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## Atmospheric particle-bound organophosphate ester flame retardants and plasticizers in a North African Mediterranean coastal city (Bizerte, Tunisia)

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12 **Abstract**

13 Organophosphate ester (OPE) flame retardants and plasticizers have been detected at  
14 generally high frequencies (70-98%) for the first time in the atmosphere over the NW  
15 African coastal Mediterranean. Results from sixty air samples (total suspended  
16 particles, TSP) collected between March 2015 and January 2016 in an urban coastal site  
17 (Bizerte, Tunisia) revealed  $\Sigma_9$ OPE concentrations of  $\sim 100$ - $1060 \text{ pg m}^{-3}$  ( $470 \text{ pg m}^{-3}$ ,  
18 median) with TCPPs, EHDPP and TiBP exhibiting the higher median concentrations ( $\sim$   
19  $110$ ,  $100$  and  $85 \text{ pg m}^{-3}$ , respectively). Spring generally exhibited the lowest  
20 concentrations, probably linked to the influence of local meteorological conditions and  
21 air mass trajectories to a lesser extent. Non-chlorinated OPEs generally predominated,  
22 in contrast to the most common reported situation in marine environments (i.e. higher  
23 abundance of chlorinated OPEs) pointing to the relevance of local OPE sources in the  
24 study area. TiBP levels were generally higher than those reported for other  
25 marine/coastal environments suggesting this OPE as a good tracer of local sources in  
26 Bizerte. Contrarily, the atmospheric levels of other abundant OPEs in the area (e.g.  
27 TCPP) seem to be in the range and/or lower than those reported for remote marine  
28 environments. These findings point to the interplay of different factors with solar  
29 irradiance (potentially enhancing atmospheric photochemical oxidation reactions) and  
30 meteorological conditions in the study area likely compensating potential local sources  
31 of some OPEs. Not all OPEs presented the same seasonality in terms of atmospheric  
32 concentrations and pattern. The estimated atmospheric dry deposition fluxes ( $\Sigma_9$ OPEs)  
33 were  $18$ - $180 \text{ ng m}^{-2} \text{ d}^{-1}$ . Up to  $\sim 9 \text{ kg y}^{-1}$  of OPEs ( $\sim 1 \text{ kg y}^{-1}$  of new organic  
34 anthropogenic phosphorus coming from OPEs) can be loaded to the shallow and  
35 enclosed Bizerte lagoon ( $\sim 130 \text{ km}^2$ ), considered as the most important aquaculture area

36 in Tunisia, with yet unknown implications for the environmental exposure and impacts  
37 in the ecosystem functioning.

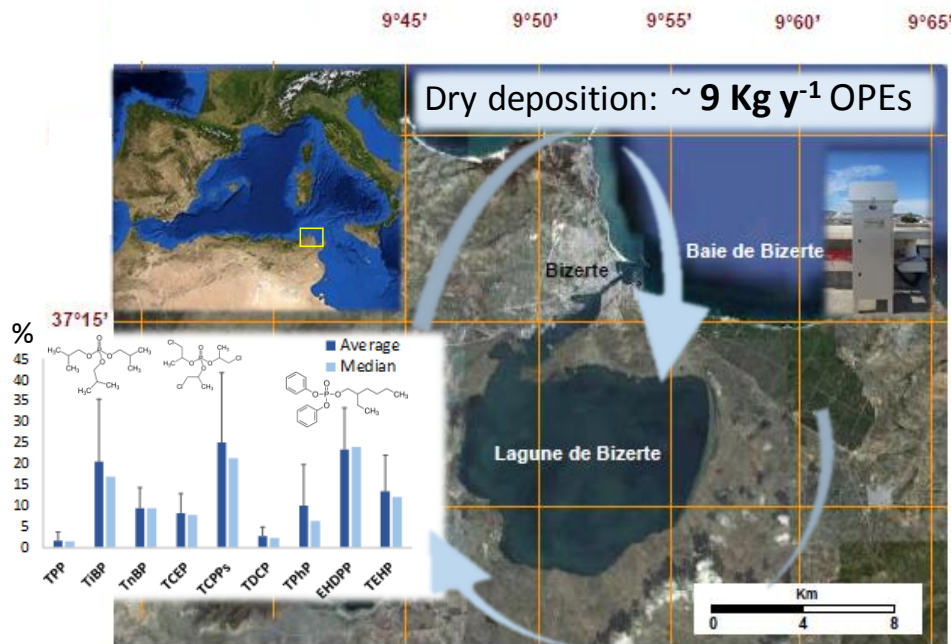
38 **Keywords:**

39 OPEs, plastic additives, marine pollution, dry deposition, environmental risk,  
40 anthropogenic organic phosphorus

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42 **Graphical Abstract**

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## 53 **1. Introduction**

54

55 There is no doubt today about the multi-media global scale occurrence of  
56 organophosphate esters (OPEs) flame retardants and plasticizers in the marine  
57 environment. OPE have been found in air, water, sediment and aquatic organisms from  
58 different marine areas of the world (Zhong et al., 2017; Wei et al., 2015; Brandsma et  
59 al., 2015; Castro- Jiménez et al., 2014; Van der Veen and de Boer, 2012, Bollmann et  
60 al., 2012; Möller et al., 2011; Kim et al., 2011), including remote environments such as  
61 the Arctic (Ma et al., 2017; Sühring et al., 2016a; Hallanger et al., 2015; Salamova et  
62 al., 2014a, Möller et al., 2012) and the most pristine areas from the tropical and  
63 subtropical Atlantic, Pacific and Indian oceans (Castro-Jiménez et al., 2016). In  
64 addition, most recent reports point to their environmental persistency, bioaccumulation  
65 and adverse effects in aquatic organisms and humans (ECHA 2008; 2009; Van der Veen  
66 and de Boer, 2012; Wei et al., 2015; Wang et al., 2015a,b). These findings have raised  
67 awareness on their environmental fate and impacts as it already happened in the past for  
68 other persistent organic pollutants (POPs). However, the magnitude and spatial  
69 distribution of OPE sources in the environment are closely linked to the recent  
70 changes/developments in international regulations, with an important expanding  
71 production and usage of OPEs from 2009 as a result of the global ban of their  
72 “predecessors” polybrominated diphenyl ethers (PBDEs) (UNEP 2009).

73

74 OPE atmospheric levels in remote areas, supposedly far from sources seem to be in  
75 many occasions within the range of levels measured in coastal areas close to suspected  
76 sources, suggesting complex atmospheric circulation patterns and different  
77 environmental processing and dynamics linked to geographic regions (Castro-Jiménez  
78 et al., 2016; Li et al., 2018). It is, therefore, crucial to better investigate the airborne

79 occurrence and loadings of OPEs to marine/coastal environments in close relation to  
80 their potential impacts. A recent study performed in the Mediterranean Sea supports the  
81 hypothesis that atmospheric aerosols can elicit a number of toxic effects in marine  
82 organisms due to the presence of legacy POPs such polychlorinated dibenzo-p-dioxins  
83 and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and high molecular  
84 weight (HMW) polycyclic aromatic hydrocarbons (PAHs) (Mesquita et al., 2016).  
85 Other POPs with recognized toxicity too, such as PBDEs and the “emerging” OPEs, can  
86 add up to the “contaminant-aerosol cocktail” (De wit, 2002; Vonderheidea et al., 2008).  
87 OPEs have been reported in both the atmospheric particle and gaseous phases, but most  
88 of the studies focus on their particle phase occurrence. The atmospheric degradation  
89 processes (e.g. photodegradation and/or OH radical oxidation) will progress more  
90 slowly for particle-bound OPEs as they will be “sheltered”, increasing therefore their  
91 long-range atmospheric transport (LRAT) potential (Liu et al., 2014). In addition, OPEs  
92 have been described to be enriched in both fine and coarse particles from the  
93 atmospheric aerosols in urban environments (Clark et al., 2017; Faiz et al., 2018).  
94 The Mediterranean Sea is a semi-enclosed environment of high ecological and socio-  
95 economic relevance (The Mermex group, 2011). This ecosystem has been documented  
96 to be largely impacted by legacy POPs and other organic contaminants (Paluselli et al.,  
97 2018; The Mermex group 2011; Berrojalbiz et al., 2011, 2011b, 2014; Castro-Jiménez  
98 et al., 2008, 2010, 2012; Mandalakis et al., 2005) as well as by plastic fragments (Cózar  
99 et al., 2015; Schmidt et al., 2018), which may be potential sources of OPEs to the  
100 overlying atmosphere in accumulation zones (Cheng et al., 2013). However, few data  
101 exist on OPE baseline levels and environmental behaviour in the Mediterranean Sea.  
102 Only one study reported surface water and sediment OPE concentrations from rivers  
103 draining into the W Mediterranean (Cristale et al., 2013), and the wide-spread OPE

104 atmospheric occurrence and inputs to surface waters far from the coast was only  
105 recently proved (Castro-Jiménez et al., 2014). Coastal measurements of OPEs of any  
106 kind are very scarce in the Mediterranean Sea, in particular in the African  
107 Mediterranean coast, where even less data on the occurrence of toxic organic  
108 contaminants are available.

109 The objectives of this work are: 1) to investigate for the first time the atmospheric  
110 occurrence of OPEs in the NW African Mediterranean coast; 2) to estimate their  
111 atmospheric dry deposition and loading in Bizerte area (Tunisia) and discuss their  
112 potential impacts.

113

## 114 **2. Materials and Methods**

115

### 116 *2.1. Area description*

117

118 A detailed area description is offered elsewhere (Barhoumi et al., 2018). Briefly, Bizerte  
119 is a medium-size city (~127 000 inhabitants), located in the north of Tunisia, between  
120 the Mediterranean Sea and the Bizerte lagoon (Figure 1). Average temperature of 22 °C,  
121 with hot summer and mild spring, frequent (200 days per year) NW winds (average  
122 speed of 6–8 m s<sup>-1</sup>) and precipitation episodes mostly in autumn and winter months,  
123 characterized the climate of Bizerte area. Even if agriculture and fishery activities are  
124 important in the area, a considerable number of light and heavy industries (i.e., cement,  
125 plastic, textile, mechanic and electronic, iron and steel metallurgy, petroleum refining  
126 and lubricants) are present (Barhoumi et al., 2018) inducing a considerable  
127 anthropogenic pressure. A certain number of studies focusing on the atmospheric  
128 pollution by legacy organic contaminants, like PAHs, PCBs and OCPs, have been



129 performed in the study area (Ben Hassine et al., 2014, Barhoumi et al., 2018). More  
130 recent measurements report on dioxin-like POPs, including PCDD/Fs and DL-PCBs and  
131 also on PBDEs (Castro-Jiménez et al., 2017) but alternative flame retardants like OPEs  
132 have never been studied to the best of our knowledge (nor in the whole NW African  
133 coastal Mediterranean).  
134



135

136 **Figure 1.** Sampling site location (Bizerte, Tunisia)

137

## 138 2.2. Sampling strategy

139

140 Integrated (48 h) aerosol samples (total suspended particles, TSP) were collected from  
141 March 2015 to January 2016 on pre-combusted quartz fibre filters (QFFs) (Whatman  
142 QMA grade, 20.3 x 25.4 cm) using a high volume air sampler (Tisch Environmental  
143 Inc., OH, USA). Overall, 60 samples were collected ( $1920 \pm 40$  m<sup>3</sup>, average volume,

144 Table S1). Sampling was conducted on the roof top (~8 m ASL) of the Faculty of  
145 Science of Bizerte (37° 16' 0.5802" N, 9° 52' 49.875" E) around 1 km far from the city  
146 center, close to the Gulf of Bizerte shoreline and Bizerte lagoon water front (Figure 1).

147

### 148 2.3. Sample processing

149

150 The samples were processed as described in Barhoumi et al. (2018). Briefly, each QFF  
151 was cut into two equal parts. One half was used for organic pollutant analyses and the  
152 other half for determination of ancillary data like TSP, total organic carbon (TOC) and  
153 organic nitrogen (TON) (Table S1). The corresponding filter halves were cut into small  
154 pieces and spiked with 250 ng of deuterated surrogate standards (tri-n-butyl- $d_{27}$ -  
155 phosphate, triphenyl- $d_{15}$ -phosphate, tris(2-chloroisopropyl)- $d_{18}$ -phosphate and tris(1,3-  
156 dichloro-2-propyl)- $d_{15}$ -phosphate). Filters were extracted with dichloromethane (DCM)  
157 (3 cycles of 5 min) using an accelerated solvent extraction system (ASE 350, DIONEX)  
158 at 100 °C, 110 bars, 100% of rinsing volume and 60 s purging time. Few grams of  
159 activated copper were added to ASE flasks to remove potential traces of sulphur. The  
160 obtained extract was rota-evaporated (with a solvent exchange into hexane) to  
161 approximately 0.5 ml and then loaded into a silica-alumina chromatography glass  
162 column (10 mm internal diameter, i.d.), prepared by adding, from bottom to top; 3 g  
163 deactivated alumina (3% w/w), 3 g activated silica, and 1 g dehydrated sodium sulphate.  
164 After conditioning with 15 mL of n-hexane, the column was subsequently eluted into  
165 three fractions (F): with 20 mL of hexane (F1), 40 mL of hexane/DCM (80:20, v/v) (F2)  
166 and 40 mL DCM/Acetone (70:30, v/v) (F3). OPEs were analysed in F3, which was rota-  
167 evaporated down to ~0.2 ml, solvent exchanged into isoctane and further concentrated  
168 under gentle nitrogen stream up to ~0.1 mL. Prior to injection, 200 ng of deuterated

169 standards (Tri-n-propyl-*d*<sub>21</sub>-phosphate, Tris(2-chloroethyl)-*d*<sub>12</sub>-phosphate and  
170 Malathion-*d*<sub>7</sub>) were added to the extracts to be used as internal standards for  
171 quantification.

172

#### 173 2.4. Instrumental Analysis

174

175 OPE analysis was conducted by gas chromatography (Agilent 7820A Series GC)  
176 coupled with mass spectrometry (Agilent 5977E MS) (GC-MS) operating in selected  
177 ion monitoring (SIM) and electron impact (EI, 70eV) mode. OPEs were quantified by  
178 the internal standard procedure. Table S2 shows selected ions for detection and  
179 quantification for each compound. The injector temperature was set at 270 °C (splitless).  
180 The separation was achieved over a 30m x 0.25mm i.d. x 0.25µm HP-5MS capillary  
181 column (Agilent J&W). The oven temperature was programmed from 90°C to 132°C at  
182 3°C/min, to 165°C at 10°C/min, to 235°C at 2°C/min, then to 300°C at 25°C/min  
183 (holding time 5min). The injection volume was of 2 µL and the helium carrier gas flow  
184 was 1 mL min<sup>-1</sup>. The temperatures of the MS transfer line; ion source, and quadrupole  
185 were set at 300, 230 and 150 °C, respectively. Samples were analysed for the following  
186 OPEs: tris-(2-chloroethyl)phosphate (TCEP; CAS: 115-96-8), tris[2-chloro-1-  
187 (chloromethyl)ethyl]phosphate (TDCP; CAS: 13674-87-8), Tris- (1-chloro-2-  
188 propyl)phosphate (TCPPs, mix of isomers; CAS: 13674-84-5), tripropyl phosphate  
189 (TPP; CAS: 513-08-6), tri-iso-butyl phosphate (TiBP; CAS: 126-71-6), tri-n-butyl  
190 phosphate (TnBP; CAS: 126-73-8), triphenyl phosphate (TPhP; CAS: 115-86-6), 2-  
191 ethylhexyl diphenyl phosphate (EHDPP; CAS: 1241-94-7), and tri(2-ethylhexyl)  
192 phosphate (TEHP; CAS: 78-42-2). TOC and TON were determined in filter subsamples

193 by high temperature combustion (CHN analyser) (Raimbault et al., 2008). Individual  
194 native OPE standards were purchased from Dr. Ehrenstorfer GmbH (Germany),  
195 whereas labeled standards tri-n-butyl- $d_{27}$ -phosphate, triphenyl- $d_{15}$ -phosphate, tri-n-  
196 propyl- $d_{21}$ -phosphate and malathion- $d_7$  were obtained from C/D/N Isotopes Inc.  
197 (Canada) and tris(2-chloroisopropyl)- $d_{18}$ -phosphate, tris(1,3-dichloro-2-propyl)- $d_{15}$ -  
198 phosphate and tris(2-chloroethyl)- $d_{12}$ -phosphate were from Cambridge Isotope  
199 Laboratories, Inc. (USA).

200

#### 201 *2.5. Quality assurance / quality control (QA/QC)*

202

203 The high volume air sampler was regularly calibrated (each month) following the  
204 manufacturer's procedure (Tisch Environmental, HIGH VOL+). QFFs were  
205 individually wrapped in double aluminium foil and baked at 450 °C overnight before  
206 sampling. After each sampling event, the filters were wrapped in the same aluminium  
207 foil and stored in double sealed plastic bags in a freezer at -20 °C before processing.  
208 The pre- and post-sampling QFF weights were determined after they were placed in a  
209 desiccator (25 °C) for 24h. Standards (natives + labelled compounds) were introduced  
210 in the chromatographic sequence to evaluate possible variations on the detection  
211 conditions during the time of analyses. Prior to use, the ASE cells were pre-cleaned by  
212 performing an "empty" ASE extraction with DCM. Three field blanks (taken in autumn  
213 - summer), consisting on baked QFFs transported to the sampling area, mounted in the  
214 sampler, and dismounted, were collected, stored and analysed concurrently with the  
215 samples. Three laboratory blanks were also performed. Blanks results are presented in  
216 Table S3. An unexpected problem occurred during the processing of one of the field

217 blanks, so results are only reported for the two remaining blanks. OPE levels in the  
218 blanks were generally low, ranging from ~1 to 14 ng for most compounds. Relatively  
219 higher blank levels were found for TiBP, EHDPP and TCPP (25 to 74 ng). However,  
220 these three OPEs exhibited the highest concentrations in the samples. These higher  
221 blank levels were suspected to come from the ASE system used for the sample  
222 extraction. A high variability was observed, in particular for the most abundant  
223 compounds, highlighting the necessity of collecting more field blanks in future long-  
224 term OPE monitoring studies. Laboratory blanks showed lower or similar levels to field  
225 blanks, so no contamination during sampling or storage occurred. Results were blank  
226 corrected by subtracting the filed blank values (autumn). Instrumental limits of  
227 detection (LODs), calculated as signal-to-noise (S/N) ratio  $> 3$ , and limits of  
228 quantification (LOQ), corresponding to a  $S/N \geq 10$ , ranged from 5 to 50 and from 10 to  
229 100 pg, respectively depending on the compound (Table S4).

230 Average method recoveries (n=60) (extraction-cleanup-analysis) as monitored by the  
231 surrogate OPEs varied from  $57 \pm 11$  to  $105 \pm 11\%$  (Table S5). In addition, spike  
232 experiments for native OPEs were conducted. Clean QFF (n=2) were spiked with a  
233 mixture of native OPE (250 ng/sample) and extracted as indicated above. Results  
234 confirm the good recoveries of our method; with an average native OPE recovery of  
235  $101 \pm 24\%$  (Table S6). Results were not corrected by recoveries. NIST SRM 2585 was  
236 analysed for target OPEs as well. This reference material is not certified for OPEs,  
237 however different laboratories have provided concentration of OPEs in this dust  
238 reference material, becoming a recommended quality control step (Fan et al., 2014,  
239 Castro-Jiménez et al., 2016). The average results for two replicates (blank corrected)  
240 proved that the analysis of OPE using the described methodologies provided

241 concentrations generally in good agreement with reported values for most OPEs (Figure  
242 S1). Deviations were found for EHDPP and TDCP, only.

243

### 244 **3. Results and discussion**

245

#### 246 **3.1. Atmospheric occurrence**

247

##### 248 *3.1.1. Detection frequency and concentrations*

249

250 The studied OPEs were detected in the aerosol samples over Bizerte city at generally  
251 high frequencies, except for TPP and TDCP (only found in 8% and 12% of the samples,  
252 respectively). Low detection frequencies of TDCP in the atmosphere has been  
253 previously reported in some environments, like in the Great Lakes (Salamova et al.,  
254 2014b). The non-chlorinated OPEs (TPhP, EHDPP, TnBP and TEHP) were generally  
255 the most frequently found (92-98%), although closely followed by the chlorinated  
256 TCEP and TCPPs (85-90%). The other alkyl-OPE measured (i.e. TiBP) was present in  
257 the 70% of the samples (Figure S2). However, the minor frequency observed for TiBP  
258 can be attributed to the blank subtraction performed (relatively high field blank levels  
259 compared to the other alkyl-OPEs) (Table S3). These results confirm the presence of  
260 OPEs at the NW Mediterranean African coast, never reported before.

261 Overall, the  $\sum_9\text{OPE}$  particle-bound atmospheric concentrations (considering only  
262 detected values) ranged from ~100 to 1060  $\text{pg m}^{-3}$  (470  $\text{pg m}^{-3}$ , median) along the  
263 sampling period with TCPPs, EHDPP and TiBP exhibiting the higher median  
264 concentrations of ~ 110, 100 and 85  $\text{pg m}^{-3}$ , respectively. Table S7 shows the compound  
265 specific concentrations for all aerosol samples. Very few OPE atmospheric

266 measurements in coastal areas have been performed so far. The vast majority of  
267 available data in marine environments come from cruise measurements. The measured  
268 values in Bizerte are generally lower than those reported across the Mediterranean Sea  
269 ( $\sum_{14}\text{OPE}$ : 400-5000  $\text{pg m}^{-3}$ ) and the SW Black Sea ( $\sum_{14}\text{OPE}$ : 1700-6000  $\text{pg m}^{-3}$ )  
270 (Castro-Jiménez et al., 2014), the E China Sea ( $\sum_8\text{OPE}$  230-2900  $\text{pg m}^{-3}$ ) (Möller et al.,  
271 2012) and tropical and subtropical areas from the Atlantic, Pacific and Indian Oceans  
272 ( $\sum_{14}\text{OPE}$ : 360-4400  $\text{pg m}^{-3}$  (Castro-Jiménez et al., 2016), but in the range of those from  
273 the North Sea ( $\sum_8\text{OPE}$ : 100-1400  $\text{pg m}^{-3}$ ) (Möller et al., 2012) and Svalbard coastal area  
274 ( $\sum_8\text{OPE}$ : 30-1450  $\text{pg m}^{-3}$ ) (Salamova et al., 2014a). However, OPE levels in Bizerte  
275 were higher than those reported for other semi-enclosed marine environments like the S  
276 China Sea ( $\sum_9\text{OPE}$ : 50-160  $\text{pg m}^{-3}$ ) (Lai et al., 2015) and also less impacted areas like  
277 the Coral Sea ( $\sum_4\text{OPE}$ : 90  $\text{pg m}^{-3}$ ) (Chen et al., 2013). These comparisons should be  
278 taken with caution though, due to the consideration of different number (and type, in  
279 some cases) of compounds included in the sums and the different seasons and years of  
280 the studies. Although it may still high variable, a more meaningful comparison would  
281 be considering individual compounds. The atmospheric levels of the predominant OPEs  
282 in Bizerte (i.e. TCPPs, EHDPP and TiBP) were individually compared with existing  
283 studies. Table 1 provides an updated compilation of atmospheric particle-bound OPE  
284 measurements in marine/coastal environments and some reference inland urban  
285 locations for comparison. Interestingly, some different trends were found compared to  
286 those of  $\sum_9\text{OPE}$ s; with TCPPs concentrations in Bizerte higher than in the E China Sea  
287 and Svalbard, but lower than those in the North Sea. TiBP levels in Bizerte appear to be  
288 generally higher than in other marine/coastal environments studied. This compound is  
289 used in a wide variety of industrial applications including building, papers, boards,  
290 plastics, rubbers, textile and directly as an additive in various products such as lacquers,

291 hydraulic fluids and floor polishes (ECHA website). Therefore, their relatively high  
292 levels measured in this study could be related to the plastic and textile industries located  
293 in Menzel Jemil city, 5 km SE of the sampling station (Figure 1) (Barhoumi et al.,  
294 2018). EHDPP concentrations in Bizerte were in the range of those reported for the  
295 Black Sea but lower than in the W Mediterranean Sea (Castro-Jiménez et al., 2014) and  
296 the tropical and sub-tropical Atlantic, Pacific and Indian Oceans (Castro-Jiménez et al.,  
297 2016).

298

299 Despite the variability that the mentioned factors may have induced, it is not completely  
300 clear why the atmospheric levels measured in Bizerte (a coastal urban city under  
301 important anthropogenic pressures) for some of the most abundant OPEs like TCPP  
302 (among others, see Table 1), are in the range and/or lower than those reported for  
303 remote coastal environments or pristine oceanic regions. Most probably a combination  
304 of differential regional emission patterns, meteorological conditions and rates of  
305 atmospheric processing can explain these data. For example, the important global solar  
306 irradiance in the Mediterranean basin (The Mermex group, 2011, Sempéré et al., 2015),  
307 reaching annual average values of  $\sim 210 \text{ W m}^{-2}$  in Bizerte city (Chelbi et al., 2015, Ben  
308 Othman et al., 2018) could enhance atmospheric degradation due to photochemical  
309 oxidation reactions. Even if these processes likely progress faster for gas-phase  
310 compounds, the atmospheric photochemical oxidation of particle-bound OPEs has also  
311 been described (Liu et al., 2014). These conditions would favour the decrease of OPE  
312 atmospheric levels, even if land-based sources could be higher than in other  
313 environments (like the Arctic, with less solar irradiation rates and colder temperatures).  
314 In addition, the huge expansion of OPE production and usage experienced in EU and  
315 other developed countries could have not yet arrived to the NW African edge of the



316 Mediterranean Sea, where OPE consumption (and related emission) may be still  
317 moderate. However, no public data on OPE production and consumption exist in this  
318 region to the best of our knowledge, highlighting the necessity of OPE emission  
319 inventories at the African Mediterranean coast.

320

### 321 *3.1.2. Atmospheric pattern and seasonality*

322

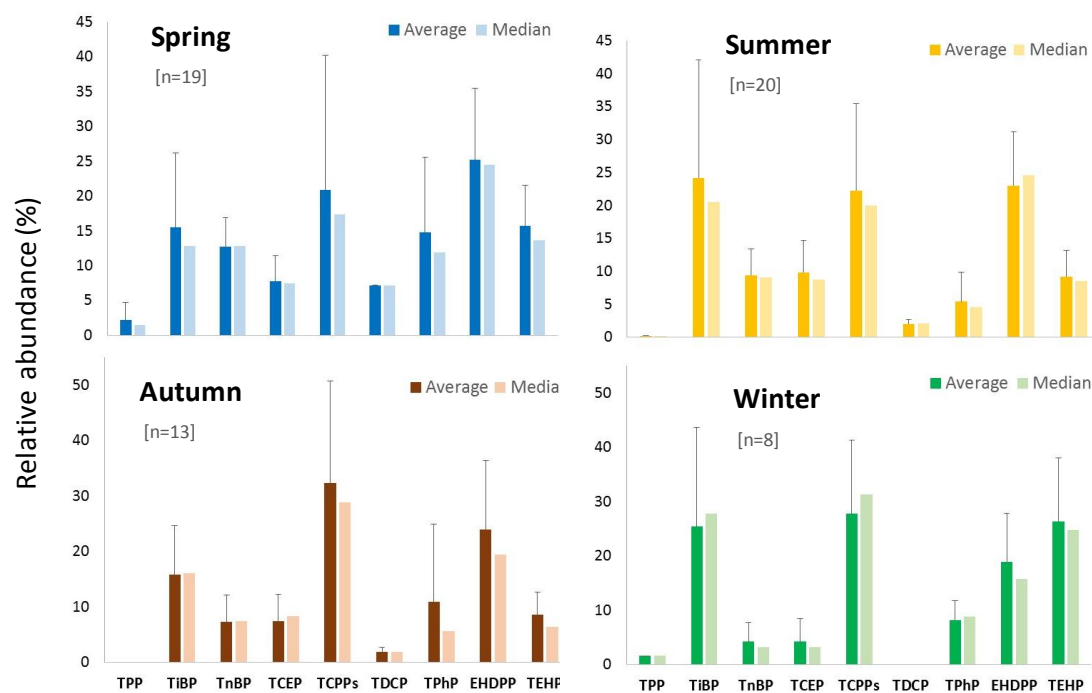
323 As indicated, TCPPs, EHDPP and TiBP exhibited the higher concentrations and  
324 therefore dominated the global OPE atmospheric pattern (n=60) over Bizerte, accounting  
325 for the 25±16 %, 23±10 %, and 20±15% of the  $\Sigma_9$ OPEs, respectively (Figure S3). A  
326 general predominance of Cl-OPEs, in particular TCPP, in atmospheric aerosols in open  
327 marine environments has been reported (Li et al., 2018; Castro-Jiménez et al., 2016;  
328 Möller et al., 2012). However, a higher relative contribution of the alkyl and aryl OPEs  
329 have been reported over urban areas or in remote areas under the suspected influence of  
330 local sources (Castro-Jiménez et al., 2016; Salamova et al., 2014a). The Cl-OPEs (as  
331 sum of TCEP, TCPP and TDCP) and the non-Cl-OPEs (as sum of TPP, TiBP, TnBP,  
332 TPhP, EHDPP and TEHP) globally (n=60) accounted for the 28% and the 72% (median  
333 values) of the  $\Sigma_9$ OPEs over Bizerte area, respectively (Table S8), generally pointing to  
334 the influence of current local OPE sources in the study area. This relative distribution is  
335 also consistent with the suspected non-Cl-OPEs sources, in particular TiBP, from the  
336 plastic industry located SE the sampling site. Generally non-Cl-OPEs are used as  
337 plasticizers, contrary to Cl-OPEs which are more commonly used as flame retardants  
338 (Wei et al., 2015). Interestingly, three samples (Prel\_22, 30, 72, Table S8) showed the  
339 opposite pattern with a clear predominance of Cl-OPEs, accounting from the 77% to  
340 88% of the  $\Sigma_9$ OPEs, in line with the most common reported situation in marine

341 environments (76% median value of predominance for Cl-OPEs) (Li et al., 2018).  
342 Indeed, the air mass back trajectories (BTs), calculated with the HYSPLIT model  
343 (Draxler and Rolph, 2011), revealed a clear Atlantic Ocean influence for those samples  
344 (Figure S4). All BTs are also available in SI (see discussion below)

345

346 Samples were grouped by seasons based on local climate of Bizerte city as follows:  
347 autumn (September, October, and November), winter (December, January), spring  
348 (March, April, and May) and summer (June, July and August). When comparing the  
349 OPE atmospheric pattern by seasons (Figure 2) with the annual pattern (Figure S3),  
350 some differences appeared. Whereas the relative distribution of Cl-OPEs appears to be  
351 pretty constant along the year, except for the winter months, when TDCP was not  
352 detected at all, some differences in the relative distribution of non-Cl-OPEs were  
353 observed. First, TiBP and TnBP showed a similar relative distribution in spring,  
354 whereas TiBP dominated over TnBP along the rest of the year, in particular in winter. In  
355 addition, EHDPP dominated the atmospheric pattern in all seasons except in winter,  
356 when TEHP exhibited higher relative concentrations. These findings point to a temporal  
357 variability on the OPE atmospheric pattern in the study area.

358



359

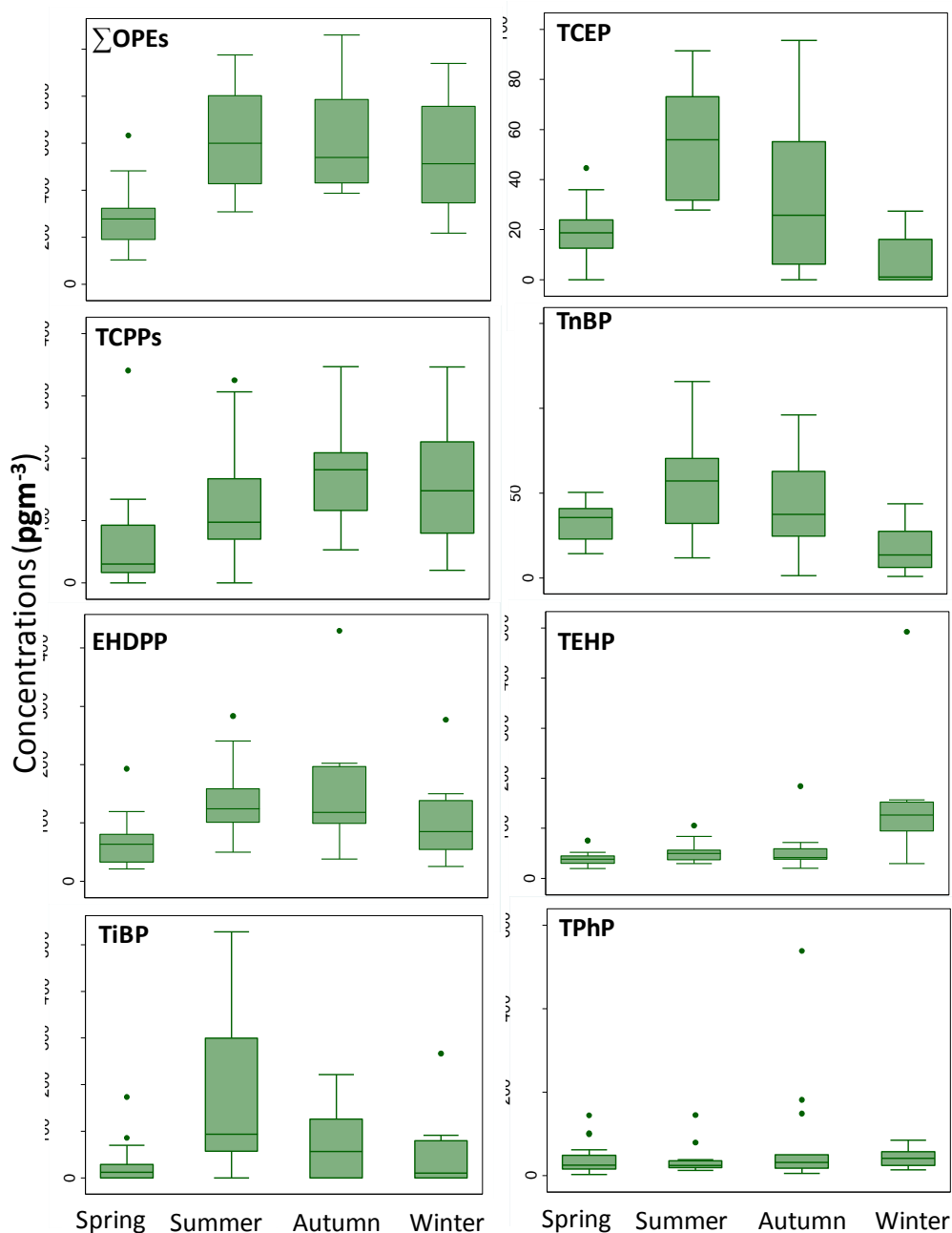
360 **Figure 2.** OPE atmospheric particle-bound pattern in Bizerte area in the different  
 361 seasons (2015-2016)

362

363 In order to further investigate the OPE seasonality in the area studied; the differences in  
 364 contaminant concentrations were evaluated as well (Figure 3). Non-parametric tests  
 365 (STATA/SE 12.1 statistical software) were used in order to investigate possible  
 366 significant differences among contaminants. For this data analysis, non-detected values  
 367 were imputed to the median value between zero and the LOD for each specific  
 368 contaminant. Results from the Kruskal-Wallis test for OPEs (TPP and TDCP were not  
 369 considered due to their low detection frequency) showed significant differences ( $p$   
 370  $\leq 0.003$ ) among seasons for the  $\Sigma$ OPEs and all individual OPEs, except TPhP (Table  
 371 S9). Contaminant concentrations (except for TPhP) were further compared by pairs of  
 372 regions (Wilcoxon rank-sum test). Each contaminant level was compared among 4  
 373 seasons resulting in a total of 6 pairs of comparisons. The False Discovery Rate (FDR)  
 374 correction (Benjamini and Hochberg, 1995; Benjamini and Yekutieli, 2001), with

375 Simes's method (Simes et al., 1986) was used to account for the effect of the multiple  
376 comparisons (Table S10).

377 Overall, the two seasons showing more significant differences were spring and summer  
378 (Table S10) with all OPEs and the  $\Sigma$ OPEs exhibiting significantly higher concentrations  
379 in summer compared to spring. Indeed, the sum of OPEs and most individual OPEs  
380 showed the lowest concentrations in spring (i.e. TCPPs, EHDPP, TiBP and TEHP) with  
381 median values from 2 to 4-fold significantly lower ( $p \leq 0.02$ ) than those measured in the  
382 other months of the year (Figure 3, Table S10). However, only three OPEs showed  
383 significant differences between the coldest (winter) and the warmest (summer) seasons,  
384 but with contrasting trends. TCEP and TnBP were the only OPEs showing significantly  
385 ( $p < 0.001$ ) higher levels (~4-fold) in summer compared to winter, whereas TEHP  
386 concentration was ~3-fold higher in winter. In addition, TEHP was the only compound  
387 exhibiting significantly ( $p \leq 0.01$ ) higher concentrations in winter (~3-fold) compared to  
388 the other three seasons, whereas TnBP showed the opposite trend, with significantly ( $p$   
389  $\leq 0.03$ ) lower levels in winter (~2-fold) compared to the other three seasons. These  
390 observations are consistent with their different relative distribution observed in the  
391 winter pattern (Figure 2).



392

393 **Figure 3.** Box plots of particle-bound atmospheric concentrations ( $\text{pg m}^{-3}$ ) of most  
 394 frequently found OPEs by season. Lines within the boxes represent the median  
 395 concentrations.

396 *3.1.3. Potential factors affecting seasonality*

397

398 OPE concentrations did not correlate with other parameters simultaneously measured in  
 399 the same samples, like TSP, TOC and TON, which ranged from 9.6 – 119.0, 1.0 – 24.5

400 and  $0.2 - 3.0 \mu\text{g m}^{-3}$ , respectively (Figure S5). The lack of correlation between some  
401 OPEs (like TCPP and EHDDP) and the atmospheric TSP and/or TOC levels over urban  
402 areas have been previously reported (Clark et al., 2017). However, the authors showed  
403 that certain OPE could correlate with other fractions of the atmospheric aerosols, the  
404 finest fractions like PM<sub>2.5</sub>. Indeed, other studies conducted in urban areas confirmed  
405 the OPE associations with PM<sub>2.5</sub> fraction (Faiz et al., 2018; Liu et al., 2016), with  
406 strong correlations reported for some OPEs, like TCEP, TnBP and TEHP (Faiz et al.,  
407 2018). The form OPEs are emitted to the atmosphere seems to be a key factor  
408 determining these associations, with higher probability of enrichment in the finest  
409 fractions for OPE directly emitted in the gas phase due to the larger surface area of fine  
410 particles compared to coarse particles (Faiz et al., 2018; Clark et al., 2017). However,  
411 these associations cannot be evaluated in the study area with available data.

412

413 TCEP, TnBP, EHDPP as well as  $\Sigma$ OPEs showed significant positive correlations with  
414 temperature ( $p \leq 0.002$ ), consistent with their higher levels found in summer (average  $T =$   
415  $26 \pm 2^\circ\text{C}$ ) compared to winter (average  $T = 12 \pm 2^\circ\text{C}$ ), in particular for TCEP and TnBP.  
416 Even if not all OPEs did show correlations with temperature, this could partially explain  
417 the lower levels generally found in spring (average  $T = 16 \pm 3^\circ\text{C}$ ) compared to summer.  
418 Temperature could play a local effect by increasing the OPE volatilization from land  
419 and water and also affecting their environmental partitioning. Interestingly, TCEP and  
420 TnBP show also a weak (but statistically significant,  $p \leq 0.001$ ) negative correlation with  
421 the relative humidity (RH). Significantly ( $p = 0.02$ ) higher RH values ( $70 \pm 7\%$ ) and  
422 slightly higher precipitation rates (9.0 mm) and wind speeds ( $17 \pm 7 \text{ km h}^{-1}$ ) were  
423 registered in spring compared to summer ( $66 \pm 5\%$ , 0.6 mm and  $15 \pm 6 \text{ km h}^{-1}$ ,

424 respectively) (Figure S5, Table S1) pointing to a most efficient atmospheric particle  
425 washout in spring, which is consistent with our observation too.

426 The BTs (Figure S6) did not really show a consistent influence on the OPE seasonality,  
427 except for punctual cases affecting the atmospheric pattern and/or concentrations (as  
428 indicated above). The BTs computed for the samples collected in spring generally had a  
429 longer air mass range with Atlantic Ocean influence, compared to those for summer,  
430 when air masses generally showed a shorter range and spent more time circulating over  
431 the W Mediterranean and continental Europe. In addition, some samples showed a clear  
432 SE influence of air mass trajectory in summer (e.g. Prel\_27, 28) leading to higher TiBP  
433 levels (Tables S7, S8) consistent too with our observation of higher levels in summer  
434 compared to spring and suspected influence of plastic industry located at the SE from  
435 the sampling site. The local wind regimes could have also an influence in the  
436 seasonality observed. Figure S7 shows the wind roses for all seasons. A general  
437 predominance of winds blowing in the sector WNW-NW was observed for all seasons  
438 except for winter, when a clear predominance for SE winds was registered. This could  
439 partially explain as well the different pattern observed in winter for non-Cl-OPEs, with  
440 higher TiBP and TEHP levels potentially coming from the plastic factory located SE  
441 from the sampling site, as discussed above. In summary, a number of factors, likely  
442 acting simultaneously, seem to be affecting the relative abundance and distribution  
443 pattern between the Cl- and non-Cl-OPEs and their atmospheric concentrations in the  
444 study area, like potential local sources and meteorological conditions, influence of air  
445 mass trajectories, the LRAT potential of some OPEs travelling from distant sources  
446 and/or the atmospheric degradation and depletion processes in the region.

447

### 448 **3.2. Atmospheric loading**

449

### 450 3.2.1. Dry deposition fluxes

451

452 Dry deposition fluxes ( $F_{DD}$ ,  $\text{ng m}^{-2} \text{d}^{-1}$ ) of target OPEs were calculated as:

453

$$454 \quad F_{DD} = 864 v_d C_A \quad [1]$$

455

456 where  $C_A$  ( $\text{ng m}^{-3}$ ) is the specific OPE volumetric concentration in the aerosol,  $v_d$  ( $\text{cm s}^{-1}$ )  
457 is the particle deposition velocity and 864 is a unit conversion factor. A reference  
458 value of  $0.2 \text{ cm s}^{-1}$  for  $v_d$  was adopted for this site. This value is within the range of  $v_d$   
459 experimentally measured (Del Vento and Dachs 2007) in coastal NW Mediterranean  
460 Sea and has recently been used in the same site for the estimation of dry deposition  
461 fluxes of other organic contaminants with similar physical-chemical properties as OPEs  
462 (Castro-Jiménez et al., 2017). Even if a degree of uncertainty is associated to this  
463 calculation due to the lack of  $v_d$  measurements during the sampling events, the selected  
464 value enables meaningful comparisons with other estimations in the study area and in  
465 the W Mediterranean Sea. Overall, the  $\Sigma_9\text{OPEs}$  atmospheric dry deposition fluxes  
466 ranged from 18 to  $180 \text{ ng m}^{-2} \text{d}^{-1}$  during the sampling period (Table S11). These fluxes  
467 were generally lower than previous dry deposition estimations performed in the W  
468 Mediterranean Sea and in the SW Black Sea (Castro-Jiménez et al., 2014) but within the  
469 range of those reported for the North Sea (Möller et al., 2011) and the Philippine Sea  
470 (Möller et al., 2012). However, the presented estimations of dry deposition are higher  
471 than those reported for other semi-enclosed environments like the China Sea (Lai et al.,  
472 2015) and also less impacted areas like the Coral Sea (Chen et al., 2013).



473 Table 2 presents the dry deposition fluxes for each OPE by season. The highest median  
474 atmospheric loading (and associated higher potential exposure) for the assemble of  
475 OPEs via atmospheric dry deposition in the study area is estimated to occur in the  
476 summer, autumn and winter months (as expected from their relative atmospheric  
477 concentrations and the assumptions considered in these calculations) with fluxes  
478 ranging from 32 to 38  $\mu\text{g m}^{-2} \text{y}^{-1}$  for these seasons. This loading is 1 to 3 orders of  
479 magnitude higher than the reported atmospheric dry deposition fluxes of PBDEs (the  
480 OPEs “predecessors”) (0.07-3.4  $\mu\text{g m}^{-2} \text{y}^{-1}$  for  $\Sigma_{27}\text{PBDEs}$ ), and even higher compared to  
481 the dry deposition fluxes estimated for other legacy POPs like PCDD/Fs, PCBs and  
482 organochlorine pesticides (OCPs) over Bizerte during the same observation period  
483 (Castro-Jiménez et al., 2017; Barhoumi et al., 2018). However, the atmospheric dry  
484 deposition fluxes of OPEs are in the lower end of those reported for  $\Sigma_{34}\text{PAHs}$  (30-1100  
485  $\mu\text{g m}^{-2} \text{y}^{-1}$ ) in Bizerte for the same period (Barhoumi et al., 2018).

486

### 487 3.2.2. *Environmental relevance and potential impacts*

488

489 According to these calculations, the nearby coastal lagoon of Bizerte ( $1.28 \times 10^8 \text{ m}^2$   
490 surface, Barhoumi et al., 2016), a well-recognized sensitive environment of ecological  
491 and socio-economic importance (the most important aquaculture area in Tunisia,  
492 annually producing around 100 tons of Pacific oysters and Mediterranean mussels,  
493 Béjaoui-Omri et al., 2014) could receive up to  $\sim 9 \text{ kg}$  of OPEs yearly. This loading of  
494 OPEs may have, yet unknown, implications for the aquatic organisms and the  
495 ecosystem functioning. The input of these hazardous compounds may elicit an effect  
496 through environmental exposure, as a single group of contaminants or in combination to  
497 other toxic organic chemicals also efficiently incorporated to this aquatic environment

498 *via* the atmosphere like PCDD/Fs, PCBs, PBDEs, OCPs and PAHs (Castro-Jiménez et  
499 al., 2017; Barhoumi et al., 2018). In addition, OPE may interfere the natural phosphorus  
500 cycle. Recent estimations performed in the Mediterranean Sea and other oceanic  
501 environments suggest that atmospheric deposition fluxes of phosphorus due to OPE  
502 deposition (and other anthropogenic organic pollutants containing phosphorus) could  
503 play an important role in the phosphorus cycle, in particular in oligotrophic  
504 environments, affecting the ecosystem structure and functioning, for example modifying  
505 primary production rates (Castro-Jiménez et al., 2014, 2016). The dry deposition fluxes  
506 of  $\Sigma_9$ OPEs given as P averaged  $\sim 10 \text{ ng}_P \text{ m}^{-2} \text{ d}^{-1}$  over Bizerte lagoon area. The maximum  
507 estimated loading of new anthropogenic phosphorus coming from OPEs was of  $\sim 1 \text{ kg y}^{-1}$   
508 <sup>1</sup>. This input is certainly small, representing only between the 0.02-0.5% of the organic  
509 phosphorus dry deposition fluxes recently estimated in the W Mediterranean Sea  
510 (Violaki et al., 2018). However, these fluxes accounted for both anthropogenic and non-  
511 anthropogenic organic compounds, and our estimates correspond exclusively to nine  
512 compounds belonging to an emerging widely diffused anthropogenic contaminant class  
513 contain phosphorous. Moreover, the reported organic phosphorous inputs for the  
514 Mediterranean (Violaki et al., 2018) correspond to the entire W Mediterranean basin,  
515 whereas the organic phosphorous amounts due to OPEs will distribute only on the  $\sim 130$   
516  $\text{km}^2$  of lagoon surface, a shallow and enclosed environment with limited water  
517 exchanges. In addition, recent studies confirmed that OPE can also exist in the  
518 atmospheric gas phase (Li et al., 2018; Sühring et al., 2016b, Castro-Jiménez et al.,  
519 2016) and the diffusive deposition fluxes (i.e. the direct input of gas phase OPE to the  
520 water dissolved phase) could be 2-3 orders of magnitude higher than the dry deposition,  
521 potentially triggering up to 1% of the reported primary production in the most  
522 oligotrophic oceanic regions (Castro-Jiménez et al., 2016). OPE could also enter Bizerte

523 lagoon by riverine inputs, a source of new anthropogenic phosphorus associated to OPE  
524 not yet evaluated. A global assessment performed with available data before the  
525 beginning of the large expansion of OPE production and usage (in 2009) estimated the  
526 human interference with the phosphorus cycle very close to a threshold of no return (i.e.  
527 irreversible disruptive effect) (Rockström et al., 2009). The not yet accounted new  
528 anthropogenic phosphorus coming from OPEs and other P-organic containing  
529 contaminants, even if small at a regional/global scale, may be contributing to reach the  
530 mentioned threshold and efforts should be devoted to study these links and the  
531 integrated impacts of OPEs in aquatic/marine ecosystems.

532

#### 533 **4. Conclusions**

534

535 Organophosphate ester flame retardants and plasticizers have been measured for the  
536 first time in the atmosphere of the NW African coastal Mediterranean Sea (Bizerte city  
537 area) confirming the general high detection frequency of most common OPEs. A  
538 general predominance of non-chlorinated OPEs has been found in the atmospheric  
539 aerosols, being different from what is commonly reported in marine environments (i.e.  
540 higher predominance of chlorinated OPEs) suggesting current local sources in the area.  
541 Some compounds could be regarded as useful tracers of local/regional specific  
542 activities/sources, like TiBP as tracer of the potential impact of plastic industries in  
543 Bizerte area. The lowest concentrations were generally found in spring, probably linked  
544 to local meteorological conditions and the LRAT of OPEs from other areas to a lesser  
545 extent. The atmospheric levels of some of the most abundant OPEs (like TCPP) in  
546 Bizerte area, a coastal urban city under important anthropogenic pressures, seem to be  
547 in the range and/or lower than those reported for remote coastal environments or

548 pristine oceanic regions. These findings suggest a combined effect of differential  
549 regional emission patterns, meteorological conditions and rates of atmospheric  
550 processing (with high solar irradiance, probably leading to a most efficient atmospheric  
551 OPE depletion processes in the area, likely compensating potential local sources). In  
552 addition, the influence of the existing regulatory frameworks in different areas of the  
553 globe may contribute to this situation. Although OPE atmospheric concentrations as  
554 sum of compounds could provide a first useful insight on their environmental levels, the  
555 environmental behaviour of OPEs should be better investigated for individual  
556 compounds. We found that not all OPEs presented the same seasonality in terms of  
557 atmospheric concentrations and pattern. The estimated dry deposition fluxes to Bizerte  
558 lagoon point to a yearly input of around ~ 9 kg of OPEs (~1 kg of new anthropogenic  
559 organic phosphorus) to this shallow and enclosed aquatic environment (~130 km<sup>2</sup>)  
560 considered as the most important aquaculture area in Tunisia, with yet unknown  
561 implications in terms of environmental exposure and impacts in the ecosystem  
562 functioning. Further research is needed to elucidate the magnitude and potential impacts  
563 of these new organic contaminants and associated sources of anthropogenic  
564 phosphorous in the study area.

565

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567

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581

582 **Supporting information available**

583

584 Additional data on the sampling and analytical procedures, QA/QC, compound-by-  
585 compound atmospheric levels and spatial distribution and deposition fluxes are  
586 presented in this section.

587

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858 **Table 1.** Updated compilation of atmospheric particle-bound OPE measurements in the marine environment and some reference urban areas  
 859 (concentrations are in  $\text{pg m}^{-3}$ , and median, standard deviation, minimum and maximum values are reported when available)  
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Region	Sampling	Date	Compounds, $\text{pg m}^{-3}$ , median [min-max]								Reference <sup>Ⓢ</sup>
			TCEP	TDCP	TCPPs	TIBP	TnBP	TPhP	EHDPP	TEHP	
<b>Northern Hemisphere</b>											
Arctic Ocean	cruise (open sea)	2007-2013	n.d. - 856	n.d. - 13	n.d. - 660	n.r.	n.d. - 97	n.d. - 1930	n.d. - 11	n.d. - 7.5	Sühring et al., 2016
Resolute Bay/Alert (Arctic)	remote (coastal)	2008-2009, 2012	n.d. - 430	n.d. - 46	n.d. - 276	n.r.	n.d. - 2340	1.2 - 96	n.d. - 40	n.r.	Sühring et al., 2016
Arctic Ocean	cruise (open sea)	Jun-September 2010	126 - 585	n.d. - 5	85 - 530	16 - 35	n.d. - 36	10 - 60	n.r.	n.d. - 6	Moller et al., 2012
Ny-Alesund (Arctic)	remote (coastal)	Jun-September 2007	<200 - 270	87 - 250	<200 - 330	<10 - 140	<200	<50	<200 - 260	n.r.	Green et al., 2008
Longyearbyen (Arctic)	remote (coastal)	September 2012-May 2013	40 - 60	2 - 294	10 - 186	n.r.	6 - 1000	1 - 50	6 - 300	1 - 40	Salamova et al., 2014
North Atlantic Ocean	cruise (open sea)	Dec 2010, Jun-Jul 2011	50 [n.d.-1230]	80 [n.d.-425]	770 [n.d.-1310]	40 [5-380]	90 [10-1700]	10 [n.d.-50]	780 [20-1730]	140 [60 - 490]	Castro-Jiménez et al., 2016
North Pacific Ocean	cruise (open sea)	Jun-September 2010	160 - 280	5 - 8	98 - 270	14 - 20	6 - 14	9 - 24	n.r.	1 - 12	Moller et al., 2012
North Pacific Ocean	cruise (open sea)	May-Jun 2011	80 [n.d.-310]	90 [n.d.-500]	640 [100-1460]	30 [3-100]	170 [20-2500]	10 [n.d.-34]	320 [100-1210]	110 [60-380]	Castro-Jiménez et al., 2016
Sea of Japan	cruise (open sea)	Jun-September 2010	237 - 1960	16 - 52	130 - 620	10 - 63	10 - 33	25 - 97	n.r.	5 - 38	Möller et al., 2012
East China Sea	cruise (open sea)	October 2009-March 2010	134	828	9	n.r.	n.r.	n.r.	n.r.	n.r.	Möller et al., 2012 & Chen et al., 2013
South China Sea	cruise (open sea)	September-October 2013	14 - 110	1 - 4	15 - 38	1 - 4	1 - 5	3 - 16	n.r.	2 - 16	Lai et al., 2015
North Sea	cruise (open sea)	March, May, July 2010	6 - 100	7 - 78	30 - 1200	n.d. - 150	n.d. - 150	4 - 150	n.r.	n.d. - 30	Möller et al., 2011
North Sea <sup>Ⓢ</sup>	coastal	August 2011-October 2012	3±2	1±0.8	10±6	9±6	6±11	3±3	n.r.	11±13	Wolschke et al., 2016
Mediterranean Sea	cruise (open sea)	Jun 2006, May 2007	220 <sup>Ⓢ</sup> [70 - 854]	75 <sup>Ⓢ</sup> [n.d. - 460]	884 <sup>Ⓢ</sup> [126 - 2340] <sup>Ⓢ</sup>	240 <sup>Ⓢ</sup> [4 - 650]	310 <sup>Ⓢ</sup> [56 - 600]	21 <sup>Ⓢ</sup> [n.d. - 80]	540 <sup>Ⓢ</sup> [n.d. - 834]	160 <sup>Ⓢ</sup> [56 - 307]	Castro-Jiménez et al., 2014
Black Sea	cruise (open sea)	Jun 2006, May 2007	490 [300 - 2420]	86 [n.d. - 97]	520 [540 - 2720] <sup>Ⓢ</sup>	150 [66 - 190]	310 [200 - 370]	35 [3 - 40]	180 [n.d. - 310]	175 [36 - 190]	Castro-Jiménez et al., 2014
Philippine Sea	cruise (open sea)	November 2010- March 2011	20 - 156	50 - 780	22 - 410	10 - 23	10 - 100	n.d. - 155	n.r.	6 - 92	Möller et al., 2012
Bonhai & Yellow Seas	cruise (open sea)	Jun-July 2016	28 [14-94]	5 [1-13]	66 [19-390] <sup>Ⓢ</sup>	12 [24-29]	5 [1-14]	3 [1-15]	n.r.	2 [n.d.-8.5]	Li et al., 2018
North Huangchen Island	remote (coastal)	May 2015-March 2016	63 [0.4-1000]	4 [n.d.-80]	26 [n.n-160] <sup>Ⓢ</sup>	24 [1-164]	8 [n.d-1100]	11 [n.d-110]	n.r.	1.5 [n.d-180]	Li et al., 2018
Huston <sup>Ⓢ</sup>	urban (inland)	September 2013	90±30 - 270±130	64±20 - 87±50	700±390 - 1200±440	n.r.	120±10 - 560±320	210±70 - 490±580	300±260 - 470±150	38±30 - 56±20	Clark et al., 2017
Great lakes <sup>Ⓢ</sup>	urban (coastal inland)	March 2012 - Dec 2014	270-334	47-100	370-390	n.r.	200-250	130-160	70-80	n.r.	Salamova et al., 2016
Great lakes <sup>Ⓢ</sup>	rural (coastal inland)	March 2012 - Dec 2014	274	15	58	n.r.	32	30	27	n.r.	Salamova et al., 2016
Great lakes <sup>Ⓢ</sup>	remote (coastal inland)	March 2012 - Dec 2014	41-46	7-11	15-36	n.r.	18-50	34-50	15	n.r.	Salamova et al., 2016
<b>Bizerte (Tunisia)</b>	<b>urban (coastal)</b>	<b>March 2015-Jan 2016</b>	<b>31 [2-96]</b>	<b>20 [7-27]</b>	<b>110 [5-347]<sup>Ⓢ</sup></b>	<b>85 [8-528]</b>	<b>36 [1-116]</b>	<b>27 [3-538]</b>	<b>100 [21-429]</b>	<b>45 [20-492]</b>	<b>This study</b>
<b>Southern Hemisphere</b>											
South Atlantic	cruise (open sea)	Jan-Feb 2011	150 [10-540]	130 [n.d.-540]	570 [20-980]	100 [30-280]	330 [120-1180]	10 [n.d.-25]	500 [n.d.-1020]	160 [50-890]	Castro-Jiménez et al., 2016
South Pacific	cruise (open sea)	Feb-April 2011	140 [34-370]	60 [n.d.-1000]	530 [50-800]	50 [15-160]	200 [50-2170]	4 [n.d.-40]	400 [260-800]	160 [40-350]	Castro-Jiménez et al., 2016
Coral Sea	cruise (open sea)	October 2009-March 2010	88	370	7	n.r.	n.r.	n.r.	n.r.	n.r.	Chen et al., 2013
Indian Ocean	cruise (open sea)	November 2010- March 2011	46 - 570	n.d. - 220	37 - 550	7 - 96	7 - 75	n.d. - 74	n.r.	4 - 50	Möller et al., 2012
Indian Ocean	cruise (open sea)	Feb-March 2011	100 [50-620]	20 [n.d.-290]	370 [30-1250]	40 [n.d.-110]	230 [70-940]	8 [n.d.-12]	370 [n.d-630]	180 [n.d-630]	Castro-Jiménez et al., 2016
Southern Ocean	cruise (open sea)	November 2010- March 2011	74	80	55	16	14	20	n.r.	7	Möller et al., 2012
Antarctic Peninsula	cruise (open sea)	October 2009-March 2010	40	76	4	n.r.	n.r.	n.r.	n.r.	n.r.	Chen et al., 2013

<sup>Ⓢ</sup> sum of three isomers; <sup>Ⓢ</sup> sum of two major isomers; <sup>Ⓢ</sup> average±SD; \* median values; <sup>Ⓢ</sup> median value correspond only to Western MED, whereas the range correspond to all basins; <sup>Ⓢ</sup> see reference section in the main manuscript for complete citation details, n.r.=not reported

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**Table 2.** OPE dry deposition fluxes ( $\text{ng m}^{-2} \text{d}^{-1}$ , median, average and range) in the different seasons (2015-2016) in Bizerte (Tunisia)

Compound	Spring [n=19]			Summer [n=20]			Autumn [n=13]			Winter [n=8]		
	Median	Average	Range	Median	Average	Range	Median	Average	Range	Median	Average	Range
TPP	0.7	0.6	(0.01 - 1.0)	0.3 <sup>b</sup>	0.3 <sup>b</sup>	/ <sup>b</sup>	n.c	n.c	n.c	1.4 <sup>b</sup>	1.4 <sup>b</sup>	/ <sup>b</sup>
TiBP	4.8	8.6	(1.7 - 30.0)	16.2	29.5	(1.4 - 91.2)	17.1	18.1	(5.8 - 38.3)	13.8	19.3	(3.6 - 46.1)
TnBP	6.1	5.6	(2.5 - 8.7)	9.9	9.8	(2.1 - 20.0)	6.5	7.5	(0.2 - 16.6)	2.8	3.4	(0.9 - 7.6)
TCEP	3.4	3.5	(0.6 - 7.7)	9.7	9.7	(4.8 - 15.8)	7.9	7.7	(1.1 - 16.5)	2.8	2.7	(0.4 - 4.7)
TCPPs <sup>a</sup>	7.3	12.6	(0.8 - 58.9)	18.2	24.2	(6.9 - 56.1)	31.4	31.7	(9.2 - 59.9)	25.5	27.5	(3.5 - 59.9)
TDCP	4.3 <sup>b</sup>	4.3 <sup>b</sup>	/ <sup>b</sup>	3.3	3.3	(1.8 - 4.6)	2.3	2.3	(1.1 - 3.4)	n.c	n.c	n.c
TPhP	4.3	7.1	(0.5 - 24.8)	4.2	5.7	(2.1 - 25.0)	5.4	15.1	(0.9 - 93.0)	7.1	7.4	(2.3 - 14.6)
EHDPP	11.0	11.9	(3.7 - 33.4)	21.4	23.3	(8.6 - 49.0)	20.4	25.4	(6.6 - 74.2)	14.7	18.5	(4.4 - 47.8)
TEHP	6.7	7.0	(3.4 - 13.1)	8.6	8.9	(5.1 - 18.2)	7.2	9.5	(3.5 - 31.8)	21.9	27.4	(5.1 - 85.0)
<b><math>\Sigma_9\text{OPEs}</math></b>	<b>48.0</b>	<b>49.5</b>	<b>(17.8 - 109.3)</b>	<b>103.7</b>	<b>107.5</b>	<b>(53.2 - 172.5)</b>	<b>93.3</b>	<b>108.0</b>	<b>(66.8 - 183.3)</b>	<b>89.2</b>	<b>95.0</b>	<b>(37.7 - 162.5)</b>

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<sup>a</sup> sum of the two major TCPP isomers; <sup>b</sup> only one detected value in the season (the values presented under median and mean correspond in this case to the only detected value), n.c = not calculated (aerosol concentrations  $\leq$  LOD)