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Organophosphorous flame retardants in biota from Svalbard, Norway

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ABSTRACT

Eight arctic species, including fish, birds and mammals, from diverse habitats (marine and terrestrial) within the Svalbard Archipelago, Norway, were screened for 14 organophosphorus flame retardant (PFR) compounds. Ten PFRs were detected: tris(2-chloroethyl)phosphate (TCEP), tris(2-chloroisopropyl)phosphate (TCIPP), tris(1,3-dichloro-2-propyl)phosphate (TDCIPP), triphenyl phosphate (TPHP); 2-ethylhexyl diphenyl phosphate (EHDPP); tris(2-butoxyethyl)phosphate (TBOEP); tritolyl phosphate (TCrP); triisobutyl phosphate (TIBP); tris(2-ethylhexyl)phosphate (TEHP); and butyl diphenyl phosphate (DPhBP). The greatest number of different PFR compounds, and the highest detection frequency were measured in capelin (*Mallotus villotus*), and the lowest in Brünnich's guillemot (*Uria lomvia*). The highest concentrations of ΣPFR, as well as the highest concentration of a single PFR compound, TBOEP, were measured in arctic fox (*Vulpes lagopus*). The presence of PFR compounds in arctic biota indicates that these compounds can undergo long-range transport and are, to some degree, persistent and bioaccumulated. The potential for biomagnification from fish to higher trophic levels seems to be limited.

Organophosphorus compounds (PFRs) have been used as flame retardants and plasticizers since the 1960s and they have been found to be ubiquitous substances in indoor environments (Wensing et al., 2005). These compounds have been proposed as alternatives to brominated flame retardants (BFRs) since the use of several BFRs, such as the penta- and octa-PBDEs (polybrominated dephenyl ethers), has recently been banned in Europe (Stockholm Convention, 2009; van der Veen and de Boer, 2012). PFRs are currently used as antifoaming agents and additives in products such as lubricants and hydraulic fluids, floor polishes and glue. The European Union (EU) used 465,000 tons of flame retardants in 2006, 8.6% (40,000 tons) of which were PFRs (SRIConsulting, 2008). The import and use of these compounds in the Nordic countries Sweden, Denmark, Norway and Finland have been estimated to be about 4000 tons per year in the period 2000–2008 (SPIN2000, 2011). Based on the large tonnage of PFRs in use, and since PFRs are additives (i.e., not chemically bound to the final product), diffusion of PFRs into the environment likely takes place. However, the distribution of specific PFRs in the environment strongly depends on their individual physio-chemical properties (Reemtsma et al., 2008; van der Veen and de Boer, 2012).

The occurrence of PFRs in natural environments was first reported in the late 1970s (Saeger et al., 1979; Sheldon and Hites, 1978). Since then PFRs have been detected in wastewater from sewage treatment plants (Marklund et al., 2005), rain and snow from urban and remote areas (Regnery and Puttmann, 2009), surface waters of lakes and rivers (Andresen et al., 2004; Quednow and Puttmann, 2009; Regnery and Puttmann, 2010), coastal and marine surface waters (Bollmann et al., 2012), and in plants (Aston et al., 1996), fish and humans (Kim et al., 2011; Sundkvist et al., 2010), indicating a wide spread of PFRs in the environment.

PFRs can be either inorganic or organic, and the organic PFRs can be divided into non-halogen PFRs and halogenated PFRs. In the halogenated PFRs chlorine is the most common halogen (van der Veen and de Boer, 2012). In this study both halogenated and non-halogen organic PFRs are included. The chlorinated PFR compounds are thought to be sufficiently stable for short- and medium-range atmospheric transportation (Regnery and Puttmann, 2009), and observations of PFRs in the marine environment (Bollmann et al., 2012) and in remote areas (Aston et al., 1996; Regnery and Puttmann, 2009, 2010), such as glacier-ice in the Arctic and particulate organic matter in Antarctic (Ciccioli et al., 1994; Hermanson et al., 2005) suggests that some PFRs are subject to long-range transport (Möller et al., 2012). Further, reported log K_{ow} values for PFR compounds range from 1.44 to 9.49 indicating

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that these compounds might be long-range transportable and bioaccumulative (van der Veen and de Boer, 2012). In addition, several the PFR compounds have been listed by Howard and Muir (2010, 2013) as potential persistent and bioaccumulative compounds. Those relevant for this study are tris(2-chloroisopropyl)phosphate (TCIPP), tris(1,3-dichloro-2-propyl)phosphate (TDCIPP) and tritolyl phosphate (TCrP).

The aim of the present study was to investigate the occurrence of 14 different PFRs in marine and terrestrial biota from the high-arctic archipelago of Svalbard, Norway. If PFRs occur in significant concentrations in arctic organisms, this would indicate that these substances do undergo long-range transport and are bioaccumulated.

Tissues for PFRs analyses were collected from eight arctic species sampled from the marine and terrestrial environment within the Svalbard Archipelago (from 74° to 81°N, and from 10° to 35°E), Norway (Fig. 1, Table 1) between 2007 and 2010. Capelin (*Mallotus villotus*) was caught using trawl nets (R/V Helmer Hansen). Whole fish were individually wrapped in aluminum foil and stored frozen in zip-lock bags until analyses. Eggs of Brünnich's guillemots (*Uria lomvia*) and glaucous gulls (*Larus hyperboreus*) were wrapped individually in aluminum foil and stored frozen in zip-lock bags. Black legged kittiwakes (*Rissa tridactyla*) were killed by neck dislocation and liver was dissected out in the laboratory, samples were individually wrapped in aluminum foil and stored frozen in zip-lock bags. Ringed seals (*Pusa hispida*) were shot with rifle on the sea ice and tissues were sampled in the field. Blubber samples were wrapped in aluminum foil and stored frozen in zip lock bags until analyses. Blood samples were collected from live-captured harbour seals (*Phoca vitulina*) using heparinized vacuum tubes. Blood from anaesthetized polar bears (*Ursus maritimus*) was collected using heparinized syringes and centrifuged in the field. Plasma from both species were was transferred to cryogenic vials and frozen. Arctic foxes (*Vulpes lagopus*) samples were collected from animals trapped near Austfjordnes, in northern Svalbard, by a local trapper. Carcasses were collected from his trap line and skinned and stored frozen, at −20 °C, for 6 to 9 months before they were autopsied in a laboratory. Liver samples were individually packed in aluminum foil.

Only new and clean equipment and materials were used to handle all of the samples collected in this study. All samples were stored frozen at −20 °C (or below) until analyses, and all samples taken in the field were frozen within 4 h. of sampling, except for the polar bear samples that were frozen within the same day.

The samples were collected during different field campaigns as part of on-going research projects. CITIES permits were held for the shipment of polar bear samples from Svalbard to mainland Norway. All other samples received approval for transfer from Svalbard to mainland of Norway by the Norwegian Food Safety Authority. Permits for collection were granted by the Governor of Svalbard, and all programs were conducted according to the regulations of, and under the permit of The Norwegian Animal Research Authority.

PFR and lipid analyses were performed at the Institute for Environmental Studies of Vrije University (VU), Amsterdam, the Netherlands. All samples were analyzed for 14 PFR compounds; Triisobutyl phosphate (TIBP), tris(2-chloroethyl)phosphate (TCEP), TCIPP, TDCIPP,

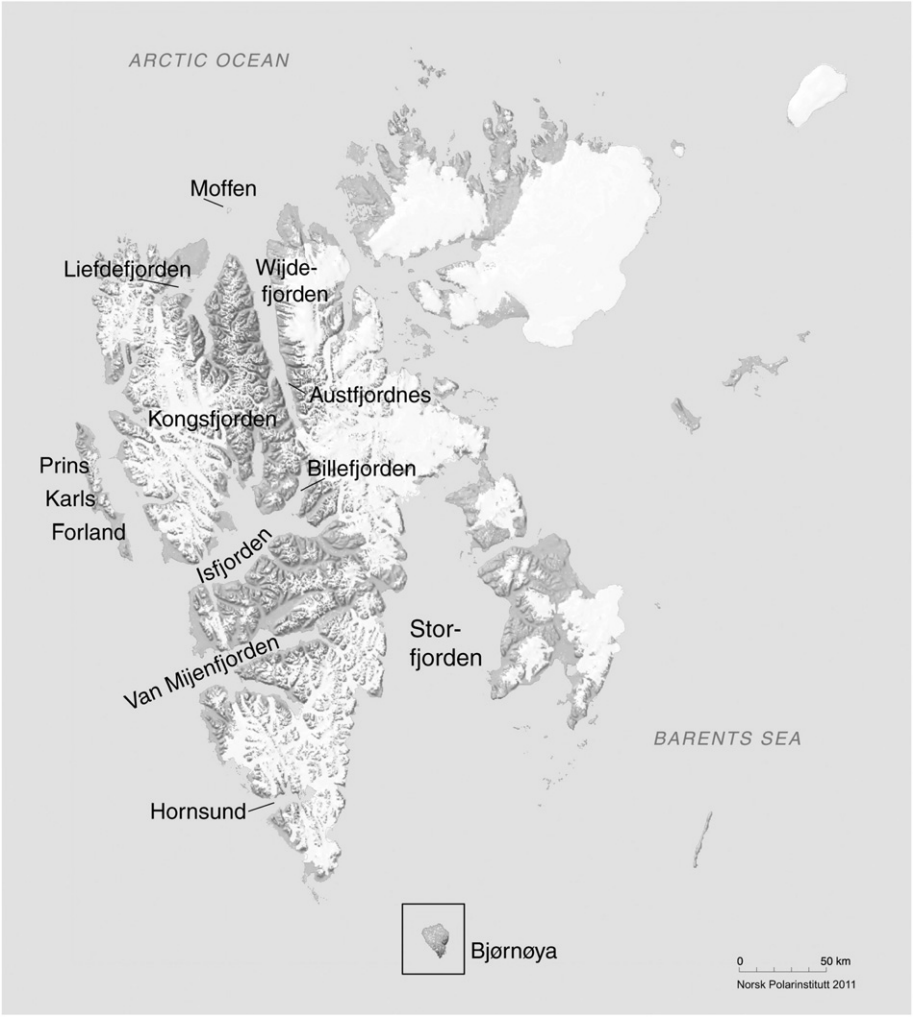

Fig. 1. Map of Svalbard with sampling locations. Sampling information for each species is given in Table 1.