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Biogeosciences Discussions

Interactive comment on "Factors controlling the temporal variability of mass and trace metal downward flux at 1000 m depth at the DYFAMED site (Northwestern Mediterranean Sea)" *by* L.-E. Heimbürger et al.

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Responses to Reviewer E.P. Achterberg

The submitted manuscript deals with total trace metal fluxes and mass fluxes for 1000 m depth traps deployed in the northwestern Mediterranean Sea. The manuscript is succinct, and lacks a good deal of detail, additional data and interpretation approaches. The paper lacks data on POC and mineral fluxes, in addition there is no effort made to compare the TM sedimentation fluxes to atmospheric inputs. No effort is made

to compare the composition of the trap material to sources. This greatly limits the importance of the paper and leaves the reader with more questions than answers. The use of scientific English requires improvements in places. The key message of the paper is not clear. What is the biogeochemical importance of the findings on TM and mass fluxes? The data is nice, and I would recommend publication after significant revision.

We did not provide POC data for two reasons: - On the one hand, our aim was to submit a short and straightforward manuscript. For this reason, one may think there is a lack of detailed data. - On the other hand, we think that introducing POC data would not make our purpose clearer. It is foreseeable that the covariance between metals and POC would be much less good than that between metals and mass. Indeed, two of us have already published temporal variations of Al/mass flux ratios at 200m depth, from sediment trap time-series at the DYFAMED site (Migon et al., 2002). These ratios exhibit maximum values in January-February (period of convection), because the mineral material supplied by atmospheric inputs has accumulated during the period of minimal transfer (period of oligotrophy/stratification), and there is not much biogenic material. On the contrary, in March-April (period of biological production), Al/mass flux ratios are significantly lower, because the transfer is now high and driven by biological productivity. By the way, atmospheric inputs have not accumulated, thus metal fluxes are lower. As a result, the percentage of biogenic material is high. Therefore, one can expect that the comparison of POC vs metal flux seasonal pattern will mirror this scenario: when POC fluxes are high, metal fluxes are minimal. This, however, does not contradict our purpose: Apart from biogenic silica and carbonates (we have not the data), mass fluxes gather both biogenic and mineral material, and the covariance between mass and metals suggests that every time particles are transferred from surface to depths, metals are found in sediment trap material. Since, in addition, there is a correlation between all metals in sediment trap samples (in spite of different emission temporal patterns: when Saharan dust events occur, loads of Al or Fe enter sea surface, but loads of Pb or Zn do not; when anthropogenic atmospheric events occur, loads of Pb

or Zn enter sea surface, but loads of Al or Fe do not), one can infer that the occurrence of Saharan dust events (or that of anthropogenic events) does not determine downward fluxes. On the opposite, biogenic particles drive fluxes of mineral material. This is in agreement with the respective size of atmospheric and biogenic particles, and with Stokesian calculations (Stokes, 1901). Ultimately, this does not contradict mineral ballasting: even if mineral material cannot sink without packaging with biogenic material, its density increases the sinking rate of biogenic particles. This is now briefly said in the manuscript.

No comparison between the composition of trap material and emission sources. Once again, we had in mind to keep the straightforwardness of the manuscript. We think such a comparison would change that feature. In addition, many papers (e.g., Guieu et al., 1997; Guerzoni et al., 1999) have stated that atmospheric deposition supplies almost totality of TMs in open Mediterranean waters, or, at least at the DYFAMED site sheltered from lateral inputs, thus the source apportionment of trap material might be out of our purpose for that specific case. Our purpose is: Whatever the origin of atmospherically-transported TMs found in sediment trap samples, they accumulate in surface waters if no hydrodynamic (sinking of dense water in winter) or biological (plankton bloom in spring) driving force carries this material to depths. In other words, basically, apart from winter mixing or packaging with biogenic material, TMs cannot sink. The correlations between TMs presented here presumably support this assumption, because while TMs of different nature, e.g., Al and Pb, do not enter surface waters at the same time (because their emission sources are different and exhibit different seasonal dynamics), they are transferred to depth at the same time, i.e. when they are driven by convection or subsequent plankton blooms.

The key message of the paper is not clear. Our purpose was certainly not well presented. The key message is: TMs are driven to depths only via winter mixing events and subsequent biological production (and, to a lesser extent, production triggered by fertilising atmospheric inputs, which may be an indirect impact of atmospheric deposi-

tion on transfer processes), and not by the occurrence of atmospheric events. Atmospheric deposition supplies TMs to surface waters, indeed, and this mineral material is likely to ballast mass fluxes, but not to determine vertical transfer. We tried to make it clearer in the revised manuscript.

Specific comments: Page 2551 Line 20: is trace metal pollution in the study region a critical issue. Are there reports of toxic effects of enhanced trace metal levels? The study site is characteristic of the open western Mediterranean, with TM concentrations relatively low (e.g., Co 32- 120pM, Ni 3.6-5.5nM, Cu 1.8-2.2nM and Cd 91-194nM, Heimbürger et al. 2008), but enhanced compared to the open ocean according to Paytan et al. (2009) for instance. To our knowledge, no toxic/inhibitory effects have been reported in the Ligurian Sea. Biological productivity does not seem to be affected by TM pollution. Significant TM pollution (as well as TM fertilisation), if any, would not change our purpose. The only available study addressing TM toxicity to phytoplankton in this region was made by Paytan et al. (2009), who observed Cu toxicity from aerosols to some phytoplankton species calculated toxicity thresholds for the red sea. We verified, using the stated Cu toxicity threshold values and mean Chlorophyll-a values from the DYFAMED site, that atmospheric Cu deposition does not inhibit primary production. Furthermore, TM concentrations in the atmospheric aerosol in this region have decreased over the past two decades for several TMs (Migon et al., 2008; Heimburger et al., 2010), which presumably has yielded reduced atmospheric deposition of TMs, as well.

Page 2551 Line 25: ...as the superimposition of Saharan inputs..... this is awkwardly phrased. The sentence has been re-phrased: “Chester et al. (1997) stated that the atmosphere of this marine region is characterized by a homogeneous European background signature disrupted by episodic Saharan dust events”.

Page 2552 (2551) Line 26: provide evidence for the relatively enhanced trace metal levels in the Mediterranean surface waters (citations and values). We provide a table summarising TM surface concentration data of the western Mediterranean. However,

we think this is not a key point of our manuscript, and, in order to keep the paper short and straightforward, we didn't want to include these data in our discussion.

Page 2552 Line 10-16: argumentation to be improved. We agree, this sentence has been rephrased. Armstrong et al. (2002) pioneered the idea that mineral material (biogenic silica, carbonate shells and atmospheric dust), rather than subsurface organic carbon (POC), determine the occurrence of deep POC fluxes. However, Passow (2004) pointed out that, despite their ballasting role, mineral particles may not cause POC fluxes. On the contrary, the occurrence of POC fluxes may determine the occurrence of mass fluxes.

Page 2553 Line 13. Sentence on NW Med coastline draining 60% of pollutants.... is not relevant to this manuscript This sentence has been removed.

Page 2553 Line 28. How was the sample desalted. Also, did the authors consider a weak leach to remove more labile (often anthropogenic TMs from particulate material). Mass retained on a 1 μm Nuclepore filter was rinsed with buffered (pH 7-10) Milli-Q water three times to remove salts (JGOFS, 1996). This is now mentioned in the revised manuscript. The removal of labile TMs by leaching was never tested. However, the use of buffered Milli-Q water probably significantly limits risks of labile TM loss.

2554 Line 14- what is MQ water? Milli-Q water is the best category of deionized water. Naming it "deionized water" does not tell enough about the quality of that water. Millli-Q is produced by Millipore, we thus write "deionised Milli-Q® Millipore water (resistivity: 18M Ohm)" in the revised manuscript.

2554 Line 16-17. I would suggest to keep in the data from 2005-2006. The ratio's will still be relevant and the sampling period may provide a good contrast. We agree. Years 2005 and 2006 are now included in the data set. One can observe that our results do not significantly change. This suggests the qualitative bias due to non rectilinear position of the traps is negligible.

2555 Line 7. Better define what a net flux means. Most processes altering the export flux, such as remineralisation, grazing, etc., occur above 1000m depth, and further major changes of the sinking matter in the water column, in terms of mass and TM concentrations, are minimal. This is now specified in the revised manuscript.

2555 Line 14-15. Atmospheric inputs are an important input of TM to the surface waters, but riverine and sedimentary TM fluxes are important as well to surface and deep waters. In the initial manuscript, we describe in the Experimental section (page 2553, first paragraph) why sources besides atmospheric deposition are negligible for this region. In the revised version, this statement is strengthened, and additional references are provided. The sentence now reads: It is broadly accepted, that 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 (Martin et al., 1989; Migon, 1993; Guerzoni et al., 1999; Martín et al., 2009).

2556 line 1-11. An alternative possible explanation for the good correlation between the TMs could be a dominant source, which obscures any smaller more variable sources. The Saharan dust could be this dominant source, obscuring European anthropogenic sources. To verify this, a comparison between atmospheric inputs to the study region with the sediment trap material fluxes is required. In addition, a comparison between the trap material and Saharan dust material (from appropriate source regions) is required. An assessment of the relative enrichment of the trap material relative to crustal and Saharan dust material would be beneficial in assessing the anthropogenic contribution to the observed trap TMs. We agree partly with Dr. Achterberg. Indeed, a comparison of aerosols, wet and dry deposition fluxes influencing this marine region would be ideal. However, we did not measure those parameters during the same time period. Saharan dust is not really a dominant source in the NW Mediterranean. For example, between July 1997 and July 1998, only 6 events exhibited a Al flux > 1000 μg m-2 d-1. The highest Al flux for this sampling year was 2425 μg m-2 d-1, against a geometric mean of 383 μg m-2 d-1. Atmospheric TM inputs and sediment trap TM

fluxes (at 200m depth) have been already compared at the DYFAMED site (see Migon et al., 2002). A recent paper involving four of us (Heimbuerger et al., 2010), confirms the idea that the northwestern marine atmosphere is characterised by a homogeneous European background signature with episodic Saharan dust episodes (Chester et al. 1997). Furthermore, we could show that natural and anthropogenic TMs in aerosol have distinct seasonal distribution patterns. Those patterns do not coincide with the marine TM fluxes presented in the present manuscript. Another convincing point is that Saharan dust events, which surely occurred during the sampling period, are not detectable in the marine export flux.

Page 2558 Line 12-15. This is awkwardly phrased We agree. This sentence has been rephrased and placed in the conclusion section.

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Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/7/C2274/2010/bgd-7-C2274-2010-supplement.pdf

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Interactive comment on Biogeosciences Discuss., 7, 2549, 2010.

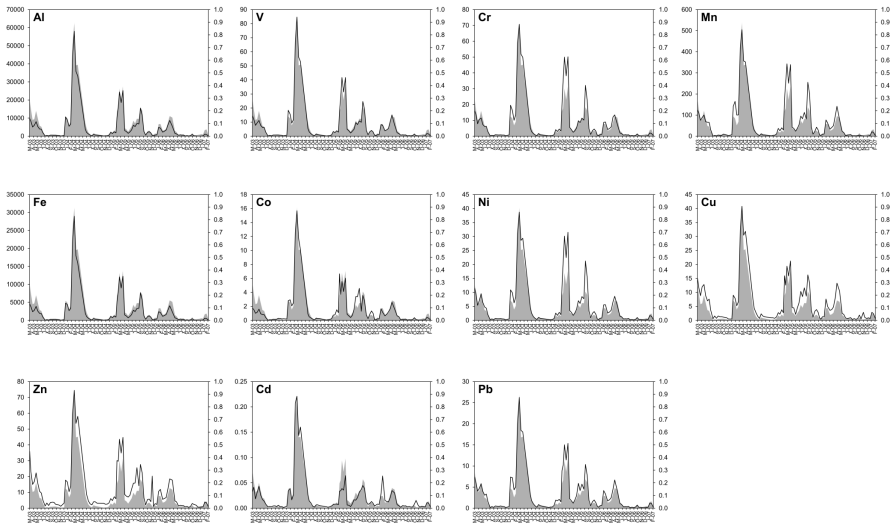

Fig. 1.

Sampling time (year)	Co (pM)	Ni (nM)	Cu (nM)	Zn (nM)	Cd (pM)	Pb (pM)	References
1983					65±16	230±92	(Béthoux et al., 1990)
				3.09±0.50	67±9	285±68	(Nicolas, 1993)
				3.9±0.54 (2.9-4.93)			(Ruiz-Pino et al., 1991)
					50-140		(Statham et al., 1985)
		4.3	2.0		40-120		(Boyle et al., 1985)
					45-190		(Copin-Montégut et al., 1986)
			2.05 (0.71-2.41)		79 (40-134)	469 (314-676)	(Ferrara and Seritti, 1989)
1987			2.4		95	300	(Seyler et al., 1989)
			2.14		62	362	(Marty and Nicolas, 1993)
1988		3.66±0.49	1.4		90±30		(Morley et al., 1989)
	40-200	2.77-7.84					(Zhang and Wollast, 1990)
1991				2.61±0.72	66±11	169±12	(Nicolas, 1993)
					53-124		(Riso et al., 1994)
1992		2-5.5	1.7-2.2		60-90		(Martin et al., 1993)
	<DL	4.0	1.4	5.0	70		(Morley and Burton, 1993)
1992/93		3.9	1.6	5.1	98	117	(Yoon et al., 1995)
1997/98					46±17		(Riso et al., 2004)
2003					70-90		(Lacan et al., 2006)

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Fig. 2.