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ARTICLE

Fluxes of particulate matter, carbonates, organic carbon and nitrogen in the northern Adriatic continental shelf: A synthesis overview

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ABSTRACT

Time series of composition and fluxes of settling particles in the marine environment, obtained by sediment traps, contribute to define the main processes driving the dynamics of particulate matter and of the time/space variability of benthic-pelagic exchanges. With this aim, the composition and seasonal and annual fluxes of settling matter, obtained from different projects and from published papers, at 13 sites of the Northern Adriatic shelf were estimated. The mean yearly particulate fluxes varied from 2763 to 14447 g m⁻² y⁻¹, from 66 to 236 gC m⁻² y⁻¹ for organic carbon (OC) flux, from 861 to 7525 g m⁻² y⁻¹ for carbonates and from 12 to 42 gN m⁻² y⁻¹ for nitrogen (N). The fluxes were characterized by high seasonal variations with marked increase in autumn or in winter with respect to spring or summer. The sink of particles occurs in relatively short episodes as about 50% of annual particle flux settles in less than 1-2 months in the western coastal area. This seasonality can be related to the riverine discharges, primary production and wind regimes of the basin. Utilizing the N/OC ratio as an index for discriminating the different origin of organic matter (*i.e.*, resuspended/riverine and autochthonous), the primary marine carbon flux was estimated to range from 10 to 28% of the OC fluxes and accounted for 8-40% of the primary production, depending on the site. Then, due to the shallow waters of the basin and to the relevant riverine inputs, the total fluxes near the sea bottom were highly dependent on resuspension and advective transport processes. The important contribution of these last processes as source of organic matter is suggested also by the comparison between fluxes determined by sediment traps with mass accumulation rates (MAR) in sediments, derived from radionuclide measurements. Indeed, the fraction of OC fluxes which is not buried in the sediment is sufficient to support the benthic respiration processes.

Key words: Organic carbon; carbonates; nitrogen; settling particulate matter; Adriatic Sea; continental shelf.

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INTRODUCTION

The continental shelves are characterised by large amounts of suspended particulate matter, derived from various sources as the autochthonous production, rivers and terrestrial runoff. The Northern Adriatic Sea (NAd) shelf receives large riverine inputs of dissolved organic carbon, nutrients, suspended solids and associated carbonates, organic carbon, nitrogen and phosphorus (Pettine *et al.*, 1998; Ludwig *et al.*, 2009; Cozzi and Giani, 2011; Cozzi *et al.*, 2012). As a result, the NAd is one of the most productive sectors of the entire Mediterranean Sea (D'Ortenzio and Ribera, 2009; Lazzari *et al.*, 2012).

In the last decade, a shift toward a general oligotrophication of the NAd has been reported (Mozetić *et al.*, 2010; Giani *et al.*, 2012; Colella *et al.*, 2016) along with an increasing trend of water acidification (Luchetta *et al.*, 2010). Since these phenomena are expected to exacerbate in the near future and expand down to the sea bottom, a

better comprehension of the benthic-pelagic coupling processes in the NAd and, in particular, the quantification of the downward particle fluxes is crucial for understanding ecosystem changes in this shallow continental shelf.

The concentration and composition of suspended particulate matter and the related downward fluxes in the NAd generally show a large spatial and temporal variability (Giani *et al.*, 2001). The typical environmental conditions (*e.g.*, shallow depth not exceeding 50 m, large riverine inputs, cyclonic circulation) and the seasonal cycle determine the persistence of rather different biogeochemical processes in the water column and at the water-sediment interface (Ogrinc *et al.*, 2003; Solidoro *et al.*, 2009).

The most common methodology for estimating the downward flux of suspended particulate matter uses sediment traps. Even if the sediment traps deployed in shallow waters are subject to different bias due to hydrodynamic effects of the flow over the trap mouth and to the presence of fouling and swimmers (Buessler *et al.*, 2007), these instruments remain a solid tool to date for

estimating the particle flux from the water column to the sea floor and its temporal variability.

Due to the cyclonic circulation and to the geographic setting of river mouths, decreasing west-east and coast-offshore gradients in suspended matter concentrations, particulate organic carbon concentrations and plankton primary production are generally observed in the NAd (Gilmartin and Revelante, 1983; Smodlaka, 1986, Giani *et al.*, 2005). Thus, our analyses considered the data obtained from a selection of sites located in three different sectors of the Northern Adriatic Sea: western coastal, eastern coastal, and offshore sectors (Fig. 1). The variables used for the analysis included the total mass flux as well as carbon, nitrogen and carbonates fluxes. We searched for and collated a large data set of downward particle fluxes measured using sediment traps in the NAd. These data, extracted from published and grey literature and partly still unpublished, were analysed to ascertain spatio-temporal scales of variability in the benthic-pelagic exchanges of this shallow area of the Adriatic Sea.

In shallow basins such as the NAd the suspended particle dynamics typically depends not only upon the allochthonous inputs, local primary production and degradation/remineralization processes, but are also largely influenced by sediment resuspension and near-bottom advective transport induced by winds and waves (Faganeli, 1989; Puškaric *et al.*, 1992; Giani *et al.*, 2001; Boldrin *et al.*, 2009). Therefore, in this study the downward fluxes of organic carbon were compared with primary production in the different areas, with an estimation of primary marine fluxes of organic carbon in this basin.

To evaluate the fraction of the settling particulate organic matter, which accumulates on the seabed, the particle flux was compared with the mass accumulation rates (MAR), allowing to estimate the organic carbon potentially available for consumption by benthic organisms or chemical oxidation.

METHODS

Study area

The NAd is subject to strong seasonal variations: in winter, because of pronounced vertical instability of the water column associated with seasonal wind mixing, Po river freshwaters are mostly confined along the NAd western coast, whereas during the period of stratification the Po river plume can extend eastwards toward the Istria peninsula (Franco *et al.*, 1992) as response to the intensity of the river discharge and to the Bora wind (Mauri *et al.*, 2007). In the northern Adriatic Sea, major primary production variations occur along the trophic gradient due to nutrient rich freshwater discharges. The range of phytoplankton production is considerable: annual values range between 60 and 90 g C m⁻² yr⁻¹ and between 130 and 210 g C m⁻² yr⁻¹ for offshore and coastal waters, respectively (Pugnetti *et al.*, 2006 and references therein).

Fluvial sediments are initially deposited on the prodelta areas with an efficient transport along the shelf (Coreggiari *et al.*, 2001), where fine sediments are deposited mainly in a belt parallel to the western coast which get wider south of the Po prodelta (Brambati *et al.*,

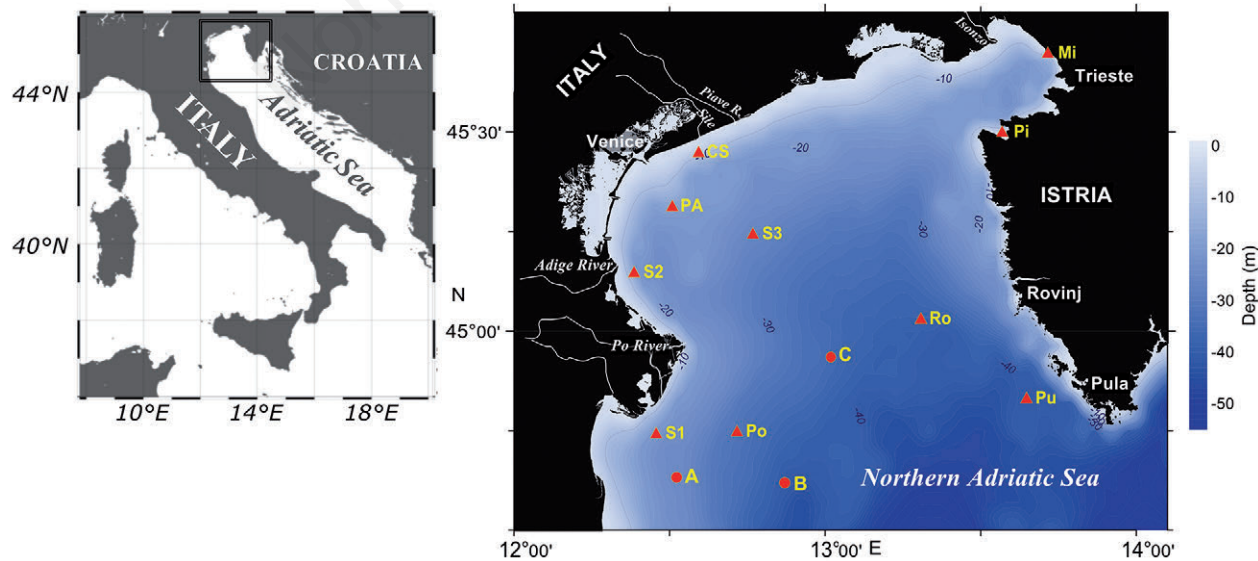


Fig. 1. Location of sediment traps deployment. Triangles indicate moored trap positions, whereas the circles represent the central position of drifting trap deployments.

1983). In NAd shallow waters the strong hydrodynamic forcing, mainly determined by NE and SE winds, can promote sediment resuspension (Wang and Pinardi, 2002; Fox *et al.*, 2004; Fain *et al.*, 2007; Boldrin *et al.*, 2009).

Mass accumulation rates in the NAd range from 0.06 to 6.6 g cm⁻² y⁻¹ (corresponding to 0.6 to 66 kg m⁻² y⁻¹) with the highest values observed in the Po and Isonzo river prodeltas (Frignani *et al.*, 2005).

Site location and sediment traps

The sediment trap data used in this work was collected in the framework of different research projects spanning from 1982 to 2010. We considered 10 sites with moored trap and 3 with drifting traps located in the NAd sites shown in Fig. 1, the metadata describing the trap deployments at the investigated sites are reported in Tab. 1.

In all the sites, the moored and the drifting traps were sited few meters above the bottom (bottom-traps). In 5 sites for moored and 2 for drifting traps an additional

upper trap was positioned in the middle of the water column. Part of sediment-trap data have been previously published (Faganeli, 1989; Puškaric *et al.*, 1992; Miquel *et al.*, 1999; Giani *et al.*, 2001; Turchetto *et al.*, 2002), but here they have been reconsidered, re-elaborated and further discussed. Other data, collected by the authors but only partially published (Boldrin *et al.*, 2006; Giani *et al.*, 2003b) or unpublished (Boldrin and De Lazzari, personal communication), have been utilised in this work.

The sites with moored traps can be geographically divided in western (sites PA, S1, S2, PO, CS), eastern (sites MI, PI, PU) and offshore (sites RO, S3) areas. Whereas, the drifting traps were located in western (site A) and offshore (sites B, C) areas.

A total of 374 moored trap samples were considered (327 for bottom-traps and 47 for upper-traps), 219 in western, 73 in the eastern and 82 in offshore areas. Overall, the sampled periods amounted to 3710 days for bottom-traps (western: 1598; eastern: 1588; offshore: 524

Tab. 1. Site geographic settings and sediment trap general information.

Area	Site	Lat. N	Long. E	Bottom depth (m)	Distance from bottom (m)	Sediment trap features			Deployment period	Sampling frequency (days)	Ref.
						Type	Surface (m ²)	Height/Width (H/W)			
<i>Moored traps</i>											
West	PA	45° 18.93'	12° 30.53'	16	2	Hydro-Bios Multi Sediment Trap	0.015	4	Several not continuous periods from 1992 to 1995	4 - 99	(1)
	S2	45° 09.00'	12° 23.15'	20	2	Technicap PPS 4/3	0.05	4	Apr-Nov 1995; Feb-Jul 1996	3 - 7	(2)
	S1	44° 44.70'	12° 27.42'	21	2, 11 (*)	Technicap PPS 4/3	0.05	4	Sep 1995-Jan 1996	2 - 4	(2)
	CS	45° 27.08'	12° 35.60'	14.5	3	Technicap PPS 4/3	0.05	4	Dec 2003-Jan 2005 with a few monthly gaps; Jul-Oct2009; Mar-May2010	6-8	(3) (4)
	PO	44° 44.00'	12° 43.00'	32	2, 12 (*)	4 PVC tubes	0.004 each	8	Jan-May 1989	20 - 30	(5)
East	MI	45° 42.02'	13° 42.93'	16	1.5	Technicap PPS 4/3	0.05	4	Jun 1998-Jul 2002	1 - 7	(6)
	PU	44° 49.00'	13° 38.30'	37	2, 12 (*)	4 PVC tubes	0.004 each	8	Jun-Dec 1989	20 - 30	(5)
	PI	45° 31.00'	13° 33.50'	16	1	6 plastic cylinders	0.003 each	5	Jul-Aug 1982; Jan-Feb 1983; Sep 1985-Jun 1986	1-3; ~15	(7)
Offshore	S3	45° 14.75'	12° 46.06'	29	4, 14 (*)	4 cylindrical tubes	0.008 each	4.5	Jun 1992-Oct 1996	4 - 96	(1) (2)
	RO	45° 02.40'	13° 18.30'	37	2, 12 (*)	4 PVC tubes	0.004 each	8	Nov 1988-Dec1989	20 - 30	(5)
<i>Drifting traps</i>											
West	A	from 44° 35.0' to 44°41.0' **	from 12° 22.1' to 12°40.4' **	13-30	5-6, 10-24 (*)	2 cone shaped	0.56 each	na	Jun 1996; Feb 1997; Jun 1997; Feb 1998	0.5 - 2	(8)
	Offshore	B	from 44° 31.2' to 44°43.9' **	from 12° 48.6' to 12°55.9' **	33-41	7-11, 30-34 (*)	2 cone shaped	0.56 each	na	Jun 1996; Feb 1997; Jun 1997; Feb 1998	0.5 - 2
C		44° 56.1'	13° 01.1'	35	8	Technicap PPS5/2	1.0	1.6	Jul 1993	1 - 2	(9)

*Distance from bottom for lower and upper traps; ** coordinates of the area of the drifting-trap deployment-

References

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|----------------------------------|--|------------------------------------|
| (1) Boldrin, unpublished data | (4) Boldrin and De Lazzari, unpublished data | (7) Faganeli, 1989 |
| (2) Giani <i>et al.</i> , 2001 | (5) Puškaric <i>et al.</i> , 1992 | (8) Turchetto <i>et al.</i> , 2002 |
| (3) Boldrin <i>et al.</i> , 2006 | (6) Giani <i>et al.</i> , 2003a | (9) Miquel <i>et al.</i> , 1999 |

days) and to 1104 days for the upper-traps (split up in: western 231, eastern 175 and offshore 698 days).

The western sites S1 and PO are located in front of the Po river delta, whereas S2 is influenced by Adige river. These rivers represent the main freshwater loads in the NAd (average discharges $1569 \text{ m}^3 \text{ s}^{-1}$ and $200 \text{ m}^3 \text{ s}^{-1}$, respectively; Cozzi and Giani, 2011). Minor rivers (Sile and Piave: $41 \text{ m}^3 \text{ s}^{-1}$ and $54 \text{ m}^3 \text{ s}^{-1}$ average discharges, respectively; Autorità di bacino dell'Adige, 2009a and 2009b, ARPAV, 2018, Verri *et al.*, 2018) influence the CS site. The site PA, located at about 15 km from venetian coast, is considered in the western area. The easternmost site (MI), in the gulf of Trieste, is affected by the Isonzo River discharge (average $82 \text{ m}^3 \text{ s}^{-1}$; Cozzi *et al.*, 2012), only during high floods. Moreover, in the eastern area we considered also other two sites (Fig. 1), one located in front of Pula (site PU; Puškaric *et al.*, 1992), and the second in the bay of Piran, in the south-eastern part of Trieste gulf (site PI), and reported earlier by Faganeli (1989).

The site S3, located at about 40 km east of Venetian coast (Giani *et al.*, 2001), and the site RO, 25 km off Rovinj (Puškaric *et al.*, 1992), are considered as representative of the offshore environment. Furthermore, drifting sediment trap located inside the Po River plume (trap A) and outside of it (traps B and C) were considered. These data were obtained from the studies carried out by Turchetto and co-workers (2002) in June 1996, June 1997, February 1997, February 1998 and by Miquel and co-workers (1999) in July 1993. More information on sites and details on deployments are reported in Tab. 1 and the localisation is shown in the Fig. 1.

Different designs of the traps were used in the deployments and could affect the efficiency of the sampling device, not easy to quantify (for a complete analysis of the biases in the sediment traps use see USGOFS, 1989). However, all the traps used were cylindrical-conical type with height to width ratios (H/W) generally ≥ 4 , required for good collection efficiency under most environmental conditions (Buesseler *et al.*, 2007).

The sampling frequency varied from 1 to 91 days. The difference in sampling timing introduces potential biases due to the fouling of the traps during prolonged absence of maintenance, though the longer sampling concerned the traps located in the offshore waters.

Treatment of sediment trap samples

The sample treatment and the analytical methods were similar in all the experiments. Collection bottles were filled with 4% formaldehyde solution of seawater collected at the same depth of the traps, buffered at pH 8.2 and filtered on a $0.4 \mu\text{m}$ Nuclepore filter (Miquel *et al.*, 1994). In the open cylindrical traps used in S3 and partially in PA, to minimize diffusive loss of poison during deployment and better retain the collected samples,

the sampling bottles, screwed at the base of the tube, were filled with 4% formaldehyde solution of a 50 g L^{-1} NaCl solution (USGOFS, 1989).

Samples treatment followed the methodology described in Heussner *et al.*, 1990. The “swimmers”, metazoan zooplankton that actively enter sediment traps and that do not contribute to the passive flux (Buesseler, 2007; Rizzo *et al.*, 2009; Miquel *et al.*, 2011), were removed manually under a dissecting microscope. To determine total mass flux (TMF) the gravimetric method was used, whereas organic carbon (OC), total carbon (TC) and total nitrogen (N) contents were determined using high temperature gas-chromatographic CHN elemental analysers. Organic carbon was measured after elimination of carbonates by acidification (Hedges, 1984). Inorganic carbon content was calculated as the difference between TC and OC; the carbonate content was calculated by assuming all inorganic carbon was CaCO_3 , using the ratio between molecular weights of CaCO_3 and C of 8.33.

Sediment-trap data analysis

The seasonal fluxes were calculated as time-weighted means. To obtain the time-weighted flux (F_{itw}), each of individual flux measurements (F_i) was weighted by the duration of collection (number of days - d_i) as: $F_{itw} = \frac{\sum(F_i d_i)}{\sum(d_i)}$. This time-weighted mean gives the best (*i.e.*, the least biased) estimate for discontinuous measurements and is used for the determination of seasonal values. Then the annual mean was calculated from the seasonal values multiplied for the season duration. The seasonal periods were defined as: winter=January-February-March; spring=April-May-June; summer=July-August-September; autumn=October-November-December.

The comparison of differences between sites and seasons was performed using the Kruskal Wallis non-parametric test. The site S1 was excluded as the data for spring were lacking. The software statistical package Statistica™, ver. 6 (StatSoft®, USA) was used.

Additional data

The flux data were integrated with available information on the composition of particulate matter and primary production of the water column and sediment properties of the sites.

The carbon export was estimated as the ratio between the OC primary downward flux and the carbon produced by phytoplankton. Annual primary production data were obtained by previous studies carried out at S1, S2 and S3 sites (Giani *et al.*, 2001), at CS site (Boldrin *et al.*, 2006) and in the gulf of Trieste (Fonda Umani *et al.*, 2007).

The elemental composition of the top first cm of sediments (0-1 cm layer) at the several stations considered was obtained from the literature and final project reports

(Faganeli *et al.*, 1991; Ogorelec *et al.*, 1991; Giani *et al.*, 1997; De Lazzari *et al.*, 2006), whereas the data for site PA are from Boldrin (unpublished data).

The fraction of sinking carbon that definitely settles on the seabed was estimated on the basis of the carbon sedimentation rates (OC_{sed}). In the absence of direct measurements in our experimental sites, we used the nearest mass accumulation rate (MAR) value measured on the basis of activity–depth profiles of ^{210}Pb and reported in the literature by Frignani *et al.* (2005) and the OC content determined in the sediments at the study sites. For the site RO the mass accumulation (MAR) rates were estimated from sediment accumulation rates (SAR) on the basis of a water content of 29.9% and a density of 2.69 g cm^{-3} .

RESULTS AND DISCUSSION

Downward fluxes and composition of settling matter

The averages of TMF and elemental composition of settling particulate matter at all the investigated sites are reported in Tab. 2.

Overall, TMF data for bottom-traps ranged between 0.05 and $293.50 \text{ g m}^{-2} \text{ d}^{-1}$, with an average of $22.35 \pm 40.87 \text{ g m}^{-2} \text{ d}^{-1}$. The downward fluxes follow the spatial trend of suspended particulate matter concentrations typically observed in the NAd (Giani *et al.*, 2003a; Boldrin *et al.*, 2005), with a clear ($p < 0.01$, Mann-Whitney U test) increase of TMF in the coastal-western area with respect to the eastern coast and the offshore areas. The western coastal sites showed higher fluxes (mean value: $30.96 \pm 49.60 \text{ g m}^{-2} \text{ d}^{-1}$), whereas the eastern sites flux was on average reduced to about 1/3 ($11.00 \pm 15.88 \text{ g m}^{-2} \text{ d}^{-1}$) and to 1/4 in the offshore sites ($7.19 \pm 9.16 \text{ g m}^{-2} \text{ d}^{-1}$), but the differences between these last two areas were not significant.

TMF in the upper-traps showed the same spatial trend of the bottom-traps, but the fluxes were about 5 time lower (average $4.63 \pm 5.79 \text{ g m}^{-2} \text{ d}^{-1}$; in the western area $7.25 \pm 7.24 \text{ g m}^{-2} \text{ d}^{-1}$; in the eastern sites $2.18 \pm 0.58 \text{ g m}^{-2} \text{ d}^{-1}$; offshore $2.09 \pm 2.13 \text{ g m}^{-2} \text{ d}^{-1}$).

The drifting-trap mass fluxes were around $0.51 \pm 0.48 \text{ g m}^{-2} \text{ d}^{-1}$, about 3% of the moored bottom-ones in the western coastal area and about 6% in the offshore. This discrepancy

Tab. 2. Daily total mass flux (TMF) and elemental composition of settling particles.

	Area	Site	Period	TMF ($\text{g m}^{-2} \text{ d}^{-1}$)			OC (%)			CaCO ₃ (%)			N (%)			OC/N (mol/mol)			Ref.
				avg	sd	n	avg	sd	n	avg	sd	n	avg	sd	n	avg	sd	n	
MOORED TRAPS	Bottom trap																		
	Western	PA	annual	20.25	30.08	39	4.10	2.66	14	34.49	14.95	14	0.53	0.40	14	9.9	1.9	14	(1)
		S2	annual	28.99	50.46	70	2.51	0.85	70	41.72	7.30	70	0.32	0.14	70	9.6	2.5	70	(2)
		S1	annual	31.90	38.32	33	2.55	1.71	33	21.45	5.09	33	0.36	0.27	33	8.6	1.1	33	(2)
		CS	annual	41.52	65.06	51	2.50	1.38	51	50.24	9.51	51	0.36	0.28	51	9.5	4.8	51	(3)
		PO	annual	26.17	14.46	3	1.93	0.61	3	22.27	10.78	3	na	na	na	na	na	na	(4)
	Eastern	MI	annual	11.37	16.50	57	3.71	1.56	59	20.29	5.69	58	0.54	0.37	59	8.6	1.4	59	(6)
		PU	annual	6.16	2.46	5	3.60	1.18	5	39.84	2.71	5	na	na	na	na	na	na	(5)
		PI	annual	12.20	8.50	na	2.50	1.00	na	na	na	na	1.00	na	na	8.1	4.2	na	(7)
	Offshore	S3	annual	6.95	10.29	48	4.07	2.00	28	28.30	7.83	28	0.49	0.24	28	10.1	4.0	28	(1,2)
		RO	annual	7.89	4.45	16	2.65	0.88	16	31.46	3.93	16	na	na	na	na	na	na	(5)
	Upper trap																		
	Western	S1	annual	7.24	7.58	21	4.50	2.48	21	18.06	6.89	21	0.80	0.55	21	7.36	1.51	21	(2)
PO		annual	7.30	2.40	2	4.15	0.64	2	32.40	7.21	2	na	na	na	na	na	na	(5)	
PU		annual	2.18	0.58	6	7.08	2.67	6	58.63	11.15	6	na	na	na	na	na	na	(5)	
S3		annual	1.51	2.87	7	10.88	5.48	7	15.10	9.03	7	1.29	0.48	7	9.65	1.63	7	(2)	
RO		annual	2.46	1.54	11	6.09	1.96	11	38.76	10.78	11	na	na	na	na	na	na	(5)	
DRIFTING TRAPS	Bottom trap																		
	Western	A	spring	0.07	0.04	2	23.27	11.41	2	10.46	14.18	2	3.70	1.74	2	7.30	0.14	2	(8)
		A	winter	1.68	2.06	2	4.04	2.03	2	39.33	26.27	2	0.70	0.50	2	7.40	1.84	2	(8)
	Offshore	B	spring	0.11	0.13	2	22.51	22.95	2	30.67	24.79	2	3.22	3.23	2	8.10	0.28	2	(8)
		B	winter	1.17	0.23	2	2.24	0.98	2	35.57	8.55	2	0.31	0.14	2	8.35	0.07	2	(8)
		C	spring	0.13	na	1	9.06	na	1	2.44	na	1	1.26	na	1	8.40	na	1	(9)
	Upper trap																		
	Western	A	spring	0.29	0.25	2	18.79	12.21	2	1.85	na	1	2.12	0.85	2	9.80	2.83	2	(8)
		A	winter	0.24	0.33	2	10.73	0.70	2	6.71	na	1	1.35	0.36	2	9.75	3.18	2	(8)
	Offshore	B	spring	0.06	0.001	2	20.56	9.40	2	23.57	30.59	2	3.86	2.47	2	6.70	1.41	2	(8)
B		winter	0.02	na	1	21.82	na	1	28.64	na	1	3.95	na	1	6.50	na	1	(8)	

avg, average; sd, standard deviation; n, number of observations, OC, organic carbon; CaCO₃, carbonates; N, nitrogen.

References

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|----------------------------------|--|------------------------------------|
| (1) Boldrin, unpublished data | (4) Boldrin and De Lazzari, unpublished data | (7) Faganeli, 1989 |
| (2) Giani <i>et al.</i> , 2001 | (5) Puskaric <i>et al.</i> , 1992 | (8) Turchetto <i>et al.</i> , 2002 |
| (3) Boldrin <i>et al.</i> , 2006 | (6) Giani <i>et al.</i> , 2003a | (9) Miquel <i>et al.</i> , 1999 |

could be considered very great but we must consider the difference in the methodology, that could reduce the lateral supply and the difference in sampling period, as more widely discussed in Buesseler *et al.* (2007). The POC fluxes in the drifting traps ranged from 1 to 82 mg m⁻² d⁻¹. The highest values are comparable to the highest ones reported for the Mediterranean Sea in the Alboran Sea (Ramondne *et al.*, 2016). The mean particulate nitrogen fluxes were 3-fold higher than those measured in the NW Mediterranean Sea (Marty *et al.*, 2009). The offshore fluxes of OC were 13 mg m⁻² d⁻¹, less than half of those measured by the more coastal traps, and more than 10-fold lower by the fluxes measured with the same approach in the gulf of Trieste (Wassmann *et al.*, 1999). The OC and N contents in the settling matter of bottom traps ranged from 0.71 to 11.30% (average 3.01±1.57%) and from 0.06 to 2.21% (average 0.42±0.29%), respectively. In the upper-traps the percentages of OC and N on TMF were about double than in the bottom ones, being on average 6.14±3.63% for OC and 0.92±0.57% for N.

At all sites, the OC content of settling particles was linearly correlated with that of N ($P \leq 0.0001$). In the upper-traps the OC/N molar ratio derived from the linear regression slope was 7.12, whilst in bottom-traps OC/N was 9.86. This difference could be attributable to a higher contribution of plankton in the upper trap than in the bottom one, where also resuspended matter can easily settle.

Carbonates, which constituted from 2 to 59% of the total mass flux, are provided by the minerals carried by rivers (calcite and dolomite), by calcareous planktonic organisms as coccolithophorids (Turchetto *et al.*, 2002; Bernardi Aubry *et al.*, 2004) or foraminifera, and by resuspension of bottom sediments containing biogenic carbonates (calcite and aragonite) from shell and skeleton debris, coralline algae (Ogorelec *et al.*, 1991) and benthic foraminifera (Puskarić *et al.*, 1992). Calcite and dolomite minerals are mostly carried in the NAd by Isonzo, Piave, Tagliamento, Brenta and Adige rivers (Bronzi *et al.*, 1979), whereas the Po River carries no dolomite, less calcite and higher amounts of silica particles. The higher content of carbonates (Mann-Whitney U test, $P < 0.05$), found in areas influenced by Adige and Brenta Rivers (site S2), by Piave (site CS) and by the outlets of the Venice lagoon (site PA), reflect the contribution of calcite and dolomite carried by the rivers with drainage basin including the dolomitic Alps, as also shown by the distribution of carbonates in the surface sediments of the NAd (Ravaioli *et al.*, 2003). High carbonate concentrations can be found also off the Istria peninsula (NE Adriatic Sea) where the sediments contain more than 50% of carbonates originating from Mesozoic sediments of Dinaric Alps (Brambati *et al.*, 1973). However, the elevated carbonate content in the trap material at PU site was likely due to a high recent biogenic contribution to the deposition of carbonates (Puskarić *et al.*, 1992).

The data obtained from sediment trap located at the site MI apparently do not support an important role of the Isonzo River as a carrier of carbonates. This incongruence is likely to be attributable to the fact that the site MI is located far from the prodelta, in a coastal zone where the carbonates in the sediments are less than 30% (Ogorelec *et al.*, 1991). Furthermore, the hydrological circulation in the gulf of Trieste is characterized, generally, by an inflow SW-NE current determining a cyclonic circulation at the sea bottom in all seasons (Bogunović and Malačič, 2009; Malačič and Petelin, 2009), preventing the direct supply of Isonzo sediments to the trap-site.

OC and N content (% of dry weight) were inversely and exponentially correlated with TMF (Fig. 2 A,B; Fig. S1). Such a “dilution effect” of OC and N within the TMF, early reported for the site S1 (Matteucci *et al.*, 1997) and observed also in other areas (*e.g.*, in NE-Mediterranean by Stavrakakis *et al.*, 2000; in southern Adriatic by Langone *et al.*, 2016; in Antarctica by Tesi *et al.*, 2012), could be related to the increase of the mineral fraction. This could be the result of OC- and N-depleted resuspended sediments captured by the traps, as well as/or of an advective transport of riverine particulate matter (Pettine *et al.*, 1998). On the other hand, carbonates increase with TMF at sites S1, S2 and PA, suggesting that the above-mentioned dilution effect is most likely due to carbonate rich particles collected by the traps. The OC/N ratio increases with TMF, according to a power fit of the type $OC/N = a(TM)^b$ at sites S1, S2 and CS (Fig. 2), possibly due to the resuspension of bottom sediments which have higher OC/N molar ratios (Tab. 3).

The fittings reported in Fig. 2 are in some cases asymptotic, then Y values tend to a given limit and this asymptotic limit was compared with the corresponding content of surficial sediments (Tab. 3). The asymptotic values differed for less than 10% from the contents of carbonates whereas for OC and N (only exception site S1) the estimated contents in settling matter were generally from 1.5- to 7-fold higher than those in the sediment (Tab. 3). These differences could be due to the degradation of labile organic matter, taking place during sediment accumulation, with respect to a more conservative component as the carbonates.

In the settling matter collected by the drifting traps the chemical composition showed a higher content of organic carbon (14.78±8.31% on average) and nitrogen (2.28±1.43% on average) with respect to the moored traps which had an OC content of 4.19±2.33% and N content of 0.63±0.41% (Tab. 2). The drifting traps in offshore waters were less influenced by resuspended sediments and riverine particulate matter as shown by the lower OC/N ratio (7.6±0.9 on average). This can be related to the short deployment period and the calm weather required during the experiments, conditions which limit particle resuspension. These ratios fall in the

range of the data reported for the eastern Mediterranean Sea by Ramondenc *et al.* (2016). The high variability of the carbonate content could be due to two opposing processes: a lower contribution of resuspended sediments and a higher contribution of the settling of coccolithoforids in offshore waters which can be important especially during winter (Godrijan, 2018; Viličić *et al.*, 2009).

Seasonal and annual fluxes

The seasonal settling fluxes for total particles, organic carbon, nitrogen and carbonates, calculated as time-weighted averages, are showed in Fig. 3.

We tested spatial and temporal differences in the fluxes, using the non-parametric ANOVA-Kruskal-Wallis test, considering, separately, 2 factors: sites and seasons (Tab. 4). Results of these tests showed that the effect of the site is significant for all parameters except for OC flux, whereas the seasons affect all the dependent variables except the CaCO_3 content.

The highest fluxes occur, with a few exceptions for OC and N fluxes, in winter or autumn (Fig. 3). In those

sites, as S1 and S2, directly influenced by the greater rivers TMF in winter were up to 9.6-fold higher than in summer. A similar difference is observed also in the

Tab. 3. Mean composition and OC/N molar ratio of surface sediments, sediment (SAR) and mass accumulation (MAR) rates.

Site	OC %	CaCO_3 %	N %	OC/N mol/mol	SAR cm y^{-1}	MAR $\text{g cm}^{-2} \text{y}^{-1}$	Ref.
Western							
PA	0.11	53.58	0.02	6.41	0.27	0.36	(1, 2)
S2	0.99	51.90	0.11	10.79	0.6	0.56	(1, 3)
S1	1.39	25.42	0.17	9.56	na	0.60	(1, 3)
CS	0.55	58.48	0.06	10.69	0.32	0.40	(1, 4)
PO	1.25	30.88	0.154	9.48	0.16	0.20	(1, 3)
Eastern							
MI	1.09	22.35	0.12	10.50	0.12	0.13	(5, 6)
PI	1.04	29.00	0.18	6.74	0.1	0.11	(5,7)
Offshore							
S3	0.32	33.68	0.04	9.75	0.13	0.16	(1, 3)
RO	0.29	25.74	0.036	9.43	0.003	0.004*	(3, 7)

*estimated on the basis of a 29.9 % of water content and a density of 2.69 g cm^{-3}

References

- (1) Frignani *et al.*, 2005
 (2) Boldrin, unpub. data
 (3) Giani *et al.*, 1997
 (4) Boldrin and De Lazzari, unpub data
 (5) Faganeli *et al.*, 1991
 (6) Giani *et al.*, 2003
 (7) Ogorelec *et al.*, 1991

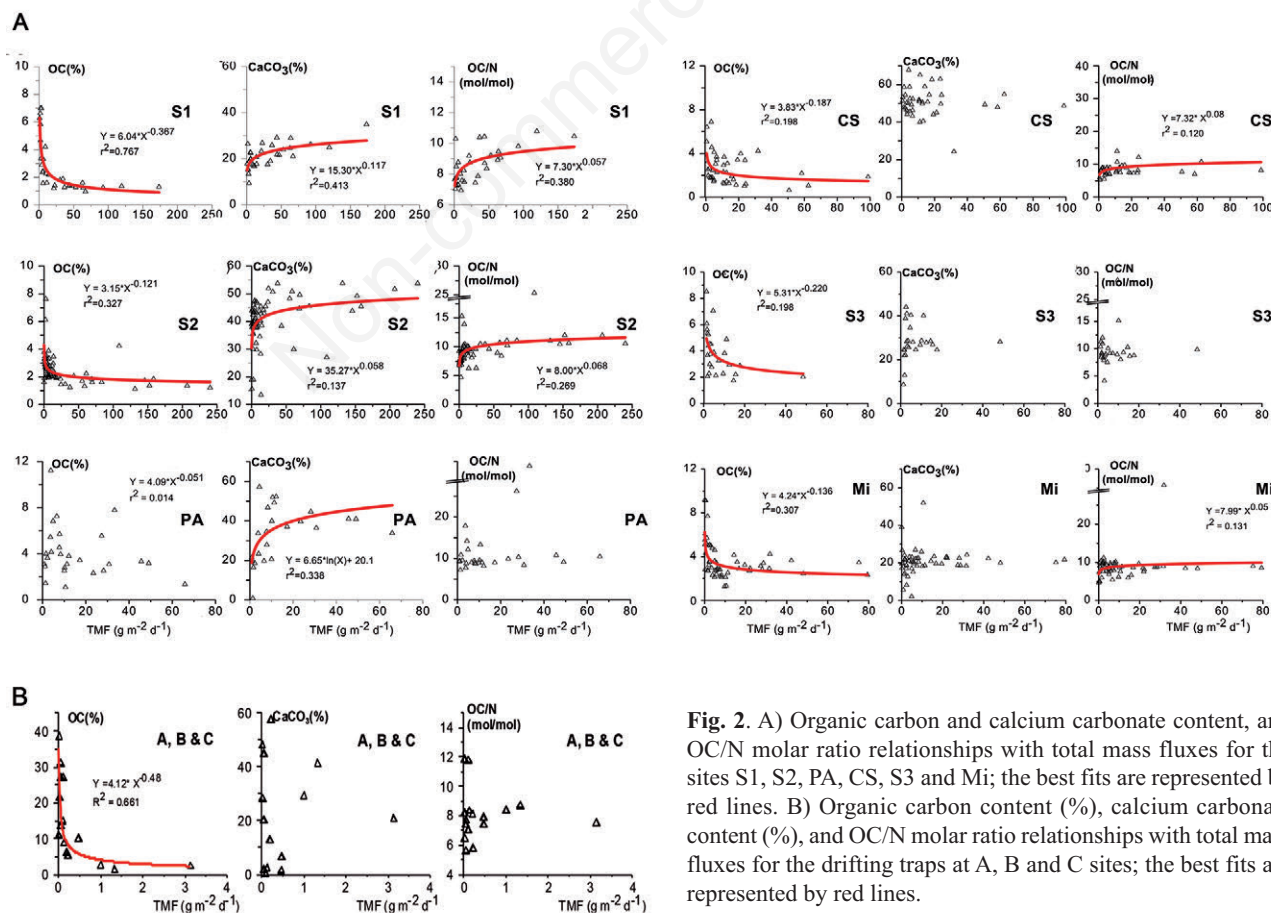


Fig. 2. A) Organic carbon and calcium carbonate content, and OC/N molar ratio relationships with total mass fluxes for the sites S1, S2, PA, CS, S3 and Mi; the best fits are represented by red lines. B) Organic carbon content (%), calcium carbonate content (%), and OC/N molar ratio relationships with total mass fluxes for the drifting traps at A, B and C sites; the best fits are represented by red lines.

organic carbon and nitrogen fluxes which were up to about 5.5 times higher in winter than in summer.

To further assess the extent of seasonal variability of the investigated fluxes, the seasonality index (SI), proposed by Berger and Wefer (1990) and Lampitt and Antia (1997), was calculated for sites S2, PA and RO, for all of which almost complete annual time series were available. SI is defined as the time (in days) needed for the deposition of 50% of the total matter sinking in one year after the ranking of the data (Fig. 4). SI for TMF varied from 26 days in site S2, to 66 in PA and up to 111 days in RO, and from 27 to 137 days for the OC flux in S2 and RO sites (the data from PA are not sufficient to complete this calculation). According to the classification proposed by Berger and Wefer (1990), the SI values allow us to define the export “strongly seasonal to pulsed” in western coastal area, since about 50% of the annual deposition settles within 1-2 months. This value is considered characteristic of areas where the sedimentation is related to events occurring at seasonal scale (riverine discharges, phytoplankton blooms) and occasional events (such as storms) strongly influence the fluxes of settling sediments in NAd. In the more oligotrophic offshore area (site RO) the 50% of sedimentation occurred in about 4-5 months and the flux appears more constant during the year.

The annual fluxes obtained from bottom traps and calculated from the seasonal weighted mean (Tab. 5), ranged from 2763 to 14447 $\text{g m}^{-2}\text{y}^{-1}$ for total mass flux, from 66 to 236 $\text{g OC m}^{-2}\text{y}^{-1}$ for organic carbon, from 12 to 42 $\text{g N m}^{-2}\text{y}^{-1}$ for nitrogen and from 861 to 7525 $\text{g m}^{-2}\text{y}^{-1}$ for calcium carbonates. The lowest fluxes were observed in the offshore area, whereas the highest occurred in the western sites located in front of the river mouths. The high fluxes measured in the western site CS could be due not only to the riverine particulate deposition but also to the presence of the artificial barriers close to the sampling site (Zennaro *et al.*, 2006). It is known that the artificial reef,

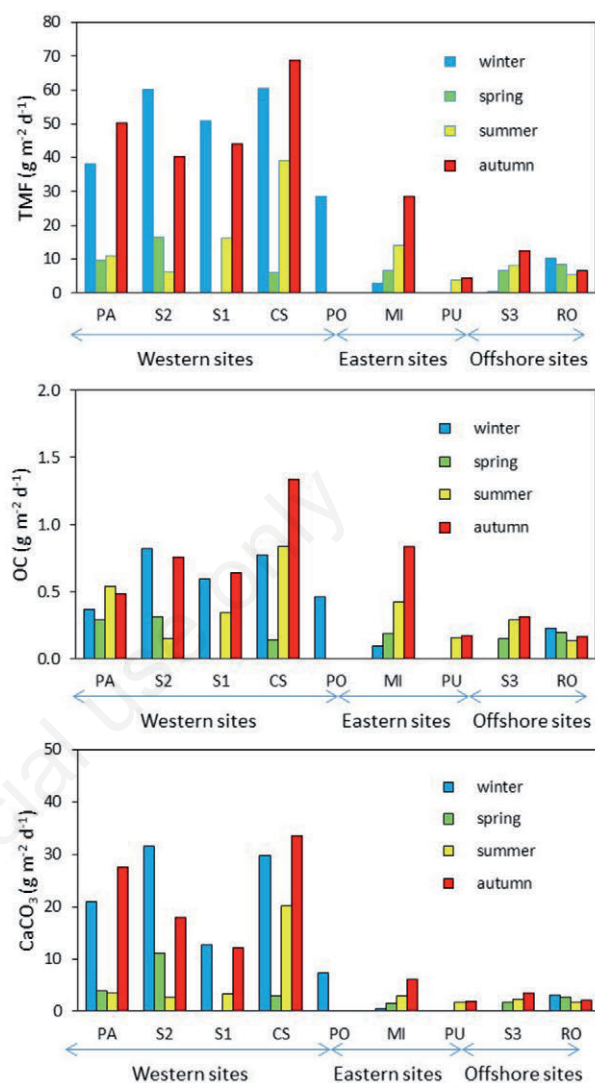


Fig. 3. Time-weighted seasonal averages of settling fluxes for total particles (TMF), organic carbon (OC) and calcium carbonates (CaCO_3) in bottom-traps.

Tab. 4. Non-parametric ANOVA-Kruskal-Wallis tests on bottom-trap fluxes and composition (%), considering 2 independent factors: sites and seasons.

Dependent Variable		Independent variable: Site		Independent variable: Season	
		Kruskal-Wallis test	P	Kruskal-Wallis test	P
TMF	$\text{g m}^{-2} \text{d}^{-1}$	H (8, N = 323) = 36.98	0.0000	H (3, N = 323) = 26.15	0.0000
OC	$\text{g m}^{-2} \text{d}^{-1}$	H (8, N = 276) = 12.92	0.1147	H (3, N = 323) = 19.33	0.0002
OC	%	H (8, N = 280) = 58.60	0.0000	H (3, N = 323) = 43.59	0.0000
CaCO_3	$\text{g m}^{-2} \text{d}^{-1}$	H (8, N = 275) = 42.12	0.0000	H (3, N = 322) = 20.01	0.0002
CaCO_3	%	H (8, N = 279) = 192.39	0.0000	H (3, N = 322) = 0.37	0.9461
N	$\text{g m}^{-2} \text{d}^{-1}$	H (5, N = 251) = 11.44	0.0433	H (3, N = 251) = 19.70	0.0002
N	%	H (5, N = 255) = 43.17	0.0000	H (3, N = 255) = 55.45	0.0000

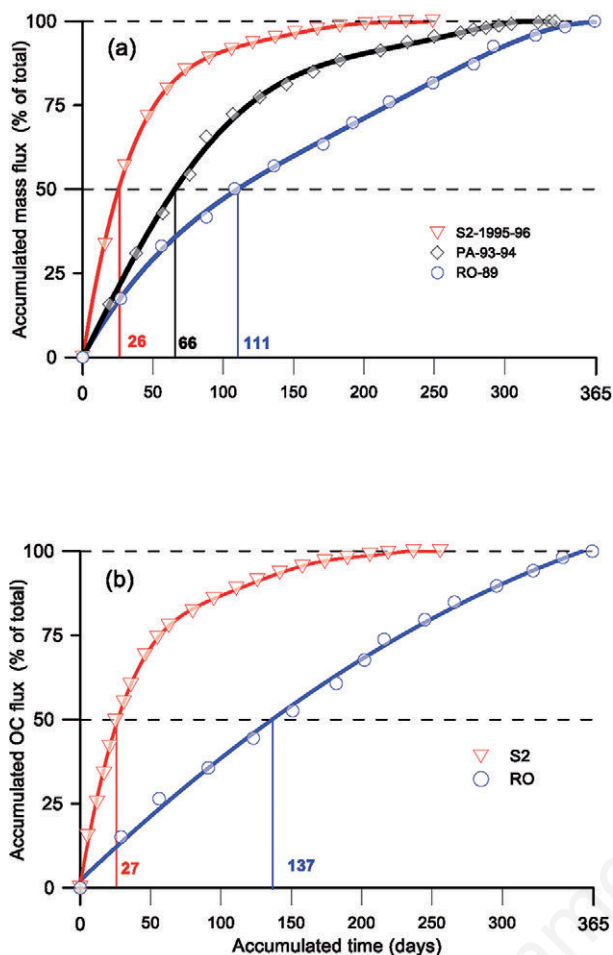


Fig. 4. Seasonal Index (SI) for accumulated total mass flux (a) and OC flux (b) for sites S2 (period June 1995-March 1996), PA (period June 1993-June 1994) and RO (period January-December 1989). The relative time values (in days) for 50% of accumulated fluxes for each parameter are reported.

modifying the hydrodynamic of the area, could increase the turbulence caused by storm events and enhance the resuspension processes (Ambrose and Anderson, 1990; Falcão *et al.*, 2009). As the CS station is shallower than the other western stations, the energy due to wind stress reaching the bottom is higher and, therefore, it generates elevated resuspended fluxes, as also evidenced by the higher values of the OC_r/OC ratio (Tab. 6). The higher annual carbonate fluxes in CS and S2 sites indicate a contribution of the riverine suspended matter discharged from the Piave and from Adige rivers, respectively, whose drainage basins include carbonate areas (Ravaioli *et al.*, 2003).

Tab. 5. Annual fluxes of particulate matter, organic carbon, carbonates and nitrogen in the bottom traps. Where the seasonal data was lacking in the computation of the annual fluxes, the value was estimated as the average of the other available values.

Site	TMF $g\ m^{-2}\ y^{-1}$	OC $g\ C\ m^{-2}\ y^{-1}$	$CaCO_3$ $g\ m^{-2}\ y^{-1}$	N $g\ N\ m^{-2}\ y^{-1}$
Western				
PA	9 920	154	5 110	16
S2	11 232	187	5 777	22
S1	13 745	198	3 545	25
CS	14 447	236	7 525	30
Eastern				
MI	4 693	141	1 009	20
PI	4435	199	na	42
Offshore				
S3	3 621	108	898	12
RO	2 763	66	861	na

na, not available

Tab. 6. Gross (OC), resuspended+riverine (OC_r) and primary (OC_p) annual fluxes of organic carbon compared to primary production (PP) and organic carbon sedimentation (OC_{sed}), calculated from mass accumulation rates.

Site	OC $gC\ m^{-2}\ y^{-1}$	OC_r $gC\ m^{-2}\ y^{-1}$	OC_p $gC\ m^{-2}\ y^{-1}$	Ref.	OC_r/OC %	PP $gC\ m^{-2}\ y^{-1}$	Ref.	OC_p/PP %	OC_{sed} $gC\ m^{-2}\ y^{-1}$	$OC-OC_{sed}$ $gC\ m^{-2}\ y^{-1}$	Ref.
Western											
PA	154	124	30	(1)	81	na	na	na	4	150	(8)
S2	187	139	48	(1,2)	74	376	(4)	13	56	131	(2, 4)
S1	198	154	44	(1,2)	78	579	(4)	8	83	115	(2, 4)
CS	236	196	40	(1)	83	121	(5)	33	22	214	(9)
Eastern											
Mi	141	102	39	(1)	72	233	(6)	17	15	127	(10, 11)
Pi	199	179	20	(3)	90	50	(7,8)	40	11	188	(12)
Offshore											
S3	108	87	21	(1)	81	80	(9)	26	5	103	(2,4)
References											
(1) This work	(4) Giani <i>et al.</i> , 1999			(7) Faganeli <i>et al.</i> , 1991			(10) Giani <i>et al.</i> , 2003				
(2) Giani <i>et al.</i> , 2001	(5) Boldrin <i>et al.</i> , 2006			(8) Bertruzzi <i>et al.</i> , 1997			(11) Giani <i>et al.</i> , 1997				
(3) Faganeli, 1989	(6) Fonda <i>et al.</i> , 2007			(9) Pugnetti <i>et al.</i> , 2006			(12) Ogorelec <i>et al.</i> , 1991				

The annual TMF estimated in the northern part of the Trieste Gulf ($4693 \text{ g m}^{-2} \text{ y}^{-1}$, site MI) is close to the flux reported in the south-eastern part of the Gulf (site PI) by Faganeli (1989). More generally, the annual OC fluxes in the whole NAd are up to two-three order of magnitude higher than those of other Mediterranean areas. The OC fluxes at southern Adriatic Pit were estimated in $3.3 \text{ g C m}^{-2} \text{ year}^{-1}$ and at northern Ionian in $2.4 \text{ g C m}^{-2} \text{ year}^{-1}$, both at 150 m depth (Boldrin *et al.*, 2002). Low value ($4.8 \text{ g C m}^{-2} \text{ year}^{-1}$) was observed also in Ligurian Sea at 80 m depth (Miquel *et al.*, 1994).

The higher fluxes observed in NAd are reasonably correlated with the high productivity of the basin (Pugnetti *et al.*, 2006) and with the presence of elevated riverine inputs (Cozzi and Giani, 2011). In addition, the shallow water of the basin (on average 35 m; Lipizer *et al.*, 2014) increases the potential effects of resuspension and sediment lateral transport.

Resuspension and riverine contributions

As already pointed out, the resuspension and sediment transport processes assume high relevance on the particle vertical fluxes in the NAd. These processes are related to the interaction between the general circulation of the water masses and the shallow bathymetry of the basin (Fain *et al.*, 2007). Moreover, the wind stress can cause resuspension and southward transport of bottom sediments, as observed during the NE-bora wind events (Wang *et al.*, 2007; Boldrin *et al.*, 2009), or when elevated wave heights resuspend sediments at shallow sites (Giani *et al.*, 2001).

Then, the particles collected by the sediment-traps can derive from different processes and have different origin. End members mixing models based on OC/N ratio and the stable carbon isotopic composition ($\delta^{13}\text{C}_{\text{OC}}$) have been frequently used in the NAd to identify the sources of organic matter in the suspended and sedimentary matter (Faganeli *et al.*, 1988; Boldrin *et al.*, 2005; Tesi *et al.*, 2007; Giani *et al.*, 2009).

In this study, to estimate the fraction that could be attributed to biological production (*primary flux*) and those due to resuspension and transport of bottom sediment (*secondary sedimentation*), a label approach based on two-end members mixing was applied, according to the methodology proposed by Gasith (1975) and previously applied in the Adriatic Sea (Faganeli *et al.*, 1989; Matteucci *et al.*, 1997; Giani *et al.*, 2001). For this purpose, N/OC was selected to distinguish resuspended sediments and/or riverine settling matter from autochthonous settling organic matter of planktonic origin (Perdue *et al.*, 2007). Organic matter derived from terrestrial and marsh vascular plants is typically depleted in nitrogen ($\text{N/OC} < 0.07$), whereas marine phytoplankton, zooplankton and bacterioplankton are characterised by

higher nitrogen content ($\text{N/OC} > 0.13$) (Goñi and Hedges, 1995; Goñi *et al.*, 2000).

To estimate the resuspended plus the allochthonous organic matter, the N/OC end members were selected for each site as they lie in different sedimentary environments. As end member representative of resuspension we considered the N/OC lower ratio (0.02 percentile of available data for each sediment trap) measured in settling matter (N/OC end members ranged from 0.07 to 0.09). As end member representative of marine particulate matter we used the 98th percentile of N/OC ratios in particulate suspended matter (N/OC end members ranged from 0.17 to 0.24). Then, the estimated resuspended or allochthonous matter transported by rivers (OC_r) on an annual basis (Tab. 6) ranged from 72 to 90% of the total particulate organic carbon fluxes. Therefore, as observed in previous studies (Matteucci *et al.*, 1997; Giani *et al.*, 2001), the dominant part of the fluxes in the NAd can be attributed to resuspension processes or riverine inputs of allochthonous particulate organic matter.

Organic carbon export and carbon accumulation in the sediments

The export of autochthonous-primary organic carbon (OC_p), calculated as the difference between OC and OC_r , was compared with the available data of primary production (Tab. 6), and the exported fraction ranged from 8 to 40%. The higher export corresponded to the site with lowest primary production (sites CS, PI and S3), whereas the lowest occurred in the most productive areas near the Po and Adige rivers (*i.e.* sites S1 and S2, respectively; Fig. 5). In these sites, even if the production is higher due to the removal of nutrient limitation, the export appears lower for the presence of elevated lateral advection and, probably, because of an intense degradation of the organic matter

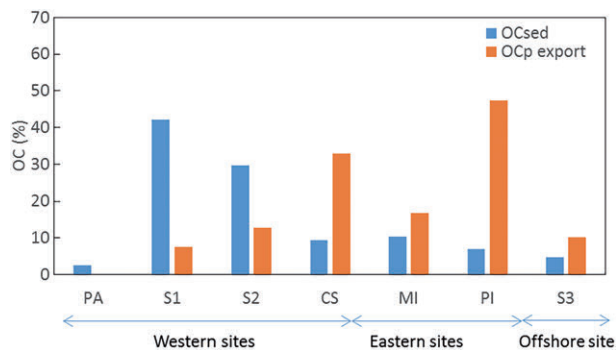


Fig. 5. Primary organic carbon exported toward the sediment with respect to primary production (OC_p export, expressed as percentage) and fraction of settled organic carbon (OC_{sed} , expressed as percentage) with respect to the gross organic carbon flux measured in the bottom traps.

due to high bacterial activities (Puddu *et al.*, 1998; Giani *et al.*, 1999). Moreover, the data and satellite images (Brando *et al.*, 2015) indicate that the influence of the riverine input on site CS is lower than in S1 and S2, and this could be likely due to the different discharges of rivers: Po >> Adige > Piave > Sile.

The organic carbon settling fluxes, as determined with the bottom sediment traps, were from 2 to 39-fold higher than the organic carbon ones, calculated from mass accumulation rates at all the sites (Tab. 6). This implies that, at all sites, a relevant fraction of the settling organic matter is not buried, rather is consumed by benthic organisms, decomposed or advected to other areas. As shown in Fig. 5, the highest % of the OC flux settles in the sediments near the Po river (site S1) and Adige river (site S2).

The mass accumulation rate (MAR) integrate the sedimentation over years and, therefore, when it is converted in flux of organic carbon, it does not reflect the deposition of the labile fraction of organic matter, which could be respired or consumed by benthic organisms on a time scale of weeks or days (Giordani *et al.*, 2002). Comparing the OC flux excess ($OC - OC_{sed}$) with the annual carbon mineralized at the sediment water – interface in the western coastal NAd, which falls in the range 54-89 $gC\ m^{-2}y^{-1}$ (Moodley *et al.*, 1998), we can estimate that from 25 to 78% of the organic carbon input to the sea bottom could be lost through benthic respiration at western coastal site under riverine influence (S1, S2, CS). If we take the respired carbon benthic fluxes estimated by Giordani *et al.* (2002) for the western NAd (100-130 $gC\ m^{-2}y^{-1}$) the incidence of the utilization of the total organic carbon particle flux rises up to 47-114%. Notwithstanding the variation of these estimates, these results suggests that a quite relevant fraction of the settling OC which is not buried in the sediments is likely consumed or remineralized at the sediment-water interface. At the sites S1, S2 and CS, highly influenced by rivers, a significant fraction of OC accumulated in the sediments results from the riverine discharge or from lateral advection. Therefore, we confirm that riverine or laterally advected labile organic matter must play a relevant role in sustaining the benthic trophic chain (Danovaro *et al.*, 2000). The particulate organic matter carried by the Po River, especially during low discharge periods, is rich in phytoplankton (Pettine *et al.*, 1998) which presumably is a source of allochthonous labile organic matter. As a matter of fact, both bacteria and meiofauna were shown to respond to frontal areas created by plumes and their associated gradients of settled organic matter particles south of the Po prodelta (Danovaro *et al.*, 2000).

CONCLUSIONS

The downward fluxes of particles in the NAd present strong gradients decreasing from west to east. The coastal

areas influenced by higher riverine inputs (Po and Adige Rivers) are characterised by higher productivity but lower carbon export when expressed as percentage of primary production. In offshore waters, primary production is lower but the organic carbon transfer to the bottom in percentage is about double with respect to the coastal areas. Downward fluxes and the elemental composition of settling matter are characterised by high seasonal variations. The sink of particles occurs in relatively short episodes as about 50% of annual flux occurs in less than 2-3 months.

In the shallow continental shelf of the northern Adriatic, resuspension and advective transport, accounting for up to 70-90% of the total organic carbon flux at annual scale, are the main processes regulating the dynamic of particles, their concentration and sedimentation. The importance of these processes is highlighted by the relevance of carbonates, which represent a substantial component of the fluxes in the north-western area of the NAd and are associated with the river inputs and with the dispersion of sediments through resuspension.

At most sites, the autochthonous organic carbon fluxes were higher than the organic carbon accumulation at the surficial sediment as estimated by radionuclide data, and this excess likely contributes to sustain the biological and chemical processes in the sediment.

In the areas influenced by higher riverine discharges, the total sedimentation of OC, estimated at annual scale, is much higher than the flux due to the primary production, then a relevant allochthonous source of organic matter is required to sustain the benthic community.

Future studies with sediment traps in the area should include a more detailed characterization of the lithogenic fraction and should also trace the organic matter sources with stable isotopes in order to better estimate the contributions of resuspension processes, and of riverine versus marine matter.

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