

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

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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

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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 μm , PM₁₀, were
85 collected on Teflon filters using a virtual impactor with an operational flow rate of 16.7 L min⁻¹.
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_{2.5} 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⁻¹ 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 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 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 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.

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308

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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.

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