Science of the Total Environment 650 (2019) 1889–1897

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Preliminary study of long-range transport of halogenated flame retardants using Antarctic marine mammals

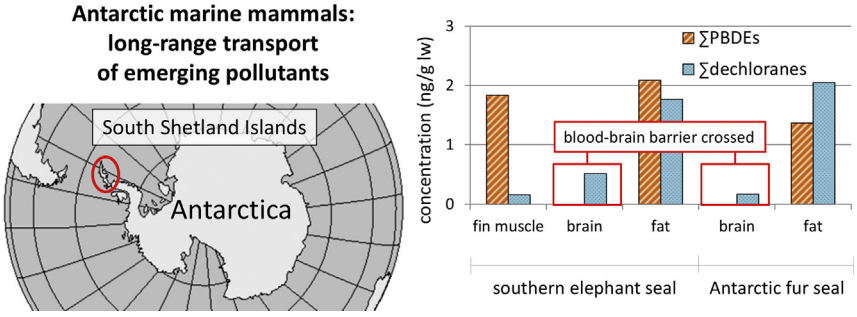
Òscar Aznar-Alemany [a], Xuefei Yang [a], Mariana B. Alonso [b], Erli Schneider Costa [c], João Paulo M. Torres [b], Olaf Malm [b], Damià Barceló [a,d], Ethel Eljarrat [a,*]

[a] Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Jordi Girona, 18, 08034 Barcelona, Spain
[b] Radioisotopes Laboratory Eduardo Penna Franca, Institute of Biophysics Carlos Chagas Filho, Federal University of Rio de Janeiro, Av. Carlos Chagas Filho, 373, 21941-902 Rio de Janeiro, Brazil
[c] Mestrado Profissional em Ambiente e Sustentabilidade, State University of Rio Grande do Sul (UERGS), Rua Assis Brasil, 842, 95400-000 São Francisco de Paula, Brazil
[d] Catalan Institute for Water Research (ICRA), Emili Grahit, 101, 17003 Girona, Spain

HIGHLIGHTS

- Long-range transport of halogenated flame retardants into Antarctic seals.
- PBDEs found in muscle, adipose and fur samples, mainly BDE-47 and BDE-28.
- Dechloranes found in all types of samples at levels comparable to PBDEs.
- Dechloranes crossed the blood-brain barrier of both species; PBDEs did not.
- Fur samples, easier to obtain, are suitable to monitor these compounds.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 May 2018
Received in revised form 19 September 2018
Accepted 21 September 2018
Available online 27 September 2018

Editor: Adrian Covaci

Keywords:
Antarctic seals
Blood-brain barrier
Fur samples
Halogenated norbornenes
Emerging flame retardants

ABSTRACT

Eight PBDE congeners, three emerging brominated flame retardants, five dechloranes and eight MeO-PBDEs were monitored in tissues (muscular, adipose, brain) and fur of southern elephant seal and Antarctic fur seal of the South Shetland Islands, Antarctic Peninsula. Total PBDEs and total dechloranes concentrations ranged between n.d.–6 ng/g lw. While PBDEs were not detected in brain tissue, Dec 602 was found in brain tissue of both seal species indicating that dechloranes —with potential neurological toxicity— could cross the blood-brain barrier. Emerging brominated flame retardants were not detected in any sample and only two MeO-PBDEs, which are of natural origin, were found. The presence of the detected compounds in biota from the Antarctic evidences their long-range transportation, being of special interest the detection of emerging compounds such as dechloranes. This is the first time that these contaminants have been detected in marine mammals from the Antarctic. BDE-47 concentrations were lower than previously reported for the same species, suggesting a successful effect of the existing regulation and bans on PBDEs.

Capsule abstract: Halogenated flame retardants were in tissues of Antarctic seals proving long-range transport. Dechloranes showed similar behaviour to PBDEs, additionally they crossed the BBB.

1. Introduction

Flame retardants (FRs) are compounds that are applied to materials to increase their fire resistance. Polybrominated diphenyl ethers

* Corresponding author at: Carrer de Jordi Girona, 18-26, 08034 Barcelona, Spain.
E-mail addresses: oaaqam@cid.csic.es (Ò. Aznar-Alemany), xuefei.yang@upc.edu (X. Yang), erli-costa@uergs.edu.br (E.S. Costa), olaf@biof.ufrj.br (O. Malm), dbcqam@cid.csic.es (D. Barceló), eeeqam@cid.csic.es (E. Eljarrat).

https://doi.org/10.1016/j.scitotenv.2018.09.287
0048-9697/

(PBDEs) are the most used family in a wide variety of indoor and outdoor products, such as household appliances, office electronics, textiles and furniture (Alaee et al., 2003). PBDEs are produced at different levels of bromination, that is, Penta-BDE, Octa-BDE and Deca-BDE commercial mixtures. They have been found in different environmental matrices (Harner et al., 2006; Guerra et al., 2010; Gorga et al., 2013), as well as in biological matrices (Norén and Meironyté, 2000; Lacorte et al., 2010). PBDEs are persistent in the environment, biomagnify in the food web and are toxic compounds that may affect hormonal regulation as well as hepatic, neuronal and thyroid activities (Branchi et al., 2003; Mikula and Svobodova, 2006).

In 2009, Penta-BDE and Octa-BDE were added to the Stockholm Convention on Persistent Organic Pollutants (POPs) (SC, 2008), with exceptions for specific uses, and their presence in formulations was reduced in North America and Europe with the commitment to stop producing them by 2013 (Schecter et al., 2010; EPA, 2014). In 2010, Deca-BDE was included in the REACH regulation (Registration, Evaluation, Authorisation and Restriction of Chemicals) (REACH, 2006) and in 2017 it was included in the Stockholm Convention.

New FRs were produced as replacements for the banned formulations (Betts, 2008), including decabromodiphenyl ethane (DBDPE), hexabromobenzene (HBB) and pentabromoethylbenzene (PBEB). Some of their properties are presumably similar to PBDEs, including their leaking into the environment (Cruz et al., 2015; Covaci et al., 2011). Not all emerging FRs are brominated. Dechlorane Plus (DP) and dechloranes 602, 603 and 604 (Dec 602, Dec 603, Dec 604) are chlorinated FRs used as substitutes for mirex since it was banned in the United States because of its toxicity (Johnson, 1976). There are reports of dechloranes' presence in environmental matrices (Sverko et al., 2007; Hong et al., 2010) and biota, including humans (Siddique et al., 2012; Houde et al., 2014).

Additionally, methoxylated PBDEs (MeO-PBDEs) are structural analogs to PBDEs. Studies indicate that MeO-PBDEs are of natural origin and not metabolites of PBDEs (Teuten et al., 2005; Nomiyama et al., 2011). It is proposed that MeO-PBDEs are synthesized by some algae, marine sponges and their associated bacteria (Malmvarn et al., 2008). These compounds are likely to be detected in marine mammals at similar concentrations to anthropogenic halogenated organic compounds (Vetter, 2006; Alonso et al., 2014).

PBDEs can be found anywhere in the world, including the Arctic and the Antarctic. Long-range atmospheric transport and ocean current transport could be the main pathways of PBDEs to remote areas although anthropogenic influence (e.g. research stations, tourism) could also influence the spatial distribution of PBDEs in the Antarctic Peninsula (Wang et al., 2012). On the other hand, few publications show data about dechloranes in remote regions. Although there are studies on dechloranes in environmental matrices from the Arctic and the Antarctic regions (Möller et al., 2010; Möller et al., 2011; Möller et al., 2012; Shen et al., 2012), only very recent publications address the presence of these compounds in biota, more specifically in the South Shetland Islands (Kim et al., 2015; Roscales et al., 2016).

The present article reports the presence of some aforementioned compounds in southern elephant seal (*Mirounga leonina*) and Antarctic fur seal (*Arctocephalus gazella*) from the South Shetland Islands. Each sample corresponded to muscular tissue from the fins, brain tissue, adipose tissue or fur. The specific aim of this study was to prove the long-range transport capacity of FRs. Furthermore, the diversity of the tissues collected allowed to evaluate if fur samples —more accessible and available— could substitute other lipid-rich tissues traditionally used for biomonitoring and to compare adipose and brain tissues samples of the same individual to judge the ability of these pollutants to cross the blood-brain barrier (BBB), which is relevant due to their proved or potential neurological effects.

2. Materials and methods

2.1. Sampling

A total of 31 samples including muscle tissue from hind flippers ($n = 5$), brain tissue ($n = 6$), adipose tissue ($n = 9$) and fur ($n = 11$) of southern elephant seal (*Mirounga leonina*) and Antarctic fur seal (*Arctocephalus gazella*) were collected in summer of 2012 during an Antarctic expedition in the framework of the Brazilian Antarctic Program (PROANTAR) in the South Shetland Islands, Antarctic Peninsula. Collection points were Hannah Point, Elephant Point and Byers Peninsula, in Livingston Island, and Penguin Island (Fig. 1). See Table 1 for the detailed number of individuals from each sampling point and the available tissue for each of them. Information about gender is not available. The biological samples were collected only from animals found dead and under Antarctic and Brazilian Environmental Agency permissions as it is a specially protected area. The carcasses were in early decomposition stages. Antarctic fur seals were adults that fed in sub-Antarctic and South American waters and southern elephant seals were pups that fed locally. The brain tissue was collected inside the

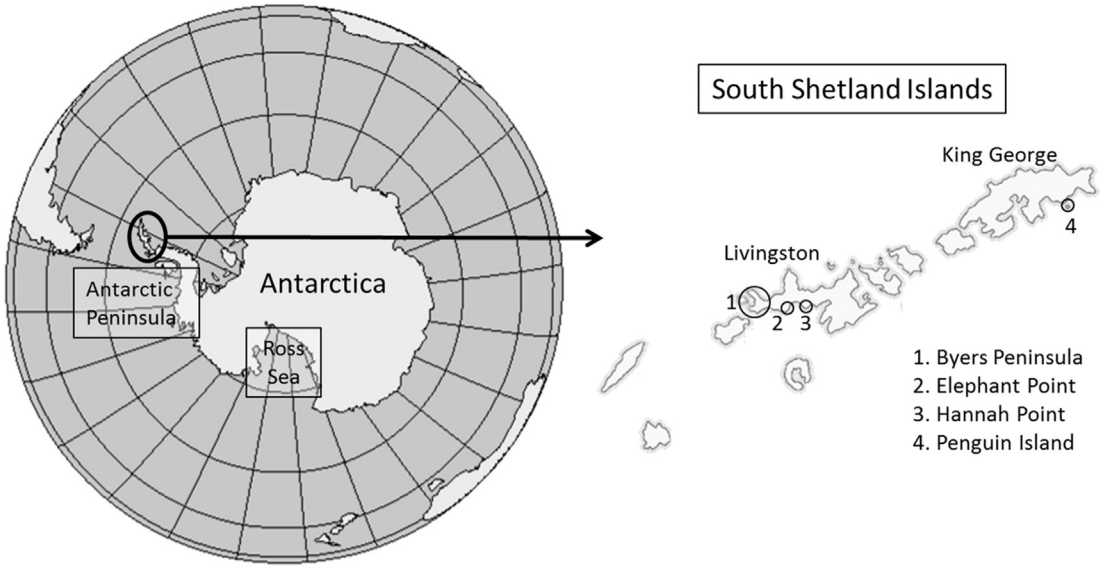


Fig. 1. Location of the samples