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**Temporal variability
of mass and trace
metal downward flux**

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Factors controlling the temporal variability of mass and trace metal downward flux at 1000 m depth at the DYFAMED site (Northwestern Mediterranean Sea)

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Abstract

Mass fluxes and trace metal (TM) fluxes were measured from samples collected in 2003 to 2005 from sediment traps deployed at 1000 m depth at the DYFAMED (Dynamique des Flux Atmosphériques en MEDiterranée) time-series station (central Ligurian Sea, 2350 m depth). A highly significant correlation is observed between all TM fluxes, whatever the nature and emission source of the TM (e.g., crustal such as Al, Fe, Co, or anthropogenic such as Zn, Cd, Pb) and the mass flux. Because these TMs originate from different emission sources, and, therefore, their atmospheric deposition to the sea surface varies with different seasonal patterns, it is suggested that fluxes of particulate organic carbon determine fluxes of TMs, and not the contrary. The seasonal sequence of the transfer of TMs to sea floor (winter convection, spring bloom and nutrient depletion of surface waters in summer and autumn) is briefly examined to highlight the concomitant temporal variability of mass and TM fluxes. This suggests that the TM downward transfer is totally controlled by the seasonal variability of biogenic carbon production, itself depending upon the intensity of winter convection. This may be a peculiarity of marine regions such as the Ligurian Sea, where hydrodynamical features (and, therefore, spring blooms) are strongly constrained by climatic and meteorological conditions (winter temperature, wind events, rain events).

1 Introduction

Metal contamination in the marine environment is a relevant problem, particularly in the Northwestern Mediterranean Sea that is subject to intense particulate and dissolved atmospheric inputs. These include anthropogenic inputs from Northern and Central Europe and pulsed Saharan dust events from Northern Africa (Guerzoni et al., 1999) containing natural crustal material. Chester et al. (1997) have described this marine region as the superimposition of Saharan inputs on a homogeneous European background signature. As a result, trace metal (TM) concentrations in Mediterranean

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surface waters are higher than in the open ocean, e.g. the Atlantic Ocean (Morley et al., 1997), and their distribution patterns in the water column suggest that the atmospheric input governs the local TM biogeochemical cycling (Béthoux et al., 1990; Migon et al., 2002).

5 Sediments integrate pollution signals (Martín et al., 2009; Sanchez-Cabeza and Druffel, 2009). Therefore, in marine environments mainly constrained by atmospheric forcing such as the Northwestern Mediterranean Sea, the accumulation of sinking particles presumably mirrors the evolution of anthropogenic emissions along its densely populated shores (~ 300 inhabitants per km^2 in 2008).

10 However, the problem remains of knowing which parameter controls the temporal variability of TM vertical flux to the seafloor. Armstrong et al. (2002) pioneered the idea that fluxes of mineral material (biogenic silica, carbonate shells and atmospheric dust), rather than subsurface particulate organic carbon (POC) fluxes, determine deep POC fluxes. However, Passow (2004) has pointed out that large aggregates (marine snow) exhibit high settling velocities (50 to 200 m d^{-1}) and presumably collect and scavenge amounts of mineral particles too small to sediment individually. For example, diatom aggregates may be efficient POC-rich carriers for inorganic material (Hamm, 2002).

15 Previous studies (Fowler et al., 1987; Migon et al., 2002) have shown that biological and biogeochemical processes occurring in the upper marine layer control the temporal variability of subsurface fluxes in the Northwestern Mediterranean. Also, Miquel et al. (1994) indicated that besides the biological processes, the vertical mixing of the water column was an important factor determining the magnitude of the vertical flux. The present paper aims to address this question through the comparison of mass fluxes and fluxes of a wide variety of TMs at 1000 m depth, over a continuous sampling of more than two years and attempts to demonstrate that all TM fluxes have the same behaviour, independently of the TM origin.

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2 Experimental

The DYFAMED (Dynamics of atmospheric fluxes in the Mediterranean Sea) time-series station (2350 m depth, 43°25' N, 7°52' E; Fig. 1) is a long-term monitoring station in the open Ligurian Sea (Northwestern Mediterranean Sea) located 28 nautical miles off continental France. The Ligurian Sea circulation is characterised by a permanent cyclonic gyre. The offshore central zone is separated from the coast by a frontal zone, across which there is a rapid horizontal change of density (Lévy et al., 1998). As a result, apart from exceptional conditions (extreme hydrodynamics and/or coastal emissions), the DYFAMED site is sheltered from lateral inputs (Béthoux et al., 1988). For this reason, the atmosphere is believed the only significant source of TMs to the open Ligurian Sea. Such hydrodynamic protection of the central Ligurian Sea is crucial, because the Northwestern Mediterranean coastline drains approximately 60% of the Western Mediterranean continental pollutants (Béthoux et al., 1988). The DYFAMED site has been used several times for the study of interactions between atmospheric deposition and open surface waters (e.g., DYFAMED and MEDFLUX programmes; see special issues Deep-Sea Research II 49, 11 (2002) and 56, 18 (2009), respectively), and it is now viewed as a reference to monitor ongoing changes in the Northwestern Mediterranean Sea.

Automated time-series sediment traps were moored at the DYFAMED site. The conical sediment traps (Technicap PPS 5, height 2.3 m, collection area 1 m²) were equipped with a programmable 24-cup collector. The sampling cups contained a solution of 2% buffered formaldehyde in filtered seawater (0.22 µm) to prevent in situ microbial degradation and grazing by swimmers. Formaldehyde has been widely used as preservative in trap time-series studies because its use reduces the loss of organic material from the trap. After recovery, the samples were stored in the dark at 4 °C. Swimmers were first removed by successive sieving through 1500 and 600 µm and further by hand-picking under the binocular microscope. The remaining samples after initial wet subsampling were then desalted and freeze-dried for further analysis and the

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estimation of mass flux (Miquel et al., 1994; Miquel and La Rosa, 1999).

Trap samples were mineralised according to the following protocol: The organic matrix was destroyed with an oxidizing attack (HNO_3), and mineral aluminosilicate matrixes were destroyed with HF. The sample was freeze-dried and weighed in 7 mL Teflon flasks, and dissolved as follows: 1) 1 mL HNO_3 65% was added to each flask. These flasks were sealed and put into larger Teflon bottles (60 mL) that act as expansion cells, overcome acidic evaporation by leaks and help to prevent contamination. This apparatus was left 5–6 h in an oven at 150°C , after which bottles and flasks were brought to room temperature and left open under laminar flow hood until a brown dry residue remained. 2) 500 μL HNO_3 65% and 500 μL HF 40% were added to the remainder. The flasks and bottles were closed and put in an oven 5-6 hours at 150°C , prior to open evaporation at room temperature under laminar flow hood, until a white dry residue was obtained. This residue was ultrasonically dissolved in 5 mL HNO_3 0.1 N. The samples were then made up with Milli-Q water to 15 mL.

Mass and TM (Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb) fluxes were analysed from 2003 to 2006. However, years 2005 and 2006 were affected by higher than usual currents. Currents $>12\text{ cm s}^{-1}$ are more likely to affect both quantitatively and qualitatively the collection of sinking particles by traps (Scholten et al., 2001; Buesseler et al., 2007). This situation occurred from 22 February to 23 June 2005, and during most of the year 2006. In order to circumvent any bias, samples from the above period of 2005 and the whole year 2006 were not considered in this study. Digested and dissolved TMs were analysed by ICP-OES, using a Perkin-Elmer Optima 3000, axial torch instrument. An ultrasonic nebuliser (CETAC) was used as sample introduction to improve the sensitivity (Desboeufs et al., 2003) up to 0.01 to 0.1 ppb level depending on the TM. The plasma power was 1250 W with a sample flow of 1 mL/min. An external calibration was performed with multi-elemental standard solutions made by a mixing of 1 g/L mono-elemental solutions from various origins. The accuracy was checked using dilutions of multi-elemental commercial solutions, and also SLRS-4 as certified reference material (CRM), but finally by analyses of CRM geo-standards GBW, BCSS and PACS.

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A good accuracy was found. Table 1 records the measured TMs with the median relative standard deviation (RSD) for all the replicate measurements of the CRMs and the recovery observed between certified and measured values. The observed recovery was then used to correct the measured values.

3 Results and discussion

Temporal evolutions of mass and TM fluxes are compared at 1000 m depth. Mineralisation processes decrease with increasing depth, and, at 1000 m depth, fluxes are considered net fluxes (Guidi et al., 2009). Raw data (mass and TM fluxes at 1000 M depth between March 2003 and December 2005, expressed in $\text{mg m}^{-2} \text{d}^{-1}$ and $\mu\text{g m}^{-2} \text{d}^{-1}$, respectively) can be found at: <http://www.obs-vlfr.fr/~heimbuerger/Files/Flux%201000m.pdf>. Seasonal and interannual variabilities of both mass and TM fluxes are compared in Fig. 2.

The outstanding feature is the strong covariance observed between the mass flux and the TM flux (Fig. 2), whatever the nature of the TM. Atmospheric deposition is the main entrance route of TMs to the open Mediterranean water column, at least for anthropogenic TMs since the beginning of the industrial era (Guerzoni et al., 1999; Martín et al., 2009). Several recent papers (e.g., Armstrong et al., 2002, 2009; François et al., 2002; Klaas et al., 2002; Lee et al., 2009) have postulated that lithogenic particles (originating mainly from atmospheric dust inputs), biogenic silica and carbonate shells can significantly control the sedimentation rate of biogenic material by ballasting biogenic matter, particularly when zooplankton faecal pellet production is low (Lee et al., 2009). This process presumably increases the density of POC aggregates (and, therefore, their sinking rates), but it is also believed capable of protecting POC from oxidation and remineralisation (De La Rocha and Passow, 2007). Atmospheric dust has been also mentioned as a possible catalyst for particle aggregation and further sinking (Lee et al., 2009).

The most striking results of this study are, however, that fluxes of a wide variety of

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TMs (e.g., anthropogenic such as Zn, Cd, Pb, or crustal such as Al, Fe, Co) exhibit in every case the same temporal variability. In addition, all TMs, whether of crustal or anthropogenic origin, are strongly and significantly ($p < 0.0001$) intercorrelated (Table 2), which suggests that all TMs are driven to depths at the same time and, therefore, gathered into the mass flux. Because these TMs originate from different emission sources, and, therefore, their atmospheric deposition to the sea surface varies with different seasonal patterns, it is hypothesized that the flux of mass determines fluxes of TMs. This means that the temporal variability of atmospherically derived TM fluxes is an effect, instead of a cause, of mass vertical transfer. As a result, mass fluxes control the temporal variability of TM removal from surface waters, as clearly suggested by the high correlations presented in Fig. 2.

The seasonal patterns of mass and TM fluxes show reproducible peaks in January–February (2004 and 2005; Fig. 2). This period corresponds to dense water formation and subsequent convection (Béthoux and Gentili, 1999). The vertical mixing driven by the cooling and/or increase of salinity of surface waters carries dissolved and particulate matter, including TMs, to depths (Migon et al., 2002). Between March and June (2003 and 2004; Fig. 2), the spring phytoplankton bloom drives the transfer of TMs to depth. This seasonal pattern suggests that, apart from convection episodes associated with dense water formation in well-defined Mediterranean areas (among which is the Ligurian Sea), the transfer of atmospheric material is almost totally driven by the magnitude and variability of biological production. This statement is in agreement with many studies that pointed out the prominent role of biological activity in the removal of TMs (e.g., Fowler et al., 1987; Buat-Ménard et al., 1989; Grotti et al., 2001; Migon et al., 2002). The efficiency of the vertical transfer under mesotrophic conditions directly depends on the intensity of the water column mixing and the subsequent diatom bloom (Marty and Chiaverini, 2010).

On the opposite, the oligotrophic season is characterised by very low transfer, due to lower biological activity. Individual dust particles have, based upon Stokesian calculations (Stokes, 1901), a negligible settling velocity (at most, $< 5 \text{ m d}^{-1}$; Buat-Ménard

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et al., 1989). Therefore, the transfer of TMs from sea surface to 1000 m depth without the driving force of hydrology or biology would require at minimum 200 days. This time being longer than the oligotrophic period (on average, ~5 months in the Northwestern Mediterranean Sea), atmospheric matter (dissolved matter and particles that do not dissolve) cannot be removed from surface waters without packaging onto large organic particles or aggregates, incorporation into faecal pellets (Fowler and Knauer, 1986; Wang and Fisher, 1998), or adsorption onto planktonic debris and faecal pellets during their sinking (Fisher et al., 1991), as observed during the mesotrophic season. Apart from winter episodes of convection, and in the absence of a significant pool of biogenic particles or aggregates, atmospherically transported TMs will thus accumulate in the surface layer in conditions of stratification, when the surface layer is nutrient-depleted (Migon et al., 2002). Total chlorophyll *a* integrated from surface to 200 m depth (*ITChl a*) usually decreases after the spring bloom (generally after July) to less than 20 mg m⁻² (Marty et al., 2002) and remains at low levels until the end of the year. However, in 2005, *ITChl a* values remained exceptionally high throughout the summer (e.g., 58 mg m⁻² in August; data available at <http://www.obs-vlfr.fr/sodyf>), and yielded significant vertical fluxes during summer (Fig. 2).

Small peaks in fluxes may be also observed between October and December. This presumably results from autumnal wind episodes that likely break the water column stratification and, therefore, bring nutrients to the surface layer and support secondary blooms (DiTullio and Laws, 1991; Goutx et al., 2000). For example, a mass peak was observed in autumn 2005 (Fig. 2), while fluxes were negligible in 2003 and 2004 at the same period. Strong easterly winds were observed early October 2005 (1st–5th) and yielded a decrease of sea surface temperature of 3.6 °C (from 20.9 to 17.3 °C) within 5 days at the METEO-FRANCE buoy “ODAS” located nearby the mooring line. Such a rapid temperature decrease suggests wave-induced deepening of the mixed layer. This would supply nutrients to the depleted surface layer, triggering an autumnal bloom as soon as calm conditions settle (probably dominated by nano- and picophytoplankton, hence the low amplitude of the observed flux; Marty et al., 2009). Most probably,

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the increase in flux observed at this period of the year resulted from such an event. In 2003 and 2004, no significant wind event and no subsequent biological production were observed between October and December. The situation observed in 2005 resulted in higher autumnal flux of mass and POC export, and, thus, higher flux of every TMs. For every TM, whatever its emission source, the same pattern strictly follows that of mass flux, which is induced by a physical cause, independently of any atmospheric supply of TMs.

Such concomitant temporal variability of mass and TM fluxes suggests that the TM downward transfer is controlled by the seasonal variability of mass flux, and not by the variability of atmospheric fluxes, the variability of mass flux being successively driven by winter convection (“flush down” effect) and biogenic carbon production. Although contrary to the widespread understanding, such a statement is, however, in agreement with studies of Passow (2004) and Passow and De La Rocha (2006). In addition, Passow and De La Rocha (2006) have observed that if mineral ballasting actually determines the downward flux of POC, this changes the way in which the biological pump is understood and modelled at present day (Ridgwell, 2003; Heinze, 2004).

4 Conclusions

Ultimately, the variability of TM fluxes is controlled by winter convection and the subsequent biological production. Hydrodynamical features of the Ligurian Sea are strongly constrained by meteorological conditions (winter temperature, wind events, rain events). As a consequence, the Ligurian spring bloom and subsequent marine fluxes below the euphotic layer are strongly dependent on climatic and meteorological conditions as well. Therefore, the understanding of the interannual/decadal variability of deep fluxes of elements in relation with climatic and meteorological changes requires i) reliable measurements of mass fluxes, including the use of proxies of such as ^{230}Th to minimise possible bias in the measurements (Rutten et al., 2000; Roy-Barman et al., 2009), and ii) good knowledge of physical (climatic and meteorological)

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parameters that determine the magnitude of winter dense water formation, as well as their interannual/decadal variability. This is very important in terms of global change, because any alteration of the climatic/meteorological conditions would significantly impact phytoplankton dynamics and, therefore, the particle flux, and this would ultimately determine the evolution of TM dynamics in the global ocean, much more than changes in the atmospheric deposition variability.

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Table 1. Certified reference material (CRM) validation results, expressed in $\mu\text{g g}^{-1}$. The median relative standard deviation (RSD, in %) is calculated from full replicates including the mineralisation step, 10 for GBW, 5 for BCSS and PACS. The median recovery observed between certified and measured values is expressed in %. Values noted * are close to the detection limit. Mean RSD values can be used to determine the uncertainty of the analytical method on each TM.

TM	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
GBW measured	78 900	107	57	3106	39 100	70	163	498	152	0.2	27
GBW RSD	3	5	7	6	6	6	9	5	6	30*	8
GBW certified	72 800	112	58.4	3330	46 000	76.7	150	424	160		
GBW recovery	108	96	97	93	85	92	109	117	95		92
BCSS measured	67 600	93	105	231	30 900	10	63	27	108	0.4	22
BCSS RSD	3	5	5	5	6	5	5	8	12	7	18
BCSS certified	62 600	94.4	123	229	33 400	11.4	55.3	18.5	119	0.25	22.7
BCSS recovery	108	98	86	101	93	89	113	147	91	163*	98
PACS measured	70 200	132	106	469	43 400	16	57	508	824	3	400
PACS RSD	2	5	2	1	1	4	9	2	6	4	5
PACS certified	64 700	127	113	470	48 700	17.5	44.1	452	824	2.38	404
PACS recovery	108	104	94	100	89	91	130	112	100	109	99
Mean RSD	3	5	5	4	4	5	8	5	8	6	10
Mean recovery	108	99	92	98	89	91	117	125	95	109	96

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Table 2. Intercorrelation matrix of the 11 TMs (59 observations per variable). All TMs, whether of crustal or anthropogenic origin, display high intercorrelation values (R^2). All intercorrelations are significant ($p < 0.0001$).

R^2	Al	Fe	Co	Mn	Cr	Ni	Cu	Cd	Pb	V	Zn
Al	1										
Fe	1.00	1									
Co	0.97	0.97	1								
Mn	0.97	0.97	0.96	1							
Cr	0.99	0.99	0.97	0.99	1						
Ni	0.97	0.97	0.95	1.00	0.99	1					
Cu	0.96	0.96	0.95	0.98	0.98	0.98	1				
Cd	0.98	0.98	0.95	0.95	0.96	0.95	0.95	1			
Pb	0.98	0.98	0.97	0.99	0.99	0.99	0.99	0.96	1		
V	1.00	1.00	0.98	0.98	0.99	0.98	0.97	0.98	0.99	1	
Zn	0.95	0.95	0.94	0.96	0.96	0.97	0.98	0.93	0.97	0.95	1

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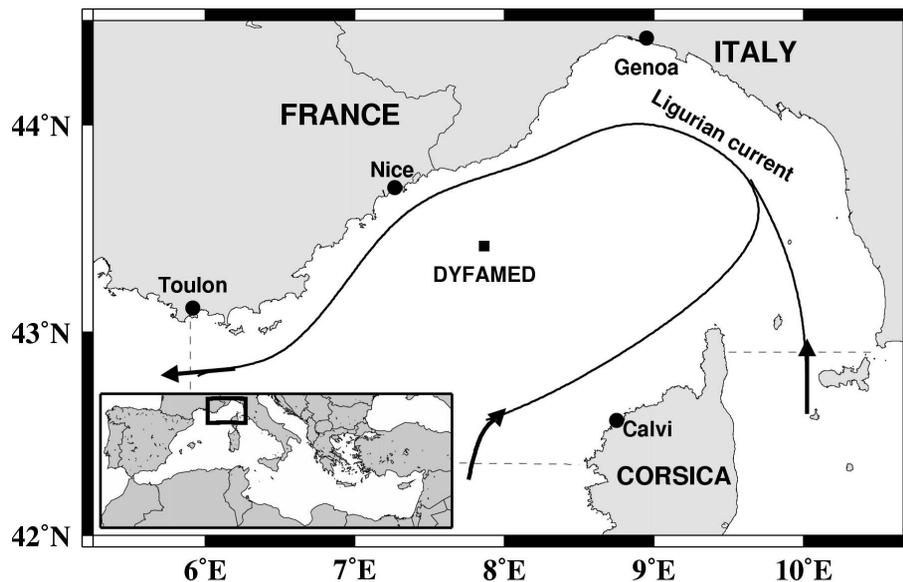


Fig. 1. Map of the Northwestern Mediterranean Sea and the location of the time-series sampling station DYFAMED.

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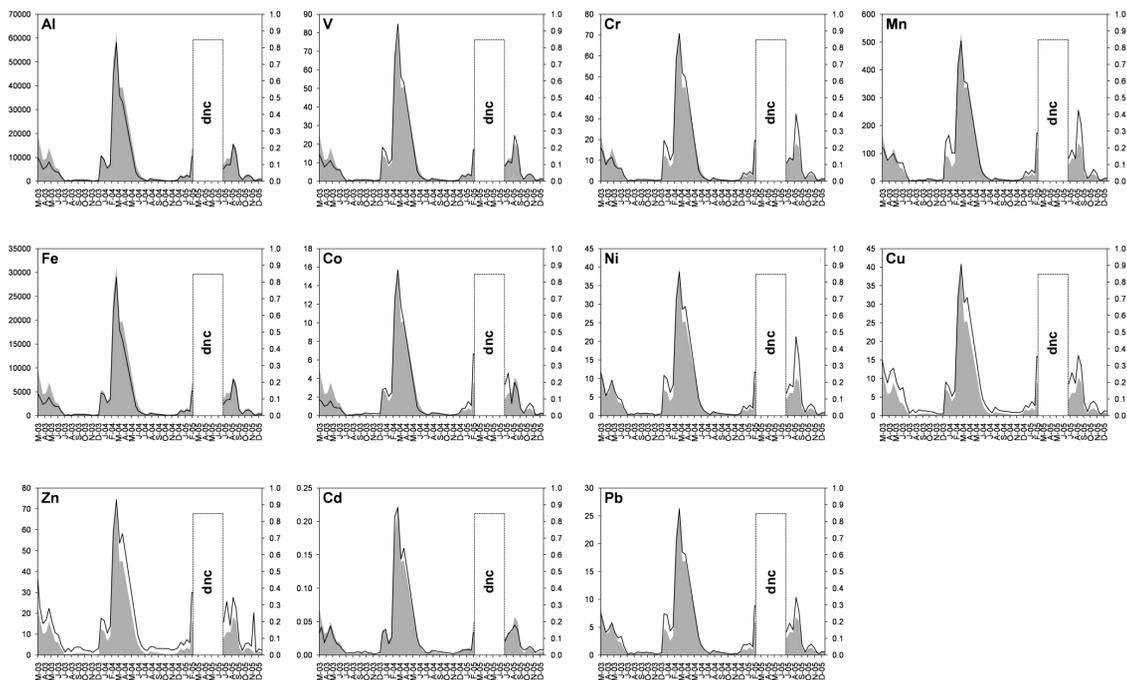


Fig. 2. Comparison of seasonal and interannual variabilities of mass and TM fluxes for the period 2003–2005. Mass (in grey) and TM (black line) fluxes are expressed in $\text{gm}^{-2} \text{d}^{-1}$ and $\mu\text{gm}^{-2} \text{d}^{-1}$, respectively; data come from a sediment trap deployed at 1000 m depth at the DYFAMED site. The correlation between mass and TM fluxes is figured by R^2 coefficients given for each TM. The data for the period 22 February to 23 June was not considered (dnc) in the present study pending calibration of the mass flux with ^{230}Th data (see text).

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