

ORGANOPHOSPHATE ESTER (OPE) FLAME RETARDANTS AND PLASTICIZERS IN THE ATMOSPHERE OVER THE GLOBAL OCEANS

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Introduction

The Stockholm Convention on persistent organic pollutants (POPs) banned the use of polybrominated diphenyl ethers (PBDEs) in 2009. These chemicals were extensively employed world-wide in the last decades mainly as flame retardants. Since then, the chemical industry has been using other suitable and “less toxic” compounds as substitutes of PBDEs. One of the chemical families which are currently employed is the organophosphate esters (OPEs), which are a group of organophosphorus flame retardants and plasticizers including halogenated (mostly chlorinated) and non-halogenated compounds¹. The production and usage of OPEs is rapidly increasing world-wide. Recent investigations point to their global atmospheric occurrence over marine environments²⁻⁵. In addition, first evidences of environmental persistency, bioaccumulation and toxic effects have been reported for some OPEs^{1,6-8}. However, there is not enough data to perform an accurate chemical risk assessment in marine environments. For example, data on OPE multi-media ambient levels, main input pathways and environmental partitioning need to be elucidated.

The objective of this study was to provide the first global assessment of OPEs atmospheric concentrations and inputs to the open waters of the main oceans of the planet. An unique set of atmospheric aerosol samples were collected during a 7-month circumnavigation campaign (MALASPINA 2010) encompassing the North and South Atlantic Ocean, the Indian Ocean and the North and South Pacific Ocean. Sampling transects are shown in Figure 1.

Materials and methods

Sampling

Atmospheric samples were collected from December 2010 to July 2011 in seven consecutive transects (L1-L7, Figure 1) encompassing all the tropical and temperate oceans between 35°N and 40°S on board of the RV Hespérides. High volume air samplers (MCV, Barcelona, Spain), installed on the upper deck of the ship, were used to gather both atmospheric gas and particle phases. The air was drawn through a pre-combusted Quartz fiber filter (QM-A; Whatman, 8x10 inches) to collect aerosol bound compounds (TSP) and then circulated through a pre-conditioned polyurethane foam (PUF) to collect chemicals present in the gas phase. The samplers were automatically stopped when wind was coming from the rear of the boat to avoid potential sample contamination from the ship emissions. A total of 115 aerosol samples were collected over the world oceans. The average sampling volume was of ~ 850 m³. Previous investigations proved that OPEs were mostly retained in the aerosol phase²⁻⁵ in various marine environments so only aerosol samples were analyzed for targeted OPEs.

Analytical determinations

QM-A filters were Soxhlet extracted with a mixture of dichloromethane/methanol (2:1, v/v) for 24h after being spiked with surrogates (Tri-n-butyl-d27 phosphate and Triphenyl-d15 phosphate). Extracts were cleaned-up in alumina columns and volumes reduced up to ~ 150ul under gentle N₂ stream. Internal standards (Tri-n-propyl-d21 phosphate and malathion-d7) were added. Analyses were performed by an Agilent 6890 Series gas chromatographer coupled with a mass spectrometer Agilent 5973 (GC/MS) and compounds were quantified by the internal standard procedure. The GC was operated in electron impact mode (EI, 70eV) and the separation was achieved in a 30m x 0.25mm i.d. x 0.25µm HP-5MS capillary column (Agilent J&W). Nine OPEs (fourteen taking into account the isomers of some of them) were analyzed: Tris-(2-chloroethyl)phosphate (TCEP), Tris[2-

chloro-1-(chloromethyl)ethyl]phosphate (TDCP), Tris- (1-chloro-2-propyl)phosphate (TCPPs, mix of isomers), Tri-iso-butyl phosphate (TiBP), Tri-n-butyl phosphate (TnBP), Triphenyl phosphate (TPhP), 2-Ethylhexyl diphenyl phosphate (EHDPP), Tri(2-ethylhexyl) phosphate (TEHP) and Tricresyl phosphate (TCrP, mix of isomers).



Figure 1. Atmospheric aerosol transects collected from December 2010 to July 2011 during the MALASPINA Expedition

Results and discussion

Ambient levels

Table 1 presents the OPE atmospheric levels over each oceanic region (Figure 1). \sum_{14} OPEs similar concentrations were obtained in all oceanic regions, ranging from ~ 0.5 to 6 ng m^{-3} . TCPPs (as sum of three isomers) dominated the atmospheric pattern in all marine environments ($53 \pm 14 \%$ of the \sum_{14} OPEs) followed by EHDPP representing the $17 \pm 7 \%$ of the \sum_{14} OPEs. The predominance of TCPPs has been previously reported for the marine atmosphere such as in the North Sea, the Mediterranean and Black Seas and over waters from East China to the high Arctic and over the Philippine Sea and the Southern Ocean²⁻⁴. This compound seems to be the most abundant over the global oceans.

Atmospheric deposition

Atmospheric dry deposition fluxes ($F_{DD} \text{ ng m}^{-2} \text{ d}^{-1}$) were calculated as $F_{DD} = v_d C_A$, 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 sea⁹. This value has been previously used in the estimation of the dry deposition of OPEs² and other organic contaminants such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs)¹⁰ and polycyclic aromatic hydrocarbons (PAHs)¹¹ from cruise measurements. However, a degree of uncertainty (factor of three) is associated to this calculation due to the lack of measurements of v_d during the cruises. Figure 2 shows the median atmospheric dry position fluxes for each compound and oceanic region studied.

Atmospheric dry deposition of \sum_{14} OPEs over the global oceans varied from 60 to $1100 \text{ ng m}^{-2} \text{ d}^{-1}$. TCPP is the compound most loaded to open marine waters, as expected from atmospheric levels, at a rate varying from 7 to $700 \text{ ng m}^{-2} \text{ d}^{-1}$ depending on the sample.

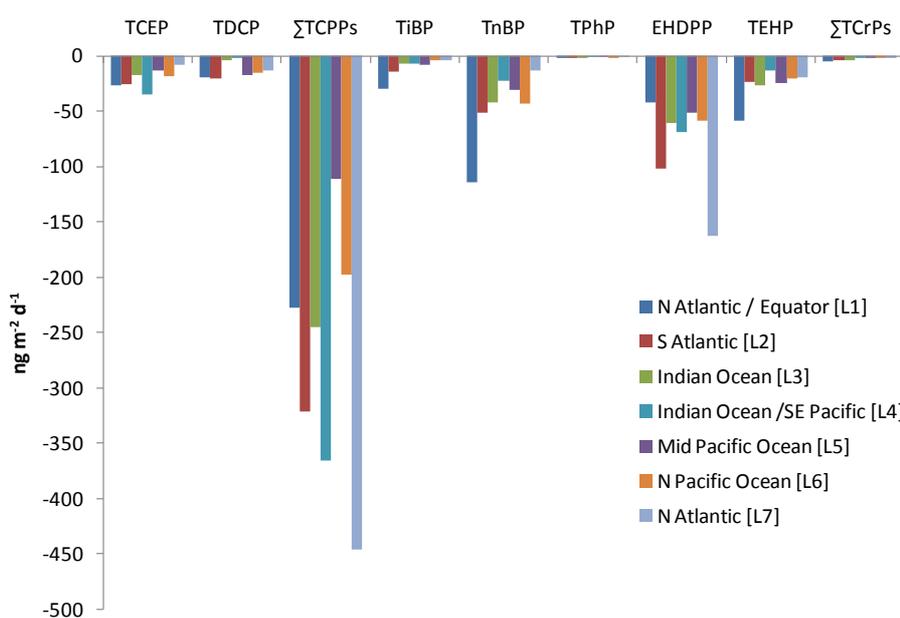
OPEs are unique compared to most of the organic contaminants studied in the atmosphere over marine environments because they contain phosphorous (P), which is an important nutrient for phytoplankton and microbial communities. In many cases, P is a *limiting nutrient*, such as in the most oligotrophic oceans and seas. A previous investigation conducted in the open Mediterranean Sea highlighted the atmospheric deposition fluxes of P due to OPE deposition as a significant fraction of reported atmospheric inputs of organic P in the Mediterranean, suggesting the relevant role that anthropogenic organic pollutants could play in the P cycle².

The dry deposition of $\Sigma_{14}\text{OPEs}$ given as P to the global oceans averaged $\sim 50 \text{ ngP m}^{-2} \text{ d}^{-1}$ ($\sim 2 \times 10^{-5} \text{ gP m}^{-2} \text{ y}^{-1}$). Further research is needed to elucidate the relevance of these organic P atmospheric inputs to the global oceans, in particular to the most oligotrophic environments.

Table 1. OPE concentrations (median, mean and range, ng m^{-3}) in the atmospheric aerosol over each oceanic region. Ranges show only detected values.

Ocean	$[\text{ng m}^{-3}]$	TCEP	TDCP	ΣTCPPs	TiBP	TnBP	TPhP	EHDPP	TEHP	ΣTCrPs	$\Sigma_{14}\text{OPEs}$
N Atlantic / Equator [L1] n=12	Median	0.16	0.11	1.32	0.17	0.66	0.01	0.24	0.34	0.03	3.13
	Mean	0.18	0.22	1.50	0.21	0.71	0.01	0.28	0.36	0.03	3.25
	Range	(0.01 - 0.47)	(0.02 - 0.54)	(0.70 - 2.73)	(0.07 - 0.38)	(0.32 - 1.71)	(0.006 - 0.02)	(0.02 - 0.50)	(0.16 - 0.89)	(0.02 - 0.06)	(0.87 - 6.16)
S Atlantic [L2] n=15	Median	0.15	0.12	1.86	0.08	0.30	0.01	0.59	0.13	0.02	3.22
	Mean	0.19	0.14	1.87	0.09	0.31	0.01	0.58	0.15	0.02	3.33
	Range	(0.04 - 0.54)	(0.03 - 0.43)	(0.60 - 3.01)	(0.03 - 0.15)	(0.12 - 0.53)	(0.002 - 0.03)	(0.04 - 1.02)	(0.05 - 0.26)	(0.01 - 0.05)	(1.03 - 5.02)
Indian Ocean [L3] n=23	Median	0.10	0.02	1.42	0.04	0.24	0.01	0.35	0.15	0.02	2.47
	Mean	0.16	0.06	1.55	0.05	0.30	0.01	0.37	0.22	0.02	2.65
	Range	(0.05 - 0.62)	(0.005 - 0.29)	(0.03 - 3.49)	(0.02 - 0.09)	(0.12 - 0.94)	(0.005 - 0.01)	(0.21 - 0.63)	(0.04 - 0.63)	(0.006 - 0.04)	(0.36 - 5.15)
Indian Ocean /SE Pacific [L4] n=7	Median	0.20	0.01	2.11	0.04	0.13	0.001	0.40	0.08	0.01	2.93
	Mean	0.22	0.01	1.81	0.05	0.17	0.001	0.44	0.18	0.01	2.74
	Range	(0.07 - 0.37)	0.01	(0.53 - 4.11)	(0.02 - 0.11)	(0.07 - 0.38)	(0.001 - 0.002)	(0.34 - 0.61)	(0.04 - 0.35)	0.01	(1.02 - 5.78)
Mid Pacific Ocean [L5] n=16	Median	0.08	0.10	0.64	0.05	0.18	0.01	0.29	0.14	0.01	1.61
	Mean	0.09	0.18	0.90	0.06	0.30	0.01	0.34	0.15	0.01	2.01
	Range	(0.02 - 0.27)	(0.01 - 1.00)	(0.14 - 2.40)	(0.006 - 0.16)	(0.05 - 2.17)	(0.001 - 0.04)	(0.12 - 0.80)	(0.08 - 0.35)	(0.006 - 0.02)	(0.59 - 4.72)
N Pacific Ocean [L6] n=22	Median	0.10	0.09	1.14	0.02	0.25	0.009	0.34	0.12	0.01	2.41
	Mean	0.11	0.13	1.22	0.03	0.52	0.012	0.41	0.13	0.02	2.55
	Range	(0.001 - 0.31)	(0.01 - 0.50)	(0.12 - 2.53)	(0.003 - 0.10)	(0.02 - 2.50)	(0.002 - 0.03)	(0.10 - 1.21)	(0.06 - 0.38)	(0.01 - 0.06)	(0.38 - 4.54)
N Atlantic [L7] n=20	Median	0.04	0.07	2.58	0.02	0.08	0.01	0.94	0.11	0.01	4.28
	Mean	0.14	0.10	2.53	0.04	0.09	0.01	0.87	0.12	0.01	3.90
	Range	(0.01 - 1.23)	(0.01 - 0.31)	(0.42 - 3.90)	(0.005 - 0.11)	(0.01 - 0.38)	(0.002 - 0.05)	(0.22 - 1.73)	(0.06 - 0.24)	(0.005 - 0.02)	(0.84 - 6.38)

Figure 2. Atmospheric dry deposition fluxes (median values, $\text{ng m}^{-2} \text{ d}^{-1}$) of OPEs at open sea in the various oceanic regions (see Figure 1 for transect identification)



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