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Organochlorine pesticides and polychlorinated biphenyls in surface soils from Ruoergai high altitude prairie, east edge of Qinghai-Tibet Plateau

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HIGHLIGHTS

- OCPs and PCBs in soils along a transect from source area to Ruoergai highland were measured
- OCP levels in wetland soils were higher than in grassland soils.
- Good correlation was observed between TOC and PCBs in the soils.
- The compounds with higher concentrations were α-HCH, β-HCH, HCB, and PCB 28.
- The POPs' behaviors in high plateau areas are similar to Polar Regions.

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ABSTRACT

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in surface soils along a transect from source areas (a petro-chemical industrial city, Lanzhou and its adjacent agricultural areas) to Ruoergai highland prairie (3552 m above sea level (a.s.l.)), where livestock farming was the only human economic activity, were studied. OCPs in Ruoergai soils were dominated by HCHs. The land types, organic carbon contents and pH affected the POP preservation in soil. OCPs and PCBs in surface soils in Ruoergai wetland and grassland showed different contamination patterns; OCP levels in wetland soils were higher than those in grassland. Significant correlations were observed between total organic carbon (TOC) contents and PCB concentrations in the soils. The land type determines TOC content in soils, which in turn was a major factor on soil concentrations of POPs. The transect was divided into two sections: The first section (Gradient I) is from Lanzhou (1740 m a.s.l.) to Luqu (2400 m a.s.l.) with decreasing agricultural activities, and the second section (Gradient II) is from Luqu to Ruoergai (3500 m a.s.l.) with grassland as the main land type. Soils of Ruoergai area were dominated by α-HCH, β-HCH, HCB, and PCB28, suggesting that the behaviors of POPs in the high plateau region were different from high mountain cold-trapping effect, and that the POPs' behaviors in high plateau region were similar to Polar Regions.

1. Introduction

Some of the semi-volatile persistent organic pollutants (POPs) can undergo long-range transport (LRT) in the form of vapor or adsorbed onto atmospheric aerosols to remote clean areas via atmospheric circulation at regional or even global scales (Wania and Mackay, 1993). These POPs may deposit onto the surface media through dry and/or wet precipitations or air–soil exchange, posing potential threat to human health and ecosystem in remote areas (Hansen 2000; UNEP 2001). More volatile components of the mixtures, such as the lower chlorinated PCBs, hop poleward more efficiently than the higher chlorinated ones, leading to a compositional shift to more volatile constituents with increasing Northern latitude (Ockenden et al., 1998).

Previous studies have shown that high mountains and cold regions become the sink and important reservoirs of POPs (Blais et al., 1998; Vandrooge et al., 2004). POPs can deposit via wet precipitation and they can be trapped by ice, snow, soils, and vegetations (Grollert et al., 1997; Weiss et al., 2000). Changes in POP composition in soil with altitude of the Peruvian Andes and the Italian Alps have been noted (Tremolada et al., 2008; Wania and Westgate, 2008). Wania and Westgate (2008) discussed the differences in the fractionation pattern along latitudinal and elevation gradients and proposed that the precipitation scavenging efficiency of organic chemicals was temperature dependent. According to the "Mountain-POP" model, POPs moving towards higher altitude along with decreasing temperature, are fractionated due to different chemico-physical properties. Several studies on POPs in top-soils from the Tibetan Plateau have been reported

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(Wang et al., 2007, 2012;P. Wang et al., 2009). However, the climate and topography of high plateaus are different from high mountains. The behaviors of POPs in high plateaus are expected to be different from ordinary high mountains, and therefore, these are ideal places to study the long-range transport of POPs via atmosphere and its relationship with seasonal change.

Up to date, little research on precipitation of POPs in highland pasture areas is available. Ruoergai (Zoige) highland prairie, located in the eastern edge of the Qinghai-Tibetan Plateau, was chosen as our study area. The altitude of Ruoergai highland is 3500 m a.s.l. on average, and livestock grazing is the major human activity. To the north (approximately 600 km) of Ruoergai area is Lanzhou city (1900 m a.s.l.), Gansu Province, representing agricultural and industrial regions. Northwesterly is prevailing in Ruoergai area in both summer (July, 2011) and winter (November, 2011). The present work investigated and quantified the levels of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in top-soils from Ruoergai highland prairie and along a transect from Lanzhou to Ruoergai high plateau. Ten OCPs and six indicator PCB congeners were analyzed by highresolution gaschromatograph-high resolution mass spectrometry (HRGC-HRMS). The aims of this paper are to further understand the behaviors of POPs in remote areas and provide information on fractionation of POPs from source areas to a high plateau prairie.

2. Methods

2.1. Research areas and the geographic setting

Ruoergai highland prairie of the Aba Tibetan and Qiang Autonomous Prefecture, is located at the eastern edge of the Qinghai-Tibetan Plateau at altitudes of 3200–3600 m a.s.l. , north of Sichuan Province, and the convergence zone of East Asia monsoon and the Qinghai-Tibetan Plateau climate system. The eco-environment is pasture and alpine wetlands. There is 808,000 hectare natural grassland in Ruoergai pasture, one of the largest three grasslands in China. The economics is mainly livestock farming (yak, sheep, and horse). Most of population is Tibetan.

The prairie has an area of 53,000 km^2, is the largest alpine wetland and a special geographic area in the World. The climate of Ruoergai highland grassland is characterized by cold weather, with annual average temperature of 2 °C, annual average precipitation of 600 mm, mostly during period between June and August. Summer is short (June and July); the average temperature in summer is 10.8 °C whereas the average temperature in winter is −5 °C. The prevailing wind is mainly westerly and northwesterly. In recent decades, the climate has changed dramatically, showing deceasing precipitation and increasing evaporation trend, especially since the 1990s. This trend has been leading to shrinking of the wetland area, water resources drastically reduced, grassland degradation, and accelerated soil desertification. The soils in the grassland are soaked in water for long time with low temperature, mainly as marsh soils, characterized by high gleization and rich organic matter and peat. Due to the cold and moist climate, low evaporation and poor drainage, the surface soils are often in a wet state, favorable to swamp development.

Lanzhou, the capital of Gansu Province, is located on the northwest of the Loess Plateau, at altitudes of 1500–2000 m a.s.l.. The average temperatures in summer and winter in Lanzhou are 21 °C and −3.9 °C, respectively. Lanzhou is a petrochemical industry city and the surrounding areas at altitude below 2500 m a.s.l. are agricultural in nature. Therefore, Lanzhou becomes a pesticide and PCB emission source area for Ruoergai highland prairie with the northwesterly wind.

2.2. Sample collection

The sampling sites ($n = 36$) in Ruoergai area are shown in Fig. 1(b). In order to distinguish the relationship between POPs in surface soils of Ruoergai high Plateau and the surrounding industrial and agricultural areas, the sampling strategy of soils was designed to be along the transect from Lanzhou to Ruoergai area at increasing altitude (Fig. 1a). The details of the samples and sampling locations are provided in Table 1. Surface soils (0–5 cm) were collected in summer (July) and winter (November) of 2011, using a small stainless shovel. The samples were wrapped in aluminum foil and stored frozen until analysis. After air-dried at room temperature, all samples were ground, sieved through a 60 mesh size, and stored in refrigerator until analysis.

2.3. Chemical analysis of OCPs and PCBs

HPLC grade Acetone, *n*-hexane, and dichloromethane were obtained from Tianjin Kermel Chemical Reagent Co. Inc., China; analytical grade methanol was from Jinan Chemical Reagent Co. Inc., China; guaranteed reagent grade sulfuric acid was from Qingdao Chemical Reagent Co. Inc., China; copper chips and analytical grade granular anhydrous sodium sulfate were from Tianjin Huazhen Chemical Reagent Co. Inc., China. Two surrogate standards (PCB209 and 2,4,5,6-tetrachloro-*m*-xylene (TMX)) and Certified Reference Materials including PCB28, PCB52, PCB101, PCB118, PCB138, PCB153, PCB180, α-, β-, γ- and δ-HCH, *p,p′*-DDD, *p,p′*-DDE, *p,p′*-DDT, *o,p′*-DDT, α- and β-endosulfans were purchased from the National Research Center for Certified Reference Materials. The quantitative standards of PCBs were from the Wellington Laboratories (Guelph, ON, Canada). The internal standards ^{13}C mass-labelled PCBs (^{13}C-PCB28, ^{13}C-PCB52, ^{13}C-PCB101, ^{13}C-PCB118, ^{13}C-PCB153, ^{13}C-PCB138, ^{13}C-PCB180 were from Accustandard USA. Granular anhydrous sodium sulfate was activated at 650 °C in a furnace for 6 h and then kept in sealed desiccators. Florisil was activated at 130 °C for 16 h before use. All glassware was cleaned in an ultrasonic cleaner and heated at 350 °C for 12 h.

The extraction and cleanup procedures for OCPs and PCBs were carried out as follows: After adding surrogate standards and mass-labelled standards to the soil samples, they were Soxhleted with 150 mL DCM for 48 h. After the extraction, 2 g copper chips were added to remove sulfur. The extract was reduced to 5–10 mL using a rotary evaporator, and then further reduced to 1 mL after 10–15 mL hexane was added. This concentration step was repeated three times and then the sample solution was transferred to a 5 mL cell, and they were passed through a silica–alumina column (7 mm i.d.; from bottom to top, 10 g 3% activated silica, 10 g 3% de-activated alumina, and 1 g dehydrated sodium sulfate). The column was eluted with 35 mL hexane/DCM (v/v ratio 1:1) solution. The eluent was reduced to 0.5 mL using a rotary evaporator, then further concentrated to 0.2 mL under a gentle high purity nitrogen gas. The sample was subject to HRGC-HRMS analysis after adding injection internal standards.

2.4. HRGC-HRMS measurement

The OCPs and PCBs in the samples were analyzed by an HRGC-HRMS system (HP-6890 high resolution gas chromatograph coupled to Finngan MAT 900XL HRMS operated in an electron impact (EI) and selective ion monitoring (SIM) mode. The GC column was a HP-5MS (30 m × 0.32 mm i.d., with film thickness of 0.25 μm). The GC conditions are as follows: the temperature settings for the injector and detector were 280 °C and 320 °C, respectively; the initial column temperature of 50 °C was held for 2 min, then increased at a rate of 10 °C min^{-1} to 180 °C, held for 2 min, and then increased to 220 °C at 2 °C min^{-1}, and to 290 °C at 10 °C min^{-1}, held for 15 min. Oxygen-free nitrogen (99.999% purity) was used as the carrier gas at a constant flow rate of 1.5 mL min^{-1}. The sample (1.0 μL) was injected with splitless injection mode. The make-up gas was high pure nitrogen.