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Atmospheric concentrations of organophosphates

At background stations in Sweden (Råö, Norunda) and Finland (Pallas)

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Summary

Organophosphate esters (OPEs) are a group of chemicals that have been used for more than a century. OPEs are widely used as flame retardants, plasticizers, anti-foaming agents and as additives in lubricants and hydraulic fluids. The results of a screening assessment carried out by Umeå University in 2004 showed that OPEs can be found in for example air, deposition and snow, both near and far from emission sources. That the atmosphere is an important route of transportation for these substances has also been shown in later studies showing that several OPEs occur in Arctic air and biota. However, they have never been part of the regular environmental monitoring program in Sweden.

The aim of this study was to get an idea of the levels of OPEs in background air and the importance of air transportation of these chemicals in Sweden and northern Finland. Sample extracts from the regular environmental monitoring program of organic pollutants in air were used for the analyses and the results were evaluated in order to propose future measurement programs. The measured OPEs were TEP, TiBP, TnBP, TCEP, TCPP, TDCP, TBEP, TEHP, TPhP, EHDPP, ToCrP and TCrP mix. TCEP, TCPP and EHDPP were measured in the highest concentrations. Unfortunately, TPhP and TCrP mix were excluded from the results due to the detection of contamination from the polyurethane plugs used as adsorbents.

To get an idea of the regional distribution, air samples were taken from the three stations, Råö at the Swedish west coast, Norunda at the east of Sweden and Pallas in northern Finland. Generally, the highest levels of OPEs were measured in Pallas and the lowest in Norunda. For TCEP and EHDPP, a geographical variation could be distinguished with highest concentrations in the north and lowest in the south. To get information about seasonal variations, sample extracts for the OPE-analyses were taken from the ordinary measurements for one year (2018), from January to December. Seasonal variations were observed for TCPP and TCEP at Råö, where higher levels were measured during the summer. In Pallas, the highest concentrations of some OPEs were instead detected in late summer. The measurements at Norunda did not show any clear seasonal variations.

The results of the measurements in this study were compared with literature data, which showed good agreement levels as well as similar relationships among different OPEs. Production figures of different OPEs were difficult to find. Although, TEP, which is reported to be produced in large quantities, was not detected in high concentrations in air at any of the stations.

Based on the results of this study, we conclude that the existing network of measurement stations, monitoring frequency, sampling and analysis procedures used within the environmental monitoring, can be used to measure organophosphates in air as well. However, the material used for the PUF adsorbent and the extraction method should be further evaluated to ensure the quality of the measurements.

Sammanfattning

Organofosfatestrar (OPEs) är en grupp kemikalier som har använts under lång tid. OPEs används i stor utsträckning som flamskyddsmedel och mjukgörare i plaster, men de används även som bl.a. antiskummedel och som tillsatser i smörjmedel och hydraul-vätskor. Resultaten från ett screeninguppdrag som utfördes av Umeå Universitet redan 2004 visar att OPEs återfinns i bl.a. luft, deposition och snö, både nära och långt ifrån källor.
Att luft är en viktig spridningsväg för dessa ämnen har visats även i senare studier då man sett att ett antal OPEs förekommer i luften i arktiska områden där de också har påträffats i biota. Trots detta har inte OPEs tidigare ingått i den reguljära miljöövervakningen i Sverige.

Syftet med denna studie var att få en uppfattning om halter av OPEs i bakgrundsluft och betydelsen av spridning av OPEs via luft i Sverige och norra Finland. Provextrakt från ordinarie mätprogram av organiska föroreningar i luft användes för analyserna, och resultaten av mätningarna utvärderades i syfte att föreslå framtida mätprogram. De OPEs som mättes var TEP, TiBP, TnBP, TCEP, TCPP, TDCP, TBEP, TEHP, TPhP, EHDPP, ToCrP och TCrP-mix. Högst halter uppmättes av TCEP, TCPP och EHDPP. Tyvärr fick TPhP och TCrP-mix exkluderas från resultaten på grund av upptäckt kontaminering från materialet av de polyuretanpluggar som användes som adsorbenter.

För att få uppfattning om regional spridning togs luftprover från de tre stationerna, Råö på svenska västkusten, Norunda på östra sidan av Sverige och Pallas i norra Finland. Generellt uppmättes de högsta halterna OPEs i Pallas och de lägsta halterna i Norunda. För TCEP och EHDPP kunde en geografisk variation urskönjas, med högst halter i norr och lägst i söder. För att studera en möjlig årstidsvariation togs provextrakt för OPE-analyser från ordinarie mätningar under ett år (2018), från januari till december. De tydligaste årstidsvariationerna observerades för TCPP och TCEP i Råö där högre halter uppmättes under sommarhalvåret. I Pallas uppmättes högst värden av vissa OPE istället under sensommaren. Mätningarna på Norunda visade inga tydliga årstidsvariationer.

I utvärderingen jämfördes resultaten av mätningarna med litteraturdata. Denna undersökning visade god överensstämning av OPE-koncentrationer och liknande relationer mellan olika OPEs. Det var svårt att finna produktionssiffror av olika OPEs. Dock visade en grov jämförelse att TEP som uppges produceras i stora mängder, inte detekterades i höga koncentrationer i luft på någon av stationerna.

Utifrån resultaten från denna studie drar vi slutsatsen att det existerande nätverket av mätstationer och mät- och analysprocedurer, som idag används inom miljöövervakningen (EMEP), även kan användas för att mäta organofosfater i luft. Dock rekommenderar vi att PUF-materialet och extraktionsmetoden vidare utvärderas för att säkerhetsställa mätningarnas kvalité.

1 Introduction

1.1 Organophosphates

Since the listing of polybrominated diphenyl esters (PBDE) as persistent organic pollutants (POPs) in the Stockholm Convention, other flame retardants (FRs) have taken their place. Substitutes are normally bromine-, chlorine or phosphate-containing organic compounds, such as organophosphate esters (OPEs). OPEs are used as flame retardants, but also, for example, as plasticizers, additives, stabilizers and they can be found in a wide range of products, see Table 1. Halogenated OPEs are generally used as flame retardants and OPEs without halogens are used as plasticizers, but some are used in both applications (AMAP 2017).

In 2006, OPEs accounted for about 11.5% of the world consumption of FRs (200 000 tonnes, 800 million USD by value) with an expected annual increase of about 5%, while in the EU, PFRs accounted for 20% of total FR consumption (Castro-Jiménez et al., 2016; Xu et al., 2016; Van Der Veen & de Boer., 2012). The total usage of OPEs in western Europe has between 2001 to 2006 increased from 83 000 t/year to 91 000 t/year (AMAP, 2017). It was expected that OPEs would be biodegradable, low-persistent and have negligible hazardous effects (Castro-Jiménez et al., 2016). However, several studies have found that OPEs are potentially bio accumulative, carcinogenic and are more environmental persistent than previously believed (Wei et al., 2015; Wang et al., 2015). Humans can be orally exposed to OPEs via ingestion of food and drinking water, transdermally, or through inhalation and unintended dust ingestion. Previous studies have found OPEs in human hair, nails, urine and breast milk and long-term exposure could for example harm the kidneys and disrupt the neurological and reproductive systems (Li et al., 2014; He et al., 2018; Alves et al., 2017).

A recent literature review on OPEs in food showed a large global spread of OPE concentrations in a variety of different food categories (Li et al., 2019). In Sweden, OPEs were mainly found in fats and oil products and in desserts. In contrast, the main polluted food categories in Australia were vegetables, fruits, dairy products and cereal, and in the US, animal products such as fish and meat were the most contaminated by OPEs. In cereal and fat/oils in Sweden the OPEs found most in food were EHDPP (2-Ethylhexyl-diphenyl phosphate) and TPhP (Tri-Phenyl phosphate), while in in China the major OPEs found in same food categories were TCEP (Tris (2-chloroethyl) phosphate) and TCPP (Tris (chloropropyl) phosphate). I Swedish mussels a high fraction of the found OPEs was TCPP while in Belgium mussels, a larger fraction of TPhP was measured (Li et al., 2019).

The results of a screening assessment carried out by Umeå University in 2004 showed that OPEs can be found in for example air, deposition and snow, both near and far from emission sources (Naturvårdsverket, 2006). That the atmosphere is an important route of transportation for these substances has also been shown in later studies showing that several OPEs occur in Arctic air and biota. However, they have never been part of the regular environmental monitoring program in Sweden.

1.2 Objectives of study

The purpose this study was to estimate the air concentrations of OPEs and to estimate the importance of atmospheric transport of these chemicals to background stations in Sweden and in northern Finland. The measurements were performed during 2018 (January-December) in order to cover seasonal variations. The procedures for sampling and analyses that are used within the national monitoring program for air and precipitation, EMEP, were used for this study (Naturvårdsverket, 2015). Hence, sample extracts from the regular measurement programme were used and analysed for organophosphates.

The results were evaluated in order to conclude whether environmental monitoring of OPEs in background air is feasible using the existing procedures for sampling and analyses and therefore can be included in the existing environmental monitoring program.

1.3 Measured OPEs and sampling locations

1.3.1 Measured OPEs

In this study 12 organophosphates (TEP, TiBP, TnBP, TCEP, TCPP, TDCP, TBEP, TEHP, TPhP, EHDPP, ToCrP, TCrP-mix) were measured in a total of 42 samples from three stations during 2018. The measured OPEs are listed in Table 1 together with information about common area uses and estimated usage, where information was available.

1.3.2 Measurement stations

Sample extracts for the analyses of OPEs during 2018 were taken from the sampling locations for organic pollutants at Råö, Norunda and Pallas. These stations are included in the national environmental monitoring network of organic pollutants in Sweden, performed by IVL on behalf of the Swedish Environmental Protection Agency and included in the EMEP network (www.emep.int). Råö is a coastal station, located at the west-coast of Sweden at the shore line. Norunda is located north of Stockholm at the east-coast of Sweden. Pallas is a joint sub-Arctic station together with the Finish Meteorological Institute (FMI) in northern Finland. The stations are shown on a map in Figure 1.

Table 1. List of measured organophosphates, common uses and estimates of global production/uses (N.F. = Not found).

Abbreviation	Name (CAS)	Common uses	Prod. (Mt)
TEP	Triethyl phosphate (78-40-0)	Industrial catalyst, polymer resin modifier, plasticizer, solvent, flame retardant etc.	28958 (2016, Global)[1]
TiBP	Tri-isobutyl phosphate (126-71-6)	Dyes, paint additives, coating additives, plasticizer	N.F.
TnBP	Tributyl phosphate (126-73-8)	Flame retardant, aircraft hydraulic fluid, solvent,	3-5[2]
TCEP	Tris (2-chloroethyl) phosphate (1155-96-8)	Flame retardant in consumer products, furniture foam, PVC, electronics	~1/year (2008, EU)[3]
TCPP	Tris (chloropropyl) phosphate (13674-84-5)	Flame retardant in flexible polyurethane foam	5-25 (2006, US)[4]
TDCP / TDCPP	Tris (1,3 -dichloro, 2-propyl) phosphate (13674-87-8)	Flame retardant in consumer products, automotive cushions.	5-25 (2006, US)[4]
TBEP	Tri (butoxyethyl) Phosphate (78-51-3)	Plasticizer for PVC, chlorinated rubber, nitriles. Emulsions of floor polishes. Flame retardant	0,5-5 (2016, US)[5]
TEHP	Tris (2-ethylhexyl) phosphate (78-42-2)	Solvent in the production of hydrogen peroxide, vinyl plasticizer	1-5 (2000, Global)[6]
TPhP	Tri-Phenyl phosphate (115-86-6)	Flame retardant, plasticizer, additive to lubricating oil and hydraulic fluid, nail polish	5-25 (2006, US)[4]
EHDPP	2-Ethylhexyl-diphenyl phosphate (1241-94-7)	Plasticizer, food packaging plastic, tubing for sausages, fireproofing in hydraulic fluids	N.F.
ToCrP	Tri-o-cresyl Phosphate (78-30-8)	Plasticizer in lacquers and varnishes, flame retardant, gasoline additive, hydraulic fluid, heat exchange medium.	N.F.
TCrP-mix	Tri-cresyl Phosphate (mix of isomers) (1330-78-5)	Flame retardants in plastics (cellulose products and PVC), hydraulic fluids, lubricants, additives.	N.F.

1.(https://www.marketwatch.com/press-release/global-triethyl-phosphate-market-prime-challenges-competitive-scenario-growth-forecast-to-2025-2019-03-13).

2.(Wikipedia.org). 3. (https://echa.europa.eu/documents/10162/f42be21b-33a3-4063-ad4d-2b0f937e41b4). 4.(AMAP, 2017).

5. (https://pubchem.ncbi.nlm.nih.gov/compound/Tris_2-butoxyethyl_-phosphate#section=Use-Classification).

6. (https://oehha.ca.gov/media/downloads/crnr/101211tris2ethylhexylphosphate.pdf).

Figure 1. Locations of the three measurement stations Råö, Norunda and Pallas, where organophosphates have been measured during 2018.

2 Methods

2.1 Sampling

The air sampling of OPEs at Råö, Norunda and Pallas was performed using high-volume samplers (HVS) equipped with a glass fiber filter which collects particle phase compounds and a series of three Polyurethane Foam (PUF) disks for collecting compounds in the gas phase, see Figure 2.

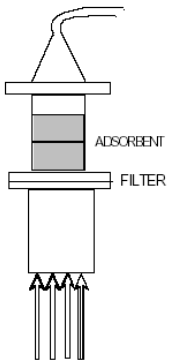

Figure 2. The principle of a high-volume sampler for collecting organic pollutants in air, including OPEs, in outdoor air. The air passes through a filter and three polyurethane foam (PUF) disks that are used as adsorbents (only two PUFs are shown in the picture).

The filters and PUF plugs were changed every week and carefully collected in aluminum foil using a clean metal tweezer. The samples were sent to the IVLs laboratory for storage in a freezer at -20°C prior the analysis.

2.2 Analysis

Weekly samples (PUFs and filters) were Soxhlet extracted for 24 hours by using acetone (GC grade from Rathburn Chemicals). The weekly sampling extracts were merged to achieve monthly samples. The total air sampling volume per month was approximately 20 000 m^3 (Råö) or less (Norunda, Pallas). The sample extracts were divided and prepared differently depending on the organic substances to be analyzed. In the case of OPEs (sample air volume 2000 m^3 for Råö and Norunda, 4000 m^3 for Pallas), the monthly sample extracts were further prepared for analysis.

An internal standard mixture was used for the organophosphate esters, consisting of phosphoric acid tri-n-amyl ester (TAP) and TPhP-d15 which was added prior to the initial extraction. The sample extracts where concentrated under gentle nitrogen stream and the solvent was changed to n-hexane. A clean-up step was performed with PSA solid phase extraction (SPE) cartridges. The OPEs analysis was carried out with a gas chromatography tandem mass spectrometry GC/MS/MS system (Agilent 7000; Agilent Technologies, Inc., Santa Clara, CA, USA) in electron impact

ionization mode (EI) with DB-5 30 m, 0.25 mm, 0.25 μm column. Integration was made with MassHunter software version B.04.00 for quantitative analysis (Agilent Technologies, Inc. 2008). All results were blank subtracted and the individual detection limits for each analyte were calculated based on the detected blank levels divided with the percentage of the extract received, and then divided with the corresponding volume of air.

3 Results

3.1 Yearly averages

The yearly averages of the 10 organophosphates, TEP, TiBP, TnBP, TCEP, TCPP, TDCP, TBEP, TEHP, EHDPP and ToCrP are presented in Figure 3 for Råö, Norunda and Pallas. TPhP and TCrP were excluded due to a suspected contamination from the PUFs (discussed in section 5.2).

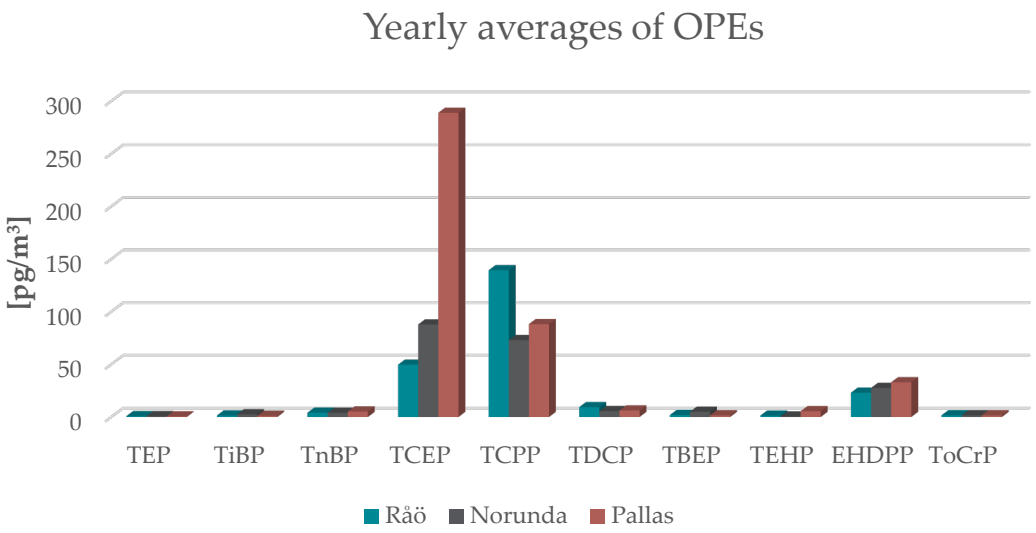

Figure 3. Yearly averages (12 sample/analyte) of measured organophosphates (TEP, TiBP, TnBP, TCEP, TCPP, TDCP, TBEP, TEHP, EHDPP, ToCrP) from January-December 2018 at Råö, Norunda and Pallas.

As Figure 3 presents, the TCEP, TCPP and EHDPP were found in the highest concentrations. TCEP represents 49% of the total concentrations of the 10 OPEs, TCPP 34% and EHDPP 10%. A potential geographical variation was observed, with higher concentrations in Pallas in the north compared to Norunda and Råö in the south, for TCEP and EHDPP especially. The dominating OPE found in Råö in the south was TCPP compared to TCEP, that was the dominating OPE at Pallas in the north. In average, the highest concentrations of the 10 OPEs were found in Pallas while the lowest concentrations were detected in Norunda. The highest concentrations of TCPP and TDCP were found at Råö in the south.

3.2 Seasonal variations

The monthly concentrations of the 10 OPEs are presented in Figure 4, 5 and 6 for Råö, Norunda and Pallas, respectively. All monthly results (including those for TPhP and TCrP) and blank values are presented in Table A1-A4 in Appendix.

At Råö where TCPP and TCEP dominated, a seasonal variation of these two chemicals was observed with higher concentrations in summer (May-September) compared to winter. Similar observations were made for EHDPP and TnBP.

At Norunda where TCEP and TCPP were found in similar concentrations, TCEP concentrations peaked in Mars and July. Somewhat higher concentrations for TCPP from Mars to August was observed. No OPE showed any clear seasonality at Norunda.

The high concentrations of TCEP at Pallas peaked in February, June, September and December. TCPP, EHDPP and TnBP showed late summer peaks in August-September. TDCP and TEHP peaked in July.

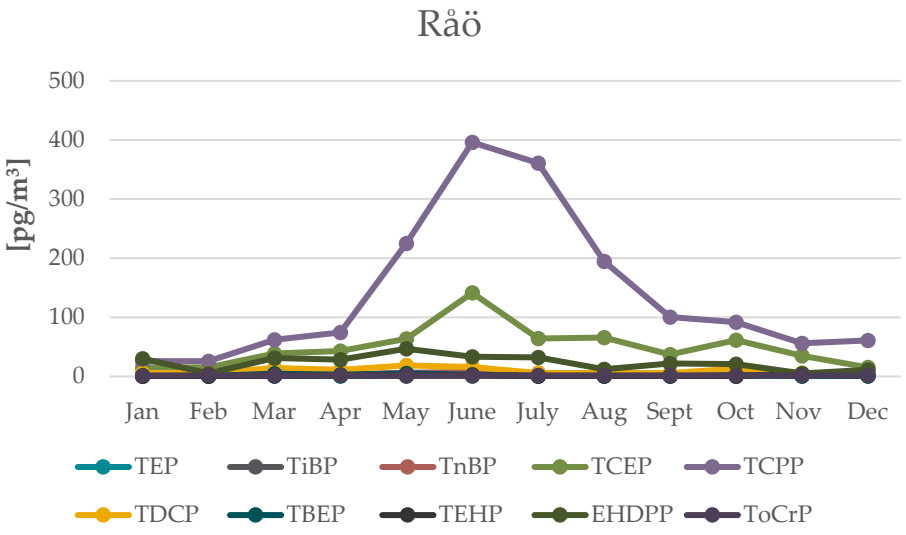

Figure 4. Measured organophosphates (TEP, TiBP, TnBP, TCEP, TCPP, TDCP, TBEP, TEHP, EHDPP, ToCrP) at the Råö station, January – December 2018.

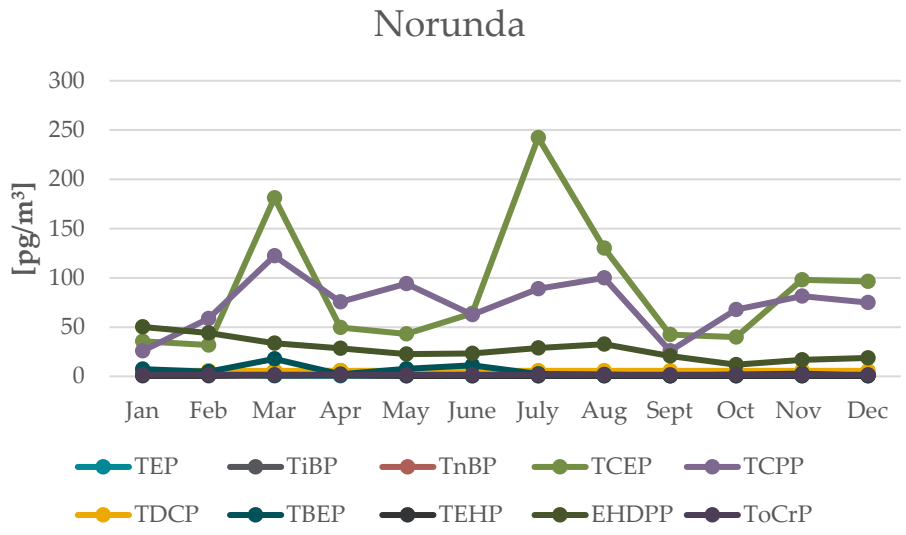

Figure 5. Measured organophosphates (TEP, TiBP, TnBP, TCEP, TCPP, TDCP, TBEP, TEHP, EHDPP, ToCrP) at the Norunda station, January – December 2018.

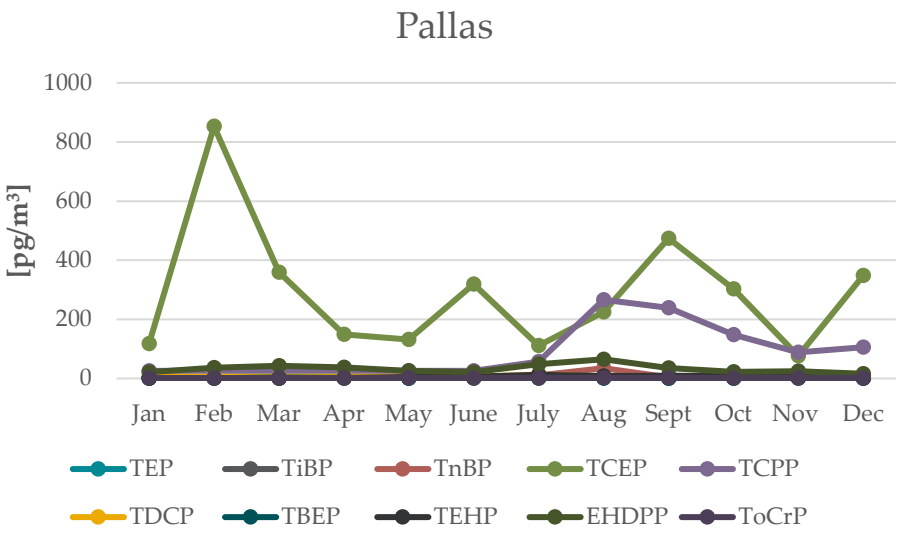

Figure 6. Measured organophosphates (TEP, TiBP, TnBP, TCEP, TCPP, TDCP, TBEP, TEHP, EHDPP, ToCrP) at the Pallas station, January – December 2018.

4 Discussion of results

The atmospheric concentrations obtained in this study for the 10 OPEs are compared to measured concentrations of organophosphates in background air reported in literature, see Table 2. Results from this study are here presented as the span from minimum to maximum obtained values. The data in Table 2 are sorted from north to south showing a somewhat higher concentration of some OPEs in the southern hemisphere compared to the northern hemisphere (e.g. TiBP, TCPP, TDCP, TEHP, EHDPP, TCrP). The concentrations found in the different studies vary (Table 2). However, we find that the concentrations obtained in this study are in comparable ranges as found in literature. TCPP, TCEP and EHDPP that were found in highest concentrations in this study are consistent with findings in other studies.

At the Zeppelin mountain at Svalbard, the dominant OPEs found were TCPP and TCEP. Higher concentrations during summer occurred for TCEP, TCPP and TnBP (Bohlin-Nizzetto et al., 2018). While the TCPP concentrations measured in this study are comparable with the results at Zeppelin mountain, the TCEP concentrations in Pallas were higher than at Svalbard and more in the same range as previously measured over the Arctic Ocean (Table 2). Also, no seasonality of TCPP and TCEP was observed in Pallas. During the oversea campaign MALASPINA, 14 different OPEs were analysed in 115 air samples collected from the tropical and subtropical Atlantic, Pacific and Indian Oceans. No trends between the southern and northern hemisphere were found and the samples were dominated by TCPP in and TnBP (Castro-Jiménez et al., 2016). It was found that TnBP was present in higher concentrations closer to the coast compared to on open sea. Castro-Jiménez et al. (2016) suggested that chlorinated OPEs, such as TCPPs are influenced by oceanic transport. TCPPs are to a greater share particle-bound than for example TnBP which has thus a longer atmospheric life-time and can be transported longer distance in the atmosphere (Castro-Jiménez et al., 2016). Therefore, it was suggested that the ratio TCPP/TnBP indicates the proximity to emission sources, with higher ratios indicating being further away from emission sources (Castro-Jiménez et al., 2016). To test this hypothesis the TCPP/TnBP ratios were calculated for Råö, Norunda and Pallas in monthly samples. The results are presented in Figure 7.

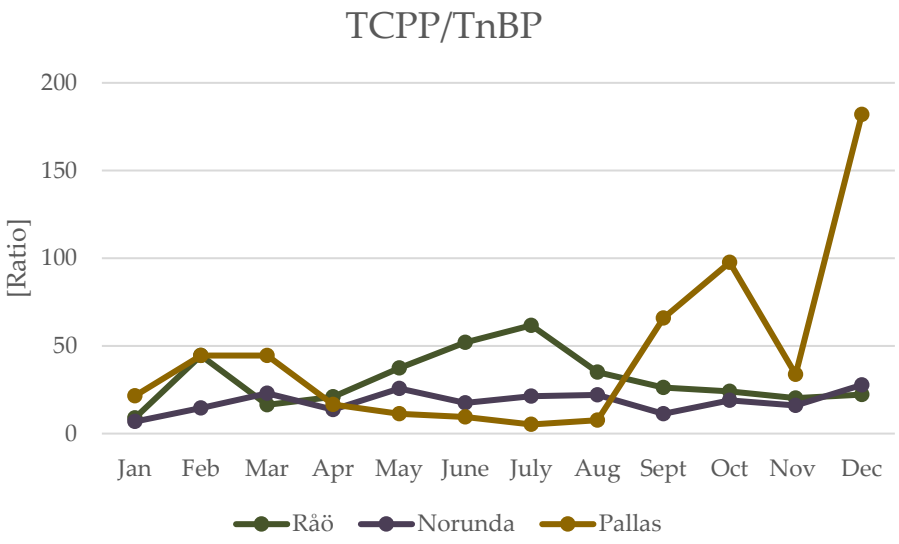

Figure 7. Calculated ratios between measured concentrations of TCPP/TnBP. Castro-Jiménez et al. (2016) suggested that small ratios indicate proximity to emission sources.

The overall lowest ratios were obtained in Pallas (TCPP/TnBP = 17), followed by Norunda (TCPP/TnBP = 18) and Råö (TCPP/TnBP = 34), which according to Castro-Jiménez et al. (2016) would indicate that Råö is furthest away from direct emission sources of OPEs. Figure 7 also shows a seasonality in TCPP/TnBP ratios that differs with location. Further research is needed to give information about the atmospheric dispersion of OPEs, the importance of secondary emission sources and long-range air transportation.

Many OPEs are considered as high-volume production chemicals. It is however hard to find available production numbers for the 12 studied OPEs, probably due to secrecy. TEP that is considered a high-volume production chemical was not detected in significant amount in air samples from Råö, Norunda or Pallas. TCEP and TCPP that were detected in highest amount in air samples had an estimated production of 1 000 ton/year (EU, 2008) and 5 000- 25 000 tons (USA, 2006), respectively. No information was found on the production volumes of EHDPP. Due to limited available information, no conclusions will be drawn regarding the ratios between production volumes and detected air concentrations of different OPEs in this study.

Table 2. Atmospheric concentrations of organophosphates reported in literature compared with achieved results in this study (min-max). MDL = Method Detection Limit (Table adapted from Castro-Jiménez et al., 2016).

Location	Sampling	Date	TEP pg/m³	TiBP pg/m³	TnBP pg/m³	TCEP pg/m³	TCPP pg/m³	TDCP pg/m³	TBEP pg/m³	TEHP pg/m³	EHDPP pg/m³	ToCrP pg/m³	Reference
Arctic Ocean	Open sea	2007-2013	-	-	<MDL - 97	<MDL - 860	<MDL - 660	<MDL - 13	-	<MDL - 7.5	<MDL - 11	-	Sühring et al., 2016
Arctic Ocean	Open sea	Jun-Sept 2010	-	16-35	<MDL - 36	130-590	85-530	<MDL - 5	-	<MDL -6	-	-	Möller et al., 2012
Resolute Bay/Alert	Coastal station	2008-2009, 2012	-	-	<MDL - 2300	<MDL - 430	<MDL - 280	<MDL - 46	-	-	<MDL - 40	-	Sühring et al., 2016
Ny Ålesund/Svalbard	Coastal station	Jun-Sept 2007	-	<10 - 140	<200	<200 - 270	<200 - 330	87-250	-	-	<200 - 260	-	Marklund et al., 2005
Ny Ålesund/Svalbard	Coastal station	Jun-Dec 2017	<3.3 - 23	1.9-15	<3 - 98	<9.1 - 29	<36 - 210	<0.3 - 1800	<MDL	<MDL	<MDL	-	Bohlin-Nizzetto et al., 2018
Longyearbyen/Svalbard	Coastal station	Sept 2012-May 2013	-	-	6-1000	40-60	10-190	2-290	-	1-40	6-300	-	Salamova et al:, 2014
Pallas, Finland	Station	Jan-Dec 2018	<1.3	<1.2 - 6.6	<1.2 - 35	76 - 850	<52 - 270	<11 - 13	<1.5 - 3.3	<0.8 - 12	16-65	<3.22	This study
Norunda, Sweden	Station	Jan-Dec 2018	<1.3 - 2.2	<1.2 - 5.3	<1.2 - 5.5	32 - 240	<52 - 120	<11	<1.5 - 18	<0.8 - 1	12-50	<3.22	This study
Råö, Sweden	Coastal station	Jan-Dec 2018	<1.3 - 2.2	<1.2 - 4.1	<1.2 - 7.6	<31 - 140	<52 - 400	<11 - 19	<1.5 - 5.2	<0.8 - 4.4	<10 - 47	<3.22	This study
North Atlantic Ocean	Open sea	Dec 2010, Jun-Jul 201	-	5-380	10-1700	<MDL -1200	<MDL -1300	<MDL -430	-	60-490	20-1700	-	Castro-Jiménez et al., 2016
North Pacific Ocean	Open sea	Jun-Sept 2010	-	14-20	6-14	160-280	98-270	5-8	-	1-12	-	-	Möller et al., 2012
North Pacific Ocean	Open sea	May-Jun 2011	-	3-100	20-2500	<MDL -310	100-1500	<MDL -500	-	60-380	100-1200	-	Castro-Jiménez et al., 2016
Sea of Japan	Open sea	Jun-Sept 2010	-	10-63	10-33	240-2000	130-620	16-52	-	5-38	-	-	Möller et al., 2012
East China Sea	Open sea	Oct 2009-Mar 2010	-	-	-	130	9	830	-	-	-	-	Cheng et al., 2013
South China Sea	Open sea	Sept-Oct 2013	-	1-4	1-5	14-110	15-38	1-4	-	2-16	-	-	Lai et al., 2015
North Sea	Open sea	Mar, May, July, 2010	-	<MDL -150	<MDL -150	6-100	30-1200	7-78	-	<MDL -30	-	-	Möller et al., 2011
Mediterranean Sea	Open sea	Jun 2006, May 2007	-	4-650	56-600	70-850	130-2300	<MDL -460	-	56-307	<MDL -830	-	Castro-Jiménez et al., 2014
Black Sea	Open sea	Jun 2006, May 2007	-	66-190	200-370	300-2400	540-2700	<MDL -97	-	36-190	<MDL -310	-	Castro-Jiménez et al., 2014
Philippine Sea	Open sea	Nov 2010-Mar 2011	-	10-23	10-100	20-160	22-410	50-780	-	6-92	-	-	Möller et al., 2012
South Atlantic	Open sea	Jan-Feb 2011	-	30-280	120-1200	10-540	20-980	<MDL-540	-	50-890	<MDL-1020	-	Castro-Jiménez et al., 2016
South Pacific	Open sea	Feb-Apr 2011	-	15-160	50-2200	34-370	50-800	<MDL-1000	-	40-350	260-800	-	Castro-Jiménez et al., 2016
Coral Sea	Open sea	Oct 2009-Mar 2010	-	-	-	88	7	370	-	-	-	-	Cheng et al., 2013
Indian Sea	Open sea	Nov 2010-Mar 2011	-	7-96	7-75	46-570	37-550	<MDL-220	-	4-50	-	-	Möller et al., 2012
Indian Sea	Open sea	Feb-Mar 2011	-	<MDL-110	70-940	50-620	30-1300	<MDL-290	-	<MDL-630	<MDL-630	-	Castro-Jiménez et al., 2016
Southern Ocean	Open sea	Nov 2010-Mar 2011	-	16	14	74	55	80	-	7	-	-	Möller et al., 2012
Antarctic Peninsula	Open sea	Oct 2009-Mar 2010	-	-	-	40	4	76	-	-	-	-	Cheng et al., 2013

5 Evaluation of existing method and recommendations for future monitoring

5.1 Method Evaluation

The results from this study were evaluated in order to propose future measurement programs. 12 OPEs were included in this study. However, analysis results for TPhP and TCrP were significantly higher compared to literature and to the other measured OPEs (see results in Table A1-A3 in Appendix). The reason might be background contamination from the material of the used PUFs. In a study by the U.S EPA, flame retardants present in flexible polyurethane foam were investigated and compared to possible substitutions on an environmental and health point of view. Polyurethane foam is normally used for many different applications including insolation, construction and furniture and is made from polyols, isocyanates, blowing agents and additives such as flame retardants, which are blended into the mix. The used flame retardant could either be very volatile or more chemically bound to the material. The desired products are either cut out from large "slabstocks", or the foam is moulded directly into the desired shape during manufacturing. TDCP and TCEP are recognized to be used most extensively in PUF material. Our blank tests, however, show no disturbance of these chemicals in the analyses. TPhP and TCrP are listed as chemicals used as flame retardants in PUF material (US EPA, 2015). Although IVL received no answer from the manufacturer regarding the content of flame retardants in their material, NILU mentioned similar problems of analysing TPhP and TCrP in air, using the same PUF material (personal communication). IVL recommends that presently used PUFs (IVL changed supplier of PUFs in 2019) should be rigorously tested for contamination before using them in the environmental monitoring of OPEs in background air.

5.1.1 Breakthrough PUFs

The sampling method for collecting the 12 OPEs was evaluated by checking the adsorbance efficiency of the used PUFs and filters. One filter and three PUFs were used in a series during all sampling. Normally the filters and the three PUFs are extracted and analysed together to form one sample. Twice during the study period (August and November), the three PUFs and the filter were extracted for Råö and analysed separately in order to study where the OPEs are adsorbed and trapped. High concentrations of a chemical on the third PUF would indicate a very volatile substance that might not be suitable to be sampled using this sampling method. The results of the breakthrough study are presented in Figure 8 for TEP, TnBP, TCEP, TCPP, TEHP and EHDPP. Remaining OPEs were under detection limit or excluded due to blank problems.

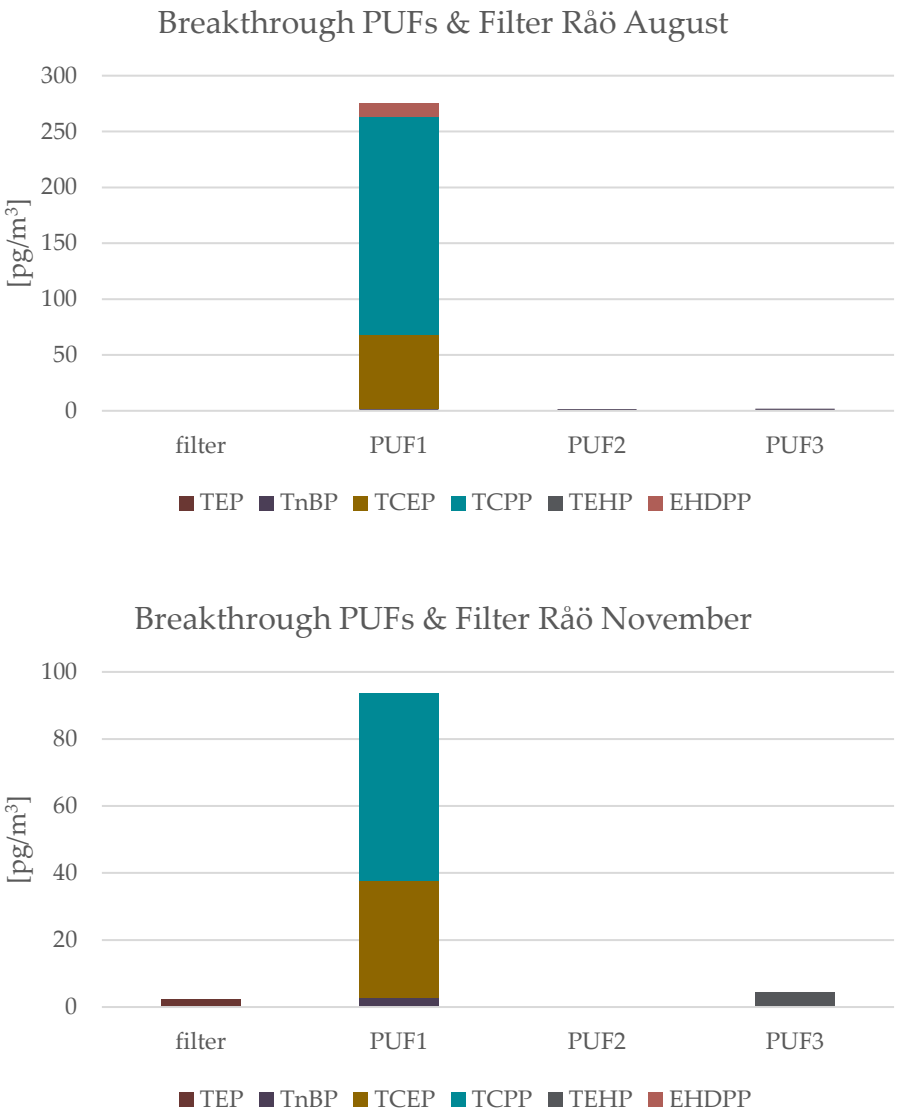

Figure 8. Concentrations of TEP, TnBP, TECP, TCPP, TEHP and EHDPP analysed in the different PUFs and filter at Råö. The test was performed twice (for August and November) during 2018 in order to study the breakthrough.

TCEP, TCPP and EHDPP were all only detected in the first PUF during both tests, showing no breakthrough and no adsorbance on the particle filter. During the August test, TnBP was detected in similar low amounts (~ 2 pg/m³) in all three PUFs. However, during the November test, TnBP was only detected in PUF1, indicating no breakthrough. TEP was during the test only detected once, on the particle filter during the November test. Generally low detected TEP concentrations were achieved in this study which could either indicate low air concentrations or inefficient sampling method. TEHP was during the first test in August only detected in PUF1 but only detected in PUF3 in November. Further breakthrough tests are recommended to support or modify the sampling method for some OPEs.

5.2 Conclusions and Recommendations

Results from OPE measurements during the test period January to December 2018 showed that the existing sampling method is feasible for the determination of OPEs in the atmosphere. This study shows that OPEs are detected in Sweden and Finland. Thus, to follow up changes in atmospheric concentrations, IVL recommends to do follow up studies of OPEs in air at Råö, Norunda and Pallas every second or third year.

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Appendix

Table A1. Organophosphates measured in air at the Råö station, Sweden.

Råö	TEP	TiBP	TnBP	TCEP	TCPP	TDCP	TBEP	TEHP	TPhP	EHDPP	ToCrP	TCrP-mix
	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³
Jan	<1.3	4.1	2.9	<31	<52	<11	<1.5	<0.8	<320	30	<3.2	5030
Feb	<1.3	<1.2	<1.2	<31	<52	<11	<1.5	<0.8	680	<10	<3.2	4600
Mar	<1.3	2.3	3.8	39	62	14	4.3	0.8	560	31	<3.2	1500
Apr	<1.3	1.6	3.6	43	74	11	2.9	1.1	600	28	<3.2	3080
May	<1.3	<1.2	6.0	64	220	19	5.2	1.9	480	47	<3.2	6400
June	<1.3	<1.2	7.6	140	400	16	2.8	2.4	690	33	<3.2	8400
July	<1.3	<1.2	5.8	64	360	<11	<1.5	0.9	890	32	<3.2	8080
Aug	<1.3	<1.2	5.6	66	190	<11	<1.5	0.9	2300	12	<3.2	14000
Sept	<1.3	1.6	3.8	37	100	<11	<1.5	0.9	700	22	<3.2	5100
Oct	<1.3	1.8	3.8	61	91	13	1.7	<0.8	490	21	<3.2	5020
Nov	2.2	<1.2	2.8	35	56	<11	<1.5	4.4	2400	<10	<3.2	12000
Dec	1.3	2.2	2.7	<31	61	<11	<1.5	1.1	1400	11	<3.2	6070

Table A2. Organophosphates measured in air at the Norunda station, Sweden.

Norunda	TEP	TiBP	TnBP	TCEP	TCPP	TDCP	TBEP	TEHP	TPhP	EHDPP	ToCrP	TCrP-mix
	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³
Jan	1.8	2.5	3.8	36	<52	<11	7.2	<0.8	<320	50	<3.2	<120
Feb	2.2	3.6	4.0	32	59	<11	4.6	<0.8	<320	44	<3.2	<120
Mar	<1.3	5.2	5.3	180	120	<11	18.0	0.9	<320	34	<3.2	<120
Apr	<1.3	5.3	5.5	50	75	<11	2.2	1.0	640	29	<3.2	140
May	<1.3	1.5	3.6	43	94	<11	7.5	<0.8	390	23	<3.2	180
June	<1.3	1.5	3.6	64	63	<11	11	<0.8	<320	23	<3.2	<120
July	<1.3	1.6	4.1	240	89	<11	2.3	<0.8	<320	29	<3.2	<120
Aug	<1.3	2.1	4.5	130	100	<11	1.8	<0.8	330	33	<3.2	<120
Sept	<1.3	<1.2	2.3	42	<52	<11	<1.5	<0.8	370	21	<3.2	<120
Oct	<1.3	1.7	3.6	40	68	<11	1.6	<0.8	<320	12	<3.2	<120
Nov	<1.3	3.0	5.0	98	81	<11	2.8	<0.8	<320	17	<3.2	<120
Dec	<1.3	1.9	2.7	96	75	<11	<1.5	<0.8	<320	19	<3.2	<120

Table A3. Organophosphates measured in air at the Pallas station, Finland.

Pallas	TEP	TiBP	TnBP	TCEP	TCPP	TDCP	TBEP	TEHP	TPhP	EHDPP	ToCrP	TCrP-mix
	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³	pg/m³
Jan	<1.3	<1.2	1.20	120	<52	<11	<1.5	<0.8	390	22	<3.2	2500
Feb	<1.3	<1.2	<1.2	850	<52	<11	<1.5	1.3	800	37	<3.2	1900
Mar	<1.3	<1.2	<1.2	360	<52	<11	3.3	<0.8	<320	43	<3.2	2300
Apr	<1.3	<1.2	1.6	150	<52	<11	1.8	1.8	1040	38	<3.2	6600
May	<1.3	<1.2	2.3	130	<52	<11	<1.5	4.7	1900	25	<3.2	16000
June	<1.3	<1.2	2.7	320	<52	<11	2.4	5.8	2100	21	<3.2	16000
July	<1.3	<1.2	11	110	56	13.00	3.2	12	3400	48	<3.2	19000
Aug	<1.3	6.6	35	220	270	<11	2.1	8.2	2700	65	<3.2	20000
Sept	<1.3	<1.2	3.6	470	240	<11	<1.5	9.2	2700	35	<3.2	25000
Oct	<1.3	<1.2	1.5	303	150	<11	<1.5	8.1	2600	23	<3.2	24000
Nov	<1.3	<1.2	2.6	76	89	<11	1.8	10	2900	24	<3.2	23000
Dec	<1.3	<1.2	<1.2	350	106	<11	<1.5	3.7	1600	16	<3.2	10500

Table A4. Transport- and analysis blanks of organophosphates in PUFs and filter.

Blanks	TEP pg/m³	TiBP pg/m³	TnBP pg/m³	TCEP pg/m³	TCPP pg/m³	TDCP pg/m³	TBEP pg/m³	TEHP pg/m³	TPhP pg/m³	EHDPP pg/m³	ToCrP pg/m³	TCrP-mix pg/m³
Transport blank Filter	0.5	0.5	0.4	10	14	3.2	0.74	0.29	150	3.5	0.12	16
Transport blank PUF	0.1	0.2	0.3	9	20	4.1	0.00	0.18	16	2.6	0.20	75
Analysis blank PUF 1	2.5	0.8	1.6	180	205	91	0.01	0.42	280	43	1.10	37
Analysis blank PUF 2	2.1	1.2	2.2	208	260	140	0.00	0.04	27	55	0.27	11
Analysis blank PUF 3	1.6	0.9	2.1	140	140	67	0.00	4.60	3400	41	0.33	230

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