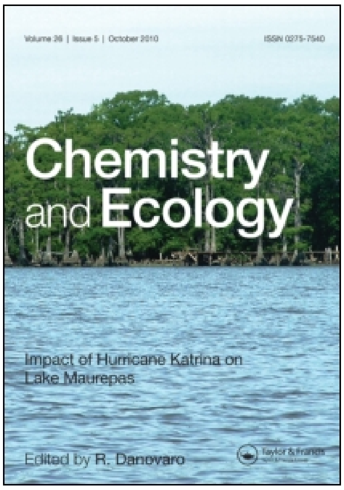

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A simplified approach to evaluate sedimentary organic matter fluxes and accumulation on the NW Adriatic Shelf (Italy)

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A simplified approach to evaluate sedimentary organic matter fluxes and accumulation on the NW Adriatic Shelf (Italy)

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Total organic carbon (TOC) and total nitrogen (TN) concentrations and fluxes were estimated in surface sediments of a shelf area in the NW Adriatic Sea (Italy), together with lithology and ^{210}Pb contents at 18 stations during four cruises (1996–1998) carried out offshore of the Po River delta. Mass accumulation rates (MAR) were ∼0.1–0.8 g cm^{-2} yr^{-1} and surface concentrations of TOC and TN were within the range of 0.5–1.4 and 0.08–0.19% of dry weight, respectively. Their spatial variability showed a direct correlation with the inputs of suspended matter from the Po River. A simplified approach to calculate average TOC and TN yearly fluxes to surface sediments over the whole area was adopted by subdividing the study area into three zones, selected on the basis of the grain size distributions and of the influence of the Po River discharge, in order to take into account major differences of sedimentological regimes on the shelf. The values of TOC ($\times 10^3$ tC yr^{-1}) and TN ($\times 10^3$ tN yr^{-1}) fluxes for these areas were, respectively, 17.9 and 2.4 near the delta, 45.2 and 6.5 for the intermediate area, and 9.5 and 1.5 for the offshore area.

Keywords: shelf sediments; coastal zone; organic matter; carbon cycling; total nitrogen; fluxes; stocks; thematic maps

1. Introduction

The shallow continental shelf of the Northern Adriatic Sea is economically one of the most important areas of the Mediterranean, in particular because of the significance of tourism and intensive fishing [1]. Nutrient dynamics is one of the most important factors controlling the trophism of the pelagic environment and the water quality in this area [2,3]. An increasing number of studies were therefore addressed to the problem of organic matter (OM) cycling within different shelf environments as a result of the increasing awareness about its role in hypoxic-anoxic crises and eutrophication, as well as in the blooming of mucilaginous aggregates. These include those devoted to benthic fluxes [4–6], the origin of OM in marine sediments [7,8], the biochemical composition of OM in marine sediments [9] and fluxes of dissolved and particulate organic carbon along the water column [10–12].

Despite nutrient availability being mainly driven by river discharge and hydrodynamics, it also depends upon the remobilisation of the surface sediments due to physical resuspension and

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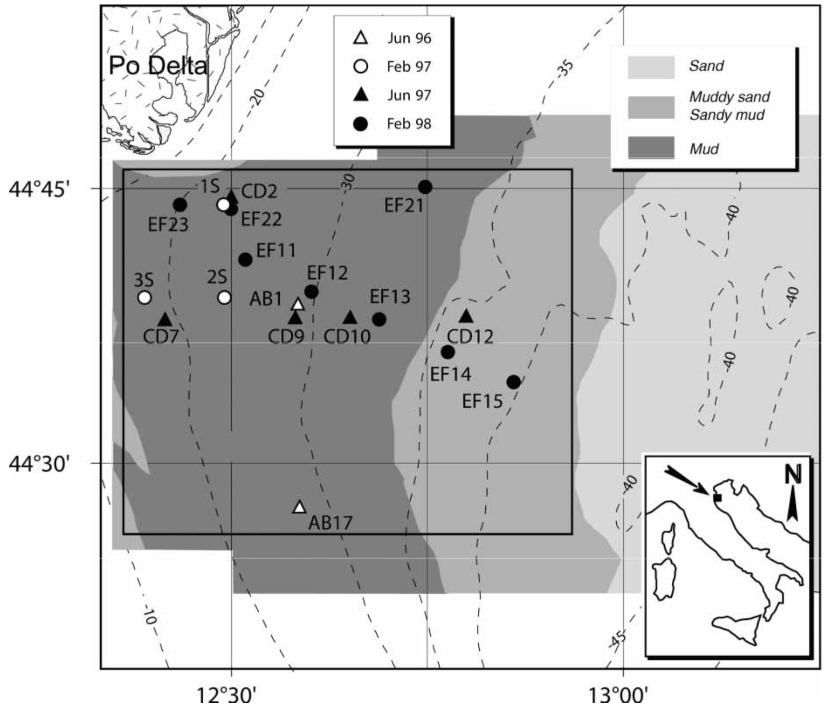


Figure 1. Study area and sampling location. Simplified grain size distribution of bottom sediment is modified from [30].

bioturbation [13] as well as to microbially mediated nutrient regeneration [6]. Core stratigraphy in these areas shows evident alternation of sediment accumulation and reworking/removal periods [14], which are indicative of variations in the sedimentation regimes [15–17] which could lead to the recycling of previously deposited OM. Calculation of the nutrient budget in the Northern Adriatic Sea should therefore include an estimate of the amount of sedimentary OM stored in shelf sediments per surface unit and an estimate of the fluxes of organic matter and bulk sediment. This information is required to evaluate the potential contribution of shelf sediments as a secondary source of OM to the food web in benthic and pelagic compartments.

The present study focuses upon an estimate of bulk sediment, total organic carbon (TOC) and total nitrogen (TN) fluxes reaching the sea floor in the NW Adriatic shelf, SE of the Po River Delta (Figure 1), as well as an estimate of TOC and TN stored within surface sediments. The investigated area was chosen as representative of the steepest land-sea gradient of sediment accumulation of the whole Adriatic Sea [17], which is representative of the main transition between the nearshore low-salinity nutrient-rich coastal waters, influenced by river runoff, and the offshore high-salinity nutrient-poor waters, mostly influenced by basin-wide circulation processes [18,19]. The collected cores were used to reconstruct recent spatial evolution of organic and inorganic sedimentary inputs along the major transport pathways of suspended matter in the area.

2. Materials and methods

2.1. *Study area*

The Adriatic Sea is the most extensive shallow continental shelf of the Mediterranean Sea (800 km from NW to SE) and represents an important source of nutrient-rich dense waters for the Eastern

Mediterranean basin [20]. The morphology and the climate of the region strongly influence the hydrodynamic features and oceanographic properties of the Adriatic Sea [18,21]. In winter, the currents are essentially of cyclonic type, forcing the river plumes southward along the Italian coast leading to a mixing of water columns in offshore areas. Strong wave motions and tidal currents may reduce, even in winter, the stratification of the coastal waters with depths of $<$10–12 m. In summer, the currents are weaker and tend to delimit small scale eddies, while the water column is frequently characterised by strong thermoclines and strong salinity gradients, due to the diffusion of freshwater inputs in the upper layer [22]. Floods from the Po River are often intense and may affect large portions of the Northern Adriatic [22].

The Northern Adriatic is a shallow and elongated epicontinental basin (average depth 35 m), with a very low slope in the Northern area and a stronger land sea gradient along the Western shelf. Fluvial inflows have shaped the sea floor morphology over a geological timescale. The present sedimentation pattern matches, quite precisely, the hydrodynamic circulation [23,24]. It consists of a narrow strip of recent coastal sands along the coast (5–10 m deep), a broad belt of muddy sediments and a wide open sandy shelf area, with little or no recent sedimentation ('relict sands').

2.2. *Experimental work*

2.2.1. *Sampling*

The Po prodelta is a gate location where sediments coming from the Northern Adriatic, delivered by rivers draining the heavy populated and industrialised areas of the NE Italy, intermingle with the Po River supply [24], whose sedimentary contribution mostly influences the hydrodynamics and physico-chemical composition of the whole Adriatic shelf.

Sediment sampling was performed along two land-sea transects across the main accumulation gradients between prodelta and offshore deposits (Figure 1), and in a discrete number of surrounding stations in order to follow the fan morphology of the prodelta accumulation area. The land-sea orientation of the two transects was normal to the coastline of the Po delta (transect EF) and of the Emilia Romagna coast (transect CD) to take into account the influence of local coastal morphology on sedimentary environments. Eighteen sediment cores (10–45 cm in length) were collected using a multicorer during four cruises of the PRISMA 2 Project between June 1996 and February 1998.

2.2.2. *Sediment lithology*

Cores were radiographed, vertically sectioned, photographed and described. Slices 0.5 cm thick were sampled in the 0–3 cm, 1 cm thick in 3–6 cm, 2 cm thick in 6–20 cm interval, and of 3 cm below 20 cm sediment depth. Slices were dried at 60°C and analysed for water content, porosity and bulk dry density [25]. Dry sediment of the surface interval (0–3 cm) was analysed, after disaggregation, for grain size, TOC and TN, whereas for ^{210}Pb analyses were carried out on all core samples.

2.2.3. *Grain size*

Grain size analyses were carried out on bulk sample after treatment with 10% hydrogen peroxide for 48 h to destroy organic aggregates. The muddy fraction was separated by wet sieving through a 63 μm mesh sieve. The transect EF was also analysed to estimate clay and silt content within the muddy fraction by a Micromeritics X-ray sedigraph, after dispersion in sodium hexametaphosphate solution and subsequent ultrasonic disaggregation (10–15 min). Sand was then separated from shell debris by dry sieving using a 250 µm mesh sieve.

2.2.4. ^{210}Pb

Activity-depth profiles of ^{210}Pb were measured in order to evaluate MAR at different locations and to calculate particle fluxes. ^{210}Pb specific activities were determined by alpha-counting ^{210}Po after [17], assuming secular equilibrium between the two isotopes. Excess ($^{210}Pb_{xs}$) activities were calculated by subtracting the ^{210}Pb supported fraction from the total. Supported ^{210}Pb was assumed constant along-core and estimated from the values (average 1 dpm g^{-1}) of the deepest sediment samples found in cores 3S, CD7 and CD12 (around 20 cm) assumed to have reached background values for this area [17]. The CF-CS model [26] was used to estimate the MAR (g cm^{-2} yr^{-1}) from the activity-depth profiles of the $^{210}Pb_{xs}$.

2.2.5. *TOC and TN*

TOC and TN concentrations were measured in the 0–3 cm interval using a FISONS NA2000 Element Analyzer, after decarbonation with 2M hydrochloric acid and drying (CV = 3–5%). Fluxes of TOC and TN for each location were calculated by multiplying mean TOC and TN concentrations of this interval by the MAR derived from ^{210}Pb activity-depth profiles.

3. Results

3.1. *Sediment characteristics*

Bottom sediments at all sites were predominantly terrigenous in origin, and varied from mud to muddy sand, rich in shell debris in the outer shelf (Table 1). Stations of the EF transect (EF11, EF12, EF13, EF14; Figure 1) showed a main dominance of clay, with values around 60–70 % d.w. which decreases toward SE to values of 28% d.w. at station EF15. Polychaetes were commonly present throughout the area. Surface sediments of stations CD7 and 3S showed a higher colonisation of benthic macrofauna (*Corbula gibba* and *Turritella* spp.) concentrated in discrete levels, with a grain size distribution similar to previous ones. This feature, together with the alternation of silt- and clay-enriched layers, suggests the episodic nature of the sedimentary input. Toward the outer shelf, sand content increases progressively up to 50% (Table 1), as does organogenic detritus (up to 25%).

3.2. *MAR and mixing*

In shelf areas, ^{210}Pb (half life of 22.3 years) is used to evaluate average MAR on a century timescale or, under the most favourable conditions, the variability of MAR on a decade timescale.

In the study area, down-core profiles of total ^{210}Pb (Figure 2) suggested the presence of a well-mixed layer, with a maximum thickness of 8 cm at station CD10, attributed to the reworking of sediments by physical/biological processes which are common on continental shelves worldwide [27,28]. Mixed layers of 5–6 cm in thickness were found in the central part of the muddy area, whereas they decrease to 3 cm in the offshore zone. Stations closer to the river delta (1S and EF23) as well as coastal stations 3S, CD7 and AB17 do not show this feature, being characterised by surface/subsurface peaks, suggesting the predominance of intermittent sediment accumulations due to spreading of the river plume.

Table 1. Mean sand, mud (silt + clay), silt, clay concentrations and porosity in surface sediments (0–3 cm). The standard deviation (SD) is reported to 1 sigma.

Station	Water depth (m)	Sand (% d.w.)	SD (% d.w.)	Mud (% d.w.)	SD (% d.w.)	Silt (% d.w.)	SD (% d.w.)	Clay (% d.w.)	SD (% d.w.)	Porosity (%)	SD (%)
AB1	29	0.4	0.1	99.6	0.1					78.0	1.5
AB17	28	0.6	0.1	99.4	0.1					77.5	1.0
1S	23	0.3	0.2	99.7	0.2					73.1	0.4
2S	25	0.7	0.2	99.3	0.2					74.5	2.2
3S	16	1.8	1.4	98.2	1.4					60.4	4.9
CD2	26	0.9	0.4	99.1	0.4					75.9	2.1
CD7	19	0.7	0.7	99.3	0.7					71.6	6.6
CD9	30	0.3	0.02	99.7	0.02					77.9	4.0
CD10	32	1.5	0.3	98.5	0.3					78.2	3.2
CD12	36	26.0	6.6	74.0	6.6					76.1	3.6
EF11	27	0.2	0.4	99.8	0.4	30.2	1.6	69.6	1.6	80.3	1.6
EF12	30	0.8	0.4	99.2	0.4	34.2	1.4	65.0	1.1	80.0	2.3
EF13	33	1.7	0.4	98.3	0.4	32.3	1.2	66.0	1.0	80.7	1.4
EF14	36	11.6	0.3	88.4	0.3	28.1	0.7	60.3	0.9	79.1	1.5
EF15	39	52.6	3.3	47.4	3.3	19.6	1.4	27.8	2.1	66.5	4.3
EF21	32									79.3	1.1
EF22	25									77.2	2.6
EF23	20									78.0	1.4

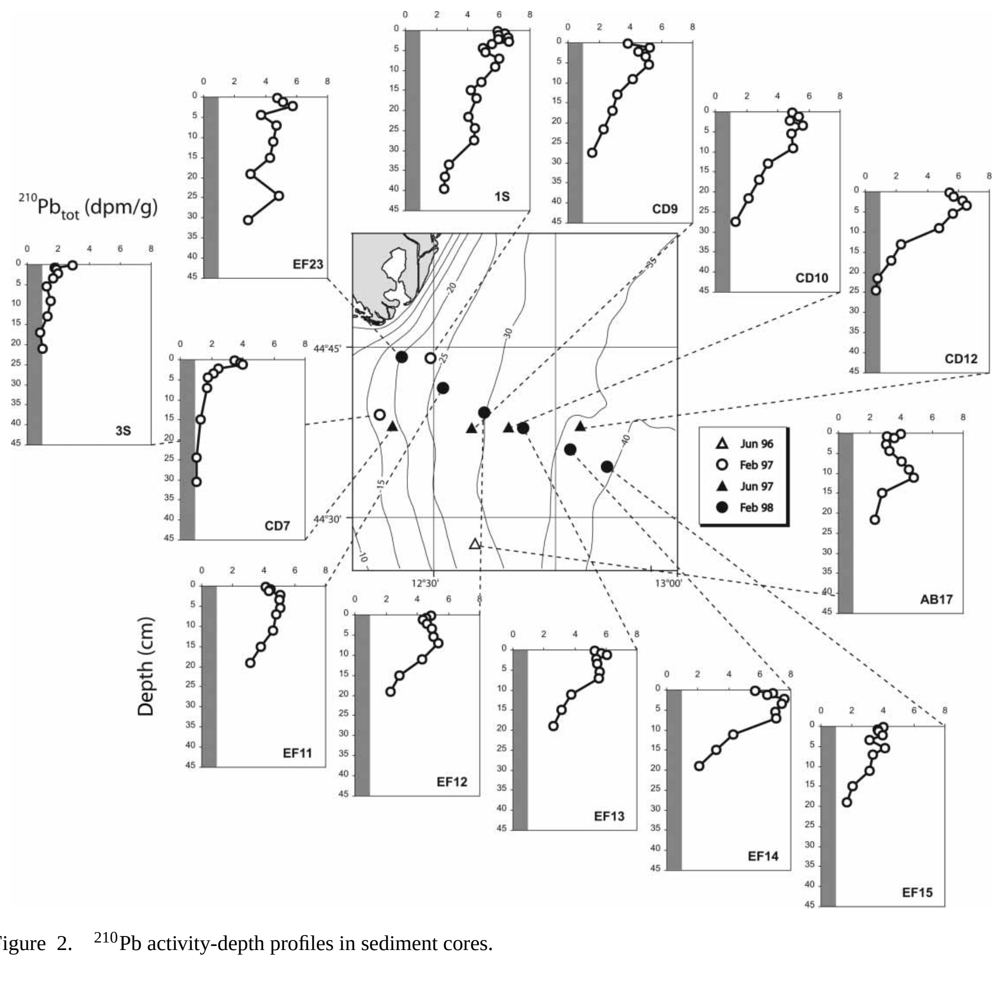


Figure 2. ^{210}Pb activity-depth profiles in sediment cores.

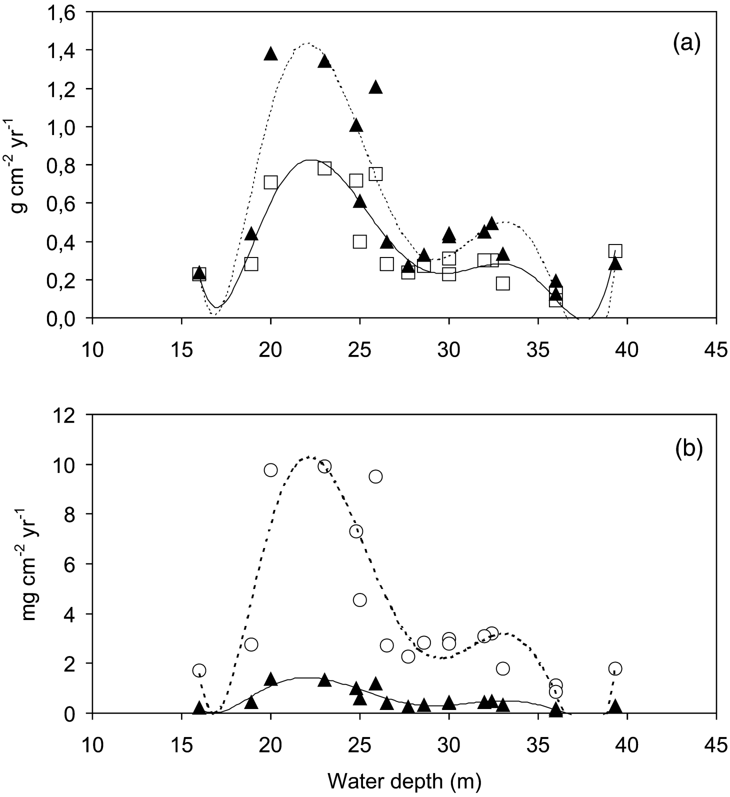


Figure 3. Comparison between (a) bulk sediment (MAR = empty squares) and TN (×1000) (filled triangles) and (b) TOC (empty circles) and TN (filled triangles) surface fluxes from land to sea (right to left). Lines represent data smoothing.

In this area, the background value of ^{210}Pb is around 1 dpm g^{-1} [17], and it was reached only in the CD transect and 3S cores. ^{210}Pb measurements show a variety of profile shapes, as a result of different sedimentary processes during deposition and burial (Figure 2) with surface activities range from 3 to 6 dpm g^{-1}. MARs were calculated for sediment cores below the mixed layer, when present. They range from 0.1 to 0.8 g cm^{-2} yr^{-1}, with values decreasing from NW to SE and from the central part of the study area towards its boundaries (Figure 3(a)), in good agreement with previous studies which give estimates of the order of 0.03 to 6.6 g cm^{-2} yr^{-1} for the whole Adriatic dataset, with an average value of 0.4 g cm^{-2} yr^{-1} [17].

In order to calculate annual average surface fluxes for the investigated area, the 3 cm interval was chosen as the 'surface interval'. This interval corresponds to a temporal accumulation of approximately 2–8 years in the study area, except for stations 3S, CD12 and EF14 which record time intervals of 13–17 years for the same sediment thickness. It thus represents averaged condition of sediment accumulation at an interannual scale occurring as a result of the main sedimentary processes acting in this area (deposition, resuspension and physical/biological mixing).

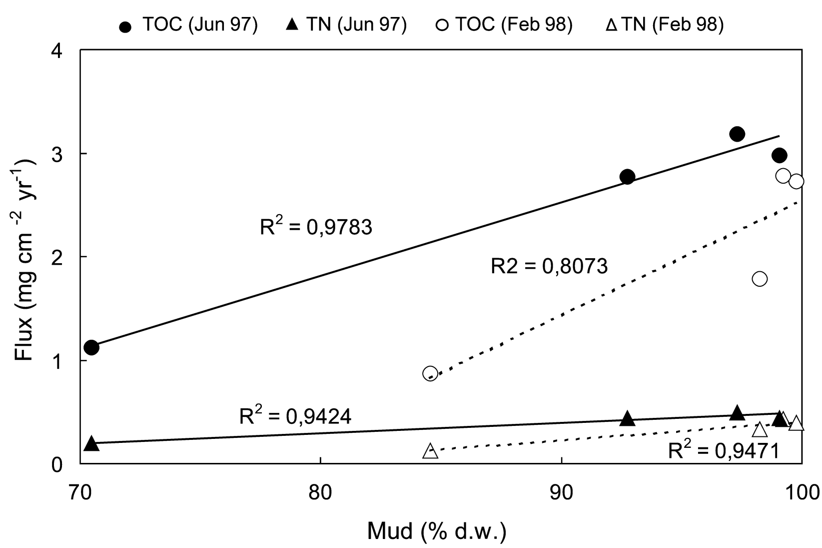
3.3. *TOC and TN fluxes*

TOC concentrations ranged from 0.4–1.8% d.w., according to different sampling sites, with an average value of about 1% d.w. for the whole dataset (Table 2). Values around 1.2–1.4% d.w. were found closer to the Po delta, then decreasing toward the open shelf, where a minimum of 0.5% d.w. was reached at site EF15. TN concentrations among cores were in the range of

Table 2. Mean total organic carbon (TOC) and total nitrogen (TN) concentrations, and C/N (as weight ratio) values in surface sediments (0–3 cm). The standard deviation (SD) is reported to 1 sigma.

Station	Water depth (m)	TOC (% d.w.)	SD (% d.w.)	TN (% d.w.)	SD (% d.w.)	C/N	SD
AB1	29	1.05	0.04	0.12	0.004	8.6	0.1
AB17	28	0.94	0.14	0.11	0.007	8.3	0.8
1S	23	1.27	0.05	0.17	0.013	7.4	0.5
2S	25	1.13	0.11	0.15	0.010	7.4	0.4
3S	16	0.74	0.19	0.10	0.021	7.2	1.2
CD2	26	1.27	0.22	0.16	0.026	7.9	0.8
CD7	19	0.99	0.34	0.16	0.019	6.2	1.8
CD9	30	0.96	0.06	0.14	0.005	6.8	0.5
CD10	32	1.06	0.14	0.17	0.014	6.4	0.5
CD12	36	0.86	0.03	0.15	0.029	5.9	1.1
EF11	27	0.97	0.05	0.14	0.010	6.9	0.6
EF12	30	1.21	0.34	0.19	0.078	6.8	1.1
EF13	33	0.99	0.09	0.19	0.058	5.7	1.4
EF14	36	0.96	0.07	0.14	0.023	6.9	0.5
EF15	39	0.51	0.04	0.08	0.006	6.3	0.2
EF21	32	1.04	0.02	0.15	0.003	6.9	0.2
EF22	25	1.01	0.13	0.14	0.020	7.2	0.2
EF23	20	1.37	0.10	0.19	0.017	7.1	0.6

0.08–0.19% d.w., with maximum values in samples taken from close to the river mouths, a minimum in the offshore sandy area and a mean value of 0.15% d.w. (Table 2). TOC/TN ratios (C/N), always expressed as weight ratio, range between 5.7 and 8.6 (Table 2) with a mean value of 7.0. TOC and TN fluxes at sampling locations followed the trend of MARs (Figure 3) and decrease in relation to the distance from the Po River mouths showing a close correlation with mud content (Figure 4), which is in turn mostly delivered by the Po River [10]. Seasonal (and



Correlation matrix

	Mud	TN	TOC
Mud	1,00000	0,72066	0,77323
TN	0,72066	1,00000	0,97260
TOC	0,77323	0,97260	1,00000

Significativity matrix

	Mud	TN	TOC
Mud	100	98,39705	99,25383
TN	98,39705	100	99,99979
TOC	99,25380	99,99979	100

Figure 4. Fluxes of total organic carbon (TOC) and total nitrogen (TN) versus mud content.

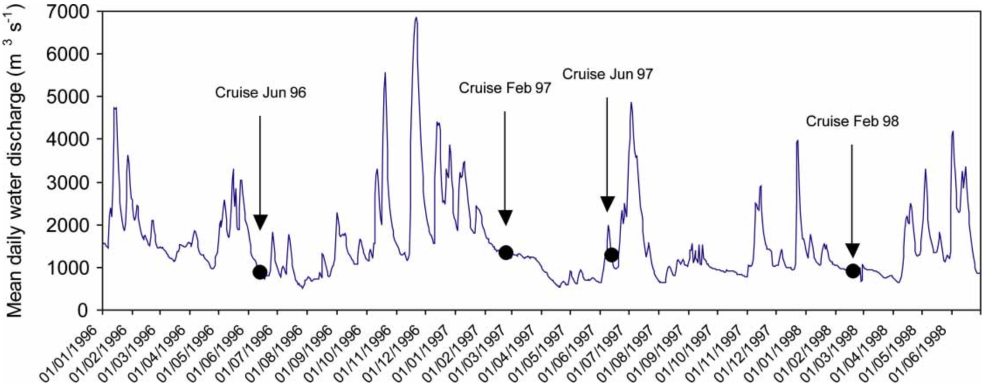


Figure 5. Mean daily water discharges of Po River at Pontelagoscuro gouge from 1 January 1996 to 30 June 1998, with location of cruise periods.

Table 3. Fluxes at the surface sediments of bulk sediment (MAR), TOC and TN at different locations in the investigated area.

Station	Water depth (m)	MAR ($g\,cm^{-2}\,yr^{-1}$)	TOC ($mgC\,cm^{-2}\,yr^{-1}$)	TN ($mgN\,cm^{-2}\,yr^{-1}$)
AB1	29	0.3*	2.8	0.3
AB17	28	0.2	2.3	0.3
1S	23	0.8	9.9	1.3
2S	25	0.4*	4.5	0.6
3S	16	0.2	1.7	0.2
CD2	26	0.8*	9.9	1.3
CD7	19	0.3	2.8	0.4
CD9	30	0.3	3.0	0.4
CD10	32	0.3	3.2	0.5
CD12	36	0.1	1.1	0.2
EF11	27	0.3	2.7	0.4
EF12	30	0.2	2.8	0.4
EF13	33	0.2	1.8	0.3
EF14	36	0.1	0.9	0.1
EF15	39	0.4	1.8	0.3
EF21	32	0.3*	3.1	0.5
EF22	25	0.7*	7.9	1.1
EF23	20	0.7	9.8	1.4

Note: *From [17].

interannual) differences between sedimentary fluxes (Figure 4) are considered to be due to different riverine regimes during sampling periods (Figure 5). TOC surface fluxes calculated for different locations (Table 3) show maximum values (above 8–9 $mg\,cm^{-2}\,yr^{-1}$) closer to the river mouths, a central sector with values of around 3–5 $mg\,cm^{-2}\,yr^{-1}$ and values of less than 2 $mg\,cm^{-2}\,yr^{-1}$ at offshore stations. The TN mean fluxes range from 0.1–1.4 $mg\,cm^{-2}\,yr^{-1}$, with an average value of 0.6 $mg\,cm^{-2}\,yr^{-1}$. Values above 1 $mg\,cm^{-2}\,yr^{-1}$ characterise the river influenced areas, whereas values below 0.6 are common in the intermediate area. Minimum values correspond to areas at water depths of about -17 m and -28 m. C/N surface values generally decrease with increasing water depth (Figure 6), suggesting a limited input to the outer shelf of terrestrial OM, which is marked by high C/N ratio due to the presence of refractory organic substances such as lignin [29].

The shelf in front of the Po prodelta records the stronger gradient of MAR of the whole Adriatic Sea from the highest, close to river mouths, to minimum values, toward the relict sands [17].

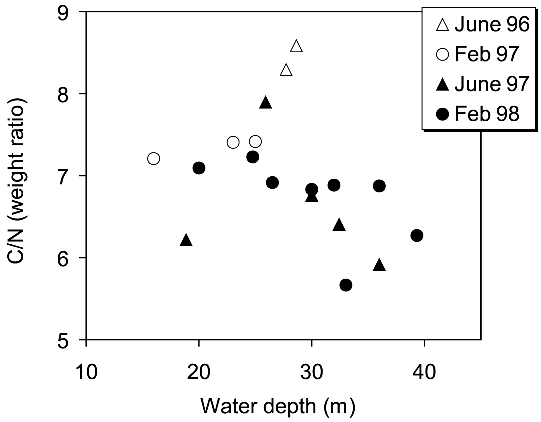


Figure 6. Behaviour of C/N weight ratio in surface sediments with increasing distance from the coast.

Since the Po River represents the major riverine source of OM as well as of muddy sediments of the Adriatic Sea [10,24], this study area is used as representative of the main OM depositional environment of the Adriatic shelf, and the simple methodology proposed to estimate TOC and TN fluxes and stocks in this area for budgeting purposes could be generally applied to the whole Adriatic and to other shelf contexts both within and outside the Mediterranean Sea.

To this aim, three sub-zones were distinguished (Figure 7) on the basis of: different grain size distributions (A = high fraction of mud (>90%) and B = sand (>10%)) and influence of Po River

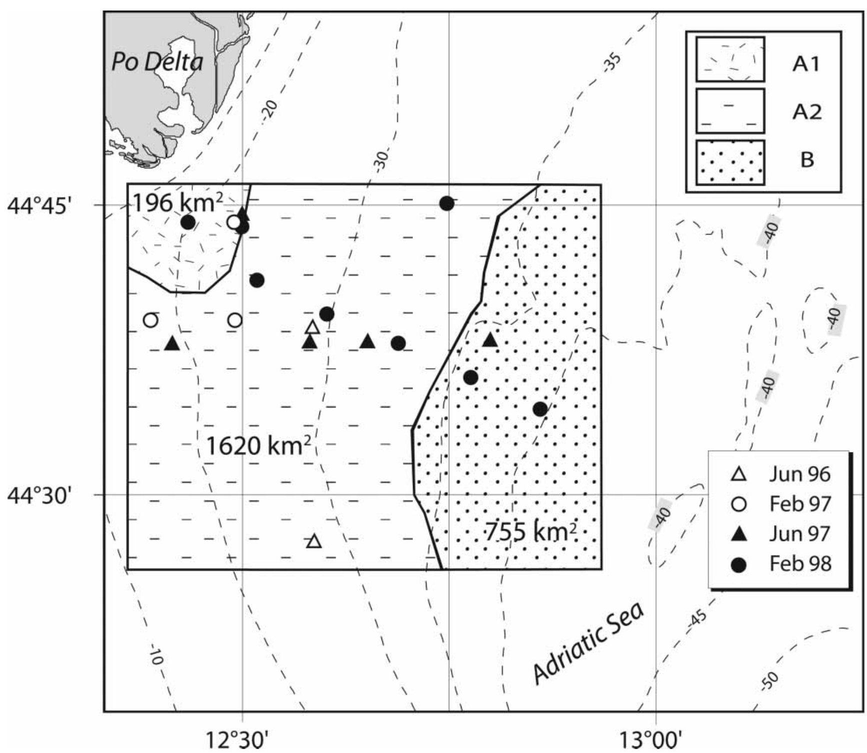


Figure 7. Areal extension of zones A1 (muddy sediments influenced by direct Po River discharge), A2 (muddy sediments influenced by basinal circulation), and B (sandy-muddy sediments corresponding to relict sands).

discharge (A1 = high (>0.7 g cm^{-2} yr^{-1}) and A2 = low (<0.7 g cm^{-2} yr^{-1}) MAR), in order to take into account different sedimentological regimes. The extension of and limits between A1, A2 and B zones were chosen on the base of the sedimentary facies recognised in this work and of the calculated MARs after cross-checking with the distribution obtained by [17] and with the sedimentological map in [30].

The surface area of each zone was multiplied by its average TOC and TN flux to obtain an estimate of their fluxes over the whole investigated area. Moreover, the estimate of the total annual amount of TOC and TN accumulated in surface sediments was integrated over the same area. Maximum and minimum fluxes were also considered to give an estimate even under different conditions of sedimentary regime: assuming the highest fluxes as corresponding to a 'flooding' season and the lowest to a 'dry' season. The concentrations of TOC and TN for station AB1, 2S, EF21, EF22 and CD2 were calculated on the base of the MAR derived by [17], since not available in the present study.

TOC yearly fluxes (tC km^{-2} yr^{-1}) for the three zones are on average 91.1 for A1, 27.9 for A2 and 12.6 for B. TN values (tN km^{-2} yr^{-1}) are 12.4 in A1, 4.0 in A2 and 2.0 in B (Table 4). These data correspond to a total mean yearly contribution to surface sediments of TOC and TN, respectively, in the three zones of 17.9 and 2.4 × 10^3 t yr^{-1} for the area directly influenced by river runoff (A1), 45.2 and 6.5 × 10^3 t yr^{-1} for the intermediate area (A2) and 9.5 and 1.5 × 10^3 t yr^{-1} for the offshore area (B) (Table 4 and Figure 8). Total amounts of TOC (×10^3 tC) and TN (×10^3 tN) present in surface sediments (0–3 cm) of the investigated area are 47 and 6 for zone A1, 292 and 45 for zone A2, and 159 and 26 for offshore locations, respectively (Table 4).

Table 4. Minimum, mean and maximum fluxes to different sea floor zones and stocks in surface sediments of the investigated area.

Zone	A1	A2	B
TOC (t km^{-2} yr^{-1})			
Min	72.9	17.1	8.7
Mean	91.1	27.9	12.6
Max	99.2	45.3	17.9
TN (t km^{-2} yr^{-1})			
Min	10.1	2.4	1.3
Mean	12.4	4.0	2.0
Max	13.8	6.1	2.9
TOC (×10^3 tC yr^{-1})			
Min	14.3	27.7	6.6
Mean	17.9	45.2	9.5
Max	19.4	73.4	13.5
TN (×10^3 tN yr^{-1})			
Min	2.0	3.9	1.0
Mean	2.4	6.5	1.5
Max	2.7	9.9	2.2
TOC (×10^3 t)			
Min	27	110	148
Mean	47	292	159
Max	69	430	170
TN (×10^3 t)			
Min	4	13	24
Mean	6	45	26
Max	10	84	28

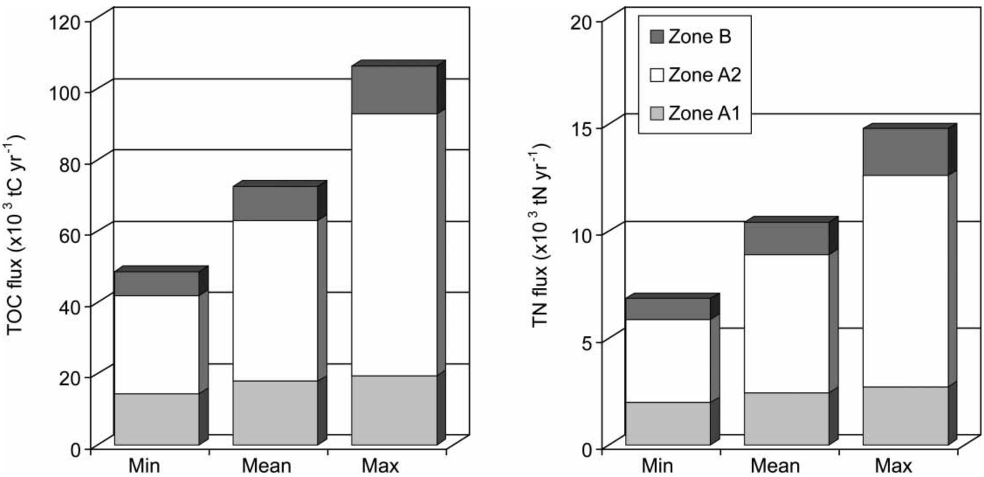


Figure 8. Contribution of zones A1, A2 and B in minimum, mean and maximum TOC and TN yearly flux regimes to the sea floor (note the different scales).

4. Discussion

All the parameters studied show strong land-sea gradients related to riverine inputs and accumulation of muddy organic-rich sediments in the prodelta. The direct links between fluxes of TOC and TN and MAR of bulk sediment, particularly of muddy sediments, found for the study samples allow a close correlation between distribution and accumulation of these elements with sedimentary characteristics of surface sediments. This seems to be an inherited characteristic from the Po riverine environment, where [10] found that the preferential transport of organic carbon in riverine sediments close to river mouths is in the particulate phase which is, in turn, strictly correlated with total suspended matter behaviour. The lack of significant processing or transformation of riverborne material within the Po estuarine system [10,31], as a result of the short residence time of waters, do not seem to significantly alter this characteristic in the shelf domain.

The presence of a two-step distribution in the MAR suggests a double sedimentary contribution to this area: a higher, inner one, directly from the Po River, where MAR values reach their maximum ($0.8\,g\,cm^{-2}\,yr^{-1}$), and the lower ($0.3\,g\,cm^{-2}\,yr^{-}1$), outer one, marking the transport pathway of sediments from the northernmost Adriatic shelf to the central basin [16,24].

A comparison with TOC concentrations of similar Mediterranean and Atlantic settings (Table 5) indicate that TOC content does not strongly vary among continental shelves, with a typical low value of 0.5% d.w. and the highest values, >0.8% d.w., being usually characteristic of areas close to river mouths. This common behaviour suggests that except for inshore locations, the role of shelves as sinks for TOC is sometimes overestimated [32]. Much higher values found off the Po River mouths, up to twice that figure, suggest that only locally, where hydrological and sedimentological conditions are favourable for organic matter accumulation, considerable amounts of TOC can be buried. The importance of the Po River as the main OM contributor to the whole Adriatic as well as to the entire Mediterranean, was already pointed out by [10] and [33].

The C/N weight ratios found in the study area (5.7–8.6) are similar to those of [10] for Po River particulate OM which show mean values of around 7.1 and that of [8] of around 6.6 for riverine, tidal and coastal suspended matter. These data demonstrate an important contribution, if not a seasonal dominance at low riverine regime [31], of freshwater OM of continental origin (e.g. freshwater phytoplankton) to riverine suspended matter. Since both freshwater and marine OM in this area could be characterised by the same C/N ratio [34], and having no available data

Table 5. TOC concentrations in surface sediments of the Mediterranean region and Atlantic continental margins (N = North, E = East, W = West).

Geographic location	TOC (% d.w.)	Reference
Gulf of Lions	0.5	[38]
Gulf of Lions (prodeltaic Rhone)	1.0–2.0	[39]
Gulf of Lions (sandy shelf)	0.3–0.50	[39]
Gulf of Lions (muddy shelf)	0.5–0.8	[39]
Gulf of Lions (slope)	0.4–1.0	[39]
N Cretan shelf	0.5–0.7	[40]
Iberian Atlantic continental shelf (depocenter)	3–4.5	[41]
Iberian Atlantic continental shelf (other)	<1	[41]
E Aegean Sea	0.4–3.0	[42]
NW European shelves	0.2–0.7	[43]
W Atlantic shelf	0.9–1.4	[44]
W Atlantic shelf (inshore)	1.6–2.9	[45]
W Atlantic shelf (offshore)	0.1–1.6	[45]
Mississippi River delta	1.2	[46]
N Adriatic Sea	0.3–1.9	[35]

about the δ^{13}C signature for the studied samples, it was not possible to precisely detect the two sources of OM in surface sediments. Nevertheless, a general criterion was used to attribute the source of OM deposited on the shelf in the study area based on recent study [34]: the sedimentary OM deposited under the direct influence of riverine sedimentary input, although present at lower concentrations, reflects the composition of the latter, at least in surface sediments, as also found by [33]. On the other hand, the shelf areas that are far from this direct input, and characterised by low MAR, are dominated by authochtonous OM derived from local marine phytoplankton blooms, as also found by [35].

The present estimate of TOC fluxes seems to confirm this hypothesis. In fact, TOC fluxes calculated for the mud-dominated area (17.1–99.2 tC km^{-2} yr^{-1}) show values that are in good agreement with previous data derived from moored sediment trap studies in the area [14,36]. These devices are used to collect particulate sediments transported along the water column as a result of different processes: vertical fluxes from the water column, advection and resuspension as found by [14] for TOC measured in surface sediments of the NW Adriatic. The calculated fluxes are otherwise higher compared to those found in the same zone using a drifting sediment trap [12], which is used to collect sediments transported within a particular water mass by following it for a certain distance, thus mostly avoiding the contribution of resuspension and lateral advection. On the other hand, they are again similar in the outer shelf stations investigated by the same authors, where they match the primary TOC flux found for the Northern Adriatic by [19] that is assumed to represent the TOC vertical flux derived only by *in situ* production, even though some minor influence of the bottom nepheloid layer was inferred. To summarise, the sedimentary TOC fluxes measured in the present study suggest that in the inshore muddy area southeast of the Po River delta, advection of riverine material and resuspension processes are responsible for most of the TOC flux, whereas in the offshore area the measured sedimentary TOC fluxes are due mostly to the vertical flux of local production.

Since OM transport to the coastal area is strictly connected to the riverine input, as seen above, with a strong influence upon the productivity cycles of the Adriatic inner shelf, the pattern of OM sedimentation in the three zones can be useful to evaluate general future scenarios of marine productivity in the NW Adriatic shelf under changing river flow regimes.

The relative contribution of the different shelf sectors to the whole TOC and TN flux of the area was then estimated, taking into account 'mean' conditions. 'Minimum' and 'maximum' flux conditions were also analysed in order to evaluate possible scenarios of different OM input

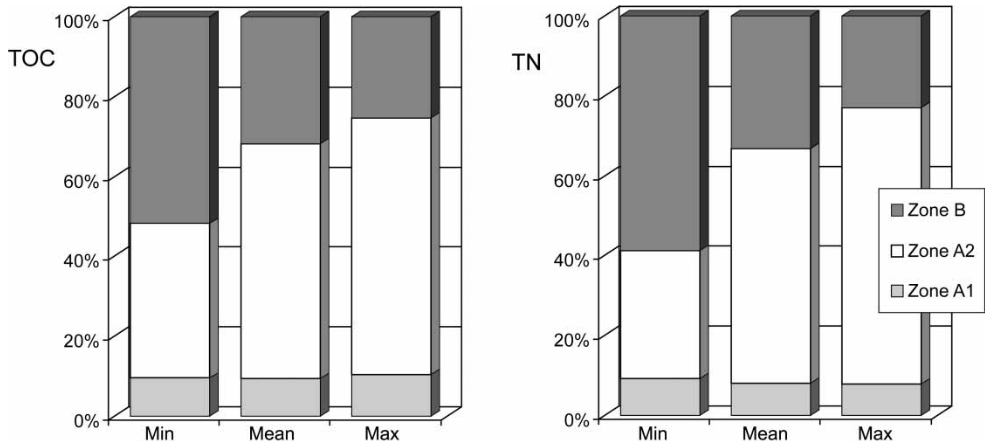


Figure 9. Comparison of relative contribution of zones A1, A2 and B in TOC and TN stocks present in surface sediments according to minimum, mean and maximum fluxes.

regimes (Figure 8). The inshore area close to river mouths particularly contributes TOC and TN during the low flux period, with values that represent around 29% of the yearly flux, whereas the opposite occurs for the intermediate zone which contributes 69% and 67%, respectively, at maximum flux. Offshore sediments are characterised by rather constant contributions of 13% and 14% respectively, under all conditions. This means that in a low flow regime, as over the last few years, the area influenced will be only zone A1 with little influence on zone A2, thus probably restricting algal blooms and productivity to very nearshore areas as a result of the limited spreading of fluvial plumes, and thus nutrients, across the shelf due to their low transport capacity of both water and sediment. In a high river flow regime, on the other hand, all the mud-dominated shelf, that is zone A1 and A2, will be involved, with a larger and more widespread chance of phytoplankton blooming as a result of the wider expansion of plumes across the shelf. On the contrary, the offshore area seems to remain untouched in both cases, probably as a result of the influence of the western Adriatic coastal current, which almost always prevents a consistent and persistent expansion of river plumes east- and southeastward [37].

As regarding TOC and TN stocks (Figure 9), zone A1 contributes under all conditions 10% and 8% of the total amount of TOC and TN, respectively, with an extension of 8% of the total shelf area considered, whereas the offshore area, with an extension less than one third of the total, accounts for the highest percentages (52% for TOC and 59% for TN), when considering minimum flux values. The intermediate zone, extending up to 63% of the total, is much more important in the presence of average (59% for both TOC and TN) to maximum (64% for TOC and 69% for TN) flux regimes. Looking at absolute values of TOC and TN stocks (Table 4), offshore sediments contain rather the same amount of OM in all flux scenarios, suggesting that this area will not be particularly influenced by changes in riverine regimes that remain within a range similar to present conditions. On the other hand, inshore areas closer to river mouths (Zone A1) will increase their stocks of 2.5 times with a shift from minimum to maximum flux conditions. For the same shift, the intermediate shelf (Zone A2) will increase its stocks by 4 times for TOC and 6.5 times for TN. These estimates are only indicative since they do not take into account the likely shift of muddy sedimentary areas offshore that will take place in response to an increase of fluvial regimes. This aspect cannot be evaluated here but should be further investigated, since changes in sea floor bathymetry and coastal morphology will certainly affect the hydrodynamics and depositional processes of the shallow NW Adriatic basin.

5. Conclusions

Although limited, this area was investigated because it is a very important site for the temporary sequestration and preservation of OM over the Adriatic shelf. Thus changes in its sedimentological regime could alter OM cycling in this coastal marine ecosystem.

^{210}Pb activity-depth profiles, together with measurements of TOC and TN concentrations in a limited number of surface samples in shelf sediments allowed the estimation of TOC and TN fluxes to the sea floor and stocks within surface sediments for each individual location.

Through the relationship of these data with the distribution of surface sediments and MARs, together reflecting different sedimentological regimes, a simplified methodology is proposed which allows data extrapolation to the whole area considered.

This was possible through careful consideration of the spatial distribution of surface sediment in the study area deriving from averaged signals from various processes occurring in the water column over very different timescales, including river inputs, thermohaline circulation and local scale hydrodynamics driven by shelf geomorphology.

The data provided here can, in fact, contribute towards an evaluation of the total reservoir of OM accumulated within the surface shelf sediments, which could be potentially available for remineralisation and recycling.

A detailed mapping of these deposits over the whole shelf could now be envisaged for integrated coastal management by local administrations, especially with regard to the displacement of bottom sediments and the evaluation of its environmental impact.

What is still poorly known for this area is the quality of OM accumulated in the shelf sediments and this is crucial for evaluating its effective role in the biogeochemical cycles of the benthic ecosystem and, therefore, labile vs. refractory nature of the sedimentary OM in this area should be further investigated.

Finally, although the methodology was applied here over a specific, very important site for the temporary sequestration and preservation of OM on the Northern Adriatic shelf, it may be applied in a general way using linked data, together with careful considerations about the main sedimentary environments, for any shallow continental shelves with important river input.

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