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Detection of tris(2,3-dibromopropyl) phosphate and other organophosphorous compounds in Arctic rivers

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ABSTRACT

The flame retardant tris(2,3-dibromopropyl) phosphate (TDBrPP) was in the 1970s banned for uses in textiles that may be in contact with the skin, owing to strong suspicions that the substance was a human carcinogen.

The substance is looked for but rarely detected in samples from the built and natural environment, but there are indications that TDBrPP is still in use. Here we report the measurement of a polymer-water partition coefficient (K_{pw}) for two types of silicone rubber (SR), allowing quantitative estimation of freely dissolved concentrations of TDBrPP by passive sampling in water. We found levels of one to two hundred picograms per litre in two Arctic rivers that were sampled during a 2014-2015 survey of contamination using passive samplers in Norwegian and Russian rivers draining into the Barents Sea. We also report the widespread presence of other organophosphorus flame retardants in this survey of eight rivers that drain into the Barents Sea.

INTRODUCTION

Tris(2,3-dibromopropyl) phosphate (TDBrPP or TDBPP) is an organophosphorus flame retardant (OPFR) that has been used in formulation with registered trades names such as FireMaster T23, Phoscon FR150 or Bromkal P67-6HP. Commercial production was initiated in the US in 1959 and applications of TDBrPP were for example for polyurethane or polystyrene foams, paints, carpets or sheets. Until a ban in 1977, children's pajamas were treated with TDBrPP with levels of 5-10% by weight. The World Health Organization (WHO) and the International Agency for Research on Cancer (IARC) identified TDBrPP as having carcinogenic effects on experimental animals (classified as a group 2A agent). The European Food Safety Authority also stated it is a likely genotoxic and carcinogenic chemical. While it is now banned or with heavily restricted usage in many countries, some international suppliers can apparently still be found[†]. Measurements of TDBrPP have been reported for house dust (Dodson et al. 2012) and seawater (Hu et al. 2014). In the vicinity of a chemical plant known to have produced the chemical, high concentrations of TDBrPP have also been measured 40 years after closure of the factory (Peverly et al. 2014).

There has been an increased focus on the measurement and understanding of the fate of OPFRs and plasticisers in the environment as a result of their use as replacement for brominated diphenyl ethers (Van der Veen &de Boer 2012). Passive sampling has previously been applied to the determination of OPFR concentrations in water with the ceramic dosimeter (Cristale et al. 2013a), with SR (Allan et al. 2013, Pintado-Herrera et al. 2016, Vrana et al. 2015), with low density polyethylene (McDonough et al. 2018) or with a modified version of the polar organic compound integrative sampler (POCIS) (Yang et al. 2017) with estimated water concentrations in ng L^{-1} to µg L^{-1} range. TDBrPP as other OPFRs is in a non-ionized form amenable to absorption-based passive sampling, and the reported $\log K_{ow}$ of 3.71 (Table 1) means that polymer-water partition coefficients (K_{pw}) for commonly used polymers (e.g. low density polyethylene and silicone rubber) are likely to be sufficiently high. We have previously shown that under similar sampling conditions, it was possible to identify a wider range of organophosphorus compounds with SR than with low density polyethylene (Allan et al. 2013). Pintado-Herrera and co-workers measured $\log K_{pw}$ values for a set of OPFRs with $\log K_{ow}$ in the range 3.7-9.5, of 4.7 to 5.9 for AlteSil™ silicone rubber (Pintado-Herrera et al. 2016). $\text{Log}K_{pw}$ for selected halogenated phosphate esters have been measured in the range 2.89-3.87 for AlteSil™ SR (Smedes 2018).

[†] http://www.chemicalbook.com/ChemicalProductProperty_EN_CB8414230.htm

In this study, we report the calibration of two types of silicone rubber for the passive sampling of TDBrPP in water. As part of a screening study for a wider range of chemicals, its presence was investigated in Arctic rivers of the North of Norway and the Russian Kola peninsula with SR passive samplers in 2014 and 2015. We also report on detection of other OPFRs in some of these rivers.

MATERIAL AND METHODS

Materials.

All glassware was either solvent rinsed or baked in a muffle furnace at 540 °C. Solvents (dichloromethane, methanol, pentane and acetonitrile) were from Rathburn (Walkerburn, Scotland) with the exception of cyclohexane (J.T. Baker, Deventer, Holland) and were of HPLC grade or better. Ultra-pure water from an Option 3, Elga™ was used for PRCs spiking and for K_{pw} measurements. Carbon dioxide (medical grade), which was used as the mobile phase in SFC, was purchased from AGA gas (Oslo, Norway). Analytical-grade standards for deuterated PAHs (d_{10}-fluorene, d_{10}-phenanthrene, d_{10}-fluoranthene, d_{12}-chrysene and d_{12}-benzo[*a*]pyrene) were from Chiron (Trondheim, Norway) and with purities >99.5%. Tri-tolylphosphate o, m, p mix (TCPs), cresyl diphenyl phosphate (DCP), tri-propylphosphate TPrP), tri-butylphosphate (TBP), Tris(2-chloroethyl)phosphate (TCEP), tris (monochloropropyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl)phosphate (TDCPP), 2-ethylhexyl diphenyl phosphate (EHDP), tris(2-ethylhexyl)phosphate (TEHP), tris(2-butoxyethyl)phosphate (TBEP), tri-isobutyl phosphate (TiBP), tris(2,3-dibrompropyl) phosphate (TDBrPP), from Sigma-Aldrich (St. Louis, MO). Butyl diphenyl phosphate dibutylphenyl phosphate (BDPhP) and tri-phenyl phosphate (TPP) were from Chiron (Trondheim, Norway), Tris(3,5-dimethylphenyl) phosphate (T35DMPP) and ^{13}C-triphenyl Phosphate (MTPP) were from Wellington Laboratories (Guelph, ON, Canada). D_{18}-tris(2-chloroisopropyl) phosphate (MTCPP), D_{15}-tris(1,3dichloro-2-propyl)phosphate (MTDCPP), D_{27}-tributylphosphate (MTBT) were obtained from Cambridge Isotope Laboratories (Tewksbury, MA, USA). The isotopically-labelled OPFRs were used as recovery standards. The AlteSil™ silicone rubber (0.5 mm thick) was obtained from Altec (Bude, UK). SSP-M823 polydimethylsiloxane (purchased from Shielding Solution Ltd, UK) also used in the K_{pw} measurement experiments was purchased from Shielding Solutions Ltd (Great Notley, UK).

Passive sampling devices.

AlteSil™ silicone rubber samplers were prepared following procedures used previously (Allan et al. 2010, Allan et al. 2013). Polymer sheets were cut to appropriate dimensions (100 cm x 2.5 cm wide) before being cleaned in a Soxhlet extractor using ethyl acetate to remove oligomers. The polymer strips were then dried to remove the ethyl acetate and placed in a glass jar for further cleaning by partitioning with methanol prior to spiking performance reference compounds (PRCs) using a methanol-water solution (Booij et al. 2002). PRCs are isotopically non-naturally occurring labelled-analogues (deuterated PAHs) of chemicals of interest, that can dissipate from the samplers during exposure. The dissipation of PRCs from the samplers during exposure allow us to estimate exchange kinetics during deployment *in-situ* (Booij et al. 1998). Once prepared, all samplers were placed in a sealed and clean metal container at -20 °C until exposure. For this work, one sample was formed of two strips and this corresponds to having 1000 cm^2 of sampling surface and a nominal sampler mass of 30 g.

Passive sampling sites and fieldwork.

Sites were selected to cover the widest range possible of rivers that flow into the Barents Sea from the Norwegian and Russian Arctic in Finnmark and Kola peninsula. On the Russian side, rivers under pressure from mining and ore processing industrial effluents and municipal and domestic sewage effluents were selected. Norwegian rivers were the Tana (catchment area of 16377 km^2, river length of 361 km, and an estimated discharge of 180 $m^3\ s^{-1}$) and Neiden (100 km long, 34 $m^3\ s^{-1}$).

Rivers in Russia included the Kola (3846 km^2, 83 km long, 44 m^3 s^{-1}), Pechenga (1829 km^2, 101 km long, 22 m^3 s^{-1}) and Titovka (1226 m^2, 83 km long, 17 m^3 s^{-1}). The two water bodies at the border between Norway and Russian and between Norway, Russia and Finland were the Grense Jakobselv (236 km^2, 45 km long, 3.2 m^3 s^{-1}) and Pasvik river (18404 km^2, 387 km long, 175 m^3 s^{-1}), respectively. For the Pasvik river, multiple sampling sites were selected to obtain a more detailed picture of contamination sources. The Pasvik watercourse originates in Lake Inari in Finland, flows into Russia and then forms the border between Norway and Russia over a distance of approximately 120 km. There is a total of seven water impoundments (hydropower reservoirs) in this part of the watercourse. Rivers selected generally differed in catchment size and number of people living within them.

Duplicate samplers were deployed at every site for each exposure period. Samplers were deployed on three occasions, (i) from September to November 2014, (ii) from May to June 2015 and (iii) from June to September 2015 at sites shown on Figure 1.

Silicone passive samplers were deployed in 2014 using standard equipment (spider holders and cylindrical canisters). Most of the samplers deployed in September 2014 could not be retrieved successfully from the rivers as a result both of icing of the rivers and human interference. Only samplers deployed in the Grense Jakobselv and those at the Pasvik Nedre sites were recovered in November 2014. These were analysed in 2015 together with control samplers. Samplers deployed in the Tana in 2014 were recovered after snowmelt in 2015. The use of metal canisters and spider holder was deemed not necessary and was believed to promote human interferences during exposure.

For deployments in 2015, one short deployment (2-3 weeks from May until June 2015) was conducted towards the end of the snowmelt period. A second longer deployment was undertaken to maximise the possibility to detect and quantify compounds present at trace levels by increasing the exposure time. For these two deployments, samplers were not enclosed in a protective cage to ensure conspicuous deployment. Samplers were directly fastened to the deployment rope/string and waste plastic bottles found on-site were used as buoys for deployment at the sampling locations in Russia. Standard deployment cages were used on the Norwegian side of the border. Despite these precautions, some samplers at certain sites were lost.

Polymer-water partition coefficient measurement.

AlteSil™ and SSP polymer-water partition coefficients for TDBrPP were measured in the laboratory by equilibrating ultrapure water and SSP SR with AlteSil™ SR pieces pre-loaded with TDBrPP. Glass bottles with glass lids were filled with one litre of ultrapure water, leaving a sufficient head space to allow effective water turbulences during shaking. Small AlteSil™ polymer pieces were cleaned and dosed with TDBrPP in a similar way to described above for samplers prepared for field exposures. Two assays with different polymer-water mass-volume ratios were prepared by placing in the glass bottles one piece of SSP and TDBrPP-dosed AlteSil™. SR-water mass-volume ratios were 20 and 500 mg/L. The two bottles were shaken at 150 rpm on an orbital shaker for 10 months, period after which concentrations in water and SR phases were expected to be at equilibrium. Assays were stopped and approximately 700 mL of water was transferred to a decanter for extraction to ensure that the quantification of TDBrPP concentration in water did not include the fraction sorbed to glass wall of the bottles. Water samples were extracted by liquid-liquid extraction with dichloromethane (DCM, 2 x 200 mL). The solvent was reduced under a gentle stream of nitrogen and solvent exchanged to acetonitrile before being reduced to a final volume of 0.5 mL for analysis. SR pieces were extracted with 200 mL of DCM. The DCM was reduced and solvent exchanged to acetonitrile before analysis. Recovery standards were added during the initial DCM extraction step. Quality control measures included a solvent blank, ultrapure water blank and water extraction recovery test. The recovery for TDBrPP extraction from water was 80.5 % while amounts in solvent and extraction blanks were below limits of detection.

Passive sampler extraction and analysis.

Following sampler retrieval, their surface was rinsed with ultrapure water and dried with a clean tissue to remove any fouling. All samplers were extracted overnight with *n*-pentane (2×200 mL) with recovery standards. The volume of pentane was reduced to 2 mL by a gentle stream of nitrogen at room temperature. Sample clean-up was using gel permeation chromatography (GPC) before PAH analysis and partitioning with acetonitrile prior to analysis for TDBrPP and other OPFRs. In addition to the use of recovery standards, we also performed spike-recovery work to assess the efficiency of the extraction, clean-up and instrumental analytical procedures. In addition to field and lab blanks/control silicone rubber passive samplers, procedural blanks were also used to assess possible contamination arising from the extraction and analysis step.

Analysis for PRCs was on an Agilent 7890A gas chromatograph that was linked to an Agilent 5975c inert XL EI/CI mass spectrometer operated in single ion monitoring (SIM) mode with electron impact ionisation (70 keV). The separation of analytes was on a DB-5MS column (30 m, -0.25 mm i.d. and o.25 µm film thickness, Agilent JW Scientific, Santa Clara, USA) following 1 µL pulsed splitless injection (pulse pressure 20 psi for 1.2 min, injector temperature of 300 °C). Helium was used as carrier with flow set to 1.2 mL min^{-1}. The temperature programme for the GC oven consisted of a step at 60 °C (held for 2 min) before an increase to 250 °C (at the rate 7 °C min^{-1}) and a final increase to 310 °C (at the rate of 15 °C min^{-1}) with this temperature held constant for a further 5 min. Temperatures for the ion source, quadrupole and transfer line were set to 230, 150 and 280 °C, respectively. Quantification was performed using the relative response of surrogate internal standards and 7-point calibration curves. Deviation (< 20%) of the qualifier ion response relative to that of the quantifier ion was used for identification.

Analysis for TDBrPP (and other organophosphorus flame retardants) was with surpercritical fluid chromatography linked to mass spectrometry (SFC/MS/MS). SFC/MS/MS analysis was performed using an ACQUITY Ultra Performance Convergence Chromatography (UPC2) system (Waters, Milford, MA) with a Quattro Premier XE tandem mass spectrometer (Waters). The SFC system was equipped with a convergence manager which controls backpressure, binary solvent manager, temperature-controlled column manager and fixed loop sample manager. The MS was equipped with an ESI source and the separation of OPFRs was achieved on an Aquity UPC2 HSS C18 column (Waters, 100 × 3.0 mm, 1,8 um particles). The SFC gradient program was: modifier 3% (2 min), 3–20 % (4.5 min), 50 % (5 min), hold 2 min, back to 3% (0.5 min) and hold 2 min. The modifier was acetonitrile: methanol (70+30, 0.1 g/L ammonium acetate and 0.01 % acetic acid). The injection volume was 3 µL, the flow rate 1.5 mL/min, the temperature of column manager was 50 °C and the active back pressure regulator (ABPR), was at 1600 Psi. A post column make-up flow (0.3 mL/min) of methanol with 0.1 % formic acid was used to enhance positive electrospray ionization. The final MS analysis conditions were as follows: capillary voltage, 3.2 kV; de solvation temperature, 400 °C; cone gas flow rate, 50 L/h; desolvation gas flow rate, 800 L/h. The mass spectrometer was operated in positive ionization mode, and data were acquired in the selected reaction monitoring (SRM) mode using three transitions (696.5>98.8, 698.5>98.8 and 700.5>98.8) for the identification of TDBrPP.

Recoveries for all OPFRs from silicone rubber samplers were in the range 69-128 % except for TCEP (< 5 %), TPrP (37 %) and TEHP (53 %). The low recoveries particularly for TCEP and TPrP can be explained by their low hydrophobicity (Van der Veen &de Boer 2012) and loss during the acetonitrile partitioning clean-up.

Passive sampling data handling.

Sampling rates, R_s (L d^{-1}) were estimated for each sampler at each site by applying the non-linear least square method to the PRC dissipation data using the methodology presented by Booij and Smedes (Booij &Smedes 2010). The model to estimate R_s from logK_{pw} was that given in Rusina et al. for AlteSil™ silicone rubber (Rusina et al. 2009) and relies on the assumptionthat the uptake in the samplers for most hydrophobic substances, including TDBrPP, is under boundary layer-control. The complete equation taking into account linear, equilibrium and partially equilibrated conditions was used to estimate dissolved concentrations of TDBrPP:

$$C_w = \frac{n_{acc}}{K_{pw}m(1 - e^{\frac{-R_s t}{K_{pw}m}})}$$

with C_w, the freely dissolved concentration (ng L^{-1}), n_{acc} the mass of TDBrPP accumulated in the sampler during exposure, *m* the mass of the silicone rubber passive sampler and K_{pw} the AlteSil-water partition coefficient measured for TDBrPP. A correction for water temperature deviating from that at which K_{pw} were measured for TDBrPP and PRCs was not applied to K_{pw} values.

RESULTS AND DISCUSSION

Polymer-water partition coefficient, K_{pw} for TDBrPP.

We expect that the experimental duration of 10 months was amply sufficient to reach equilibrium between the TDBrPP concentrations in the two pieces of silicone rubber and in water at 20 °C. Final water and silicone rubber concentrations were 37 and 87 ng L^{-1} and 95-965 ng g^{-1}, respectively. This translated to log$K_{pw,SSP}$ and log$K_{pw,AlteSil™}$ of 3.40 and 3.97 L kg^{-1} (Table 1). Relative percent differences between the two measurements that included differences in TDBrPP spiking levels and silicone rubber mass/water volume ratios, were perfectly acceptable. In general, these silicone rubber-water partition coefficients are not very high but in agreement with reported/calculated logK_p values of 3.71[‡]. In general, lower logK_{pw} have been reported for SSP silicone rubber than for AlteSil™ (Gilbert et al. 2016). This is also the case for TDBrPP.

Estimates of freely dissolved TDBrPP concentrations.

The sampling rates for AlteSil™ silicone rubber passive samplers estimated using PRCs and the NLS method (Booij &Smedes 2010) had an average of 17 L d^{-1} but varied from 0.9 L d^{-1} for the samplers deployed in the Tana river for 264 days to 101 L d^{-1} for an 87 day-long exposure in the Pasvik river. These are shown in Table 2. The variability of R_s between duplicate samplers exposed at each site was in most case very low with relative percent differences (RPDs) values ranging from 2 to 30 %. One exposure in the Pasvik resulted for unknown reasons in a factor of two difference in R_s for duplicate samplers. Water velocity or turbulences at the different passive sampler exposure sites can result in large differences in sampling rates (Booij et al 2003). While an R_s of 4-20 L d^{-1} for 1000 cm^2 of sampling surface is a totally acceptable range, values over 100 L d^{-1} or under 1 L d^{-1} are relatively uncommon. The low sampling rate could be due to the extremely low river water temperature or even frozen conditions for a large period of the deployment. High sampling rates have been obtained in the past with towed deployments or the use of dynamic passive sampling (Allan et al. 2011, Vrana et al. 2015).

[‡] http://www.chemspider.com/Chemical-Structure.29089.html

Considering the instrumental limits of quantification for TDBrPP, the sampling rates and exposure times, limits of quantification for TDBrPP in water were below 100 pg L^{-1}.

TDBrPP was not detected in preparation or field control samplers extracted and analysed within the same batches of analysis as exposed samplers. It was also not found in any extracts from passive samplers exposed in the Grense Jakobselv, Kola, Neiden, Tana and Titovka rivers. However, as shown in Table 2, surprisingly it was found above limits of quantification at three stations: at Sites 5 and 8 (Kuetsjarvi and Salmijarvi sites) in river Pasvik and at Site 11 in the Pechenga river. For Sites 8 and 11, TDBrPP was detected during one of the two sampling periods only. Importantly however, when TDBrPP was found above limits of quantification, it was consistently detected in both duplicate samplers with on average masses absorbed of 49, 22 and 24 ng per sampler for samplers exposed at Sites 5, 8 and 11 (Table 2). RPDs were 8.3, 56 and 39 % for Sites 5, 8 and 11, respectively, and slightly higher than those generally observed for silicone rubber based passive sampling of more commonly analysed target chemicals such as PAHs or PCBs. Freely dissolved concentrations in water for the Pasvik and Pechenga rivers were calculated from masses accumulated and sampling rates according to the methodology presented above. As shown in Table 2, these were in the range of 0.1-0.2 ng L^{-1}.

Nowadays, the presence or occurrence of TDBrPP in the natural environment is only sparsely reported since it was removed from the market in the US and in many countries in Europe in the 1970s after it was found to have potential to be carcinogenic and genotoxic. In Europe, it was regulated under the European Union's Directives 79/663/EEC 83/264/EEC regarding restrictions on the use of certain dangerous substances. Li et al. (Li et al., 2014) did not find TDBrPP in any drinking water samples from their screening study in China (Li et al. 2014). TDBrPP was also not found in wastewater treatment plant samples (Woudneh et al. 2015). TDBrPP was also not found in surficial sediment samples collected from various locations in the Western Scheldt estuary in the Netherlands (López et al. 2011). However, Hu et al. did consistently detect TDBrPP in seawater samples collected in coastal area of the yellow and East China Sea in the vicinity of major Chinese coastal cities (Hu et al. 2014). Concentrations for TDBrPP were in the range of 20 to 500 ng L^{-1}. The source of TDBrPP is likely to be manufacturing or use and release to the environment through municipal and industrial wastewater effluents. This is perhaps not surprising since suppliers of this chemical can apparently be found in China. High organophosphorus flame retardant concentrations in riverine environments have also been attributed to urban/populated areas and their release associated with wastewater treatment plant effluents (Cristale et al. 2013b). In our case, the lower TDBrPP concentrations observed are more likely to result from use and emission through wastewater treatment plants rather than production. This indicates possible continued use of garments and/or other plastics such as polyurethane or polystyrene that contain TDBrPP. In the case of the River Pasvik, the closest town from which wastewater effluent discharges may occur is the town of Nikel with roughly twelve thousand inhabitants (census of 2010) on the shores of lake Kuetsjarvi. For the Pechenga, the passive sampler exposure site was upstream from the town of Pechenga and only smaller settlements are found upstream (Luostari and Korzunovo). Using LDPE passive samplers, McDonough et al. (2018) did consistently detect TDBrPP in East Lake, Cape Bounty in the Canadian Arctic at concentrations of 100-300 pg L^{-1} which is relatively unexpected considering the remoteness of the site. It was also measured at that concentration level in Artic surface waters of Allen Bay. However, they did not find it at any depths for two moorings in the Fram Straight in the North Atlantic (McDonough et al. 2018).

TDBrPP was found above limits of quantification in 62 and 38 % of dust samples from Californian homes sampled in 2006 and 2011, respectively (Dodson et al. 2012). The mean concentration for dust from 16 homes was 1000 ng g^{-1} for 2006 samples and significantly lower than this for 2011 samples (40 ng g^{-1}). Considering the hydrophobicity of TDBrPP (expected $\log K_{oc}$ of 3.29), it will sorb to sedimentary organic matter in a riverine system. Therefore, sustained presence in these aquatic environments may be confirmed by analysis of sediment from depositional areas in these rivers.

Presence of other OPFRs in water.

TCPP, TiBP, TPP, TnBP, EHDP, TDCPP, and TEHP were found in blank samplers. For TCPP, TiBP, and TEHP, levels in field blanks were similar to those in preparation blanks, which shows that sampler contamination was from preparation and manipulation in the field did not result in further contamination. The presence of TCPP, TiBP, TnBP and TPP in procedural blanks but at a lower level than passive sampler blank indicates that some of the contamination observed also results from the extraction and analysis step. For TPP, TnBP, TDCPP and EHDP, substantially higher masses were observed in field blanks than in preparation blanks. Information on blank levels was used to decide whether OPFR amounts found in exposed samplers can legitimately be attributed to uptake during exposure.

As shown in Table 3, the lowest number of OPFRs detected were for the Grense Jakobselv (Site 1) and for the two sites the furthest upstream on the Pasvik (Sites 7 and 9). This is not surprising since these are rivers and sampling locations with very little human impact. The highest number of OPFRs consistently detected and with largest amounts were for the Pechenga (Site 11) and Sites 5 and 8 on the river Pasvik (Kuetsjarvi and Salmijarvi). These data are consistent with detections of TDBrPP. Notably, despite the low recoveries, TCEP was consistently detected in duplicate extracts from these two of these sampling locations. OPFRs listed in Table 3 including DCP, TBEP, TnBP and TiBP were detected in most rivers sampled in this study and this is consistent with the suite of OPFRs seen for example in storm waters in Oslo (Ruus 2017). EHDP was found in sampler extracts from all rivers, however the very variable and sometimes high amounts found in field blanks prevent us from reporting detection although its presence in these aquatic environment is likely (Ruus 2017). BDPhP, DBPhP, T35DMPP and TPrP were not detected in any exposed or blank samplers.

Conclusion.

Although passive sampling can be conducted with different types of devices since OPFRs generally span a wide range of hydrophobicity, relatively little work has been done to calibrate the uptake of organophosphorus compounds in passive sampling devices. The ceramic dosimeter was calibrated for the sampling of selected OPFRs by Cristale et al. with R_s in mL d^{-1} resulting in limits of detection in the ng L^{-1} range for 3 week-long deployments (Cristale et al. 2013a). Pintado-Herrera et al. included selected OPFRs in the laboratory-based measurement of silicone rubber-water partition coefficients and polymer diffusion coefficients (Pintado-Herrera et al. 2016). Measurements of K_{pw} values for OPFRs have been undertaken and K_{pw} values exist but remain unpublished. With 30 g and 1000 cm^2 of sampling surface, R_s values in the range of L d^{-1} can be obtained for SR. However, since $\log K_{pw}$ for the two SR calibrated here are below 4 for TDBrPP, it is likely that sampling is undertaken at equilibrium for this compound for deployments of one month or longer. The SR-based passive sampling solution presented here permit limits of detection equivalent to values as low as 20 pg L^{-1} in river water. Screening of extracts for a range of OPFRs confirms the presence of these many of these chemicals in Arctic rivers of Finnmark region in Norway and Kola peninsula in Russia. The narrowest numbers of OPFRs in sampler extracts were observed at riverine sampling locations with expected lowest level of human impact.

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Table 1. Selected physico-chemical parameters of tris(2,3-dibromopropyl) phosphate (TDBrPP) and measured polymer-water partition coefficients for AlteSil™ and SSP silicone rubber.

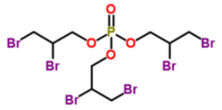
Structure	
MW (g mol^{-1})	697.6
logP	3.71^{a}, 5.39^{b}
logK$_{pw,\ AlteSil™}$	3.40 (*11 %*)^{c}
logK$_{pw,\ SSP}$	3.97 (*34 %*)^{c}
^{a}from Chemspider; ^{b}from Chemicalize; ^{c}Relative percent difference (RPD) of K$_{pw}$ based on duplicate measurement with two SR-water mass-volume ratios	

Table 2. Masses absorbed, estimated sampling rates (R$_s$) and freely dissolved concentrations in water (C$_w$) for TDBrPP in silicone rubber passive samplers exposed in seven Arctic rivers.

	River	Exposure Deployment	Retrieval	Time (d)	R$_{s\text{-}TDBrPP}$ (L d^{-1})*	n$_{ACC}$ (ng)*	C$_w$ (pg L^{-1})*
1	Gr. Jakobselv	25.05.2015	13.06.2015	19	7.1 (*9*)	< 5	< 50
		13.06.2015	16.09.2015	95	4.8 (*30*)	< 5	< 26
3	Kola	27.05.2015	11.06.2015	15	5.1 (*8*)	< 5	< 80

		11.06.2015	14.09.2015	95	4.0 (*24*)	< 5	< 28
4	Neiden	13.06.2015	14.09.2015	93	6.6 (*25*)	< 5	< 22
5	Pasvik	11.06.2015	06.09.2015	87	101 (*2*)	**49.1 (*8.3*)**	**201 (*10*)**
6		25.05.2015	13.06.2015	17	7.7 (*8*)	< 5	< 47
7		25.05.2015	13.06.2015	19	5.2 (*3*)	< 5	< 62
		13.06.2015	14.09.2015	93	9.5 (*2*)	< 5	< 21
8		26.05.2015	11.06.2015	16	29.0 (*4*)	**22.2 (*56*)**	**156 (100)**
9		11.06.2015	06.09.2015	87	5.0 (114)	< 5	< 40
11	Pechenga	27.05.2015	13.06.2015	17	27.3 (*15*)	< 5	
		13.06.2015	16.09.2015	95	24.1 (*25*)	**24.0 (*39*)**	**96 (*41*)**
12	Tana	22.09.2014	13.06.2015	264	0.9	< 5	< 32
		13.06.2015	13.09.2015	92	6.8 (*4*)	< 5	< 22
13	Titovka	11.06.2015	06.09.2015	87	13.0 (*31*)	< 5	< 45

*relative percent differences (RPDs) based on duplicate measurements are given in brackets

Table 3. Detection of OPFRs in silicone rubber passive sampler extracts after exposure in Arctic rivers

		TCEP	TCP	DCP	TEHP	TBEP	TDCPP	TnBP	TPP	TiBP	TCPP
	Blanks/controls				✓		✓	✓	✓	✓	✓
1	Gr. Jakobselv				✓	✓	✓			✓	
3	Kola			✓	✓	✓	✓	✓		✓	✓
4	Neiden			✓	✓	✓	✓	✓	✓	✓	
5	Pasvik	✓	✓	✓		✓	✓	✓	✓	✓	✓
6				✓	✓	✓	✓	✓			✓
7				✓	✓	✓					✓
8			✓	✓	✓	✓	✓	✓	✓	✓	✓
9				✓		✓				✓	✓
11	Pechenga	✓	✓	✓		✓	✓	✓	✓	✓	✓
12	Tana			✓		✓	✓	✓	✓	✓	✓
13	Titovka		✓	✓	✓	✓		✓		✓	

Note: Relative standard deviations of OPFR masses found in blanks were below 20 % except for TiBP and TnBP. Here, detection in exposed samplers means quantification of masses of individual OPFRs over three times levels found in field blanks, with OPFRs measured in duplicate passive samplers and for all exposure periods within a single sampling location.

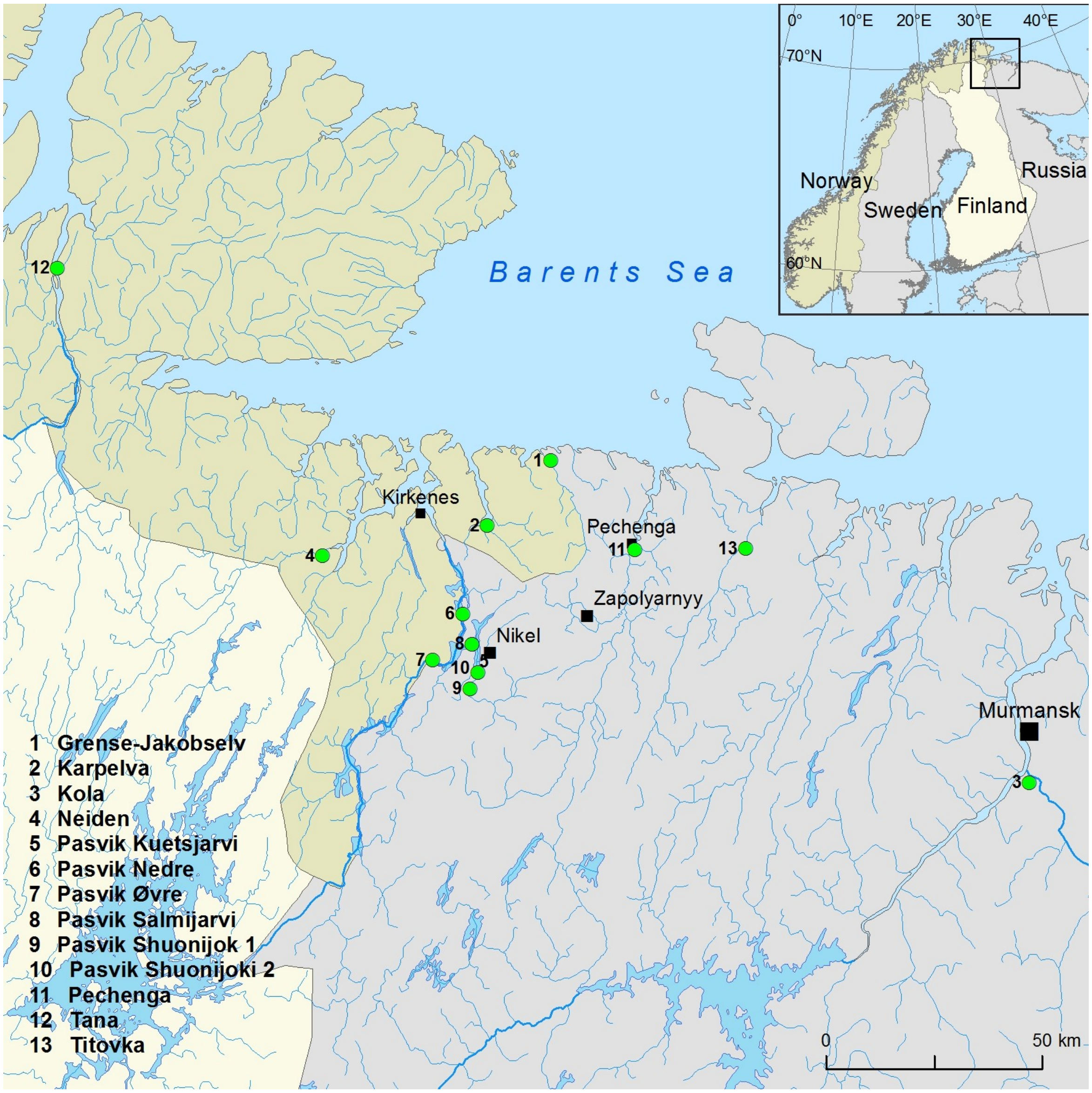


Figure 1. Overview of rivers and sampling sites in the Finnmark region and Kola peninsula