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The significance of atmospheric inputs of major and trace metals to the Black Sea

C. Theodosi [a], S. Stavrakakis [b], F. Koulaki [a], I. Stavrakaki [b], S. Moncheva [c], E. Papathanasiou [b], A. Sanchez-Vidal [d], M. Koçak [e], N. Mihalopoulos [a,*]

[a] Environmental Chemistry Processes Laboratory, Department of Chemistry, University of Crete, P.O. Box 2208, 71003 Heraklion, Greece
[b] Hellenic Centre for Marine Research, Institute of Oceanography, Anavyssos, Greece
[c] Institute of Oceanology, BAS Parvi Mai Str. No 40, Varna 9000, Bulgaria
[d] GRC Geociències Marines, Universitat de Barcelona, 08028 Barcelona, Spain
[e] Institute of Marine Sciences, Middle East Technical University, P.O. Box 28, 33731 Erdemli-Mersin, Turkey

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ABSTRACT

To estimate the role of atmospheric deposition on Black Sea biogeochemistry, the chemical composition (particulate matter, carbon, major and trace metals) of both atmospheric deposition and sediment traps material was studied.
Lithogenic material was found to be the most abundant constituent in sediment traps (31–34%) followed by carbonates (CC; 21%) and particulate organic carbon (POC; 10%).
Particulate matter fluxes in sediment traps were low from January to March with maxima from November to December for both depths (930 m and 1930 m). Particulate organic carbon and lithogenic material present common peaks with particulate matter, indicating that during blooms, phytoplankton produces aggregates and sweep from the surface both lithogenic and anthropogenic elements which are transported rapidly to the deep.
Atmospheric deposition was found to supply quantitatively a considerable amount of major and trace metals to the seawater of the Black Sea. More precisely, on average from the surface towards the deeper water layers of the Black Sea 26% and 83% of Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb fluxes were provided by atmospheric deposition, demonstrating its significant role as an external source of major and trace metals in the area.

1. Introduction

The atmosphere is a significant route by which both natural and anthropogenic compounds are transported from land-based sources to coastal and offshore waters (e.g., Duce et al., 1991; Jickells, 1995). This is of particular importance for semi-enclosed seas, such as the Mediterranean and the Black Sea, due to the relative proximity of land-based emissions and densely populated coastal areas (Guerzoni et al., 1999; Kubilay et al., 2002). As a consequence, the impact of increased anthropogenic trace metal inputs is visible in the Mediterranean Sea sediments (Heimbürger et al., 2012). In several oceanic regions, vertical export fluxes appear to reflect seasonal features of both atmospheric inputs and primary production (Deuser, 1986; Jickells et al., 1998; Migon et al., 2002).

The Black Sea is the world's largest permanently anoxic marine basin and therefore is an intriguing field of investigation regarding the evolution of its biogeochemical structure (Konovalov and Murray, 2001; Murray et al., 1995). The water column is stratified into an upper oxygenated surface layer (80–150 m deep) and the underlying permanent anoxic waters. The surface circulation pattern is dominated by a general cyclonic circulation pattern with local central gyres or cyclonic rings in the eastern and western Black Sea basins (Boguslavskiy et al., 1976).

In examining the vertical export flux, both vertical effects and lateral processes must be considered. Seasonal changes in biological activity, resuspension of shelf sediments and the input of fluvial matter, can modify the supply of suspended and sinking material in the Black Sea (Hay, 1987; Heussner et al., 2006; Honjo et al., 1987). The dominant primary producers are *Emiliania huxleyi*, diatoms and dinoflagellates (Benli, 1987; Sorokin, 1983). Diatoms predominantly bloom in spring, whilst *E. huxleyi*, and to a lesser degree dinoflagellates, in summer and autumn. The basin-wide correlation of the upper-most laminated sediment sequence suggests either the existence of basin-wide blooms or if production is highly regional, effective dispersal of the biogenic particles across the basin before settling (Hay et al., 1990).

The Black Sea has become a focus of research due to potential adverse effects of contaminated urban, industrial, and agricultural runoffs to the ecosystem. Over the last three decades, increased human activities have consequently increased the inorganic nitrogen and phosphorus inputs to the Black Sea (Konovalov and Murray, 2001; Oguz and Velikova, 2010; Oguz et al., 2006). Rivers and atmospheric deposition are expected to be the most important external sources

* Corresponding author.
E-mail address: mihalo@chemistry.uoc.gr (N. Mihalopoulos).

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of pollutants and nutrients to the Black Sea, however their relative contribution has been poorly assessed (Kubilay et al., 1995). Indeed up to now the majority of the studies focused on the role of rivers as source of nutrients (Ludwig et al., 2010), whilst little attention was given to the role of atmospheric deposition (Kubilay et al., 1995). Compared to the atmosphere, rivers are mainly point sources. More than half of the terrigenous input to the Black Sea is believed to be supplied by the Danube River alone. Another 25% enters in the southeastern corner of the Black Sea from the rivers Kizil Irmak, Yesil Irmak, Coruh, Rioni and other Caucasian rivers (Shimkus and Trimonis, 1974). However, after the recent dam constructions on the Danube River and the political changes in the early 1990's slight but significant decreasing trends are observed especially important in the case of N and P inputs (Ludwig et al., 2010) to the northwestern Black Sea. Consequently, given the strong impact of the Danube nutrients for biological productivity in the Black Sea, it is not unlikely that this may have had an impact on primary production in the Black Sea on the whole (Humborg et al., 1997; Ludwig et al., 2010).

With regards to the Black Sea trace metals budget Guieu et al. (1998) addressed the importance of the Danube River estuary in the shelf area of the north-western Black and found that the concentrations of elements Al, Mn, Fe, Zn, Ni, Cd and Pb were surprisingly low for an area where serious contamination has been suspected. Moreover, the concentrations of metals in the particulate fraction were similar to those in other major rivers of the world, whilst the surface distribution of the dissolved metals in the studied area showed a limited influence of the Danube on the concentrations observed for the open sea. Finally, for these metals, the concentrations of the open Black Sea surface waters were of the same order of magnitude as concentrations in the Mediterranean surface waters (Guieu et al., 1998).

The aim of this study is to present a detailed data-set on the atmospheric deposition of major and trace metals (Al, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) establishing a reliable quantitative budget of atmospheric inputs to the Black Sea.

To our knowledge this is the first effort towards trying to unravel the contribution of atmospheric inputs on biogeochemical cycling of major and trace metals in the Black Sea. The significance of atmospheric deposition of metals (e.g. Fe, Mn) on seawater productivity in the Black Sea was examined by comparing the atmospheric inputs with the vertical export flux collected with sediment traps. Thus, the importance of atmospheric inputs as an external source of these elements to Black Sea water column was quantified.

2. Experimental

2.1. Sampling sites

Atmospheric deposition and aerosol samples were collected at two locations bordering the Black Sea: Varna (43.18°N, 27.91°E) and Sinop (42.02°N, 35.09°E), respectively. Sediment traps were deployed at water depths of 930 m and 1930 m in the south west Black Sea (43° 01,812N, 29° 28,498E). The sites of atmospheric and seawater samplings are depicted in Fig. 1.

2.2. Sampling and analytical techniques

2.2.1. Atmospheric deposition samples

At Varna bulk (wet and dry) deposition samples were collected with a monthly interval from April 2008 to September 2009. The sampling device was made of a 4 L polyethylene (HDPE) bottle, with a polyethylene funnel (surface = 113 cm^2) attached at the top. A polyester mesh (mesh-opening of 33 μm) at the base of the funnel prevents contamination of the sample by plant debris or insects. The collector was installed 2 m above the roof of the Institute of Oceanology located 30 m away from the seashore without important industrial activity in the vicinity. More details on the sampling system and limitations can be found at Guieu et al. (2010) and Markaki et al. (2010).

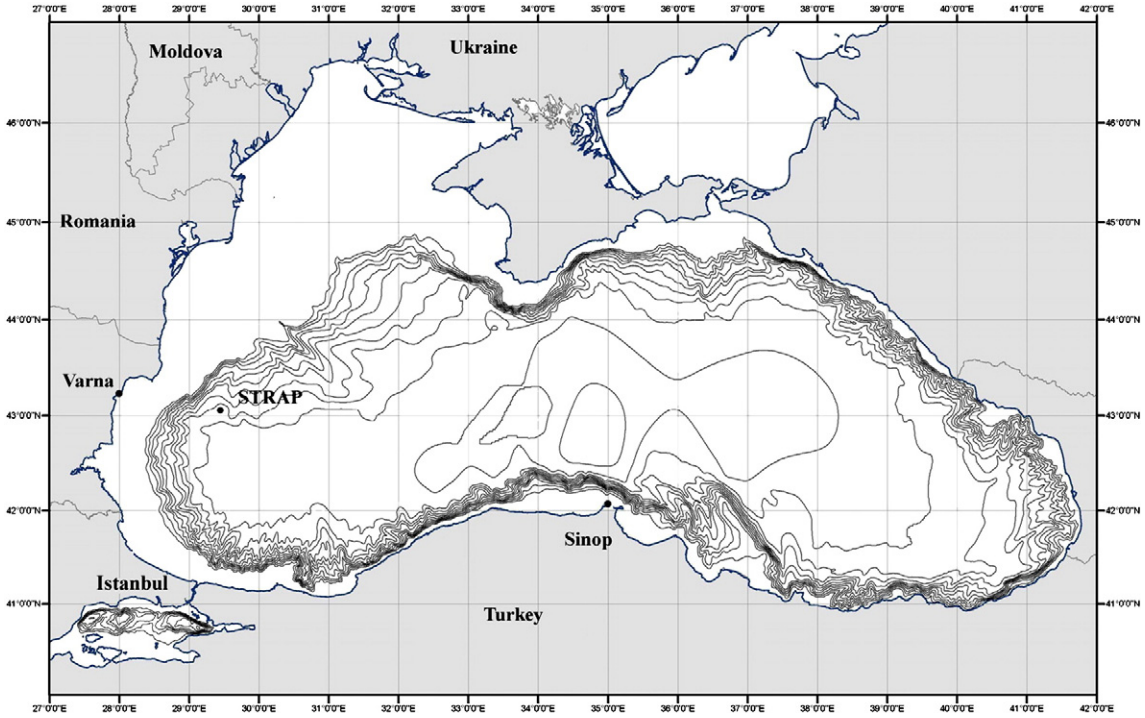

Fig. 1. Locations of the three sampling sites across the Black Sea: circle: sediment trap deployment (43° 01,812N, 29° 28,498E), Varna (43.18°N, 27.91°E) and Sinop (42.02°N, 35.09°E).

Bulk deposition samples were filtered immediately after collection, through a pre-weighed polycarbonate filter (Millipore, Isopore Membrane, pore size 0.4 μm, diameter 47 mm) and particulate matter mass was estimated by pre and post weighting each filter. All samples were acidified using a 0.74 M nitric acid solution and stored at 5 °C until analysis.

2.2.2. Aerosol samples

A Gent-type PM_{10} stacked filter unit (SFU) sampler was used to collect atmospheric particles in two size ranges namely, coarse ($10\ \mu m > D_a > 2.5\ \mu m$) and fine ($D_a < 2.5\ \mu m$) at a rural sampling site situated at the Sinop University, Faculty of Fisheries on the coast of Central Black Sea. The site was located 200 m away from the sea at 10 km distance from the city of Sinop (approx. 200,000 inhabitants), in an area covered by trees and grass. The sampling campaign commenced in April 2009 and ended in December 2009. During this period, a total of 516 aerosol filters (256 daily coarse and fine samples) were collected with a temporal resolution of 24 h. After collection, $PM_{10-2.5}$ and $PM_{2.5}$ concentrations were determined gravimetrically and a part of the filter (1/4) was analyzed after acid digestion for major and trace metals as described in Section 2.2.4.

2.2.3. Sediment trap samples

In the Southwest Black Sea (43° 01,812N, 29° 28,498E; Fig. 1), samples were collected on a two-week basis for 13 months (October 2007 until October 2008) and 19 months (October 2007 until April 2009) at the water depths of 930 and 1930 m, respectively using two time series sediment traps (Technicap PPS3/3; Heussner et al., 1990). Immediately after recovery every sample was divided into aliquots, for total mass flux, particulate organic carbon (POC), elemental carbon (EC), carbonates (CC) and trace metals determination. Details are given by Stavrakaki et al. (2009).

2.2.4. Analysis

An acid microwave digestion procedure followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Electron X Series) was applied to measure major (Al, Ca, Mn and Fe) and trace metal (V, Cr, Ni, Cu, Zn, Cd and Pb) concentrations in atmospheric deposition, aerosol and particles from sediment trap samples, following the technique described in detail by Theodosi et al. (2010a). A microwave digestion system (Berghof MWS-2) using teflon vessels (DAP — 60 K, 60 mL/40 bar) and concentrated nitric acid (puriss. p.a., Fluka Prod. No. 84380) was used. The heating program applied was 30 min heating at 180 °C and 999 W of microwave power. This first step was repeated and then it was followed by heating at 100 °C and 800 W of microwave power for 20 min. After cooling to room temperature, the digested solution was transferred to an acid-cleaned polyethylene container and stored in the freezer prior to ICP-MS analysis. Recoveries obtained for certified reference materials (MESS-3, GBW 07313 and BCSS-1) were excellent, ranging from 90.0 to 104.1% for all studied elements except Al (60%) which was corrected accordingly. Indium (In, CPI International, S4400-1000241) was added as an internal standard to the samples before ICP-MS analysis and calibration curves were performed for each analytical batch using standard certified solutions by CPI International ($R^2 = 0.9999$). The detection limits, defined as three times the standard deviation of the blank value, were (in $\mu g\ L^{-1}$): Al = 0.55, Ca = 18.95, V = 0.08, Cr = 0.03, Mn = 0.09, Fe = 2.35, Ni = 0.41, Cu = 0.39, Zn = 0.76, Cd = 0.02 and Pb = 0.03.

Analysis of sediment trap material for EC, was performed using the thermal-optical transmission (TOT) technique (Birch and Cary, 1996), using a Sunset Laboratory OC/EC Analyzer described in detail by Theodosi et al. (2010b). POC and CC were determined according to Monaco et al. (1990). CC fluxes were determined by multiplying inorganic carbon fluxes by a factor of 8.33, whilst the lithogenic matter was estimated using Fe or Al as tracers of lithogenic material assuming a relative ratio of 4.5% or 7.1% for each sample (Guieu et al., 2002; Wedepohl, 1995).

3. Results and discussion

3.1. Atmospheric deposition of metals in the Black Sea

Fig. 2a presents total atmospheric mass fluxes and fluxes of all the studied elements. Statistical analysis (not shown) performed between the measured species showed significant correlations ($p < 0.01$) between almost all elements independent of their origin: crustal (Al, Fe, Ca, Mn), anthropogenic (Pb, Cr, V, Ni) or mixed (Cu, Zn) indicating similar variability (Heimbürger et al., 2010; Pacyna and Pacyna, 2001). This is clearly seen in Fig. 2b that presents time series of bulk atmospheric deposition mass, Al and Pb daily fluxes, representing crustal and anthropogenic originated elements respectively. A similar pattern in their variability is also evident for all measured elements with maxima during spring and autumn in 2008. Trajectory analysis indicates significant Sahara dust influence during these seasons. Air mass origin in association with frequent rain (almost during all months without a clear seasonal trend) as well as the long sampling period could explain the common variability of all measured species.

Our data on total metals deposition in Black Sea are in the same range with the values reported for the Mediterranean (Guieu et al., 2010; Heimbürger et al., 2011; Theodosi et al., 2010a). The representativity of Varna deposition data for the Black Sea is investigated by comparison with dry deposition of trace metals calculated from aerosol observations at Sinop (Fig. 1) and reported in Table 3.

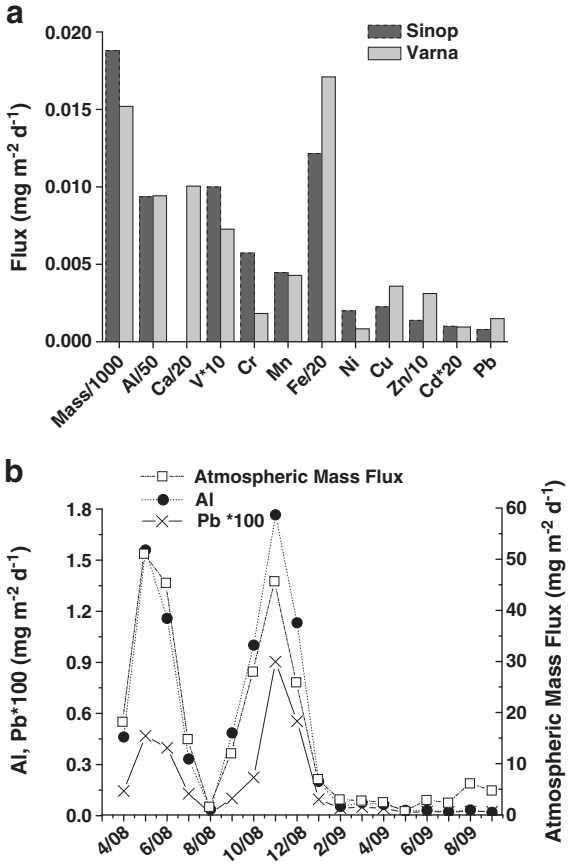

Fig. 2. (a) Atmospheric fluxes of major and trace metals (mg m^{-2} d^{-1}) in Varna (04/2008–09/2009) and Sinop (04/2009–12/2009) and (b) Seasonal variations of aluminum, lead and atmospheric mass fluxes (mg m^{-2} d^{-1}) in Varna, Bulgaria.

Dry deposition flux of a metal x (DF_x) was calculated as the product of concentration (C_x) and deposition velocity (V_d) according to Seinfeld and Pandis (1998).

$$DF_x = C_x \cdot V_d \quad (1)$$

The mean values of the deposition velocity adopted here were 2 cm s^{-1} for the coarse particles and 0.1 cm s^{-1} for the fine (Duce et al., 1991; Koçak et al., 2005). The DF_x was calculated using the metal concentrations (fine plus coarse concentrations) measured from the aerosols samples collected at Sinop and the aforementioned dry deposition velocities. Although Sinop data covers different sampling period and dry deposition represents only part (about 30–60%) of the total deposition, the calculated dry deposition values at Sinop fall within the range of those measured at Varna. It is therefore reasonable to conclude on the representativity of Varna bulk deposition data of trace metals for the whole south Black Sea.

3.2. Fluxes of particulate matter, particulate organic carbon, major and trace metals through the water column

Table 1 recapitulates the average, standard deviation and median of particulate matter, carbon and trace metals fluxes measured at the sediment traps deployed at the two depths. Values are reported both in terms of fluxes and mass ratios. POC accounts for about 10% at both depths, CC for about 21% and lithogenic material for 31–34%.

Multi regression analysis was performed between the various elements at both depths for both fluxes and mass ratios. Table 2 depicts the statistical significant correlations between all elements both in terms of fluxes (2a) and mass ratios (2b) for the trap at 930 m depth. Similar results have been observed for the sediment trap at 1930 m depth. It is noteworthy that statistically significant correlations ($R^2 > 0.33$, $p < 0.01$) are observed between elements of same origin (e.g., Al, Fe, Mn; crustal origin) but also between elements of different origin (e.g., Fe vs EC, V, Ni, Cd, Pb). For instance, Fe displays high correlation values with V and Mn, for both fluxes and mass ratios. The correlation with the latter was somehow expected as both Fe and Mn have a crustal origin and both are transition metals equally affected by the changes in the redox conditions. However, the correlation between Fe and V, emitted by heavy oil combustion was not expected. Particularly interesting is the intercorrelation of crustal originated elements such as Al, Ca and Fe. Regarding Al, which is a tracer of lithogenic material, a strong correlation was observed with V ($R^2 = 0.83$) in the shallower depth, whilst in the case of Ca with organic matter and EC. All trace metals, with the exception of Zn, independent of their source, display significant correlation values between them as well as with EC (in terms of fluxes). The fact that most trace metals, whether of crustal or anthropogenic origin, display significant correlations, suggests that the transfer mechanism that drives major and trace metals from surface waters to the deep is the same.

Taking into account that anthropogenic elements such as V, Ni, Cd and EC mainly exist in the fine mode (Koulouri et al., 2008) and those of crustal origin in the coarse one, the good correspondence between the flux of lithogenic and anthropogenic constituents suggests that removal occurs largely by incorporation into larger sinking "marine snow" aggregates and fecal pellets during sporadic intense plankton blooms. The coherence of metals maxima with those of particulate organic carbon corroborates this hypothesis (see below).

Fig. 3a–f presents time series of fluxes of particulate matter, carbon (organic, elemental and carbonates), lithogenic material and Pb (characteristic of anthropogenic metals) at both depths. In the following paragraphs a short description of each parameter is given.

3.2.1. Particulate matter distribution

The annual cycle of particulate matter flux presents a significant seasonal variation at both depths with a minimum peak during winter and three well distinguished maxima, two of them in autumn

Table 1
The average, standard deviation and median of particulate matter, carbon and trace metals fluxes and mass ratios (in parenthesis) measured at the sediment traps samples deployed at 930 m and 1930 m, respectively.

mg m^{-2} d^{-1} (mg g^{-1})	930 m (n = 21)		1930 m (n = 27)	
	Average ± st. dev	Median	Average ± st. dev	Median
Particulate matter	109 ± 79.1	84.6	75.9 ± 56.2	69.6
Lithogenic	35.7 ± 41.4	23.3	22.8 ± 20.2	17.8
POC	11.7 ± 9.47	8.09	9.88 ± 8.41	7.61
	(105 ± 44.4)	(87.9)	(101 ± 35.5)	(97.2)
EC	4.22 ± 4.67	3.03	2.53 ± 2.44	1.81
	(35.6 ± 13.7)	(33.8)	(30.3 ± 14.6)	(26.7)
CC	26.1 ± .37.5	17.4	22.9 ± 21.5	13.6
	(207 ± 133)	(156)	(211 ± 108)	(204)
Al	2.67 ± 3.16	1.56	1.72 ± 1.20	1.51
	(2.42 10^{1} ± 1.62 10^{1})	(1.57 10^{1})	(47.9 ± 69.0)	(19.9)
Ca	16.0 ± 18.9	12.2	8.35 ± 10.2	2.68
	(133 ± 63.2)	(138)	(107 ± 91.2)	(74.3)
V	2.80 10^{-3} ± 3.38 10^{-3}	2.03 10^{-3}	1.89 10^{-3} ± 1.86 10^{-3}	1.33 10^{-3}
	(2.47 10^{-2} ± 1.41 10^{-2})	(2.30 10^{-2})	(2.74 10^{-2} ± 1.62 10^{-2})	(2.25 10^{-2})
Cr	6.36 10^{-3} ± 7.18 10^{-3}	3.97 10^{-3}	4.19 10^{-3} ± 3.19 10^{-3}	3.55 10^{-3}
	(5.54 10^{-2} ± 2.92 10^{-2})	(5.59 10^{-2})	(7.69 10^{-2} ± 7.30 10^{-2})	(5.83 10^{-2})
Mn	2.44 10^{-2} ± 2.25 10^{-2}	1.98 10^{-3}	1.83 10^{-2} ± 1.62 10^{-2}	1.28 10^{-2}
	(0.224 ± 0.102)	(0.224)	(0.300 ± 0.214)	(0.227)
Fe	1.61 ± 1.87	1.05	1.03 ± 0.907	0.799
	(13.8 ± 6.94)	(12.5)	(15.5 ± 9.12)	(15.1)
Ni	4.56 10^{-3} ± 4.89 10^{-3}	2.98 10^{-3}	3.36 10^{-3} ± 2.84 10^{-3}	2.6310^{-3}
	(3.93 10^{-2} ± 1.46 10^{-2})	(3.91 10^{-2})	(7.16 10^{-2} ± 1.34 10^{-1})	(3.78 10^{-2})
Cu	8.19 10^{-3} ± 6.99 10^{-3}	5.59 10^{-3}	6.01 10^{-3} ± 5.86 10^{-3}	3.98 10^{-3}
	(7.56 10^{-2} ± 3.24 10^{-2})	(7.59 10^{-2})	(0.105 ± 0.106)	(7.75 10^{-2})
Zn	0.315 ± 0.551	7.98 10^{-2}	0.165 ± 0.208	5.68 10^{-2}
	(4.29 ± 9.91)	(0.963)	(3.72 ± 9.91)	(0.634)
Cd	2.80 10^{-4} ± 5.74 10^{-4}	1.13 10^{-4}	1.33 10^{-4} ± 1.33 10^{-4}	9.66 10^{-5}
	(2.16 10^{-3} ± 1.98 10^{-3})	(1.59 10^{-3})	(4.02 10^{-3} ± 8.58 10^{-3})	(1.71 10^{-3})
Pb	6.03 10^{-3} ± 1.77 10^{-2}	1.96 10^{-3}	1.82 10^{-3} ± 1.60 10^{-3}	1.52 10^{-3}
	(3.55 10^{-2} ± 5.53 10^{-2})	(2.63 10^{-2})	(3.87 10^{-2} ± 6.34 10^{-2})	(2.46 10^{-2})

Table 2
Coefficients of determination (R^2) between the elements analyzed at the sediment traps samples at 930 m both as fluxes (a; mg m^{-2}) and mass ratios (b; mg g^{-1}). All correlations are significant for $R^2 > 0.33$ ($p < 0.01$).

a

930 m (mg m^{-2})	Al	Ca	V	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb	OC	EC	CC
Al	1.00													
Ca	0.60	1.00												
V	0.96	0.64	1.00											
Cr	0.84	0.70	0.89	1.00										
Mn	0.88	0.74	0.93	0.83	1.00									
Fe	0.95	0.73	0.98	0.88	0.95	1.00								
Ni	0.87	0.81	0.92	0.90	0.93	0.95	1.00							
Cu	0.69	0.77	0.79	0.76	0.91	0.83	0.89	1.00						
Zn									1.00					
Cd	0.73	0.41	0.85	0.77	0.73	0.78	0.71	0.65		1.00				
Pb	0.79	0.41	0.86	0.78	0.71	0.80	0.70	0.60		0.98	1.00			
POC								0.36				1.00		
EC	0.63	0.92	0.68	0.78	0.73	0.76	0.84	0.78	0.50	0.51			1.00	
CC		0.67					0.39	0.34					0.58	1.00

b

930 m (mg g^{-1})	Al	Ca	V	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb	OC	EC	CC
Al	1.00													
Ca		1.00												
V	0.83		1.00											
Cr			0.46	1.00										
Mn	0.61		0.80		1.00									
Fe	0.80		0.92		0.70	1.00								
Ni	0.43		0.60	0.47	0.43	0.50	1.00							
Cu					0.33			1.00						
Zn									1.00					
Cd										1.00				
Pb			0.33				0.35			0.72	1.00			
POC												1.00		
EC		0.40											1.00	
CC														1.00

(October and November) and one in late spring (May, Fig. 3a, b). Both the observed levels and the seasonal variation of particulate matter fluxes are in agreement with the results reported by previous studies in the area (Hay et al., 1990; Muramoto et al., 1991; Osawa et al., 2005). Although particulate matter flux variability at both depths presents similarities, especially during mixing period, no statistically significant correlation exists indicating no direct connection between the two depths. Cross correlation factor (CCF) between particulate matter flux of the 930 m and 1930 m traps shows the highest correlation coefficient at lag 1 (one lag offset corresponds to one sampling interval which is 15.5 days), indicating a sinking speed of around 67 m day^{-1}, which is comparable with the sinking speed given by Honjo et al. (1987). The above estimated average sinking speed implies transport time from surface down to the first sediment trap within 2 weeks. Thus good correspondence between atmospheric deposition and sediment traps material is expected if atmosphere is a significant external source.

3.2.2. Carbon distribution

At both depths POC flux presents the same maxima as particulate matter, indicating a connection between particulate matter maxima and phytoplankton blooms (Fig. 3c, d). During the bloom, phytoplankton produces aggregates and sweeps from the surface both lithogenic and anthropogenic elements which are transported rapidly to the deep water. At the shallower trap POC presents 3 maxima, whilst only two for CC and EC. The maximum in POC and CC fluxes during late spring (May) is an indicative of the coccoliths bloom (Cokacar et al., 2001; Moncheva et al., 2010). CC, consisting of coccoliths within fecal pellets, is the dominant component almost 75% of the particulate matter fluxes as also observed by Hay et al. (1990). The autumn maximum could be assigned to dinoflagellates bloom as indicated by the low contribution in carbonates. Of particular interest are the maxima of EC fluxes during late spring and autumn in the 930 m trap. EC is considered to be a very good tracer of combustion (Kim et al., 2000). Sciare et al. (2008) showed that important biomass burning events occur around Black Sea region in spring and summer. Combustion materials could accumulate in surface seawater and rapidly transfer to the shallower sediment trap during blooms. The association of EC with combustion material such as V (Fig. 3c, d) indicates also significant contribution from burning activities. Interestingly even at the deeper trap EC presents a summer maximum in agreement with our hypothesis.

3.2.3. Major and trace metals distribution

The data presented is the first detailed data set for major and trace metals in sediment traps for the Black Sea. Muramoto et al. (1991) reported Fe fluxes for sediment traps deployed at 2000 m at two locations in the southern Black Sea ranging from 2.79 ± 2.49 at the coastal site, to 0.67 ± 1.14 mg m^{-2} d^{-1} at the open ocean site, within the range of our measured values (Table 1). For Fe, these authors also concluded that non-pyritic or non-sulfidic Fe comprises a significant proportion of total Fe.

All maxima of major and trace metal fluxes were found to be associated to POC and particulate matter fluxes indicating similar behavior, most probably aggregation of lithogenic material with fecal pellets and rapid transfer to the water depth. Lithogenic material calculated using Fe or Al as tracer contributes 31 to 34% of the particulate matter flux at both depths. This is in agreement with the results reported by Hay and Honjo (1989) (34%) and Hay et al. (1990) (40.8%).

Fig. 4(a–f) compares fluxes (mg m^{-2} d^{-1}) and mass ratio (mg g^{-1}) for carbon (organic, elemental and carbonates), Fe, V and Cd at 930 m. Statistical significant correlations have been observed between fluxes and mass ratio for all the above mentioned elements indicating that fluxes variability, presented in the previous section,

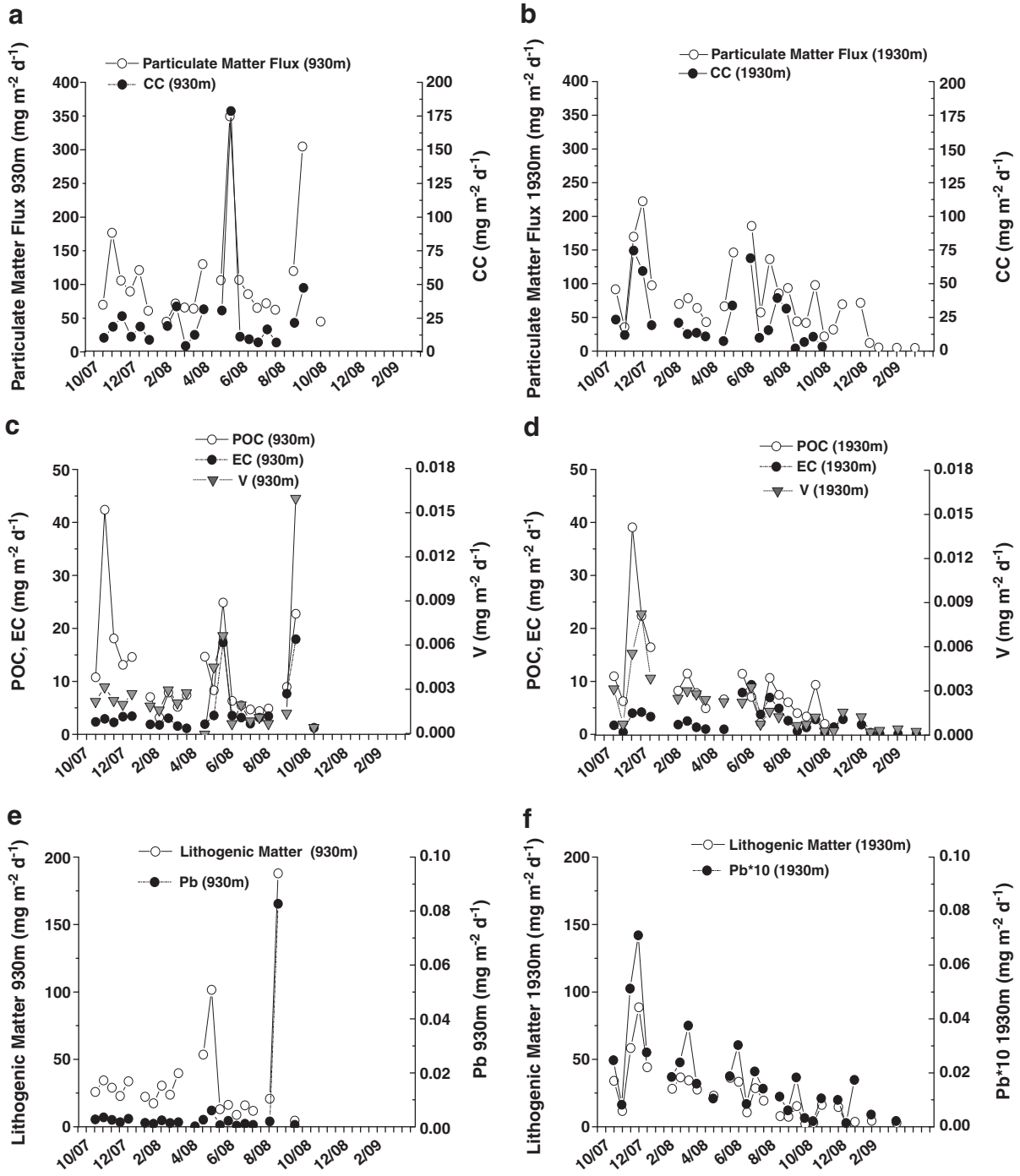

Fig. 3. Time series of fluxes of particulate matter and carbonates (a, b), particulate organic, elemental carbon and vanadium (c, d) lithogenic and lead (e, f) at both depths (930 and 1930 m). All fluxes are expressed in mg m^{-2} d^{-1}.

was not only driven by mass flux variability. For instance, as far as carbonaceous species are concerned a reasonable agreement between maxima of fluxes and mass ratios occurs for EC and CC and in lesser extent for POC. Similar situation can be seen for trace elements and lithogenic material (Fig. 4d–f). Lithogenic material (Fig. 4d) at the shallow trap presents 3 maxima; two in spring (March and May 2008) and one in autumn (September 2008) with values of 63, 51 and 62%, respectively. At the same time lithogenic contribution reaches its minimum values during summer (12–22%) and especially during the coccoliths bloom.

4. Atmospheric versus vertical fluxes through the seawater column

Once metals are deposited to sea surface, regardless of their sources, they are assimilated by marine biota, dissolved, accumulate in the mixed layer, transferred directly through the water column, etc. In the latter case metals, along with fecal pellets from biota, will be collected by sediment traps. In general dissolved matter is removed from surface waters via its assimilation by phytoplankton. Phytoplankton is likely to accumulate reactive trace elements (in particular, metals) by assimilation or adsorption processes (Fisher, 1985,

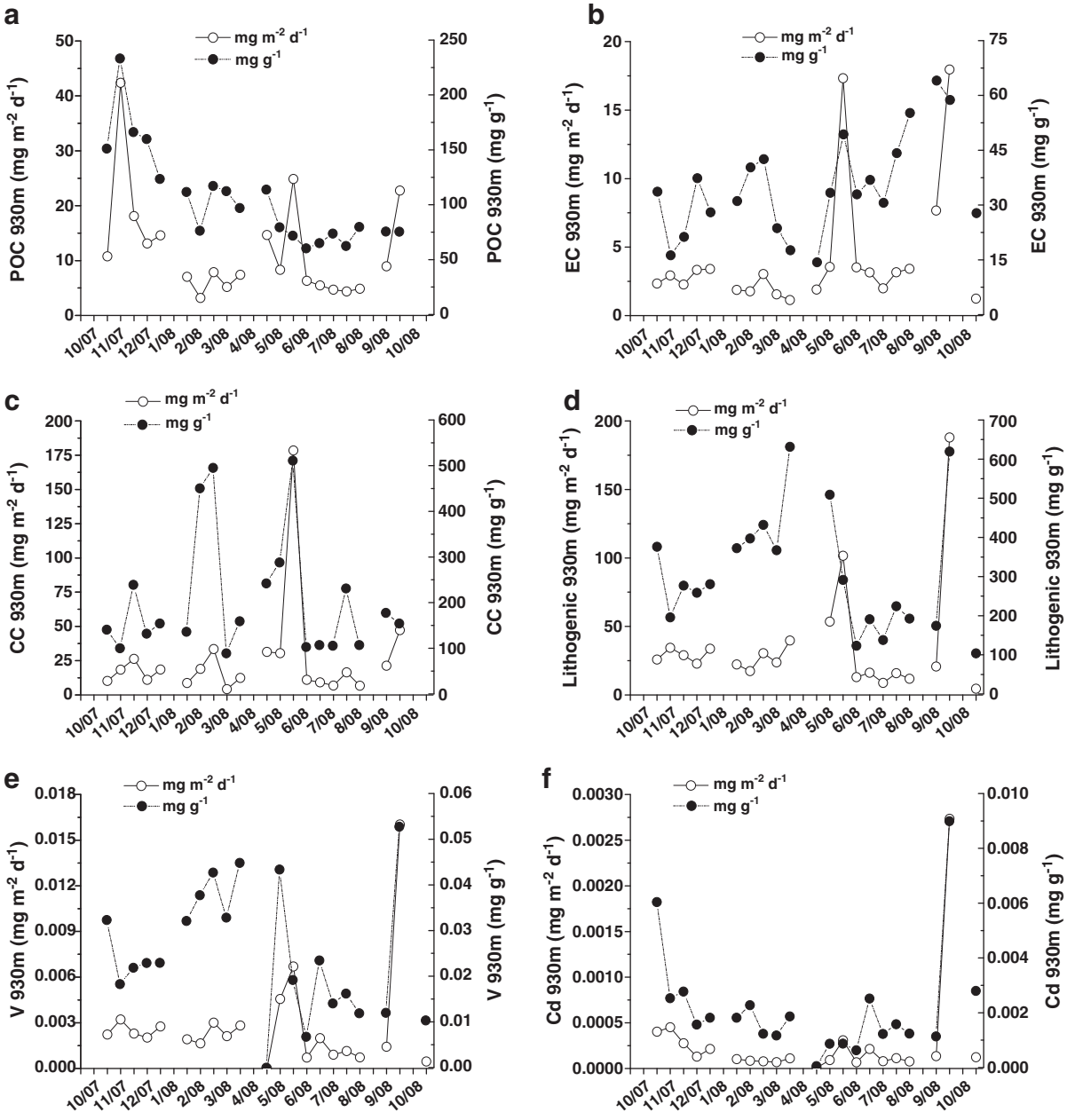

Fig. 4. Time series of particulate organic carbon (a), elemental carbon (b), carbonates (c), lithogenic material (d), vanadium (e) and cadmium (f) at 930 m for both fluxes (mg m^{-2} d^{-1}) and mass ratio (mg g^{-1}).

1986). The removal of atmospheric particulate matter is linked to biological packaging into large organic particles, e.g. adsorption onto phytoplanktonic debris or incorporation into fecal pellets (Deuser et al., 1983; Fowler and Knauer, 1986; Fisher et al., 1991). Thus by comparing input (atmospheric deposition) with the outflow from the marine upper layer, an estimation of the importance of atmospheric deposition can be obtained.

The atmospheric deposition estimates of major and trace metals derived during the current study are compared in Table 3 with results from sediment traps at both depths. Two estimates of atmospheric bulk deposition are presented covering each sampling period of the sediment traps. In Fig. 5 the percentage of atmospheric deposition in Varna needed to balance sediment trap fluxes referring to the common sampling period is also reported.

Lithogenic matter is a major component of particle fluxes of atmospheric deposition and marine export data. Overall, dust from atmospheric deposition can account for 25–77% of dust in the water column of the Black Sea; whereas, atmospheric inputs of mass contribute also significantly (19–29%) to the particulate matter measured in sediment traps in the Black Sea.

For the majority of the studied elements, atmospheric deposition represents a significant external source. Moreover for a number of elements (Al, V, Cr, Fe, Mn, Cu, Pb), atmospheric deposition provides quantitatively more than a quarter of the amount of metals collected by the sediment traps at the shallower waters and all or even more at 1930 m (average 30% and 96%, respectively). For the remaining metals (Cd, Ni and partly Zn) atmospheric deposition is also a significant external source contributing at least 10 and 40% to the sediment trap values at

Table 3
Daily atmospheric and seawater particulate matter fluxes (mg m^{-2} d^{-1}) in the Black Sea.

Metals mg m^{-2} d^{-1}	Atmospheric flux			Particulate matter flux in water column			
	Sinop, 04/09–12/09	Varna, 04/08–10/08	Varna, 04/08–04/09	930 m, 04/08–10/08	930 m, 10/07–10/08	1930 m, 04/08–04/09	1930 m, 10/07–04/09
Dust	5.40	10.8	10.4	43.4	35.7	13.5	22.8
Mass	18.8	24.5	19.8	131	109	69.3	78.8
Al	0.468	0.719	0.641	2.95	2.55	1.17	1.72
Ca	–	0.297	0.263	20.8	16.0	7.92	8.35
V	1.00E-03	1.07E-03	1.00E-03	3.15E-03	2.80E-03	1.02E-03	1.89E-03
Cr	5.73E-03	2.50E-03	2.43E-03	8.56E-03	6.36E-03	3.37E-03	4.19E-03
Mn	4.47E-03	6.27E-03	5.52E-03	2.47E-02	2.44E-02	1.11E-02	1.83E-02
Fe	0.243	0.487	0.469	1.95	1.61	0.609	1.03
Ni	2.00E-03	1.20E-03	1.13E-03	5.65E-03	4.56E-03	2.32E-03	3.36E-03
Cu	2.26E-03	4.43E-03	4.88E-03	8.83E-03	8.19E-03	3.38E-03	6.01E-03
Zn	1.38E-02	6.28E-02	4.16E-02	0.254	0.315	0.111	0.165
Cd	4.97E-05	2.95E-05	5.50E-05	3.60E-04	2.80E-04	8.29E-05	1.33E-04
Pb	7.87E-04	1.73E-03	2.00E-03	9.31E-03	6.03E-03	1.13E-03	1.82E-03

930 m and 1930 m, respectively (Fig. 5). All the above results clearly indicate the importance of atmospheric inputs to the biogeochemical cycling of trace elements into the Black Sea.

5. Conclusion

The role of atmospheric deposition of major and trace metals on Black Sea's biogeochemical cycling has been assessed by comparing the results from atmospheric deposition data with sediment traps data deployed at two depths in the southern Black Sea.

At the sediment traps, significant correlation has been observed between particulate matter, POC and lithogenic material. The good correspondence between the flux of biogenic, lithogenic and anthropogenic matter suggests that removal occurs largely by incorporation into larger sinking "marine snow" aggregates and fecal pellets during sporadic intense plankton blooms.

Atmospheric deposition presents an important seasonal variability driven by meteorology, especially air masses origin and precipitation. The observed bulk deposition fluxes of major and trace metals are within the range of the reported values for the Mediterranean Sea. By comparing atmospheric deposition fluxes of metals with data from sediment trap collectors, the significant role of the atmosphere as an external source of major and trace metals to the southern Black Sea has been demonstrated.

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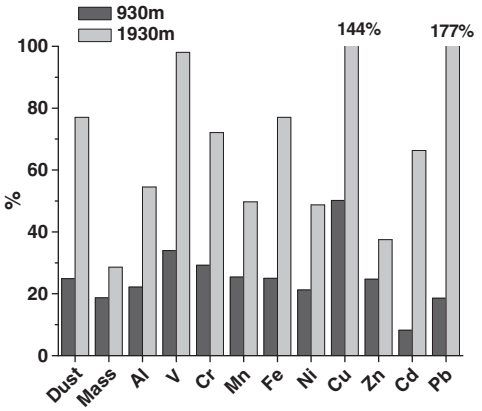

Fig. 5. Percentage of atmospheric deposition of mass, lithogenic material, major and trace metals in sediment traps, during the common sampling periods (4/08–10/08 at 930 m and 4/08–4/09 at 1930 m).

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