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Humic acids contribution to sedimentary organic matter on a shallow continental shelf (northern Adriatic Sea)

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ABSTRACT

The shallow northern Adriatic Sea receives large river runoff, predominantly from the Po River, which is the main allochthonous source of nutrients and organic matter. The origin and quality of organic matter deposited in the sediments can influence the degradation processes and oxygen consumption in the bottom waters as well as the fate of many pollutants. Therefore the humic acids (HA) were quantified in surface and sub-surface sediments collected in an area of the north-western Adriatic platform south of Po River. HA showed to have a relevant contribution to sedimentary organic matter. HA content in sediments were positively correlated with the organic carbon concentration and negatively with redox potential and pH, particularly in sub-surface reduced sediments, suggesting their important role in the diagenetic processes taking place in anoxic conditions. Elemental composition of HA extracted from surface and sub-surface sediments showed a wide range of variation of the C_{org}/N ratios which could be due to a mixed (terrestrial and marine) origin and/or an elevated bacteria degradation of nitrogen during diagenesis processes in sediments. The spectroscopic ratios A_2/A_4 and A_4/A_6 of HA confirmed a mixed origin with a high degree of condensation of the HA extracted from sediments.

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1. Introduction

A substantial proportion of the so-called refractory organic matter (OM) in waters and sediments is constituted by humic substances (HS) which are formed from the decomposition of plant, animal and microbial tissues and tend to be more recalcitrant than their precursors (Coates et al., 2002).

HS are one group of organic molecules commonly studied as generic tracers, such as operationally defined fractions or functional group analysis, useful to describe bulk OM. They are defined according to fractionation schemes based on solubility under various pHs (Aiken et al., 1985). Though HS were considered refractory organic material, especially in anoxic environments as sediments, recent research showed that humic acids (HA) could play an important role as electron sinks for anaerobic respiratory bacteria and fermentative bacteria by stimulating the mineralization of complex organic carbon compounds in the absence of O_2 (e.g.: Lovley et al., 1996). HS can bind both hydrophobic and hydrophilic species (e.g.: Lafrance et al., 1990); they can act as stimulatory agents for marine phytoplankton (Prakash and Rashid, 1968) and are electron donors in photo-oxidation reactions in marine environments (Zepp et al., 1987). Moreover HS can determine the fate of many heavy metals (e.g.: Ashley, 1996; Fengler et al., 1994; Nissenbaum and Swaine, 1976; Wasserman et al., 1998) and of different classes of hydrophobic pollutants as polyaromatic hydrocarbons and alkylphenols that can be found associated to the humic sedimentary OM (e.g.: Poerschmann et al., 2007).

The Po River is the main OM source of the northern Adriatic (NA) Sea and significantly affects its coastal and pelagic ecosystems. The NA is an area particularly subject to hypoxic and anoxic events affecting bottom waters during the summer (e.g.: Justić et al., 1987) and to sporadic massive occurrence of mucilaginous aggregates (Precali et al., 2005). The sediment accumulation rates and the physico-chemical conditions of the sea bottom, as oxygen concentration, redox potential and pH, can influence the degradation and transformations of OM in particular of the HS, which may account for up to 80% of the organic carbon pool in marine sediments (Rashid, 1985). Only recently HS were characterized in the sediments of the NA Sea though their incidence on the bulk organic matter and their role in the early diagenesis of OM is still poorly known. Previous results showed that the humic and fulvic acid concentrations were inversely correlated to the distance from the coast (Calace et al., 2006a). Moreover, the humic and fulvic acids, closely correlated to the total organic content and to the total

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phosphorus content, suggesting a primarily *in situ* formation of the HA (Calace et al., 2006a). Nevertheless, the River Po can act both as carrier of humified compounds and as supplier of allochthonous organic matter whose decomposition products lead to the formation of HS.

The aim of this study is to quantify the contribution of HA to sedimentary OM and to investigate on the HA origin in a shallow continental platform influenced by riverine inputs. For this purpose a characterization approach based on stable carbon isotope ratios (e.g.: Stuermer et al., 1978; Malcolm, 1990), C_{org}/N ratios and absorption spectra of HA (Nissenbaum and Kaplan, 1972; Fooken and Liebezeit, 2000; Moreda-Piñeiro et al., 2006) have been employed to investigate the autochthonous or allochthonous sources of HA.

2. Regional setting

Freshwater and sedimentary input to the sea is mostly constrained along the western coast of the NA basin. The water circulation generally follows the Italian coast during winter, whereas in summer the plume may extend eastwards to the Croatian coast due to the seasonal stratification of the water column and weakening of the Western Adriatic Coastal Current (Franco and Michelato, 1992). The NA, in particular in its western part, is subject to hypoxia in the bottom waters, at the end of a high stability period in autumn (Degobbis, 1989; Socal et al., 2008) or in summer after high riverine discharges (Degobbis, 1989; Rachev et al., 2006). The coastal area immediately south of the Po river delta is a shallow sub-area of the NA where local depletion of oxygen frequently occurs in summer (Montanari et al., 1984). The intense sedimentation of riverine particulate matter and of phytoplankton blooms coupled with strong thermohaline stratification, high temperatures (>29 °C, e.g.: Socal et al., 2008) and reduced turnover time of bottom waters are the triggers of the hypoxia/anoxia events in this sub-area.

Close to the Po River mouth muddy sediments deposition is greatest in water depth <10 m (Fox et al., 2004), with a sediment accumulation rate of $\sim 1–2$ cm yr^{-1} decreasing rapidly to a few mm yr^{-1} from the prodelta southwards (Frignani et al., 2005).

3. Materials and methods

3.1. Sampling

Shelf bottom sediments were sampled during a survey carried out on board R/V Daphne II from May 14th to 27th 2004 at depths ranging from 4 to 18 m by a box-corer equipped with a sampling box of $17 \times 10 \times 23$ 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–-seas transects up to 10 km off the coast (Fig. 1). The sediment cores were sectioned into a surface layer (Table 1), representing the active sedimentation, and a sub-surface layer (Table 1), 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 analyses were kept at $+4$ °C, the methods and the data have been described in a previous work (Giani et al., 2009). 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. 5267), 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 standard) for the calibration of Eh.

3.2. Laboratory analyses

Organic carbon (C_{org}) and total nitrogen (N) were determined in surface and sub-surface sediments and HA extracted from the sediments by using a CHNS-O Elemental Analyser Fison (Italy) mod. EA1108, calibrated with acetanilide as standard. C_{org} was determined after removal of carbonates with HCl 1 N (Nieuwenhuize et al., 1994). Weight percentages of N were determined following the same procedure, without acidification. The detection limit of the method was 0.4 μmol for carbon and 0.9 μmol for nitrogen. The reproducibility of C_{org} determination was $\leq 3\%$ whereas that of N was $\leq 5\%$. C_{org} and N concentrations in sediments were expressed as weight percentage of the element on the dry sediment. The isotopic ratio ($\delta^{13}C$) of surface and sub-surface sediments were determined after removal of carbonates by HCl treatment (Nieuwenhuize et al., 1994). The $\delta^{13}C$ ratios were determined by the Isotope Ratio Mass Spectrometer (Delta Plus, Thermo Finnigan) coupled with a CHNSO Analyser Fisons (Italy) mod. EA1108. The results were expressed in the usual $\delta^{13}C$-notation in parts per mil (‰) from the international standard VPDB (Vienna Pee Dee Belemnite). The analytical precision of measurements was 0.2%. Sucrose IAEA-CH6 was used as certified reference material.

3.3. Humic acids extraction and characterization

The extraction of HA from sediments was performed following the methods of the International Humic Substance Society modified by Moreda-Piñeiro et al. (2004). HS comprise three basic components: humin, HA and fulvic acid (FA) defined according to their solubilities: humin is the fraction which is insoluble at all pH, HA is insoluble at pH < 2.0, and FA is soluble at all pH.

1–3 g dry weight of samples was shaken with 10 mL of 0.1 mol L^{-1} HCl for 1 h. After centrifugation at 4000 rpm, the precipitate was neutralised with 1 mol L^{-1} NaOH and then added with an alkaline solution of NaOH (0.1 mol L^{-1}) to pH 9. The suspension was shaken for 4 h. The humin precipitate, separated by centrifugation, was washed with deionized MilliQ water and 0.1 mol L^{-1} HCl three times. The alkaline extract was acidified at pH 2 (6 mol L^{-1} HCl) and was allowed to stand for 12 h in order to separate FA from HA. HA precipitate, separated by centrifugation, was re-dissolved in 0.1 mol L^{-1} NaOH and reprecipitated by 6 mol L^{-1} HCl. This procedure was repeated twice. The precipitate was treated with 0.3 mol L^{-1} HF, and then separated by centrifugation, washed twice with MilliQ water, frozen at -20 °C for at least 48 h, and freeze dried at -40 °C.

Carbon, nitrogen and $\delta^{13}C$ were determined on the freeze dried HA by the same methods described for sediment without HCl treatment to remove carbonates.

HA content in sediments was expressed as mg C/g sediment (dry weight) and as % of HA-carbon on the total C_{org} in sediment.

The UV–visible spectra of HA were performed by dual beam UV–vis spectrophotometer ATI Unicam UV2 with 1 cm-path length quartz cells and 2 nm-slit width. The spectra were recorded in the 250–800 nm range against MilliQ water blank. HA were solubilized with 1 mmol L^{-1} NaOH.

The terrestrial (F_t), riverine (F_r) and marine (F_m) fractions of the sedimentary organic matter have been estimated by Giani et al. (2009) using a three end member mixing model and they are used to investigate the possible relationships of the OM fractions with the HA.

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