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Research paper

Elemental variations in glacier cryoconites of Indian Himalaya and Spitsbergen, Arctic

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ABSTRACT

Cryoconite samples were collected from two different climatic domains i.e., the Sutri Dhaka glacier, western Himalaya India and Svalbard glaciers, the Spitsbergen, Arctic, to understand the elemental source and elemental deposition patterns. The data of geochemical analysis suggest that the Himalayan cryoconite samples accumulate higher concentrations as compared to the cryoconite samples of the Arctic glaciers. The concentration of lithophile elements (Cs, Li, Rb and U) was recorded higher in the cryoconite holes of the Himalayas, especially, in the lower to the higher parts of the glacier, whereas, lower concentrations were recorded in the Arctic samples. Chalcophile elements in the Himalayan cryoconites are enriched in As and Bi while the Arctic cryoconite samples show a higher concentration of Bi, Pb and As. The higher concentrations are responsible for influencing the ecosystem and in human health related issues. Siderophile elements (Co, Fe, Mn and Ni) show high concentrations in the Himalayan samples, whereas, the Arctic samples show minor variations and low elemental concentration in these elements, respectively. In addition, a few elements, such as Ag, Mg, and Ca show higher concentration in the Himalayan glacier samples. Ca also occurs in high concentrations in Arctic glacier samples. R-mode factor analysis of the Himalayas (Arctic) samples indicate that the elements are distributed in four (three) factors, explaining 89% (90%) of the variance in their elemental distribution. The Factor 1 suggests statistically significant positive loadings for most of the lithophile, chalcophile and siderophile elements of the "Himalayan" and the Arctic cryoconite samples. The sample-wise factor score distribution shows a considerable variation in the sampling locations along the glaciers of both the regions. Factors 2 and 3, demonstrate insignificant loading for most of the elements, except statistically significant positive loading in some of the elements of the both, Himalayan and Arctic "cryoconites". The higher elemental concentration in the cryoconites of the Himalayan region may be an indicator of the natural processes and/or attributed to the rapid industrialization in the Asian countries.

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1. Introduction

Cryoconite is a dark coloured, dust material transported by wind and deposited on the surface of snow or ice (Wharton et al., 1985), which is an aggregate of minerals and organic dust, together with microorganisms. The surface of glaciers is able to accumulate large

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amounts of airborne pollutants bound to extracellular polymeric substances secreted by the microorganisms (Nagatsuka et al., 2014a; Łokas et al., 2016). Once the dust material is deposited on glacial surface, it absorbs more solar radiation than the surrounding ice, creating melt holes (cryoconite holes) with distinct, "shaft-like" structures (Takeuchi, 2002; Singh et al., 2012a,b). The dark colour of minerals and organic matters in the cryoconite can reduce the albedo of glaciers and increase their ice melting (Kohshima et al., 1993; Wientjes et al., 2011). The mineral dust may also affect the microbial population of filamentous cyanobacteria and green algae, which are likely to incorporate nutrients from mineral particles as

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well as the dissolved components in snow and ice (Nagatsuka et al., 2010; Wientjes et al., 2011). The studies on minerals in cryoconites are important for correlation of biological activity and recent changes in glacial mass balance. Since glaciers and ice sheets constitute a significant part of the land and hydrosphere with sites of high biological production, the understanding of the cryoconites is of great significance.

Mountainous and high altitudinal terrain of the Himalaya and Arctic regions support permanent ice cover, which is significantly influenced by the natural processes of erosion, transportation and deposition. Chemical weathering and associated soil development on glacial forelands has increased with time, since the last glaciation (Darmody and Thorn, 1997). Cryoconite dust are transported by winds from the local outcrops in the atmosphere (Singh et al., 2012a,b). In order to recognise the effect of natural processes and/ or anthropogenic disturbances, the elemental composition and concentration of the glaciers are required to be analyzed at regular intervals. Any unprecedented increase in the elemental values needs to be verified against the various pollution factors that may be affecting the area. Cryoconites collected from the Hans Glacier in the SW Spitsbergen reveal high concentrations of anthropogenic Pu, Cs, Sr and natural Pb radionuclides (Łokas et al., 2016).

The Himalayan Mountain range is the second largest ice mass after the Polar region (Wagnon et al., 2007). Environmental monitoring of the major, minor and trace elements in the Himalayan samples was earlier carried out from lichens (Bergamaschi et al., 2002), surface sediments of river systems (Ramesh et al., 2000), meltwater chemistry (Sharma et al., 2013), fresh-snow (Mayewski et al., 1983; Shrestha et al., 1997; Marinoni et al., 2001; Kang et al., 2002, 2004, 2007; Balerna et al., 2003; Lee et al., 2008), debris cover (Sharma et al., 2016) and aerosols (Cong et al., 2010). The resulting data from glacier soil samples revealed that the biogeochemical properties affect the diversity of microbial communities (Pradhan et al., 2010; Shivaji et al., 2011; Srinivas et al., 2011). Rapid industrialisation, in the Asian countries, has become one of the greatest contributors of anthropogenic pollutants. Earlier studies revealed that the industrial and domestic processes, namely combustion of fossil fuels and production of non-ferrous metals and bulk release of trace metals such as, As, Cr, Cu, Ni and Zn into the atmosphere, have an adverse impact on the Himalayan ecosystem (Pacyna and Pacyna, 2001; Pacyna et al., 2007). Mining activities and tourism activities in these regions may also affect the equilibrium of this system.

Earlier studies (Bøggild et al., 2010; Wientjes et al., 2011) showed that the minerals in the cryoconite on the Arctic glaciers are likely to be derived from local sources rather than from the aeolian dust from distant areas. Rapid changes in many parts of the Earth's surface has been related to recent climate warming and human activities (IPCC, 2007). This in turn may result in changes in atmospheric transport and sources of mineral dust on the glaciers. Several studies have been carried out to monitor the environmental impacts on Arctic glaciers by studying the geochemistry of aerosols (Pacyna et al., 1984; Maenhaut et al., 1989; Wadham et al., 2006; Eleftheriadis et al., 2009), lake sediments (Boyle et al., 2004; Rose et al., 2004), snow and cryoconite (Snyder-Conn et al., 1997) etc. Barrie (1986) and Pacyna et al. (1985) revealed that the air pollution occurs in the Arctic through long-range pollutants, while Aldahan et al. (2000) analyzed the element stratigraphy in quaternary sediments of the Arctic Ocean. Ruman et al. (2012) reported the pollutants present in different components of the environment of Svalbard Archipelago. Recent studies were carried out on elemental chemistry of different habitats in Svalbard, such as sediments of Kongsfjord (Lu et al., 2013; Singh et al., 2015a), glacier ice cores (Singh et al., 2015b), permafrost (Singh et al., 2012b) and lichens (Singh et al., 2012a).

The Himalayas and the Arctic, although geographically apart represent a regime of Cryosphere with similar climatic conditions. No comparative study on the elemental variations of cryoconites of the two regions has been attempted so far. The present study attempts to fill up this knowledge gap.

2. Materials and methods

2.1. Study area and sample collection

Cryoconites samples were collected from two different climatic regions, i.e., one from the Sutri Dhaka glacier of the Chandra basin, Himalayan region and other from the Austre and Vestre Brøggerbreen glaciers of the Spitsbergen, Arctic region (Fig. 1). The Sutri Dhaka glacier (25.4 km²) is located in the Chandra valley of Lahaul and Spiti district of Himachal Pradesh, western Himalayas, India. The Austre Brøggerbreen (11.7 km²) and the Vestre Brøggerbreen (5.3 km²) glaciers are situated on the western part of the Spitsbergen, Arctic. The samples were collected from 12 different locations (H1-H12) spread over in the ablation zone of the Sutri Dhaka glacier, between altitudes of 4634 and 5177 m. Six samples (A1–A6) were collected, from different sites of the Austre Brøggerbreen glacier at an elevation of 598 m. Another five samples (A7-A11) were collected, from the Vestre Brøggerbreen glacier at the altitude of 99–184 m. The sampling was performed following contamination-free procedures as suggested by Veysseyre et al. (2001). All the samples of were labelled and stored in insulated box, at -20 °C (Arctic samples) and sub-zero temperature (Himalavan samples), and transported subsequently to the laboratory of National Centre for Antarctic and Ocean Research (NCAOR), Goa, India for further analyses.

2.2. Geochemical analysis

Finely grounded powdered samples were oven-dried at 110 °C. 0.5 g of each sample was digested completely in the microwave (Ethos 1, M/s. Milestone, s.r.l, Italy) by adding 3 mL of 69% sub-pure HNO₃ (SubPUR M/s. Milestone, s.r.l, Italy), 1 mL suprapure 30% HCl (Merck, Darmstadt, Germany) and 1 mL of 30% H₂O₂ (Merck specialities Pvt. Ltd, India). The acid digestion was carried out by raising the temperature up to 180 °C (within 20 min) and later held for 15 min at 180 °C temperatures. The Milli-Q deionised water was used to make the dissolved solution up to 50 mL. The digested samples were analyzed by ICP-MS (X Series II, Thermo Fisher Scientific, Bremen, Germany). Continuous calibration was performed with standard and blank solutions during the course of measurements. Instrumental conditions were optimized, followed by auto-tuning of mass calibration procedure and detector cross calibration using the Thermo tune solution. Standard solutions were prepared in 1% HNO₃ using 10 mg/L (30 elements) CertiPUR ICP multi-element standard solution XXI for MS (Merck, Darmstadt, Germany) except Ca and Mg standard solution prepared from 1000 mg/L CertiPUR Single element standard (Merck, Darmstadt, Germany). The geochemical analysis was carried out for each sample-using standard $(\mu g/L)$ and blank $(\mu g/L)$ samples (details are given in Supplementary Table 1). Elemental concentrations such as (1) Lithophiles (Ba, Cr, Cs, Li, Rb, Sr, U, and V), (2) Chalcophiles (As, Bi, Cd, Cu, Pb, and Zn) and (3) Siderophiles (Co, Fe, Mn, and Ni) were measured in triplicate and were recorded in mg/kg. Elemental concentrations in the Himalayas and the Arctic glaciers cryoconites were compared with the continental crustal values, earlier estimated by Gao et al. (1998) for the East China and Shaw et al. (1967, 1976) for the Canadian Precambrian shield, respectively. The concentration of the As and Cs values were compared with those given by Rudnick and Gao (2003).

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