Available at www.scientevents.com/proscience/

ScientEvents

ProScience 1 (2014) 174-179

ProScience

Conference Proceedings

1st International Conference on Atmospheric Dust - DUST2014

Atmospheric deposition fluxes of aluminium, iron and trace metals in a coastal station on the nw-Alboran Sea, (w-Mediterranean)

Esperanza Liger[1*], Pedro Cañada[2], Concepcion Dueñas[3],
M. Carmen Fernandez[3], Sergio Cañete[2], Elisa Gordo[2], Manuel Pérez[4]

[1]Department of Applied Physics II, University of Málaga, Málaga, 29071, Spain
[2]Central Research Facilities, University of Málaga, Málaga, 29071, Spain
[3]Department of Applied Physics I, University of Málaga, Málaga, 29071, Spain
[4]Department of Radiology and Health Physics, University of Málaga, 29071, Spain

Abstract

The atmosphere is an important transport route by which natural and polluted compounds are carried from their natural or anthropogenic emission sources inland to the coast or offshore. Different studies have found atmospheric transport to be the main form of pollutants transportation from the continent to the sea in the Western Mediterranean area. This study reports preliminary information of deposition samples collected during the rainy season (October 2012-March 2013) at a coastal Mediterranean sampling site at the NW-Alboran Sea. The Alboran Sea is a very interesting case study regarding the atmospheric input because the atmospheric chemistry is dominated by the influences of natural (mainly from the Sahara) and human activity. Filtrates and filters were analyzed by ICP-MS for selected heavy metals. Atmospheric fluxes of eight trace metals (Cd, Cr, Cu, Ni, Mn, Pb, V and Zn) with Al as a crustal reference and Fe for its potential role in marine productivity were determined to evaluate their presence in their different bio-available forms.

Keywords: Atmospheric deposition; Minor and trace metals; Soluble and insoluble fractions; Mediterranean Sea; Alboran Sea.

---

[*] *Corresponding Author: eliger@uma.es*

Selection and peer-review under responsibility of DUST2014 Scientific Committee
DOI:10.14644/dust.2014.028

1. Introduction

The input of trace metals from the atmosphere to the water column plays a key role in ocean biogeochemical processes and is particularly important in a semi-enclosed sea like the Mediterranean (Guieu et al, 1997; Guerzoni et al., 1999). Available data show poor spatial representation, as most of the deposition data refer to the northwestern zone. The Alboran Sea, in particular, is a very interesting case study as regards the atmospheric input because the atmospheric chemistry is dominated by antagonistic influences of natural (mainly from the Sahara) and human activity due to the relative proximity of land-based sources and densely populated shores. The biogeochemical impact of desert dust also remains a matter of discussion regarding its contribution for different major and minor elements to terrestrial and marine systems and especially its potential fertilizing role by supplying micronutrients as iron. Several studies have provided contrasting estimates on the relative role of dry vs. wet deposition in the Mediterranean region. As a first approximation, the bio-available fraction (the most interactive with living organisms) is often described as the atmospheric input which remains dissolved in a natural water layer and it includes the dissolved material in rainwater and the soluble fraction of dry deposition (Sandroni & Migon, 2002).Therefore, in deposition studies it is important to distinguish between the dissolved and suspended fractions. This study reports preliminary information collected during a sampling campaign of atmospheric deposition in a semi-urban station on the south-eastern coast of the Iberian Peninsula with the aim to raise awareness on the deposited amount of particulate matter. A quantification of different metal deposition fluxes in their soluble and insoluble fractions, with Al as a crustal reference and Fe for their potential role in marine productivity, was made in order to determine the contribution to the atmospheric deposition and its role as an external source of major and trace metals to the Alboran Sea. It is known that fallout is not linear (less intense over the open sea by a factor two, approximately, with a similar number of rain events, but it is generally admitted that data from coastal stations indicate atmospheric fluxes over the open sea (Sandroni & Migon, 2002). The main goal of this study is to add to existing knowledge on trace metal deposition to the western Mediterranean Sea magnitude and modes of atmospheric inputs.

2. Materials and methods

The sampling site is in the north-west of the city of Málaga (36°43′40″ N; 4°28′8″ W), 5 km inland from the coastline (Fig. 1). The city lies in the south of the Iberian Peninsula on the shores of the Alboran Sea, the Mediterranean's westernmost basin and 100 km east of the Gibraltar Strait. The city is almost completely surrounded by mountains, which cause a special wind regime. As in other coastal localities nearby with a similar setting, the predominant winds are easterly and westerly. Furthermore, due to its geographical vicinity with the African continent, our study area is frequently affected by intrusions of air masses with high concentrations of atmospheric particulate matter.

Sampling presented for this study was carried out during the peak of the rainy season (autumn and winter months). Atmospheric deposition samples were collected on the flat roof of the Central Research Facilities (SCAI building) at the University of Málaga using standard rain collection device (funnel 27 cm diameter; 2 L polyethylene collection bottle). Samples of bulk deposition (TD; n = 15), wet deposition (WD; n = 12) and dry deposition (DD; n=2) were collected from October 2012 to March 2013.

Fig. 1. Map of the area and location of the sampling point.

The sampling duration of total atmospheric deposition was typically one week. Bulk deposition contains the wet deposition flux and the gravitational sedimentation fraction of the dry deposition. In addition to the normal operation, we added event samples collected for shorter (one to several days) intervals according to various forecasts on dust concentration in the atmosphere and precipitation. We used dust forecasts provided by CALIMA network (www.calima.es). In the case of samples in absence of precipitation, the collector was cleaned with 1000 mL of MilliQ grade distilled water. In presence of precipitation the rainwater was collected and then the collector was cleaned with distilled water. Within the lapse of 24 h, samples were filtered through pre-weighted 0.45 µm pore size Millipore filters (47 mm diameter) to separate insoluble and soluble fraction. The weight of particulate material was obtained by weighing the filters, once dried and the insoluble fraction was measured in the solid residue deposited in the filters. Blank values corresponding to blank filters were subtracted from measured concentrations. Filtrates and filters were analyzed by ICP-MS (inductively coupled plasma mass spectrometry) for selected heavy metals. Data treatment included the calculation of daily atmospheric fluxes of different trace metals using the concentration in deposition samples, volume collected, area of the funnel and number of days deployed to give a value in mg m^{-2} day^{-1}. Meteorological variables were provided by the Spanish National Institute of Meteorology (AEMET) from the nearest station network. The origin of the air masses reaching the study region was interpreted based on: (a) HYSPLIT back trajectories from the Air Resources Laboratory (available at http://www.arl.noaa.gov) (Draxler and Rolph, 2013). (b) Dust Regional Atmospheric model (http://www.bsc.es/projects/earthscience/BSC-DREAM/) operated by the Barcelona Supercomputing Center. Principal component analysis (PCA) and the following Varimax rotation (SPSS 22.0) were carried out to extract major factors explaining variances and to find the groups of elements with similar behaviour.

3. Results and discussion

A total of 29 deposition samples were collected between Oct-2012 and Mar-2013. The highest rainfall was during November (233.4 mm), followed by October (125.3 mm) and March (104.7 mm). Lower rainfall amount were recorded in December (12.3 mm), January (25.0 mm) and February (70.3 mm). It is interesting to note the great rainfall amount recorded during this period (570 mm on 73 rainy days) compared to the average annual precipitation in Málaga (500 mm) due to torrential rainfalls that occurred during these months. During winter the subtropical high-pressure belt is shifted to the south, allowing mid-latitude storms to enter the region from the open Atlantic and bringing enhanced amounts of rainfall to the Mediterranean.

Deposition fluxes (mg m^{-2} day^{-1}) of Al as a crustal reference and Fe for their potential role in marine productivity are presented in Fig. 2 in their soluble and insoluble fractions measured in our sampling point for the period of time considered. African dust outbreaks and precipitations occurring simultaneously are highlighted in a different colour. Measured parameters show well-defined episodic variations. The identification of African events was confirmed by means of backward trajectories computed in the vertical velocity model (starting point at 12 UTC from LC coordinates run backwards for 72 h) at 500, 1500, 3000 m a.s.l and BSC-DREAM8b v2.0 dust images. The origin of these autumn-winter events was mainly from the North and West Sahara and samples presented a high variability in the Fe/Al ratio. According to Rodríguez et al. (2001), in the period January–June transport of Saharan dust toward Spain is mainly due to the cyclonic activities over the West or South of Portugal, while in the summer this transport is governed by the anticyclonic activities over the East or Southeast of Iberian Peninsula. Future works will be focused on time-series measurements of the elemental composition of the particulate phase of selected 'Saharan rains' collected at this northern border of the Alboran Sea coast.

Additionally, soluble and insoluble daily deposition fluxes (mg m^{-2} day^{-1}) in this coastal Mediterranean station for different metals that exhibit a more or less marked anthropogenic, and sometimes toxic, character are given in Table 1. The contribution of the soluble fraction in deposition fluxes was usually greater for all metals, in particular for Cd, V and Zn. The exceptions were Al, Fe and Pb. Maximum values in soluble and insoluble forms were recorded in WD samples (samples identification are given in brackets). In most parts of Europe wet deposition fluxes of elements and ions dominate over dry deposition fluxes. The high autumn-winter deposition rate found in this coastal station can be well explained by the greater rainfall amount in these months compared with the annual average precipitation in Málaga and suggest that the heavy metal fluxes were mainly controlled by the number and amount of rainfall during these months.

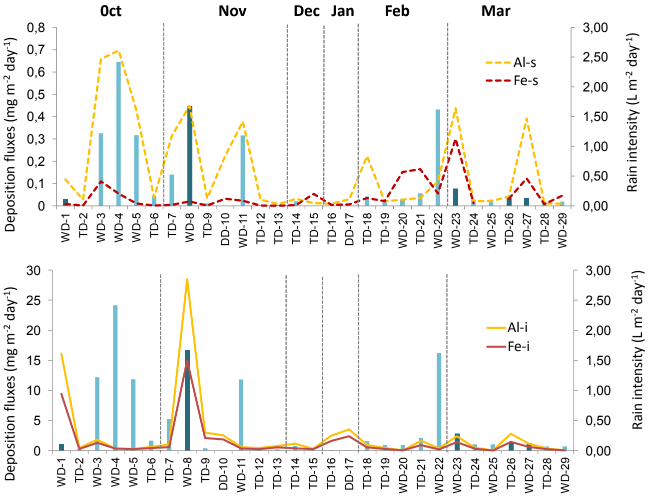

Fig. 2. Daily-scale variability of Al and Fe deposition flux rates in dissolved and suspended fractions during the rainy season.

Table 1. Average deposition fluxes (mg m^{-2} day^{-1}) of various metals in the insoluble (i) and soluble (s) fractions during the October 2012 - March 2013 period in Málaga.

METAL	N	Mean	Std.Dev.	Max. (Sample ID)
Al (i)	29	2.56E+00	5.79E+00	2.85E+01 (WD- 8)
Al (s)	29	1.66E-01	2.09E-01	6.96E-01 (WD- 4)
Cd (i)	29	2.92E-05	7.87E-05	3.93E-04 (WD- 8)
Cd (s)	24	2.56E-04	5.88E-04	2.90E-03 (WD- 4)
Cr (i)	29	4.88E-03	8.26E-03	3.79E-02 (WD- 8)
Cr (s)	27	7.30E-03	1.58E-02	6.04E-02 (WD-23)
Cu (i)	29	6.85E-03	9.38E-03	4.42E-02 (WD- 8)
Cu (s)	27	7.80E-03	1.05E-02	4.00E-02 (WD- 4)
Fe (i)	29	1.48E+00	3.13E+00	1.50E+01 (WD- 8)
Fe (s)	28	4.56E-02	6.79E-02	3.00E-01 (WD-23)
Mn (i)	29	1.84E-02	3.50E-02	1.48E-01 (WD- 8)
Mn (s)	29	1.64E-02	2.34E-02	9.21E-02 (WD-23)
Ni (i)	29	5.12E-03	1.22E-02	6.61E-02 (WD-8)
Ni (s)	28	6.35E-03	7.46E-03	2.75E-02 (WD-23)
Pb (i)	29	1.04E-02	2.95E-02	1.56E-01 (DS- 1)
Pb (s)	26	5.55E-03	9.82E-03	4.00E-02 (WD- 4)
V (i)	29	4.28E-03	8.57E-03	4.09E-02 (WD- 8)
V (s)	29	7.92E-03	1.43E-02	7.04E-02 (WD- 4)
Zn (i)	29	2.20E-02	3.81E-02	1.81E-01 (WD- 4)
Zn (s)	29	9.10E-02	1.89E-01	8.89E-01 (WD- 1)

Table 2. Results of the Varimax rotated PCA showing loadings with independent factors (PC).

METAL	*Soluble fraction*			*Insoluble fraction*	
	PC1 (58.4%)	PC2 (21.2%)	PC3 (8.3%)	PC1 (80.7%)	PC2 (11.2%)
Na	0.295	**0.769**	0.257	**0.952**	0.230
Mg	0.336	**0.815**	0.254	**0.658**	**0.689**
Al	**0.758**	0.540	0.079	**0.967**	0.222
Si	**0.877**	0.403	0.029	**0.849**	0.391
K	**0.772**	0.573	-0.040	**0.963**	0.254
Ca	0.231	**0.870**	0.225	0.265	**0.940**
V	**0.859**	0.345	0.062	**0.961**	0.268
Cr	-0.187	0.217	**0.930**	**0.933**	0.351
Fe	0.050	0.321	**0.894**	**0.960**	0.267
Ni	**0.615**	0.319	**0.675**	**0.912**	0.108
Mn	-0.002	**0.897**	0.229	**0.922**	0.358
Cu	**0.910**	0.205	-0.067	**0.740**	0.567
Cd	**0.934**	0.071	0.058	**0.804**	0.338
Pb	**0.935**	0.033	0.023	0.070	**0.916**
Zn	**0.936**	0.068	0.049	0.679	0.609

The calculation of principal components were performed on both fractions to evaluate the correlations among different elements and to find the groups of elements with similar behaviour for the identification of the sources of particulate matter and their relative quantifications. The results of the Varimax-rotated PCA (Table 2) show that three PC account for 87.9% of the total variance of the data set for the soluble fraction. For the insoluble fraction only two PC were found, which explains 91.9% of the total variance and metals correlate in a different way compared with the soluble fraction.

4. Conclusions

This study reports the results of a preliminary data set from an autumn-winter campaign and the analysis focused on heavy metal atmospheric deposition at this coastal station on the NW-Alboran Sea. Deposition fluxes were marked by meteorological conditions and the external influence of other emissions on a regional scale and the frequency and magnitude of African outbreaks. During this period, wet deposition has shown an important transport route for metals when rainy events occur. Even in the absence of significant industrial and energy production point sources, the Varimax rotation of PCA results identified factors including urban-industrial emission, crustal and marine aerosols and wind transport explaining over 80% of the variance. Assuming that data from Málaga account for atmospheric inputs to the NW-Alboran Sea, the present work attempts to provide an estimation of the potentially seawater labile material for this marine area. Sudden increases in heavy metal deposition in the dissolved form can be an important input into biochemical cycles in the NW-Alboran Sea. The partitioning between dissolved and particulate phases within the marine surface layer is obviously needed to address the issue of the biogeochemical fate of atmospherically deposited trace metals and more research is needed for a deeper understanding of such depositional processes in this interesting area of the W-Mediterranean.

5. Acknowledgements

This study was financed by the Spanish Ministry of Economy and Competitiveness, (Project CTM12-37598-C02). The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and to Barcelona Supercomputing Center for the images provided by the BSC-DREAM8b and the NMMB/BSC-Dust models used in this study.

References

Draxler R.R., Rolph G.D. (2013). HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, College Park, MD.

Guerzoni S., Chester R., Dulac F., Herut B., Loÿe-Pilot M.D., Measures C., Migon C., Molinaroli E., Moulin C., Rossini P., Saydam C., Soudine A., Ziveri P. (1999). The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea. Progress in Oceanography, 44, 147-190.

Guieu C., Chester R., Nimmo M., Martin J.M., Guerzoni S., Nicolas E., Mateu J., Keyse S. (1997). Atmospheric input of dissolved and particulate metals to the north-western Mediterranean. Deep-Sea Research II, 44, 655-674.

Sandroni V., Migon C. (2002). Atmospheric deposition of metallic pollutants over the Ligurian Sea: labile and residual inputs. Chemosphere, 47, 753-764.