JOURNAL OF ENVIRONMENTAL SCIENCES 28 (2015) 8–13

Available online at www.sciencedirect.com

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JOURNAL OF ENVIRONMENTAL SCIENCES

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Distribution characteristics and indicator significance of Dechloranes in multi-matrices at Ny-Ålesund in the Arctic

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ARTICLE INFO

Article history:
Received 28 March 2014
Revised 20 July 2014
Accepted 21 July 2014
Available online 15 November 2014

Keywords:
Dechloranes
Arctic
Multi-matrices
Distribution characteristic
Ratio
Source analysis

ABSTRACT

In recent years, Dechloranes have been widely detected in the environment around the world. However, understanding and knowledge of Dechloranes in remote regions, such as the Arctic, remain lacking. Therefore, the concentrations of 5 Dechloranes in surface seawater, sediment, soil, moss, and dung collected from Ny-Ålesund in the Arctic were measured with the concentrations 93 pg/L, 342, 325, 1.4, and 258 pg/g, respectively, which were much lower than those in Asian and European regions. The mean ratios of anti-Dechlorane Plus (DP) to total DP (f_{anti}) in seawater, sediment, soil, moss, dung, and atmospheric samples were 0.36, 0.21, 0.18, 0.27, 0.66, and 0.43, respectively. Results suggested that the main source of DP in seawater, sediment, soil, and moss was long-range atmospheric transport. However, the ratio identified in dung was different, for which the migration behavior of the organism is probably the main source of DP.

Introduction

Halogenated (usually brominated or chlorinated) flame retardants are chemicals that are extensively used in consumer products, including electronic equipment, textiles, furniture, and automobiles, to improve their resistance to fire (Guerra et al., 2011). Dechloranes (Decs), as highly chlorinated flame retardants, were reported to have flame-retardant properties similar to that of mirex. Decs, developed by Hooker Chemicals and Plastics (now known as OxyChem), partially replaced mirex for non-agricultural applications after use of the latter was restricted during the 1970s because of its toxicity (INCHEM, 2010). Decs include Dec 602 ($C_{14}H_4Cl_{12}O$), Dec 603 ($C_{17}H_8Cl_{12}$), Dec 604 ($C_{13}H_4Br_4Cl_6$), and Dechlorane Plus (DP, $C_{18}H_{12}Cl_{12}$, also called as Dechlorane 605). These substances are hexachlorocyclopentadiene Diels–Alder adducts that contain a basic bicyclo[2,2,1]-heptene structure (Milne, 2005). Dec 602 is used in fiberglass-reinforced nylon-6 at 18% by weight (Chanada and Roy, 2007). Dec 604 is used in Molykote AS-810 silicone grease (10% to 30%) produced by Dow Corning USA to lubricate metal-to-metal and metal-to-plastic substrates in electro-mechanical applications (MatWeb, 2009). Dec 604 has also been reported as an impurity (2%) in a commercial product of mirex (NTP, 1990). DP is used as a flame retardant in electrical hard plastic connectors in television and computer monitors, wire coating, and furniture (Betts et al., 2006). Technical DP mixture is composed primarily of two isomers, the

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http://dx.doi.org/10.1016/j.jes.2014.07.019

syn- and *anti*-isomers. The different physical and chemical properties of DP isomers can lead to dissimilar persistence in the environment (Hoh et al., 2006; Zhu et al., 2007).

Decs have become a ubiquitous contaminant in the environment. Accordingly, environmental concerns have emerged because of the widespread detection and persistence of Decs in the environment and their bioaccumulation in biota (Feo et al., 2012; Xian et al., 2011). Decs 602, 603, and 604 were detected in sediments and fish (Jia et al., 2011; Qiu et al., 2007; Sverko et al., 2010). DP was detected in various environmental matrices, including air (Ren et al., 2008; Wang et al., 2010b), indoor dust (Zhu et al., 2007), water (Möller et al., 2010), soil (Ma et al., 2011), sediments (Sverko et al., 2010; Qiu et al., 2007), plants (Chen et al., 2011; Qiu and Hites, 2008), biota (Sverko et al., 2010; Tomy et al., 2007; Wu et al., 2010; Zhang et al., 2011), and human serum (Ren et al., 2009), in North America, Europe, and China.

Information on the environmental occurrence, fate, and behavior of Decs is still limited. Most studies on Decs have been conducted near manufacturing areas. However, Decs are bio-accumulative, persistent, and can undergo long-range atmospheric transport. There is evidence that Decs are emitted by several means into the environment, and are even transported into remote regions, including the North and South Poles as well the Qinghai–Tibet Plateau area. Ny-Ålesund is one of the northernmost human settlements in the world. It is situated in Kongsfjorden, an inlet on the west coast of Spitsbergen, which is the largest of the Svalbard Islands. Most of the animal and plant species in the islands have been identified in Spitsbergen, making the town an optimal base to conduct Arctic research. Thus, the settlement was chosen as the study area in this research. The objective of this study is to provide the levels of Decs in multi-matrices in Ny-Ålesund to analyze the source of this flame retardant in the Arctic area by using the isomer ratio profiles of DP in environmental matrices.

1. Materials and methods

1.1. Sampling and preparation

Concurrent surface seawater and sediment sampling was conducted in King's Bay. Surface soil (upper 5 cm), moss, and reindeer dung were simultaneously collected. Atmospheric samples in the gaseous phase were collected using polyurethane foam. Particle-bound analytes in air were collected on a quartz fiber filter in July 2012 in the Ny-Ålesund area (78°55′N, 11°56′E), Svalbard in the Arctic Circle (Fig. 1). Only damp-dry dung was collected to reduce the influence of secondary Decs input/loss after excretion. The average temperature during sampling was 5°C. All samples were kept in aluminum foil and stored at −20°C after sampling. Soil, sediment, moss, and reindeer dung samples were freeze-dried, ground, and sieved (80 mesh) prior to analysis.

1.2. Materials

Dec 602 (95%), Dec 603 (98%), and Dec 604 (95%) were purchased from Toronto Research Chemical Inc. (Toronto Research Chemical Inc., Ontario, Canada). A standard mixture of DP, which contained *syn*- and *anti*-DP, was obtained from AccuStandard, Inc. (AccuStandard Inc., Connecticut, USA). Meanwhile, the internal standard of polychlorinated biphenyl 209 (99%) was acquired from J&K Scientific Ltd. (Beijing, China). All organic solvents used in the study (dichloromethane, *n*-hexane) were pesticide grade. Water was purified by a Milli-Q system. Silica, neutral alumina, and anhydrous sodium sulfate were purchased from Merck (Darmstadt, Germany).

1.3. Extraction, cleanup, and analysis

Approximately 5 g sediment, soil, moss, and dung (reindeer and bird) samples mixed with the surrogate standard were extracted *via* accelerated solvent extraction with 50 mL hexane/dichloromethane (DCM) (1:1, *V*/*V*). Activated copper powder was added to the extracts of sediment and soil to remove elemental sulfur. The seawater samples, C18 and glass fiber filter (GFF), were extracted and analyzed separately to obtain information on their respective water and particle phases. Approximately 8.0 L surface seawater samples were collected by C18 (the water phase) and GFF (the particle phase) at each station, and the C18 and GFF samples were soaked for 12 hr with 50 mL hexane/DCM (1:1, *V*/*V*) and were extracted in an ultrasonic bath for 30 min. The procedure was repeated twice. Air samples were collected by a high-volume air sampler (HiVol) equipped with GFF to capture particles and a PUF plug for the gas Decs. The HiVol operated at an average flow rate of 1.0 m^3/min and the total sampled air volume averaged about 2880 m^3. These samples were Soxhlet-extracted for 24 hr using hexane/DCM (1:1, *V*/*V*). The raw extracts of all samples were evaporated to 5 mL with a rotary evaporator and were transferred to a multi-layer column filled from the bottom with 2 g activated silica gel, 4 g neutral alumina, and 1 cm anhydrous Na_2SO_4 (pre-soaked in hexane). The extracts were then eluted with 70 mL hexane/DCM (1:1, *V*/*V*) mixture and were further evaporated under a gentle N_2 stream. The sample was solvent-exchanged to hexane (500 μL).

Decs were analyzed on an Agilent 6890 N gas chromatograph coupled with a 5973I mass spectrometer (MS, Agilent Technologies, Inc. Santa Clara, California, USA) using the negative chemical ionization mode with methane as the ionization gas fitted with a DB-5HT capillary column (0.25 mm i.d. × 30 m × 0.10 μm film thickness, J&W Scientific, Inc., Santa Clara, California, USA). The injection volume was 1.0 μL in the splitless mode. Helium was used as the carrier gas at a flow rate of 1.0 mL/min. The gas chromatography oven was programmed as follows: initial 80°C for 2 min, ramped at 20°C/min to 180°C, then 5°C/min to 250°C and held for 2 min, then 30°C/min to 310°C and held for a final 5 min. The MS transfer line was held at 275°C. The temperature of the ion source and the quadrupole was 150°C. The instrument was operated in selected ion monitoring mode (*m*/*z* 606.0, 608.2, and 610.0 for Dec 602; *m*/*z* 628.0, 630.0, and 634.0 for Dec 603; *m*/*z* 569.0, 608.0, and 612.0 for Dec 604; *m*/*z* 646.0, 645.0, and 649.0 for *syn*-DP and *ant*-DP).

1.4. Quality control

Different measures were performed to assess the accuracy and reliability of the obtained data. Field and laboratory blanks (method blanks) were extracted and analyzed in the same manner as field samples. The method detection limits (MDLs) were derived from mean blank values plus thrice the standard deviation; for compounds with no blank, from the