



Source, diagenesis, and fluxes of particulate organic carbon along the western Adriatic Sea (Mediterranean Sea)

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ABSTRACT

In this study, we investigated the modern organic carbon (OC) cycling along the clinoform-shaped deposit that developed after the attainment of the modern sea-level in the Adriatic Sea (~5.5 kyr cal BP). Newly acquired data were combined with published results to characterize the (i) origin, (ii) diagenesis, and (iii) fluxes of OC along the Adriatic clinoform. $\delta^{13}\text{C}$, $\Delta^{14}\text{C}$, and lignin phenols were used to constrain the composition of OC accumulating in surface sediments. Sediment cores collected at different water depths were used to describe the early diagenesis during burial in different regions. In addition, on the basis of an extensive number of accumulation rates and OC data, we assessed the flux of OC to the seabed and its burial. Our results showed that terrigenous OC is the dominant OC source in the Po prodelta mainly in the form of pre-aged soil-derived OC and vascular plant fragments. Along the clinoform, both $\Delta^{14}\text{C}$ and the concentration of lignin-derived phenols decreased with increasing distance from the Po prodelta indicating the influence of an additional pool of aged OC that gradually becomes more important because of its selective preservation during the sediment transport. As a result, degradation rates (k) decreased along the clinoform as a function of the sediment oxidative history. The calculated half-life of reactive OC ($t_{1/2}$) was ~14.6 yrs in the Po prodelta whereas topset/forest deposits south of this region exhibited higher values, ~100 yrs, indicating the presence of refractory material. In the distal bottomset region, the $t_{1/2}$ was particularly high ranging from ~255 to ~912 yrs. Because of the significant southward component of the sediment transport, the OC deposition in the southern surface sediments exceeded the local OC input via rivers (ratio deposition/input 1.2). Conversely, the northern Adriatic was characterized by a marked imbalance (ratio deposition/input 0.3–0.5). According to our calculations, the OC flux to the seabed along the clinoform was ~309 Gg of C per year whereas the OC burial was ~180 Gg of C per year, corresponding to an overall burial efficiency of ~59%.

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1. Introduction

Clinoform-shaped deposits are ubiquitous sedimentological bodies of modern continental margins, including both carbonate and silicoclastic platforms. They formed after the attainment of the modern sea level high-stand (mid-late Holocene) when river outlets and shoreline migrated landward. Their shape and thickness are affected by a series of factors including relative sea level, sediment supply, depositional regime, and sediment type (Pirmez et al., 1998). Typical clinoforms developing along continental margins consist of a prograding body capped by aggrading topsets that become thinner upwards. Clinoforms formed over the last few thousands of years were described along the inner shelf of diverse settings: tectonically passive margins, such as the Amazon prodelta (Nittrouer et al., 1986),

active margins, such as the Ganges–Brahmaputra setting (Goodbred et al., 2003) and several epicontinental-shelves (Alexander et al., 1991).

As clinoform-shape deposits are essential building blocks of the infill of sedimentary basins (Mitchum et al., 1977; Vail et al., 1977), they are sites of intense organic carbon (OC) deposition and account for a significant fraction of the OC burial in the ocean during interglacial periods. In addition to the high deposition rates, the OC burial in these deposits is promoted by the relatively low reactivity of the land-derived material being diagenetically pre-altered and matrix-protected against degradation (Mayer, 1994; Mead and Goñi, 2008). Furthermore, hypopycnal coastal plumes experience intense new primary productivity constituting another pool of organic biomass accumulating along the clinoform body (Lohrenz et al., 1990; Campanelli et al., 2011). However, in high energy environments, some clinoforms can act as efficient incinerators where OC burial is limited by the prolonged residence of particles in refluxing suboxic mobile mud (e.g. Fly river delta, Gulf of Papua; (Aller and Blair, 2004).

In this biogeochemical study, we focused on sigmoidal clinoforms that are generally associated with low-energy environments (Pirmez

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et al., 1998; Cattaneo et al., 2007). In particular, we characterized the modern accumulation, degradation, and burial of OC along the late-Holocene sigmoid in the Western Adriatic Sea (Mediterranean Sea) (Fig. 1). This sedimentary body consists of a mud wedge recognizable on seismic profiles as a progradational unit lying on top of the maximum flooding surface that marks the time of maximum landward shift of the shoreline attained around 5.5 kyr cal BP (Correggiari et al., 2001; Cattaneo et al., 2003). Along shore-normal sections, this mud wedge exhibits quasi flat topsets in shallow waters and a gradual increase in the slope of foreset beds (0.5°, Correggiari et al., 2001) (Fig. 1b,c). In the last two decades, several projects have investigated sediment dynamics and organic geochemistry along the Adriatic mud wedge (PRISMA 1, PALICLAS, EURODELTA, US/EU EuroSTRATAFORM, PASTA, VECTOR) (Langone et al., 1996; Epping and Helder, 1997; Giani et al., 2001; Giordani et al., 2002; Ravaioli et al., 2003; Frignani et al., 2005; Palinkas and Nittrouer, 2006; Tesi et al., 2006; Miserocchi et al., 2007; Palinkas and Nittrouer, 2007; Tesi et al., 2007, 2008a; Giani et al., 2009, 2010; Tesi et al., 2011; Weltje and Brommer, 2011). All these studies increased our understanding of strata formation and organic matter cycling in this epicontinental margin. With this study, our overarching goal was to combine the results gained during these projects with newly acquired data to (i) further characterize the origin of sedimentary OC accumulating in surface sediments, (ii) investigate the reactivity of OC during burial along the Adriatic muddy deposit, and (iii) assess fluxes to seabed and burial of OC along the uppermost strata. Furthermore, because the accumulation is not necessarily linked to a specific river due to sediment transport along the shelf (Frignani et al., 2005; Palinkas and Nittrouer, 2006; Cattaneo et al., 2007), another important goal of this study was to characterize the spatial distribution of OC deposition and burial along the Adriatic clinoform. Our study benefited from an extensive number of radionuclide-based sediment accumulation rates (^{210}Pb and ^{137}Cs) and numerous biogeochemical data of surface sediments and sediment cores. Newly acquired data were obtained to fill up gaps in the existing biogeochemical dataset in order to have a synoptic overview of the Adriatic mud-wedge. Specific details regarding the source of the data used in this study will be provided in the text.

2. Background

2.1. The late-Holocene mud wedge

The Adriatic shelf has three major features: (1) epicontinental margin characterized by a microtidal regime, (2) clastic sources mainly located on the western side where a series of rivers discharge into the sea (i.e., line-source system, Palinkas and Nittrouer, 2006) and (3) thermohaline cyclonic circulation (Poulain, 2001) that transports sediments southwards along the Italian coast (Fain et al., 2007) (Fig. 1a).

As a result of these forcings, a continuous belt of deltaic and shallow-marine deposits forms the late-Holocene mud wedge along the western Adriatic shelf (Fig. 1b). This shallow deposit reaches up to 35 m in thickness (north of the Gargano promontory) and encompasses three connected depositional elements (Cattaneo et al., 2003): (a) the Po delta system, (b) the central Apennine fine-grained deposit fed by numerous steep rivers characterized by high sediment yields (Apennine Rivers), and (c) the Gargano subaqueous delta in the southern region, away from any direct river input. In volume this deposit is the major component of the late-Holocene Highstand System track formed after the attainment of the present sea level highstand (ca. 5.5 cal kyr BP, Correggiari et al., 2001). On seismic reflection profiles (Fig. 1c) the late-Holocene mud wedge exhibits a clinoform-shaped architecture characterized by three distinctive elements: (1) “topset” beds, shallow and low-angle deposits, (2) “foreset” beds, the central and steepest strata

characterized by relatively high accumulation, and (3) “bottomset” beds, gently inclined strata in the deepest region of the clinoform. Thickness and slope of these elements vary along the mud wedge based on environmental forcings such as oceanographic conditions, sediment supply, and accommodation space (Cattaneo et al., 2003). Sedimentation outside the clinoform is negligible and not recognizable using seismic profiles.

Anthropogenic- and climate-induced changes affected both growth and internal architecture of the Adriatic clinoform throughout the late-Holocene (Cattaneo et al., 2003). In its initial stage, after the attainment of the present sea level highstand, clinoform progradation was relatively low. Changes in pollen abundances showed at least two significant intervals of deforestation since the late Bronze Age (ca. 3700 yrs before present) that resulted in increased soil erosion and sediment supply to the shelf. Subsequently, significant progradation occurred during the Little Ice Age (ca. 500–100 yrs BP) because of considerable precipitations that characterized this period (Cattaneo et al., 2003). Since War World II, natural and artificial subsidence, riverbed excavation, and increased reservoir constructions have resulted in slowing down the rate of progradation. In spite of the hydropower management, sediment supply to the Po prodelta is still highly episodic because of flood events that ensure a rapid supply and deposition of land-derived material in the coastal ocean (Palinkas and Nittrouer, 2006; Wheatcroft et al., 2006). Conversely, the sediment delivery along the Apennine stretch suffered particularly from reservoir constructions and discharge regulation. As a result, most of the upper sediments lack laminated beds typical of event-driven deposition (Palinkas and Nittrouer, 2006; Wheatcroft et al., 2006). According to a recent sediment budget (Frignani et al., 2005), roughly one-fourth of the material enters the Adriatic Sea via the Po River (12.2 Tg of sediments). The remaining material is supplied by northern rivers draining the eastern Alps (3.2 Tg of sediments) and short, steep rivers draining the Apennine Mountains (29.7 Tg of sediment) (Fig. 1a).

3. Datasets

3.1. Data from the literature

3.1.1. Sediment accumulation rates (SARs) and mass accumulation rates (MARs)

Three recent 100-yr sediment budgets along the late-Holocene mud wedge were carried out by Frignani et al. (2005) and Palinkas and Nittrouer (2006, 2007). All budgets are based on radioisotope geochronology (mainly ^{210}Pb and ^{137}Cs). In this study we combined these datasets to gain a better spatial data distribution. The final collection of accumulation rates is composed of 231 point measurements spread all over the western continental shelf (Fig. 2a).

3.1.2. Biogeochemical data of surface sediments

A significant number of surface sediments were collected along the Adriatic shelf in the last decade. Tesi et al. (2006, 2007) and (Ogrinc et al., 2005) analyzed the elemental composition of surface sediments collected along the western and northern Adriatic shelf. Additional published data of surface sediments collected in various regions of the Adriatic margin (Epping and Helder, 1997; Giani et al., 2001; Giordani et al., 2002; Miserocchi et al., 2007; Giani et al., 2009, 2010) were added to obtain a final dataset of 383 measurements of OC (Fig. 2b). All sediment samples used in this study were collected via either box-corer or light gravity core built to preserve intact the sediment/water interface. Most of the surface sediments (258) are 1 cm thick (0–1 cm sediment interval; Epping and Helder, 1997; Tesi et al., 2006; Miserocchi et al., 2007; Tesi et al., 2007). The rest of the surface sediments encompass the uppermost 2 cm (0–2 cm sediment interval). Finally, some of the aforementioned studies presented additional biogeochemical data including carbon

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