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Response of polar regions to emerging organic pollutant organophosphorus esters (OPEs), a review

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Abstract Polar regions are free from major anthropogenic impact due to their remoteness. However, certain pollutants can be transported there via atmospheric and/or oceanic circulations. Here we present an overview of current research on organophosphorus esters (OPEs) in polar regions by reviewing the literature on distribution, source and transport of OPEs. Current research on OPEs reveals significant anthropogenic influences in both polar regions. As well as the expected occurrence in the Arctic, OPEs were found on the Antarctic Ice Sheet up to 650 km from the coast, and the OPE concentrations were higher at high elevation due to cold climate retention. The immediate source of OPEs for inland Antarctica might be the Southern Ocean surrounding the continent, where OPEs in aerosols and seawater showed comparable concentrations to remote areas in the European Arctic. A positive correlation between aerosol OPEs in the open water and the surface vortex of ocean currents indicates that these compounds may be transported and accumulated in the ocean currents. The Antarctica Circumpolar Current accumulates them in the marginal seas of Antarctica.

Keywords Antarctica, organophosphorus esters, Southern Ocean, ice sheet

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1 Introduction

Polar ecosystems are vulnerable mainly due to their physical environment and lack of complexity (Block, 1994). However, despite its pristine and unspoiled features (Hughes et al., 2011), Antarctica is also threatened by contaminants from tourism and scientific expeditions (Stewart et al., 2005), as well as long range transported pollution (Bargagli, 2006). Though it is the only continent where indigenous people and industry are absent, industrial pollutants could be transported to Antarctica via various pathways, as humanity has become the dominant environmental force (Caro et al., 2012). The detection of dichlorodiphenyltrichloroethane (DDT) and other organochlorine pesticides in Antarctica (Sladen et al., 1966; Peterle, 1969) initiated the concept of persistent organic pollutants (POPs). POPs are defined as toxic organic pollutants which are subject to long-range transport, degradation resistance and bioaccumulation (Jones and De Voogt, 1999). In the subsequent decades, much research was done in this field (Weber and Goerke, 2003; Kallenborn et al., 2013; Vecchiato et al., 2015), and an expanding

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human footprint was uncovered (Penna, 2010), especially in Antarctica (Hughes et al., 2013). Concerns were also raised about the impact of scientific expeditions and other anthropogenic impacts on Antarctica (Jabour, 2009; Pertierra et al., 2013). Considering that DDTs has been phased out from the 1970s, and additional POPs have been banned since 2004 as the Stockholm Convention came into effect, they become more and more inappropriate for evaluating current response of remote regions on anthropogenic impact (Wu et al., 2011; Dodson et al., 2012). Therefore it might be helpful to investigate new organic pollutants in Antarctica.

New chemicals are being continuously introduced to the environment. Some of these new compounds may qualify as POPs, but time is needed for these classifications to take effect. For example, some long-chain perfluoroalkylated compounds were found to be toxic after several decades of market production (Hekster et al., 2003; Lau et al., 2004). Now they are detected in polar regions (Smithwick et al., 2006; Dietz et al., 2008; Benskin et al., 2012), indicating their global distribution. Octa-polybrominated diphenyl ethers (PBDEs) and other flame retardants were listed in the Stockholm Convention in 2009, and since have been phased out by most European and American countries. As alternatives, organophosphorus esters (OPEs) were introduced to the plastic industry (Stapleton et al., 2012). These flame retardants and plasticizers were added to almost every plastic product (Stapleton et al., 2009). Unlike common additives, OPEs are only physically mixed with plastic products (Reemtsma et al., 2008). Hence, they are readily released to the environment due to lack of chemical bonding.

Similar to PBDEs, OPEs have also been found to be toxic in recent years, e. g. tricresyl phosphate (TCrP) can cause reproductive effects (Latendresse et al., 1993), triphenyl phosphate (TPhP) damages the skin and nerve conductivity (Saboori et al., 1991), and tris(2-chloroethyl) phosphate (TCEP) is carcinogenic (Umezu et al., 1998; Ren et al., 2008). As OPEs were found in human urine (Möller et al., 2004) and breast milk (Sundkvist et al., 2010), they could be a potential health risk to the public. Degradation experiments also showed some persistence of OPEs, especially chloro alkyl-phosphates like TCEP (Kawagoshi et al., 2002). A mass balance model based on measured OPE concentrations in the North Sea waters revealed infinite half-lives of TCEP (Andresen et al., 2007), which further confirmed its persistence. Recent research has revealed their presence in various indoor environments (Carlsson et al., 1997; Sjödin et al., 2001; Marklund et al., 2003; Hartmann et al., 2004), as well as in precipitation and surface water in Europe (Fries and Püttmann, 2001; Andresen et al., 2004; Regnery and Püttmann, 2009; Regnery and Püttmann, 2010b), seawater and aerosol in the North Sea (Andresen et al., 2007; Möller et al., 2011), montane lakes in Italy (Bacaloni et al., 2008) and even in polar regions. These studies were mainly conducted in Europe and North America, where intensive production and usage could be assumed, and the long range transport of OPEs is still to be investigated. In fact, it is possible to find OPEs in polar regions, despite remoteness from local industry, because semi-volatile compounds like OPEs can undergo global distillation and condense in polar regions via cold condensation (Wania and Mackay, 1996). It is also possible that these compounds can be enclosed in secondary organic aerosols and transported to polar regions with them (Zelenyuk et al., 2012).

2 Analytical methods for OPEs

As OPEs are ubiquitous in the indoor environment (Hartmann et al., 2004; Wensing et al., 2005) and almost any plastic products (Stapleton et al., 2011), extra caution is needed for their quantitative analysis. Aerosol samples are the most common matrix for OPE investigation, with atmospheric particulate samples collected on glass fiber filters and quartz fiber filters, in order to avoid any plastic. The filters were usually baked at over 400°C to remove any possible OPEs during manufacture of the filters (Quintana et al., 2007). In some cases, aerosol samples were sonicated in water to extract OPEs (Cheng et al., 2013b). In other cases, Soxhlet extraction was used to extract OPEs in the particulate samples (Möller et al., 2012; Salamova et al., 2014). A clean-up step could be employed to purify the OPEs with deactivated silica gel (Möller et al., 2012), but it is not always necessary (Sühring et al., 2016),

OPEs have also been investigated in snow samples (Cheng et al., 2013a), biota samples (Hallanger et al., 2015) and sediment samples (Ma et al., 2017). The snow samples were collected with perfluorinated tools and containers, then treated in a similar way to the extracted aerosol samples (Cheng et al., 2013a). Sediment samples were collected with metal tools to avoid possible contamination from plastic. The samples were extracted and analyzed in a similar way to the aerosol samples mentioned above (Ma et al., 2017). Biological samples were more complex. Blood samples were centrifuged and plasma was sonicated with formic acid:2-propanol (4:1, v/v), then mixed with water:2-propanol (4:1, v/v) and diluted with water. The precipitated fraction was loaded onto HLB SPE cartridges that were conditioned with 5% methanol, then OPEs were eluted with dichloromethane:isooctane (3:1). Other biota samples were homogenized and extracted with dichloromethane:aceton (1:1, v/v) in an accelerated solvent extraction (ASE) device. Acetone was removed by evaporation after extraction and then fractionated on a silica gel column in isooctane. The matrix was removed with 12 mL of 15% diethyl ether in hexane, then the cyclic OPEs were eluted with 30 mL of 15% diethyl ether in hexane, and finally aliphatic OPEs were collected with 30 mL acetone (Hallanger et al., 2015).

The OPEs are usually quantified with gas chromatography − mass spectrometry (GC-MS) (Möller et al., 2012; Salamova et al., 2014) or liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) (Cheng et al., 2013a; Cheng et al., 2013b; Hallanger et al., 2015). Isotopic surrogates and internal standards are often spiked into samples for quality control (Möller et al., 2012; Hallanger et al., 2015). Because OPEs are ubiquitous in indoor environments and even chemical laboratories (Rodríguez et al., 2006; García-López et al., 2008), field and experimental blanks are usually employed to evaluate possible contamination in sampling and analysis procedures. Aerosol field blanks were collected by passive sampling without the air pump on (Möller et al., 2012) or by retrieving the filter immediately after putting it on the sampler (Cheng et al., 2013b). For the snow samples, field blanks were collected by leaving purified water in an open sample bottle when collecting field samples. The field blanks were then sealed and analyzed in the same way as the snow samples (Cheng et al., 2013a). Experimental blanks are included with high-purity water with actual samples in most studies. A group of three experiment blanks are often processed and the limit of detection is defined as the mean blank value plus three standard deviation(Sühring et al., 2016), although in some studies the mean blank value was used as limit of detection while the mean blank value plus three standard deviation was used as a limit of quantification (Cheng et al., 2013a).

3 OPEs in the Arctic

The Arctic is more prone to industrial pollution, such as OPEs, than Antarctica because of its proximity to larger populations and industry in the northern hemisphere (Candelone et al., 1995; Akimoto, 2003). Indeed, OPEs were found in the Canadian Arctic and European Arctic in numerous environmental samples. Besides sub-Arctic investigations on seawater (Bollmann et al., 2012) and aerosol samples (Möller et al., 2011) in the North Sea, much work has also been done in the European high Arctic, especially in Svalbard.

Salamova et al. (2014) measured 13 OPEs and 45 brominated and chlorinated flame retardants (BFRs) in 34 atmospheric particle samples from Longyearbyen on Svalbard, where a coal mining community of ~2100 resident is located. Five out of 13 measured OPEs were not detected in any samples. Nonchlorinated OPEs tri-n-butyl phosphate (TnBP) and 2-ethylhexyl diphenyl phosphate (EHDPP) were the predominant congeners, and were detected in all the samples. The total concentrations of OPEs were two orders of magnitude higher than total BFRs. This is not unexpected because OPEs are one of the major alternative groups of chemicals for BFRs, which are gradually being discontinued. However, this study was conducted near a relatively large human settlement, and may not represent OPE occurrence in other remote regions in the Arctic.

In a study of transported OPE contamination, Hallanger et al. (2015) reported ten OPEs in capelins, kittiwakes, gulls, seals and polar bears from the Svalbard Archipelago, with a further four OPEs that did not show up in any of their samples. Animal tissue, egg, liver and blood samples were collected and kept frozen until analysis. The comprehensive detection frequencies of each compound were between 5.3% and 17%, showing a minor impact of OPEs on Svalbard biota. However, one of the most important food sources for Arctic sea birds and mammals, the fish species capelin, had higher or similar OPE concentrations compared to sea birds and mammals. This result indicated that OPEs in this study were not subject to significant biomagnification, although the authors did raise the concern that the selected tissues might not be appropriate for assessing biomagnification.

The Bering Strait is another Arctic region that may experience high anthropogenic pollution, because it is between two major continents, Asia and North America. Eight OPEs were investigated in aerosol samples in this region by Möller et al. (2012). They found TCEP and tri(chloropropyl) phosphate (TCPP) were the dominant OPEs in Arctic aerosols, and air mass back trajectories showed clear origin from the Asian continent. In sediment samples from the same region, Ma et al. (2017) also found TCEP and TCPP were major contributors to an increase in total OPEs towards the Central Arctic Ocean, suggesting that they were more prone to long range transport. By comparing their OPE results with PBDE results, these authors suggested a higher efficiency of OPEs for transport to, and accumulation in, the remote Arctic. Given the continued production and use of most OPEs, remote marine sediments may be a major repository for them.

In North America, Sühring et al. (2016) investigated 14 OPEs in 117 air samples from research stations (land-based) and ship-based cruises in the Canadian Archipelago and vicinity. They found the total OPE concentration to be a few hundreds pg·m^{-3}. In general, chlorinated OPE concentration were around two orders of magnitude higher than that of nonchlorinated OPEs, and the difference in total concentrations of these two groups was statically significant (p<0.05, student t test). This finding suggested chlorinated OPEs may be more persistent than nonchlorinated OPEs (Kawagoshi et al., 2002; Andresen et al., 2007) and have a larger amount of production and usage (van der Veen and de Boer, 2012). However, there were two exceptions, namely TPhP (triphenyl phosphate) and TnBP, which are both nonchlorinated OPEs but were found at high concentrations. TPhP was found at high concentrations in ship-based samples while TnBP concentrations were high in land-based samples. TnBP was quantified in only one ship-based sample. Similarly, EHDPP and tris-meta-cresyl phosphate (TmCP) were also quantified in about 70% of land-based samples, but in less than 20% of ship-based samples. The authors argued that these three OPEs had local sources like airports and settlements, rather than long-range transport. In geographic trends, chlorinated OPE concentrations were high near major river mouths, and decreased at higher latitude in open water. In contrast, nonchlorinated OPEs did not show any spatial patterns in open water. TPhP was the only compound that showed a significant temporal trend (*p*=0.044) with a doubling time of 335 d, while tris(2-ethylhexyl) phosphate (TEHP) was marginal with a 31% annual decrease (*p*=0.075). Sühring et al. (2016) suggested three potential transport pathways to the Arctic for OPEs, namely local source, river transport and atmospheric transport for TnBP, chlorinated OPEs and TPhP, and nonchlorinated OPEs, respectively.

4 Detection of OPEs in Antarctica

Unlike the Arctic region, Antarctica is far from major anthropogenic pollution, and the population and industry are much smaller in the Southern Hemisphere (Candelone et al., 1995; Akimoto, 2003). However, OPEs have also been found in remote areas of the Southern Hemisphere, even on the Antarctic Ice Sheet. During the 27th Chinese National Antarctic Research Expedition (CHINARE), a total of 120 surface snow samples were collected at 10 km intervals along the transect between Zhongshan Station (69°22′24″S, 76°22′40″E) and Dome A (80°22′51″S, 77°27′23″E) in the austral summer from 2010 to 2011 (Figure 1). A route was established for multiple year expeditions, and the vehicles travelled 30 m downwind of this route, while samples were collected at least 50 m upwind in order to exclude any possible contamination. Fresh snow samples were collected directly with 500 mL bottles and kept frozen before analysis. OPEs were concentrated by passing melted snow through HLB Solid Phase Extraction (SPE) columns. A 3 mL Waters Oasis HLB SPE column was first activated with 3 mL acetonitrile and then with 3 mL of purified water. The melted snow sample was then passed through the column at a speed of no more than 3 mL·min^{-1}. No breakthrough experiment was conducted because the expected OPE concentrations in snow samples were very low, hence the capacity of the columns was assumed to be enough. Field blanks were processed for each ten samples, by leaving purified water in an open sample bottle when collecting field samples. The field blanks were then sealed and analyzed in the same way as the samples. OPE concentrations were determined with an HPLC-tandem-MS system equipped with a Waters XTerra C18 column (2.1 mm by 150 mm, 5 μm). A detailed description of this method can be found in our previous paper (Cheng et al., 2013a). Three experiment blanks were run with Milli-Q water accompanying each seven samples. The limit of detection of a specific sample was defined as the average concentration of corresponding blanks, and the limit of quantification was calculated as the average of corresponding blanks plus three times of standard deviation.

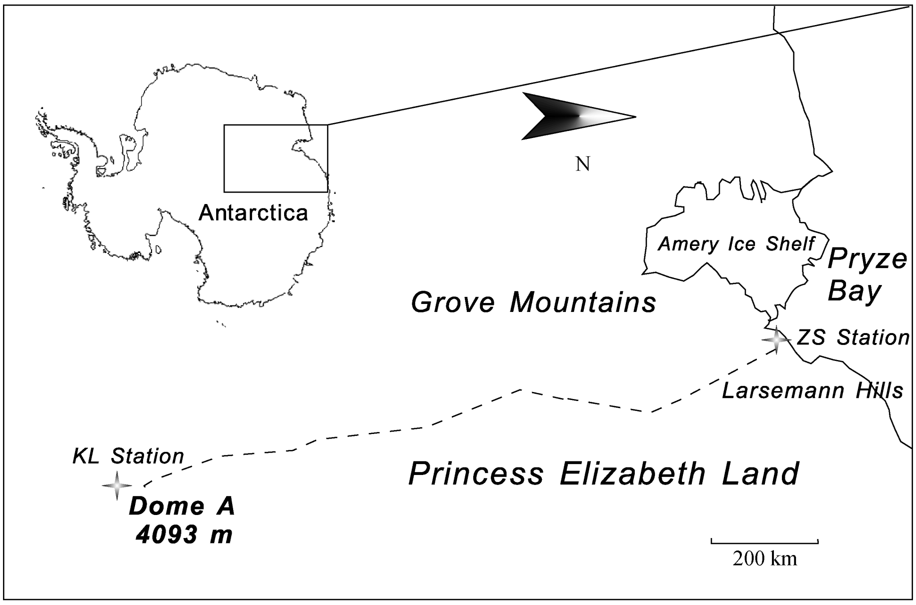

Figure 1 Sample locations on the Antarctic Ice Sheet. Dot line indicates the set route for multi years expedition, surface snow samples were collected at 10 km intervals. Vehicles were travelling at least 30 m downwind while samples were collected at least 50 m upwind. ZS Station = Zhongshan Station, KL Station = Kunlun Station.

Twelve OPEs were analyzed, but five of them were not detected in any of these samples (Table 1). TPhP, TPrP and EHDPP were detected in less than 40% of samples, and the first two were not quantified in any samples. This result implied limited long range atmospheric transport of the eight compounds listed at the bottom of Table 1. The other four OPEs, namely TCPP, TCEP, TBP and TBEP were detected in most samples, and TCEP was quantified in more than half of the samples. The difference in detection rates of these analyzed OPEs might be ascribed to their different physical and chemical properties. Alkyl and aryl OPEs are subject to degradation in the environment: their half-lives in seawater are only a few months (Andresen et al., 2007). Hence TMP, TEP, TPhP and TPrP may degrade during transport to Antarctica. Furthermore, TMP and TEP have low molecular weight and they are the most volatile of the analyzed compounds (Dobry and Keller, 1957; Meylan and Howard, 1993). They might enter the atmosphere again after deposition, leaving an insufficient amount in the snow to be detected. In contrast, TDCP has a high molecular weight with a chloro substituent (Meylan and Howard, 1993), and hence might not be volatile enough to transport to the inland ice sheet. TnBP and TCrP concentrations were higher in the experiment blanks than those in the samples, probably due to contamination from the high-purity water instrument (García-López et al., 2008). TBP concentrations were high in both blanks and samples, hence this compound was detected in most samples but only quantified in less than 20% of samples.

Table 1 OPEs analyzed in snow samples from the Antarctic Ice Sheet.

Abbr.	Full name	Ion fragments/($m \cdot z^{-1}$)	Quantified	Detected
TCEP	Tri(2-chloroethyl) phosphate	233, 177	60/120	120/120
TnBP	Tri-n-butyl phosphate	186, 113	21/120	118/120
EHDPP	2-ethylhexyl diphenyl phosphate	152, 251	11/120	11/120
TBEP	Tributoxyethyl phosphate	299, 199	6/120	115/120
TCPP	Tri(chloropropyl) phosphate	99, 174, 176	1/120	120/120
TPrP	Tripropyl phosphate	141, 99	0/120	43/120
TPhP	Triphenyl phosphate	215, 77	0/120	8/120
TCrP	Tricresyl phosphate	165, 243	0/120	0/120
TDCP	Tri(dichloroporpyl) phosphate	191, 99	0/120	0/120
TEHP	Tri(2-ethylhexyl) phosphate	113, 99	0/120	0/120
TEP	Triethyl phosphate	126, 99	0/120	0/120
TMP	Trimethyl phosphate	109, 79	0/120	0/120

Notes: “Detected” was defined as the average concentration of three corresponding blanks, and “Quantified” was defined as the average of three corresponding blanks plus three times of the standard deviation.

TCEP had the highest quantification rate among the analyzed OPEs, being quantified in 50% of samples. In particular, it was quantified in 60 out of the first 61 samples closest to Zhongshan Station, but it was not quantified in any samples further towards Dome A. As there were no other significant pathways to transport TCEP to the inland ice sheet, it can be reasonably postulated that TCEP was transported there via atmospheric circulation, either in gaseous phase or combined with particulate matter (Zelenyuk et al., 2012). Hence the significant difference between inland samples and coastal samples could be an indication of zones which received different atmospheric deposition. The change point of TCEP concentration was at around 650 km from the coast, at 2770 m above sea level. Oxygen stable isotopes in Antarctic snow also show an abrupt change at around 2000 m elevation (Masson-Delmotte et al., 2008), suggesting different sources of water vapor for the snow that falls in inland and coastal zones. Oxygen isotopes showed similar patterns to TCEP along the Dome A transect (Ding et al., 2010; Xiao et al., 2013). Multi-year accumulation monitoring suggested different accumulation rates on the two sides of the 600—700 km zone (Ding et al., 2011; Ding et al., 2015). Studies on inorganic ions along the transect between Zhongshan Station and Dome A also revealed large fluctuations of sea salt ions and marine sulfate at around 700 km from the coast (Li et al., 2015b). Formate and acetate profile along this transect also showed different distribution styles around the 600 km point (Li et al., 2015a). All these, despite their significantly different properties, indicate distinctly different origins of atmospherically transported material between the inland and coastal Antarctic Ice Sheet. The TCEP concentration in the three samples closest to coast were among the highest, but the concentration in the fourth sample was among the lowest. This difference could be ascribed to the possible influence of intruding cyclones in the coastal areas.

TCEP concentrations in the snow samples showed a significant positive correlation with elevation (Figure 2). Numerous studies have revealed the accumulation of semi-volatile pollutants at high elevation and cold environments (Blais et al., 1998; Blais et al., 2003; Davidson et al., 2003; Demers et al., 2007). Hence the high TCEP concentrations at high altitudes could be a result of cold climate retention (Wania and Mackay, 1993). Research on OPEs in alpine lakes also found several-fold higher concentrations in remote montane lakes than those at lower altitudes (Regnery and Püttmann, 2010a). With a rapidly changing global climate and melting polar ice (Rothrock et al., 1999; Parkinson and Comiso, 2013; Paolo et al., 2015), the condensed TCEP and other OPEs may be an important legacy pollutant in the future, either as free chemicals or as a result of the released microplastic (Obbard et al., 2014).

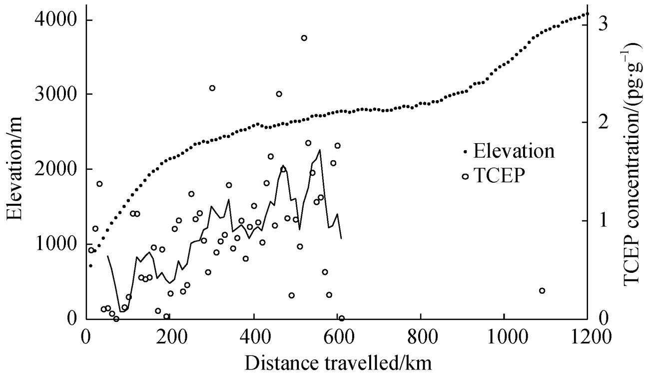

Figure 2 Distribution of TCEP at the transect from Zhongshan Station to Dome A. Elevations are in solid dots, TCEP concentrations are in open circles. Solid line indicates 5-point moving average of TCEP concentrations.

5 Source of OPEs in Antarctica

OPEs are semi-volatile compounds (Meylan and Howard, 1993; Mäkinen et al., 2009), their relatively short atmospheric half-life could not support their long-range transport to Antarctica from major northern hemispheric sources. Alternatively, they may be absorbed or enclosed in secondary aerosols or other particulate matter and transported with these materials (Hallquist et al., 2009; Zelenyuk et al., 2012; Waxman et al., 2013). This mechanism may explain the presence of alkyl OPEs in organic particulates from Terra Nova Bay (Ciccioli et al., 1994). Their most likely carrier is plastic debris in the ocean, which contains a few percent of OPEs (Stapleton et al., 2009). The amount of plastic debris dumped annually into the ocean is estimated to be in the millions of tons in the United States alone, and it comprises 40% to 80% of floating debris in the oceans (Thompson et al., 2004; Barnes et al., 2009). This debris is carried globally by ocean circulations and found on remote coasts (Derraik, 2002; Ryan et al., 2009; Browne et al., 2011), even in sub-Antarctic (Walker et al., 1997; Convey et al., 2002). Thus, OPEs may reach remote regions with floating debris in the ocean like other chemical contaminants (Teuten et al., 2009; Van et al., 2012). Furthermore, plastic debris was found to accumulate in ocean gyres (Law et al., 2010). Up to five tons of plastic debris were retrieved in one square kilometer at the center of the North Pacific Central Gyre in the 1970's (Colton et al., 1974), which is remote from any continents or major population. Recent research revealed more than 200000 pieces of plastic in the Atlantic subtropic gyre, and the amount of plastic debris was three times higher in the center of the gyre compared to the periphery (Law et al., 2010). We suggest that the high density of plastic debris in the ocean gyres may act as local source of OPEs to the atmosphere.

In order to examine this hypothesis, we analyzed seawater and aerosol samples collected on a circumpolar cruise of the R/V *XUE LONG* icebreaker in the Southern Ocean. Aerosol samples were collected on pre-baked glass fiber filters with a high-volume air sampler. The sampler was installed at the bow of the ship, in order to eliminate any possible pollution from the ship. In addition, an automatic control system with a wind sensor shut down the sampler when wind was coming from behind. The aerosol filters were stored in a fridge until analysis. 70 square centimeters of each filter was cut off and sonicated to extract OPEs. Field blanks were employed to control data quality. Instrumental analysis of the aerosol extracts was similar to that for snow samples. Details of the analytical method can be found in Cheng et al. (2013b).

Though the OPE concentrations in the Southern Ocean were much lower than those in East Asia and New Zealand, they were still comparable to results from remote regions in the northern hemisphere (Möller et al., 2011; Möller et al., 2012) (Figure 3). This result indicated a potential local source of atmospheric OPEs. No significant correlations were found between OPE concentrations and climatic parameters such as air temperature, pressure or wind speed, suggesting that they are not affected by atmospheric conditions, which confirmed that they were not subject to long range atmospheric transport. Relatively high OPE concentrations were found near expedition stations, especially near the Antarctic Peninsula, where dozens of stations are located (Figure 3). However, the OPE concentrations dropped significantly once the ship left the Peninsula, which further supported a lack of long range atmospheric transportation. Therefore, OPE emissions from the expedition stations could not explain the widespread presence of OPEs in the Southern Ocean. Furthermore, high concentrations of OPEs were found in the open water of the Weddell Sea and the Bellingshausen Sea, where no expedition stations are located (Figure 3).

Besides the atmospheric circulation, ocean currents are another important pathway of long range transportation of pollutants (Wania, 2006; Czub et al., 2008). The Antarctic continent is surrounded by a circumpolar ocean current, which forms a dynamic barrier of floating debris (Schmitz, 1996). Plastic debris is trapped at Antarctic shorelines, and does not easily escape once it enters this current (Turner et al., 2009). Furthermore, the Antarctic Circumpolar Current forms local gyres, among which the most important are the Ross Gyre and Weddell Gyre (Gouretski, 1999; Michels et al., 2002). Relatively high OPE concentrations were found in these two gyres (Figure 3), supporting the hypothesis that ocean gyres could act as the local source of atmospheric OPEs. A correlation between ocean surface vorticity and OPE concentrations further confirmed the relationship between ocean gyres and OPEs. With local sources contributing to OPEs in the atmosphere, OPEs can be transported to the Dome A traverse route via local atmospheric circulation. Hence, we conclude that transport of plastic debris by ocean surface currents is a significant mechanism for OPEs to reach Antarctica.

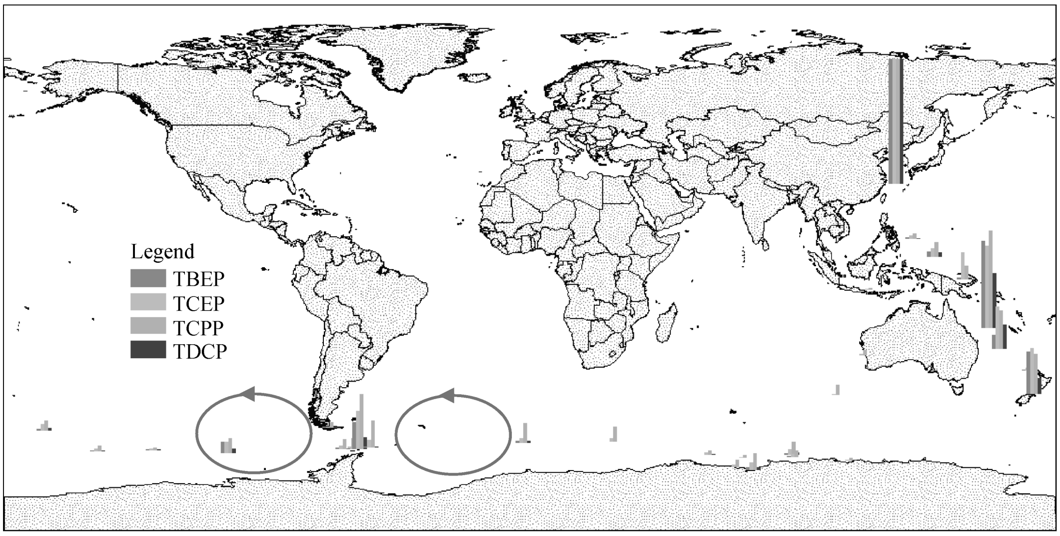

Figure 3 Relative OPE concentrations in aerosol samples in the Southern Ocean and West Pacific. The concentrations of each OPEs in the sample collected at Shanghai Port, China was used as 100% and concentrations in the other samples were normalized to them. Blue circles indicate major ocean gyres in the Southern Ocean

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References

Akimoto H. 2003. Global air quality and pollution. Science, 302(5651): 1716–1719

Andresen J A, Grundmann A, Bester K. 2004. Organophosphorus flame retardants and plasticisers in surface waters. Sci Total Environ, 332(1–3): 155–166

Andresen J A, Muir D, Ueno D, et al. 2007. Emerging pollutants in the North Sea in comparison to Lake Ontario, Canada, data. Environ Toxicol Chem, 26(6): 1081–1089

Bacaloni A, Cucci F, Guarino C, et al. 2008. Occurrence of organophosphorus flame retardant and plasticizers in three volcanic lakes of Central Italy. Environ Sci Technol, 42(6): 1898–1903

Bargagli R. 2006. Antarctic ecosystems: environmental contamination, climate change, and human impact. Berlin: Springer

Barnes D K A, Galgani F, Thompson R C, et al. 2009. Accumulation and fragmentation of plastic debris in global environments. Philos Trans R Soc Lond B Biol Sci, 364(1526): 1985–1998

Benskin J P, Muir D C G, Scott B F, et al. 2012. Perfluoroalkyl acids in the Atlantic and Canadian Arctic Oceans. Environ Sci Technol, 46(11): 5815–5823

Blais J M, Schindler D W, Muir D C G, et al. 1998. Accumulation of persistent organochlorine compounds in mountains of western Canada. Nature, 395(6702): 585–588

Blais J M, Wilhelm F, Kidd K A, et al. 2003. Concentrations of organochlorine pesticides and polychlorinated biphenyls in amphipods (*Gammarus lacustris*) along an elevation gradient in mountain lakes of western Canada. Environ Toxicol Chem, 22(11): 2605–2613

Block W. 1994. Terrestrial ecosystems: Antarctica. Polar Biol, 14(5): 293–300

Bollmann U E, Möller A, Xie Z Y, et al. 2012. Occurrence and fate of organophosphorus flame retardants and plasticizers in coastal and marine surface waters. Water Res, 46(2): 531–538

Browne M A, Crump P, Niven S J, et al. 2011. Accumulation of microplastic on shorelines woldwide: sources and sinks. Environ Sci Technol, 45(21): 9175–9179

Candelone J P, Hong S M, Pellone C, et al. 1995. Post-Industrial Revolution changes in large-scale atmospheric pollution of the northern hemisphere by heavy metals as documented in central Greenland snow and ice. J Geophys Res Atmos, 100(D8): 16605–16616

Carlsson H, Nilsson U, Becker G, et al. 1997. Organophosphate ester flame retardants and plasticizers in the indoor environment: analytical methodology and occurrence. Environ Sci Technol, 31(10): 2931–2936

Caro T, Darwin J, Forrester T, et al. 2012. Conservation in the anthropocene. Conserv Biol, 26(1): 185–188

Cheng W H, Sun L G, Huang W, et al. 2013a. Detection and distribution of Tris (2-chloroethyl) phosphate on the East Antarctic ice sheet. Chemosphere, 92(8): 1017–1021

Cheng W H, Xie Z Q, Blais J M, et al. 2013b. Organophosphorus esters in the oceans and possible relation with ocean gyres. Environ Pollut, 180: 159–164

Ciccioli P, Cecinato A, Brancaleoni E, et al. 1994. Chemical composition of particulate organic matter (Pom) collected at Terra-Nova Bay in Antarctica. Int J Environ Anal Chem, 55(1–4): 47–59

Colton J B Jr, Knapp F D, Burns B R. 1974. Plastic particles in surface waters of the northwestern Atlantic. Science, 185(4150): 491–497

Convey P, Barnes D K A, Morton A. 2002. Debris accumulation on oceanic island shores of the Scotia Arc, Antarctica. Polar Biol, 25(8): 612–617

Czub G, Wania F, McLachlan M S. 2008. Combining long-range transport and bioaccumulation considerations to identify potential arctic contaminants. Environ Sci Technol, 42(10): 3704–3709

Davidson D A, Wilkinson A C, Blais J M, et al. 2003. Orographic cold-trapping of persistent organic pollutants by vegetation in mountains of western Canada. Environ Sci Technol, 37(2): 209–215

Demers M J, Kelly E N, Blais J M, et al. 2007. Organochlorine compounds in trout from lakes over a 1600 meter elevation gradient in the Canadian Rocky Mountains. Environ Sci Technol, 41(8): 2723–2729

Derraik J G B. 2002. The pollution of the marine environment by plastic debris: a review. Mar Pollut Bull, 44(9): 842–852

Dietz R, Bossi R, Rigét F F, et al. 2008. Increasing perfluoroalkyl contaminants in East Greenland polar bears (*Ursus maritimus*): a new toxic threat to the Arctic bears. Environ Sci Technol, 42(7): 2701–2707

Ding M H, Xiao C D, Jin B, et al. 2010. Distribution of δ^{18}O in surface snow along a transect from Zhongshan Station to Dome A, East Antarctica. Chin Sci Bull, 55(24): 2709–2714

Ding M H, Xiao C D, Li Y S, et al. 2011. Spatial variability of surface mass balance along a traverse route from Zhongshan Station to Dome A, Antarctica. J Glaciol, 57(204): 658–666

Ding M H, Xiao C D, Li C J, et al. 2015. Surface mass balance and its climate significance from the coast to Dome A, East Antarctica. Sci China Earth Sci, 58(10): 1789–1797

Dobry A, Keller R. 1957. Vapor pressures of some phosphate and phosphonate esters. J Phys Chem, 61(10): 1448–1449

Dodson R E, Perovich L J, Covaci A, et al. 2012. After the PBDE phase-out: a broad suite of flame retardants in repeat house dust samples from California. Environ Sci Technol, 46(24): 13056–13066

Fries E, Püttmann W. 2001. Occurrence of organophosphate esters in surface water and ground water in Germany. J Environ Monit, 3(6): 621–626

García-López M, Rodríguez I, Cela R. 2008. Evaluation of liquid–liquid microextraction using polypropylene microporous membranes for the determination of organophosphorus flame retardants and plasticizers in water samples. Anal Chim Acta, 625(2): 145–153

Gouretski V. 1999. The large-scale thermohaline structure of the Ross Gyre // Spezie G, Manzella G M R. Oceanography of the Ross Sea Antarctica. Milano: Springer, 77–100

Hallanger I G, Sagerup K, Evenset A, et al. 2015. Organophosphorous flame retardants in biota from Svalbard, Norway. Mar Pollut Bull, 101(1): 442–447

Hallquist M, Wenger J C, Baltensperger U, et al. 2009. The formation, properties and impact of secondary organic aerosol: current and emerging issues. Atmos Chem Phys, 9(14): 5155–5236

Hartmann P C, Bürgi D, Giger W. 2004. Organophosphate flame retardants and plasticizers in indoor air. Chemosphere, 57(8): 781–787

Hekster F M, Laane R W P M, De Voogt P. 2003. Environmental and toxicity effects of perfluoroalkylated substances // Reviews of environmental contamination and toxicology. New York, NY: Springer, 99–121

Hughes K A, Fretwell P, Rae J, et al. 2011. Untouched Antarctica: mapping a finite and diminishing environmental resource. Antarc Sci, 23(6): 537–548

Hughes K A, Cary S C, Cowan D A, et al. 2013. Pristine Antarctica: threats and protection. Antarc Sci, 25(1): 1

Jabour J. 2009. National Antarctic programs and their impact on the environment // Kerry K R, Riddle M. Health of Antarctic wildlife. Berlin, Heidelberg: Springer, 211–229

Jones K C, De Voogt P. 1999. Persistent organic pollutants (POPs): state of the science. Environ Pollut, 100(1–3): 209–221

Kallenborn R, Breivik K, Eckhardt S, et al. 2013. Long-term monitoring of persistent organic pollutants (POPs) at the Norwegian Troll station in Dronning Maud Land, Antarctica. Atmos Chem Phys, 13(14): 6983–6992

Kawagoshi Y, Nakamura S, Fukunaga I. 2002. Degradation of organophosphoric esters in leachate from a sea-based solid waste disposal site. Chemosphere, 48(2): 219–225

Latendresse J R, Azhar S, Brooks C L, et al. 1993. Pathogenesis of cholesteryl lipidosis of adrenocortical and ovarian interstitial cells in F344 rats caused by tricresyl phosphate and butylated triphenyl phosphate. Toxicol Appl Pharm, 122(2): 281–289

Lau C, Butenhoff J L, Rogers J M. 2004. The developmental toxicity of perfluoroalkyl acids and their derivatives. Toxicol Appl Pharm, 198(2): 231–241

Law K L, Morét-Ferguson S, Maximenko N A, et al. 2010. Plastic accumulation in the North Atlantic Subtropical Gyre. Science, 329(5996): 1185–1188

Li C J, Xiao C D, Shi G T, et al. 2015. Spatiotemporal variations of monocarboxylic acids in snow layers along a transect from Zhongshan Station to Dome A, eastern Antarctica. Atmos Res, 158–159: 79–87

Li C J, Xiao C D, Shi G T, et al. 2016. Spatial and temporal variability of marine-origin matter along a transect from Zhongshan Station to Dome A, Eastern Antarctica. J Environ Sci, 46: 190–202

Ma Y X, Xie Z Y, Lohmann R, et al. 2017. Organophosphate ester flame retardants and plasticizers in ocean sediments from the North Pacific to the Arctic Ocean. Environ Sci Technol, 51(7): 3809–3815

Mäkinen M S E, Mäkinen M R A, Koistinen J T B, et al. 2009. Respiratory and dermal exposure to organophosphorus flame retardants and tetrabromobisphenol A at five work environments. Environ Sci Technol, 43(3): 941–947

Marklund A, Andersson B, Haglund P. 2003. Screening of organophosphorus compounds and their distribution in various indoor environments. Chemosphere, 53(9): 1137–1146

Masson-Delmotte V, Hou S, Ekaykin A, et al. 2008. A review of Antarctic surface snow isotopic composition: observations, atmospheric circulation, and isotopic modeling. J Clim, 21(13): 3359–3387

Meylan W M, Howard P H. 1993. Computer estimation of the Atmospheric gas-phase reaction rate of organic compounds with hydroxyl radicals and ozone. Chemosphere, 26(12): 2293–2299

Michels K H, Kuhn G, Hillenbrand C D, et al. 2002. The southern Weddell Sea: combined contourite-turbidite sedimentation at the southeastern margin of the Weddell Gyre // Stow D A V, Pudsey C, Howe J C, et al. Deep-water contourite systems: modern drifts and ancient series, seismic and sedimentary characteristics. London: Geological Society, 305–323

Möller A, Xie Z Y, Caba A, et al. 2011. Organophosphorus flame retardants and plasticizers in the atmosphere of the North Sea. Environ Pollut, 159(12): 3660–3665

Möller A, Sturm R, Xie Z Y, et al. 2012. Organophosphorus flame retardants and plasticizers in airborne particles over the northern Pacific and Indian Ocean toward the polar regions: evidence for global occurrence. Environ Sci Technol, 46(6): 3127–3134

Möller K, Crescenzi C, Nilsson U. 2004. Determination of a flame retardant hydrolysis product in human urine by SPE and LC–MS. Comparison of molecularly imprinted solid-phase extraction with a mixed-mode anion exchanger. Anal Bioanal Chem, 378(1): 197–204

Obbard R W, Sadri S, Wong Y Q, et al. 2014. Global warming releases microplastic legacy frozen in Arctic Sea ice. Earth's Future, 2(6): 315–320

Paolo F S, Fricker H A, Padman L. 2015. Volume loss from Antarctic ice shelves is accelerating. Science, 348(6232): 327–331

Parkinson C L, Comiso J C. 2013. On the 2012 record low Arctic sea ice cover: combined impact of preconditioning and an August storm. Geophys Res Lett, 40(7): 1356–1361

Penna A N. 2010. The human footprint: a global environmental history. Malden, Mass: Wiley-Blackwell

Pertierra L R, Hughes K A, Benayas J, et al. 2013. Environmental management of a scientific field camp in Maritime Antarctica: reconciling research impacts with conservation goals in remote ice-free areas. Antarc Sci, 25(2): 307–317

Peterle T J. 1969. DDT in Antarctic snow. Nature, 224(5219): 620

Quintana J B, Rodil R, López-Mahía P, et al. 2007. Optimisation of a selective method for the determination of organophosphorous triesters in outdoor particulate samples by pressurised liquid extraction and large-volume injection gas chromatography–positive chemical ionisation–tandem mass spectrometry. Anal Bioanal Chem, 388(5–6): 1283–1293

Reemtsma T, Quintana J B, Rodil R, et al. 2008. Organophosphorus flame retardants and plasticizers in water and air I. occurrence and fate. TrAC Trends Anal Chem, 27(9): 727–737

Regnery J, Püttmann W. 2009. Organophosphorus flame retardants and plasticizers in rain and snow from Middle Germany. CLEAN Soil Air Water, 37(4–5): 334–342

Regnery J, Püttmann W. 2010a. Occurrence and fate of organophosphorus flame retardants and plasticizers in urban and remote surface waters in Germany. Water Res, 44(14): 4097–4104

Regnery J, Püttmann W. 2010b. Seasonal fluctuations of organophosphate concentrations in precipitation and storm water runoff. Chemosphere, 78(8): 958–964

Ren X H, Lee Y J, Han H J, et al. 2008. Effect of tris- (2-chloroethyl)-phosphate (TCEP) at environmental concentration on the levels of cell cycle regulatory protein expression in primary cultured rabbit renal proximal tubule cells. Chemosphere, 74(1): 84–88

Rodríguez I, Calvo F, Quintana J B, et al. 2006. Suitability of solid-phase microextraction for the determination of organophosphate flame retardants and plasticizers in water samples. J Chromatogr A, 1108(2): 158–165

Rothrock D A, Yu Y, Maykut G A. 1999. Thinning of the Arctic sea-ice cover. Geophys Res Lett, 26(23): 3469–3472

Ryan P G, Moore C J, Van Franeker J A, et al. 2009. Monitoring the abundance of plastic debris in the marine environment. Philos Trans R Soc B Biol Sci, 364(1526): 1999–2012

Saboori A M, Lang D M, Newcombe D S. 1991. Structural requirements for the inhibition of human monocyte carboxylesterase by organophosphorus compounds. Chem Biol Interact, 80(3): 327–338

Salamova A, Hermanson M H, Hites R A. 2014. Organophosphate and halogenated flame retardants in atmospheric particles from a European Arctic site. Environ Sci Technol, 48(11): 6133–6140

Schmitz W J Jr. 1996. On the world ocean circulation: Volume II, the Pacific and Indian oceans/a global update. Woods Hole, Massachusetts: Woods Hole Oceanographic Institution

Sjödin A, Carlsson H, Thuresson K, et al. 2001. Flame retardants in indoor air at an electronics recycling plant and at other work environments. Environ Sci Technol, 35(3): 448–454

Sladen W J L, Menzie C M, Reichel W L. 1966. DDT residues in Adelie penguins and a crabeater seal from Antarctica. Nature, 210(5037): 670–673

Smithwick M, Norstrom R J, Mabury S A, et al. 2006. Temporal trends of perfluoroalkyl contaminants in polar bears (*Ursus maritimus*) from two locations in the North American Arctic, 1972 - 2002. Environ Sci Technol, 40(4): 1139–1143

Stapleton H M, Klosterhaus S, Eagle S, et al. 2009. Detection of organophosphate flame retardants in furniture foam and U.S. house dust. Environ Sci Technol, 43(19): 7490–7495

Stapleton H M, Klosterhaus S, Keller A, et al. 2011. Identification of flame retardants in polyurethane foam collected from baby products. Environ Sci Technol, 45(12): 5323–5331

Stapleton H M, Sharma S, Getzinger G, et al. 2012. Novel and high volume use flame retardants in US couches reflective of the 2005 PentaBDE phase out. Environ Sci Technol, 46(24): 13432–13439

Stewart E J, Draper D, Johnston M E. 2005. A review of tourism research in the polar regions. Arctic, 58(4): 383–394

Sühring R, Diamond M L, Scheringer M, et al. 2016. Organophosphate esters in Canadian Arctic air: occurrence, levels and trends. Environ Sci Technol, 50(14): 7409–7415

Sundkvist A M, Olofsson U, Haglund P. 2010. Organophosphorus flame retardants and plasticizers in marine and fresh water biota and in human milk. J Environ Monit, 12(4): 943–951

Teuten E L, Saquing J M, Knappe D R U, et al. 2009. Transport and release of chemicals from plastics to the environment and to wildlife. Philos Trans R Soc Lond B Biol Sci, 364(1526): 2027–2045

Thompson R C, Olsen Y, Mitchell R P, et al. 2004. Lost at sea: where is all the plastic? Science, 304(5672): 838

Turner J, Bindschadler R, Convey P, et al. 2009. Antarctic climate change and the environment. Cambridge: Scientific Committee on Antarctic Research

Umezu T, Yonemoto J, Soma Y, et al. 1998. Tris(2-chloroethyl)phosphate increases ambulatory activity in mice: pharmacological analyses of its neurochemical mechanism. Toxicol Appl Pharmacol, 148(1): 109–116

Van Der Veen I, De Boer J. 2012. Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. Chemosphere, 88(10): 1119–1153

Van A, Rochman C M, Flores E M, et al. 2012. Persistent organic pollutants in plastic marine debris found on beaches in San Diego, California. Chemosphere, 86(3): 258–263

Vecchiato M, Argiriadis E, Zambon S, et al. 2015. Persistent Organic Pollutants (POPs) in Antarctica: occurrence in continental and coastal surface snow. Microchem J, 119: 75–82

Walker T R, Reid K, Arnould J P Y, et al. 1997. Marine debris surveys at Bird Island, South Georgia 1990–1995. Mar Pollut Bull, 34(1): 61–65

Wania F, Mackay D. 1993. Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. Ambio, 22(1): 10–18

Wania F, Mackay D. 1996. Peer reviewed: tracking the distribution of persistent organic pollutants. Environ Sci Technol, 30(9): 390A–396A

Wania F. 2006. Potential of degradable organic chemicals for absolute and relative enrichment in the Arctic. Environ Sci Technol, 40(2): 569–577

Waxman E M, Dzepina K, Ervens B, et al. 2013. Secondary organic aerosol formation from semi- and intermediate-volatility organic compounds and glyoxal: relevance of O/C as a tracer for aqueous multiphase chemistry. Geophys Res Lett, 40(5): 978–982

Weber K, Goerke H. 2003. Persistent Organic Pollutants (POPs) in antarctic fish: levels, patterns, changes. Chemosphere, 53(6): 667–678

Wensing M, Uhde E, Salthammer T. 2005. Plastics additives in the indoor environment—flame retardants and plasticizers. Sci Total Environ, 339(1–3): 19–40

Wu X G, Lam J C W, Xia C H, et al. 2011. Atmospheric concentrations of DDTs and chlordanes measured from Shanghai, China to the Arctic Ocean during the Third Chinese Arctic Research Expedition in 2008. Atmos Environ, 45(22): 3750–3757

Xiao C, Ding M, Masson-Delmotte V, et al. 2013. Stable isotopes in surface snow along a traverse route from Zhongshan Station to Dome A, East Antarctica. Clim Dyn, 41(9–10): 2427–2438

Zelenyuk A, Imre D, Beránek J, et al. 2012. Synergy between secondary organic aerosols and long-range transport of polycyclic aromatic hydrocarbons. Environ Sci Technol, 46(22): 12459–12466