

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

2 Amelia F. Longo<sup>1</sup>, Ellery D. Ingall<sup>1\*</sup>, Julia M. Diaz<sup>1§</sup>, Michelle Oakes<sup>1‡</sup>, Laura E. King<sup>1</sup>,  
3 Athanasios Nenes<sup>1,2,3</sup>, Nikolaos Mihalopoulos<sup>3,4</sup>, Kaliopi Violaki<sup>4</sup>, Anna Avila<sup>5</sup>, Claudia R.  
4 Benitez-Nelson<sup>6</sup>, Jay Brandes<sup>7</sup>, Ian McNulty<sup>8</sup> and David J. Vine<sup>8</sup>

5 <sup>1</sup>School of Earth and Atmospheric Sciences, Georgia Institute of Technology, 311 Ferst Drive,  
6 Atlanta, GA 30332-0340, USA.

7 <sup>2</sup>School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst  
8 Drive, Atlanta, GA 30332-0340, USA.

9 <sup>3</sup>Foundation for Research and Technology, Hellas, Patras 70013, Greece.

10 <sup>4</sup>University of Crete, Department of Chemistry, Iraklion 71003, Greece.

11 <sup>5</sup>CREAF, Universitat Autònoma de Barcelona, Bellaterra 08193, Spain.

12 <sup>6</sup>Department of Earth & Ocean Sciences & Marine Science Program, University of South  
13 Carolina, Columbia, SC 29208, USA.

14 <sup>7</sup>Skidaway Institute of Oceanography, 10 Ocean Science Circle, Savannah, GA 31411, USA.

15 <sup>8</sup>Advanced Photon Source, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL  
16 60439, USA.

17 <sup>§</sup>Present address: Biology Department, Woods Hole Oceanographic Institution, Woods Hole,  
18 MA 02543, USA.

19 <sup>‡</sup>Present Address: Environmental Protection Agency, National Center of Environmental  
20 Assessment, Research Triangle Park, NC 27711, USA.

21 \*Correspondence to: [ingall@eas.gatech.edu](mailto:ingall@eas.gatech.edu)

22 School of Earth and Atmospheric Sciences, Georgia Institute of Technology, 311 Ferst Drive,  
23 Atlanta, GA 30332-0340, USA

25 **Key Points**

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

29 **Keywords**

30 Mediterranean, phosphorus, aerosol

31 **Abstract** Biological productivity in many ocean regions is controlled by the availability of the  
32 nutrient phosphorus. In the Mediterranean Sea, aerosol deposition is a key source of phosphorus  
33 and understanding its composition is critical for determining its potential bioavailability. Aerosol  
34 phosphorus was investigated in European and North African air masses using Phosphorus Near  
35 Edge X-ray Fluorescence Spectroscopy (P-NEXFS). These air masses are the main source of  
36 aerosol deposition to the Mediterranean Sea. We show that European aerosols are a significant  
37 source of soluble phosphorus to the Mediterranean Sea. European aerosols deliver on average  
38 3.5 times more soluble phosphorus than North African aerosols and furthermore are dominated  
39 by organic phosphorus compounds. The ultimate source of organic phosphorus does not stem  
40 from common primary emission sources. Rather, phosphorus associated with bacteria best  
41 explains the presence of organic phosphorus in Mediterranean aerosols.

42 **Index Terms**

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

45

46

## 47 **1. Introduction**

48 Atmospheric deposition is an important source of nutrients to oligotrophic ocean regions  
49 [*Graham and Duce, 1982; Mahowald et al., 2008*]. In the Eastern Mediterranean Sea, biological  
50 productivity is strongly limited by the vital nutrient phosphorus [*Krom et al., 2010; Krom et al.,*  
51 *1991*], with aerosol deposition accounting for at least one third of all phosphorus inputs [*Ganor*  
52 *and Mamane, 1982*]. Large dust plumes, clearly visible in satellite images, stretch from North  
53 Africa to the Mediterranean Sea. Perhaps as a consequence of this visible and obviously  
54 significant contribution, previous studies have mainly focused on Northern Africa as the major  
55 source of nutrients to the Mediterranean [*Escudero et al., 2011; Ganor and Mamane, 1982;*  
56 *Guerzoni et al., 1999*]. Despite the eastern Mediterranean basin receiving air masses from  
57 Europe at least 70% of the time [*Kouvarakis et al., 2001*], phosphorus within European-sourced  
58 aerosols has not been as extensively studied due to comparatively lower mass deposition. Yet, it  
59 is the composition of the aerosol and the ability of microorganisms to assimilate nutrients from  
60 this source, i.e. bioavailability that must also be considered.

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

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

## 78 **2. Methods**

### 79 **2.1 Ambient aerosol collection**

80 Air masses originating in North Africa and Europe were sampled at the Finokalia research  
81 station (35°32'N, 25°67'E), a remote site on the island of Crete, Greece, located 70 km from the  
82 nearest major city. This site was chosen as it is isolated from both local and regional influences  
83 [*Markaki et al.*, 2003], making it an ideal location for examining the transport of long range  
84 aerosols. Samples of particulate matter with an aerodynamic diameter < 10  $\mu\text{m}$ , PM<sub>10</sub>, were  
85 collected on Teflon filters using a virtual impactor with an operational flow rate of 16.7 L min<sup>-1</sup>.  
86 Samples were collected over a one to three day period from 2009-2011 during which either  
87 North African or European air masses dominated (Table S1). A total of fourteen samples were  
88 analyzed, five from European and nine from North African air masses (Table S1), hereafter  
89 referred to as simply European and North African samples. Hybrid Single Particle Lagrangian  
90 Integrated Trajectory Model (HYSPLIT) [*Draxier and Hess*, 1998; *Izquierdo et al.*, 2012] back  
91 trajectories were completed for each sample in order to confirm the geographic origin of the air  
92 masses sampled. HYSPLIT back trajectories were calculated between 1000 m and 3000 m above

93 ground level for five days preceding sample collection (Figure S1). HYSPLIT back trajectories  
94 were computed at 3000 m to confirm dust events. Dust is either homogeneously distributed from  
95 0 to about 3000 m, during spring and autumn dust events, or is found in a layer between 2500 –  
96 4000 m during summer and autumn dust events [Kalivitis *et al.*, 2007]. HYSPLIT back  
97 trajectories computed at 1000 m show the origin of air masses within the boundary layer; this  
98 height is chosen, rather than the more conventional heights of 0 m or 500 m to avoid orographic  
99 problems. While HYSPLIT back trajectories do not guarantee that pure end members were  
100 sampled, the air masses were dominated by either North African or European origins. Ambient  
101 aerosol samples were stored at -20°C until analysis.

## 102 **2.2 Emission source collection**

103 Emissions from ultra-low sulfur diesel fuel and gasoline were collected using US  
104 Environmental Protection Agency protocols under typical urban driving conditions [Oakes *et al.*,  
105 2012b]. Coal fly ash from an electrostatic precipitator, provided by The Southern Company, was  
106 aerosolized and collected with a PM<sub>2.5</sub> cyclone inlet sampler [Oakes *et al.*, 2012b]. Smoke  
107 produced from the burning of materials collected from coniferous and deciduous trees native to  
108 Georgia, USA, was sampled during a controlled biomass burning experiment using a cyclone  
109 inlet sampler placed 3.5 m above the burn area at a flow rate of 16.7 L min<sup>-1</sup> for approximately  
110 30 minutes. The ash produced from the biomass burning experiment was also analyzed.  
111 Although emission sources were not collected from European or North African locations, source  
112 materials presented here are considered to be reasonably similar to those found in Europe and  
113 North Africa. Thus, these emission source end members are used as a proxy for primary  
114 phosphorus sources found in European and North African air masses. In addition, the following  
115 commercially available source materials were analyzed: pollen (*Quercus ruba*; Sigma P7895),

116 the bacteria *Azotobacter vinelandii* (Sigma A2135), and the bacteria *Bacillus subtilis* (Sigma  
117 B4006). These commercially available materials were handled and analyzed in the same manner  
118 as the phosphorus standards (Supporting Information). Emission source samples were stored at -  
119 20°C until analysis.

### 120 **2.3 Total phosphorus and soluble phosphate determination**

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

### 136 **2.4 Synchrotron-based X-ray spectromicroscopy**

137 Samples were analyzed on the X-ray fluorescence microscope located at beamline 2-ID-B at  
138 the Advanced Photon Source, Argonne National Laboratory. The beamline is optimized to

139 examine samples over a 1-4 keV energy range using a focused X-ray beam with a spot size of  
140 approximately  $100 \text{ nm}^2$  [McNulty *et al.*, 2003]. Phosphorus Near Edge X-ray Fluorescence  
141 Spectroscopy (P-NEXFS) data were collected in two modes that differ based on spatial  
142 resolution. In the first mode, individual phosphorus-rich particles with a diameter of greater than  
143 1 micron identified in X-ray fluorescence maps; these particles were then interrogated with  
144 micro P-NEXFS. The individual phosphorus-rich particles seen in X-ray fluorescence maps are  
145 obvious contributors to total sample phosphorus. However, much of the total phosphorus on an  
146 aerosol filter can also be contained in particles that are less phosphorus-rich and therefore less  
147 apparent in X-ray fluorescence maps. Therefore, in the second mode, large areas of the filters  
148 were also examined with an unfocused beam (spot size =  $0.28 \text{ mm}^2$ ) to obtain bulk spectra  
149 representative of the average phosphorus phase present.

150 In order to maximize the number of samples analyzed in the allotted time, X-ray fluorescence  
151 maps were created by rastering the focused beam in  $0.5 \text{ }\mu\text{m}$  steps with an incident energy of  
152 2185 eV. At this resolution, individual phosphorus-rich particles were clearly discernible.  
153 P-NEXFS spectra were collected over an energy range of 2130 to 2210 eV in 0.33 eV steps,  
154 using a 1 s dwell time at each step. Each P-NEXFS measurements for both bulk and individual  
155 phosphorus-rich particles were repeated at least three times, in a single position, creating a  
156 minimum effective dwell time of 3 s. X-ray spectromicroscopy data were collected using an  
157 energy dispersive silicon drift detector (Ketek with a  $5 \text{ mm}^2$  sensitive area). A flow of helium  
158 was introduced between the X-ray optical hardware and the sample to reduce X-ray backscatter.  
159 An in-line monitor stick composed of fluorapatite was measured with each sample in order to  
160 identify and correct for any potential drift in monochromator energy calibration that occurred

161 during analyses [*de Jonge et al.*, 2010]. Clean areas of Teflon and cellulose acetate filters were  
162 examined as blanks and showed negligible background signal.

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

## 167 **2.5 P-NEXFS data analysis**

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

180 The data for an individual P-NEXFS spectrum was normalized to create a relative intensity  
181 value of approximately 1 for post edge area of the spectra ( $> 2160$  eV). The data were also  
182 processed using a three-point smoothing algorithm built into the software. Smoothing did not  
183 appreciably change the data, other than removing high frequency noise. The standard database



184 used in our spectral linear combination fitting included phosphorus minerals and inorganic  
185 phosphorus compounds discussed in Ingall et al. [2011], as well as a variety of organic  
186 phosphorus compounds (Supporting Information). An iterative process was used to refine the  
187 standard database used to model the sample spectra. First, complex, high temperature, and high-  
188 pressure minerals, unlikely to be major components of aerosol phosphorus were excluded from  
189 the database [Oakes et al., 2012a]. Second, the database was narrowed through elimination of  
190 standards with low contribution (i.e. less than 10%) or poor fit (i.e. high R-factor) during initial  
191 linear combination fitting. Finally, the composition of individual phosphorus-rich particles  
192 determined using micro P-NEXFS helped to guide the choice of standards for the modeling of  
193 bulk P-NEXFS spectra.

194 Spectra can be very similar within certain compound classes like phosphorus esters  
195 (Figure S2) and mineral classes like apatites [Ingall et al., 2011]. Also, insufficient quantities of  
196 a specific mineral or compound in a sample can also lead to underestimation of the specific  
197 compound during linear combination fitting [Hesterberg, 2010]. We therefore generalized our  
198 results into four chemical classes, apatite, metal phosphates, alkali and alkaline earth metal  
199 phosphates, and organic phosphorus + polyphosphate, with distinct implications for phosphorus  
200 solubility and bioavailability. The apatite chemical class includes fluorapatite, hydroxyapatite,  
201 carbonate fluorapatite and carbonate hydroxyapatite and chlorapatite. Minerals in the metal  
202 phosphate chemical class have a dominant metal cation like iron, copper, or manganese and  
203 include vauxite, cornetite, wardite, and wolfeite. Alkali and alkaline earth metal phosphates  
204 (hereafter referred to as alkali phosphates) include sodium phosphate and calcium dihydrogen  
205 phosphate; these phases typically have high solubility. The final chemical class, organic

206 phosphorus + polyphosphate, includes organic compounds like adenosine-5'-triphosphate (ATP),  
207 lipids (and other phosphorus esters), and polyphosphates, all compounds of biological origin.

208

### 209 **3. Results and Discussion**

#### 210 **3.1 Ambient aerosols**

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

227 Previous studies based on sequential extraction techniques have shown that apatite is the  
228 most abundant phosphorus phase followed by oxide-associated phosphorus in North African-

229 sourced air masses [Anderson *et al.*, 2010; Nenes *et al.*, 2011]. Our results suggest  
230 organic phosphorus + polyphosphate as well as alkali phosphates account for a large fraction of  
231 the phosphorus in the North African derived aerosol (Figure 2). The oxide-associated  
232 phosphorus fraction determined by sequential extraction techniques can include labile organic  
233 phosphorus as well [Anderson *et al.*, 2010]. Therefore, our finding of organic phosphorus +  
234 polyphosphate in North African-sourced aerosols could be consistent with chemical extraction  
235 methods and suggests organic phosphorus is present in the oxide-associated fraction identified in  
236 these studies. The presence of alkali phosphates in North African air masses may reflect  
237 recycling of apatite-derived phosphorus. At low pH, apatite more readily dissolves into aerosol  
238 water droplets [Anderson *et al.*, 2010] that are subsequently dehydrated, possibly resulting in  
239 supersaturation of these droplets with respect to alkali phosphates. If sulfuric acid is the  
240 dominant acidic species present, aerosol water content may continue to be high even at low pH,  
241 which further facilitates dissolution of phosphorus.

242 Soluble phosphorus percentage shows the strongest correlation with the relative abundance  
243 of organic phosphorus + polyphosphate (Figure 3). However, the correlation coefficient of 0.61  
244 indicates that significant variability in this relationship exists, likely tied to the abundance and  
245 solubility of specific organic phosphorus compounds *within* the defined chemical class. Organic  
246 phosphorus compounds exhibit a wide range of structures and compositions that are generally  
247 not possible to distinguish with P-NEXFS (Supporting Information). These species, in turn,  
248 differ in terms of phosphorus solubility. Also, acidification of normally insoluble phosphorus  
249 phases can increase phosphorus solubility [Nenes *et al.*, 2011]. Anthropogenic emissions are  
250 well-documented sources of acidic species [Nenes *et al.*, 2011] and have also been linked to  
251 more soluble forms of aerosol phosphorus [Izquierdo *et al.*, 2012; Zamora *et al.*, 2013]. Varying

252 quantities of acidic species [Nenes *et al.*, 2011] entrained in European and North African air  
253 masses would likely lead to different levels of phosphorus solubilization during atmospheric  
254 transport.

### 255 **3.2 Emission Sources**

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

275 examined here. In fact, when various emission sources were used as standards in spectral linear  
276 combination fitting, fits containing bacteria as a standard produced the best results for ambient  
277 aerosols sampled from both North African and European air masses.

278

#### 279 **4. Conclusions**

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

294

295

296

297 **Acknowledgments.** This material is based upon work supported by the National Science  
298 Foundation under Grants OCE 1060884 and OCE 1357375, and the data used to produce these  
299 results is available upon request to the corresponding author. Any opinions, findings, and  
300 conclusions or recommendations expressed in this material are those of the authors and do not  
301 necessarily reflect the views of the National Science Foundation. Use of the Advanced Photon  
302 Source is supported by the U.S. Department of Energy, Office of Basic Energy Sciences under  
303 contract No. DE-AC02-06CH11357. NM and KV acknowledge support from European Union  
304 (European Social Fund) and Greek national funds through the Operational Program "Education  
305 and Lifelong Learning" of the National Strategic Reference Framework Research Funding  
306 Program, ARISTEIA. We thank John Jansen at Southern Co. and Bill Preston at the EPA for  
307 providing source emission samples. Finally, we thank Terry Lathem for the volcanic ash sample.

308

309 **References**

- 310 Ajiboye, B., O. O. Akinremi, and A. Jurgensen (2007), Experimental validation of quantitative  
311 XANES analysis for phosphorus speciation, *Soil Science Society of America Journal*, 71(4),  
312 1288-1291.
- 313 Anderson, L. D., K. L. Faul, and A. Paytan (2010), Phosphorus associations in aerosols: What  
314 can they tell us about P bioavailability?, *Marine Chemistry*, 120(1-4), 44-56.
- 315 Artaxo, P., J. V. Martins, M. A. Yamasoe, A. S. Procopio, T. M. Pauliquevis, M. O. Andreae, P.  
316 Guyon, L. V. Gatti, and A. M. C. Leal (2002), Physical and chemical properties of aerosols in  
317 the wet and dry seasons in Rondonia, Amazonia, *Journal of Geophysical Research-Atmospheres*,  
318 107(D20).
- 319 Aspila, K. I., H. Agemian, and A. S. Y. Chau (1976), A semi-automated method for the  
320 determination of inorganic, organic and total phosphate in sediments., *Analyst*, 101, 187-197.
- 321 Baker, A. R., T. D. Jickells, M. Witt, and K. L. Linge (2006), Trends in the solubility of iron,  
322 aluminium, manganese and phosphorus in aerosol collected over the Atlantic Ocean, *Marine*  
323 *Chemistry*, 98(1), 43-58.
- 324 Bauer, H., A. Kasper-Giebl, M. Loflund, H. Giebl, R. Hitzemberger, F. Zibuschka, and H.  
325 Puxbaum (2002), The contribution of bacteria and fungal spores to the organic carbon content of  
326 cloud water, precipitation and aerosols, *Atmospheric Research*, 64(1-4), 109-119.
- 327 Beauchemin, S., D. Hesterberg, J. Chou, M. Beauchemin, R. R. Simard, and D. E. Sayers (2003),  
328 Speciation of phosphorus in phosphorus-enriched agricultural soils using X-ray absorption near-  
329 edge structure spectroscopy and chemical fractionation, *Journal Of Environmental Quality*,  
330 32(5), 1809-1819.

331 Benitez-Nelson, C. R. (2000), The biogeochemical cycling of phosphorus in marine systems,  
332 *Earth-Science Reviews*, 51(1-4), 109-135.

333 Burrows, S. M., W. Elbert, M. G. Lawrence, and U. Poschl (2009), Bacteria in the global  
334 atmosphere - Part 1: Review and synthesis of literature data for different ecosystems,  
335 *Atmospheric Chemistry and Physics*, 9(23), 9263-9280.

336 Chamard, P., F. Thiery, A. Di Sarra, L. Ciattaglia, L. De Silvestri, P. Grigioni, F. Monteleone,  
337 and S. Piacentino (2003), Interannual variability of atmospheric CO<sub>2</sub> in the Mediterranean:  
338 measurements at the island of Lampedusa, *Tellus Series B-Chemical and Physical Meteorology*,  
339 55(2), 83-93.

340 Chen, H. Y., T. H. Fang, M. R. Preston, and S. Lin (2006), Characterization of phosphorus in the  
341 aerosol of a coastal atmosphere: Using a sequential extraction method, *Atmospheric*  
342 *Environment*, 40(2), 279-289.

343 de Jonge, M. D., D. Paterson, I. McNulty, C. Rau, J. A. Brandes, and E. Ingall (2010), An energy  
344 and intensity monitor for X-ray absorption near-edge structure measurements, *Nuclear*  
345 *Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and*  
346 *Associated Equipment*, 619(1-3), 154-156.

347 Draxler, R. R., and G. D. Hess (1998), An overview of the HYSPLIT\_4 modelling system for  
348 trajectories, dispersion and deposition, *Australian Meteorological Magazine*, 47(4), 295-308.

349 Escudero, M., A. F. Stein, R. R. Draxler, X. Querol, A. Alastuey, S. Castillo, and A. Avila  
350 (2011), Source apportionment for African dust outbreaks over the Western Mediterranean using  
351 the HYSPLIT model, *Atmospheric Research*, 99(3-4), 518-527.

352 Ganor, E., and Y. Mamane (1982), Transport of Saharan dust across the Eastern Mediterranean,  
353 *Atmospheric Environment*, 16(3), 581-587.



354 Graham, W. F., and R. A. Duce (1982), The atmospheric transport of phosphorus to the western  
355 North-Atlantic, *Atmospheric Environment*, 16(5), 1089-1097.

356 Guerzoni, S., et al. (1999), The role of atmospheric deposition in the biogeochemistry of the  
357 Mediterranean Sea, *Progress in Oceanography*, 44(1-3), 147-190.

358 Hamza, W., M. R. Enan, H. Al-Hassini, J. B. Stuut, and D. de-Beer (2011), Dust storms over the  
359 Arabian Gulf: a possible indicator of climate changes consequences, *Aquatic Ecosystem Health*  
360 *& Management*, 14(3), 260-268.

361 Hesterberg, D. (2010), Chapter 11 - Macroscale Chemical Properties and X-Ray Absorption  
362 Spectroscopy of Soil Phosphorus, in *Developments in Soil Science*, edited by S. Balwant and G.  
363 Markus, pp. 313-356, Elsevier.

364 Ingall, E., J. Brandes, J. Diaz, M. de Jonge, D. Paterson, I. McNulty, W. Elliott, and P. Northrup  
365 (2011), Phosphorus K-edge XANES spectroscopy of mineral standards, *Journal of Synchrotron*  
366 *Radiation*, 18, 189-197.

367 Izquierdo, R., C. R. Benitez-Nelson, P. Masque, S. Castillo, A. Alastuey, and A. Avila (2012),  
368 Atmospheric phosphorus deposition in a near-coastal rural site in the NE Iberian Peninsula and  
369 its role in marine productivity, *Atmospheric Environment*, 49, 361-370.

370 Kalivitis, N., E. Gerasopoulos, M. Vrekoussis, G. Kouvarakis, N. Kubilay, N. Hatzianastassiou,  
371 I. Vardavas, and N. Mihalopoulos (2007), Dust transport over the eastern Mediterranean derived  
372 from Total Ozone Mapping Spectrometer, Aerosol Robotic Network, and surface measurements,  
373 *Journal of Geophysical Research-Atmospheres*, 112(D3).

374 Kouvarakis, G., N. Mihalopoulos, A. Tselepidis, and S. Stavrakaki (2001), On the importance of  
375 atmospheric inputs of inorganic nitrogen species on the productivity of the eastern Mediterranean  
376 Sea, *Global Biogeochemical Cycles*, 15(4), 805-817.

377 Krom, M. D., K. C. Emeis, and P. Van Cappellen (2010), Why is the Eastern Mediterranean  
378 phosphorus limited?, *Progress in Oceanography*, 85(3-4), 236-244.

379 Krom, M. D., N. Kress, S. Brenner, and L. I. Gordon (1991), Phosphorus limitation of primary  
380 productivity in the eastern Mediterranean Sea, *Limnology and Oceanography*., 36(3), 424-432.

381 Mackey, K. R. M., K. Roberts, M. W. Lomas, M. A. Saito, A. F. Post, and A. Paytan (2012),  
382 Enhanced Solubility and Ecological Impact of Atmospheric Phosphorus Deposition upon  
383 Extended Seawater Exposure, *Environmental Science & Technology*, 46(19), 10438-10446.

384 Mahowald, N., et al. (2008), Global distribution of atmospheric phosphorus sources,  
385 concentrations and deposition rates, and anthropogenic impacts, *Global Biogeochemical Cycles*,  
386 22(4).

387 Markaki, Z., K. Oikonomou, M. Kocak, G. Kouvarakis, A. Chaniotaki, N. Kubilay, and N.  
388 Mihalopoulos (2003), Atmospheric deposition of inorganic phosphorus in the Levantine Basin,  
389 eastern Mediterranean: Spatial and temporal variability and its role in seawater productivity,  
390 *Limnology and Oceanography*, 48(4), 1557-1568.

391 McInnes, K. L., T. A. Erwin, and J. M. Bathols (2011), Global Climate Model projected changes  
392 in 10 m wind speed and direction due to anthropogenic climate change, *Atmospheric Science*  
393 *Letters*, 12(4), 325-333.

394 McNulty, I., et al. (2003), The 2-ID-B intermediate-energy scanning X-ray microscope at the  
395 APS, *Journal De Physique Iv*, 104, 11-15.

396 Murphy, J., and J. P. Riley (1962), A modified single solution method for the determination of  
397 phosphate in natural waters, *Analytica Chimica Acta*, 27, 31-36.

398 Nenes, A., M. D. Krom, N. Mihalopoulos, P. Van Cappellen, Z. Shi, A. Bougiatioti, P. Zarmas,  
399 and B. Herut (2011), Atmospheric acidification of mineral aerosols: a source of bioavailable  
400 phosphorus for the oceans, *Atmospheric Chemistry and Physics*, *11*(13), 6265-6272.

401 Oakes, M., R. J. Weber, B. Lai, A. Russell, and E. D. Ingall (2012a), Characterization of iron  
402 speciation in urban and rural single particles using XANES spectroscopy and micro X-ray  
403 fluorescence measurements: investigating the relationship between speciation and fractional iron  
404 solubility, *Atmospheric Chemistry and Physics*, *12*(2), 745-756.

405 Oakes, M., E. D. Ingall, B. Lai, M. M. Shafer, M. D. Hays, Z. G. Liu, A. G. Russell, and R. J.  
406 Weber (2012b), Iron Solubility Related to Particle Sulfur Content in Source Emission and  
407 Ambient Fine Particles, *Environmental Science & Technology*, *46*(12), 6637-6644.

408 Prietzel, J., A. Dümig, Y. Wu, J. Zhou, and W. Klysubun (2013), Synchrotron-based P K-edge  
409 XANES spectroscopy reveals rapid changes of phosphorus speciation in the topsoil of two  
410 glacier foreland chronosequences, *Geochimica Et Cosmochimica Acta*, *108*(0), 154-171.

411 Ravel, B., and M. Newville (2005), ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-  
412 ray absorption spectroscopy using IFEFFIT, *Journal of Synchrotron Radiation*, *12*, 537-541.

413 Ridame, C., and C. Guieu (2002), Saharan input of phosphate to the oligotrophic water of the  
414 open western Mediterranean Sea, *Limnology and Oceanography*, *47*(3), 856-869.

415 Zamora, L. M., J. M. Prospero, D. A. Hansell, and J. M. Trapp (2013), Atmospheric P deposition  
416 to the subtropical North Atlantic: sources, properties, and relationship to N deposition, *Journal of*  
417 *Geophysical Research-Atmospheres*, *118*(3), 1546-1562.

418

419

420

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

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

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

437  
438





