

## Air-seawater gas exchange fluxes of Organophosphate esters in the North Atlantic and Arctic

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### Introduction

Organophosphate esters (OPEs) are a group of man-made industrial chemicals which have been widely applied in many industrial processes and household products, such as flame-retardants, plasticizers, antifoaming agents, and additives in hydraulic, lacquers, and floor polishes.<sup>1</sup> Recently, the production and usage of OPEs have increased continually as OPEs can be used in many cases as substitutes of polybrominated diphenyl ether (PBDEs). From 1992 to 2013, the worldwide OPEs consumption volume increased from 102,000 to 370,000 tons. In 2013, the global usage of flame retardants (FRs) was estimated at 1,950,000 tons, of which approximately 19% were OPEs, which was comparable with brominated flame retardants (BFRs, 21%).<sup>2</sup>

In this work, the air-seawater gas exchange fluxes of OPEs in the North Atlantic and Arctic are estimated, and the comparison of OPEs levels in the Arctic and other global remote areas are performed. This work will improve the understanding of the long range transport and the fate of OPEs in the Arctic ecosystem.

### Materials and Methods

Air samples were collected with a high volume air sampler onboard the FS Polarstern in the northeast Atlantic and the Arctic Ocean (50°N–80°N) in June 2014. Atmospheric particle samples were collected with a glass fiber filter (GFF: diameter, 150 mm, pore size, 0.7 µm) and following with a PUF/XAD-2 resin column for gaseous phase. Each air sample was collected with the high-volume air pump operating at ~15 m<sup>3</sup>/h for 24 to 48 h. Field blanks were prepared by shortly espousing the columns to the sampling site. PUF/XAD-2 and GFF samples were stored at 4°C and -20°C in a cooling room, respectively. 1L seawater samples were collected in glass bottles from the ship's intake system located in the keel (depth: 11 m), and stored at 4°C in a cooling room.

Air sample pretreatment and analysis followed the approach given by Möller et al.<sup>3</sup> Briefly, PUF/XAD-2 and GFFs were spiked with 20 ng of d27-TnBP, d12-TCEP and d15-TPhP as surrogates, and extracted with MX-Soxhlet using dichloromethane (DCM) for 16 h. Eight hundred milliliters (800 mL) of seawater from each sample were performed with liquid-liquid extraction using 50 ml DCM three times. All samples were concentrated down to 150 µl and then spiked with 500 pg <sup>13</sup>C<sub>6</sub>-PCB 208 as the injection standard. The samples were then analyzed using a gas chromatograph couple to a triple quadrupole mass spectrometer (GC-MS/MS) equipped with a programmed temperature vaporizer

(PTV) injector (Agilent, USA).

The equilibrium status (or direction) of the air-seawater gas exchange was estimated based on Eq. (1):

$$f_A / f_W = C_A RT_A / (C_w H) \quad (1)$$

where  $f_A / f_W$  is the fugacity ratio,  $C_A$  and  $C_w$  are the gaseous and dissolved concentrations in air and seawater ( $\text{pg}/\text{m}^3$ ),  $H$  is the Henry's law constant ( $\text{Pa}/\text{m}^3/\text{mol}$ ) corrected by the given water temperature and the salinity. Generally,  $f_A / f_W = 1$  means a system at equilibrium, whereas  $f_A / f_W < 1$  and  $f_A / f_W > 1$  indicate volatilization and deposition, respectively. Considering large uncertainties existing with  $H$  values of OPEs, we assume that the value of  $f_A / f_W$  from 0.3 to 3 showing a system at dynamic equilibrium.<sup>4</sup>

Air-seawater gas exchange fluxes were estimated using the modified Whitman two-film resistance model:

$$F_{AW} = K_{OL} (C_w - \frac{C_A}{H}) \quad (2)$$

where  $F_{AW}$  is the flux ( $\text{pg}/\text{m}^2/\text{day}$ ),  $K_{OL}$  ( $\text{m}/\text{day}$ ) is the gas phase overall mass transfer coefficient.  $F_{AW} < 0$  represent OPEs deposition from air into seawater, and  $F_{AW} > 0$  represent their volatilization from seawater into air.

## Results and Discussion

**OPEs concentrations.** The concentrations of eight OPEs have been investigated in both particle and gaseous phases. The sum concentrations of the eight OPEs ( $\sum\text{OPE}$ ) ranged from 35 to 343  $\text{pg}/\text{m}^3$ , with a mean of  $98 \pm 98 \text{ pg}/\text{m}^3$ . The three chlorinated OPEs accounted for  $88 \pm 5\%$  of the total OPEs. In gaseous phase, the concentrations of  $\sum\text{OPE}$  ranged from 7 to 163  $\text{pg}/\text{m}^3$  (mean,  $40 \pm 53 \text{ pg}/\text{m}^3$ ). In the particle phase, the range was from 29 to 180  $\text{pg}/\text{m}^3$  (mean,  $58 \pm 48 \text{ pg}/\text{m}^3$ ) for  $\sum\text{OPE}$  concentration. TCEP was the dominant OPE in both the gaseous and particle phases. Particle phase OPEs contributed to  $67 \pm 17\%$  of the total OPEs on average.

**Air-seawater gas exchange fluxes.** The equilibrium status ( $f_A / f_W$ ) and fluxes ( $F_{AW}$ ) of air-water gas exchange for four major OPEs (TCEP, TCPP, TiBP, TnBP) were estimated in this study, the results are shown in Figure 1. The  $f_A / f_W$  values of TCEP were from  $3 \times 10^{-5}$  to 0.7, indicating that volatilization from seawater to air dominated in all samples. The fluxes of TCEP ranged from 4 to 1019  $\text{ng}/\text{m}^2/\text{day}$ . For TCPP, there was a net volatilization directions, with all  $f_A / f_W$  values lower than 0.3, and the fluxes ranged from 60 to 12131  $\text{ng}/\text{m}^2/\text{day}$ . As to TiBP and TnBP, the  $f_A / f_W$  values were all lower than 0.3, with the fluxes ranged from 7 to 616  $\text{ng}/\text{m}^2/\text{day}$  for TiBP and 3 to 919  $\text{ng}/\text{m}^2/\text{day}$  for TnBP. These results indicated air-sea exchange processes may interfere with long-range transport potential for OPEs and drive their remobilization in Arctic summer (or ice free period).

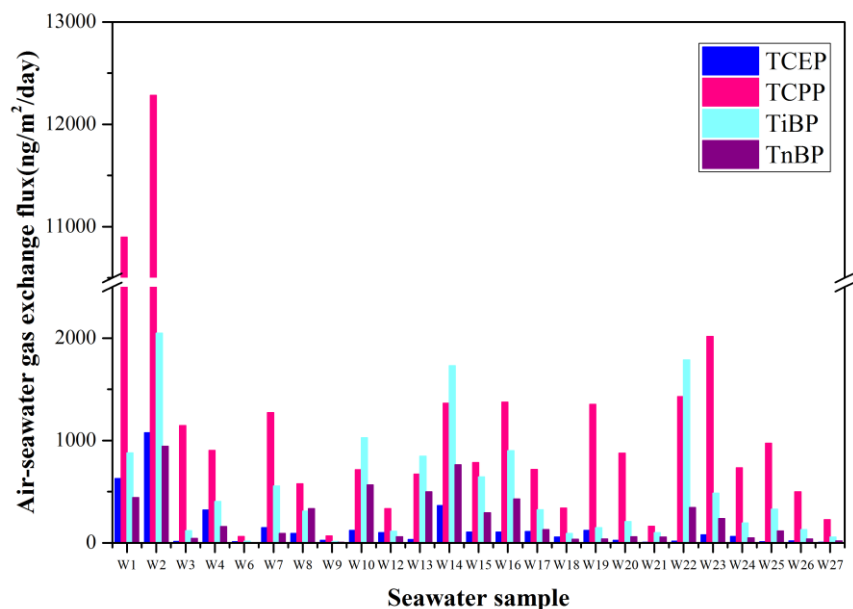


Figure 1. Air-water exchange fluxes of four major OPEs over the sea in the North Atlantic and the Arctic

**Comparison of OPEs levels in the air of global remote areas.** OPEs concentrations that measured in the air of different remote areas are shown in Figure 2. Chlorinated OPEs (TCPP, TCEP, and TCDP) have been reported as dominating OPEs congeners in different geographic regions, except from an Arctic site. The mean total OPEs concentrations varied from 100  $\text{pg}/\text{m}^3$  in this study to 2800  $\text{pg}/\text{m}^3$  over Black Sea.<sup>5</sup> High concentrations ( $>1000 \text{ pg}/\text{m}^3$ ) were presented in three areas, i.e. East Asia like the East China Sea and Japan Sea,<sup>6,7</sup> Europe such as Mediterranean Sea and Black Sea,<sup>5</sup> North America like the Great Lakes.<sup>8</sup> The Western Europe, North America and East Asia are the highest consumption regions for flame retardants.<sup>9</sup> In 2013, the usage of OPEs in Western Europe (110,000 tons) and North America (70,000 tons) accounted for approximately 30% and 20% of worldwide usage, respectively. The consumption of OPEs in China was 179,000 tons in 2012.<sup>10</sup> But relatively low concentrations were also detected in those areas like 100  $\text{pg}/\text{m}^3$  over the South China Sea and 400  $\text{pg}/\text{m}^3$  over the North Sea.

The ratios of TCEP to TCPP mean concentrations were  $<1$  in Europe, which was adverse in East Asia (range from 1.8 to 15). This might result from TCEP has been replaced by TCPP in the Europe while it was continue used in East Asia.<sup>11</sup> In indoor air and dust, the TCEP/TCPP ratios are generally  $<1$  in Europe, while, it depends in East Asia, as the ratios  $>1$  in southern China<sup>12</sup> and Beijing<sup>13</sup>,  $<1$  in Hangzhou of China<sup>14</sup> and a new house of Japan,<sup>15</sup>  $\sim 1$  in a lab of Japan<sup>15</sup>. However, the ratios are all found  $>1$  in polar areas and open oceans except the Indian Ocean (0.9).<sup>7</sup> This might result from the slower photochemical degradation of TCEP than TCPP in the atmosphere.<sup>16</sup> The half-life of TCEP (17.5 h) is two times as long as TCPP (8.6 h) in gaseous phase, while lack data for particle phase in the atmosphere.

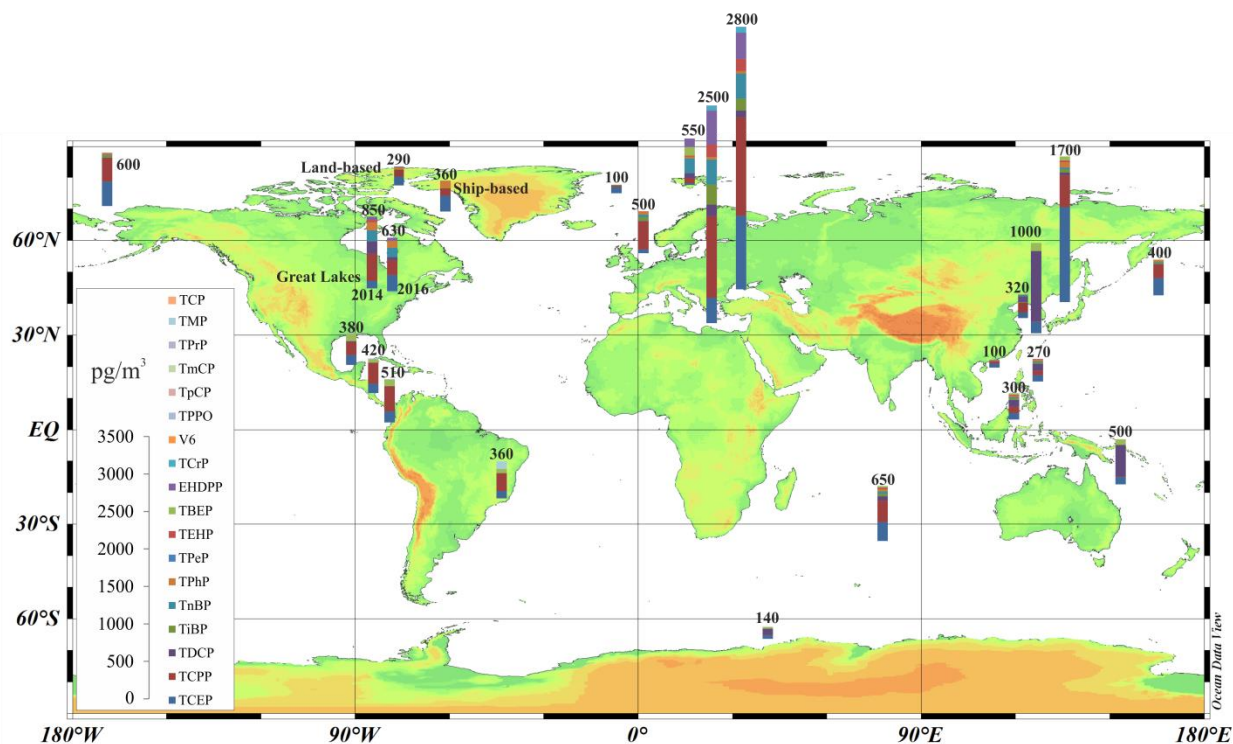


Figure 2. The OPEs concentrations in the atmosphere in different remote areas

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