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ORGANOPHOSPHATE ESTERS: CURRENT KNOWLEDGE ON PROPERTIES AND ENVIRONMENTAL BEHAVIOUR, FATE AND CONTAMINATION FROM A MULTI-MEDIA PERSPECTIVE IN THE ARCTIC

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Introduction

Organophosphate esters (OPEs), and mainly OP triesters, are high production volume chemicals and have been in use since the 1970s[1,2]. OP triesters are used as flame retardants (FRs), plasticizers, and as performance additives to engine oils and found in hydraulic oils plastics, foams, textiles, floor polishes, waxes and furniture. In recent years the production and use of some OP triesters have been increasing, and coincident with the regulation and phase-out of brominated FR substances such as polybrominated diphenyl ethers (PBDEs) (e.g. penta-BDEs), and hexabromocyclododecane. The estimated annual consumption of OPEs in Western Europe increased from approximately 83,000 metric tonnes/y in 2001 to 91,000 metric tonnes/y in 2006[3]. Production volumes for TDCIPP, TPHP, and TCIPP (see Table 1) in the United States of America increased from less than 14,000 metric tonnes/y in the mid-1980s, to 5,000 to 25,000 metric tonnes/y in 2006, and to approximately 38,000 metric tonnes/y in 2012[4]. With respect to the Arctic, in a 2010 review on FRs and related compounds in the circumpolar Arctic, OPEs were not mentioned yet as contaminants in any media compartment[5]. The objective of the present study is to review what is currently known form a multi-media perspective on OPEs (OP triesters) in the Arctic, as well as physical-chemical properties and processes that could affect OP triester fate in Arctic abiotic and biotic environments.

Materials and methods

The present study reviewed the literature on physical-chemical properties, transformation and environmental levels in multi-media of OP triesters in the Arctic. This Arctic review is part of a recent 2016 assessment of contaminants of emerging concern in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP). The reported OP triester analyses and sample concentrations were determined either by HPLC-MS/MS, UPLC-MS/MS or GC-MS based methods. Table 1 lists OP triesters where there is published literature reporting on levels in Arctic media.

Results and discussion

There is a considerable lack of measured values on the physical-chemical properties of OP triesters. For measured values that have been reported there are significant uncertainties in the physical-chemical properties. OP triester physical-chemical property values have been modelled and thus are considered more as estimated values[6,7]. It is known that OP triester water solubility decreases with increasing molecular mass. Most OP triesters appear to be hydrolytically stable at neutral pH but can be hydrolysed under more basic pH conditions[8]. OP triester properties of solubility, relatively high vapour pressures and general resistance to hydrolysis at neutral pH imply relatively high environmental mobility including to the Arctic. Where hydrolysis half-lives are equal, the OP triesters with lower masses are more likely to be found in the aquatic environment than those with higher molecular masses. Most of the OP triesters have been reported to have positive log K_{ow} values, which means they are more lipophilic than hydrophilic (log K_{ow} values have been reported in the range of 0 to 10)[2]. The wide range of Henry's law constant values of OP triesters indicates that their distribution in air and water, such as in the oceans, is predicted to be highly variable.

Since 2010, there has been little reported information on OPEs (in air and biota only) in Arctic media (Table 1). Liu et al.[10] reported on heterogeneous reactions between OH radicals and OP triesters coated on inert particles. The degradation of these particle-bound OP triesters was observed as a result of OH exposure, and second-order rate constants were derived for the heterogeneous loss of TPHP, TEHP, and TDCIPP. Atmospheric lifetimes were estimated to be 5.6, 4.3 and 13 days, for TPHP, TEHP and TDCIPP, respectively, and this OH radical oxidation was consistent with the assumption that OP triesters can undergo medium or long-range transport, including to the Arctic. A recent modelling exercise on the long-range transport OP triesters to the Arctic found some evidence suggesting that the chlorinated OP triesters may be transported to the Arctic via rivers enabled by their high solubility and persistence in water[7,11].

In various parts of the Arctic, OP triesters were reported in air samples taken on board of the Amundsen Icebreaker as part of the Northern Contaminants Program (NCP; Canadian Federal Ministry of Indigenous and Northern Affairs (INAC)) and ArcticNet between 2007-2013 (Figure 1; note the references cited). OP triesters identified in arctic air were: TCEP TCIPP, TPHP, EHDPP and TDCIPP (see Table 1 for full chemical names). Reports on OP triesters in Arctic biota are at present extremely limited. However, new wildlife studies outside the Arctic strongly suggest that OP triester residue concentrations in tissues and other body compartments and eggs of exposed wildlife are much lower than reported in abiotic environmental samples. Only one report appears to currently exist on OP triesters in biota and in Arctic freshwater environments. McGoldrick et al.[15] investigated OP triesters in whole body homogenates of lake trout and walleye collected from Canadian lakes, including from Great Bear Lake just above the Arctic Circle. In a lone and semi-Arctic study in avian wildlife, Eulaers et al.[16] very recently screened for 6 OP triesters in feathers and blood plasma of white-tailed sea eagle nestlings from Trøndelag, Norway (just below the Arctic Circle). Another recent screening study measured OP triesters in eight arctic species, including fish, birds and mammals, from the Svalbard Archipelago, Norway. Of the 14 OP triesters examined, only 10 were detectable.

In another recent study, polar bear adipose and liver sample pairs from 2012-2015 collected from western and southern Hudson Bay were screened for a suite of 15 OP triesters[17]. Both the liver and adipose samples contained low- to sub-ng/g (ww) concentrations of TCEP, TCIPP, TNBP, TPHP and/or TBOEP. As suspected for other Arctic wildlife and fish, low tissue levels of OP triesters in these polar bears appears to be largely attributed to rapid OP triester metabolism. However, more research is necessary on the whole for Arctic wildlife. To our knowledge, there are currently no published reports of OP triesters in the terrestrial Arctic environment.

It is apparent that there is currently a dearth of information on OPEs in abiotic and biotic compartments of the Arctic. As a consequence, environment spatial or temporal trends in the Arctic are currently unknown. There is evidence of long-range transport of OPEs to the Arctic as they have been reported in Arctic air (particles). It is important to note that atmospheric OPE concentrations in the Arctic have been reported to be two orders of magnitude higher than those of PBDEs. In limited biotic studies, much lower OPE concentrations have been found in Hudson Bay polar bears, in lake trout as well as plasma, feathers and eggs from birds at the fringe of the Arctic Circle (i.e. northern Norway), and in fish, seabirds, seals, Arctic fox and polar bear from Svalbard.

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Table 1. Summary of Arctic media for which OPEs (OP triesters) have been reported.

		Atmosphere		Terrestrial		Freshwater			Marine		
OP triester*	Abbreviation (CAS#)	Air	Snow	Soil	Biota	Water	Sed.	Biota	Water	Sed.	Biota
Tris(2-chloroethyl) phosphate	TCEP (115-96-8)	X						X			X
Tris(2-chloroisopropyl) phosphate**	TCIPP (13674-84-5)	X						X			X
Tris(1,3-dichloro-2-propyl) phosphate	TDCIPP (13674-87-8)	X						X			X
Triphenyl phosphate	TPHP (115-86-6)	X						X			X
Tri-n-butyl phosphate	TNBP (126-73-8)	X						X			X
Tris(methylphenyl) phosphate	TMPP (1330-78-5)										X
2-Ethylhexyl-diphenyl phosphate	EHDPP (1241-94-7)	X									X
Tris(2-butoxyethyl) phosphate	TBOEP (78-51-3)	X						X			X
Tris(2-ethylhexyl)phosphate	TEHP (78-42-2)	X									X
Tris(isobutyl) phosphate	TIBP (126-71-6)	X									X
Butyldiphenyl phosphate	DPhBP (2752-95-6)										X

* See Bergman et al. (2012) for a complete listing of OP triester chemical abbreviations.
** TCIPP represents tris(2-chloroisopropyl) phosphate as indicated; however, there are seven additional structural isomers of TCIPP with unique CAS# (i.e. 26248-87-3, 76025-08-6, 76649-15-5, 6145-73-9, 137909-40-1, 137888-35-8 and 1067-98-7) (see Truong et al.[9] for isomer details).

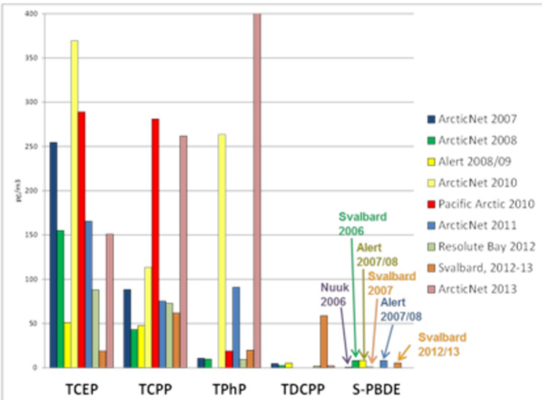

Figure 1. Average concentrations of PFRs in Arctic air, 2007-2013. ArcticNet 2007: shipboard August in the Labrador Sea and Hudson Bay areas; ArcticNet 2008: shipboard Beaufort Sea in May-June; Alert 2008/09: land based Dec 2008 to Aug 2009 (blank problems for TPHP); Pacific Arctic 2010: ship based Bering-Chukchi-Beaufort Seas summer of 2010 is from Möller et al.[12]); ArcticNet 2011: shipboard central and east archipelago; Resolute Bay: land based July 2012; Svalbard in 2012-2013: land based (Salamova et al.[13]) and ArcticNet 2013: ship board in Barrow Strait and McClure Strait. Compared to the sum-PBDEs (11-35 BDEs) in Greenland (Nuuk), Svalbard and the Alert monitoring station (see Xiao et al.[14]) for references and Salamova et al.[13].