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P-NEXFS Analysis of Aerosol Phosphorus Delivered to the Mediterranean Sea

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Key Points

- Synchrotron-based techniques are effective tools for characterizing aerosols
- Phosphorus in European and North African air masses is compositionally distinct
- European aerosols deliver substantial soluble phosphorus to the Mediterranean

Keywords

Mediterranean, phosphorus, aerosol

AbstractBiological productivity in many ocean regions is controlled by the availability of the nutrient phosphorus. In the Mediterranean aerosol deposition is a key source of phosphorusand understanding its composition is critical for determining its potential bioavailability. Aerosol phosphoruswas investigated in European and North African air masses using PhosphorusNear Edge X-ray Fluorescence Spectroscopy (P-NEXFS). These air masses are the main source of aerosol deposition to the Mediterranean Sea. We show that aerosols originating in Europe represent asignificant source of solublephosphorus to the Mediterranean. European aerosols deliver on average 3.5 times more soluble phosphorus than North African aerosols and furthermore are dominated by organic phosphorus compounds. The ultimate source of organic phosphorus does not stem from common primary emission sources. Rather, phosphorus associated with bacteria best explains the presence of organic phosphorus in Mediterranean aerosols.

Index Terms

Composition of aerosols and dust particles, aerosols and particles, nutrients and nutrient cycling, major and trace element geochemistry

1. Introduction

Atmospheric deposition is an important source of nutrients to oligotrophic ocean regions [*Graham and Duce*, 1982; *Mahowald et al.*, 2008].In the Eastern Mediterranean Sea, biological productivity is strongly limited by the vital nutrient phosphorus [*Krom et al.*, 2010; *Krom et al.*, 1991], with aerosol deposition accounting for at least one third of all phosphorus inputs [*Ganor and Mamane*, 1982]. Large dust plumes, clearly visible in satellite images, stretch from North Africa to the Mediterranean Sea. Perhaps as a consequence of this visible and obviously significant contribution, previous studies have focused on this region as a source of nutrients to the Mediterranean [*Escudero et al.*, 2011; *Ganor and Mamane*, 1982; *Guerzoni et al.*, 1999].Despite the eastern Mediterranean basin receiving air masses from Europe at least 70% of the time[*Kouvarakis et al.*, 2001], phosphorus supplied to the Mediterranean by European-sourced aerosols has not been as extensively studied due to comparatively lower mass deposition. Yet, it is the composition of the aerosol and the ability of microorganisms to assimilate nutrients from this source, i.e. bioavailability that must also be considered.

Phosphorus bioavailability has traditionally been linked to the composition and abundance of different chemical phases [*Beauchemin et al.*, 2003; *Mackey et al.*, 2012]. Phosphorus is thought to be bioavailable when present as highly soluble inorganic compounds as well as simple organic molecules. Assessments of phosphorus bioavailability in aerosols have been challenged by current analytical limitations. Typically, studies of aerosol phosphorus rely upon sequential chemical extraction or leaching techniques to assess the composition, and therefore the potential bioavailability of phosphorus[*Anderson et al.*, 2010; *Chen et al.*, 2006; *Izquierdo et al.*, 2012; *Markaki et al.*, 2003; *Ridame and Guieu*, 2002]. These techniques have painted a complex picture of aerosol phosphorus composition, showing that phosphorus occurs

in a number of different phases including organic, inorganic, and mineral forms and that these phases can undergo many transformations in response to environmental conditions [*Anderson et al.*, 2010; *Baker et al.*, 2006; *Chen et al.*, 2006; *Nenes et al.*, 2011]; however, phases used to calibrate extraction methods were developed for soil and marine sediment analysis, thus may not be entirely representative of phosphorus phases found in aerosol. Here we combine novel synchrotron-based techniques with traditional analyses to show that European aerosols contribute phosphorus to the Mediterranean Sea that is vastly different in phosphorus composition and solubility than North African aerosols.

2. Methods

2.1 Ambient aerosol collection

Air masses originating in North Africa and Europe were sampled at the Finokalia research station (35°32'N, 25°67'E), a remote site on the island of Crete, Greece, located 70 km from the nearest major city.The Finokalia research station was chosen to be as far away from any local or regional influences as possible[*Markaki et al.*, 2003]. This makes the samples most representative of long range transport. Samples of particulate matter with an aerodynamic diameter of less than 10 µm, PM10, were collected on Teflon filters using a virtual impactor with an operational flow rate of 16.7 L min^{-1}. Samples were collected over a one to three day period while either North African or European air masses dominated from 2009 – 2011 (Table S1). A total of fourteen samples were analyzed, five from European air masses and nine from North African air masses (Table S1), hereafter referred to as simply European and North African samples. Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) [*Draxier and Hess*, 1998; *Izquierdo et al.*, 2012]back trajectories were completed for each sample in order to confirm the geographic origin of the air masses sampled. HYSPLIT back trajectories were

calculated between 1000 m and 3000 m above ground level for five days preceding sample collection (Figure S1). HYSPLIT back trajectories were computed at 3000 m to check for dust events. Dust is either homogeneously distributed from 0 to about 3000 m, during spring and autumn, or is found in a layer between 2500 -4000 m during summer and autumn[*Kalivitis et al.*, 2007]. HYSPLIT back trajectories computed at 1000m show the origin of air masses within the boundary layer; this height is chosen, over 0 m or 500 m, to avoid orographic problems. While HYSPLIT back trajectories do not guarantee pure end members were sampled, the air masses were dominated by either North African or European origins. Ambient aerosol samples were stored at -20^{o}C until analysis.

2.2 Emission source collection

Emissions from ultra-low sulfur diesel fuel and gasoline were collected using US Environmental Protection Agency protocols under typical urban driving conditions [*Oakes et al.*, 2012b]. Coal fly ash from an electrostatic precipitator, provided by The Southern Company, was aerosolized and collected with a PM2.5 cyclone inlet sampler [*Oakes et al.*, 2012b]. Smoke produced from the burning of materials collected from coniferous and deciduous trees native to Georgia, USA, was sampled during a controlled biomass burning experiment using a cyclone inlet sampler placed 3.5 m above the burn area at a flow rate of 16.7 L min^{-1} for approximately 30 minutes. The ash produced from the biomass burning experiment was also analyzed. Although emission sources were not collected from European or North African locations, source materials presented here are considered to be reasonably similar to those found in Europe and North Africa. Thus, these emission sources can be used as a proxy for primary phosphorus sources found in European and North African air masses. In addition to the above emission sources, the following commercially available source materials were analyzed: pollen (*Quercus*

ruba; Sigma P7895), the bacteria *Azotobacter vinelandii* (Sigma A2135), and the bacteria *Bacillus subtilis* (Sigma B4006). This commercially available material was handled and analyzed in the same manner as phosphorus standards (Supporting Material). Emission source samples were stored at -20˚C until analysis.

2.3 Total phosphorus and soluble phosphate determination

Total phosphorus was measured for all samples with a technique employing high temperature combustion (550°C for 2 hours) followed by extraction in acid (1N HCl, agitated for 24 hours) [*Aspila et al.*, 1976]. The extracts were centrifuged prior to analysis to remove suspended particles. Total phosphorus content was measured using standard spectrophotometric techniques [*Murphy and Riley*, 1962]. Soluble phosphate was determined for all samples collected at the Finokalia research station. For these samples half of a Teflon filter was extracted by sonicating with 15 ml of nanopure water (Milli-Q, resistivity: 18.2 MΩ-cm) for 45 minutes. Prior to analysis, each extracted solution was filtered through polyethersulfone membrane (PES) filters (0.45 µm pore size diameter), to remove suspended particles. A Dionex AS4A-SC column with ASRS-ULTRA-II suppressor in autosuppression mode of operation was used for the analysis of dissolved inorganic phosphate (DIP). The reproducibility of the measurements defined as standard deviation of five consecutive analyses was better than 2%. The detection limit, defined as 3 times the standard deviation of the blank, was 0.06 µM DIP.

2.4 Synchrotron-based X-ray spectromicroscopy

Samples were analyzed on the X-ray fluorescence microscope located at beamline 2-ID-B at the Advanced Photon Source, Argonne National Laboratory. The beamline is optimized to examine samples over a 1-4 keV energy range using a focused X-ray beam with a spot size of approximately 100 nm^2[*McNulty et al.*, 2003]. Phosphorus Near Edge X-ray Fluorescence

Spectroscopy (P-NEXFS) data were collected in two modes that differ based on spatial resolution. In the first mode, individual phosphorus-rich particles with a diameter of greater than 1 micron identified in X-ray fluorescence maps; these particles were then interrogated with micro P-NEXFS. The individual phosphorus-rich particles seen in X-ray fluorescence maps are obvious contributors to total sample phosphorus. However, much of the total phosphorus on an aerosol filter can also be contained in particles that are less phosphorus-rich and therefore less apparent in X-ray fluorescence maps. Therefore, in the second mode, large areas of the filters were also examined with an unfocused beam (spot size = 0.28 mm^2) to obtain bulk spectra representative of the average phosphorus phase present.

In order to maximize the number of samples analyzed in the allotted time, X-ray fluorescence maps were created by rastering the focused beam in 0.5 µm steps with an incident energy of 2185 eV. At this resolution, individual phosphorus-rich particles were clearly discernable. P-NEXFS spectra were collected over an energy range of 2130 to 2210 eV in 0.33 eV steps, using a 1 s dwell time at each step. Each P-NEXFS measurements for both bulk and individual phosphorus-rich particles were repeated at least three times, in a single position, creating a minimum effective dwell time of 3 s. X-ray spectromicroscopy data were collected using an energy dispersive silicon drift detector (Ketek with a 5 mm^2 sensitive area). A flow of helium was introduced between the X-ray optical hardware and the sample to reduce X-ray backscatter. An in-line monitor stick composed of fluorapatite was measured with each sample in order to identify and correct for any potential drift in monochrometer energy calibration that occurred during analyses [*de Jonge et al.*, 2010]. Clean areas of Teflon and cellulose acetate filters were examined as blanks and showed negligible background signal.

P-NEXFS provides essentially the same information as another commonly cited technique, P-XANES (X-ray Absorption Near Edge Structure) spectroscopy. The two techniques differ primarily in the method of signal detection.P-NEXFS uses the X-ray fluorescence signal which is inversely proportional to the absorption signal used in a XANES measurement.

2.5 P-NEXFS data analysis

Linear combination fitting is an effective tool for the deconvolution of spectra of known mixtures [*Ajiboye et al.*, 2007]. Using Athena software [*Ravel and Newville*, 2005], individual particle and bulk P-NEXFS spectra were fit with characterized phosphorus standard materials using the linear combination approach to determine both speciation and relative abundance of phosphorus phases [*Prietzel et al.*, 2013]. Additionally, bulk P-NEXFS spectra of ambient aerosol were fit using emission sources rather than standards; this approach was used to determine if phosphorus in ambient aerosol could be accounted for solely by emission sources. Athena used a non-linear, least-squares minimization approach to fit spectra of unknown materials with spectra of standard materials and computes an error term, R-factor, to quantify the goodness of fit produced by a particular linear combination of standard P-NEXFS spectra. The linear combination of standards that yielded the lowest R-factor reflected the best fit [*Ravel and Newville*, 2005].

The data for an individual P-NEXFS spectrum was normalized to create a relative intensity value of approximately 1 for post edge area of the spectra (> 2160 eV). The data were also processed using a three-point smoothing algorithm built into the software. Smoothing did not appreciably change the data, other than removing high frequency noise. The standard database used in our spectral linear combination fitting included phosphorus minerals and inorganic phosphorus compounds discussed in Ingall et al. 2011, as well as a variety of organic phosphorus

compounds (Supporting Material). An iterative process was used to refine the standard database used to model the sample spectra. First, complex, high temperature, and high-pressure minerals, unlikely to be major components of aerosol phosphorus were excluded from the database [*Oakes et al.*, 2012a]. Second, the database was narrowed through elimination of standards with low contribution (i.e. less than 10%) or poor fit (i.e. high R-factor) during initial linear combination fitting. Finally, the composition of individual phosphorus-rich particles determined using micro P-NEXFS helped to guide the choice of standards for the modeling of bulk P-NEXFS spectra.

Spectra can be very similar within certain compound classes like phosphorus esters (Figure S2) and mineral classes like apatites [*Ingall et al.*, 2011]. Also, insufficient quantities of a specific mineral or compound in a sample can also lead to underestimation of the specific compound during linear combination fitting [*Hesterberg*, 2010]. We therefore generalized our results into four chemical classes, apatite, metal phosphates, alkali and alkaline earth metal phosphates, and organic phosphorus + polyphosphate, with distinct implications for phosphorus solubility and bioavailability. The apatite chemical class includes fluorapatite, hydroxyapatite, carbonate fluorapatite and carbonate hydroxyapatite and chlorapatite. Minerals in the metal phosphate chemical class have a dominant metal cation like iron, copper, or manganese and include vauxite, cornetite, wardite, and wolfeite. Alkali and alkaline earth metal phosphates (hereafter referred to as alkali phosphates) include sodium phosphate and calcium dihydrogen phosphate; these phases typically have high solubility. The final chemical class, organic phosphorus + polyphosphate, includes organic compounds like adenosine-5'-triphosphate (ATP), lipids (and other phosphorus esters), and polyphosphates, all compounds of biological origin.

3. Results and Discussion

3.1 Ambient aerosols

Aerosol phosphorus from North African air masses was on average 15.5 ± 14.1% soluble. In contrast, aerosol phosphorus from European air masses was on average 54.0 ± 5.6% soluble (Figure 1). Despite European-sourced aerosols having less total phosphorus than North African aerosols, the mass of soluble phosphorus per mass of aerosol is comparable (Figure 1). Consistent with our findings based on our limited sample set, sequential extraction methods have shown that anthropogenically-influenced air masses, such as those originating in Europe, tend to have more soluble phosphorus than North African aerosol [*Anderson et al.*, 2010; *Izquierdo et al.*, 2012]. Our bulk P-NEXFS measurements further showed that European-sourced aerosols were dominated by the organic phosphorus + polyphosphate chemical class and were on average composed of 93.8 ± 13.9% organic phosphorus + polyphosphate and 6.2 ± 13.9% metal phosphate, with no alkali phosphates or apatite (Figure 2). In contrast, the average phosphorus composition of North African-sourced aerosols was 32.3 ± 33.2% apatite, 24.9 ± 29.5% alkali phosphates, 24.8 ± 26.9% organic phosphorus + polyphosphate, and 18.1 ± 27.2% metal phosphate (Figure 2). Micro P-NEXFS analysis revealed that individual phosphorus-rich particles from European and North African air masses were often solely comprised of organic phosphorus + polyphosphate or apatite, respectively.

Previous studies based on sequential extraction techniques have shown that apatite is the most abundant phosphorus phase followed by oxide-associated phosphorus in North African-sourced air masses [*Anderson et al.*, 2010; *Nenes et al.*, 2011]. Our results suggest organic phosphorus + polyphosphate as well as alkali phosphates account for a large fraction of the phosphorus in the North African derived aerosol (Figure 2). The oxide-associated phosphorus

fraction determined by sequential extraction techniques can include labile organic phosphorus as well [*Anderson et al.*, 2010]. Therefore, our finding of organic phosphorus + polyphosphate in North African-sourced aerosols could be consistent with extraction studies and suggest organic phosphorus is present in the oxide-associated fraction identified in these studies. The presence of alkali phosphates in North African air masses may reflect recycling of apatite-derived phosphorus. At low pH, apatite more readily dissolves into aerosol water droplets [*Anderson et al.*, 2010] that are subsequently dehydrated, possibly resulting in supersaturation of these droplets with respect to alkali phosphates. If sulfuric acid is the dominant acidic species present, aerosol water content may continue to be high even at low pH, which further facilitates dissolution of phosphorus.

Soluble phosphorus percentage shows the strongest correlation with the relative abundance of organic phosphorus + polyphosphate (Figure 3). However, the correlation coefficient of 0.61 indicates that significant variability in this relation exists. Solubility is likely tied to the abundance of specific organic phosphorus compounds *within* the defined chemical class. Organic phosphorus compounds exhibit a wide range of structures and compositions that are generally not possible to distinguish with P-NEXFS (Supporting Material). These species, in turn, differ in terms of phosphorus solubility. Also, acidification of normally insoluble phosphorus phases can increase phosphorus solubility [*Nenes et al.*, 2011]. Anthropogenic emissions are well-documented sources of acidic species [*Nenes et al.*, 2011] and have also been linked to more soluble forms of aerosol phosphorus [*Izquierdo et al.*, 2012; *Zamora et al.*, 2013]. Varying quantities of acidic species [*Nenes et al.*, 2011] entrained in European and North African air masses would likely lead to different levels of phosphorus solubilization during atmospheric transport.

3.2 Emission Sources

In addition to ambient aerosol samples, several common emission sources were analyzed with bulk P-NEXFS. Spectral linear combination fitting showed that pollen and the bacteria *Bacillus subtillis* and *Azotobacter vinelandii* were dominated by organic phosphorus + polyphosphate. Coal fly ash, diesel, volcanic ash, and biomass burning ash were comprised of apatite, metal phosphates and organic phosphorus + polyphosphate. Neither gasoline nor biomass burning emissions showed a discernable phosphorus edge, so phosphorus composition could not be characterized for these sources. Spectral linear combination fits based only on source emission spectra for ambient aerosol samples were usually inferior to fits utilizing phosphorus compounds and minerals. The dissimilarity between source emissions and ambient aerosol suggest either that atmospheric processing strongly modifies phosphorus composition or that another unknown phosphorus source is a dominant aerosol component. For example, aerosol production by plants and other organisms is a possible source of organic aerosol phosphorus [*Artaxo et al.*, 2002; *Benitez-Nelson*, 2000]. Biogenic pathways involved in aerosol production remain uncertain [*Artaxo et al.*, 2002; *Benitez-Nelson*, 2000]; however, primary emissions from vegetative cover could also account for the dominance of organic phosphorus + polyphosphate class seen in European air masses. Microbial cells have also been recognized as an important natural component of aerosol [*Bauer et al.*, 2002; *Burrows et al.*, 2009]. Due to a globally ubiquitous distribution[*Bauer et al.*, 2002; *Burrows et al.*, 2009], bacteria are potentially a key contributor to the organic fractions present in both the North African and European aerosol examined here. In fact, when emission sources were used as standards in spectral linear combination fitting, fits containing bacteria as a standard, produced the best results for both ambient aerosols sampled from North African and European air masses.

4. Conclusions

This work demonstrates, based on our limited data set, that synchrotron-based techniques provide valuable insights into the composition and therefore the factors influencing the solubility and bioavailability of phosphorus in aerosols. The distinctively higher phosphorus solubility in European aerosol is attributed largely to the presence of organic phosphorus. Preliminary evidence suggests that this organic phosphorus may be associated with bacteria;however,further research is necessary to specifically characterize the organic phosphorus containing phasesand determine the prevalence of bacteria in Mediterranean aerosols. Shifts in wind direction observed over seasonal and inter-annual timescales [*Chamard et al.,* 2003] have been suggested as a key factor controlling the delivery of vital nutrients to marine systems [*Hamza et al.*, 2011]. Climate simulations suggest that European-sourced windswill be more prevalent over the Mediterranean Sea than North African-sourced winds in the future [*McInnes et al.*, 2011]. If phosphorus in European aerosol is consistently shown to be 3.5 times more soluble than North African aerosol, the increased European influences will lead to more soluble phosphorus loading to the Mediterranean Sea and ultimately more biological productivity.

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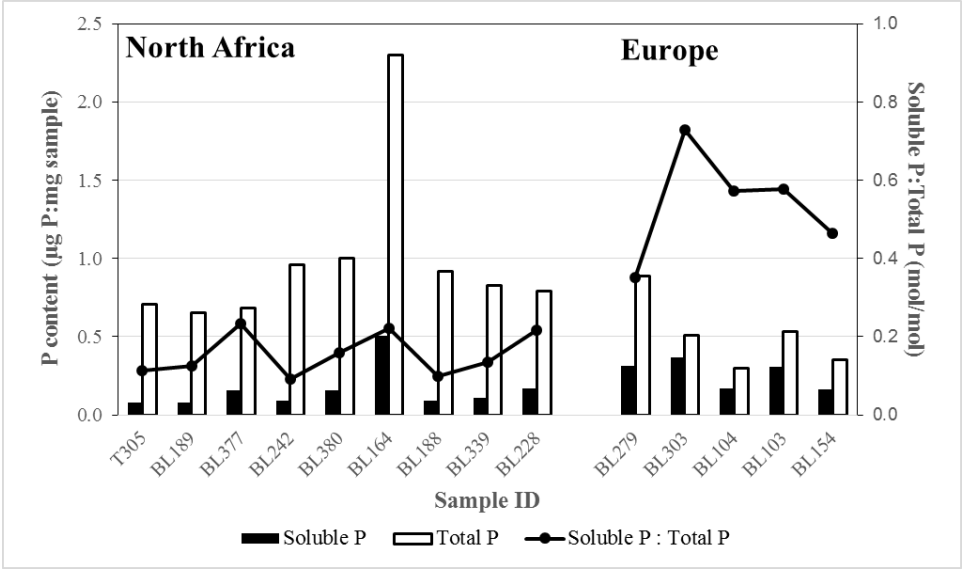

406

407 **Figure 1**. The soluble and total phosphorus contained in Mediterranean aerosols are shown for
408 air masses originating in Europe and North Africa. Total phosphorus content (white) and soluble
409 phosphorus content (black) show both European and North African samples are potential sources
410 of phosphorus to the Mediterranean Sea. The molar ratio of soluble phosphorus to total
411 phosphorus (line) expressed as a percentage shows European aerosol can be up to 4.7 times more
412 soluble than North African aerosol. Typically, the reproducibility for measuring soluble
413 phosphorus and total phosphorus are 2% and 10%, respectively.

414

415

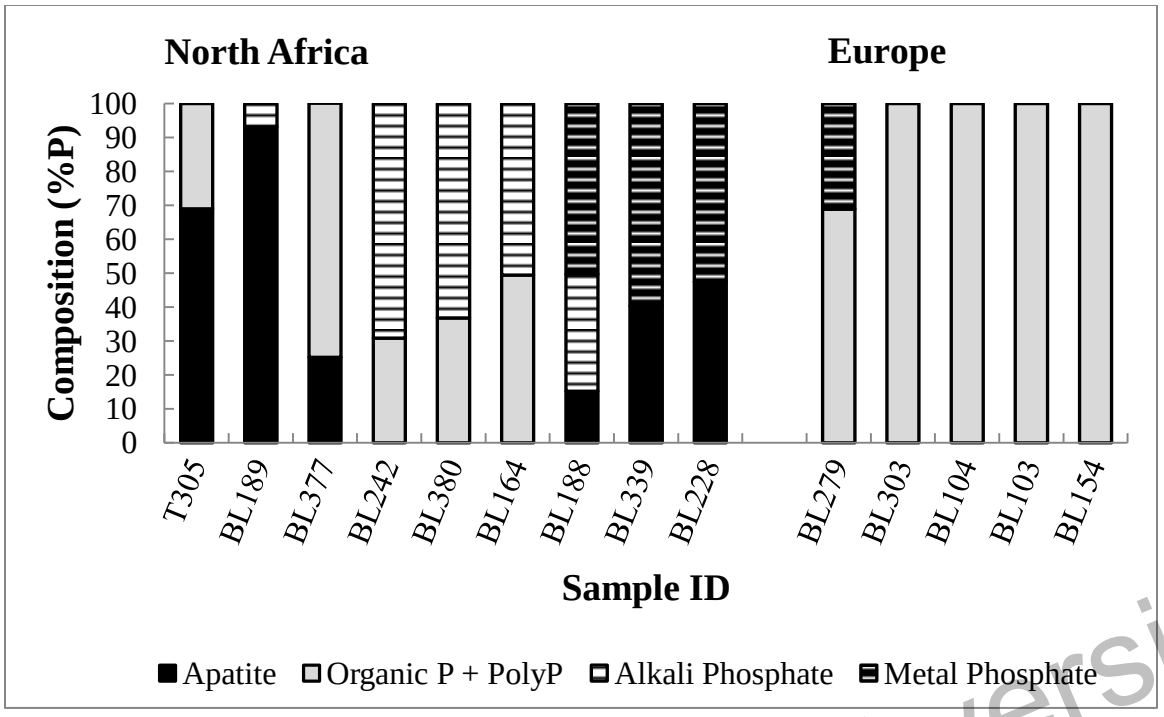

Figure 2. Linear combination fitting of each aerosol spectra was used to determine the phosphorus composition in each sample. The distribution of apatite (black), organic phosphorus + polyphosphate (grey), alkali phosphates(white striped), and metal phosphates (black striped) determined through linear combination fitting are shown for each sample.

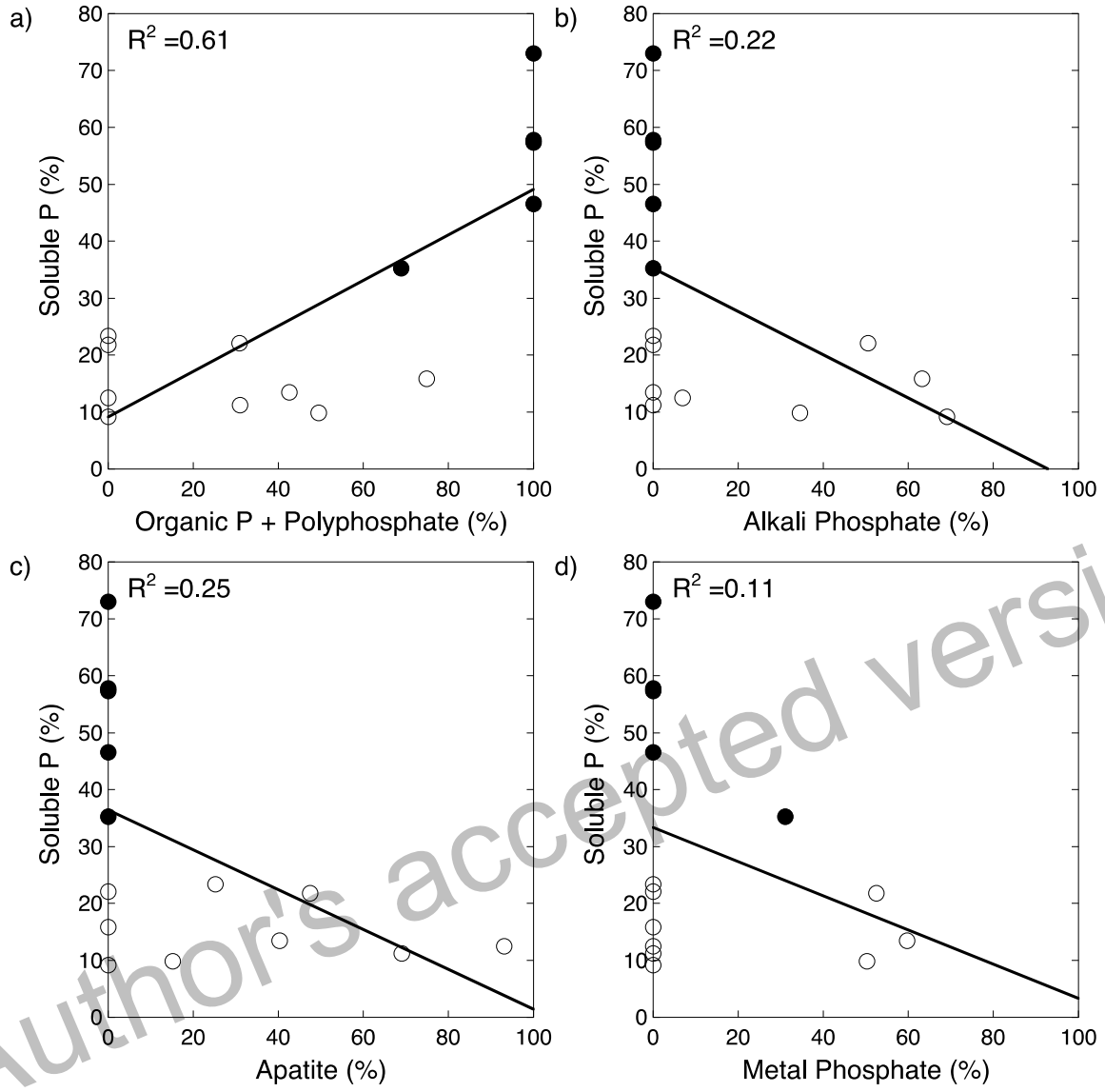

Figure 3. Plots of percent soluble phosphorus versus phosphorus composition are shown for North African (○) and European (•) sourced aerosol samples. The only chemical class showing a notable correlation with solubility is organic phosphorus + polyphosphate (a) suggesting that this class does in part influence solubility.