

The influence of air mass origin to the solubility of atmospheric P

Violaki K., Nikolaou P., Kanakidou M., Mihalopoulos N.

The role of air mass origin in the solubility of atmospheric Phosphorus (P) in aerosol and wet deposition samples collected in the Eastern Mediterranean atmosphere was investigated. Volume weighted mean (VWM) concentration of Total dissolved Phosphorus (TDP) was estimated at 2.7 μM . The percentage contribution of DIP (dissolved phosphate), DOP (dissolved organic Phosphorus) and CP (condensed inorganic P) to TDP was 7%, 86% and 7%, respectively. Particulate phosphorus (TPP) was accounting for 23% of total P. TIP (particulate inorganic P) and POP (particulate organic P) contributed to TPP by 38% and 62%, respectively. Maximum levels of P species, for both soluble and insoluble fractions, were associated with S/SW winds, suggesting African dust as an important source of P species over the area. The highest solubility of PO_4^{3-} present in PM_{10} aerosols was observed within the N/NW sector together with the highest levels of nss-sulfate, while the lowest solubility was observed during dust outbreak events.

Violaki K.^{*}, Nikolaou P., Kanakidou M., Mihalopoulos N.

Environmental Chemistry Processes Laboratory, Department of Chemistry, University of Crete, P.O. Box 2208, 71003 Heraklion, Greece

^{*}corresponding author e-mail: kviolaki@chemistry.uoc.gr

1 Introduction

Phosphorus is a key nutrient and controls the primary productivity in large areas of the open ocean, especially in P-limited, such as Eastern Mediterranean Sea. An increase in the atmospheric flux of bioavailable P is expected to increase primary productivity which in turns enhances carbon dioxide removal from the atmosphere. Recently it was shown that acid processes in the atmosphere can dramatically increase the fraction of bioavailable P in dust deposited to the ocean (Nenes et al. 2011). The acidity of the atmosphere is mainly chemically produced by precursors of anthropogenic origin (e.g. emitted by fossil fuels combustion).

The present study aims to investigate the sources, forms and biogeochemical significance of soluble and insoluble atmospheric P at a remote site in the East Mediterranean, in relation to the prevailing air mass origin. The area is ideal for this study because is the crossroad of polluted air masses from north and central Europe and of Sahara dust (south air masses). Wet deposition samples have been collected during two years period (2012-2013) and analyzed for P speciation while the solubility of P was examined in PM₁₀ atmospheric particles.

2 Data and Methodology

2.1 Sampling

Wet deposition. During two years period (2012-2013) rainwater was collected on an event basis using wet-only collectors installed at Finokalia monitoring station (25°60' E, 35°24' N). Finokalia is a remote marine site on the northern coast of Crete, considered as representative background area of Eastern Mediterranean atmosphere. Details about Finokalia can be found elsewhere (Mihalopoulos et al. 1997). Immediately after collection the rain samples (N=43) were filtered through a pre-weighed 0.45 µm cellulose filter. The non-filterable mass was regarded as insoluble matter. From the solution three aliquots were obtained. The first was immediately used for pH determination, in the second, 50–100 µl of chloroform were added as a biocide and stored in the refrigerator at 4 °C until further analysis. The third was stored at -18 °C for P analysis. All analyses were performed within a month after the collection.

PM₁₀ atmospheric samples. Daily aerosol particles (N=36) with aerodynamic diameter less than 10 µm (PM₁₀) were collected at Finokalia monitoring station using a sequential sampler SEQ47/50 (Sven Leckel) during 4 months (February-May 2013). The flow rate of the sampling system was 38 L min⁻¹. Both samplers were using quartz fiber filters (Pall flex membrane filters, 47 mm) precombusted at 550°C for five hours to minimize organic contamination.

2.2 Methodology

The speciation of P in rain samples was determined according to the analytical protocol referred in Standard Methods for the Examination of Water and Wastewater (20th Edition). Total Phosphorus (TP) in both soluble and insoluble matter was measured after acid digestion of samples according to Persulfate Digestion Method; TP was measured colorimetrically as PO₄³⁻ at 690nm using the stannous chloride method. TP recoveries obtained with the use of certified reference materials (MESS-3) were found to be to 98±12%. Dissolved Phosphate (DIP) was determined as HPO₄²⁻ by Anion Chromatography (IC), while Total acid hydrolized Inorganic Phosphorous (TIP) was determined after mild oxidation of sample (pH=1.6) with sulfuric acid (0.02M), separately in filtrate and filterable sample. Organically bound phosphates were determined in both soluble (DOP) and insoluble matter (POP) by subtracting

TIP from TP, while the condensed phosphates (pyro-, meta-, and other polyphosphates), called CP, were determined only in the soluble fraction by subtracting HPO_4^{2-} from soluble TIP.

Total Phosphorus (TP) in PM_{10} particles was measured by acid digestion of filter part (3 cm^2) with concentrated nitric acid (puriss. p.a., Fluka Prod. No. 84380) 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. These solutions were finally analyzed by Inductively Coupled Argon Plasma Optical Emission Spectrometer (ICP-OES) which uses an Echelle optical design and a Charge Injection Device (CID) solid-state detector (iCAP 6000 spectrometer by Thermo). TP recoveries obtained by the use of certified reference materials (MESS-3) ranged from 90–104%.

Part of the filters (2.5 cm^2) was extracted by sonication for 45 min in nanopure water (Milli-Q, $R < 18 \text{ M}\Omega \text{ cm}^{-1}$) for the measurement of main ions. The extraction efficiency of this method is higher than 98% for all compounds of interest. Chloroform of 100–150 μl was added as a biocide till the analysis of main ions. A Dionex AS4A-SC column with ASRS-300 4mm suppressor in auto-suppression mode of operation was used for the analysis of anions (Cl^- , Br^- , NO_3^- , SO_4^{2-} , HPO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$) in rain samples and aerosol extractions. All the anions were determined with isocratic elution at 1.5 ml min^{-1} of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ eluent. For the cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) a CS12-SC column was used with a CSRS-300 4mm suppressor. Separation was achieved under isocratic conditions with MSA (20 mM) eluent and flow rate of 1.0 ml min^{-1} . The reproducibility of the measurements was better than 2% and the detection limit ranged from 1 to 3 ppbv for the main anions and cations. Blanks were always below the detection limits.

3 Results

3.1 P speciation in wet deposition samples

A total of 43 rain events were collected over two years period (2012–2013) at Finokalia. The VWM concentration of TDP was estimated at $2.7 \mu\text{M}$, while the percentage contributions of DIP, DOP and CP to TDP were found to be 7%, 86% and 7%, respectively. Particulate phosphorus (TPP) was accounting for 23% of the total P while the percentage contribution of TIP (particulate inorganic P) and POP (particulate organic P) to TPP were 38% and 62%, respectively.

To investigate the role of air mass origin in P speciation in rainwater, rain samples ($N=31$) were distributed into three classes (N/NW, S/SW & E/NE) corresponding to the main wind sectors influencing the area. Significant contribution was found for the organically bound P, both as DOP and POP, within all sectors (Fig. 1, 2). In terms of absolute values both DOP and POP follow nicely the nss-Ca^{2+} (Fig. 1, $r^2=0.8$, $n=10$ for the S/SW sector) and mass levels variability (Fig. 2) indicating important contribution from dust of organic P in the rain. In the N/NW sector significant correlation ($r^2=0.7$, $n=13$) between soluble organic P and nss-sulfate was found, indicating anthropogenic influence on the levels of DOP.

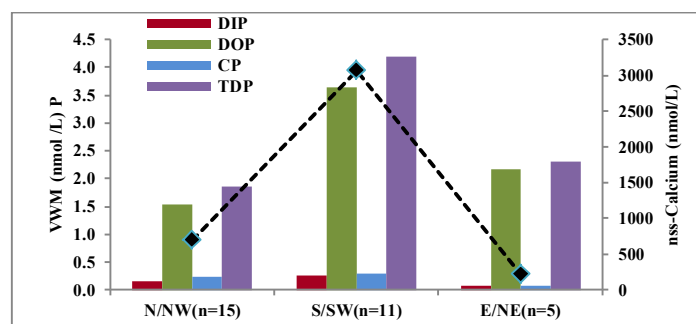


Fig. 1. The influence of air mass origin to the speciation of soluble P in rain samples.

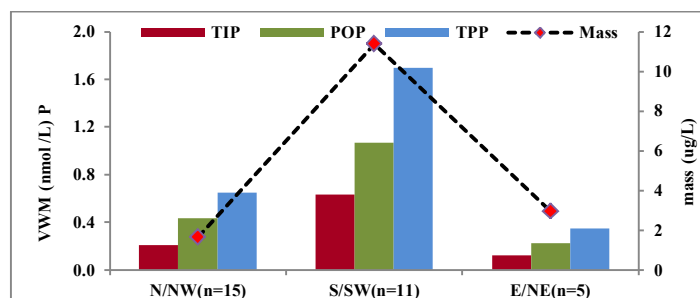


Fig. 2. The influence of air mass origin to the speciation of insoluble P in rain samples.

3.2 The role of air mass origin to the solubility of P species

Following the hypothesis that acid processing of mineral aerosols is a major pathway for the production of water soluble P in the atmosphere (Nenes et al., 2011), the solubility of P species in different wind sectors was also investigated. Five-day back trajectories corresponding to rain and PM₁₀ aerosol samples were calculated using HYSPLIT (Draxler and Rolph 2003). In Fig. 3 the influence of air mass origin on the solubility of P species in rain samples is presented. Higher solubility was observed for inorganic P species (phosphate and inorganic condensed P species such as apatite, meta-, ortho-phosphate etc) in N/NW sector. Winds from that sector transport anthropogenic pollution from N/NW Europe over the East Mediterranean, including gaseous acids contributing to the acidity of the atmosphere (Seinfeld and Pandis 2006).

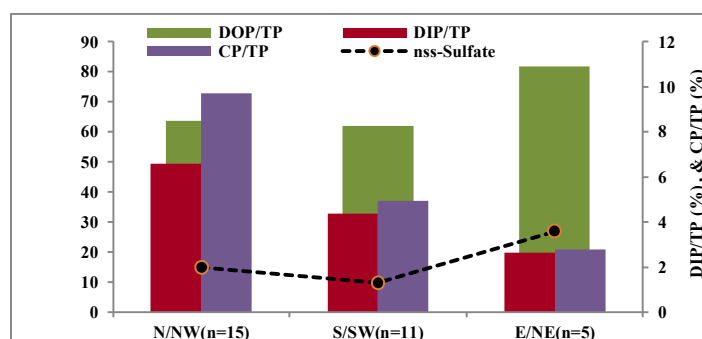


Fig. 3. The influence of air mass origin to the solubility of P species in rain water samples.

Increased solubility of P in PM₁₀ aerosol was observed mainly in the N/NW sector together with the higher concentration of nss-sulfate, while the lowest solubility of P was observed during the dust outbreak from Sahara desert (Fig. 4). The acidity of the atmosphere appeared

to play an important role in the increased DIP/TP ratio in N/NW wind sector, with significant correlations between PO_4^{3-} solubility and nss-sulfate ($r^2=0.8$, $n=11$).

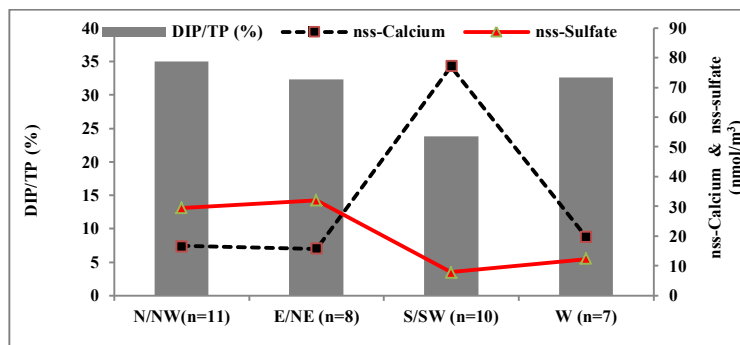


Fig. 4. The influence of air mass origin to the solubility of PO_4^{3-} in PM_{10} atmospheric particles.

4 Conclusions

During this study we investigated the P speciation in wet deposition samples and PM_{10} particles in East Mediterranean atmosphere under the influence of different air mass origin. DOP and POP accounted for the main form of P at both soluble and particulate fractions and independently of air mass origin indicating significant contribution from anthropogenic and natural (dust) sources. The anthropogenic source under N/NW winds enrich the atmosphere with more soluble P compared to dust, with inorganic species to prevail when compared with the other sectors. Finally, the highest solubility of PO_4^{3-} in PM_{10} aerosols was observed within the N/NW sector while the lowest solubility was observed during the dust outbreaks

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