# **Riverine Carbon and the Sedimentary Record on the Continental Shelves**

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### LONG-TERM GOALS

The long-term goal of our research is to improve the understanding of the behavior of terrestrial organic carbon on continental shelves. More specifically this project seeks to link the rates, the routes and the fate of organic carbon to the continental-margin sediment dynamics.

## **OBJECTIVES**

The field work is carried out in the northern Adriatic margin in the framework of the EuroSTRAFORM program. Our approach is to use the signature of the organic matter in order to: 1) trace the initial distribution of flood sediments on the shelf (spatial variability); 2) trace the physical and biological reworking of the flood layer (temporal variability); 3) discriminate between Po and Apennine riverine inputs; 4) identify flood layers in the stratigraphic records; 5) estimate the particulate organic carbon discharged during the 2000 flood event; 6) evaluate the overall organic carbon accumulation on the Adriatic continental shelf at monthly and 100-year time scales; 7) provide the overall partition between terrestrial and marine origin of the organic matter, based on a refined assessment of the end-member values of  $\delta^{13}$ C.

## APPROACH

River-dominated continental shelves, such as the Northern Adriatic, receive inputs of organic matter from allochthonous and autochthonous sources. Allochthonous sources of particulate matter include terrestrial (vascular detritus or soil) organic matter and freshwater (riverine or lake algae) or estuarine phytoplankton. Autochthonous particles are due to coastal biological productivity by phytoplankton, microphytobenthos and higher plants, and chemoautotrophic production.

The organic matter bears the geochemical signature of its sources, and thus can serve as a tracer of the transport and mixing of riverine particles in the shelf and slope environments. Because of shallow water depth and associated rapid sedimentation processes of the flood sediment pre-depositional degradation is not affecting the original signature of the organic matter.

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The approach comprise the quantification of  $C_{org}$  content, carbon stable-isotope composition and C/N ratio on sediments and suspended matter.

The stable isotopic composition of organic carbon has been widely used as an indicator of the sources and transport pathways of organic matter on continental margin sediments. Terrestrial plants are impoverished in <sup>13</sup>C compared to marine phytoplankton. Other factors, as temperature and plankton species composition can induce differences in isotopic fractionation, nevertheless in the Adriatic continental shelf, the  $\delta^{13}C_{org}$  signature most likely directly reflects the provenience of organic carbon (Faganeli et al., 1994).

A more quantitative assessment of the organic carbon origin in estuarine and coastal areas is achieved applying a mixing model based on C/N and  $\delta^{13}C_{org}$  data and the contribution of three distinct organic carbon sources: terrestrial (T), riverine (R) and marine (M) phytodetritus, with the riverine one including freshwater and estuarine phytoplankton in undifferentiated way. Major assumptions of the model are that the end-member compositions are representative of the organic matter sources in the study area and that diagenetic reactions do not significantly alter their values.

An opportunity to directly follow riverine particulate matter on a continental shelf over monthly and yearly time-scales was provided in late October 2000, when the Po River in the Northern Adriatic experienced a major flood. Rapid response cruises were carried out soon after the flood reached the sea; a hydrological survey for the characterization of the plume and a box coring cruise for sediment sampling was carried out. Po prodelta stations were re-occupied several times each year at seasonal frequency. Starting from April 2002 investigations were extended along the Apennine margin. The field work ended in May-June 2003.

## WORK COMPLETED

Box cores and suspended matter were collected near the Po delta in December 2000, 1 month after the major flood. Sample collection was repeated in January 2001, June 2001, October 2001, January 2002 and April 2002. During the last cruise was investigated also the central Adriatic shelves. During FY2003 three more oceanographic cruises were conducted comprising both Po prodelta environment and Apennine margin. Approximately a total of 500 surface sediment and 700 suspended matter samples have been collected and analyzed for carbon stable-isotope, C<sub>org</sub>, and N determination at ISMAR Elemental Analyses and Mass Spectrometry laboratory in Bologna.

Sediment vertical profiles from selected box and kasten core were also sampled. These analyses were started. A new PhD student, Tommaso Tesi, joined our group in February 2004. His work is supported from the ONR EuroSTRATAFORM Program.

In addition the ISMAR-SGM has supported the fieldwork by providing logistical help (lab and office space, refrigerator storage, field equipment, vessel use, and relationship with local authorities) to researchers involved in the EuroSTRATAFORM program.

### RESULTS

In the Po River prodelta surface sediments mean organic C contents for each cruise ranged between 0.87 % and 1.22 %, with an overall average value of  $1.00 \pm 0.26$  wt% (taking into account the 265 samples collected in 95 different stations during 9 seasonal cruises), not presenting a clear seasonal variability (Fig. 1).

In December 2000, the  $\delta^{13}C_{org}$  distribution of surface sediments of the Po prodelta, sampled after the Po River flood, ranged from -25.9 ‰ to -23.1 ‰ with the lightest values close to the coast and a trend toward heavier values going offshore with increasing water depth, as a consequence of the decrease of the contribution of terrestrial organic carbon and the increase of that of marine origin. The organic carbon content of surface sediments follows the same pattern of distribution as of the river plume, with the highest values recorded in a central belt shifted southward of the Pila and Goro-Gnocca river mouths. These areas nearly match those characterized by the highest thickness of the Fall-2000 flood deposit, as suggested by <sup>7</sup>Be penetration (Palinkas et al., in press) and sedimentary structures revealed by X-radiographs (Wheatcroft et al., submitted).

The composition of the end-members for the organic matter sources in the study area were defined (Boldrin et al., in press), and the origin of organic carbon estimated utilizing a mixing model based on  $\delta^{13}C_{org}$  values and C/N molar ratios. We have chosen to plot N/C rather than C/N ratios because the former are more robust statistically, since the higher number (% OC) is in the denominator, and behave linearly in end member mixtures. The compositional ranges of each end-member depicted in Fig. 2A are derived from previously published studies. It is well apparent that the most part of our samples converge toward the terrestrial end member (Fig. 2A). Samples collected during the different cruises indicate that there are not marked seasonal differences in the sedimentary organic matter (Fig. 2B), even for the samples collected soon after the 2000-flood event. The lacking of compositional differences between samples collected during flood or no-flood events, in addition to the surface distributions of OC contents and stable isotopes, suggest that similar processes may control their composition. This supports the hypothesis that in present-day conditions, the sediment accumulation in the main Po prodelta lobes is river-dominated (Correggiari et al., in press). On the other hand, much of the Po sedimentation that occurs during non-flood periods is subsequently eroded and dispersed by southward-flowing currents (Fain et al., submitted).

Unlike the Po prodelta sediments, the average composition of the particulate organic carbon collected at the same time offshore the Po River delta is closer to the marine end-member (Fig 2B). Furthermore, the average compositions of both particulate and sedimentary OC on the Apennine Margin, south of the study area, are somewhat similar to that of Po prodelta POC (Fig. 2B).

The apparent mismatch between sedimentary and particulate  $\delta^{13}C_{org}$  values in the Po prodelta had been already pointed out (Miserocchi et al., 2003), and tentatively attributed to a preferential remineralization of more-labile marine organic matter during early diagenesis relative to its proportion in bulk organic carbon (Boldrin et al., submitted), as suggested by Aller (1998) and Aller and Blair (2004) for other coastal environments.

Within the Apennine rivers, we did not find clear evidences of localized organic C input. The values of  $\delta^{13}C_{org}$  become less negative along the sediment dispersal system, which implies a progressive dilution

of the Po river organic C signature. Nevertheless, the proportion of terrestrial organic matter prevails in sediment accumulating north of the Pescara river.

 $\delta^{13}C_{org}$  was shown to be a good tracer of flood events in the recent stratigraphic record. It also revealed seasonal changes that were tentatively attributed to terrestrial input in front of the Po river delta and to degradation processes in the Central Adriatic. Finally, sediment accumulation rate played a strong role in the flux of organic C to the sea bed.

Our research is related to that of two other groups. First we are collaborating with Paul Hill and Tim Milligan, in order to examine the relationship between organic carbon and particle grain size.

Second, we are working with Dan Orange in evaluating the origin of anomalous sub-surface shallow gas concentrations in the Po prodelta delta and along the Adriatic western coast. The hypothesis is that in the Po delta, flood deposits deliver significant amounts of terrigenous organic matter that can be rapidly buried on the prodelta, effectively removing this organic matter from oxidation and biological uptake, and leading to enhanced methanogenesis (Orange et al., in press). In areas unaffected by rapid/thick flood deposition, or in between flood events, the gas data suggests that reworking of the surficial sediment between flood events effectively oxidizes and mineralizes organic matter (derived from both marine and terrestrial sources) and limits bacterial methanogenesis in the subsurface



Figure 1. Distribution of  $C_{org}$  content (% wt) on surface sediment from the Po prodelta area during different seasonal cruises. Enclosed circles indicate station location.



#### Figure 2.

A) Elemental and isotopic compositions of Po River prodelta sediments, colored boxes represent end members (Riverine, Marine and Terrestrial) compositional ranges from published studies. The most part of samples converge toward the terrestrial end member.

B) Elemental and isotopic compositions of Po River prodelta sediments represented as seasonal cruise averages, vertical and horizontal bars represent standard deviation value. Averages for Apennine surficial sediment and for particulate organic carbon both in Apennine and Po prodelta area are also depicted. colored boxes represent end members (Riverine, Marine and Terrestrial) compositional ranges from published studies. The average compositions of both particulate and sedimentary OC on the Apennine Margin, are somewhat similar to that of Po prodelta POC.

#### **IMPACT/APPLICATIONS**

Studying the sedimentary processes that affect the distribution and preservation of organic matter on the continental shelves, will provide key insight to understand the role this environment as sinks for  $C_{org}$  with respect to the global carbon cycle.

#### TRANSITIONS

No transitions, see related projects.

#### **RELATED PROJECTS**

Our research is related with several other EuroSTRAFORM groups. In detail stringent collaboration is active with: Chuck Nittrouer (UW) which provide dates for recent surface sediments; Paul Hill (UDal) and Tim Milligan (BIO) in order to inspect the relationships between organic carbon content and particle grain size; and with Rob Wheatcroft (OSU) to characterize the role the biological and/or physical reworking of the flood layer. Furthermore, we are working with Dan Orange (UCSC) in

evaluating the origin of anomalous sub-surface shallow gas concentrations in the Po prodelta delta and along the Adriatic western coast.

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