Chemosphere 92 (2013) 1017–1021

Contents lists available at SciVerse ScienceDirect

Chemosphere

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

Detection and distribution of Tris(2-chloroethyl) phosphate on the East Antarctic ice sheet

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HIGHLIGHTS

- First ever report of OPEs detection on Antarctic ice sheet and inland Antarctica.
- First ever report of TCEP distribution on Antarctic ice sheet.
- Positive correlation between TCEP and elevation, suggesting cold condensation.
- The surrounding seas could be pollution sources of Antarctic ice sheet.

ARTICLE INFO

Article history:
Received 30 November 2012
Received in revised form 6 March 2013
Accepted 17 March 2013
Available online 18 April 2013

Keywords:
Organophosphorus esters
Antarctic ice sheet
Long range transport
TCEP

ABSTRACT

Use of PBDEs (Polybrominated Diphenyl Ethers) has been restricted in Europe and North America in recent years. As substitute products with similar properties, OPEs (Organophosphate Esters) are now used as alternatives to PBDEs. Recent research has revealed that, similar to PBDEs, OPEs are also environmentally hazardous like PBDEs. Thus knowledge of their distribution and transport is needed to understand the extent of risk. However, studies on environmental OPEs mainly focus on Europe and North America. Knowledge in the southern hemisphere is very limited. In this study, we analyzed fresh snow samples collected along the transect from Zhongshan Station to Kunlun Station, East Antarctica. Several OPEs were detected in this transect, among which Tris(2-chloroethyl) phosphate (TCEP) had the highest frequency of quantification. It was quantified in most samples from the coastal half of the transect and was detected but not quantified in most samples in the inland half. We show that TCEP at this transect probably originated from the ocean around Antarctica. This study is the first to report the presence of TCEP on the Antarctica ice sheet, providing evidence of its long range transport from the source regions. This work also indicate that TCEP can transport hundreds of kilometers in the Antarctica.

1. Introduction

Plastic products are a vital part in modern human life. In order to adjust their properties, especially to prevent fire, additives and flame retardants are added in plastic products. OPEs and PBDEs were two widely used plastic additives in the past (Wang et al., 2011). Europe and the United States in 2004, and Canada in 2008, have restricted the use of PBDEs, due to their health and environmental hazards, including persistence, bioaccumulation and toxicity (Xia et al., 2011). As PBDEs become restricted in more countries, OPEs are increasingly used in the plastic industry. In 2006 alone, approximately 91 000 tons of OPEs were consumed worldwide (Wang et al., 2011).

OPEs had not been proved to be persistent in the environment until the 1980s. In fact, triaryl and trialkyl OPEs are degradable (Muir et al., 1983). However, chlorinated alkyl OPEs are quite persistent (Kawagoshi et al., 2002). In recent years, more and more toxicities of OPEs have been discovered. For example, TCEP has been shown to be carcinogenic, reproductive and neural toxic (Umezu et al., 1998; Ren et al., 2008). TPhP is an allergen (Saboori et al., 1991) and TCrP is toxic to the adrenal cortex and reproduction system of mice (Latendresse et al., 1993). Furthermore, TDCP and TPhP could inhibit human hormone activity and damage human sperm (Meeker and Stapleton, 2010). World Health Organization has established several Environmental Health Criteria in the 1990s for OPEs (Hartmann et al., 2004). European Chemicals

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0045-6535/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2013.03.038

Agency has also published a list of "very high concern" chemicals, including several OPEs. The increasing recognition of OPEs as health hazards has attracted much attention in both policy making and scientific research (Stapleton et al., 2011).

Unlike other additives, OPEs are not chemically conjugated to plastic products (Reemtsma et al., 2008). Thus they can be easily released into the environment. OPEs have been found in indoor environment in Europe and the United States (Hartmann et al., 2004; Staaf and Ostman, 2005; Wensing et al., 2005), surface water and precipitation in Europe (Fries and Püttmann, 2001; Andresen et al., 2004; Regnery and Puttmann, 2010b), atmosphere and sea water in the North Sea (Andresen et al., 2007; Moller et al., 2011), alpine lakes in Italy (Bacaloni et al., 2008), human milk and urine (Moller et al., 2004; Sundkvist et al., 2010), and in Arctic (Moller et al., 2012). However, investigation of OPEs has mainly focused on Europe and North America. Studies in the southern hemisphere and Antarctica are limited (Ciccioli et al., 1994; Moller et al., 2011). We herein present an investigation of twelve OPEs along the transect from Zhongshan Station to Kunlun Station, East Antarctica. We then discuss the possible atmospheric transport of OPEs on the Antarctic ice sheet. To our best knowledge, this is the first report of the presence of OPEs on the Antarctic ice sheet.

2. Materials and methods

2.1. Geological characteristics of the study sites

Kunlun Station (80°25′01″S, 77°06′58″E) is located approximately 7 km southwest to Dome A (80°22′51″S, 77°27′23″E), the highest elevation point on the Antarctic ice sheet. The sample collection was part of the transect between Kunlun Station and Zhongshan Station (69°22′24″S, 76°22′40″E). Zhongshan Station is on the Larsemann Hills, which is located at the coast of Prydz Bay in East Antarctica. This region is free of ice in austral summer. The fresh snow between the last sampling point (69°36′04″S, 76°24′36″E) and Zhongshan Station had partly melted at the time of sampling. As a result, it was impossible to sample fresh snow, thus this part of the transect was not included in this study.

2.2. Sample collection

During the 27th CHINARE (2010–2011), a set of 120 fresh snow samples were collected along the transect from Zhongshan Station to Kunlun Station at an interval of 10 km. Only superficial loose snow was sampled to ensure that the samples were all fresh snow. Each snow sample was collected and stored in a 500 mL LDPE bottle. The bottles were pre-cleaned by 10% nitric acid (MOS grade) for three times, n-hexane (HPLC grade) for three times, methanol (HPLC grade) for three times and purified water (18.2 MΩ) for three times successively. The sampling route is shown in Fig. 1. The vehicles travelled downwind about 30 m to the west of the set route, and we collected samples upwind about 30 m to the east of the set route. This sampling strategy and the constant east wind in this area ensured that no contaminant from the vehicles was taken into the samples. During the 28th CHINARE (2011–2012), three surface sea water samples were collected in Prydz Bay near Zhongshan Station with clean Teflon bottles.

2.3. Extraction and analysis of OPEs

The fresh snow samples were analyzed with an HPLC/MS/MS system equipped with a Waters XTerra C18 column (2.1 mm × 150 mm, 5 μm). The column temperature was kept constant at 45 °C. Mobile phase A was water and B was acetonitrile. The gradient set was as follows: 0–10 min linear gradient 50–55% B, 10–15 min linear gradient 55–83% B, 15–22 min steady 50% B for rinse. Twelve OPEs including TMP (Trimethyl phosphate), TEP (Triethyl phosphate), TCEP (Tris(2-chloroethyl) phosphate), TPrP (Tripropyl phosphate), TCPP (Tris(2-chloroisopropyl) phosphate), TDCP (Tris(dichloro-2-propyl) phosphate), TPhP (Triphenyl phosphate), TnBP (Tri-n-butyl phosphate), TBEP (Tris(2-butoxyethyl) phosphate), TCrP (Tricresyl phosphate), EHDPP (2-Ethylhexyl

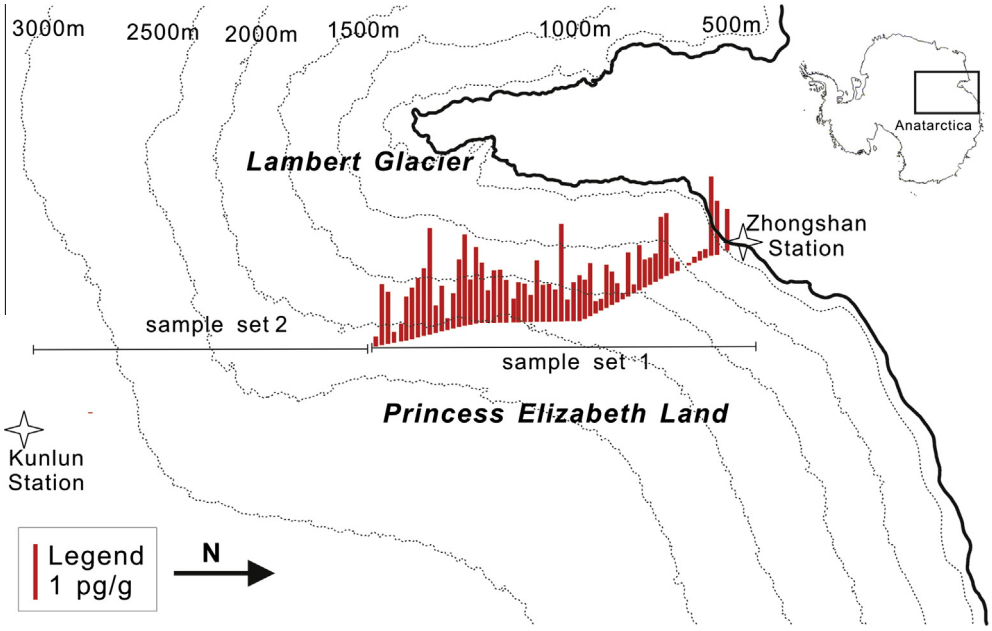

Fig. 1. Results of superficial snow samples collected during the 27th CHINARE. Superficial snow was sampled every 10 km. Bars along the transect represent TCEP concentrations of superficial snow samples. Samples between Kunlun Station and the 60th sample (74°56′34.8″S, 76°58′24.3″E), which were referred to as sample set 1, were not quantified except in one with a very low concentration. Map in the upper right shows the relative location of our study area in the Antarctica. Dash lines in the main screen indicate contour lines at 500 m intervals.