



## Temporal and diurnal analysis of trace elements in the Cryospheric water at remote Laohugou basin in northeast Tibetan Plateau



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### HIGHLIGHTS

- New data were presented on temporal and diurnal change of trace elements in Cryospheric water.
- Trace elements showed evident diurnal change with a peak concentration at about 15:00–17:00.
- Diurnal change of trace elements was influenced by runoff level and pH.
- Heavy metals (e.g. Ni, Zn, Mo, Sb and Pb) were partially from anthropogenic sources.

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### ABSTRACT

An evaluation of glacial meltwater chemistry is needed under recent dramatic glacier melting when water resources might be significantly impacted. This study investigated trace elements variation in the meltwater stream, and its related aquatic environmental information, at the Laohugou (LHG) glacier basin (4260 m a.s.l.) at a remote location in northeast Tibetan Plateau. We focused on the spatial, temporal and diurnal change of trace elements during the glacier ablation period. Results showed evident elements spatial difference on the glacier surface meltwater, as most of the elements showed increased concentration at the terminus compared to higher elevations sites. Dominant elements in the meltwater were Ba, Sr and Cr, whereas elements with high enrichment factors (EFs) were Sb, Ni, Mo and Zn. Temporal change of some trace elements concentration (e.g. Sc, Cu, and Rb) indicated increasing trend with accelerated snow-ice melting, whereas others (e.g. Ni, Zn, and Pb) showed decreasing trend. We find that, trace elements showed evident diurnal change and a peak value of concentration was observed each day at about 15:00–17:00, and the diurnal change was influenced by runoff level and pH. Moreover, EFs calculations revealed that heavy metals were partially originated from regional anthropogenic sources. Overall, the accelerated diurnal and temporal snow-ice melting (with high runoff level) were correlated to increased elemental concentration, pH, EC and elemental change mode, and thus this work is of great importance for evaluating the impacts of accelerated glacier melting to meltwater chemistry and downstream ecosystem in the northeast Tibetan Plateau.

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## 1. Introduction

Glacier meltwater chemistry enables us to understand the cryospheric influences on chemical denudation, biogeochemical cycling and glacial ecosystems (Jones et al., 1999; Brown, 2002; Brown and Fuge, 1998). A few studies on minor and trace elements have been performed in alpine glacial hydrological systems (Boutron et al., 1995; Hodson et al., 2005; Mitchell et al., 2004,

2006; Dong et al., 2015; Sun S et al., 2016; Sun X, et al., 2016; Huang et al., 2014). The quantity and transport mode of trace elements influence their bioavailability downstream of glacial headwater catchments. Trace elements have potential in the solute-provenance and flow-routing studies, and their enrichment in meltwater has implications for downstream aquatic environments (Mitchell et al., 2004). Glacier meltwater is usually low solute concentrations than that of other rural sites as its snow-ice based formation process. For example, previous study at the Wright Valley of the Antarctic showed that, the element concentrations (e.g. Mn, Fe and Ni) are lower than those in world's stream waters (Green et al., 2005). The Tibetan Plateau, usually called "the third pole" (Yao et al., 2012), is one of the most remote and isolated regions in the world. However, element measurements for glacier meltwater from this area have been rare, usually due to the harsh natural conditions and logistic difficulties.

Glacier meltwater in the northeast Tibetan Plateau provides headwaters for some rivers that influence regional water availability and food security in surrounding arid regions in northwest China. However, trace elements variation in the glacier meltwater on the northeast Tibetan Plateau have not been investigated, despite their importance as bio-limiting nutrients or toxic metals in freshwater and other aqueous systems (Chester, 1990; Manahan, 1991), and their importance in downstream assessment of anthropogenic stream pollution (Mitchell et al., 2006). Moreover, an evaluation of glacial meltwater chemistry is needed under recent dramatic glacier melting when water resources might be significantly impacted (Kang et al., 2010). Analyzing diurnal change of meltwater chemistry is an important starting point to investigate dramatic glacier change influences to meltwater. Expanded interest in diel cycles during the past years has helped demonstrate the importance of, and the interconnections among, biogeochemical processes in down streams (Nimick et al., 2011; Gammons et al., 2015).

The Qilian Shan Station of Glaciology and Ecologic Environment (high station) is situated in the Laohugou glacier basin (LHG) on the northern slope of the western Qilian Mountains, in the northeast Tibetan Plateau (Fig. 1). Due to its high elevation (4260–5100 m.a.s.l) and long distance (200 km) from local pollution sources, the high station is well suited for temporal change investigation of glacier meltwater chemistry. There exist 44 glaciers in the LHG basin, with the largest glacier of glacier No.12 with an area of 20 km<sup>2</sup>. The large amount of meltwater from the LHG basin is very important water resource for the Shule River in the downstream of arid regions. Based on continues sampling of glacier meltwater in LHG basin during summer 2014, this study can provide a first valuable dataset on trace elements variation and new evidence on the water quality and aquatic environment of the glacier meltwater at a remote location of the northeast Tibetan Plateau, and give an evaluation of glacier meltwater geochemistry under recent dramatic glacier melting.

In this study, we focused on the changes in chemical behavior of trace elements in the glacier meltwater stream at the LHG basin during the whole ablation period of 2014 and associated aquatic environmental information. With the elevation rise on the glacier surface, the behavior and fate of trace element transportation may have changed. Thus we worked to find out the spatial distribution of various trace elements in the meltwater of distinct elevation along the glacier surface, and to compare the difference between the glacier terminus sampling sites and other higher elevation sites. The main objectives of this study are to measure the concentrations of trace element in the meltwater and its temporal and diurnal change mode, investigate their possible sources of trace element in the meltwater stream, and finally evaluate the impacts of accelerated glacier melting to glacier meltwater geochemistry in northeast Tibetan Plateau.

## 2. Sampling and lab analysis

We collected the glacier meltwater stream samples at different elevations in the remote LHG glacier basin of the northern Tibetan Plateau (Fig. 1). The LHG Glacier basin (39°20'N, 96°34'E, with the altitude of 4200–5200 m a.s.l.) is located at the northern slope of western Qilian Mountains with typical continental climatic conditions (Dong et al., 2014). The Laohugou Glacier No.12 is the most typical glacier at the basin, with a length of 10 km and an area of 20 km<sup>2</sup>, and was divided into two branches at the altitude of 4560 m a.s.l., providing large amount of glacier meltwater runoff to the glacier basin in summer. There are many large cities surrounding in the LHG glacier area, such as Yumen city and Jiuquan city, etc.

During the glacier ablation period in 2014, we collected meltwater stream samples at the terminus (4260 m a.s.l.) of Laohugou Glacier No. 12 at 14:00, with a frequency of every two-day across June–September 2014, and also collected meltwater samples on the glacier surface meltwater river in different elevations along the Laohugou glacier No.12 surface (see Fig. 1b). A total of 107 samples of meltwater were acquired, including 42 glacier surface meltwater river samples along different elevations in the glacier No.12 (from the elevation of 4260–5010 m a.s.l.) and 65 samples of temporal change at the terminus of Glacier No.12 in 4260 m a.s.l. As in this work we collected samples at the glacier terminus and also the glacier surface with different elevations, thus we will not consider the influence to elements from drainage system at the LHG glacier bottom. Moreover, we collected the samples far away from the surface moraine, avoiding influence of moraine and local dust inputs to trace elements. However, there exists large amount of cryoconite in the glacier ablation zone, from the elevations of 4300–4600 m a.s.l. Cryoconite deposited on mountain glaciers with dark color typically consists of mineral dust particles (large partially) and other components, such as black carbon and organic particles (Dong et al., 2016; Grzesiak et al., 2015), which acted as light absorbing impurity and may contribute to crustal elements to the glacier meltwater stream.

Pre-cleaned Low-density polyethylene (LDPE) 60 mL bottle (Nalgene®) was used for the sample collection. Glacier meltwater trace-metal samples were collected in the field by first rinsing the bottles three times before collection and using 'clean hands, dirty hands' techniques. Sample gloves were changed between each collected sample. Stream trace and major element samples were filtered using 0.45 µm pore size Nuclepore polycarbonate membrane filters and then acidified to 2% (v/v) using Optima HNO<sub>3</sub> within 2 days of collection, to dissolve the trace elements associated with atmospheric particles and to prevent their adsorption onto the walls of the bottles. Stream samples were filtered using triple-acid-cleaned (10% HCl, 10% HNO<sub>3</sub>, 1% Optima HNO<sub>3</sub>) filter towers into clean bottles, and were kept frozen until transported to the lab for analysis. All samples were melted at room temperature and the concentrations of trace elements were determined directly by a Thermo Scientific Element 2 inductively coupled sector-field mass spectrometry (ICP-SF-MS) at the Analytical Laboratory of Beijing Research Institute of uranium Geology. Finally, 18 trace elements (Li, Be, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Nb, Mo, Cd, Sb, Cs, Ba, Tl, and Pb) and 9 REEs (La, Ce, Pr, Nd, Sm, Eu, Th, U, and Yb) were analyzed. Quality assurance and quality control (QA/QC) of elements analysis were completed to inspect contamination of samples in both field and laboratory, and to ensure the reliability of our results. Trace-element samples were handled and filtered entirely in a Class 100 laminar flow hood using Nitrile polyethylene gloves. Non-powder vinyl clean room gloves and masks were worn to avoid possible contamination during the sampling and laboratory analysis. All samples were kept frozen until laboratory analysis.

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