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Seasonal Variation and Deposition of Atmospheric Organophosphate Esters in the Coastal Region of Shanghai, China

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Abstract

The coastal megacity Shanghai is located in the center of the Yangtze River Delta, a dominant flame retardants (FRs) production region in China, especially for organophosphate esters (OPEs). This prompted us to investigate occurrence and seasonal changes of atmospheric OPEs in Shanghai, as well as to evaluate their sources, environmental behavior and fate as a case study for global coastal regions. Atmospheric gas and particle phase OPEs were weekly collected at two coastal sites - the emerging town Lingang New Area (LGNA), and the chemical-industry zone Jinshan Area (JSA) from July, 2016 - June, 2017. Total atmospheric concentrations of the observed OPEs were significantly higher in JSA (median of 1800 pg m$^{-3}$) than LGNA (median of 580 pg m$^{-3}$). Tris(1-chloro-2-propyl) phosphate (TCPP) was the most abundant compound, and the proportion of three chlorinated OPEs were higher in the particle phase (55%) than in the gas phase (39%). The year-round median contribution of particle phase OPEs was 33%, which changed strongly with seasons, accounting for 10% in summer in contrast to 62% in winter. Gas and particle phase OPEs in JSA exhibited significant correlations with inverse of temperature, respectively, indicating the importance of local/secondary volatilization sources. The estimated fluxes of gaseous absorption were almost 2 orders of magnitude higher than those of particle phase deposition, which could act as sources of organic phosphorus to coastal and open ocean waters.

Key Words

organophosphate esters, atmospheric deposition, seasonal trends, gas-particle
partitioning, coastal region

1. Introduction

Organophosphate esters (OPEs) are toxic, high production volume synthetic organic chemicals, mainly used for decades as flame retardants (FRs) and plasticizers (Hou et al., 2016; Veen and Boer, 2012; Wei et al., 2015). Elevated concentrations of OPEs were detected in both populated and remoted regions, suggesting OPEs spreading globally (Ma et al., 2017; McDonough et al., 2018; Wu et al., 2020). Hence OPEs are increasingly dwarfing other FRs as chemicals of emerging concern (CECs). The environmental behavior and fate of atmospheric OPEs is not well understood, especially for their gas/particle partitioning, which is essential for semi-volatile organic compounds (SVOCs) (Lohmann et al., 2000). Although initial research suggested atmospheric OPEs were predominantly present in the particle phase (Castro-Jimenez et al., 2014; Möller et al., 2011; Salamova et al., 2014), recent modeling results indicated OPEs with specific physicochemical properties and certain atmospheric levels of total suspended particles (TSP) should be mostly in the gas phase (Sühring et al., 2016b; Zhang et al., 2016). Recent changes in methodology, including the usage of glass fiber filter (GFF) instead of quartz fiber filter (QFF) to minimize gas-phase sorption of hydrophilic OPEs and GC-MS/MS systems for instrument analysis, resulted in their higher detection in the gas phase (Okeme et al., 2018; Wolschke et al., 2016).

The coastal region has been reported as the source of many anthropogenic pollutants, however, limited studies focused on the occurrence of atmospheric OPEs in the coastal
region, where OPEs concentrations are possibly controlled by both continental and ocean air masses (Li et al., 2018; Möller et al., 2011; Wolschke et al., 2016). Similar to other SVOCs, the coastal atmospheric OPEs would be transported to the open ocean, deposited to the surface water and further participate in the oceanic biogeochemical cycles (Galbán-Malagón et al., 2012; Galbán-Malagón et al., 2013). Particle phase OPEs might be more easily scavenged along the transport pathway, compared to the dynamic air-sea gas exchange process (Halsall et al., 2001), although there might be higher resistance of particle phase OPEs to OH- radical initiated oxidation (Liu et al., 2014). In addition to the interest in quantifying the oceanic sink of atmospheric OPEs, their bioaccumulation and ecotoxicological impact in aquatic organisms, OPEs could also be a source of organic phosphorus (P) in seawater, and could serve as an additional P sources, especially in P-limited marine environments (Castro-Jimenez et al., 2014; Castro-Jimenez et al., 2016).

The coastal city of Shanghai is a world-renowned metropolis with a high population density, urbanization, and active economic development, and also featuring an internationally important port. The Yangtze River Delta, where Shanghai is located, is one of the dominant FRs production area in China (Zhang, 2014). Moreover, Shanghai also serves as a transport pathway for anthropogenic pollutants moving downstream from mainland China to the open East China Sea (Wang et al., 2019). Therefore, the coastal region of Shanghai represents an ideal site for field measurement of atmospheric OPEs, while results and conclusions can be applied to assess other coastal regions in the world. In this study, atmospheric gaseous and particle samples were weekly
collected and analyzed for OPEs at two coastal sites of metropolis Shanghai for one year by the improved sampling and analysis method, using GFF instead of QFF to collect particle phase and GC-MS/MS systems for instrument analysis. The aims of this study were to: i) provide the first comprehensive assessment of the atmospheric gas and particle phase OPEs in the coastal region of Shanghai; ii) examine the annual/seasonal variation of OPEs and investigate potential influencing factors; iii) explore the gas-particle partitioning of OPEs; iv) estimate their atmospheric loadings to coastal waters.

2. Materials and Methods

2.1. Sampling

Atmospheric samples were weekly collected at two coastal sites of Shanghai, LGNA and JSA, for one year from July, 2016 - June, 2017. Both of these two sites were along the north shore of Hangzhou Bay. One sampling sites is in the Lingang New Area (LGNA), which is located in the southeast corner of Shanghai, with the Yangshan International Hub Port in the south. The other sampling sites is in the Jinshan Area (JSA), which is located in the southwest of Shanghai, representing a typical coastal base of petrochemical industry (Figure 1). Atmospheric OPEs were sampled actively by a high-volume air sampler, equipped with double GFFs (diameter: 150 mm, pore size: 0.7 mm), used to trap particle phase OPEs, followed by a PUF/XAD-2 resin glass column for collection of gaseous OPEs. Both filters and glass columns were stored at -20 °C until analysis. Details on the air sampling information, including sampling date, duration and volume are summarized in Table S1. The meteorological data, including temperature, wind direction, wind speed and relative humidity, were obtained from
2.2. Extraction, Analysis, QC/QA

The pretreatment procedure of air samples followed the method published by Xie et al. (Xie and Ebinghaus, 2008). Briefly, both GFF and PUF/XAD-2 were spiked with 20 ng surrogates, including d_{12}-TCEP, d_{15}-TPhP, and d_{27}-TnBP, prior to separate Soxhlet extractions using dichloromethane (DCM) for 16 h. Then the extracts were concentrated down to 150 µl and spiked with 500 pg ^13C_6-PCB 208 as the injection standard. A gas chromatograph (Agilent 7890A) coupled to a triple quadrupole mass spectrometer (Agilent 7010A, GC-MS/MS), equipped with an Agilent programmed temperature vaporizer (PTV) injector was used for instrument analysis. The MS transfer line and the high sensitivity electron impact ionization source (HSEI) were held at 280 and 230 °C, respectively. The MS/MS was operated in Multiple Reaction Monitoring (MRM) mode. The GC was fitted with two HP-5MS columns (15 m × 0.25 mm i.d. 0.25 µm film thickness, J&W Scientific). The oven temperature program was 50 °C for 2 min, 20 °C min^{-1} to 80 °C, 5 °C min^{-1} to 250 °C, and then 15 °C min^{-1} to 300 °C for 10 min. The quantifier ions are listed in Table S2.

The samples were analyzed for 13 OPEs (Table S3), including three chlorinated OPEs, TCPPs (tris(1-chloro-2-propyl) phosphate, including three isomers), TCEP (tris(2-chloroethyl) phosphate), and TDCPP (tris(1,3-dichloro-2-propyl) phosphate); nine alkyl OPEs, TEP (triethyl phosphate), TnBP (tri-n-butyl phosphate), TiBP (tri-iso-butyl phosphate), TPeP (tripentyl phosphate), TBEP (tris(2-butoxyethyl) phosphate), TEHP (tris(2-ethylhexyl) phosphate), THP (trihexyl phosphate), TPrP (tripropyl...
phosphate), TiPrP (tri-iso-propyl phosphate); as well as one aryl OPEs, TPhP (triphenyl phosphate). The calibration linearity ($R^2$) for each compound is also listed in the Table S2.

All solvents we used were residue grade and purchased from LGC Standards (Wesel, Germany). For QC/QA, in order to remove organic residue, all glassware was baked out at 450°C for 8h, and the GFFs were also baked at 450 °C for 12h prior to deployment. The PUF/XAD-2 resin columns were stepwise cleaned up using DCM, hexane/acetone (1:1, V:V), and methanol for 16 h prior to deployment. Field blanks were collected at both sampling sites by exposing both GFF and PUF/XAD-2 resin glass column to the atmosphere on site and storing them together with the samples. Procedure blanks were performed together with each batch of samples. The method detection limits (MDL) were calculated as the mean plus 3 times of the standard deviation ($3\sigma$) of field/procedure blanks and listed in Table S4. All OPEs we reported in this study were blank corrected and the original data below the corresponding MDL were reported as not detected (n.d.). The recoveries of $d_{12}$-TCEP, $d_{15}$-TPhP, and $d_{27}$-TnBP were $107 \pm 38\%$, $125 \pm 40\%$ and $99 \pm 28\%$, respectively.

2.3. Air Mass Back Trajectory

The air mass origins of the two sampling sites were evaluated using air mass back trajectories calculated by the MeteoInfo Software based on NOAA HYSPLIT model (Draxler and Hess, 1997). Air mass back trajectories were calculated in 6 h steps tracing back the air masses for everyday at the height of 500m. Cluster-mean trajectories were conducted for each month, each season, and the whole year. The cluster-mean air mass
back trajectories for the whole year are displayed in Figure S1.

2.4. Statistical Analysis

In this study, the spearman’s correlation coefficient was calculated to assess the correlations by IBM SPSS 21 software, because the dataset of pollutant concentrations in the environment do not follow a normal distribution. The nonparametric ANOVA test (Kruskal–Wallis Test) were adopted to analyze significant differences of OPE concentrations. A value of 0.05 was used as the p-value to determine statistical significance. Linear regression was performed by Origin 2018. The original data below the MDL was replaced by 2/3 of the blank subtracted MDL value for the statistical analysis.

3. Results and Discussion

3.1. Detection, Comparison and Profile of Atmospheric OPEs

For all samples collected in LGNA and JSA, the detection frequencies of OPEs in gas phase were above 90%, except for TiPrP, TPrP and TBEP in the range of 50% - 61%. For OPEs in particle phase, TiPrP and TPrP were detected in 5% and 14%, TBEP, TEP and TDCPP were detected in 43% - 75%, and the remaining compounds were detected in >90% of all samples (Table S5).

Statistical and detail information of individual OPE concentrations are listed in Table 1 and Table S6. At LGNA, total atmospheric concentrations of the observed OPEs ($\Sigma_{13}$OPEs) ranged from 100 – 3,700 pg m$^{-3}$, with the mean ± standard deviation and median value of 950 ± 950 pg m$^{-3}$ and 580 pg m$^{-3}$, respectively. The median
concentrations of the major OPEs detected were in the decreasing order of TCPPs (110 pg m\(^{-3}\)) > TiBP (73 pg m\(^{-3}\)) > TnBP (68 pg m\(^{-3}\)) > TCEP (48 pg m\(^{-3}\)) > TEP (35 pg m\(^{-3}\)) > TPhP (32 pg m\(^{-3}\)) > TEHP (30 pg m\(^{-3}\)). Generally, concentrations of the gaseous phase \(\Sigma_{13}\)OPEs\(_{gas}\) (range 42 - 3000 pg m\(^{-3}\), mean and median of 650 ± 710 pg m\(^{-3}\) and 390 pg m\(^{-3}\)) were higher than those detected in the particle phase \(\Sigma_{13}\)OPEs\(_{particle}\) (range 13 - 2200 pg m\(^{-3}\), mean and median 300 ± 410 pg m\(^{-3}\) and 150 pg m\(^{-3}\)).

At the more populated JSA site, \(\Sigma_{13}\)OPEs in the atmosphere ranged from 390 – 4,900 pg m\(^{-3}\), with the mean and median concentration of 2000 ± 1100 pg m\(^{-3}\) and 1800 pg m\(^{-3}\), that were significantly higher than those detected in LGNA (p < 0.01). The dominant OPEs observed in JSA were somewhat different from those in LGNA, with the median concentrations in the decreasing order of TCPPs (400 pg m\(^{-3}\)) > TEHP (200 pg m\(^{-3}\)) > TEP (190 pg m\(^{-3}\)) > TPhP (180 pg m\(^{-3}\)) > TiBP (170 pg m\(^{-3}\)) > TCEP (160 pg m\(^{-3}\)), indicating different potential sources from LGNA. The cluster-mean year-round air mass back trajectories indicated that air masses from open ocean accounted for 80% and 38% at LGNA and JSA, respectively (Figure S1). Therefore, OPEs in LGNA were greatly diluted compared with those in JSA. Similar to LGNA, concentrations of the gaseous phase \(\Sigma_{13}\)OPEs\(_{gas}\) (range 120 - 3200 pg m\(^{-3}\), mean and median 1300 ± 800 pg m\(^{-3}\) and 1300 pg m\(^{-3}\)) were generally higher than those detected in the particle phase \(\Sigma_{13}\)OPEs\(_{particle}\) (range 42 - 3500 pg m\(^{-3}\), mean and median 700 ± 730 pg m\(^{-3}\) and 490 pg m\(^{-3}\)) at JSA (Figure S2).

Our results were 1-2 orders of magnitude lower than those detected in urban and suburban Shanghai (\(\Sigma_{7}\)OPEs median 4400 ng m\(^{-3}\) in Baoshan District and 16600 ng m\(^{-3}\)
in Xujiahui District) collected during 2008, although almost all OPEs (95%) were observed in particle phase (Ren et al., 2016). While compared with previous studies that measured OPEs in both gas and particle phase (Table S7), $\Sigma_{13}$OPEs in the JSA were generally comparable with those detected in the inland urban sites, such as Beijing-Tianjin-Hebei (BTH) region, China ($\Sigma_8$OPEs median 1100–1600 pg m$^{-3}$) (Zhang et al., 2019), Greater Toronto Area, Canada ($\Sigma_9$OPEs mean 1800 pg m$^{-3}$) (Saini et al., 2019) and Great Lakes region, US ($\Sigma_{14}$OPEs median 1300 pg m$^{-3}$ in Cleveland and 880 pg m$^{-3}$ in Chicago) (Wu et al., 2020); while $\Sigma_{13}$OPEs in LGNA were comparable with those detected in suburban Beijing ($\Sigma_8$OPEs median 460 pg m$^{-3}$) and rural site in Great Lakes ($\Sigma_{14}$OPEs median 410 pg m$^{-3}$ in Sturgeon Point, New York) (Wu et al., 2020), but were relatively higher than those detected in a seaside village Büsum, Germany ($\Sigma_8$OPEs mean 47 pg m$^{-3}$) (Wolschke et al., 2016) and remote sites of Great Lakes ($\Sigma_{14}$OPEs median 86 and 100 pg m$^{-3}$ in Sleeping Bear Dunes and Eagle Harbor, Michigan) (Wu et al., 2020). Moreover, compared with the open ocean measurements, our results were higher than OPEs observed in the North Huangcheng Island in Bohai Strait ($\Sigma_9$OPEs median 210 pg m$^{-3}$), Bohai and Yellow Seas, China ($\Sigma_9$OPEs median 280 pg m$^{-3}$) (Li et al., 2018), North Sea, Germany ($\Sigma_8$OPEs mean 370 pg m$^{-3}$) (Möller et al., 2011), as well as the North Atlantic to the Arctic ($\Sigma_8$OPEs mean 98 pg m$^{-3}$) (Li et al., 2017). However, compared with OPEs in Northwestern Pacific, concentrations in the JSA were comparable with one offshore sampling sites in Hangzhou Bay ($\Sigma_{11}$OPEs 1900 pg m$^{-3}$), indicated the continuous releasing of OPEs from continent to the offshore region; while OPEs in LGNA were generally comparable with levels in the open Northwestern
Pacific (Na et al., 2020), that further demonstrated OPEs in LGNA might be more significantly affected by the marine air masses.

The compositional profile of atmospheric OPEs is shown in Figure 2 and Figure S3. Among all the 13 detected OPEs, TCPPs was the most abundant compound, with mean contributions of 30 ± 23% and 28 ± 12% to $\Sigma_{13}$OPEs in LGNA and JSA, respectively. Although only three chlorinated OPEs were observed in this study, their contributions to $\Sigma_{13}$OPEs were comparable with the other nine alkyl OPEs at both sites. Specifically, chlorinated and alkyl OPEs averagely contributed 46 ± 20% and 48 ± 19% in LGNA, 44 ± 10% and 44 ± 10% in JSA. While the aryl OPE – TPhP averagely accounted for 6.6 ± 4.3% and 12 ± 5.1% of total OPEs in LGNA and JSA, respectively. The abundance of chlorinated OPEs, especially TCPPs in the atmosphere was consistent with recent measurements in Beijing-Tianjin-Hebei (BTH) of China, Great Lakes of North America, Greater Toronto Area of Canada, as well as previously detected in TSP of Shanghai (Ren et al., 2016; Saini et al., 2019; Wu et al., 2020; Zhang et al., 2019).

3.2. Seasonal Trends and Potential Influencing Factors of Gas and Particle Phase OPEs

As shown in Figure 3, $\Sigma_{13}$OPEs displayed a seasonal variation in LGNA, with the mean concentrations in the order of winter (1300 pg m$^{-3}$) > summer (1100 pg m$^{-3}$) ≈ autumn (1100 pg m$^{-3}$) > spring (530 pg m$^{-3}$). The highest concentrations were at the end of autumn and early winter, with $\Sigma_{13}$OPEs averaging 1700 pg m$^{-3}$ and 1600 pg m$^{-3}$ in November and December. While OPEs also displayed quite high levels in August (mean 1500 pg m$^{-3}$). Different seasonal trends of total OPE concentrations were observed at...
JSA, with the mean concentrations in the order of autumn (2500 pg m$^{-3}$) > winter (2100 pg m$^{-3}$) > summer (1900 pg m$^{-3}$) > spring (1400 pg m$^{-3}$). In addition to the relatively higher $\Sigma_{13}$OPEs shown from October to January (mean 2200 - 3700 pg m$^{-3}$), OPEs also displayed quite high levels in July (mean 2500 pg m$^{-3}$).

It is noticeable that the gas and particle phase OPEs displayed different seasonal variations (Figure 3). OPEs in the gas phase generally exhibited higher concentrations in warmer months, especially in JSA, in contrast to relatively higher concentrations of OPEs in particle phase in colder months. As presented in Figure 4 (Table S8), the ln $C_g$ ($\Sigma_{13}$OPEs) and seven individual OPE compound in JSA exhibited significant and negative correlations with inverse temperature (1/T), indicated the gaseous OPEs were mainly controlled by local sources, as well as some secondary sources, such as volatilization from soil, vegetation and water surface, due to the semi-volatile property of OPEs (Saini et al., 2019; Shoeib et al., 2014). Since OPEs are additive retardants and do not covalently bind to the material to which they are added, higher temperatures may mobilize and promote volatilization and emissions from factories, buildings and vehicles (Marklund et al., 2003). However, the temperature dependence of gaseous OPEs in LGNA were not as obvious as JSA. Only three of thirteen detected OPEs (TCPPs, TPeP and TBEP) exhibited significant and negative correlations with 1/T; While the ln $C_g$ ($\Sigma_{13}$OPEs) and 1/T in LGNA showed negative but insignificant correlations, indicating both local sources and advection from distant sources contributed to air loadings of gaseous OPEs in LGNA. Air mass back trajectories in LGNA also demonstrated the more significant impact of ocean air masses (Figure S1).
A partial dependence of gaseous OPEs on temperature were also displayed in the Great Toronto region (Saini et al., 2019; Shoeib et al., 2014).

For OPEs in the particle phase, the $\ln C_p (\Sigma_{13} \text{OPEs})$ and $1/T$ in both LGNA and JSA showed positive and significant correlations (Figure 4). Most individual OPE compound in the particle phase (eleven in LGNA and twelve in JSA) also showed positive and significant relationship with $1/T$ (Table S8). These phenomena might be due to higher TSP levels during winter-time as well as the intrinsic physicochemical properties, in particular the temperature dependence of octanol-air partition coefficient ($K_{OA}$) of OPEs (Zhang et al., 2019). Low temperature conditions potentially reduced volatilization of SVOCs, but increased cold condensation of OPEs. To some extent, this also explained the detected higher contribution of particle phase OPEs in the polar regions (Li et al., 2017; Möller et al., 2012; Sühring et al., 2016a). Moreover, compared to dynamic air-sea gas exchange process, OPEs in particle phase might be more easily scavenged by atmospheric dry deposition, which has already been demonstrated for other SVOCs, such as polycyclic aromatic hydrocarbons (PAHs) (Halsall et al., 2001; Ma et al., 2013). Hence the temperature dependence of OPEs particle phase in LGNA were not as obviously affected by air masses from open ocean as gaseous OPEs.

As far as the relationships between OPE concentrations and relative humidity were concerned (Table S9), gas phase OPEs at both sites generally did not show significant correlations with relative humidity, and the same was observed for OPEs in the particle phase in JSA. However, the total OPE concentrations and ten individual OPEs in particle phase in LGNA displayed negative and significant relationship with relative...
humidity, further demonstrated that the moist marine air mass brought low concentrations of particle phase OPEs.

3.3. Gas/particle Partitioning

The particle phase fraction of an OPE (Φ) was calculated by equation (1) to evaluate the gas-particle partitioning:

$$\Phi = \frac{C_p}{C_g + C_p}$$

where $C_p$ (pg m$^{-3}$) and $C_g$ (pg m$^{-3}$) are the concentrations of particle phase and gas phase OPEs, respectively.

The calculated values of Φ ranged from 7.0% for TEP to 43% for TEHP in LGNA. While in JSA, Φ values ranged from 4.0% for TEP to 49% for TDCPP, but TiPrP was only detected in the gas phase. The mean contribution of particle phase OPEs ($\Sigma_{13}$OPE$_{\text{particle}}$) were 36% ± 23% and 34% ± 25% to $\Sigma_{13}$OPEs in LGNA and JSA, respectively (Figure S4). These particle fractions were slightly lower than those reported for the German North Sea coast town (45%) (Wolschke et al., 2016), Bohai and Yellow Seas of China (51 ± 21%) (Li et al., 2018), and Great Lake in North America (26%-87%) (Wu et al., 2020), but obviously lower than those in Beijing-Tianjin-Hebei (BTH) region (80 ± 22%) (Zhang et al., 2019), and North Huangcheng Island in Bohai Strait of China (82 ± 17%) (Li et al., 2018). Our calculated Φ values were significantly and positively associated with their $K_{OA}$ and negatively correlated with their subcooled liquid vapor pressure ($\log P_L$) at both sites (Figure 5), supporting the use of $K_{OA}$ and $P_L$ as effective physicochemical properties to evaluate/predict the gas/particle partitioning.
of SVOCs (Liagkouridis et al., 2015; Reemtsma et al., 2008; Sühring et al., 2016b; Wang et al., 2017; Yaman et al., 2020). Modeling results indicated OPEs with log $K_{OA} < 10$ and a log $P_L > -5.0$ ($P_L$ in Pa) should not be limited to the particle phase (Sühring et al., 2016b), consistent with the field measurement results of this study. Interestingly, the average proportion of chlorinated OPEs were relatively higher in particle phase (~55%) than those in the gas phase (~40%) at both sites (Figure 2). That might be due to the overall relatively higher $K_{OA}$ and lower $P_L$ of chlorinated OPEs than aryl- or alkyl-OPEs (Sühring et al., 2016b).

Strong seasonal variations of gas-particle partitions for all OPE compounds were observed; the dependence of gas and particle phase OPEs on temperature were diametrically opposite. The observed $\Phi$ values were higher in winter (median 62%) than those observed in summer (median 10%, Figure 6 and Table S10). Specifically, $\Phi$ values showed significant and positive relationship with $1/T$ in both LGNA and JSA (Figure 4), indicated the high sensitivity of gas-particle partitioning to temperature variations. Higher TSP levels during winter-time and the temperature dependence of $K_{OA}$ of OPEs were also important factors to explain observations.

A previous study suggested that some sampling artifact, specifically the adsorption of hydrophilic gas-phase OPEs on the water film formed on the surface of GFFs, could be causing deviations in partitioning behavior of OPEs (Okeme et al., 2018). Hence, the high relative humidity would result in relatively higher particle phase distribution of OPEs if sampling artifact existed. However, the negative and significant correlations between relative humidity and $\Phi$ value for total OPEs and most individual OPE
compound in both LGNA and JSA (Table S9) indicated the sampling process of this research effectively avoided the possible sorption of hydrophilic OPEs onto water film covering GFFs.

3.4. Dry Particle Deposition Fluxes

Based on the concentrations of OPEs we measured in the particle phase, the dry deposition fluxes ($F_{\text{dry}}$, ng m$^{-2}$ day$^{-1}$) were calculated via equation (2):

$$F_{\text{dry}} = C_p \times v_d$$ (2),

where $C_p$ is the concentrations of particle phase OPEs (pg m$^{-3}$), and $v_d$ is the deposition velocity (cm s$^{-1}$). A value of 0.55 cm s$^{-1}$ was adopted for $v_d$ in the present study, which was recommended for pollutants concentrated in smaller particles over the Yellow Sea (Gao et al., 1992) and used in the coastal sea of China (Li et al., 2018).

In LGNA, the dry deposition fluxes of $\Sigma_{13}$OPEs ranged from 6.0 – 1000 ng m$^{-2}$ day$^{-1}$ (mean: 140 ng m$^{-2}$ day$^{-1}$), and was dominated by TCPPs and TCEP (mean: 35 and 31 ng m$^{-2}$ day$^{-1}$). In JSA, the dry deposition fluxes range of $\Sigma_{13}$OPEs was estimated as 20 – 1700 ng m$^{-2}$ day$^{-1}$, with the mean of 330 ng m$^{-2}$ day$^{-1}$; higher than those of LGNA ($p < 0.01$). TCPPs also exhibited the highest fluxes (mean: 100 ng m$^{-2}$ day$^{-1}$), followed by TEHP, TPhP and TDCPP, with the mean fluxes of 60, 55 and 43 ng m$^{-2}$ day$^{-1}$, respectively. Similar to the seasonal variation of particle phase OPEs, the dry deposition fluxes of OPEs also displayed the highest value during winter and showed significant temperature dependence at both sites (Figure 7).

OPEs detected in JSA and LGNA generally represent the offshore deposition fluxes
into the East China Sea. Compared with other coastal region of China, the dry
deposition fluxes of OPEs from LGNA (median: 70 ng m\(^{-2}\) day\(^{-1}\)) were similar to those
published for the Bohai and Yellow Seas (median: 70 ng m\(^{-2}\) day\(^{-1}\)) (Li et al., 2018), but
higher than previously reported for the South China Sea (16 ± 6.7 ng m\(^{-2}\) day\(^{-1}\)) (Lai et
al., 2015) and those of the North Atlantic and the Arctic Ocean (5.0 ± 4.0 ng m\(^{-2}\) day\(^{-1}\))
(Li et al., 2017). However, OPEs deposited from JSA (median: 230 ng m\(^{-2}\) day\(^{-1}\)) was
higher than above mentioned regions. Therefore, based on the results of this and
previous studies, the dry deposition fluxes of OPEs along the southeast coast of China
were generally in the order of East China Sea > Bohai and Yellow Seas > South China
Sea.

3.5. Estimation of Absorption of OPEs

The diffusive gross absorption \(F_{\text{abs}}, \text{ng m}^{-2} \text{ d}^{-1}\) of gas phase OPEs was estimated via
equation (3):

\[
F_{\text{abs}} = \frac{v_{a/w} \times C_g}{K_{aw,T_2}} \quad (3),
\]

where \(C_g\) is the gas phase concentrations (pg m\(^{-3}\)), \(v_{a/w}\) (cm day\(^{-1}\)) is the overall air-
water transfer velocity, \(K_{aw,T_2}\) is the dimensionless Henry’s Law constant of sampling
temperature \(T_2\). The \(K_{aw}\) value we used were the median value estimated by EPI Suite,
SPARC, Absolv and other available data as listed in the previous study (Sühring et al.,
2016b). Further details on the calculation of \(v_{a/w}\) are provided in Text S1.

In LGNA, the gross diffusive fluxes of \(\Sigma_{13}\)OPEs ranged from 750 – 37,000 ng m\(^{-2}\)
day\(^{-1}\) (mean: 9,300 ng m\(^{-2}\) day\(^{-1}\)), and was dominated by TCPPs and TCEP (mean: 4,200
and 2,500 ng m$^{-2}$ day$^{-1}$). These fluxes were comparable with those in JSA, with range and mean fluxes of 850 – 36,000 ng m$^{-2}$ day$^{-1}$ and 13,000 ng m$^{-2}$ day$^{-1}$. Dominant compounds were TCPP, TCEP and TPhP, with the mean fluxes of 5,000, 3,000 and 2,000 ng m$^{-2}$ day$^{-1}$, respectively (Figure 7). It is noticeable that the fluxes of gaseous absorption were almost 2 orders of magnitude higher than those of particle phase deposition. Similarly, it was estimated that the atmosphere - ocean diffusive exchange of OPEs could be 2–3 orders of magnitude larger than dry deposition across the tropical and subtropical Atlantic, Pacific, and Indian Oceans (Castro-Jimenez et al., 2016). These diffusive absorption fluxes should be interpreted with caution due to the uncertainty of $K_{aw}$ values. Dissolved OPEs in coastal waters and open ocean would volatilize to the atmosphere, and the difference between absorption and volatilization fluxes represent the net diffusive air-water exchange fluxes of OPEs. Previous studies with simultaneous OPE air and water measurements indicated OPEs underwent net gas-phase deposition in the Great Lakes with much human activities in vicinity (Ma et al., 2021), but net volatilization/equilibrium in the open ocean (Li et al., 2017; McDonough et al., 2018).

3.6. Implication for the Biogeochemical Cycles

In addition to atmospheric particle dry deposition and gaseous absorption, OPEs would also enter the marine environment through wet deposition (Rodgers et al., 2018), riverine input (Bollmann et al., 2012; Wang et al., 2015), WWTP effluents (Rodgers et al., 2018; Un-Jung et al., 2017), among others. Considering the continuous large
volume production and application, OPEs will continue to be released into the coastal environment and further transported to the open oceans through long-range atmospheric transport, ocean currents, atmospheric deposition and participate in the oceanic biogeochemical cycles. Recent studies suggested that OPEs could be microbi ally hydrolyzed to inorganic P (Vila Costa et al., 2019), which is the essential limiting factor for eutrophication in some coastal waters, such as East China Sea due to imbalance of nitrogen (N) and P caused by excessive N nutrients (Zhang et al., 2007). P also acts as the limiting nutritional factor even in the open ocean, such as the North Atlantic Ocean (Moore et al., 2013). The input of element P can be further derived based on the molecular weight of specific OPE compound. The estimated average inputs of P to the ocean were 960 ng P m\(^{-2}\) day\(^{-1}\) and 1,400 ng P m\(^{-2}\) day\(^{-1}\) in LGNA and JSA due to gaseous diffusive of OPEs, in contrast to 14 ng P m\(^{-2}\) day\(^{-1}\) and 30 ng P m\(^{-2}\) day\(^{-1}\) in LGNA and JSA due to atmospheric dry deposition, respectively. However, the importance of microbial degradation of anthropogenic OPEs and the resulting effects on nutrient balance and primary productivity based on field measurement and on-site culture remain unknown. Therefore, understanding the biogeochemical cycle of OPEs and the relationship with P cycles in coastal water and open ocean environment, especially the P-limited region still need further systematic discussion.

4. Conclusion

This research demonstrated the abundance of atmospheric OPEs in the representative chemical-industry zone of coastal megacity Shanghai. These OPEs mainly originated
from local volatilization sources, although some were diluted by air masses from open ocean. Strong seasonal variations were observed for both gas and particle phase OPEs, as well as their gas-particle partitions due to the intrinsic physical-chemical properties and the changing TSP levels. Moreover, atmospheric OPEs impact coastal waters, with higher gas phase absorption fluxes than the particle phase deposition fluxes. The inputs of OPEs to East China Sea through wet deposition and riverine discharges need further study. Further research should also be focused on the biogeochemical cycle of OPEs and the relationship with P cycles in coastal water and open ocean environment.

Acknowledgement

We acknowledge funding from the National Natural Science Foundation of China (41976211) and Shanghai Pujiang Talent Program of Shanghai Science and Technology Committee (19PJ1404200). We thank Qi Yang from Shanghai Meteorological Service for providing meteorological data. All data, including sampling information, meteorological data, instrument method, OPE concentrations, physicochemical properties are available in Supporting Information.

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Ma, Y., Xie, Z., Lohmann, R., Mi, W., Gao, G., 2017. Organophosphate ester flame retardants and plasticizers in ocean sediments from the North Pacific to the Arctic Ocean. Environmental Science & Technology 51, 3809-3815.


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measured data. Environmental Science & Technology 50, 6644-6651.


Table 1. Summary statistics for the concentration of gas and particle phase OPEs (pg m$^{-3}$) in LGNA and JSA

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<tr>
<th>Lingang New Area</th>
<th>Compound</th>
<th>n</th>
<th>Gas Phase</th>
<th>Range</th>
<th>Mean ± SD</th>
<th>Median</th>
<th>Particle Phase</th>
<th>Range</th>
<th>Mean ± SD</th>
<th>Median</th>
<th>Gas + Particle Phase</th>
<th>Range</th>
<th>Mean ± SD</th>
<th>Median</th>
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<tbody>
<tr>
<td>TCEP</td>
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<td>n.d. - 810</td>
<td>87 ± 170</td>
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<td>0.87 - 1100</td>
<td>66 ± 180</td>
<td>9.0</td>
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<td></td>
<td>8.0 - 1500</td>
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<tr>
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<tr>
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<td></td>
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<td>24 ± 40</td>
<td>6.5</td>
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</tr>
<tr>
<td>TEP</td>
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Figure 1. Location of two sampling sites in the coastal region of megacity Shanghai
Figure 2. The average proportions of chlorinated, alkyl and aryl OPEs in gas and particle phase at LGNA and JSA (The error bars indicate the standard deviations of the proportion).
Figure 3. Trends of gas phase, particle phase and total OPEs in LGNA (a) and JSA (b)
Figure 4. Natural logarithm of gaseous and particle OPE concentrations ($\ln C_g$ and $\ln C_p$) and particle phase fraction ($\Phi$) as plotted against inverse of
temperature (1000/T, Kelvin) in LGNA and JSA

Figure 5. Mean of particle phase fraction (Φ) as plotted against octanol-air partition coefficient (log $K_{OA}$) (a) and subcooled liquid vapor pressure (log $P_L$, Pa) (b) of OPEs in LGNA and JSA (Log $K_{OA}$ at 298 K are obtained from Sühring et al., 2016b, Wang et al., 2017, Liagkouridis et al., 2015, Yaman et al., 2020; Log $P_L$ at 298 K are obtained from Sühring et al., 2016b, Reemtsma et al., 2008; Both Log $K_{OA}$ and Log $P_L$ were listed in Table S3)
Figure 6. Seasonal variations in particle-phase fractions ($\Phi$) of individual OPEs in LGNA (a) and JSA (b)
Figure 7. Mean dry deposition and absorption fluxes of OPEs to coastal waters of LGNA and JSA