

# Estimate atmospheric fluxes of nutrients and trace metals using an atmospheric deposition collection system in the Western Mediterranean Sea

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The atmospheric inputs to the Mediterranean Sea play a significant role in marine nutrient cycles during the summer period of surface water stratification. This is the case for macronutrients (P and N) (Loÿe-Pilot et al., 1990; Pulido-villena et al., 2010) and micronutrients such as Fe (Bonnet and Guieu, 2006), and also possibly trace metals such as Co, Ni, Mo, Mn, Zn and Cd which play an essential role in phytoplanktonic activity (Morel and Hudson., 1985). It is necessary to estimate the mass flux of nutrients and trace metals associated in atmospheric inputs and their bioavailability to assess their role in phytoplanktonic activity. To do this, many studies focused on macronutrient P and micronutrient Fe, however there are little data for trace metal deposition to Mediterranean Sea.

A network of mass deposition measurements was installed around the western Mediterranean basin on islands or coasts: Le Casset, Frioul Island and Cape Corsica (France), Mallorca Island (Spain), Lampedusa Island (Italy), and Medenine (Tunisia) since 2011 to estimate the dynamic of Saharan dust deposition events. This network is based on an automatic sampler named CARAGA collecting weekly bulk insoluble fraction flux of total atmospheric deposition, mainly composed of mineral dust (Laurent et al., 2015).

In order to estimate mass flux of nutrients and trace metals, we tested the relevance to use CARAGA samples for measuring the chemical composition of atmospheric deposition. In a first time, the contribution of the insoluble fraction was compared to total deposition by measuring elemental mass loss during simulated rain events. During the collection in situ, we lost by dissolution in water 0.39-1.09% of Al and 0.11-0.68% of Fe, but 10.27-15.60% of P. For trace metals, this loss presents less than 5%, except Zn (5.79-9.22%), Cu (2.55-6.58%) and Mn (3.67-15.82%). For mass measurements, CARAGA samples are ignited at 550°C to eliminate organic matters. The impact of this ignition on elemental composition was checked from dust and soot analogues. Results show a mass loss of nutrients and trace metals of less than 5%. Finally, the various tests show that the CARAGA samples are relevant to estimate the total mass fluxes of nutrients and trace metals with uncertainties better than 10% for Al, Fe and trace metals, except Mn (15%) and P (around 20%).

Annual mass fluxes of nutrients and trace metals have been estimated for samples of Corsica, Mallorca, Lampedusa and Medenine for 2013 and 2014 (table 1).

Table 1: Annual mass flux of nutrients and trace metals in kg km<sup>-2</sup> yr<sup>-1</sup> in 2013 and 2014 for 4 sites: Cape Corsica, Mallorca, Lampedusa and Medenine

Station	Cape Corsica		Mallorca	Lampedusa		Medenine
Position	40°00N-9°21E		39°15N-3°03E	35°31N-12°37E		33°21N-10°30E
Year	2013	2014	2013	2013	2014	2013
Fe	533.7	80.9	1351.4	3390.5	140.7	1215.4
P	11.7	4.3	31.8	17.4	12.4	32.5
Cd	0.01	0.002	0.02	0.18	0.004	0.03
Co	0.6	0.2	1.5	0.4	0.6	2.1
Cr	3.6	0.9	3.5	3.6	1.5	2.9
Cu	0.69	0.16	1.4	5.3	0.7	2.1
Mn	5.1	0.9	12.6	5.9	2.0	21.0
Ni	0.9	0.2	2.3	28.3	1.0	1.4
V	1.4	0.2	2.8	3.7	0.5	3.8
Zn	1.9	0.7	3.7	525.5	1.4	4.6

By comparing elemental mass ratios to Al of CARAGA samples with reference values of Saharan dust, we find that Zn, Cu, Ni and Cr have been widely influenced by anthropogenic sources, and that this influence had a large spatial variability.

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