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

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Abstract

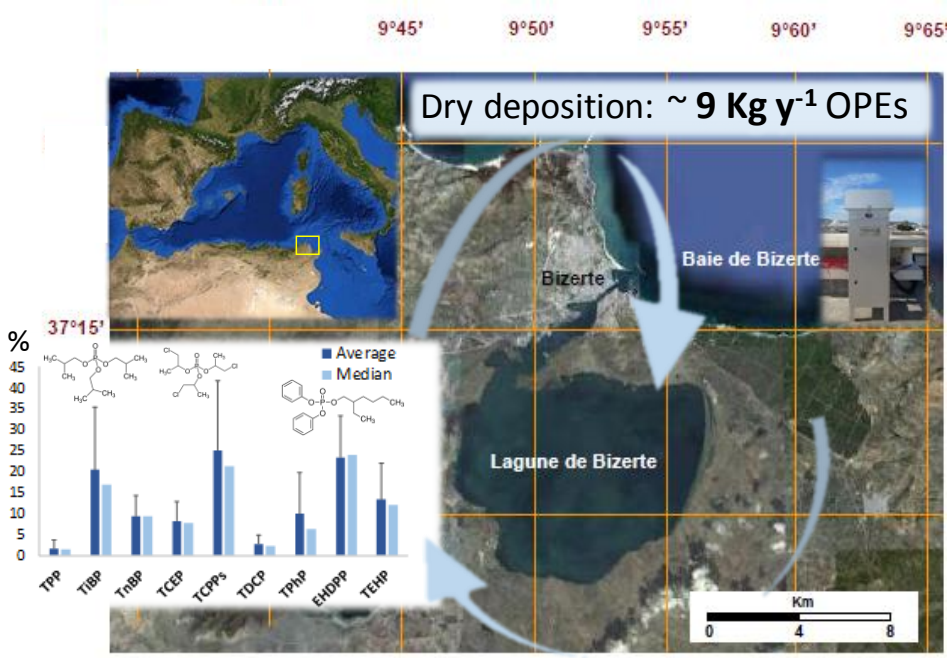
Organophosphate ester (OPE) flame retardants and plasticizers have been detected at generally high frequencies (70-98%) for the first time in the atmosphere over the NW African coastal Mediterranean. Results from sixty air samples (total suspended particles, TSP) collected between March 2015 and January 2016 in an urban coastal site (Bizerte, Tunisia) revealed $\sum_9$OPE concentrations of ~100-1060 pg m^{-3} (470 pg m^{-3}, median) with TCPPs, EHDPP and TiBP exhibiting the higher median concentrations (~ 110, 100 and 85 pg m^{-3}, respectively). Spring generally exhibited the lowest concentrations, probably linked to the influence of local meteorological conditions and air mass trajectories to a lesser extent. Non-chlorinated OPEs generally predominated, in contrast to the most common reported situation in marine environments (i.e. higher abundance of chlorinated OPEs) pointing to the relevance of local OPE sources in the study area. TiBP levels were generally higher than those reported for other marine/coastal environments suggesting this OPE as a good tracer of local sources in Bizerte. Contrarily, the atmospheric levels of other abundant OPEs in the area (e.g. TCPP) seem to be in the range and/or lower than those reported for remote marine environments. These findings point to the interplay of different factors with solar irradiance (potentially enhancing atmospheric photochemical oxidation reactions) and meteorological conditions in the study area likely compensating potential local sources of some OPEs. Not all OPEs presented the same seasonality in terms of atmospheric concentrations and pattern. The estimated atmospheric dry deposition fluxes (Σ_9OPEs) were 18-180 ng m^{-2} d^{-1}. Up to ~9 kg y^{-1} of OPEs (~1 kg y^{-1} of new organic anthropogenic phosphorus coming from OPEs) can be loaded to the shallow and enclosed Bizerte lagoon (~130 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.

Keywords:

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

Graphical Abstract



1. Introduction

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

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

occurrence and loadings of OPEs to marine/coastal environments in close relation to their potential impacts. A recent study performed in the Mediterranean Sea supports the hypothesis that atmospheric aerosols can elicit a number of toxic effects in marine organisms due to the presence of legacy POPs such polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and high molecular weight (HMW) polycyclic aromatic hydrocarbons (PAHs) (Mesquita et al., 2016). Other POPs with recognized toxicity too, such as PBDEs and the "emerging" OPEs, can add up to the "contaminant-aerosol cocktail" (De wit, 2002; Vonderheidea et al., 2008). OPEs have been reported in both the atmospheric particle and gaseous phases, but most of the studies focus on their particle phase occurrence. The atmospheric degradation processes (e.g. photodegradation and/or OH radical oxidation) will progress more slowly for particle-bound OPEs as they will be "sheltered", increasing therefore their long-range atmospheric transport (LRAT) potential (Liu et al., 2014). In addition, OPEs have been described to be enriched in both fine and coarse particles from the atmospheric aerosols in urban environments (Clark et al., 2017; Faiz et al., 2018).

The Mediterranean Sea is a semi-enclosed environment of high ecological and socio-economic relevance (The Mermex group, 2011). This ecosystem has been documented to be largely impacted by legacy POPs and other organic contaminants (Paluselli et al., 2018; The Mermex group 2011; Berrojalbiz et al., 2011, 2011b, 2014; Castro-Jiménez et al., 2008, 2010, 2012; Mandalakis et al., 2005) as well as by plastic fragments (Cózar et al., 2015; Schmidt et al., 2018), which may be potential sources of OPEs to the overlying atmosphere in accumulation zones (Cheng et al., 2013). However, few data exist on OPE baseline levels and environmental behaviour in the Mediterranean Sea. Only one study reported surface water and sediment OPE concentrations from rivers draining into the W Mediterranean (Cristale et al., 2013), and the wide-spread OPE

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

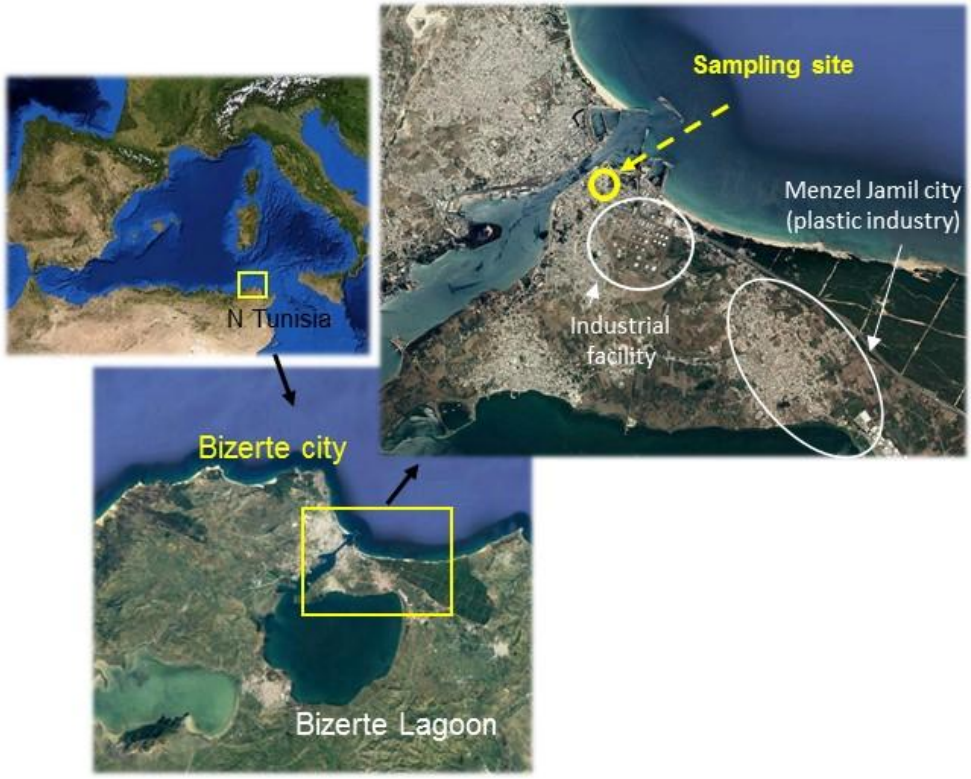
The objectives of this work are: 1) to investigate for the first time the atmospheric occurrence of OPEs in the NW African Mediterranean coast; 2) to estimate their atmospheric dry deposition and loading in Bizerte area (Tunisia) and discuss their potential impacts.

2. Materials and Methods

2.1. Area description

A detailed area description is offered elsewhere (Barhoumi et al., 2018). Briefly, Bizerte is a medium-size city (~127 000 inhabitants), located in the north of Tunisia, between the Mediterranean Sea and the Bizerte lagoon (Figure 1). Average temperature of 22 °C, with hot summer and mild spring, frequent (200 days per year) NW winds (average speed of 6–8 m s^{-1}) and precipitation episodes mostly in autumn and winter months, characterized the climate of Bizerte area. Even if agriculture and fishery activities are important in the area, a considerable number of light and heavy industries (i.e., cement, plastic, textile, mechanic and electronic, iron and steel metallurgy, petroleum refining and lubricants) are present (Barhoumi et al., 2018) inducing a considerable anthropogenic pressure. A certain number of studies focusing on the atmospheric 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±40 m^3, 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 flanks 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 isooctane and further concentrated
168 under gentle nitrogen stream up to ~0.1 mL. Prior to injection, 200 ng of deuterated

standards (Tri-n-propyl-d_{21}-phosphate, Tris(2-chloroethyl)-d_{12}-phosphate and Malathion-d_7) were added to the extracts to be used as internal standards for quantification.

2.4. Instrumental Analysis

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

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

2.5. Quality assurance / quality control (QA/QC)

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

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

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

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

3. Results and discussion

3.1. Atmospheric occurrence

3.1.1. Detection frequency and concentrations

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

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

measurements in coastal areas have been performed so far. The vast majority of available data in marine environments come from cruise measurements. The measured values in Bizerte are generally lower than those reported across the Mediterranean Sea ($\sum_{14}$OPE: 400-5000 pg m^{-3}) and the SW Black Sea ($\sum_{14}$OPE: 1700-6000 pg m^{-3}) (Castro-Jiménez et al., 2014), the E China Sea ($\sum_{8}$OPE 230-2900 pg m^{-3}) (Möller et al., 2012) and tropical and subtropical areas from the Atlantic, Pacific and Indian Oceans ($\sum_{14}$OPE: 360-4400 pg m^{-3} (Castro-Jiménez et al., 2016), but in the range of those from the North Sea ($\sum_{8}$OPE: 100-1400 pg m^{-3}) (Möller et al., 2012) and Svalbard coastal area ($\sum_{8}$OPE: 30-1450 pg m^{-3}) (Salamova et al., 2014a). However, OPE levels in Bizerte were higher than those reported for other semi-enclosed marine environments like the S China Sea ($\sum_{9}$OPE: 50-160 pg m^{-3}) (Lai et al., 2015) and also less impacted areas like the Coral Sea ($\sum_{4}$OPE: 90 pg m^{-3}) (Chen et al., 2013). These comparisons should be taken with caution though, due to the consideration of different number (and type, in some cases) of compounds included in the sums and the different seasons and years of the studies. Although it may still high variable, a more meaningful comparison would be considering individual compounds. The atmospheric levels of the predominant OPEs in Bizerte (i.e. TCPPs, EHDPP and TiBP) were individually compared with existing studies. Table 1 provides an updated compilation of atmospheric particle-bound OPE measurements in marine/coastal environments and some reference inland urban locations for comparison. Interestingly, some different trends were found compared to those of $\sum_{9}$OPEs; with TCPPs concentrations in Bizerte higher than in the E China Sea and Svalbard, but lower than those in the North Sea. TiBP levels in Bizerte appear to be generally higher than in other marine/coastal environments studied. This compound is used in a wide variety of industrial applications including building, papers, boards, plastics, rubbers, textile and directly as an additive in various products such as lacquers,

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

Despite the variability that the mentioned factors may have induced, it is not completely clear why the atmospheric levels measured in Bizerte (a coastal urban city under important anthropogenic pressures) for some of the most abundant OPEs like TCPP (among others, see Table 1), are in the range and/or lower than those reported for remote coastal environments or pristine oceanic regions. Most probably a combination of differential regional emission patterns, meteorological conditions and rates of atmospheric processing can explain these data. For example, the important global solar irradiance in the Mediterranean basin (The Mermex group, 2011, Sempéré et a., 2015), reaching annual average values of ~210 W m^{-2} in Bizerte city (Chelbi et al., 2015, Ben Othman et al., 2018) could enhance atmospheric degradation due to photochemical oxidation reactions. Even if these processes likely progress faster for gas-phase compounds, the atmospheric photochemical oxidation of particle-bound OPEs has also been described (Liu et al., 2014). These conditions would favour the decrease of OPE atmospheric levels, even if land-based sources could be higher than in other environments (like the Arctic, with less solar irradiation rates and colder temperatures). In addition, the huge expansion of OPE production and usage experienced in EU and 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 patter (n=60) over Bizerte, accounting
325 for the 25±16 %, 23±10 %, and 20±15% of the $\sum_9$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 at 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 $\sum_9$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 $\sum_9$OPEs, in line with the most common reported situation in marine

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

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

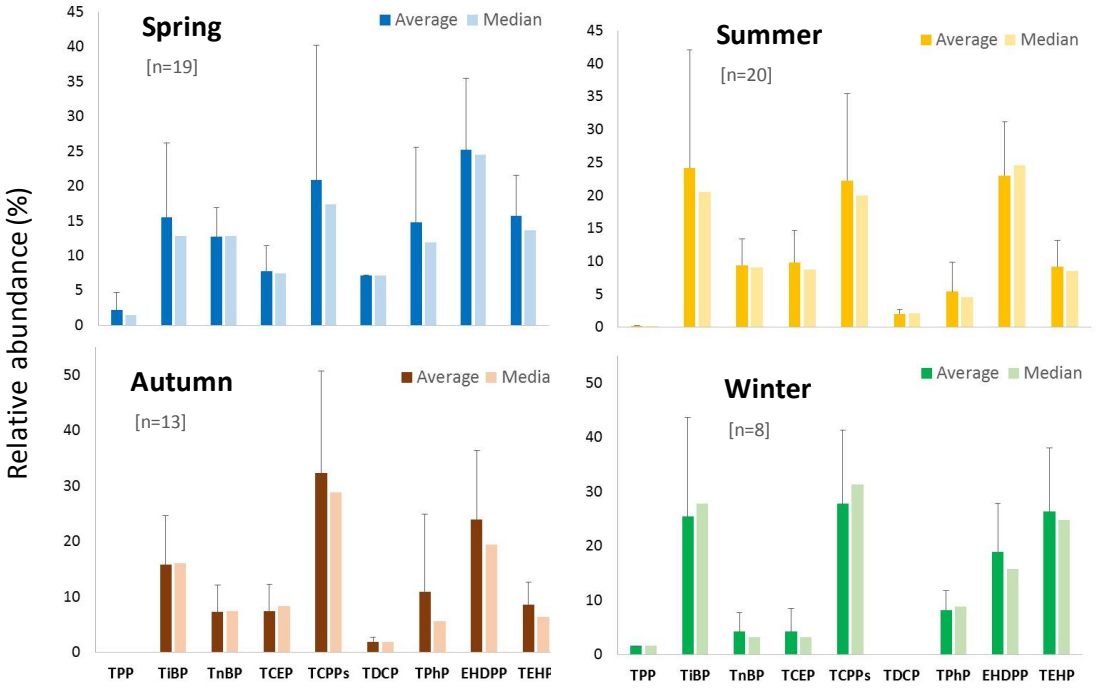


Figure 2. OPE atmospheric particle-bound pattern in Bizerte area in the different seasons (2015-2016)

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

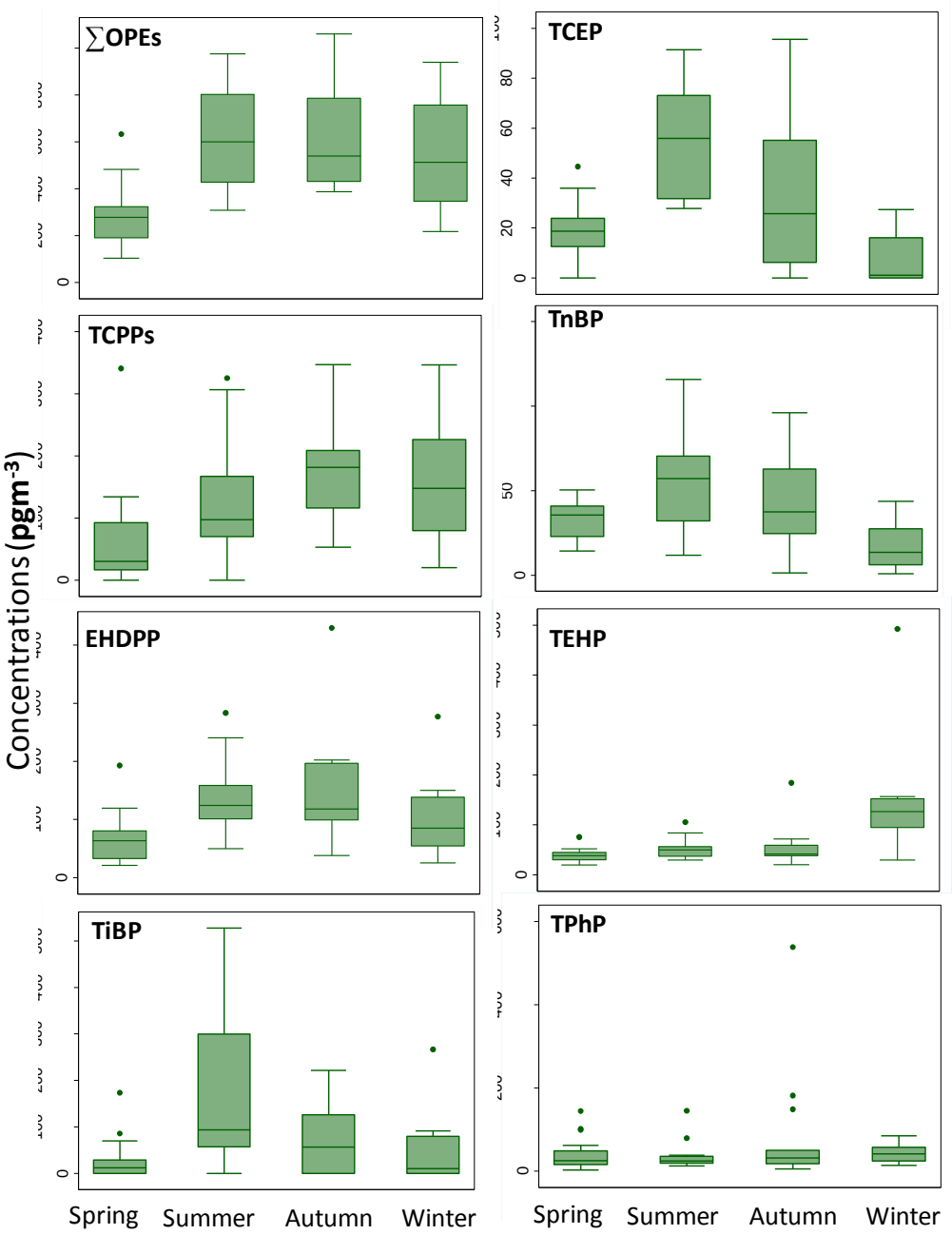


Figure 3. Box plots of particle-bound atmospheric concentrations (pg m^{-3}) of most frequently found OPEs by season. Lines within the boxes represent the median concentrations.

3.1.3. Potential factors affecting seasonality

OPE concentrations did not correlate with other parameters simultaneously measured in 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 μg 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 PM2.5. Indeed, other studies conducted in urban areas confirmed
405 the OPE associations with PM2.5 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 ΣOPEs showed significant positive correlations with
414 temperature ($p \leq 0.002$), consistent with their higher levels found in summer (average T=
415 26±2°C) compared to winter (average T=12±2°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±3°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±7%) and
422 slightly higher precipitation rates (9.0 mm) and wind speeds (17±7 km h^{-1}) were
423 registered in spring compared to summer (66±5%, 0.6 mm and 15±6 km h^{-1},

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

The BTs (Figure S6) did not really show a consistent influence on the OPE seasonality, except for punctual cases affecting the atmospheric pattern and/or concentrations (as indicated above). The BTs computed for the samples collected in spring generally had a longer air mass range with Atlantic Ocean influence, compared to those for summer, when air masses generally showed a shorter range and spent more time circulating over the W Mediterranean and continental Europe. In addition, some samples showed a clear SE influence of air mass trajectory in summer (e.g. Prel_27, 28) leading to higher TiBP levels (Tables S7, S8) consistent too with our observation of higher levels in summer compared to spring and suspected influence of plastic industry located at the SE from the sampling site. The local wind regimes could have also an influence in the seasonality observed. Figure S7 shows the wind roses for all seasons. A general predominance of winds blowing in the sector WNW-NW was observed for all seasons except for winter, when a clear predominance for SE winds was registered. This could partially explain as well the different pattern observed in winter for non-Cl-OPEs, with higher TiBP and TEHP levels potentially coming from the plastic factory located SE from the sampling site, as discussed above. In summary, a number of factors, likely acting simultaneously, seem to be affecting the relative abundance and distribution pattern between the Cl- and non-Cl-OPEs and their atmospheric concentrations in the study area, like potential local sources and meteorological conditions, influence of air mass trajectories, the LRAT potential of some OPEs travelling from distant sources and/or the atmospheric degradation and depletion processes in the region.

3.2. Atmospheric loading

449

450 *3.2.1. Dry deposition fluxes*

451

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

453

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

455

456 where C_A (ng m^{-3}) is the specific OPE volumetric concentration in the aerosol, v_d (cm s^{-1}) is the particle deposition velocity and 864 is a unit conversion factor. A reference value of 0.2 cm s^{-1} for v_d was adopted for this site. This value is within the range of v_d experimentally measured (Del Vento and Dachs 2007) in coastal NW Mediterranean Sea and has recently been used in the same site for the estimation of dry deposition fluxes of other organic contaminants with similar physical-chemical properties as OPEs (Castro-Jiménez et al., 2017). Even if a degree of uncertainty is associated to this calculation due to the lack of v_d measurements during the sampling events, the selected value enables meaningful comparisons with other estimations in the study area and in the W Mediterranean Sea. Overall, the Σ_9OPEs atmospheric dry deposition fluxes ranged from 18 to 180 ng m^{-2} d^{-1} during the sampling period (Table S11). These fluxes were generally lower than previous dry deposition estimations performed in the W Mediterranean Sea and in the SW Black Sea (Castro-Jiménez et al., 2014) but within the range of those reported for the North Sea (Möller et al., 2011) and the Philippine Sea (Möller et al., 2012). However, the presented estimations of dry deposition are higher than those reported for other semi-enclosed environments like the China Sea (Lai et al., 2015) and also less impacted areas like the Coral Sea (Chen et al., 2013).

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

3.2.2. Environmental relevance and potential impacts

According to these calculations, the nearby coastal lagoon of Bizerte (1.28 $x10^8$ m^2 surface, Barhoumi et al., 2016), a well-recognized sensitive environment of ecological and socio-economic importance (the most important aquaculture area in Tunisia, annually producing around 100 tons of Pacific oysters and Mediterranean mussels, Béjaoui-Omri et al., 2014) could receive up to ~ 9 kg of OPEs yearly. This loading of OPEs may have, yet unknown, implications for the aquatic organisms and the ecosystem functioning. The input of these hazardous compounds may elicit an effect through environmental exposure, as a single group of contaminants or in combination to other toxic organic chemicals also efficiently incorporated to this aquatic environment

via the atmosphere like PCDD/Fs, PCBs, PBDEs, OCPs and PAHs (Castro-Jiménez et al., 2017; Barhoumi et al., 2018). In addition, OPE may interfere the natural phosphorus cycle. Recent estimations performed in the Mediterranean Sea and other oceanic environments suggest that atmospheric deposition fluxes of phosphorus due to OPE deposition (and other anthropogenic organic pollutants containing phosphorus) could play an important role in the phosphorus cycle, in particular in oligotrophic environments, affecting the ecosystem structure and functioning, for example modifying primary production rates (Castro-Jiménez et al., 2014, 2016). The dry deposition fluxes of Σ_9OPEs given as P averaged ~10 $ng_P\ m^{-2}\ d^{-1}$ over Bizerte lagoon area. The maximum estimated loading of new anthropogenic phosphorus coming from OPEs was of ~1 $kg\ y^{-1}$. This input is certainly small, representing only between the 0.02-0.5% of the organic phosphorus dry deposition fluxes recently estimated in the W Mediterranean Sea (Violaki et al., 2018). However, these fluxes accounted for both anthropogenic and non-anthropogenic organic compounds, and our estimates correspond exclusively to nine compounds belonging to an emerging widely diffused anthropogenic contaminant class contain phosphorous. Moreover, the reported organic phosphorous inputs for the Mediterranean (Violaki et al., 2018) correspond to the entire W Mediterranean basin, whereas the organic phosphorous amounts due to OPEs will distribute only on the ~ 130 km^2 of lagoon surface, a shallow and enclosed environment with limited water exchanges. In addition, recent studies confirmed that OPE can also exist in the atmospheric gas phase (Li et al., 2018; Sühring et al., 2016b, Castro-Jiménez et al., 2016) and the diffusive deposition fluxes (i.e. the direct input of gas phase OPE to the water dissolved phase) could be 2-3 orders of magnitude higher that the dry deposition, potentially triggering up to 1% of the reported primary production in the most oligotrophic oceanic regions (Castro-Jiménez et al., 2016). OPE could also enter Bizerte

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

4. Conclusions

Organophosphate ester flame retardants and plasticizers have been measured for the first time in the atmosphere of the NW African coastal Mediterranean Sea (Bizerte city area) confirming the general high detection frequency of most common OPEs. A general predominance of non-chlorinated OPEs has been found in the atmospheric aerosols, being different from what is commonly reported in marine environments (i.e. higher predominance of chlorinated OPEs) suggesting current local sources in the area. Some compounds could be regarded as useful tracers of local/regional specific activities/sources, like TiBP as tracer of the potential impact of plastic industries in Bizerte area. The lowest concentrations were generally found in spring, probably linked to local meteorological conditions and the LRAT of OPEs from other areas to a lesser extent. The atmospheric levels of some of the most abundant OPEs (like TCPP) in Bizerte area, a coastal urban city under important anthropogenic pressures, seem to be 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^2)
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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Supporting information available

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

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Table 1. Updated compilation of atmospheric particle-bound OPE measurements in the marine environment and some reference urban areas (concentrations are in pg m^{-3}, and median, standard deviation, minimun and maximum values are reported when available)

Region	Sampling	Date	Compounds, *pg m^{-3}*, median [mix-max]								
			TCEP	**TDCP**	**TCPPs**	**TiBP**	**TnBP**	**TPhP**	**EHDPP**	**TEHP**	**Reference[&]**
Northern Hemisphere											
Artic 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
Artic 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[c]	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[#] [70 - 854]	75[#] [n.d. - 460]	884[#] [126 - 2340][a]	240[#] [4 - 650]	310[#] [56 - 600]	21[#] [n.d. - 80]	540[#] [n.d. - 834]	160[#] [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][a]	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][a]	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][a]	24 [1-164]	8 [n.d-1100]	11 [n.d-110]	n.r.	1.5 [n.d-180]	Li et al., 2018
Huston[c]	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[*]	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[*]	rural (coastal inland)	March 2012 - Dec 2014	274	15	58	n.r.	32	30	27	n.r.	Salamova et al., 2016
Great lakes [*]	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
Bizerte (Tunisia)	**urban (coastal)**	**March 2015-Jan 2016**	**31 [2-96]**	**20 [7-27]**	**110 [5-347][b]**	**85 [8-528]**	**36 [1-116]**	**27 [3-538]**	**100 [21-429]**	**45 [20-492]**	**This study**
Southern Hemisphere											
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
Antartic 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

[a] sum of three isomers; [b] sum of two major isomers; [c] average±SD; * median values; [#] median value correspond only to Western MED, whereas the rangee correspond to all basins; [&] see reference secion in the main manuscript for complete citation details, n.r =not reported

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

	Spring [n=19]			Summer [n=20]			Autumn [n=13]			Winter [n=8]		
Compound	Median	Average	Range	Median	Average	Range	Median	Average	Range	Median	Average	Range
TPP	0.7	0.6	(0.01 - 1.0)	0.3[b]	0.3[b]	/ [b]	n.c	n.c	n.c	1.4[b]	1.4[b]	/ [b]
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[a]	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[b]	4.3[b]	/ [b]	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)
Σ_9OPEs	48.0	49.5	**(17.8 - 109.3)**	103.7	107.5	**(53.2 - 172.5)**	93.3	108.0	**(66.8 - 183.3)**	89.2	95.0	**(37.7 - 162.5**

[a] sum of the two major TCPP isomers; [b] 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 calcualted (aerosol cocentrations ≤LOD)