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### Seasonal and pluri-annual variability of sediment accumulation and organic matter fluxes in the Northwestern Adriatic shelf and its relationship with the frontal system

Francesca Alvisi<sup>a</sup>; Mauro Frignani<sup>a</sup>; Mariangela Ravaioli<sup>a</sup>

<sup>a</sup> CNR, Istituto di Geologia Marina, Bologna, Italy

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# SEASONAL AND PLURI-ANNUAL VARIABILITY OF SEDIMENT ACCUMULATION AND ORGANIC MATTER FLUXES IN THE NORTHWESTERN ADRIATIC SHELF AND ITS RELATIONSHIP WITH THE FRONTAL SYSTEM

FRANCESCA ALVISI\*, MAURO FRIGNANI and  
MARIANGELA RAVAIOLI

*Istituto di Geologia Marina, CNR – Via P. Gobetti, 101-40129 Bologna, Italy*

Twenty eight short sediment cores, collected along six transects in two areas influenced by the frontal system formed by the Po River, were analysed for  $^{234}\text{Th}$  and  $^{137}\text{Cs}$  in order to improve our knowledge on short time scale sediment deposition, accumulation and mixing. Sedimentological and mineralogical parameters were also analysed.

The decreasing  $^{137}\text{Cs}$  activities and C/N values in surface sediments indicate a decreasing input of terrestrial material during the study period. Furthermore, low excess thorium activities and inventories at some sites, together with low sedimentary organic matter concentrations in the southern area, suggest that the productivity in summer 1997 was lower than in 1996. Temporal and spatial shifts of the front exert a strong influence on short time scale deposition of particulate matter in the northern area, while the front position is more stable in the southern area, influencing both seasonal and interannual deposition.

The comparison between apparent seasonal and pluri-annual accumulation rates suggests, for the northern area, a sedimentation pattern characterized by temporal deposition of material on to the sea floor, with periodical resuspension. The net apparent accumulation is  $0.1\text{--}0.4\text{ g cm}^{-2}\text{ yr}^{-1}$ . The same occurs for the southern area, where values are higher, probably due to the longer persistence of the frontal system in the same area over the years. Here, both seasonal and pluri-annual deposition showed the same pattern, but seasonal values were two to three times higher with a net apparent accumulation rate of  $0.3\text{--}0.8\text{ g cm}^{-2}\text{ yr}^{-1}$ .

Organic carbon and nitrogen concentrations are generally less than 1.3 and 0.2% d.w., with lower values in the southern area. By contrast, mass fluxes showed higher values in the southern area, while the rate of removal over a pluri-annual time scale is generally high.

*Keywords:* Adriatic Sea; Sediment accumulation; Frontal system; Variability

## 1. INTRODUCTION

Seasonal and inter-annual changes of density structures along the water column are among the most important factors affecting biogeochemical and sedimentological processes in the Adriatic Sea (Artegiani *et al.*, 1997a). The changes in water density strongly affect the dynamics of biological and sedimentological processes, thus influencing vertical and horizontal transport of particles within the basin (e.g. Frascati *et al.*, 1988). In this context, the study of biogeochemical processes and particle transport is of crucial importance. The frontal system

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\*Corresponding author. E-mail: francesca.alvisi@igm.bo.cnr.it

delimits a coastal area, physically different from the offshore oligotrophic waters, that is strongly affected by anthropogenic inputs of chemicals. Therefore, the frontal line acts as a physical barrier that influences the dispersal of the suspended matter and dissolved materials delivered to the sea by the Po River and by several minor rivers along the NE Italian coast. To better understand the effects of frontal formation and dynamics on the behaviour of the Adriatic system, it is important to quantify the flux to the sea floor of both lithogenic and biogenic particulate materials over different time scales. The aim of this study was to provide a contribution to the knowledge of the biogeochemical cycles through quantitative first order estimates of short time-scale deposition and long-term accumulation of sedimentary material, and related fluxes of organic carbon and nitrogen in different areas subject to the influence of the front.

## 2. STUDY AREA AND SAMPLING STRATEGY

The Adriatic Sea is an elongated basin with a very low slope gradient in the northern area and a stronger land sea gradient along the western shelf. The water circulation is dominated by a cyclonic gyre which causes an overall sediment transport and deposition along the Italian coast. The general circulation of the Northern and Central Adriatic Sea has two different seasonal regimes (Franco *et al.*, 1982; Malanotte and Bergamasco, 1983; Orlich *et al.*, 1992; Artegiani *et al.*, 1997a, 1997b).

Sampling was carried out in two different sectors, which are differently affected by the frontal system. The first, located immediately south of the Po delta, was chosen to evaluate direct and indirect effects of the frontal system produced by the Po River plume offshore the Emilia-Romagna coast. The second, facing the Marche Region, was studied to understand the effects of the front far from the Po delta, where the slope of the shelf is steeper. Sampling locations were chosen in order to: 1) follow the frontal area spatial evolution, 2) reconstruct the time evolution of the sedimentary inputs at fixed locations, and 3) follow deposition and accumulation processes along the main transport pathways of the Northwestern Adriatic basin.

## 3. MATERIALS AND METHODS

Sampling was carried out along transects crossing the frontal line in two different seasons: June and February were taken as representative of a summer and a winter situation. The sampling strategy was based on the collection of two/three cores land ward and sea ward with respect to the frontal line. Each time, some other stations were sampled to evaluate the spatial variability of the single site and to compare different sedimentological environments. During the first cruise (June, 1996), all stations were located within the frontal system.

Sediment cores (10–45 cm long) were collected using a multicorer during four cruises, carried out in June, 1996, February and June, 1997, and February, 1998 on the R/V “Urania”. All cores were radiographed, vertically sectioned, photographed and described. Slices 0.5–2 cm thick were sampled and dried at 60°C. Water content, porosity and bulk dry density were determined according to Berner (1971), assuming a sediment density of 2.5 g cm<sup>-3</sup>. Grain size analyses were carried out by wet sieving through a 60 µm mesh sieve to separate

the muddy fraction, after a pre-treatment with hydrogen peroxide. Sands were then separated from shell debris by dry sieving using a 250  $\mu\text{m}$  mesh sieve. Dry sediment was analysed, after disaggregation, for organic carbon, total nitrogen and radiotracers. Organic carbon (OC) and total nitrogen (assumed to be equivalent to organic nitrogen, ON), were measured by means of a Fisons CHNS Elemental Analyzer after a treatment with 2N hydrochloric acid to eliminate the carbonates.  $^{234}\text{Th}$  and  $^{137}\text{Cs}$  activities were measured by gamma spectrometry according to Frignani *et al.* (1991). Excess  $^{234}\text{Th}$  ( $^{234}\text{Th}_{\text{xs}}$ ) activities were calculated subtracting the fraction in equilibrium with  $^{238}\text{U}$  from the total. Supported  $^{234}\text{Th}$  was obtained from the values shown by samples at depth in cores, checked by repeating the analysis after several half lives.

Apparent accumulation rates were calculated from  $^{137}\text{Cs}$  on the basis of the mass depth of the two peak activities (1963 and 1986). Short timescale accumulation rates were obtained from  $^{234}\text{Th}_{\text{xs}}$  depth penetration divided by four months (5 half-lives) and then referred to one year. This procedure, used in absence of a depth profile, provides rough estimates, which could be considered maximum limits. Organic carbon and total nitrogen fluxes were obtained by multiplying mass accumulation rates by their concentrations in the surface sediment (0–0.5 cm).

## 4. RESULTS AND DISCUSSION

The results of radiochemical and organic matter analyses of the surface layers (0–0.5 cm) are shown in Figures 1 and 5. The stations of the three study transects of each zone are grouped along the horizontal axis numbered from land to sea and positioned relatively to their front lines (vertical lines in the diagrams). In Figure 1 from left to right in each diagram, the transects of February, 1997 (cores 20, 21 and 16), June, 1997 (cores 7, 9, 10 and 12) and February, 1998 (cores 11, 12, 13, 14 and 15) are shown. Figure 5 shows the transects relative to February, 1997 (cores 1, 2, 3 and 4), June, 1997 (cores 13, 14, 15 and 16) and February, 1998 (cores 2, 3, 4 and 5). In the northern area, during February, 1997 cruise, the frontal system was located further offshore, where the sediment is made of relict sands difficult to sample. At that time, the cores were collected onshore, in the mud belt, far from the front and are, thus, located in the diagram parallel to the stations sampled in June, 1997 to compare similar locations in different seasons and with different frontal influences.

### 4.1. Northern Area

The shallow area is characterised by clay sediments, colonised by polychaetes of different species and few molluscs (*Turritella*, *Corbula*). The stratigraphy of the mud belt cores (February, 1997/20 and 21, June 1997/7, 9, 10, February 1998/11, 12, 13 and 14) shows a certain degree of bioturbation, due to macrobenthos activity, that destroys primary sedimentary structures, which are generally represented by flat laminations. Offshore stations (February 1997/16, June 1997/12 and February 1998/15) display a coarser lithology with up to 50% of sand and abundant shell debris and biogenic detritus. These stations are located in the transitional area between the pelitic mud belt and the offshore relict sands.

$^{137}\text{Cs}$  surface activities decrease from 15–18 to 5–8  $\text{Bq kg}^{-1}$  as the distance from the delta increases, with a pattern independent on the frontal position (Fig. 1). The inventories for the

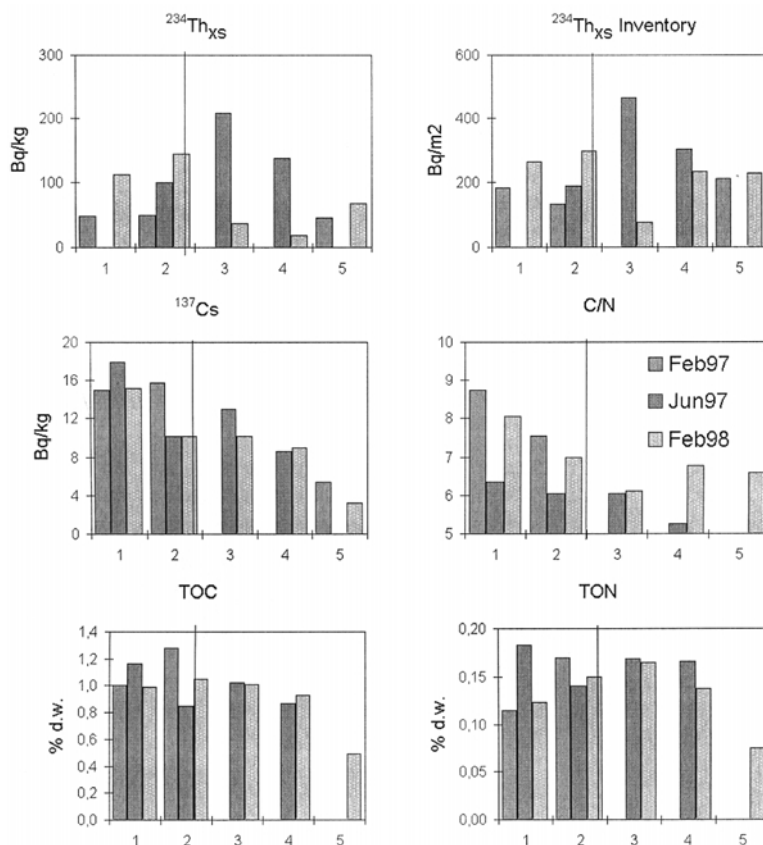


FIGURE 1 Seasonal distribution of  $^{234}\text{Th}_{\text{XS}}$  activities and inventories,  $^{137}\text{Cs}$  activities, C/N, TOC, and TON in surface sediment samples along the transects of the northern area. Vertical lines represent the frontal location.

surface layer (0.5 cm thick), follow the same pattern, with values decreasing from  $85 \text{ Bq m}^{-2}$  to nearly nothing (Fig. 2). These distributions point out the role of the Po River in supplying  $^{137}\text{Cs}$ , as already recognized by previous authors (Albertazzi *et al.*, 1984; Frignani and Langone, 1991; Albertazzi *et al.*, 1992; Delfanti *et al.*, 1997).

Surface  $^{234}\text{Th}_{\text{XS}}$  activities span between 0 and  $250 \text{ Bq kg}^{-1}$  with the highest values close to the frontal system. In general, all activities are lower in winter than in summer, and largely influenced by the distance from the frontal line. In fact, higher activities are recorded at the locations close or behind the frontal line, both in summer and winter (Fig. 1). We obtained values of  $77 \text{ Bq kg}^{-1}$  in February 1997/20 and 21 cores, with the frontal system located much offshore which increased to about  $160 \text{ Bq kg}^{-1}$  in presence of the frontal system (February 1998/11 and 12). These results suggest a strong influence of the front, that probably enhances both deposition of suspended matter and scavenging of  $^{234}\text{Th}$  within the frontal system, due to the very shallow water column, the vicinity of the river mouths and the confinement of the water that reduces their dynamics.

Such an influence appears even more evident in the warm season, when the concentration of suspended matter is higher, due to an enhanced production associated with a stratification

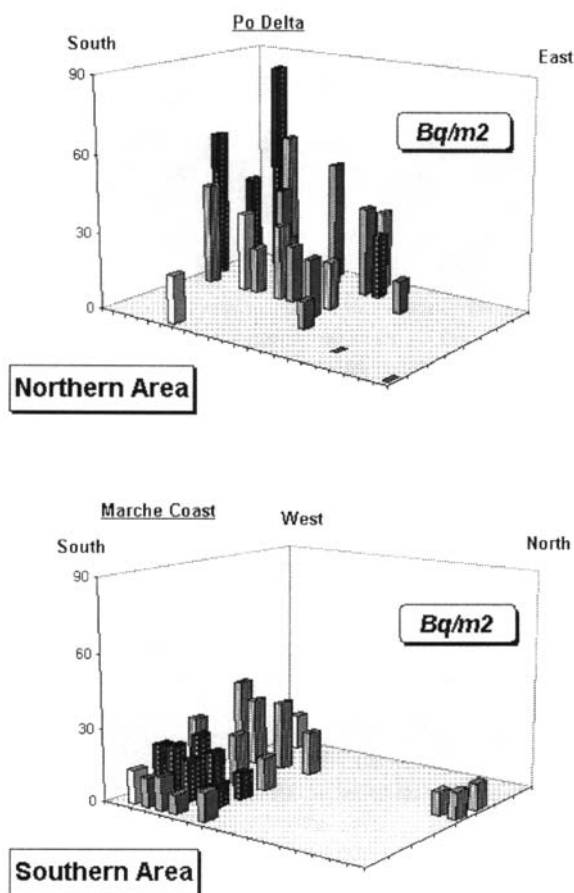


FIGURE 2 Spatial distribution of  $^{137}\text{Cs}$  inventories in surface sediments (0–0.5 cm) of the two investigated areas. Different bar patterns refer to the four cruises.

of the water column that probably increases both the residence time in the water column and the scavenging capability of the suspended particles.

$^{234}\text{Th}_{\text{xs}}$  vertical profiles account for a deeper penetration of the radiotracer during the warm season (Fig. 3), probably due to the enhanced biological activity on the sea floor linked to the high input of particulate organic matter and favoured by the warm temperature on the bottom.

The distribution of organic carbon and nitrogen in surface sediments is not clearly linked to the frontal system location (Fig. 1). Organic nitrogen concentrations are generally low, from 0.12 to 0.18% dw. Values relative to shallow sites are higher in summer and lower in winter. Organic carbon concentrations show the same pattern, ranging from 0.9 to 1.3% dw. The C/N ratio (Figs. 1 and 4) shows values always lower than 10, thus suggesting a dominance of the autochthonous input of organic matter to the sediment. However, there is a land-sea gradient in the northern area, which is higher in winter time. This pattern suggests a relatively more important contribution of organic riverborne material to the sediment in winter (Faganeli *et al.*, 1990).

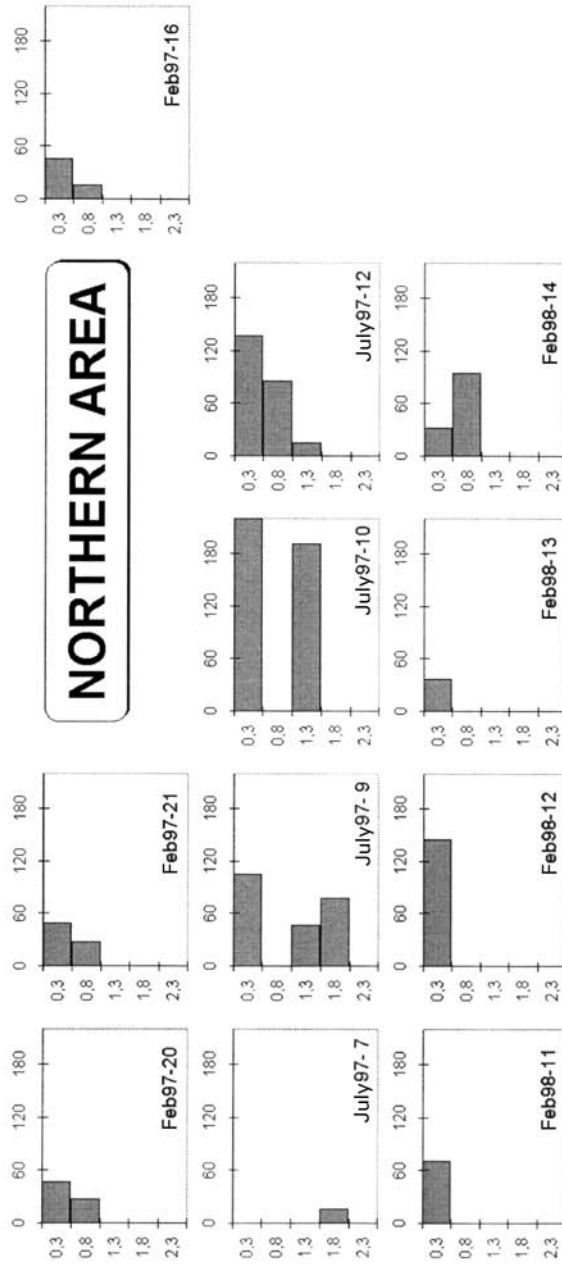


FIGURE 3 Activity/depth profiles of  $^{234}\text{Th}_{\text{xs}}$  along the transects of the northern area. Label indicates sampling cruises and site number.

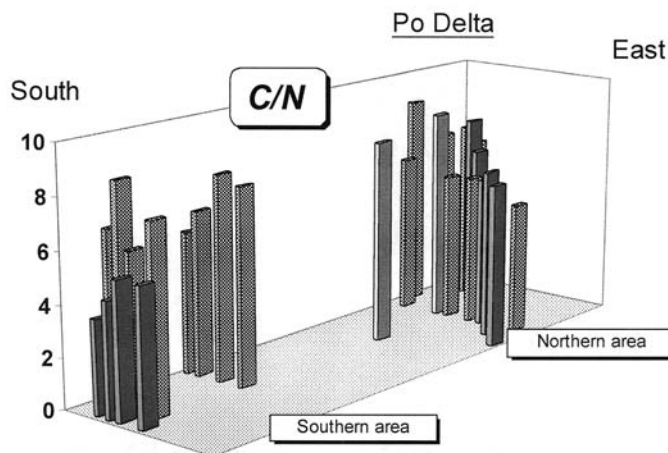


FIGURE 4 C/N ratio in surface sediment samples in the study area. Different bar patterns refer to the four cruises.

#### 4.2. Southern Area

Sediment cores from the southern area are characterised by difference in silt and clay enriched layers. Together with the presence of tanathocenoses, this pattern reflects sedimentation pulses with colonisation stages and sudden inputs of sediment that buried the benthic fauna. The shallow stations are subject to sand inputs brought during storm events, clearly recognizable in surface sediments down to a depth of 18–20 m. Below this depth, coarse sediments are progressively mixed with the fine particles.

Due to some analytical problems, thorium data regarding stations 13 and 16 of the transect sampled in summer 1997 are missing, and this reduces the reliability of the comparison between the different seasons. The stations across the front show higher  $^{234}\text{Th}_{\text{xs}}$  activities (Fig. 5) with respect to the more distal ones. Again this is a surprising result, because high fluxes of sedimentary material should dilute the radiotracer. The high activities could be due to preferential scavenging, related to the composition of the suspended matter and to the spatial stability of the frontal system in this area. Behind the frontal line, thorium activities are lower, due to both the very shallow environment and the coarser sediment grain size. The highest  $^{234}\text{Th}_{\text{xs}}$  activities, characteristic of the two distal stations, reflect the higher depth of the water column, the enhanced residence time of particles and the very fine grain size of the sedimentary material. Furthermore, high  $^{234}\text{Th}_{\text{xs}}$  inventories in deep water sediments, found especially in winter, suggest a possible displacement of the shallow water sediments offshore, due to the enhanced water dynamics (Artegiani *et al.*, 1997a and 1997b), with phases of resuspension and redeposition of sedimentary material over the sea floor. The higher summer inventories of thorium underneath the frontal system account for a preferential vertical precipitation of the particles probably favoured by low bottom water dynamics and by water column stratification.  $^{137}\text{Cs}$  distribution in surface samples appears dependent upon the frontal system (Fig. 5), as seen for thorium. This behaviour suggests that caesium is mainly of atmospheric origin in this area and its depositional pattern is influenced only by marine dispersal processes, without the superimposed effect of a direct continental input. Nevertheless, some continental input of caesium seems to be recognizable in the slight de-



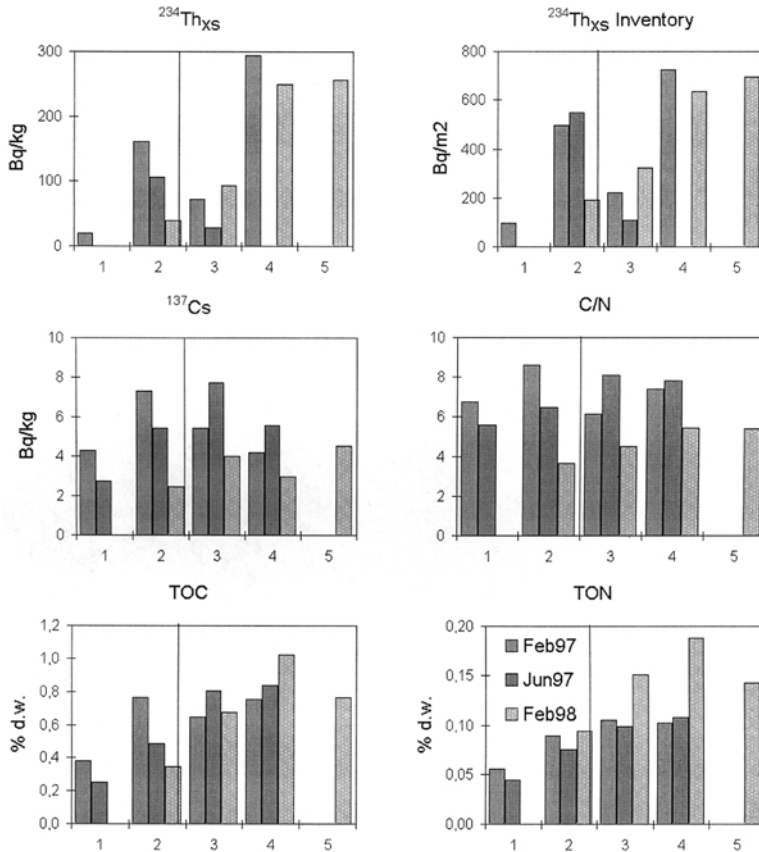


FIGURE 5 Seasonal distribution of  $^{234}\text{Th}_{\text{xs}}$  activities and inventories,  $^{137}\text{Cs}$  activities, C/N, TOC, and TON in surface sediment samples along the transects of the southern area. Vertical lines represent the frontal location.

crease of the activities, during the study period, suggesting a decreasing river delivery as shown by the pattern in the northern area.

Organic carbon and nitrogen concentrations in the three seasons show some interesting features. Organic nitrogen always displays the same pattern, but values are lower in June 1997 and higher during winters. Organic carbon shows a shift of the highest value toward deeper waters over the same period. The C/N ratio (Figs. 4 and 5) shows a decrease in February, 1998, thus suggesting an increased importance of autochthonous organic matter. In general, the behaviour of biogenic material, such as OC and nitrogen, seems to be primarily influenced by the lithology of the sea floor with low values close to the coast and higher values corresponding to the mud belt. However, there could be also an effect of depletion behind the front line, probably due to the enhanced benthic degradation of organic material induced by the frontal system itself.

#### 4.3. Accumulation Rates and Fluxes

We calculated apparent accumulation rates, based on both  $^{234}\text{Th}_{\text{xs}}$  and  $^{137}\text{Cs}$  profiles, for sediments collected in winter, 1997 (southern area) and 1998 (northern area) (Fig. 6). Since

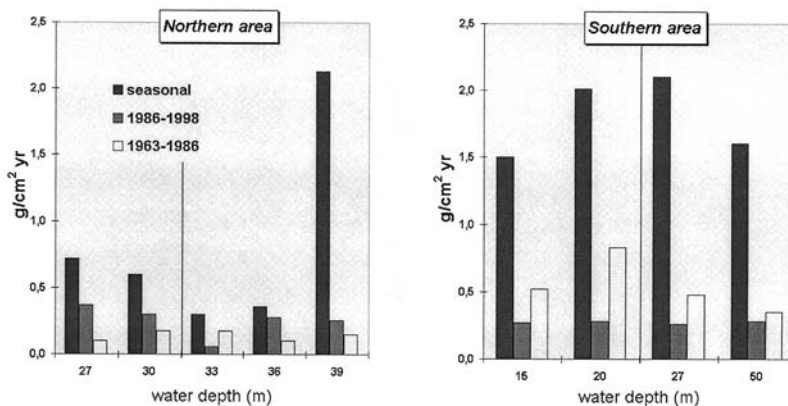


FIGURE 6  $^{234}\text{Th}_{\text{xs}}$ - and  $^{137}\text{Cs}$ -derived accumulation rates for the two investigated areas. Vertical lines represent frontal location.

$^{234}\text{Th}_{\text{xs}}$  depth distributions reflect slow bioturbation, as suggested by very poor penetration of thorium within the sediment column (only 0.5 cm in most cases), mixing effects were not considered. Thorium-derived rates were called 'seasonal', because they represented a winter situation, but they are referred to an annual scale to be compared with caesium-derived rates, calculated for the two periods: 1963–86 and 1986–1998.

In the northern area, seasonal apparent accumulation rates range between 0.3 and 0.7  $\text{g cm}^{-2} \text{yr}^{-1}$  in the mud belt and 2.1  $\text{g cm}^{-2} \text{yr}^{-1}$  in the sandy area. The pluri-annual rates are 0.3–0.4  $\text{g cm}^{-2} \text{yr}^{-1}$  for the period 1986–1998, and become generally low for the period 1963–86 (around 0.2  $\text{g cm}^{-2} \text{yr}^{-1}$ ). These results can be affected by the tendency of  $^{137}\text{Cs}$  to migrate through interstitial waters along concentration gradients. Obviously this process tends to affect the older peak more, favoured by the much longer time interval in which this process can act, whereas the rates derived from the Chernobyl radio-caesium are more reliable. The caesium-derived values are in good agreement with previous studies in the

area (Sticchi, 1990; Frignani and Langone, 1991) and show only minor fluctuations, probably linked to local shift of the mud distribution. In particular, we can observe a decreasing trend from the coast down to a water depth of 33 m (station February, 1998), with an inversion further offshore. This pattern could be linked to the presence of two main sedimentary components, the Po-derived material deposited mainly close to the coast, and the northern Adriatic-derived material deposited further offshore (Frasconi *et al.*, 1984; Ravaioli, 1986). The station at 33 m depth might represent a 'nodal' point with constant low accumulation rates. The 'seasonal' rates are much higher than decadal rates, suggesting episodes of rapid deposition alternated with events of sediment resuspension and displacement as shown also by Price *et al.* (1993). Highly significant differences in accumulation rates were obtained in sandy offshore sediment (station February 1998; depth 39 m) due to the same alternation of deposition and resuspension events, coupled with physical mixing. At this station, in fact, the sediment is mainly made of sands, up to 50%, together with shell debris, and the new fine sediment deposited is periodically washed by deep currents (Artegiani *et al.*, 1997a).

The apparent fluxes of organic carbon and nitrogen were calculated (Fig. 7) using the accumulation rates derived from radiotracers both on seasonal and decadal time scales. The sea-

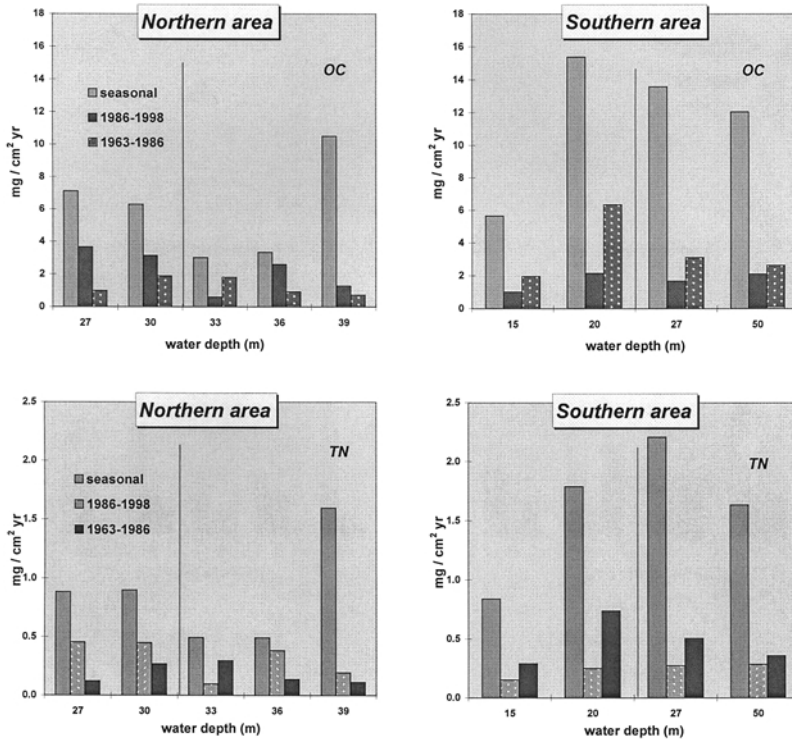


FIGURE 7 Organic carbon and total nitrogen fluxes calculated for the two study areas. Vertical lines represent frontal location.

sonal fluxes of carbon and nitrogen are comprised within the intervals 7–10.5 and 0.5–1.6  $\text{mg cm}^{-2} \text{yr}^{-1}$ . They are much higher, sometime even double or more, than the decadal ones (0.5–3.5 and 0.1–0.4  $\text{mg cm}^{-2} \text{yr}^{-1}$ ), due to both diagenesis and periodic removal of these species from the surface sediments. These latter processes, in particular, are efficient close to the coast where up to a half of the seasonal apparent deposition is removed. The removal effect is even higher at the offshore location for the reasons already mentioned.

In the southern area, the pattern is different. The seasonal apparent mass accumulation rates are high at all stations, with a distribution similar to those calculated for the period 1963–86, but characterized by different values (1.5–2.1  $\text{g cm}^{-2} \text{yr}^{-1}$  versus 0.4–0.7  $\text{g cm}^{-2} \text{yr}^{-1}$ ). On the contrary, the rates for the period 1986–97 were more or less constant around 0.25  $\text{g cm}^{-2} \text{yr}^{-1}$ , very similar to the values obtained for the northern zone, thus suggesting a sort of regular spatial distribution of sediment deposition on the western continental shelf over a decadal time scale. Moreover, the higher short timescale rates recorded in the southern area and the diverse pattern along the transects can be due to different mechanisms of sediment distribution: in the northern area, the location of the frontal system was quite different in time and space, as seen during the four cruises. Therefore, even if the concentration of the particulate matter in the water column is always rather high, sediment dispersion is conditioned by the movement of the frontal system. In the southern area, on the contrary, the position of the frontal system is more stable in space and time, and causes a focusing of sedimentary material in the same areas. This behaviour seems to be persistent

over a pluriannual time scale and could result in the higher accumulation of material along the coastal area of the Marche Region.

The apparent fluxes of organic matter in the southern area are higher than the northern ones, according to higher mass accumulation rates. The OC seasonal fluxes range between 5.8 and 15.0 mg cm<sup>-2</sup> yr<sup>-1</sup>. The minimum, located close to the coast, is clearly influenced by the coarse sediment lithology and the highest value, found at ca. 20 m depth, is probably due to both the focusing of sedimentary material and the input of terrestrial organic material. The same pattern characterises the period 1963–86, but with lower values (2–6 mg cm<sup>-2</sup> yr<sup>-1</sup>) suggesting a persistence over a pluri-annual timescale of the sedimentary conditions recorded on a seasonal scale. The total nitrogen shows a very similar pattern with values ranging between 0.8–2.2 mg cm<sup>-2</sup> yr<sup>-1</sup> on a seasonal scale and 0.3–0.8 mg cm<sup>-2</sup> yr<sup>-1</sup> on an pluri-annual scale. The maximum value is located at 27 m depth, in disagreement with both pluri-annual fluxes and OC concentration patterns. This feature could be the result of a possible change in the relative composition of the organic matter at the front station, reflecting a higher continental input during this period, as suggested by the C/N values of the same transect (Fig. 5, February, 1997).

## 5. CONCLUSIONS

In the northern area, the <sup>234</sup>Th<sub>xs</sub> behaviour points out that the frontal system strongly influences the short time scale deposition of particulate matter. Its role is enhanced by the large spatial shift occurring over this shallow area which causes a wide distribution of the sedimentary material on the continental shelf over a pluri-annual time scale. Temporal and spatial shifts of the frontal system are less important in the southern area, with a sound effect on both seasonal and interannual deposition. The land sea slope gradient of this area and the presence of seasonal currents parallel to the coast seem to influence the deposition and resuspension of the fresh sedimentary material with a net offshore transport.

Both areas show a decrease of the input of river-borne material to the sea floor during the study period as suggested by decreasing <sup>137</sup>Cs surface activities and C/N values. The low excess thorium activities and inventories observed at some sites and the low organic matter concentrations in bottom sediments of the southern area suggest that summer, 1997, was less productive than the 1996 one.

Apparent accumulation rates suggest that the two areas show different behaviours with respect to the distribution and deposition of fine material on the sea floor. The northern area is characterized by relatively low rates, decreasing with the increasing distance from the Po delta, with also a clear decreasing trend going offshore. Moreover, it seems that there is an inflection point around 33 m water depth, where the main influence on sediment accumulation changes from the Po input to the northern Adriatic gyre. The comparison between seasonal and pluri-annual apparent mass accumulation rates suggests a temporary deposition of material on the sea floor, half of which is periodically resuspended and transported further south with a net accumulation of 0.1–0.4 g cm<sup>-2</sup> yr<sup>-1</sup>, depending on the different locations.

The southern area shows higher sedimentary fluxes with respect to the northern area, probably related to the longer persistence on the same area of the frontal system over the years with a deeper centre between 20–27 m water depth. A similar pattern of seasonal and inter-annual deposition was observed, with former values two to three times higher, with a net input of material of 0.3–0.8 g cm<sup>-2</sup> yr<sup>-1</sup>.

Organic carbon and nitrogen in the sediment are generally lower than 1.3 and 0.2%, with lower values in the southern area. On the contrary, the fluxes show lower values in the northern area while a higher rate of removal over a pluri-annual time scale is recorded in both areas.

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