THE SIGNIFICANCE OF ATMOSPHERIC INPUTS OF DISSOLVED AND PARTICULATE TRACE METALS TO THE EASTERN MEDITERRANEAN SEAWATER

Nikolaos Mihalopoulos [1]*, Christina Theodosi [1] and Zambia Markaki [1]

[1] Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, 71003 Voutes, Heraklion, Crete, Greece - mihalo@chemistry.uoc.gr

Abstract

Atmospheric deposition is a potential source of trace metals of continental origin to oceanic areas. Trace metals speciation (Fe, Al, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) was studied in atmospheric deposition (wet and dry) collected at a remote location in the Eastern Mediterranean Sea. Elemental concentrations were measured using ICP-MS, while Dissolved Reactive Fe (DSRFe: Fe (II) and Fe(III)) was determined spectrometrically. Atmospheric deposition was also compared with long-term trace metals data in sediment traps.

Keywords: Eastern Mediterranean, Atmospheric Input, Sediments, Metals

Introduction

The atmosphere is a significant source, especially for oligotrophic oceanic areas and semi-enclosed seas, such as the Mediterranean, due to the relative proximity of land-based sources and densely populated shores [1]. Riverine inputs are limited and localized and will not affect offshore sites such as the Cretan or the Levantine sea [2]. Thus atmospheric input may play an important role in the supply of bioavailable nutrients to surface waters and hence marine biological productivity. Therefore a comparison between dry and wet deposition of metals would be noteworthy regarding the bioavailability and toxicity of metals in the marine system.

Materials and Methods

Atmospheric deposition samples, wet and dry, were collected at Finokalia (35°20?N, 25°40?E), a remote coastal site in the Northeast part of Crete, in the Eastern Mediterranean over a two year period (January 2005–December 2006). After collection all samples were filtered through pre weighed 0.45 μm nitrocellulose filters. The sediment traps were moored for seven years in the Southern Cretan Sea (along 45°06?E, 500m and 1715m depth). The sediment trap samples were collected from 1999 until 2005, on a two–week basis and immediately after collection an aliquot was filtered through a precombusted and pre-weighted quartz fiber filters (Whatman QMA, diameter 47mm) for further analysis. An acid microwave digestion procedure followed by Inductively Coupled Plasma Mass Spectrometry was applied to measure metal concentrations in sediment trap and deposition samples.

Results and Discussion

Partitioning of atmospheric deposition between soluble and insoluble fractions demonstrated that Fe, V, Cr and Pb are mainly in the particulate form. For Cd, Zn, Mn and Cu, the dissolved fraction represents 60-68% of the total atmospheric input. Mean solubility for all metals in both wet and dry deposition appears to be related to pH and dust mass. More precisely solubility is decreasing with increasing pH values and increasing dust mass. For Pb, when the dust load is 0-70mg m^{-2} solubility reaches up to 74%, whereas dust >500mg m^{-2} leads to much lower Pb solubility is 0.3%. Cr, Mn and Cu are removed from the Eastern Mediterranean atmosphere by dry deposition, while Zn and Fe almost equally by wet and dry deposition whereas the rest of the studied metals via wet deposition.

In sediment traps, a significant correlation was observed between mass fluxes at 600m and 1715m indicating a quite good homogenicity in our system. Total mass flux presents two maxima: The first during spring, while the second one during autumn. Both are due to the increase in productivity and deposition of atmospheric dust. Similar seasonal trend was observed for Fe and Pb, elements characteristic of crustal and anthropogenic sources respectively, indicating similarity in transport mechanism independent of the trace metals origin. Dust is the main component of the sediment material as it accounts for about 40-44% of the mass. In addition a coherence between marine and atmospheric dust fluxes was observed. Annual deposition of atmospheric dust and dust in sediment traps are equal, in terms of fluxes, suggesting that atmospheric dust can be transferred in full down to 600 and 1715m.

Regarding the trace metals, our results suggested that atmospheric deposition is sufficient to balance their levels in the water column, indicating the predominant role of atmospheric deposition as external source of these elements in the area. Indeed DSRFe levels deposited were sufficient to account for the dissolved iron levels in seawater, therefore dissolved iron in the Mediterranean Sea could be exclusively attributed to atmospheric deposition. Cr, Mn, Fe, Zn, and Pb atmospheric deposition supplies 57- 84% of the amount collected in sediment traps. Total atmospheric depositions of Cu, Ni and Cd are equal to the fluxes from sediment trap deployment.

References

1 - Duce, R. A. and Tindale N. W., 1991. Atmospheric transport of iron and its deposition in the ocean. *Limnology and Oceanography*, 36, 17 15-I 726.

2 - Statham, P. J., Hart, V., 2005. Dissolved Iron in the Cretan Sea (Mediterranean). *Limnolology and Oceanography*, 118–124.