Environmental Pollution 196 (2015) 134–140

Contents lists available at ScienceDirect

Environmental Pollution

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

Polychlorinated biphenyls in surface soils of the Central Tibetan Plateau: Altitudinal and chiral signatures

Guo-Li Yuan [a, b, *], Yong Sun [b], Jun Li [b], Peng Han [b], Gen-Hou Wang [b]

[a] State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Beijing 100083, China
[b] School of the Earth Sciences and Resources, China University of Geosciences, Beijing 100083, China

ARTICLE INFO

Article history:
Received 16 August 2014
Received in revised form
1 October 2014
Accepted 4 October 2014
Available online

Keywords:
Polychlorinated biphenyls
Chiral signature
Enantiomeric fraction
Tibetan Plateau
Altitudinal change

ABSTRACT

The soils in the Central Tibetan Plateau (CTP), which is a unique background region, play an important role in the fate of the global cycling of polychlorinated biphenyls (PCBs). Forty-four soil samples from across the CTP were collected at altitudes between 3711 m and 5352 m, and the concentrations of 122 PCB congeners were measured from 66.98 to 150.81 ng/kg. The concentration of PCBs was positively correlated with the sampling altitude and clay content. Furthermore, enantiomeric fractions (EFs) of CB-95, CB-136 and CB-149 in soils of CTP were first determined. A (+)-enantiomer excess was identified for CB-136 and CB-149 in all of the samples investigated. Additionally, enantiomer-specific excess was found for CB-95. The dominance of enantiomer-specific excess decreased with increased the sampling altitude and congener concentration. It is likely that the addition of enantiomeric mixtures of PCBs from the atmosphere changed the EFs in the soils according to the altitude.

1. Introduction

Background soils play an important role in the global fate and distribution of persistent organic pollutants (POPs) (Meijer et al., 2003). Such soils can be significant environmental reservoirs, sinks or sources for these chemicals, receiving inputs of POPs via atmospheric deposition and potentially exchanging them with the atmosphere (Schuster et al., 2011). POPs in background surface soils are a potential secondary source of pollutants in the atmosphere through the air–soil exchange (Cabrerizo et al., 2011).

Polychlorinated biphenyls (PCBs) are a well-known class of pollutants. Given their inherent stability, PCBs are difficult to eliminate from environmental matrices. Because their use has been banned for several decades, concentrations of PCBs in arctic and European background air have decreased (Hung et al., 2010; Schuster et al., 2010). Nevertheless, Schuster et al. (2011) found a smaller net average decline of PCBs in surface soil from 2008 compared with data sets from 1998. Although contaminated soil and water represent important secondary sources of PCBs (Li et al., 2010; Zhang and Lohmann., 2010), manmade products continue to remain the primary sources of PCBs (Chen et al., 2014). Background soils not only receive inputs of PCBs via atmospheric deposition, but they also serve as secondary source of PCBs into the atmosphere (Cabrerizo et al., 2011).

The Tibetan Plateau (TP), which covers over 2.5 million km^2 at an average elevation of over 4000 m, has long been regarded as one of the most remote and isolated regions in the world. As a unique background region, POPs in the soils of the TP are deposited by long-range atmospheric transport (LRAT) (Chen et al., 2008; Wang et al., 2010). Our recent investigations found that the soil in the Central Tibetan Plateau (CTP) is contaminated with PAHs, OCPs and PBDEs (Yuan et al., 2012a, 2012b, 2014a, 2014b). The detection of PCBs in the atmosphere (Wang et al., 2010) indicates that the CTP receives a continuous influx of PCBs. However, less attention has been given to PCBs in soils, except for the detection of 25 congeners along a transect (Wang et al., 2009). Recently, Zheng et al. (2012) reported the soil concentration of 25 PCB congeners at the east edge of TP. However, their study area is ca. 1000 km far away from the region of CTP. Although the distribution of PCBs in Chinese and global surface soils has been reviewed (Ren et al., 2007; Li et al., 2010; Cui et al., 2012), data for PCB concentrations in the CTP region are still absent because of the difficulty in sampling. So, it is significant to investigate the distribution and detail composition of PCBs in region of CTP.

The chiral signatures of PCBs provide clear evidence that biodegradation is occurring in the field soils (Harner et al., 2000; Borja et al., 2005). Chiral signatures have been used as powerful

---

* Corresponding author. State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Beijing 100083, China.
E-mail address: yuangl@cugb.edu.cn (G.-L. Yuan).

http://dx.doi.org/10.1016/j.envpol.2014.10.006
0269-7491/© 2014 Elsevier Ltd. All rights reserved.

tools to investigate environmental and biological processes of PCBs (Lehmler et al., 2010), such as the implications of source apportionment (Robson and Harrad, 2004; Asher et al., 2007) and biotransformation (Zhai et al., 2011; Chen et al., 2014). Enantioselective degradation of PCBs was determined in background soils collected on a transect from the southern U.K. to Norway in 2008, while racemic mixtures of PCBs were found in air samples from 2006 to 2008 along the same route (Schuster et al., 2011). Although primary emission sources continue to be the dominant source of PCBs in the atmosphere, secondary sources, such as the volatilization of PCBs from soils, is likely to become an important supply in the future as the contribution from primary sources shrinks (Bidleman et al., 2012). To our knowledge, less attention has been paid on the EF of PCBs in TP.

The main goals of this study were: (1) to investigate the distribution and detail composition of PCBs in surface soils of the CTP; (2) to firstly reveal the chiral signature of PCBs in CTP; and (3) to explore possible influencing factors on the distribution and enantioselectivity of PCBs.

2. Materials and methods

2.1. Sampling

All of the samples were collected during August 2010. Forty-four surface soil samples across the CTP were collected at altitudes between 3711 m and 5352 m above sea level. The detailed sampling and storing methods have been described previously (Yuan et al., 2014b). Sample site locations are shown in Fig. 1, and additional information is provided in Table S1 (Supplementary Materials).

2.2. Chemicals

Four PCBs standard solutions (125 congeners), a surrogate standard (CB-30 and CB-204), internal standards (CB-65 and CB-155), and Aroclor 1242 were purchased from AccuStandard Inc (New Haven, CT). The PCB calibration mixtures were quantitatively diluted with *iso*-octane. Standard reference material GBW08307 (reference soil for PCBs congeners analysis, including CB-28, 52, 77, 81, 101, 118, 114, 105, 138, 153, 167, 156, 157 and 180) was obtained from the National Research Center for Certified Reference Materials of China. Additional experimental details, including solvents, grade, and the pre-treating process, are identical to those used previously (Yuan et al., 2012a, 2012b).

2.3. Sample preparation and achiral analysis

Ten grams of soil were ground with anhydrous sodium sulfate into a free-flowing powder. Each sample was then extracted with 50 mL of hexane/acetone (1:1, vol/vol) by ultrasonication for 4 min and then centrifuged. This process was repeated three times, and the extracts were combined. The concentrated extracts were evaporated to 1 mL in a Kuderna–Danish concentrator under a gentle N_2 stream for cleanup. Before extraction, the samples were spiked with the surrogate standards (CB-30 and CB-204). Extracts were cleaned by using a chromatography column (20 cm × 15 mm i.d.) containing the following: 2 g of silver nitrate silica (10% concentrated silver nitrate, wt/wt), 1 g of activated silica gel, 3 g of basic silica gel, 1 g of activated silica gel, 4 g of acid silica gel (44% concentrated sulfuric acid, wt/wt), 1 g of activated silica gel and 2 g of anhydrous sodium sulfate. The PCB fraction was eluted with 100 mL of hexane. The elution was then evaporated with a rotary evaporator and then reduced to 50 μL under a gentle N_2 stream for analysis. CB-65 and CB-155 were added as the internal standards.

Achiral analysis was performed using an Agilent 6890 gas chromatograph (GC) coupled with an Agilent 5973 mass spectrometer (MS) using electron impact ionization in the SIM mode. The separation was performed on a fused silica capillary column (DB-5MS, 30 m × 0.25 mm i.d. and 0.25 μm film thickness). The GC column temperature program for PCBs was 75 °C (2 min), 15 °C/min to 150 °C, and 2.5 °C/min to 280 °C (15 min).

2.4. Enantiomeric analysis

Enantiomer analysis was conducted using the Agilent GC–MS in the EI/SIM mode noted previously. Determination of the enantiomers of CB-95, CB-136 and CB-149 were performed on a ChiraSil-Dex column (25 m × 0.25 mm × 0.25 μm, 2,3,6-tri-O-methyl β-CD; Varian-Chrompack, Middelburg, the Netherlands). The GC column temperature program for these PCBs was 100 °C (1 min), 20 °C/min to 160 °C, 4 °C/min to 210 °C, and 210 °C (10 min). The ions *m/z* 323.9 and 325.9 were selected for monitoring CB-95, and the ions *m/z* 359.9 and 361.9 were selected for CB-136 and CB-149,

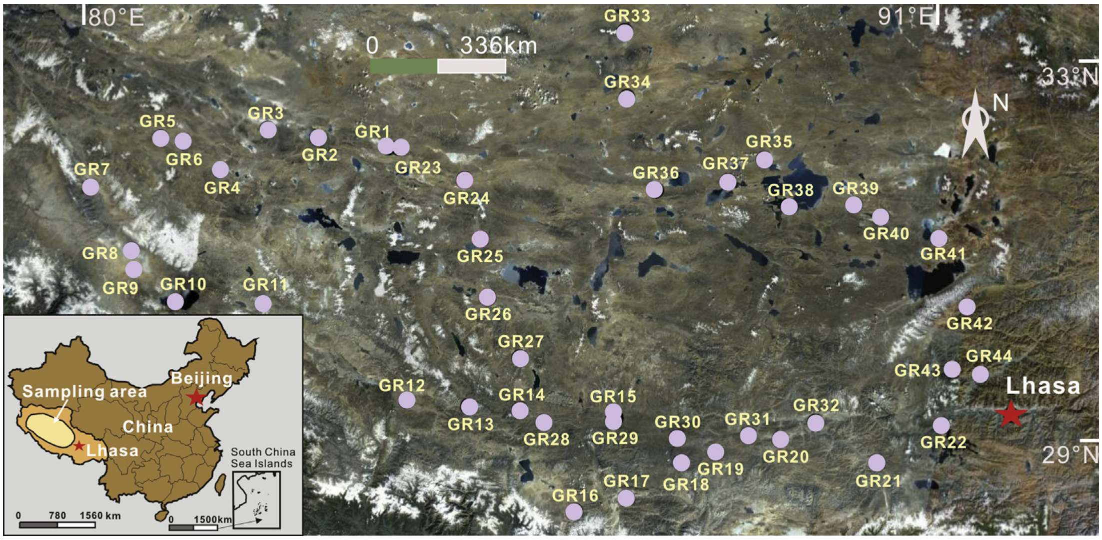

Fig. 1. Map showing sampling site locations.