



## Composition and sources of polycyclic aromatic hydrocarbons in cryoconites of the Tibetan Plateau glaciers



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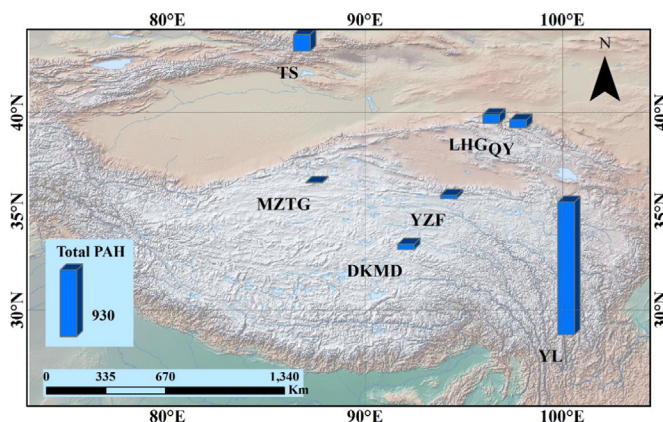
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### HIGHLIGHTS

- PAHs in cryoconite from seven glaciers of the Tibetan Plateau were presented.
- The highest  $\Sigma$ PAHs contents were found in the southeastern Tibetan Plateau.
- Total organic carbon and grain size were minor factors affecting PAHs values.
- Low toxic equivalent quantity of PAHs in most of glaciers suggested a limited biological risk.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 22 July 2016

Received in revised form 19 September 2016

Accepted 19 September 2016

Available online xxx

Editor: Jay Gan

#### Keywords:

Tibetan Plateau

Glacier

Cryoconite

Polycyclic aromatic hydrocarbon

### ABSTRACT

Dark-colored cryoconite can absorb substantial solar radiation, reduce the surface albedo of glaciers, and thus greatly accelerate glacier melting. Organic matters in cryoconites such as polycyclic aromatic hydrocarbons (PAHs) are kind of the light absorbing compositions. In this study, 15 PAHs containing 3–7 rings were identified in 61 cryoconites samples collected from seven glaciers over the Tibetan Plateau (TP). The average concentration of total PAHs in cryoconites samples was in the range of 6.67–3906.66 ng g<sup>-1</sup> dry weight. The highest average total PAH concentration was found in the southeastern TP, followed by the northern TP. The central TP contained the lowest amount of PAHs. Moreover, correlation analysis showed that total organic carbon (TOC) and grain size were only a minor factor for the accumulation of PAHs in cryoconites of the TP. Factor analysis and diagnostic ratios indicated that the PAHs were produced mainly from the incomplete combustion of coal, fossil fuels and biomasses. The exhaust gas of locomotives also contributed to the accumulation of PAHs in the glaciers. The PAHs in these seven glaciers showed low toxic equivalent quantity (TEQ), and thus had low biological risk. Nevertheless, the pollution of PAHs in the southeastern TP needs to be addressed.

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## 1. Introduction

Cryoconite is a dark-colored spherical particulate transported onto a glacier surfaces via aeolian processes, landslides from valley walls, and supraglacial and englacial entrainment (Macdonell and Fitzsimons, 2008; Mcintyre, 1984). It is a mixture originating from the local, regional and remote sources through both natural and anthropogenic pathways (Tieber et al., 2009). Global warming has led to the retreat and thinning of many glaciers throughout the Tibetan Plateau (TP) over the past decades (Yao et al., 2012; Kang et al., 2015). Dark-colored cryoconite on the surfaces of glaciers can absorb substantial solar radiation, reduce the surface albedo of glaciers, and thus significantly accelerate glacier melting (Fujita, 2002; Takeuchi et al., 2005). Cryoconite usually resides in cryoconite holes and in the entire ablation areas of glaciers in high alpine environments.

Previous studies have suggested that the dark coloration of humic substances in cryoconite is attributed to their highly conjugated molecular bonds including benzene rings and polyethylene chains, which can effectively absorb visible light over a wide range of wavelengths (Takeuchi, 2002). Polycyclic aromatic hydrocarbons (PAHs) are a class of organic contaminants composed of two or more fused benzene rings within a conjugated system. They are some of the most disturbing contaminants on both regional and global scales because of their persistence, transportation over long ranges, and potential carcinogenesis and mutagenesis (Guo et al., 2010; Lang et al., 2008). PAHs are also considered as a typical indicator of human activity (Vehviläinen et al., 2001). The levels of PAHs are strongly correlated to regional energy consumption and degrees of industrialization and urbanization (Metre et al., 2000).

The TP is sensitive to environmental changes and thus is an excellent area for studying the distribution of organic contaminants in remote regions. The glaciers on the TP currently serve as a “sink” of pollutants and can release accumulated organic contaminants as the temperature increase. This discharge of pollutants may become a threat to both human health and the ecosystem in the future. Cryoconite organic matter may also play an important role in accelerating the melting of glaciers because it can absorb visible light (Takeuchi, 2002; Xu et al., 2010). Numerous studies on the organic matters in cryoconite holes have been published in recent years (Xu et al., 2010; Pautler et al., 2013). However, the PAHs in the cryoconites on the TP glaciers have been rarely reported up to now. In the present study, cryoconite samples were collected from seven glaciers, from the south to the north of the TP. The contents and spatial distribution of PAHs in cryoconites of the TP glaciers were investigated and the possible sources of these organic contaminants were determined. This work can provide a basic information for studying the organic matters in cryoconite and further for assessing the effects of PAHs on alpine environments.

## 2. Materials and methods

### 2.1. Study area

Yulong (YL) Snow Mountain (27°40'N, 100°10'E) is located in the southeastern TP as a part of the southern Hengduan Mountains (Fig. 1). It is characterized by maximum annual precipitation of 3100 mm and relatively high temperatures, with average annual and summer temperature of −6 °C and 1–5 °C at the equilibrium line (Zhang et al., 2012).

Dongkemadi (DKMD) glacier (33°05'N, 92°04'E) is located on the northern slope of Tanggula Pass of the central TP (Fig. 1). It is 2.8 km long and its equilibrium line altitude (ELA) lies at 5620 m a.s.l. (Xiao et al., 2002). Yuzhufeng (YZF) glacier (35°39'N, 94°14'E) is located at the summit of the eastern Kunlun Mountains in the northern TP (Fig. 1), and has a maximum highest elevation of 6178 m a.s.l. and a snowline at 5100–5300 m a.s.l. (Wu et al., 2001). Muztagh (MZTG) glacier (36°40'N, 87°30'E) is situated at the ridge of the central Kunlun Mountains with

an area of 71.70 km<sup>2</sup>. It belongs to the watershed between the Milan and Che'erchen rivers at an elevation of 6973 m a.s.l. (Fig. 1). Its inventory number is 5Y624E34 (Xing et al., 2016).

Qiyi (QY) glacier (39°14'N, 97°46'E) and Laohugou (LHG) No.12 glacier (39°26'N, 96°33'E) are on the western Qilian Mountains with the Badain Jaran and Tengger Deserts in its north and the Qaidam basin in its south (Fig. 1). These two glaciers are surrounded by many large deserts and wastelands and have a typical continental climate (Dong et al., 2013).

Tianshan (TS) is an active intracontinental mountain belt that extends over 2500 km in the east-west direction across central Asia. The eastern branch of the Urumqi glacier No. 1 (43°06'N, 86°48'E) riverhead is located in the eastern TS and is surrounded by the Taklimakan Desert to the south, the Gurbantungut Desert to the north, and the Gobi Desert to the east (Fig. 1). The glacier's ELA was approximately 4055 m a.s.l. in 1959–2003 (Li et al., 2001).

The TP covers climatic regions from the monsoon region to the areas affected by westerly depressions, and the climate changes from warm and wet to cold and dry. Consequently, the vegetation coverage in the region gradually decreases from the south to the north over the plateau.

### 2.2. Sample collection

Cryoconite samples were collected from seven glaciers of the TP in July and August 2014 (Fig. 1), which was during the summer ablation season. Specifically, samples were collected with a stainless steel scoop from the superimposed ice surface or the bottom of cryoconite holes in the ablation area of glaciers. The numbers of collected samples were 9, 5, 5, 3, 14, 11, and 14 from the Baishui No. 1 glacier on YL Snow Mountain, DKMD glacier, YZF glacier, MZTG glacier, LHG glacier, QY glaciers, and TS Urumqi No. 1 glacier, respectively. All samples were placed into previously cleaned glass bottles that were then immediately stored in Whirl-Pak® bags and frozen in a refrigerator. The samples were transported to the laboratory and were stored at −20 °C until further analysis.

### 2.3. Chemicals and reagents

Hexamethylbenzene, perdeuterated PAHs surrogate standards (including phenanthrene-*d*10, chrysene-*d*12, and perylene-*d*12), and 15 PAHs containing 3–7 aromatic rings were purchased from Sigma-Aldrich. The 15 PAHs were includes: phenanthrene (Phe); anthracene (Ant); fluoranthene (Flu); pyrene (Pyr); retene (Ret); benzo[*a*]anthracene (BaA); chrysene (Chry); benzo[*b*]fluoranthene (BbF); benzo[*k*]fluoranthene (BkF); benzo[*a*]pyrene (BaP); perylene (Pery); indeno[1,2,3-*cd*]pyrene (InP); dibenzo[*a,h*]anthracene (DbA); benzo[*g,h,i*]perylene (BgP); and coronene (Cor). HPLC grade Hexane (HEX), dichloromethane (DCM) and methanol (MeOH) were used for all sample preparation and analyses. Silica gel (80–100 mesh) and alumina (120–200 mesh) were activated in an oven at 150 °C and 180 °C, respectively, for 12 h. Deionized water was obtained from a Milli-Q system.

### 2.4. Extraction and analysis of PAHs

The cryoconite samples were freeze-dried at −70 °C and were ground into powder. About 10–20 g of the powder was extracted with 9:1 (v/v) DCM: MeOH for 72 h in a Soxhlet apparatus and desulfurized with activated copper. The extract was concentrated up to 2–3 mL and was passed through a chromatographic column packed with pre-activated alumina and silica gel (3:1 w/w) for cleanup and fractionation. The top of the column was covered with 0.5 g anhydrous sodium sulfate to remove the residual water. The column was eluted with 45 mL DCM, the eluent was concentrated and solvent-exchanged into 10 mL *n*-hexane which further reduced to approximately 1–2 mL by rotary evaporation at 40 °C and was then evaporated to 500 μL in hexane under a

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