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Organophosphate Ester (OPE) Flame Retardants and Plasticizers in the Open Mediterranean and Black Seas Atmosphere

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S Supporting Information

ABSTRACT: The presence of organophosphate ester (OPE) flame retardants and plasticizers has been confirmed for the first time in the atmosphere over the Mediterranean and Black Seas. Atmospheric aerosol samples were collected during two West−East oceanographic cruises across the Mediterranean and in the southwest Black Sea. This comprehensive assessment of baseline concentrations of aerosol phase OPEs, spatial distribution, and related deposition fluxes reveals levels ranging from 0.4 to 6.0 ng m^{-3} for the $\sum_{14}$OPEs and a lack of significant differences among sub-basins. Levels measured across the Mediterranean Sea and in the Black Sea are in the upper range or higher than those from previous reports for the marine atmosphere, presumably due to proximity to sources. From 13 to 260 tons of OPEs are estimated to be annually loaded to the Mediterranean Sea open waters from the atmosphere. Tris-(1-chloro-2-propyl)phosphate (TCPP) was the most abundant compound over the atmosphere of all the Mediterranean and Black Sea sub-basins, and therefore the chemical reaching surface waters at a higher extent by dry deposition. The atmospheric deposition fluxes of phosphorus due to OPE deposition is a significant fraction of known atmospheric inputs of new organic phosphorus (P), suggesting the relevant role that anthropogenic organic pollutants could play in the P cycle.
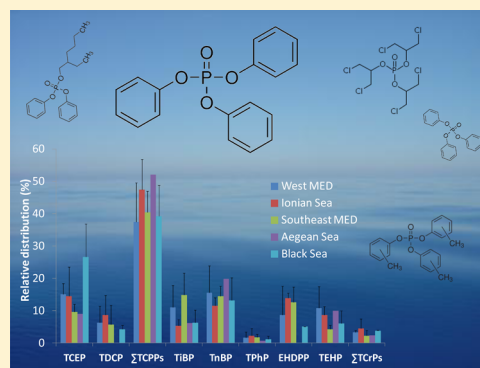
INTRODUCTION

The Mediterranean and Black Seas are under intense anthropogenic pressure because of their semienclosed nature, surrounded by highly populated areas (more than 400 million people). Sources of organic contaminants in the region include coastal urbanization, industry, energy generation/consumption, transportation systems, tourism and recreation, agriculture, fisheries, forestry and mining.[1,2] These pressures result in the emission of semivolatile organic contaminants such as persistent organic pollutants (POPs) and related compounds to the Mediterranean atmosphere. The atmospheric pathway of semivolatile POPs accounts for the main input of these toxic chemicals to the marine environments around the world, especially at open sea.[3,4] In the particular case of the Mediterranean Sea, the atmospheric occurrence and deposition of polycyclic aromatic hydrocarbons (PAHs),[5−9] polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs),[10−13] polychlorinated biphenyls (PCBs),[8,10−12,14−17] polybrominated diphenyl ethers (PBDEs),[8,12,16] and some organochlorine pesticides (OCPs),[10,17] have been investigated in the last decades for both coastal sites and open sea. Conversely, the reported occurrence of organic pollutants in the Black Sea's atmosphere is restricted to a few coastal measures of PAHs in urban or semiurban locations,[18,19] and measurements of PCDD/Fs, PAHs, PCBs, and OCPs at the open southwest Black Sea atmosphere.[9,13,17]

Atmospheric inputs of contaminants, such as those of PAHs, can be higher than those from rivers in some Mediterranean basins (e.g., northwest Mediterranean).[5] Recent estimates using comprehensive field measurements have provided clear evidence of the relevant role of the atmosphere as a source of organic pollutants to the Mediterranean Sea. For instance, an atmospheric loading of toxic chemicals ranging from 2100 to 4360 ton yr^{-1} (as sum of PAHs, PCBs, PCDD/Fs, OCPs, and PBDEs) was estimated for the open Mediterranean Sea.[20] Figures for the Black Sea are not as comprehensive as for the Mediterranean Sea, but ∼500 tons of PAHs are estimated to be deposited to Black Sea open waters annually.[9] However, there is a dearth of quantifying the atmospheric levels and inputs to marine waters of other emerging pollutants, such as organophosphate esters (OPEs) in the region. These chemicals are a group of organophosphorus flame retardants and plasticizers which are nowadays widely employed in many industrial applications and household products.[21] OPEs are used in many cases as substitutes of PBDEs since their recent ban by the Stockholm Convention in 2009. Some OPEs have been reported to be persistent in the environment (e.g., tris[2-chloro-1-(chloromethyl)ethyl]phosphate, TDCP) and to bio-

accumulate in the food chain.[21,22] In addition, some halogenated OPEs have been found to exhibit various toxic effects. For instance, tris-(1-chloro-2-propyl)phosphate (TCPP) is considered to be potentially carcinogenic and tris-(2-chloroethyl)phosphate (TCEP) is toxic to aquatic organisms and carcinogenic for animals.[21−24] The usage of TCEP and TCPP in Europe in year 1995 was reported to be of ~2000 and ~23 000 tons, respectively,[21] and in 2006 phosphorus flame retardants (all known families) were already responsible for 20% of the global flame retardant consumption in Europe (~93 000 tons).[21]

OPEs have been described at high concentrations in the Great Lakes atmosphere,[25] but at lower concentrations in remote coastal sites in Northern Finland and Norway.[26,27] Recent investigations pointed to the global atmospheric occurrence of OPEs over marine environments, even in remote regions of the world.[28−30] The presence of OPEs in the mentioned environments has been mainly linked to anthropogenic sources, and provides scientific evidence of their transport from distant sources and their global distribution associated mainly to long-range transport of aerosols. In addition, atmospheric deposition of OPEs could be a new significant source of organic phosphorus (P) to the marine environment. Phosphorus is a key nutrient for marine phytoplankton and microbial communities, and organic phosphorus plays an important role in the biogeochemical cycle of phosphorus, especially relevant for marine bacterial populations and its role on the carbon cycle.[31] Therefore, there is an increasing interest to quantify the atmospheric inputs of organic phosphorus to the marine environment,[32] and an important fraction of it could be due to anthropogenic substances, such as OPEs.

The scarcity of data on production and consumption of OPEs in the Mediterranean region together with the lack of experimental confirmation of their presence in the regional atmosphere and deposition to seawaters makes it difficult to evaluate the exposure to organisms and biogeochemical significance of this class of pollutants. The overall objectives of this work are (1) to provide the first comprehensive assessment of OPE aerosol phase concentrations in the open Mediterranean and Black Seas atmosphere; (2) to estimate their atmospheric loading to open waters via dry deposition; and (3) to compare these inputs of OPEs with the reported modeled inputs of total organic phosphorus in the marine environment.

■ EXPERIMENTAL SECTION

Study Region and Sampling. The Mediterranean Sea covers an area of around 2.5×10^6 km^2 and has a connection to the Atlantic Ocean through the strait of Gibraltar (~14 km wide). The Black Sea is virtually isolated and only connected to the eastern Mediterranean Sea through the Bosphorus strait. It represents an area of 4.2×10^5 km^2. These two marine basins are semienclosed environments with limited water exchanges and are threatened by the intense human activity in the area. A detailed description of the studied area has been recently reported elsewhere.[33]

Air samples were collected during two sampling cruises performed in June 2006 and May 2007 on board of the R/V *García del Cid.* The campaigns started and finished in Barcelona, with Istanbul and Alexandria being the intermediate stops, respectively. Details on the sampling campaign can be found in the Supporting Information (SI), Text S1. Briefly, air samples were collected by using high volume samplers installed on the upper deck on the ships' bow. The samplers were automatically stopped when wind was blowing from the poop of the vessel to avoid potential contamination by the ship exhausts, and only sampled when the wind came from the front (160 degrees sector). Additionally, the samplers were manually switched off when the boat was stopped. The gas phase was sampled with polyurethane foams (PUFs), whereas aerosol phase collection was achieved on quartz fiber filters (QFFs). Sampling volumes varied from 140 to 950 m^3 depending on the sample (SI, Table S1). Ten PUFs were initially analyzed, but targeted OPEs were below the limits of detection (LOD), consistent with previous reports indicating that OPEs are mostly associated with the atmospheric aerosol phase at open sea in the marine environment worldwide.[28,29] Therefore, only aerosol samples were considered. A total of 23 aerosol samples were analyzed for OPEs (SI, Figures S1 and Table S1).

Analysis. Details on the OPE extraction and analytical procedures are presented in SI, Text S2. Briefly, QFFs were spiked with phenanthrene-d10 and chrysene-d12 labeled standards before Soxhlet extraction (24 h). The extracts were rota-evaporated and fractionated on alumina columns, and OPEs were eluted in the second and third fraction with an hexane/dichloromethane mixture. Extracts were then concentrated to 50−150 μL under gentle nitrogen flow. Prior to injection, syringe labeled standards (tri-*n*-propyl-d21 phosphate and malathion-d7) were added to the extracts to be used as internal standards for quantification. OPE analysis was performed by high resolution gas chromatography−low resolution mass spectrometry (HRGC−LRMS). Samples were analyzed for the following OPEs: TCEP, TDCP, TCPPs (mix of isomers), tri-iso-butyl phosphate (TiBP), tri-*n*-buthyl phosphate (TnBP), triphenyl phosphate (TPhP), 2-ethylhexyl diphenyl phosphate (EHDPP), tri(2-ethylhexyl) phosphate (TEHP) and tricresyl phosphate (TCrP, mix of isomers).

Quality Assurance/Quality Control (QA/QC). The QA/QC procedures are detailed in SI, Text S3. Summarizing, field and procedural blanks (for sampling and analysis) were collected and analyzed with the samples. Aerosol phase blank values (QFF blanks) are reported in SI, Table S2 . Only 50% of the compounds were detected in the blanks, with mean levels ranging from 0 to 18% of sample values, depending on the sample and the compound, except for TPhP which reached ~40% of the sample value. However, this higher percentage occurs because the TPhP exhibited the lowest ambient levels. Results were blank corrected. Procedural blanks showed similar levels to field blanks so no contamination of samples during sampling and storage occurred.

Standards (natives + labeled compounds) were introduced in the chromatographic sequence to evaluate possible variations during the time of analyses. Chromatographic peaks of target compounds were only considered when their abundance was at least three times higher than the noise. Instrumental LODs (calculated as signal-to-noise ratio >3) ranged from 0.1 to 1 pg m^{-3} depending on the compound (SI, Table S3). Average method recoveries (extraction−cleanup−analysis) in the aerosol samples ranged from 42 to 68% depending on the sample and surrogate. Results were not corrected by recoveries.

Data Statistical Analysis. Since the data set was not normally distributed, a nonparametric test was used in order to investigate possible significant differences among contaminants. The software employed was STATA/SE 12.1.
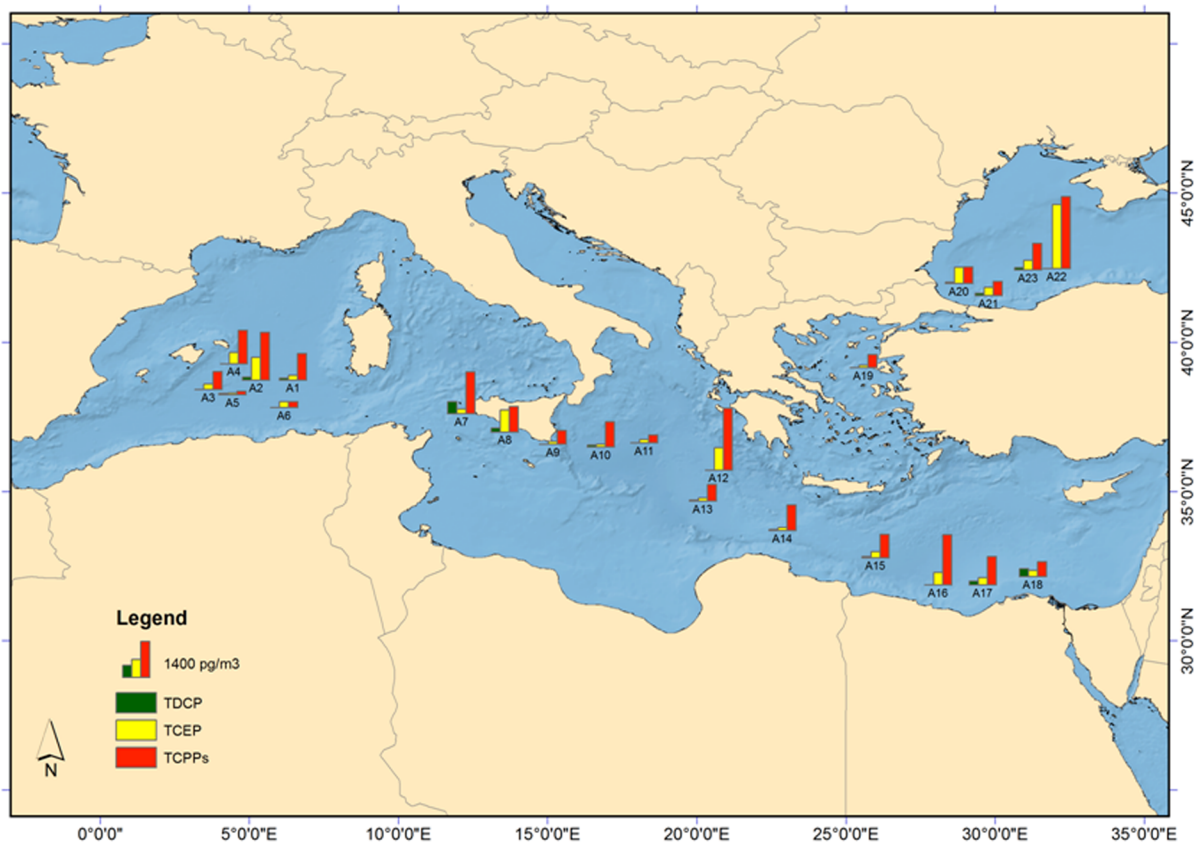
Figure 1. Spatial distribution of TCEP, TDCP, and TCCPs (the most potentially hazardous OPEs) across the Meiterranean and in the Black Sea.
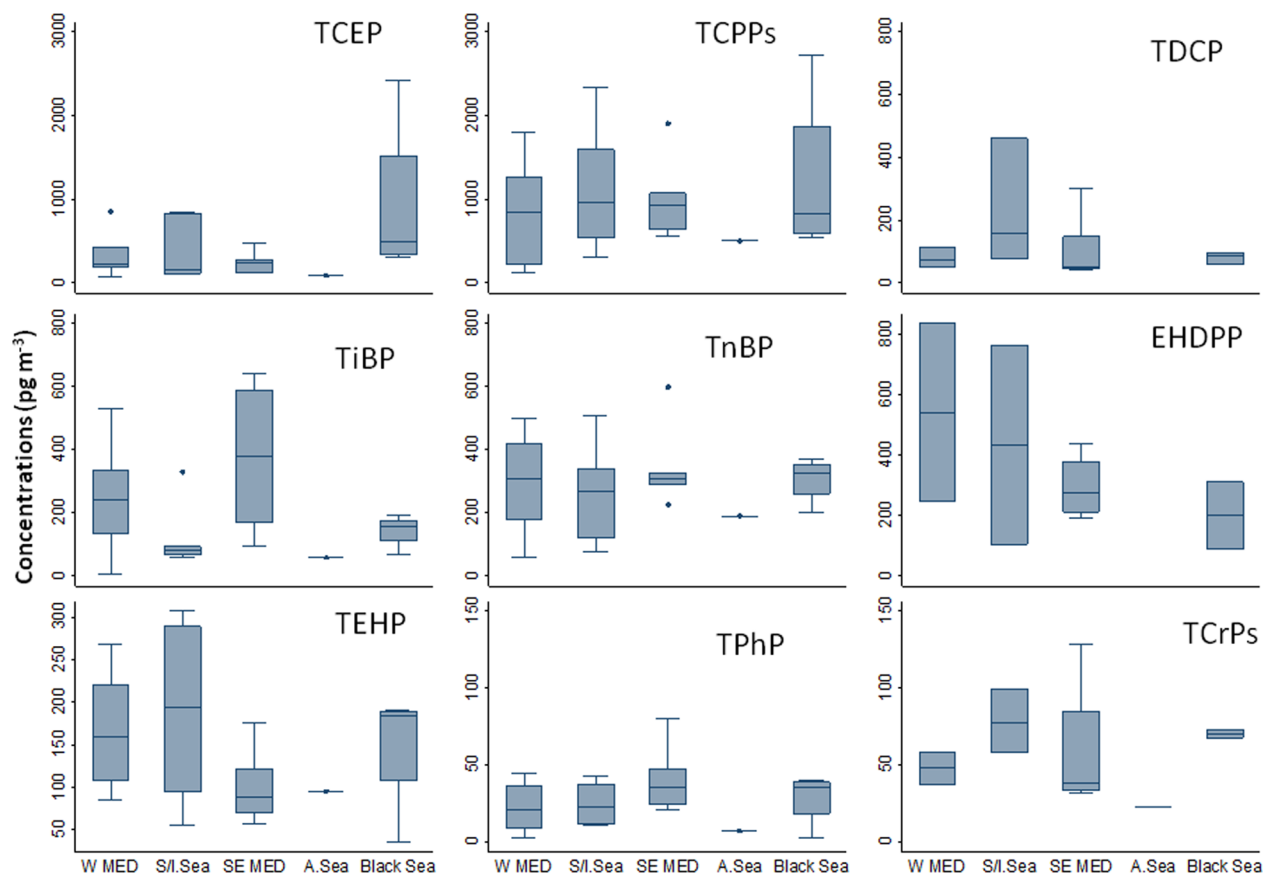

Figure 2. Box plots of atmospheric concetrations (pg m^{-3}) of targeted OPE by basin. Lines within the boxes represent the median concentrations.

■ RESULTS AND DISCUSSION

Atmospheric Occurrence of OPEs. All targeted OPEs were detected in the atmosphere across the Mediterranean Sea and in the southwest Black Sea. Detection frequency varied as follows: among the halogenated OPEs, TCEP and TCPPs were detected in all samples, whereas TDCP was detected in 60% of the samples. Among the nonhalogenated OPEs, TnBP, TiBP, and TEHP were detected in all samples, while TPhP, TCrP (as sum of four isomers), and EHDPP were detected in 90%, ∼50%, and ∼40% of the samples, respectively. $\sum_{14}$OPE concentrations varied from 0.4 to 5.0 ng m^{-3} in the Mediterranean Sea. Slightly higher levels were measured in the southwest Black Sea, ranging from 2.0 to 6.0 ng m^{-3}. Figure 1 shows the spatial distribution of the halogenated OPEs (the most potentially hazardous) in all transects. Samples were grouped by basins in order to study the interbasin variability of OPE atmospheric concentrations (Figure 2). Median, mean concentrations, and ranges in the various sub-basins are presented in SI, Table S4, whereas compound by compound concentrations for all aerosol samples are reported in SI, Table S5. For a more meaningful comparison of pollutant concentration among basins, a nonparametric statistical test (Kruskal−Wallis rank test) was performed for each contaminant as well as for the $\sum_{14}$OPEs. Results from the test show that single OPE concentrations measured in the various basins are not significantly different. The limited amount of samples per basin and the high within-basin variability could explain these results.

TCPPs (as sum of three isomers) dominated the atmospheric pattern (SI, Figure S2) in all basins (42 ± 10% of the $\sum_{14}$OPEs) followed by TnBP and TCEP representing the 14 ± 5% and the 15 ± 8% of the $\sum_{14}$OPEs, respectively. Indeed, the spatial distribution of $\sum_{14}$OPEs across all the studied basins was mostly dominated by one of the TCPPs (Figure 1 and SI, Figure S3). The predominance of TCPPs has been previously reported for the marine atmosphere such as in the North Sea, over waters from East China to the high Arctic and over the Philippine Sea and the Southern Ocean.[28,29] In the case of the North Sea, the authors argued that dominant concentrations of TCPPs were most probably the result of the industrial replacement of TCEP by TCPP in Europe motivated by the reduced toxicity of TCPP in comparison to TCEP. It has also been reported that TCPP represents approximately 80% of the chlorinated phosphorus flame retardants in Europe, and is by production volume the most important OPE.[21] Interestingly, the atmospheric concentrations of two of the chlorinated OPEs (i.e., TCEP and TCPPs) clearly peaked in the Black Sea (Figure 1, SI, Figure S3, sample A22), whereas those of the other chlorinated compound (i.e., TDCP) peaked close to Sicily (Figure 1, SI, Figure S3, sample A7). Nonhalogenated OPEs also showed this differential behavior. For example, TiBP and TPhP exhibited the highest levels at sample A17 in the southeast Mediterranean, close to Alexandria, while the highest concentration of EHDPP was measured in the western Mediterranean (sample A2) (SI, Figure S3). This fact highlights the high compound specific within-basin variability which can be attributed to the differential behavior and sources among contaminants.

The highest $\sum_{14}$OPEs atmospheric levels were found in samples in the southeast Mediterranean (A12 and A16) and in the Black Sea (A22), whereas the lowest level was measured in a sample from the Western Mediterranean (A5) (SI, Table S5).

$\sum_{14}$OPEs concentrations in samples A12, A16, and A22 were 10 to 15 times higher than those measured in A5. Three-day air mass back trajectories (BTs) at 15 and 500 m over sea level were calculated for these samples showing the maximum and minimum levels by using the HYSPLIT model.[34] BT analysis revealed air masses circulating over coastal sites from the Aegean Sea and the Istanbul area for the samples with the highest OPE levels (SI, Figure S4). In addition, the higher level in sample A16 reflect the proximity of the Nile Delta and Alexandria urban area (around 4 million inhabitants). The influence of the Alexandria's region has also been described for PAH aerosol-phase concentrations for the same samples.[9] In contrast, air masses arriving from the Atlantic through the Strait of Gibraltar to the sampling site in the western Mediterranean registered the lowest level of OPEs in the aerosol phase. This provides a reasonable explanation for the observed spatial distribution of concentrations pointing to coastal sites and large coastal cities as a source of atmospheric OPEs to the region.

Very limited data are available on atmospheric levels of OPEs from cruise measurements at open sea for comparison. Table 1 shows existing targeted OPE levels measured at open waters in different oceans or seas of the world and in remote sites for comparison. The geographically closest available data come from measurements undertaken in 2010 in the North Sea ($\sum_8$OPEs: 110 − 1400 pg m^{-3}).[28] Measurements carried out between 2009 and 2010 in an oceanographic campaign starting in China and encompassing western Australia and the Southern Ocean reported $\sum_4$OPEs atmospheric levels ranging from a few hundred pg m^{-3} to around 1 ng m^{-3} in samples collected near China.[30] Another similar survey undertaken between 2010 and 2011, this time covering as well transects reaching the high Arctic in addition to the Southern Ocean, reported $\sum_8$OPEs levels ranging from 230 to 2900 pg m^{-3} and from 120 to 1700 pg m^{-3} for the Arctic and Antarctic expeditions, respectively.[29] When considering the sum of OPEs, the atmospheric concentrations measured across the Mediterranean Sea (400−5100 pg m^{-3}), and in the Black Sea (1700−6160 pg m^{-3}) are in the upper range or higher than the previous reports for the marine atmosphere (samples below LODs are not considered in the concentration ranges of $\sum$OPEs). Although these comparisons may provide an overall picture of total levels in various marine environments worldwide, caution should be taken because the number, and sometimes the specific compounds, included in the sums may be different. In addition, the sampling took place in different years and seasons (Table 1) so the climatic conditions could have contributed to a different atmospheric occurrence of OPEs. Indeed, when examining individual compounds (Table 1) it can be seen that TCEP exhibited higher atmospheric concentrations in the Sea of Japan compared to those measured in the Mediterranean Sea. Moreover, atmospheric concentrations of TPhP measured in the Mediterranean and Black Seas were within the same range or lower than those reported for the oceans or seas around the world, in particular when compared to the levels found in the North Sea. This variability on levels for single OPEs may reflect the different usages and sources. For example, in similar semienclosed environments surrounded by highly populated areas and industrial zones such as the Sea of Japan and the Mediterranean and Black Seas, the predominant OPEs are different. The fact that TCEP predominated in the Black Sea and the Sea of Japan compared to the Mediterranean Sea may be pointing to a higher usage of TCEP in those areas and to a minor degree of replacement of TCEP by TCPP compared to

Table 1. Atmospheric Levels of the OPE Targeted in This Study Measured at Open Sea in Different Oceans/Seas of the World and in Remote Sites

location (ref)	sampling	location type	date	compounds^a, pg m^-3								
				TCEP	TDCP	ΣTCPPs	TiBP	TnBP	TPhP	EHDPP	TEHP	ΣTCrPs
North Sea [28]	cruise	open sea	March, May, July 2010	6–160	7–78	38–1200	nd–150	nd–150	4–290	nr	nd–31	nr
Sea of Japan [29]	cruise	open sea	June–September 2010	237–1960	16–52	130–620	11–63	10–33	25–97	nr	5–38	nr
Northern Pacific Ocean [29]	cruise	open sea	June–September 2010	160–280	5–8	98–270	14–21	6–4	9–24	nr	1–12	nr
Philippine Sea [29]	cruise	open sea	November 2010–March 2011	20–156	50–780	22–411	10–23	10–100	nd–155	nr	6–92	nr
Indian Ocean [29]	cruise	open sea	November 2010–March 2011	46–570	nd–220	37–550	7–96	7–75	nd–74	nr	4–51	nr
East China Sea [30]	cruise	open sea	October 2009–March 2010	134	828	9	nr	nr	nr	nr	nr	nr
Coral Sea [30]	cruise	open sea	October 2009–March 2010	88	370	7	nr	nr	nr	nr	nr	nr
Southern Ocean [29]	cruise	open sea	November 2010–March 2011	74	80	55	16	14	19	nr	7	nr
Near Antarctic Peninsula [30]	cruise	open sea	October 2009–March 2010	41	76	4^b	nr	nr	nr	nr	nr	nr
Artic Ocean [29]	cruise	open sea	June–September 2010	126–585	nd–5	85–530	16–35	nd–36	10–60	nr	nd–6	nr
Ny-Alesund (Artic) [27]	s. station^c	coastal site	June–September 2007	<200–270	87–250	<200–330	<10–140	nr	<50	260	nr	nr
Mediterranean Sea (This study)	cruise	open sea	Jun 2006, May 2007	70–854	nd–460	126–2340	4–650	56–600	nd–80	nd–834	56–307	nd–128
Black Sea (This study)	cruise	open sea	Jun 2006, May 2007	300–2417	nd–97	540–2722	66–190	202–370	3–40	nd–310	36–190	nd–73

^aNotation: nr = not reported; nd = not detected. ^bEstimated value from the source document (Figure 2, ref 30). ^cCoastal sampling station.

the Mediterranean Sea, more affected by the situation in Europe (most air mass back trajectories came from Europe in this study). Unfortunately, no information regarding production and uses of OPEs in the Mediterranean and Black Sea regions are available to confirm this hypothesis.

Atmospheric Deposition of OPEs to the Mediterranean and Black Seas. Since both sampling cruises were performed during summer or late spring/summer, in the absence of precipitation events, and taking into account the clear predominance of OPEs in the aerosol phase, as confirmed by our own experiments and consistent with previous reports at open waters in other oceanic regions,[28,29] the atmospheric deposition was considered to be represented by the dry deposition fluxes. Dry deposition fluxes (F_{DD} ng m^-2 d^-1) were calculated as

$$F_{DD} = v_d C_A \qquad ([1])$$

where C_A is the volumetric concentration of OPEs in the aerosol phase (ng m^-3), v_d (cm s^-1) is the deposition velocity of particles. A value of 0.2 cm s^-1 (173 m d^-1) for v_d has been chosen as representative of marine aerosols at high sea.[35] This value has been previously used in the estimation of the dry deposition of other organic contaminants such as PCDD/Fs and PAHs over the Mediterranean Sea.[9,13] However, a degree of uncertainty (factor of 3) is associated to this calculation due to the lack of measurements of v_d during the cruises.

Atmospheric dry deposition fluxes (median values) for each study region as estimated using eq [1] are presented in Figure 3. Median, mean, and range of fluxes for single contaminant in
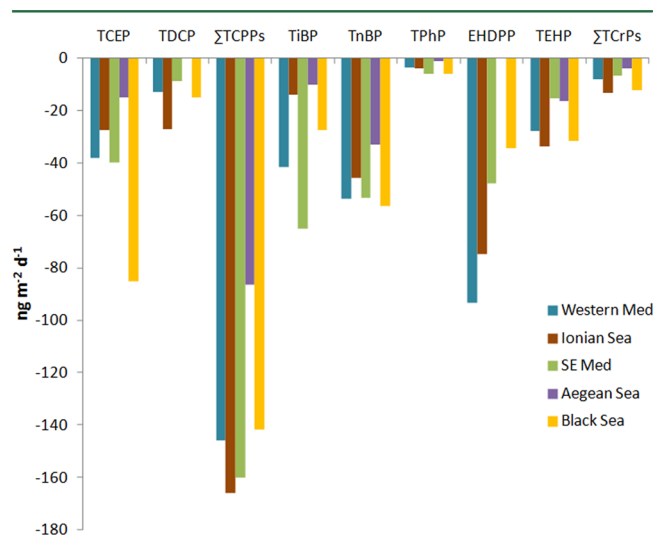

Figure 3. Atmospheric dry deposition fluxes (ng m^-2 d^-1, median values) of OPE over surface open waters in the studied marine basins.

each basin are given in SI, Table S6, whereas values for all samples are shown in SI, Table S7. Atmospheric dry deposition of $\sum_{14}$OPEs over the Mediterranean and the Black Seas varied from 70 to 880 ng m^-2 d^-1 and from ~300 to 1060 ng m^-2 d^-1, respectively (SI, Table S6). The atmospheric loading to marine waters is dominated by TCPPs as expected from atmospheric levels, ranging from 22 to 400 ng m^-2 d^-1 and from 90 to 470 ng m^-2 d^-1 in the Mediterranean and Black Seas, respectively. It is possible that there is a seasonality in the atmospheric concentrations of OPEs that cannot be elucidated here, thus leading to different depositional fluxes for the different seasons. In addition, wet deposition may have a higher relevance for

other seasons, since precipitation events follow a clear seasonality in the Mediterranean climate regime. Regardless of these limitations, extrapolating the estimates of the dry deposition fluxes of OPEs for the whole year, the total atmospheric inputs ($\sum_{14}$OPEs) in the western Mediterranean Sea, the Ionian Sea and the southeast Mediterranean Sea are very similar (20−250, 40−240 and 100−260 ton y^{-1}, considering surfaces of 8.5×10^{11} m^2, 7.5×10^{11} m^2, and, 9.6×10^{11} m^2, respectively). The lowest atmospheric loading of OPEs was estimated for the Aegean Sea (13 ton y^{-1} considering a surface of 2.1×10^{11} m^2). The estimated atmospheric inputs of OPEs in the Black Sea ranged from ∼50 to 170 ton y^{-1} considering a surface of 4.4×10^{11} m^2). Mediterranean Sea open waters receive therefore from 13 to 260 tons of OPEs (as sum of 14 compounds) each year from the atmosphere. These deposition fluxes correspond to a yearly input of P varying from 1 to 26 tons to the Mediterranean Sea open waters.

Are OPEs Relevant for the Phosphorus Cycle? The $\sum_{14}$OPEs aerosol phase concentrations given as P averaged 0.25 ng$_P$ m^{-3} and ranged from 0.04 to 0.8 ng$_P$ m^{-3}. These concentrations of organic P are 2 orders of magnitude lower than the total P reported for NW Mediterranean aerosol.[36] However, organic P may play an important role for microbial communities that can take advantage of the use of this source of an often limiting nutrient such as P. In fact, phosphate ester groups are common in biological organic molecules (e.g., phospholipids, DNA, RNA) and thus there are specific enzymes able to degrade organic phosphate ester compounds, suggesting that OPEs could be degraded by bacteria, even though to the best of our knowledge this has not been confirmed experimentally. An important issue is whether OPEs introduced to seawater by dry deposition are bioavailable. Even though OPEs are generally hydrophobic compounds, they will undergo particle−water partitioning once introduced in the water column. The dissolved phase compounds will be bioavailable, and if degraded, further OPEs will partition from the aerosol particles to the dissolved phase due to a particle to water fugacity gradient.

There is a raising interest to quantify the relevance and role of the organic P inputs play on the oceanic biogeochemical cycles.[32] The Mediterranean Sea is colimited by P, as other oligotrophic regions of the global oceans.[31] The anthropogenic sources of organic P to the environment are poorly characterized, and current estimates of anthropogenic organic P only account for some organophosphorus pesticides[32] but have not accounted for the contribution of OPEs and other potential families of organic compounds containing P. The dry deposition of $\sum_{14}$OPEs given as P, averaged 40 ng$_P$ m^{-2} d^{-1} (or 1.5×10^{-5} g$_P$ m^{-2} y^{-1}). The predicted atmospheric deposition of total organic phosphorus in the Mediterranean Sea is about 2×10^{-4} g$_P$ m^{-2} y^{-1}, with an order of magnitude of uncertainty.[32] Therefore, the quantified atmospheric deposition of $\sum_{14}$OPEs to the Mediterranean sea is of the same order of magnitude of the previous account for total anthropogenic organic P (which omitted OPEs), especially if we consider that the deposition velocities used in nutrient biogeochemical models are usually those determined for inorganic P, which are 5 to 20 times higher[36] than those used here. This exploratory analysis of the relevance of the deposition inputs of families of organic pollutants containing P, as $\sum_{14}$OPEs, suggests that there is a need of quantifying the depositional fluxes of these compounds for the global oceans. In addition, the relevance of the

concentrations and fluxes for other families of anthropogenic organic pollutants containing P, and other nutrients such as nitrogen should be explored. The characterization of such anthropogenic perturbation of the nutrient cycles, would help to understand the interactions between emissions of organic pollutants and biogeochemical cycles of nutrients and their ecological relevance. The full dimension of the importance of organic pollutants as a driver of environmental changes during the anthropocene,[37] will only be determined once we elucidate its coupling with the other vectors of global change,[38] the nutrient cycles being a key node of ecosystem functioning.

ASSOCIATED CONTENT

Supporting Information
Additional data on the sampling and analytical procedures, QA/QC, compoud-by-compound atmospheric levels, spatial distribution and deposition fluxes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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