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Evidence for persistent organic pollutants released from melting glacier in the central Tibetan Plateau, China☆

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ABSTRACT

Glacier alluvial deposits record persistent organic pollutants (POPs) not only derived from the atmospheric deposition but also from the release of glacial melting. The evidence for melting glacier in the Tibetan Plateau (TP) as a secondary source of pollutants is introduced through investigating the concentration of organochlorine pesticides (OCPs) in four deposited profiles collected at the edge of the Changwengluozha glacier. Two concentration peaks were observed for dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs) in the past century. The first peak was observed in the 1970s, corresponding with the heavy usage of HCHs and DDTs in the surrounding countries and regions. The second one was in 2000 when the production and usage of DDTs and HCHs were strictly limited, which possibly indicated a significant release from melting glacier. This result was further supported by the enantiomeric fraction values for α-HCH and *o,p′*-DDT. On the other hand, the dramatic increase of polycyclic aromatic hydrocarbons (PAHs) from atmospheric deposition, which was associated with the socioeconomic development in Tibet, shaded the release of PAHs from melting glacier. This study reveals not only the air deposition history of legacy POPs but also a substantial release of OCPs from glacier to the adjacent environment. Our research supports the hypothesis that the melting glacier in the TP represents a secondary source of OCPs, which is consistent with the findings in the Alps glaciers.

1. Introduction

Because of long-range atmospheric transport (LRAT), persistent organic pollutants (POPs) can reach and affect remote ecosystems at high latitude and altitude (Khairy et al., 2016; Wania, 2003; Wania and Westgate, 2008). In alpine mountain areas, the cold-trapping of POPs occurs during LRAT due to low-temperature condensation at higher altitude (Arellano et al., 2011; Wania and Westgate, 2008). Glaciers, covering large parts of Polar Regions and mountainous areas, are one type of important reservoir for POPs. A significant amount of POPs may deposit into glaciers in a period of high environmental pollution and be stored in ice layers during the following years (Pavlova et al., 2014, 2015; Steinlin et al., 2014, 2015). Melting glaciers would result in a substantial release of POPs, which is proposed as the "glacier hypothesis" (Bogdal et al., 2009). This phenomenon has been found in the Alps (Bettinetti et al., 2008, 2011; Bogdal et al., 2008, 2009; Schmid et al., 2011), alpine regions of Canada (Lafrenière et al., 2006), and Antarctica (Geisz et al., 2008). Reasonably, pristine ecosystems in other regions, such as Tibetan Plateau, may also be affected by the delayed release of environmental contaminants which had been extensively emitted in the history.

The Tibetan Plateau (TP) covers an area of over 2.5 million km^2 with an average elevation of higher than 4000 m, and it is also called "the third pole" of the earth. In this plateau, there are 36,800 glaciers which cover an area of 49,873 km^2 with a total volume of 4561 km^3 (Yao et al., 2007). Due to global warming, initial retreat of the glaciers in the plateau was observed from the late 1980s and glacier volume had lost 39.41 km^3 in 2002 compared with the volume in 1980 (Yu et al., 2012). By analyzing the glacial ice core, concentration peaks were found in the 1970s for legacy organochlorine pesticides (OCPs) and in the 1990s for legacy polycyclic aromatic hydrocarbons (PAHs), resulting from their extensive emission (Wang et al., 2008). Most recently, OCP concentrations in some sedimentary cores of the plateau were determined, showing

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an increasing trend in the 1990s (Cheng et al., 2014), which was tentatively explained as the influence of melting glaciers. If so, some crucial evidence is needed to confirm the release of POPs directly from melting glacier, representing a "secondary source" in the plateau similar to that found in the Alps (Schmid et al., 2011).

In this study, legacy POPs were analyzed in the alluvial deposits at the edge of the Changwengluozha glacier in the central Tibetan Plateau, including chiral analysis. The goal is to reveal the potential influences of the hypothesized secondary source (melting glacier) on DDTs, HCHs and PAHs in the unique ecosystem at high altitude. Alluvial deposits at the edge of the glacier are the residues of meltwater flow. With the ice melting into water, formerly trapped chemicals in ice are adsorbed as deposits. Thus, the secondary source of POPs resulting from melting glaciers would be archived in specific layers of the alluvial deposits. Compared to lake sediments, alluvial deposits should more accurately record the variations of POPs from melting glaciers because the loss of POPs during the transporting process may be reduced significantly.

2. Materials and methods

2.1. Study site, sampling and statistical methods

The Changwengluozha glacier is 6028 m above sea level, and is at least 200–300 km away from the nearest small town of Gaize and more than 1000 km away from Lhasa in Tibet. There was almost hardly historical anthropogenic activities in the depopulated area. This glacier is dominated by continental climatic condition with limited precipitation and classified as continental type, one prevalent type of glacier in the TP (Yao et al., 2012). In four vertical profiles (denoted P1, P2, P3 and P4) of alluvial deposits, 51 samples were collected, including 18 samples in P1, 13 in P2, 10 in P3 and 10 in P4 (Table S1 in Supplementary Material, SM). In each profile, the samples were collected from surface to bottom and sectioned onsite at an interval of 2.5 cm. All of the samples were collected in August 2011. The sampling sites at altitudes from 5080 to 5234 m are shown in Fig. 1, and more detailed location information is outlined in Table S2 in SM. The temperature time series data were obtained from the observatory station located in Gaize area provided by National Meteorological Administration (http://data.cma.cn). At such an altitude higher than 5000 m with annual average temperature lower than freezing point, the degradation of POPs is negligibly weak (Yuan et al., 2014c, 2015a). Moreover, the low water solubility and low volatilization of POPs from low temperature meltwaters implied the limited losses of POPs in this case. Thus, POPs archived in deposits would be supposed to mainly maintain the original composition from melting glacier. Methods for sampling and storage were the same as those reported previously (Yuan et al., 2014b). Curve fitting analysis of the concentration trends was performed using the software of Matlab R2016a (MathWorks) for windows.

2.2. Chemicals

The 23 OCPs standard solutions (Table S3 in SM), and 16 PAHs standard solutions (Table S4) were purchased from Cambridge Isotope Laboratories (Andover, MA). In addition, four deuterated PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}) and 2,4,5,6-tetrachloro-m-xylene (TCMX) (J&K Chemical, U.S.) were, respectively, used as surrogate standards for PAHs and OCPs to monitor the extraction procedure. Racemic standards of α-HCH and *o,p′*-DDT were obtained from Ehrenstorfer GmbH, Augsburg, Germany. Additional details, including the producer, grade, and pre-treating process, were provided previously (Yuan et al., 2014b, 2014c).

2.3. Geochronology

Dating of the vertical profiles was based on the analysis of 137Cs and 210 Pb by γ-rays spectrometry. A constant rate of supply (CRS) dating model (Appleby, 2001) was used for the chronology calculation (Fig. S1 in SM). Average sedimentation rates were determined to be 0.69 cm/a for profile P1, 0.67 cm/a for P2, 0.55 cm/a for P3 and 0.61 cm/a for P4. More detailed information on dating methods is given in Supplementary Material.

2.4. Extraction and analysis

The extraction of OCPs and PAHs was performed separately using the same processes. 10 g of sample was freeze-dried and homogenized with anhydrous sodium sulfate. The mixture was packed into a clean centrifuge tube, then 20 ml of acetone/n-

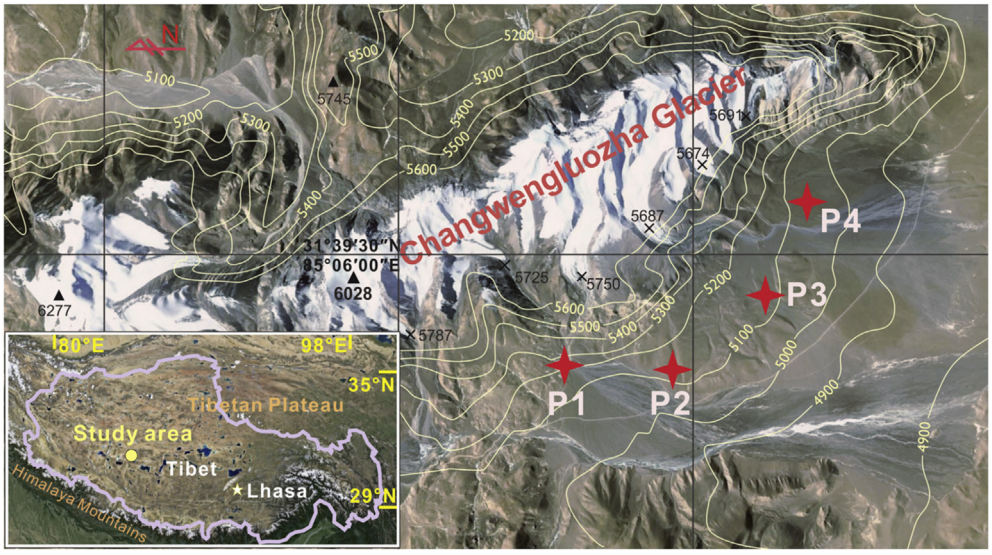

Fig. 1. Map showing the Changwengluozha glacier with sampling sites. The grid represents 5 km. (Bottom left) Overview map of Tibet showing the location of the study area.