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ORGANOPHOSPHATE ESTER FLAME RETARDANTS AND PLASTICIZERS IN THE GLOBAL OCEANIC ATMOSPHERE

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Abstract

Organophosphate esters (OPEs) are widely used as flame retardants and plasticizers and have been detected ubiquitously in the remote atmosphere. Fourteen OPEs were analysed in one hundred fifteen aerosol phase samples collected from the tropical and subtropical Atlantic, Pacific and Indian oceans during the MALASPINA circumnavigation campaign. OPEs were detected in all samples with concentrations ranging from 360 to 4400 pg m⁻³ for the sum of compounds. No clear concentration trends were found between the Northern and Southern hemispheres. The pattern was generally dominated by Tris-(1-chloro-2-propyl)phosphate (TCPP), although Tri-n-butyl phosphate (TnBP) had a predominant role in samples close to continents and in those influenced by air masses originating in continents. The dry deposition fluxes of

aerosol phase $\sum_{14}\text{OPE}$ ranged from 4 to 140 $\text{ng m}^{-2} \text{d}^{-1}$. An estimation of the OPE gas phase concentration and gross absorption fluxes by using three different sets of physical chemical properties suggested that the atmosphere-ocean diffusive exchange of OPEs could be two-three orders of magnitude larger than dry deposition. The associated organic phosphorus inputs coming from diffusive OPEs fluxes were estimated to potentially trigger up to 1.0 % of the reported primary production in the most oligotrophic oceanic regions. However, the uncertainty associated to these calculations is high and mostly driven by the uncertainty of the physical chemical properties of OPEs. Further constraints of the physical chemical properties and fluxes of OPEs are urgently needed, in order to estimate their environmental fate and relevance as a diffusive source of new organic phosphorus to the ocean.

Keywords: Marine pollution, aerosols, dry deposition, emerging contaminants, OPEs

TOC art

43 **Introduction**

44

45 Organophosphorus flame retardants (PFRs) have been used as substitutes of
46 polybrominated diphenyl ethers (PBDEs) after their almost-complete ban by the
47 Stockholm convention on persistent organic pollutants (POPs) in 2009.¹ The shifting of
48 the flame retardants market from PBDEs to PFRs has led to a rapid increase of the
49 world-wide consumption of these chemicals. Organophosphate esters (OPEs) are a
50 group of PFRs also used as plasticizers, and includes halogenated and non-halogenated
51 compounds.² The annual global consumption of PFRs, including OPEs, reached ~ 300
52 000 tonnes in 2011³ and a 5% annual increase (average annual growth rate) is expected
53 according to a recent market study.⁴

54 OPEs were thought to be degradable enough as to exhibit low persistency in the
55 environment and low Long Range Atmospheric Transport (LRAT) potential. Estimates
56 of half-life times in the environment are particularly short for the atmospheric gas
57 phase.⁵ In addition, OPEs were thought to elicit negligible hazardous effects in the
58 environment as compared to PBDEs. However, last scientific evidences contradict these
59 initial assumptions in an increasing number of cases. The fact that OPEs have been
60 found in indoor and outdoor environments (in biotic and non-biotic compartments) in
61 rural, urban and industrial areas,⁶ but also in remote regions,⁷⁻⁹ proves their multi-media
62 global occurrence and high potential for LRAT, consistent with the latest reports
63 highlighting the longer atmospheric half-lives for particle-bound OPEs.¹⁰ Evidence of
64 their environmental persistency, bioaccumulation and adverse effects in aquatic
65 organisms and humans have also been reported.^{2,6,11-14} These observations have raised
66 awareness on their environmental fate and impacts as it already happened in the past for
67 other POPs.

68

69 The open ocean constitutes an extensive and sensitive remote area of our planet
70 providing early warning on global chemical pollution. OPEs enter the oceanic
71 environment by atmospheric deposition like other semi-volatile organic contaminants
72 (SVOCs),¹⁵⁻¹⁹ even though oceanic transport may also be important for some OPEs.²⁰
73 Current investigations focusing on the atmospheric occurrence and loading of OPEs in
74 these large remote oceanic regions have been undertaken by dedicated oceanographic
75 campaigns usually covering only one or few of the sub-regions of the ocean/sea of
76 interest, probably due to logistic and opportunistic limitations. The majority of the
77 measurements have been performed in a number of marine regions from the Northern
78 hemisphere (NH): i.e. Arctic Ocean,^{8,9,21} North Pacific Ocean,²¹ Sea of Japan,²¹ China
79 Sea,^{22,23} North Sea,²⁴ Mediterranean and Black Seas²⁵ and the Philippine Sea.²¹ A limited
80 number of studies have been conducted in the Southern hemisphere (SH): i.e. Coral
81 Sea,²² Indian Ocean²¹ and Southern Ocean.^{21,22} In addition to the interest in quantifying
82 the oceanic sink of OPEs and their ecotoxicological impact, OPEs are also a source of
83 organic phosphorus for the most oligotrophic marine environments,²⁵ not yet quantified
84 globally.

85 We report here results from a unique set of atmospheric samples collected during a 7-
86 month circumnavigation campaign (MALASPINA 2010), covering the tropical and
87 subtropical areas of the North and South Atlantic and Pacific Oceans, and the Indian
88 Ocean. The main objectives of this study were: (1) to provide the first global assessment
89 of the occurrence of OPEs in the tropical and subtropical oceanic atmosphere, and (2) to
90 estimate their depositional fluxes to oceanic waters, and its associated organic
91 phosphorus input to the oceans.

92

93 **Materials and Methods**

94 *Study region and sampling*

95

96 A total of 115 atmospheric samples were collected from December 2010 to July 2011 in
97 seven consecutive transects (L1-L7, Figure S1) during the MALASPINA
98 circumnavigation campaign on board of the RV Hespérides, encompassing all the
99 tropical and temperate oceans between 35°N and 40°S. High volume air samplers
100 (MCV, Barcelona, Spain), installed on the upper deck of the ship (above the bridge),
101 were used to gather the atmospheric particle phase as explained elsewhere^{17, 19} (Text
102 S1). Briefly, the air was drawn through pre-combusted quartz fiber filters (QFFs) to
103 collect aerosol-bound compounds (total suspended particles, TSP). The samplers were
104 automatically stopped when wind was coming from the rear of the boat to avoid
105 potential sample contamination from the ship emissions. The average sampling volume
106 was of $\sim 850 \text{ m}^3$ (details for all sampling events are reported in Table S1). Most of
107 existing studies performed in marine environments report that OPEs are mainly found in
108 the aerosol phase,²¹⁻²⁵ so we focussed on the aerosol samples as the analytical method
109 had been optimized for the aerosol phase. Very recent measurements proved that most
110 common OPEs can also exist in the atmospheric gas phase in a coastal site,²⁶ and
111 modelling estimations seem to confirm their atmospheric gas-particle partitioning.²⁷
112 We processed 10 of the polyurethane foams used to sample the gas phase compounds,
113 which were collected and analysed as explained elsewhere.¹⁹ Few of the targeted OPEs
114 could be detected and not for all samples with a high variability in surrogate recoveries
115 (results not shown). Most probably, this was due to the fact that the sampling, extraction
116 and fractionation methods had not been specifically optimized for OPEs in PUF
117 samples, and thus gas phase analysis was not further pursued. Below we discuss OPE

118 gas phase concentrations calculated by gas-particle partitioning using reported estimates
119 of the octanol-air partition coefficient (K_{OA}).

120

121 *Analysis*

122

123 Briefly, QFFs were spiked with Tri-n-butyl-d27 phosphate and Triphenyl-d15
124 phosphate labelled standards and were Soxhlet extracted (24h). The extracts were rota-
125 evaporated and fractionated on alumina columns as reported elsewhere.^{17,25} (details in
126 Text S2). OPEs were eluted in the second and third fraction with
127 hexane/dichloromethane and dichloromethane/methanol mixtures, respectively. Extracts
128 were then concentrated to 50 – 150 μ L under a gentle nitrogen flow. Prior to injection,
129 labelled standards (Tri-n-propyl-d21 phosphate, and malathion-d7) were added to the
130 extracts to be used as internal standards for quantification. OPE analysis was conducted
131 by gas chromatography (Agilent 6890 Series GC) coupled with a mass spectrometer
132 (Agilent 5973 MS) (GC-MS) operating in selected ion monitoring (SIM) and electron
133 impact (EI, 70eV) mode and compounds were quantified by the internal standard
134 procedure (Table S2 shows selected ions for detection and quantification for each
135 compound). The injector temperature was set at 280 °C and the splitless mode was used.
136 The separation was achieved in a 30m x 0.25mm i.d. x 0.25 μ m HP-5MS capillary
137 column (Agilent J&W). The oven temperature was programmed from 90°C (holding
138 time 1min) to 170°C at 8°C/min, to 250°C at 4°C/min, then to 300°C at 10°C/min
139 (holding time 9min). The injection volume was of 2 μ l and the helium carrier gas flow
140 was 1 ml min⁻¹. The temperatures of the MS transfer line and the ion source were set at
141 280 °C and 230 °C, respectively.

142 Samples were analysed for the following OPEs: Tris-(2-chloroethyl)phosphate (TCEP),
143 Tris[2-chloro-1-(chloromethyl)ethyl]phosphate (TDCP), Tris- (1-chloro-2-
144 propyl)phosphate (TCPPs, mix of isomers), Tri-iso-butyl phosphate (TiBP), Tri-n-butyl
145 phosphate (TnBP), Triphenyl phosphate (TPhP), 2-Ethylhexyl diphenyl phosphate
146 (EHDPP), Tri(2-ethylhexyl) phosphate (TEHP) and Tricresyl phosphate (TCrP, mix of
147 isomers).

148

149 *Quality assurance /Quality control (QA/QC)*

150

151 The QA/QC procedures are detailed in Text S3. Summarizing, field and laboratory
152 (procedural for sampling and analysis) blanks were collected and analysed concurrently
153 with the samples. Blank values are reported in Table S3. Mean blank levels in the
154 aerosol phase were in general very low ranging from 0 to 8% of sample values,
155 depending on the sample and the compound, except for TPhP which reached a
156 maximum of ~ 30% of the sample amount. However, this higher percentage is due to
157 the fact that TPhP exhibited the lowest ambient levels, since the absolute blank (amount
158 of chemical) was in the same range as other OPEs. Results were blank corrected by
159 subtracting individual OPE total blank average levels (n=20) from the corresponding
160 sample levels. Procedural blanks showed lower or similar levels to field blanks so no
161 contamination of samples during sampling and storage occurred.

162 Standards (natives + labelled compounds) were introduced in the chromatographic
163 sequence to evaluate possible variations on the detection conditions during the time of
164 analyses. Chromatographic peaks of target compounds were only considered when their
165 abundance was at least 3 times higher than the instrumental noise. Instrumental limits of

166 detection (LODs) (calculated as signal-to-noise ratio > 3) ranged from 0.06 to 0.6 pg m⁻³
167 depending on the compound (Table S4). The method recovery (extraction-clean up-
168 analysis) varied from 41 to 85 % (median values, Figure S2). Results were not corrected
169 by recoveries. A clear chromatographic peak identification and quantification was
170 feasible in all aerosol samples.

171 NIST SRM 2585 was analysed for target OPEs. This reference material is not certified
172 for OPEs, however nine different laboratories have provided concentration of OPEs in
173 this dust reference material, becoming a recommended quality control step.²⁸ The
174 average results for five replicates (blank corrected) proved that the analysis of OPE
175 using the described methodologies provided concentrations in good agreement with
176 reported values for most OPEs (Figure S3). Deviations were found for EHDPP and
177 TCrPs, only.

178

179 *Data statistical analysis*

180

181 Since the data set was not normally distributed, non-parametric tests (Kruskal-Wallis
182 and Wilcoxon rank-sum) were used in order to investigate significant differences
183 among pollutant's levels. The effect of multiple comparisons was taken into account by
184 applying the False Discovery Rate method. The software employed was STATA/SE
185 12.1. Details are presented in Text S4, Table S5 and Figure S4.

186

187 **Results and discussion**

188

189 **Global atmospheric occurrence of OPEs**

190

191 *Detection frequency, atmospheric concentrations and pattern*
192
193 Most OPEs (i.e. TnBP, TiBP, TEHP, EHDPP, and the chlorinated TCPPs and TCEP)
194 were detected in the aerosol samples over the global tropical and subtropical oceans at
195 considerably high frequencies (90 – 100%), confirming that these chemicals have
196 equally reached remote waters from the NH and SH (Figure 1, Figure S5). However, the
197 detected frequency of other OPEs like TPhP and TCrPs point to a reduced occurrence in
198 the SH, in particular in the Indian Ocean, being only found in ~ 20 % (up to ~ 90% the
199 in NH) and ~ 10% (up to ~ 80% in the NH) of the samples, respectively (Figure S5).
200 Detection frequency of TDCP in the Indian Ocean was also low (detected in 44% of the
201 samples collected in this region).

202
203
204 **Figure 1.** Box plots of atmospheric aerosol concentrations (ng m^{-3}) of targeted OPEs
205 across the tropical and subtropical regions of the major oceans (lines within the boxes

206 represent the median concentrations). Detection frequency (%) are numbers at the
207 bottom squares. This comparison is shown in log-scale in Figure S6.

208

209 $\sum_{14}$ OPE aerosol phase concentrations varied from 360 to 4400 pg m^{-3} (1800 pg m^{-3} ,
210 median) across the studied oceanic regions with TCPPs, EHDPP and TnBP dominating
211 the OPE pattern with median concentrations of ~ 610 , 390 and 220 pg m^{-3} , respectively
212 (Figure 1). Median, mean concentrations, and ranges in the various oceanic regions are
213 presented in Table S6, whereas compound specific concentrations for all aerosol
214 samples are reported in Table S7.

215

216 The atmospheric aerosol pattern of OPEs showed a general predominance of TCPPs in
217 around half of the samples (Figure 2A), with TCPP contributing from $38 \pm 9\%$ to $48 \pm$
218 13% of the $\sum_{14}$ OPEs. EHDPP and TnBP were also abundant accounting from the $18 \pm$
219 13% to $40 \pm 11\%$, and from the $4 \pm 2\%$ to $19 \pm 11\%$ of the $\sum_{14}$ OPEs, respectively.
220 However, the other half of samples showed a higher contribution of TnBP (from $19 \pm$
221 5% to $30 \pm 14\%$, Figure 2B). This pattern was mostly observed in samples collected
222 closer to the coast (like in Brazil area) or for which air masses (air mass back
223 trajectories, BTs, calculated with HYSPLIT model²⁹) showed a general continental
224 influence (SW Mexico, NW Africa, S Africa and Madagascar and New Zealand)
225 (Figure S7), but also in some SH regions with lower TCPP and higher TnBP
226 abundances, respectively.

227 The dominant role of non-chlorinated OPEs, such as TnBP in the atmospheric pattern
228 have been mostly reported in areas under the influence of suspected sources and in
229 urbanized regions.^{9,20,21,30} Conversely, the predominance of chlorinated OPEs, in
230 particular TCPPs, in the atmospheric pattern has been previously reported for other

231 marine areas in the NH and SH, such as in the North Sea,²⁴ the Sea of Japan,²¹ the
232 Mediterranean and Black Seas,²⁵ the Indian and Southern oceans,²¹ the East and South
233 China Sea, and the Coral Sea.^{22,23} Oceanic transport has been suggested to be important
234 for chlorinated OPEs.²⁰

235
236 **Figure 2.** Relative predominance of OPEs in the global oceanic atmospheric aerosol.
237 Columns show mean values + standard deviation of samples exhibiting a general TCPP
238 predominance (A) and those showing higher contribution of TnBP (B) for each region.

239

Most probably, the longer atmospheric half-lives of particle-bound TCPPs compared to TnBP⁹ will result in a weathering of the atmospheric pattern during LRAT from the source areas to the open ocean. The atmospheric pattern weathering during LRAT has been described for other SVOCs such as dioxins^{18,31,32}. The TCPP/TnBP ratio could provide information regarding the atmospheric weathering of OPE, and as an indicator of OPEs sources from land. In general, the smaller the ratio the higher the probability of proximity to sources (Table S8). For instance, the TCPP/TnBP ratio in this study ranged from 0.1 to 75 (Table S8), with the lowest ratios in the SH and in regions with air mass back trajectories influenced by land.

249

Aerosol phase OPE spatial distribution

251

Figure 3 shows the spatial distribution of the three most abundant OPEs. TCPPs and EHDPP follow a similar pattern with high levels in the Atlantic Ocean and an overall wide-spread distribution in both hemispheres. Contrarily, TnBP showed in general lower levels in the Atlantic but concentrations peaked in samples from the NE Pacific Ocean and NE Atlantic, with land influenced air mass BT (Figure S7). Differences in spatial distribution were also observed for the other OPEs (Figure S8). For instance, TDCP, TCEP, TPhP and TCrPs were generally less abundant in the SH and presented specific concentration peaks in some samples from the NH, whereas TEHP was found to be more abundant in the SH. The diverse spatial pattern of the individual OPEs may be the result of different sources for different individual compounds, and different physical-chemical properties and degradation pathways affecting their global cycling.

263

Figure 3. Spatial distribution of the most abundant OPEs (i.e TCPPs, EHDPP and TnBP) found in the global tropical and subtropical oceanic atmosphere.

Figure S9 shows the box plots for individual contaminant concentrations per oceanic region (as grouped in Figure S1). Statistically significant differences among oceanic regions (Kruskal-Wallis rank test, $p = 0.0001 - 0.0046$) were found in the concentration of $\sum_{14}\text{OPEs}$ and for all OPEs except for TEHP (Table S5). Contaminant concentrations (except for TEHP) were further compared by pairs of regions (Wilconxon rank-sum test) (Figure S4). The observed trends are far from being homogenous and are strongly

contaminant dependent. Not all contaminants exhibited consistent higher levels in one hemisphere over the other. Thus, TCEP, TiBP and TnBP exhibit higher levels (~3 fold, median values) in the South Atlantic than in the North Atlantic. However, only TiBP was higher in the South Pacific (~2 fold, median values) compared to the North Pacific (Table S6, Table S7) and TPhP concentration was higher in the North Pacific compared to the South (~2 fold, median values). The two regions showing more significant differences were the North Atlantic and the Indian ocean, with TDCP, EHDPP and TCrPs showing higher levels (2-5 fold, median values) in the North Atlantic, and the opposite trend for TCEP, TnBP and TPhP (1-2 fold higher levels in the Indian Ocean) was observed. This fact is highlighting the high compound specific variability in a given oceanic region and between the NH and SH. In general, the continental influence of the air masses gave rise to higher levels and changes in the atmospheric pattern (as discussed above). This situation mostly happened closer to the continental coasts at both hemispheres and in the Indian Ocean which is affected by northern air masses in the mid troposphere.¹⁷ The influence of air masses is probably coupled with regionally dependent different use of individual OPE, and weathering during LRAT.

In addition, the variable amounts of the atmospheric TSP over the different oceanic regions affected the observed spatial patterns explaining part of the concentration variability. For example, when normalizing atmospheric concentrations by TSP (Table S9), the median $\sum_{14}\text{OPEs}$ concentrations are similar for the North Atlantic ($23.5 \text{ ug g}^{-1}_{\text{TSP}}$) and the Indian ocean ($22.6 \text{ ug g}^{-1}_{\text{TSP}}$) (Figure S10 and Table S9), while the median volumetric concentrations was higher for the North Atlantic. High aerosol phase concentrations of semi-volatile organic pollutants such as dioxins and polycyclic aromatic hydrocarbons (PAHs) have also been observed in some oceanic gyres such as the Indian Ocean.^{17,18}

Table 1 gathers existing data on OPE aerosol phase atmospheric concentrations from cruise measurements and remote coastal sites in various marine regions of the world. The majority of the studies have been performed in the NH. The present work complements those studies and fills important data gaps for some oceanic regions such as the open Atlantic and the South Pacific Oceans. Concentrations of halogenated OPE measured during the MALASPINA campaign in the NH are generally in the upper-end range of those reported for the most remote environments from this hemisphere (Table 1). Higher concentrations were found for some non-halogenated OPEs like TnBP and EHDPP, whereas TiBP and TCrPs were within the range of those levels in remote regions. The higher TnBP levels correspond mostly to the samples collected closer to the coast or with BT showing continental influence, as well as in the SH. Previous cruise measurements performed in the North Pacific Ocean²¹ revealed generally lower OPE concentrations, except for TCEP and TPhP, with levels in the range of our measurements in North Pacific. However, even if both cruises sampled the same ocean, they had different geographical coverage. Regarding the SH, the concentrations measured during the MALASPINA expedition in the South Atlantic, Pacific and the Indian Oceans are generally higher than those reported for the most remote areas, in the southern Ocean²¹ and near the Antarctic peninsula.²² However, our concentrations compare well with the previously reported levels in the Indian Ocean.²¹ The comparison of concentrations from different field studies should be made with caution as most previous studies did not report the concentrations from reference materials which limits the interlaboratory comparability (potential quantification bias), and used different sampling approaches including different deployment times (potential sampling bias due to OPE degradation). Sampling deployment times ranged from 12 to 24 hours in this work.

324 *Atmospheric dry deposition of OPEs to the global oceans*

325

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

327

$$328 \quad F_{DD} = 864 v_d C_A \quad [1]$$

329

330 where C_A is the volumetric concentration of OPEs in the aerosol phase (ng m^{-3}), and v_d
331 (cm s^{-1}) is the deposition velocity of particles. v_d were predicted using the recently
332 developed empirical parameterization derived from field measurements during the same
333 MALASPINA circumnavigation cruise¹⁷:

334

$$335 \quad \text{Log}(v_d) = -0.261 \text{Log}(P_L) + 0.387 U_{10} * \text{Chl}_s - 3.082 \quad [2]$$

336

337 where U_{10} (m s^{-1}) is the wind speed at 10 m over sea surface, Chl_s (mg m^{-3}) is the
338 chlorophyll a concentration in surface waters, and P_L (Pa) is the chemical vapor
339 pressure of each OPE congener. This equation predicts higher depositional fluxes for
340 the less volatile (more hydrophobic) chemicals, and higher depositional fluxes in those
341 oceanic regions with higher wind speed, and higher phytoplankton biomass due to the
342 formation of a surface microlayer enhancing the deposition of hydrophobic fine
343 aerosols. ³³ U_{10} and Chl_s were measured during the sampling campaign¹⁷ and P_L values
344 for OPEs were taken from literature³⁴. The v_d calculated using equation [2] ranged from
345 0.001 to 0.10 cm s^{-1} depending on the oceanic region and compound (Figure S11).
346 Figure 4 shows the OPE atmospheric dry deposition fluxes for each sampling point and
347 compound. Median, mean and range of fluxes for single contaminant in each region are
348 presented in Table S10, whereas values for all samples are shown in Table S11.

349 Atmospheric dry deposition fluxes of $\sum_{14}\text{OPEs}$ across the major oceans of the Earth
350 varied from 4 to 140 $\text{ng m}^{-2}\text{d}^{-1}$ (Figure 4, Table S11).

351

353 **Figure 4.** Atmospheric dry deposition fluxes ($\text{ng m}^{-2} \text{d}^{-1}$) to surface waters of the
354 tropical and subtropical regions of the major oceans

355

356 The atmospheric loading to marine waters is dominated by TCPPs, the most abundant
357 OPE detected, with higher deposition fluxes in the North Pacific and Indian Oceans
358 (higher v_d values calculated for these regions, Figure S11) reaching up to 35 $\text{ng m}^{-2}\text{d}^{-1}$
359 (median value) in the North Pacific (Table S10). The annual dry deposition fluxes
360 ($\sum_{14}\text{OPEs}$) in the Pacific (considering a surface of $1.7 \times 10^{14} \text{ m}^2$) and Indian (surface of
361 $7.4 \times 10^{13} \text{ m}^2$) Oceans ranged from 1 to $\sim 7 \text{ Kt y}^{-1}$ and from 0.1 to 4 Kt y^{-1} , respectively.
362 Generally lower annual deposition fluxes (0.2 to 2.5 Kt y^{-1}) were estimated for the
363 Atlantic Ocean (surface of $8.2 \times 10^{13} \text{ m}^2$). The surface waters of the tropical and
364 subtropical oceans receive a resulting yearly integrated amount of ~ 2 to 13 Kt y^{-1} of
365 OPEs (sum of 14 compounds) from the overlying atmosphere as a result of the dry
366 deposition of particle-bound OPEs.

367

368 **OPEs as a source of new organic phosphorus (P) to the open ocean**

369

370 The anthropogenic impacts of OPEs, and other organophosphorus hazardous chemicals,
371 may not be limited to toxic effects to wildlife and humans as reported so far, but also to
372 the interactions with the natural phosphorous cycle²⁵. Phosphorus is often a limiting
373 nutrient in large oceanic regions,^{35,36} but current estimates of phosphorus deposition to
374 oceanic regions are mostly based on the assessment (measurements and model
375 estimations) of inorganic phosphorus.³⁷ There is a raising interest to quantify the
376 relevance and role of the organic phosphorus inputs (a fraction poorly characterized) on
377 the oceanic biogeochemical cycles.³⁷

378 The dry deposition of $\sum_{14}\text{OPEs}$ given as organic phosphorus to the global oceans varied
379 from 0.5 to 12 ngP m⁻² d⁻¹ (or from $\sim 2 \times 10^{-7}$ to 4×10^{-6} gP m⁻² y⁻¹). Assuming the
380 phosphorus input coming from aerosol phase OPEs is bioavailable for planktonic
381 organisms, it is estimated that it could trigger a primary productivity (using the Redfield
382 ratio) accounting for around 0.001% of the primary productivity measured in the
383 oligotrophic oceanic gyres during the MALASPINA campaign (100 - 600 mg C m⁻² d⁻¹)
384 ³⁸ or in other field studies (18 - 360 mg C m⁻² d⁻¹)³⁹.

385 The P_L range of the targeted OPEs in this study varied from 0.00002 Pa (TEHP) to 1.7
386 Pa (TiBP). This P_L range is similar to that of other SVOCs with a well described
387 atmospheric gas-particle partitioning such as polychlorinated biphenyls (PCBs), PAHs
388 and some organochlorinated pesticides (OCPs)^{40,41}. The issue of weather OPEs are
389 found in the gas phase is extremely relevant for understanding and predicting their
390 environmental fate. We know from other semi-volatile POPs that diffusive air-water
391 exchange is the main depositional process. The diffusive atmospheric deposition (air-
392 water exchange) of other SVOC with similar physical-chemical properties as OPEs,
393 such as PAHs and PCBs, can be various orders of magnitude larger than the dry
394 deposition fluxes in marine environments, in particular for the most volatile compounds

395 ^{40, 41}. In addition, this mechanism is the dominant pathway of SVOC loading to aquatic
396 environments far from the coast due to a decrease in marine aerosol abundance in the
397 open ocean ^{40, 41}.

398 Early works provided concentrations of OPEs in the gas phase over the North Sea, ²⁴
399 with concentrations accounting from 15 to 65% of atmospheric OPEs. Recently, it has
400 been reported that gas phase OPEs are predominant over a coastal site ²⁶, consistent
401 with their predicted gas-particle partitioning from P_L and K_{OA} . ²⁷ We estimated the gas
402 phase concentrations of OPEs for each sampling event from the measured aerosol phase
403 concentrations and K_{OA} ⁴². K_{OA} values have been estimated for a wide range of OPEs⁵
404 using three different approaches: the EPI Suite, SPARC and ABSOLV. The three
405 estimates of the values of K_{OA} for OPEs are different by orders of magnitude ⁵, leading
406 to a very high variability of the predicted OPE gas phase concentrations. For example,
407 the predicted median TCPP gas phase concentrations for the oceanic atmosphere were
408 of $\sim 46\ 000\ \text{pg m}^{-3}$ (EPI Suite), $\sim 369\ 000\ \text{pg m}^{-3}$ (SPARC), and $\sim 1500\ \text{pg m}^{-3}$
409 (ABSOLV). The large variability in predictions is also true for other OPEs with lower
410 P_L . The predicted median gas phase concentrations of EHDPP were $\sim 60\ \text{pg m}^{-3}$ (EPI
411 Suite), $\sim 300\ \text{pg m}^{-3}$ (SPARC), $\sim 0.1\ \text{pg m}^{-3}$ (ABSOLV). Due to the lack of reports of gas
412 phase concentrations for OPEs in most previous field studies, even in those where gas
413 phase OPEs were targeted, one could think that the lower values predicted by the
414 ABSOLV method would be close to the environmental levels. However, this cannot be
415 assured until oceanic gas phase concentrations of OPEs are measured. In any case, these
416 gas phase concentrations could be supporting important air-water diffusive fluxes of
417 OPEs to the global oceans.

418 The diffusive gross absorption (F_{Abs} , $\text{ng m}^{-2} \text{d}^{-1}$) of gas phase OPEs was estimated by,
419

$$F_{Abs} = k_{AW} \frac{C_G}{H'} \quad [3]$$

421

422 Where C_G is the gas phase concentrations (ng m^{-3}), k_{AW} is the air-water mass transfer
423 coefficient, estimated as previously reported^{40, 41}, and H' is the dimensionless Henry's
424 Law constant. We estimated F_{Abs} using the H' estimated from the EPI Suite, SPARC,
425 and ABSOLV methods, which also show a large variability⁵.

426 The estimated mean gross diffusive fluxes of $\Sigma_{14}\text{OPEs}$ were of $60\,000 \text{ ng m}^{-2} \text{ d}^{-1}$ (EPI
427 Suite), $200 \text{ ng m}^{-2} \text{ d}^{-1}$ (SPARC), and $6000 \text{ ng m}^{-2} \text{ d}^{-1}$ (ABSOLV). TCEP, TCPP, TiBP,
428 and TnBP are the main OPEs contributing to this diffusive flux. The estimated average
429 global inputs of P to the ocean due to gross diffusive air-water exchange were of 6600
430 $\text{ngP m}^{-2} \text{ d}^{-1}$ (EPI Suite), $24 \text{ ngP m}^{-2} \text{ d}^{-1}$ (SPARC), and $620 \text{ ngP m}^{-2} \text{ d}^{-1}$ (ABSOLV). The
431 estimated mean primary productivity that the diffusive air-water exchange of OPEs
432 could trigger due to inputs of bioavailable P would be of $0.3 \text{ mg C m}^{-2} \text{ d}^{-1}$ (EPI Suite),
433 $0.001 \text{ mg C m}^{-2} \text{ d}^{-1}$ (SPARC), and $0.03 \text{ mg C m}^{-2} \text{ d}^{-1}$ (ABSOLV). These diffusive inputs
434 of P (from OPEs) account from 0.0002% to more than 1% of primary production in the
435 oligotrophic oceans, and the upper-end estimates are one order of magnitude larger than
436 phosphorus diffusive inputs previously considered by biogeochemical models³⁷. It is
437 noteworthy that this is a potential input of new (non-recycled) organic phosphorus to the
438 ocean, but this input cannot be constrained until the uncertainty related to OPE's
439 physical-chemical properties is significantly reduced.

440 Several studies have reported changes in primary production and chlorophyll a
441 concentrations during the last century.^{43,44} Environmental and climatic change can
442 induce an increase or decrease of primary production due to a number of factors.^{43,44}
443 The figures obtained here for organic phosphorus inputs due to OPEs, even if their
444 gaseous deposition fluxes have an uncertainty of orders of magnitude, suggest that these

445 chemicals, acting together with other anthropogenic pollutants containing P and N,
446 could be triggering small perturbations of the regional/global oceanic primary
447 production, and of comparable magnitude than those observed during the anthropocene.
448 This would suggest another, yet neglected, interaction of the anthropogenic
449 chemosphere with the other vectors of global change. Further work on the oceanic
450 occurrence of OPEs, including waterborne long range transport, and determination of
451 physical chemical properties of OPEs is urgently needed to constrain the uncertainty on
452 their environmental fate and relevance.

453

454

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456

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471

472 **Supporting information available**

473

474 Additional data on the sampling and analytical procedures, QA/QC, compound-by-
475 compound atmospheric levels, spatial distribution and deposition fluxes are presented in
476 this section. This information is available free of charge via the Internet at
477 <http://pubs.acs.org/>

478

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671

672 **Table 1.** Compilation of existing measurements of OPE atmospheric levels (aerosol concentrations except where otherwise indicated) in different
673 oceanic regions of the world. Median concentrations and range (in brackets) are shown for this study.
674

	Sampling	Location type	Date	Compounds, $pg\ m^{-3}$									
				TCEP	TDCP	Σ TCPPs	TtBP	TnBP	TPhP	EHDPP	TEHP	Σ TCrPs	
Northern Hemisphere													
Arctic Ocean ²⁰	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	n.d. - 12 ^(b)	
Resolute Bay & Alert (Canada, Arctic) ²⁰	Remote	Coastal site	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.	n.d. - 1.7 ^(c)	
Arctic Ocean ²¹	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	n.r.	
Ny-Alesund (Svalbard, Arctic) ⁷	Remote	Coastal site	Jun-September 2007	<200 - 270	87 - 250	<200 - 330	<10 - 140	<200	<50	<200 - 260	n.r.	n.r.	
Longyearbyen (Svalbard, Arctic) ⁹	Remote	Coastal site	September 2012-May 2013	40 - 60	2 - 294	10 - 186	n.r.	6 - 1000	1 - 50	6 - 300	1 - 40	n.r.	
North Atlantic Ocean ^{This study}	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]	10 [n.d. - 30]	
North Pacific Ocean ²¹	Cruise	Open sea	Jun-September 2010	160 - 280	5 - 8	98 - 270	14 - 20	6 - 14	9 - 24	n.r.	1 - 12	n.r.	
North Pacific Ocean ^{This study}	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]	5 [n.d.-30]	
Sea of Japan ²¹	Cruise	Open sea	Jun-September 2010	237 - 1960	16 - 52	130 - 620	10 - 63	10 - 33	25 - 97	n.r.	5 - 38	n.r.	
East China Sea ²²	Cruise	Open sea	October 2009-March 2010	134	828	9	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	
South China Sea ²³	Curise	Open sea	September-October 2013	14 - 110	1 - 4	15 - 38	1 - 4	1 - 5	3 - 16	n.r.	2 - 16	n.r.	
North Sea ^{24 (a)}	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	n.r.	
Mediterranean Sea ²⁵	Cruise	Open sea	Jun 2006, May 2007	70 - 854	n.d. - 460	126 - 2340	4 - 650	56 - 600	n.d. - 80	n.d. - 834	56 - 307	n.d. - 128	
Black Sea ²⁵	Cruise	Open sea	Jun 2006, May 2007	300 - 2420	n.d. - 97	540 - 2720	66 - 190	200 - 370	3 - 40	n.d. - 310	36 - 190	n.d. - 73	
Philippine Sea ²¹	Cruise	Open sea	November 2010- March 2011	20 - 156	50 - 780	22 - 410	10 - 23	10 - 100	n.d. - 155	n.r.	6 - 92	n.r.	
Southern Hemisphere													
South Atlantic ^{This study}	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]	9 [n.d. - 20]	
South Pacific ^{This study}	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]	6 [n.d.-8]	
Coral Sea ²²	Cruise	Open sea	October 2009-March 2010	88	370	7	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	
Indian Ocean ²¹	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	n.r.	
Indian Ocean ^{This study}	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]	2 [n.d. - 5]	
Southern Ocean ²¹	Cruise	Open sea	November 2010- March 2011	74	80	55	16	14	20	n.r.	7	n.r.	
Near Antarctic Peninsula ²²	Cruise	Open sea	October 2009-March 2010	40	76	4 ^a	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	

n.r. = not reported; (a) atmospheric concentrations correspond to the sum of gas+particle phases, (b) three TCrP isomers analyzed, (c) two TCrP isomers analyzed

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