Source contribution in nutrients and trace metals atmospheric deposition in the western Mediterranean

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RATIONALE:

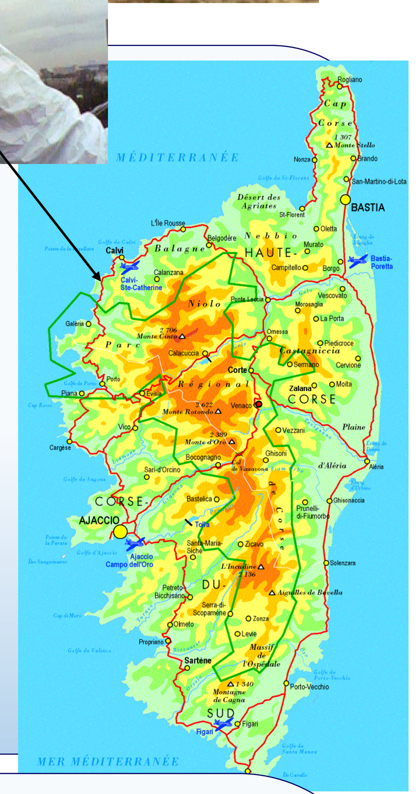
Mediterranean Sea MS is a typical oligotrophic region where the atmospheric deposition of aerosols constitutes the main source of major nutrients, as N, P or Fe to the surface open waters of the MS in the summer/autumn period. In a context of anthropogenic changes,, it is crucial to distinguish between anthropogenic vs natural atmospheric inputs of nutrients in order to assess how the evolution of chemical atmospheric forcing will modify the marine nutrient cycling.

Here, we show a 3.5-yr time continuous series of nutrients (N, P, Si) and trace metals (As, Cr, Cu, Fe, Mn, Ni, V, Zn) total deposition fluxes in Corsica. We applied a statistical method of source apportionment on these data for estimating the contribution of various sources on the inputs of these elements.

CONCLUSION:

A 3.5 years of time-series on total nutrients deposition show that the N and P annual fluxes are very close with an average ratio N:P (=36) which is higher than Redfield ratio. Zn and Mn predominate TMs inputs.

Biomass burning and sporadic dust events enables intense and short nutrients and TMs inputs. But the anthropogenic sources are usually the major providers of nutrients and trace metals inputs, except for Cr, V, Si and Fe which are mainly associated to dust deposition.



SAMPLING SITE AND METHOD:

Total bulk deposition, i.e. dry + wet deposition, was sampled weekly from March 2008 to October 2011. Sampling was conducted at Cap Cuittone (42.44°N; 8.66°E, 190m above sea level). The site of sampling is on the Mediterranean coast of the National Corsica Park (Parc Naturel Régional de Corse) at 16 km to the SSE of Calvi, the main city in the part of the island which has no important industry. Consequently, the data from this site could be considered representative of the open western Mediterranean Sea.

Total deposition was sampled using an open collector with a PTFE Teflon® funnel associated to 500 mL polypropylene bottle neck. Before deployment, the sampling bottles are preloaded with 50mL of hydrochloric acid and weighed. Each week, before collection, the internal surface of the funnel is rinsed with the hydrochloric acid content of a 60 mL bottle, taking care to flush the entire surface. P, Si and Trace metals are analysed by ICP-AES in the dissolved phases and by X-ray fluorescence for particulate phases. Total N is estimate as the dissolved N measured by ionic chromatography.

NUTRIENT AND TRACE METALS FLUXES:

Deposition fluxes for the major nutrients and trace metals (TMs) during the 3.5 years of sampling, i.e. 195 samples, are presented in the Figure 1. Among major nutrients, the most abundant nutrients in bulk deposition is Si followed by P and N which have fluxes in the same order of magnitude. For trace metals, the highest annual fluxes are observed for Zn, Mn and Cu whereas that the other metals have fluxes inferior of one order of magnitude. Except for Ni, the standard deviation on the mean fluxes are superior to 15%, and reach than 50% for P, As and Cu, meaning a large inter-annual variability of their deposition.

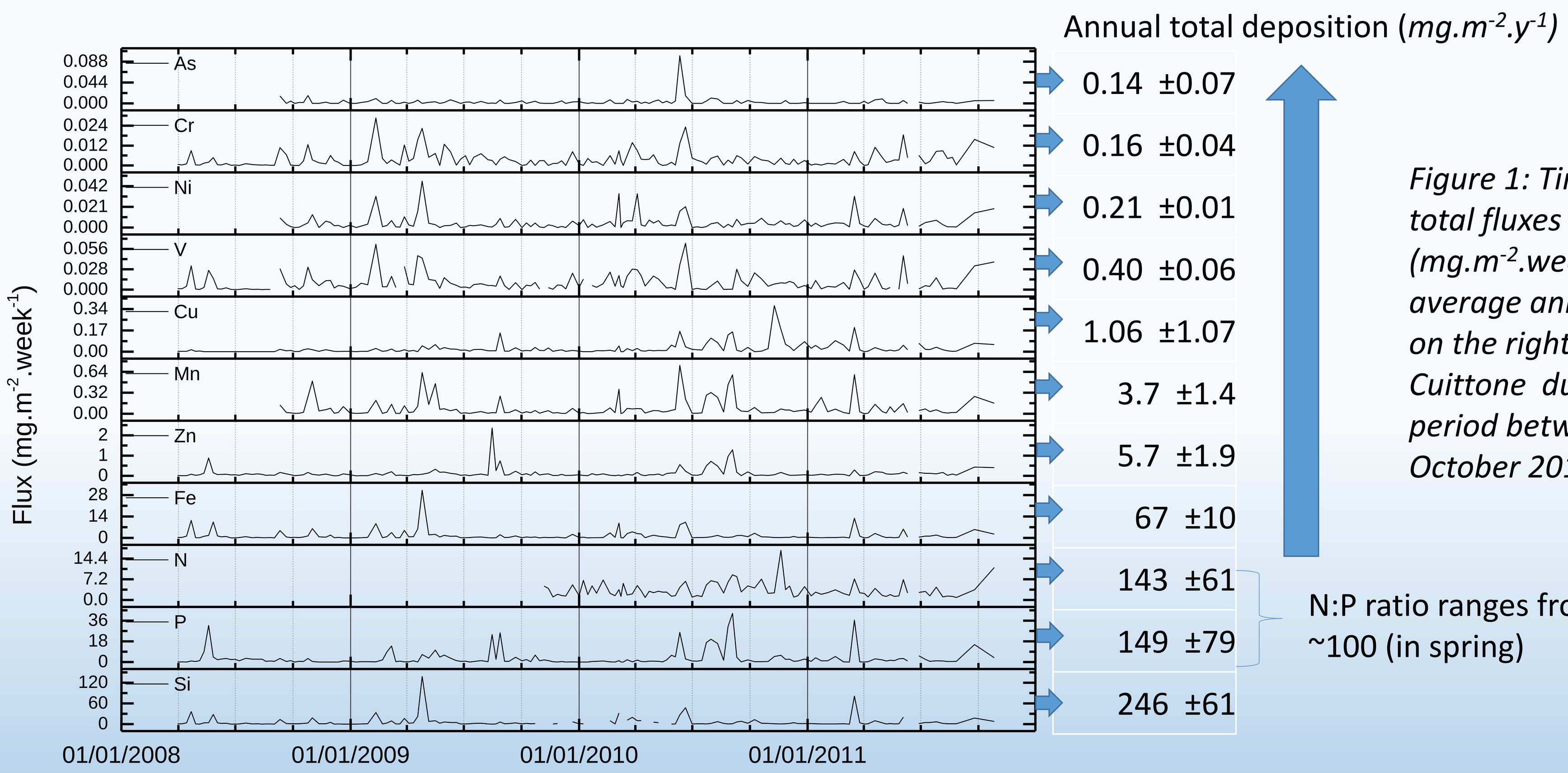


Figure 1: Time-series of weekly total fluxes of nutrients and TMs ($mg.m^{-2}.week^{-1}$, on the left) and average annual flux ($mg.m^{-2}.y^{-1}$, on the right) on the station of Cap Cuittone during the sampling period between March 2008 and October 2010.

SOURCE APPORTIONMENT:

Specific events

The results emphasize a large difference of timing of deposition fluxes for the various elements, meaning various sources. Due to the sporadic pattern of specific events as dust storm or biomass burning, it is known that the fluxes of elements associated to these sources are often important on a short period. From tracers time-series (Al, Ti, Pb, Na..), satellite product (Figure 2) and air-mass trajectories (Hysplitt model), we identified 6 extremes events during the sampling period: 5 dust storms and 1 biomass burning.

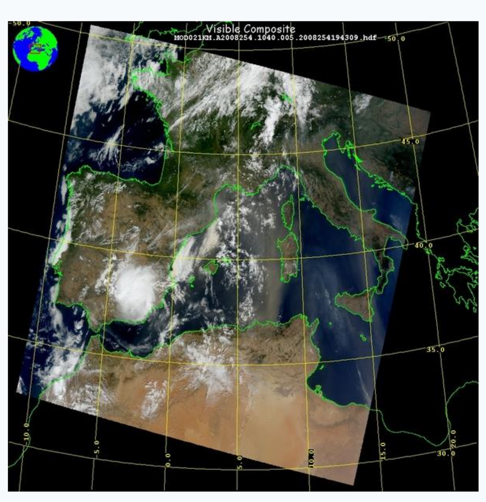


Figure 2: Dust storm of 10/09/2008 (AOD from TERRA RGB level 2)

Dust storms represent more than 35% of total cumulated fluxes, confirming the importance of these extreme dust inputs as sources of these nutrients. However for the others nutrients and TMs, these events are less than 15% of total fluxes.

The biomass burning event is crucial for As deposition, since this event represent 25% of the cumulated fluxes on the 3.5 years of sampling.

EPA method

The source identification analysis of the deposition data was carried out by EPA PMF method. We applied EPA PMF v5.0 (Norris et al., 2014) to the matrices of tracers, nutrient and trace element total deposition measurements. We included all valid samples , excluding the samples that we identified as extreme outliers (i.e. 6 samples). We used source signatures based on the combination of elements within each factor and the elemental ratios for known source tracers. Finally, the solution with 3 sources was the most reasonable to describe the various sources in Corsica (Figure 3): dust (Al, Ti, Ca), marine aerosols (Na, Mg, S) and anthropogenic aerosols (Pb, K, nssS).

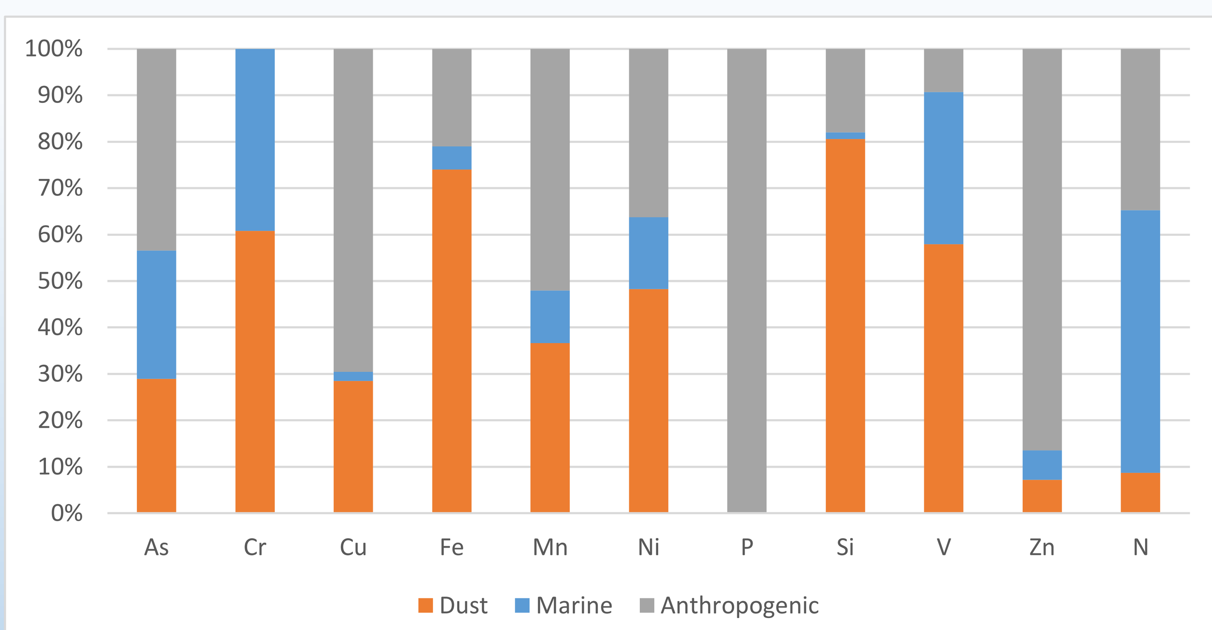


Figure 3: Contribution of proposed sources (%) for nutrients and TMs deposition

The results show that the anthropogenic sources predominates the continuous inputs of majors nutrients and TMs, except Cr, V, Fe and Si. P deposition is completely associated to anthropogenic inputs out of the sporadic dust events. For N deposition, the inputs associated to marine sources are quasi-similar with the anthropogenic inputs. However, this difference of sources could suggest a difference of N speciation in the inputs (inorganic nitrate vs organic nitrate?).