of coarser grain-size, whereas the riverine and marine organic fractions were mainly accumulating near the coast and offshore, respectively.

1. Introduction

Estuarine areas are an important sink for organic carbon as it is thought that around 44% of organic carbon is buried in deltaic sediments (Hedges and Keil, 1995). The shallow north-western Adriatic Sea receives significant freshwater inputs which enhance the productivity of its waters (Revelante and Gilmartin, 1976). In the northern Adriatic Sea, the Po River is the main freshwater source and accounts for approximately 50% of the total riverine input (Degobbis et al., 1986) affecting the general hydrodynamics of the basin through the introduction of low salinity water at its western boundary (Artegiani et al., 1997). The other Italian rivers, even if less important, exert an important local influence, especially close to their mouths and in nearby coastal areas. The Po is considered to be the main contributor of organic carbon (C_{org}) to the Mediterranean basin with its discharge of 25×10^4 t C_{org} yr^{-1} (Pettine et al., 1998). In addition, the organic matter (OM) and nutrients load discharged by the Po River significantly influence the productivity and trophic dynamics of the northern Adriatic Sea (Pettine et al., 1998). Land plants, soil-derived carbon and freshwater plankton are the main contributors to the OM transported by rivers (e.g.: Mook and Tan, 1991; Kendall et al., 2001). Besides their aquatic *in situ* produced C_{org} and the land-derived OM, rivers also vehiculate to the sea the organic load of anthropogenic origin (e.g.: sewage and farm wastewaters). Within the shallow North Adriatic shelf, the autochthonous OM is mainly produced by phytoplankton (e.g.: Pugnetti et al., 2005), phytobenthos (Epping and Helder, 1997; Kemp et al., 1999; Cibic et al., 2008) and macrophytes (Sfriso et al., 1987; Kemp et al., 1999).

The different sources of organic matter can play a relevant role in determining its cycling in the Northern Adriatic basin where they can contribute to hypoxic and anoxic events affecting bottom waters during the summer (Montanari et al., 1984; Justič et al., 1987) and to the formation of mucilaginous aggregates (Precali et al., 2005). Moreover, changes in the riverine discharges (Alvisi et al., 2006), nutrient concentrations (Degobbis et al., 2000; Tedesco et al., 2007) and carbon cycles (Pugnetti et al., 2008) have been recently observed in the North Adriatic.

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Carbon stable isotope ratios ($\delta^{13}C$) method is widely used to determine origin (aquatic vs. terrestrial or autochthonous vs. allochthonous) and fate of OM in water column and sediments (e.g.: Fry and Sherr, 1984). Modelling changes in particulate organic matter (POM) $\delta^{13}C$ composition with simple two end-member mixing models, where the end-members were respectively $\delta^{13}C$ values of typical terrestrial and marine organic matter (Salomons and Mook, 1981) has proven to be reasonably successful when applied to large rivers. The combined use of $\delta^{13}C$ and C_{org}/N ratios can improve POM provenance discrimination (Matson and Brinson, 1990; Thornton and McManus, 1994).

The relative abundance of terrestrial and riverine C_{org} sources in the Northern Adriatic has been estimated by a three sources model based on $\delta^{13}C$ and N/C ratios of OM (Boldrin et al., 2005; Miserocchi et al., 2007). Recently it has been shown that the sedimentary OM deposited in front of the Po River is the result of a mixture of highly aged and modern organic carbon (Tesi et al., 2008) and a four end-member mixing model was applied to discriminate the land vegetation and the soil OMs from the riverine-estuarine and marine sources (Tesi et al., 2007).

The purpose of this study is to investigate the origin of the OM in recent sedimentary OM of a North Adriatic coastal area influenced by riverine waters.

2. Regional setting

Fluvial inflows to the Adriatic have shaped the sea floor morphology over a geological timescale. The present sedimentation pattern matches, quite precisely, the hydrodynamic circulation (Tomadin, 2000; Ravaioli et al., 2003). It consists of a narrow strip of recent coastal sands along the coast (5–10 m deep), a broad belt of muddy sediments (10–20 m deep) and a wide-open sandy shelf area (<25 m deep) with little or no recent sedimentation ("relict sands").

Freshwater and sedimentary inputs to the sea are mostly constrained along the western coast of the basin. The water flow generally follows the Italian coast during winter, whereas in summertime the plume may extend eastwards until the Croatian coast also thanks to the seasonal stratification of the water column and weakening of the Western Adriatic Coastal Current (Franco and Michelato, 1992; Wang and Pinardi, 2002). In addition to this, the northern Adriatic shelf is a relatively low-energy environment with small tidal range and wave heights where much of the sediment delivered during flood events remain in its initial location (Palinkas and Nittrouer, 2007).

The character of the fluvial input in the coastal area could be very different during high and low flow regimes. In low condition, the POM transported by river is mostly characterised by fresh organic material produced within the river and to a lesser extent of detritus coming from the drainage basin. On the contrary, as the flow regime increases, the POM become more and more enriched in detritus fraction of terrestrial origin both organic and inorganic derived mostly by soil erosion and resuspension of bottom river sediments (Boldrin et al., 2005).

The sea floor of the investigated area is characterised by a double influence due to: the Po River with a N–S gradient, since the main river mouths are located in the northern part of it (Fig. 1) and the Emilia Romagna rivers with a W–E gradient. In the study area, fine sediment accumulation takes place in shallow coastal waters (Fig. 1) with increase in south or south-west of Po River delta and north of Reno River mouth. This is the result of the interaction between the river inputs, the North Adriatic Coastal Current and the local hydrodynamics influenced by the coastline morphology (Dal Cin, 1983; Artegiani et al., 1997), where the Po delta protrusion determines a shadow effect S–SW of it leading to high accumulation of fine material even at shallow depth.

The Po River has a drainage basin of 71×10^3 km^2, 44% of which is devoted to agricultural activities. During the last decades the river has been canalised for more than a half of its 650 km length by the construction of artificial levees (Marchetti, 2002) to prevent the overflow of the alluvial plain. The southern distributaries (Po delle Tolle, Po di Gnocca and Po di Goro) of the Po River delta (Fig. 1) transport about 35% of the total water flux (Syvitski and Kettner, 2007).

During the last 20 years, the Po River had a mean daily outflow of 1465 m^3 s^{-1} and was characterised by a biannual seasonal flooding mainly due to snowmelt in May and rainfall in October–November (Tedesco et al., 2007). The most relevant flooding usually occurs in autumn (Degobbis et al., 2000) with discharges higher than 6000 m^3 s^{-1}.

Deposition of muddy sediments transported by the Po River is greatest close to the river mouth in water depth < 10 m (Fox et al., 2004), with a sediment accumulation rate of ~1–2 cm yr^{-1} in the prodelta area decreasing rapidly southwards to a few mm yr^{-1} (Frignani et al., 2005). Occasional flooding can determine maximal deposition rates up to 6 cm yr^{-1}, at depth proximal to 10 m, near the Po della Pila distributaries (Palinkas et al., 2005) which carries about 60% of the total river discharge (Syvitski and Kettner, 2007). Po River daily outflows measured at Pontelagoscuro during sampling within the river were 505 m^3 s^{-1} on August 3rd 2004, 743 m^3 s^{-1} on March 15th 2005 and 277 m^3 s^{-1} on July 21st 2005. These values are well below the mean daily outflow of 1465 m^3 s^{-1} reported by Tedesco et al. (2007).

The Reno River is the second river after the Po of the Emilia Romagna Region, both in terms of length (210 km) and dimension of the drainage basin (4.9×10^3 km^2). The flow regime characterised by mean daily discharge of 35 m^3 s^{-1} is determined by rainfall with floods mainly concentrated in spring and autumn (Billi and Salemi, 2004). At Voltascirocco, about 9 km upstream from the river mouth, the water course is closed by a floodgate built in the second half of the 1950s. Recent measures pointed out the reduction to half of its solid bottom transport with respect to the period 1929–1978 (Mattarelli et al., 2004). At present, the river mouth is oriented northward thus delivering its water and sedimentary yield towards the Po delta when the floodgate is periodically opened.

3. Methods

3.1. Field methods

Shelf bottom sediments were sampled during a survey carried out onboard the R/V Daphne II from May 14th to 27th 2004 by means of a box-corer equipped with a sampling box of 17 × 10 × 23 cm. The sediments were collected at 28 sites, located in the coastal area influenced by the Po and Reno rivers between the Po di Goro and the Ravenna harbour, along 8 land-sea transects up to 10 km from the coast (Fig. 1). The sediment cores were sectioned into a surface layer (~0–2 cm), representing the active sedimentation and a sub-surface layer (~2–4 cm) representing the already-consolidated deposition, defined according to lithostratigraphic and sedimentological characteristics. Different aliquots were sub-sampled for geochemical analyses and immediately frozen at −20 °C. Additionally, samples for grain-size and mineralogical analyses were kept at +4 °C. The pH and oxidative–reductive potential (Eh) were determined on aliquots of each sample using combined glass electrode (mod. 50 52) and a platinum combined electrode (mod. 52 67), respectively, with a Crison portable pH-meter (mod. 25). Two buffer solutions at pH 4.01 (potassium and disodium phosphates) and at pH 7.00 (potassium hydrogen phthalate) were used for the calibration of pH and a ferric solution in sulphuric acid at Eh = 468 mV (Crison redox