Trace Metals in PM10 Particles over the Eastern Mediterranean

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Daily aerosols samples have been collected in a remote coastal site on the northeast part of Crete island (Greece), in Finokalia and analyzed for ions, trace metals, organic (OC) and elemental carbon (EC). The main purpose was to determine the general characteristic of trace metals variability in this background area and identify their sources, which have their origin in Europe and Africa. The highest concentrations of crustal elements are related with dust events from southeast regions, according to backward trajectories. By contrast, anthropogenic elements showed increased concentrations when air masses were coming from the European zone. The reliability of our results was verified by mass closure, which showed a very good agreement between individual chemical aerosols species and particulate mass. Moreover, an estimation of the phosphorus solubility in aerosols, was performed in this study. The median P solubility for our samples was 34%, while during dust events, the solubility dropped to 20%, due to the alkaline environment.

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1 Introduction

Atmospheric aerosols play a significant role in the atmosphere, and their presence causes several both local and global impacts, with the most important being those on human health, acid deposition and climate changes. The sources of these aerosols vary depending on location and time. They include motor vehicle exhausts, vegetative burning, industrial emissions, soil and road dust. Annually, 3400 million tones of atmospheric aerosols are emitted at global level, of which 10% are of anthropogenic origin and 85% are of natural primary origin (IPCC 2001).

Being far from significant anthropogenic sources, the atmospheric monitoring station of the University of Crete at Finokalia, is an ideal place for background aerosol studies in the Eastern Mediterranean. However, there is evidence that atmospheric transport of trace elements from anthropogenic activities in European countries and natural land-sources around the Mediterranean Sea, influences the biogeochemical cycles of elements in the area (Herut et al. 2001). Therefore, there is an urgent need for undertaking a systematic study of chemical composition of aerosols in this area and appraisal of primary and chemical (secondary) sources of them.

Deposition of atmospheric aerosols plays an important role in supplying nutrient and trace metals, including nitrogen, phosphorus, and iron, over the Eastern Mediterranean. Mediterranean Sea is considered to be among the most oligotrophic seas of the world (Bethoux et al. 1998, Bosc et al. 2004). It is clear that atmospheric metal inputs can profoundly influence primary production in the oceans and hence the global carbon cycle and climate system. Thus processes which control metal solubility in the atmosphere are fundamentally important in governing oceanic biogeochemical cycles and biological productivity. Previous studies have highlighted the pH influence on trace metal solubility (Desboeufset al. 2001, 2005).

In the present study, to investigate the chemical composition of aerosols in this background area, daily samples of PM_{10} (atmospheric particles of diameter smaller than 10 μm) were collected and analyzed for Al, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, P, Na, K, As, Cd, Co, Sn, Ba, Hg and Pb. Special attention was paid on the calculation of dust content, as dust is the major source of aerosol particles. The total particulate mass was also measured at Finokalia station and compared with the sum of ionic, dust, elemental carbon and particulate organic carbon masses. Finally, the impact of air masses origin on phosphorus solubility was also examined.

2 Data and Methodology

Particulate matter sampling was performed at Finokalia during the period between October of 2012 and May of 2013. Daily PM_{10} particles were collected on quartz fiber filter using a Leckel GmbH sampler. All filters were pre- and post-weighed using a 5-digit microbalance.
Samples were analyzed for Al, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, P, Na, K, As, Cd, Co, Sn, Ba, Hg and Pb by Inductively Coupled Plasma Optical Emission (ICP-OES, iCAP 6000 Series). The filters were subjected to digestion with concentrated nitric under controlled conditions (Berghof Microwave System-2, Teflon vessels (DAP – 60K, 60ml/40bar)). After cooling to room temperature, the digested solution was transferred to an acid-cleaned polyethylene container and stored in the freezer until the analysis day.

3 Results

3.1 General Characteristics of Chemical Composition

Figure 1 shows the mean concentrations of trace metals measured in PM_{10} samples at Finokalia. Ca, Al and Fe exhibit the highest values due to their crustal origin, while lower mean concentrations are found for anthropogenic elements, specifically Cd, Cu and Ni. The ratio of PM_1/PM_{10} is also shown in Figure 2. All the metals present ratios lower than 0.6, which indicates the natural – crustal origin of them. Generally, the distribution of trace metals in coarse or fine mode exhibits similarities to the distribution results of previous study in Finokalia (Koulouri et al. 2008b).

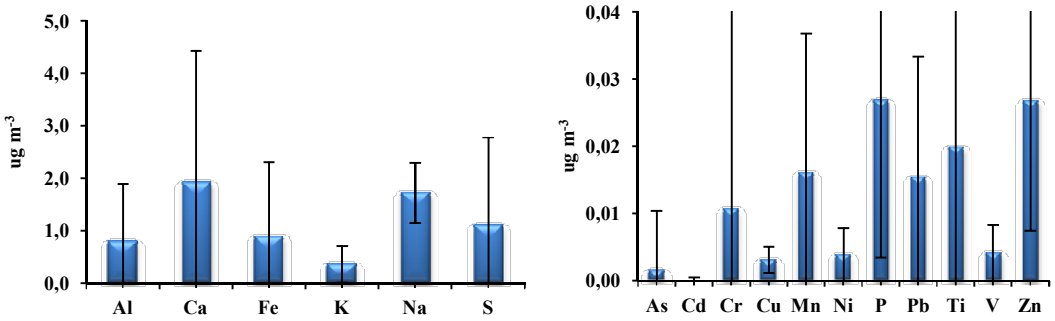

Fig. 1: Mean concentrations of trace metals measured in PM_{10} at Finokalia in μg m^{-3}

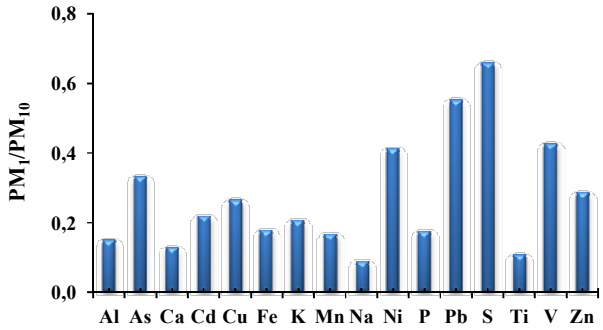

Fig. 2: Contribution of fine fraction aerosol to the metals in total (PM_{10}) aerosol.

The high values of crustal elements (Ca, Al, Fe) observed in the samples highlight the importance of airborne dust particles. This was the most remarkable feature of the entire sampling period, while the m increased concentrations of these elements were marked during the dust episodes, identified by running the NOAA Hysplit Model (Hybrid Single –Particle Langrangian Integrated Trajectory). This public domain model (http://www.arl.noaa.gov/ready/hysplit4.html) is documented in the international literature (Draxler and Hess, 1998).

According to air mass backward trajectories, Ca, Al and Fe daily maximum values were occurring when air masses were moving along the North African region sweeping through the sources of mineral aerosols and carrying Saharan dust to our measuring site. Dust episodes are more pronounced during spring and autumn in the Eastern Mediterranean (Kubilay et al. 2000; Kocak et al. 2004). During these episodes, mean concentrations of Fe, Al and Ca were 1.52, 1.63 and 3.56 μg m^{-3}, respectively, which were at least two times higher than those observed during non-dust events. Similar results were presented for dust events at Erdemli (Kocak et al. 2007).

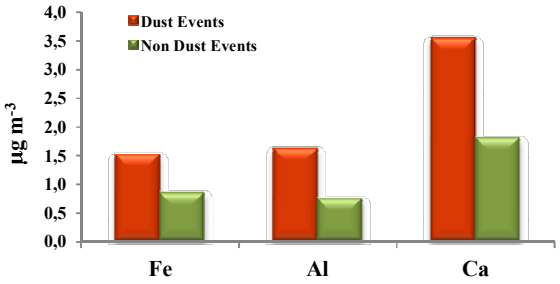

Fig. 3: Mean concentrations of crustal elements in PM_{10} particles, during dust- or non-dust- events

Anthropogenic elements, such as Zn, Pb and Ni, exhibited maximum values, during the beginning of dry season when air masses arriving at Finokalia, originated from the anthropogenically impacted regions at northeast and northwest, as indicated by air mass back trajectories analysis. Thus, during non- dust events, when air masses were originating mainly from these regions, higher concentrations were observed for anthropogenic elements than during dust events (Fig. 4).

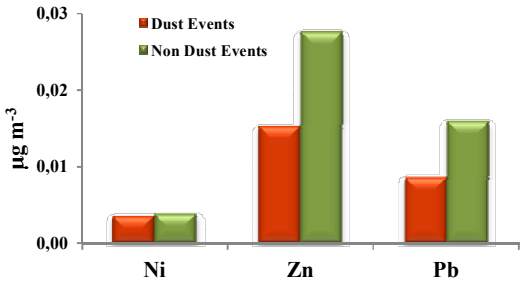

Fig. 4: Mean concentrations of anthropogenic elements in PM_{10} particles, during dust or non-dust events

To assess the extent of pollution in the study area, the observed concentrations of trace elements were compared to the observations reported for other Mediterranean coastal locations. For most metals, the measured concentrations are in good agreement with those reported in the literature (Gullu et al. 2000). Exceptions are found for the concentrations of soil-related elements, Al and Fe, which are lower than reported in literature. These exceptions could be attributed to the intensity of dust events during the measured period.

3.2 Calculation of Dust Content

Dust material was estimated using Al, Fe, Ca and Ti as indicators of crustal material. The statistically significant high correlation coefficients between these elements confirm their common origin (Fig. 5).

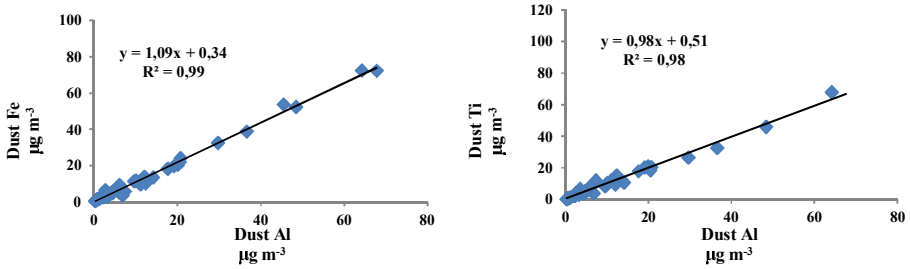

Fig. 5: Dust content of PM_{10} at Finokalia, estimated using different elements as indicators of crustal material

3.3 Solubility of Trace Metals

Solubility is defined as the fraction of the soluble metal concentration to its total (soluble plus particulate) concentration (Baker et al. 2006). Solubility of elements can be influenced by a number of factors, including the origin of particles (crustal or anthropogenic) (Guieu et al. 1997), the grain size of aerosols and the pH (Colin et al. 1990). This study focuses on the solubility of phosphorus in PM_{10}.

The median P solubility calculated for our aerosol samples was 34%. The solubility of P is inversely related to the presence of dust, as it can be seen in Figure 6 that reports P solubility versus Al concentrations (μgr m^3) (Fig. 6). Specifically, phosphate in mineral dust is predominantly bound to Fe oxides or associated with Ca, Mg, Al and Fe minerals which are known to be weakly soluble (Ridame and Guieu 2002). On the opposite, Figure 6b demonstrates increasing P solubility in acidic environment (i.e. high SO_4^{2-}/Ca^{2+} equivalent ratio). When sulfuric acid that is one of the main acids in the atmosphere, is present in sufficient amounts into mineral aerosolsit overcomes the available carbonate buffer capacity. This causes aerosol pH to drop to low values and increases the solubility of phosphorus (Meskhidze et al. 2003; Stumm and Morgan, 1996).

Solubility of P was about 20% when air masses were coming from Saharan regions. During non–dust events, P solubility showed considerably higher value (37%). A similar behavior for P solubility has been reported for aerosols over the northwestern Atlantic (36%) (Graham and Duce, 1982) and for Saharan- and European-origin aerosols (median P solubility of 25% and 45%, respectively) collected at coastal sites in Israel (Herut et al. 1999).

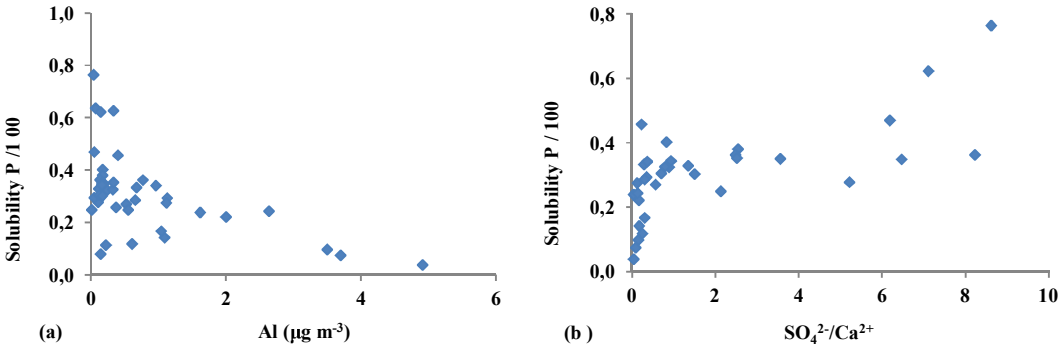

Fig. 6: Correlation between P solubility and (a) Al concentrations, (b) SO_4^{2-}/Ca^{2+} equivalent ratio**.**

3.4 Mass Closure

Mass closure was studied, in order to compare the gravimetric particulate mass to the mass that arises from the sum of different aerosol components. These aerosol components are Ionic Mass, Dust, Particulate Organic Matter (POM) and EC. The particulate organic matter (POM) was estimated by multiplying the measured OC by a conversion factor of 2.1, which corresponds to the ratio of organic mass to organic carbon, as determined for the area by Sciare et al. (2005) and references within.

Absorption of water by aerosol particles has a major effect on their physical and chemical properties. The presence of water in particles accounts for a significant part of the differences between chemically and gravimetrically measured concentrations, thus it is important to determine its fraction.

Figure 7a shows the temporal variation of the aerosol mass concentration, on monthly mean observations, derived from both gravimetric measurements (PM_Gravimetric) and chemical analysis (Chemical Species). The good correlation (Figure 7b), between these

measurements, with slope close to 1, indicates that our hypotheses and especially the calculations for dust, water and carbonaceous aerosols were realistic.

Dust, is a major component of the total PM_{10} mass, since it accounts for up to 48% followed by IM (23%) and carbonaceous material (10%) (Fig. 7c).

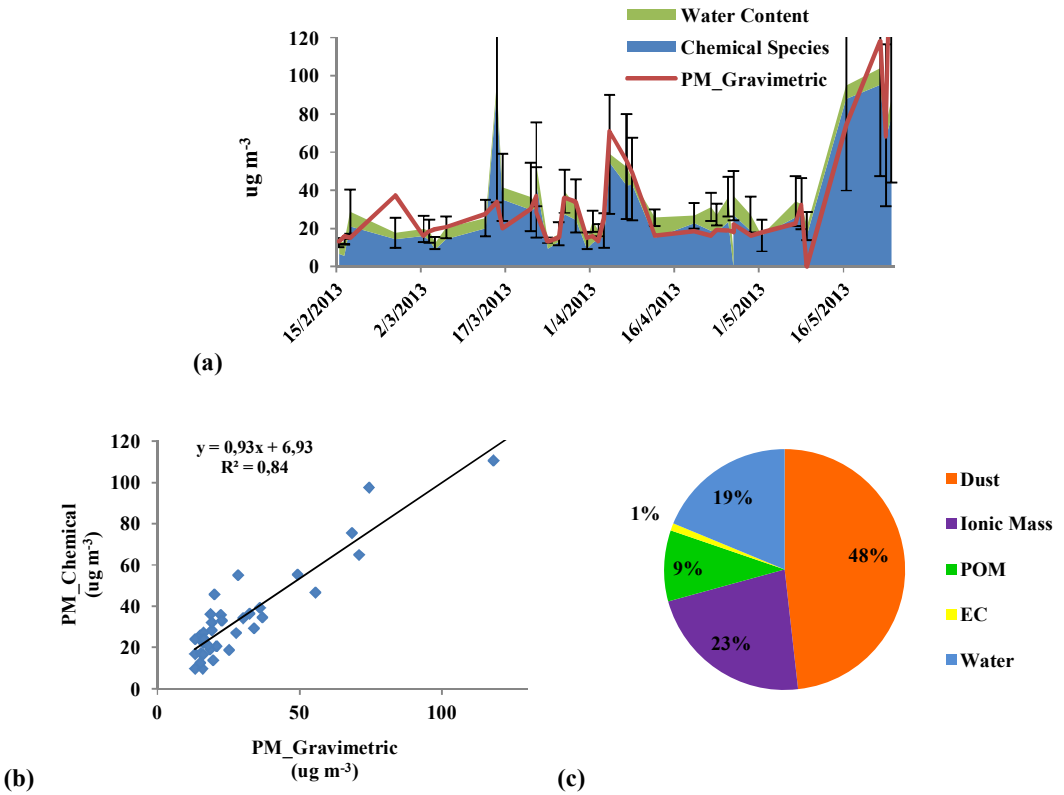

Fig. 7: (a) Chemical mass closure, on a monthly a monthly mean observations, for PM_{10} in Finokalia, (b) Correlation between PM derived as the sum of measured chemical species and gravimetric measurements, (c) Percentage contribution of different chemical species in the PM mass closure

4 Conclusions

The concentrations of trace elements measured at Finokalia from October of 2012 to May of 2013, were presented in this study. Aerosol species concentrations indicate day-to-day variability due to the impact of air masses of different origin in the area. Anthropogenic and crustal sources of atmospheric particles affect the Eastern Mediterranean atmosphere as demonstrated by air mass back trajectory analysis and the determination of chemical composition in size segregated aerosol samples.

During the sampling period, 23 dust episodes with variable intensity were identified using the NOAA Hysplit Model for air mass back trajectory calculations. The strongest dust transport episodes occurred in February and May, with the concentrations of crustal elements rising up to 10 μg m^{-3}, during these episodes. The levels of anthropogenic elements, such as V and Ni in PM_{10} at Finokalia, were also strongly influenced by air mass origin, with the highest levels observed during air mass transport from north European countries.

An extended study of the solubility of P was also presented. Mean solubility for P appears to be related to pH and dust content. Also, mass closure was attempted on monthly values to compare the gravimetric mass and the measured total ionic mass, dust, EC and POM masses. The unidentified component was investigated in order to eliminate the difference between gravimetric and chemical measurements and it was found that water absorbed by sulphate and

nitrate particles significantly contributes to mass closure. The main constituents of particulate mass during the measured period were found to be dust and ionic mass contributing up to 48% and 23%, respectively.

However further studies are required to better understand the seasonality of PM_{10} aerosols in this background area and investigate the solubility of P and other trace elements present in PM_{10} as a function of aerosol pH.

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