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Occurrence of organochlorine pesticides in the environmental matrices from King George Island, west Antarctica

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ABSTRACT

Antarctica is considered as a final sink of many persistent organic pollutants (POPs). This work aims to investigate the levels, distributions and potential sources of organochlorine pesticides (OCPs) with HRGC/HRMS technique. Twenty-three OCPs were measured in various environmental matrices from King George Island, west Antarctica. The total concentrations (Σ_{23}OCPs) were at quite low levels, ranging 93.6–1260 pg g^{-1} dry weight (dw) in soil and sediment, 223–1053 pg g^{-1} dw in moss and 373–812 pg g^{-1} dw in lichen. Hexachlorobenzene (HCB), dichloro-diphenyl-trichloroethane (DDT) and its metabolites (especially *p,p′*-DDE) and hexachlorocyclohexanes (HCHs) were the main contaminants in all samples. Lower α-HCH/γ-HCH and higher *p,p′*-DDE/*p,p′*-DDT ratios compared with the technical products indicated long-range atmospheric transport (LRAT) of recent lindane and aged technical DDT. Significant dependence of many OCPs concentrations on total organic carbon (TOC) was observed. Apart from LRAT, local biotic activities could also contribute and influence the spatial distribution of the contaminants.

1. Introduction

The occurrence of persistent organic pollutants (POPs) in Antarctica, which is the most isolated continent on Earth, has been recognized as a research priority (Nash, 2011). These compounds with high toxicity, high persistence and bioaccumulation can disperse widely into the environment after released and be transported over long distance from source to colder areas including the Polar Regions (Wania and MacKay, 1996). Therefore, Antarctica is considered to be a final sink of POPs due to the combination of its environmental conditions and the physicochemical properties of the compounds themselves.

Organochlorine pesticides (OCPs) are listed as typical POPs in the Stockholm Convention, which were once widely produced and used globally with a long history. Detection of OCPs (dichloro-diphenyl-trichloroethane (DDT), hexachlorocyclohexane (HCH), heptachlor epoxide and dieldrin) from Antarctic wildlife was reported in 1960s for the first time (Sladen et al., 1966; Tatton and Ruzicka, 1967), and since 1990 there was a restriction and reduction of the global production and usage of nine OCPs listed in "Dirty Dozen" (UNEP, 2001). The primary sources of OCPs such as HCHs and hexachlorobenzene (HCB) have been reduced consequently during the last decades (Breivik et al., 2004). However, they are still found ubiquitously in almost all the environmental matrices such as air, water, snow, soil and biota in Antarctica. For instance, Kang et al. (2012) detected α-HCH, γ-HCH and HCB with concentrations of 17.5–83.2, 33–137 and n.d.–182 pg L^{-1}, respectively, in snow samples collected from the coast of east Antarctica. Galbán-Malagón et al. (2013a) reported that levels of HCHs (sum of α-, β- and γ-HCH) and HCB in seawater samples from west Antarctica in 2008 and 2009 were 1.2–12.3 pg L^{-1} and 0.41–0.98 pg L^{-1}, respectively. In the meantime, they investigated HCHs and HCB in the atmosphere from Antarctic Peninsula, and the gas phase concentrations of α-HCH, γ-HCH and HCB were 0.04–5.8, 0.07–7.1 and

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2.2–49.7 pg m^{-3}, respectively (Galbán-Malagón et al., 2013b). Cold condensation and global fractionation during the long-range atmospheric transport (LRAT) were proposed as the main mechanism by which POPs ultimately reach the Polar Regions (Wania and MacKay, 1996). Apart from the LRAT, possible local impact (e.g., biotic activities) may also contribute to the environmental pollution in Antarctica (Evenset et al., 2007; Roosens et al., 2007).

Although the investigations of OCPs in Antarctic soil have been conducted previously at several sites, like the east Antarctic coast (Negoita et al., 2003), Victoria Land (Borghini et al., 2005), James Ross Island (Klánová et al., 2008) and Deception and Livingstone Islands (Cabrerizo et al., 2012), there is a limitation of data on HCB, HCH (α- and γ-HCH), DDT and dichlorodiphenyldichloroethylene (DDE) due to the limit of detection capability of gas chromatography (GC) combined with electron capture detector (ECD) or low resolution mass spectrometry (LRMS) which are commonly employed in these studies. Detailed information regarding OCPs in Antarctic soil and terrestrial vegetation is still scarce (Cabrerizo et al., 2012). High resolution gas chromatography coupled with high resolution mass spectrometry (HRGC/HRMS) can provide more reliable results for POPs at trace levels compared with GC/LRMS (Kang et al., 2012). The method detection limits (MDLs) for OCPs using HRGC/HRMS are reported at relatively low levels (0.3–2.0 pg g^{-1} in solid) (US EPA, 2007), which is lower than those by GC/LRMS method (US EPA, 1998). However, limited studies on OCPs in Antarctica were conducted with HRGC/HRMS technique. In this work, HRGC/HRMS was therefore applied for analyzing twenty-three OCPs in various environmental samples from west Antarctica. The objective was to: (1) investigate the levels and distribution patterns of OCPs in this pristine area; (2) assess the potential sources in this region based on the abundant data. To our best knowledge, this is one of the very few studies analyzing so many OCP compounds in Antarctic areas.

2. Materials and methods

2.1. Reagents and materials

Target OCPs were: HCB, α-, β-, γ- and δ-HCH, *o,p*′- and *p,p*′-DDT, *o,p*′- and *p,p*′-DDE, *o,p*′- and *p,p*′-dichlorodiphenyldichloroethane (DDD), *trans*-chlordane (TC), *cis*-chlordane (CC), *oxy*-chlordane (OxC), heptachlor (HEPT), *cis*- and *trans*-heptachlor epoxide (HE), *trans*-nonachlor (TN), *cis*-nonachlor (CN), aldrin, dieldrin, endrin and mirex. All ^{13}C-labeled standards of OCPs including surrogate standards (LCS, ES-5349), injection standards (IS, EC-5350) and calibration solutions (CS1-CS6, ES-5348) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Pesticide-grade dichloromethane (DCM) and *n*-hexane, and HPLC-grade acetonitrile from J.T. Baker Company Inc. (Fairfield, OH, USA), nonane and alkaline alumina from Sigma (St. Louis, USA), C_{18} reversed-phase Solid Phase Extraction (SPE) cartridges (LC-18 SPE, 1 g, 6 mL) from Supelco Inc. (Bellefonte, PA, USA), silica gel 60 (0.063–0.100 mm particle diameter) from Merck (Darmstadt, Germany) and guaranteed grade anhydrous sodium sulfate from the domestic market were used for the entire analysis. Prior to use, silica gel, alkaline alumina and anhydrous sodium sulfate were baked at 550 °C for 12 h, 600 °C for 24 h and 660 °C for 6 h, respectively.

2.2. Sample collection

Natural soil ($n = 7$), dropping-amended soil ($n = 3$), sediment ($n = 1$), moss (*Sanionia uncinata*, $n = 7$) and lichen (*Usnea aurantiacoatra*, $n = 6$) samples were collected from Fildes Peninsula at King George Island, west Antarctica and the neighboring Ardley Island. Many international research stations (including Chinese Great Wall Station, Chilean Frei Station and Russian Bellingshausen Station, etc.) are located in Fildes Peninsula, and Ardley Island is an important settlement for the penguins and migrating birds. Nine sampling sites scattered in the vicinity of Chinese Great Wall Station (62°12′59″S, 58°57′52″ W) (Fig. 1) and sample details are listed in Table S1 in the Supporting information. Field sampling was conducted in the austral summer of December 11th 2009–January 17th 2010, during the 26th Chinese Scientific Research Expedition to Antarctica. All the samples were sealed in clean plastic bags and transported to the laboratory in Beijing, China and stored frozen (−20 °C) until analysis. A detail description of sampling was presented elsewhere (Wang et al., 2012).

2.3. Sample extraction and cleanup

Prior to extraction, the samples were freeze-dried and homogenized, and soil and sediment were sieved through 16-mesh sieve. The procedures of sample extraction and cleanup followed the reported method (Chen et al., 2014). Pesticide extraction was carried out from 5 g of dried samples using an Accelerated Solvent Extractor (ASE300, Dionex, USA) with a mixture of *n*-hexane: DCM (1/1, v/v) at 150 °C and 1500 psi (10.3 MPa), after spiking with the ^{13}C-labeled standards (OCPs-LCS). Two static cycles of 8 min were applied for complete extraction. Prior to cleanup, activated copper was added to the extracts to remove sulfur. The extracts were then purified by multilayer columns packed with 10 g of silica gel, 5 g of alumina (deactivated with 3% H_2O) and 5 g of anhydrous sodium sulfate from the bottom up. The column was preconditioned with 60 mL *n*-hexane: DCM (1/1, v/v) and eluted with 100 mL *n*-hexane: DCM (1/1, v/v). The eluates were evaporated to almost dryness using rotary evaporator, and redissolved in 0.2–0.3 mL acetonitrile for further cleanup through C_{18} reversed-phase SPE sorbents. The SPE cartridges were pre-rinsed with 6 mL of acetonitrile and eluted with 12 mL acetonitrile.

Similar to soil and sediment, 2.0 g lichen or moss samples were extracted using ASE and purified directly by multilayer silica/alumina columns and C_{18} reversed-phase SPE cartridges as described above without sulfur removal. All the eluates were finally concentrated into 20 μL nonane in GC-micro-vials by a gentle stream of nitrogen and spiked with the OCPs-IS before instrumental analysis.

2.4. Instrumental analysis

Instrumental analysis was performed using an HRGC/HRMS system (DFS, Thermo Fisher, USA) with an electron impact (EI^+) ion source. The HRMS was operated in selected ion recording (SIR) mode at mass resolution ≥ 8000. The electron emission energy was set to 45 eV, and the source temperature was 230 °C. Exactly 1 μL solution was injected into HRGC in splitless mode with a 30 m DB-5MS fused silica capillary column (J&W, Scientific, 0.25 μm film thickness, 0.25 mm i.d.). Helium was the carrier gas with a constant flow of 1.0 mL min^{-1}. The GC temperature was programmed as: 60 °C held for 1.5 min, increased to 140 °C at 10 °C min^{-1}, then to 220 °C at 4 °C min^{-1} and 250 °C at 2 °C min^{-1}, and finally ramped to 300 °C at 8 °C min^{-1}.

2.5. Quality assurance/quality control (QA/QC)

All the target compounds were analyzed using HRGC/HRMS with an isotope-dilution method. The isotopic ratios between the two main ion pairs were within ±15% of the theoretical values. OCPs-LCS were utilized for identification and quantification, and OCPs-IS was added for recovery calculation. For every set of