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Chemistry and isotopic composition of precipitation and surface waters in Khumbu valley (Nepal Himalaya): N dynamics of high elevation basins

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HIGHLIGHTS

- Ionic concentrations in rain are the regional background deposition concentrations.
- In non-monsoon seasons, the Himalayas are not a barrier for airborne pollution.
- The chemistry of stream water is dominated by the dissolution of calcite and gypsum.
- N deposition fluxes do not adequately predict N concentrations in stream waters.

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ABSTRACT

We monitored the chemical and isotopic compositions of wet depositions, at the Pyramid International Laboratory (5050 m a.s.l.), and surrounding surface waters, in the Khumbu basin, to understand precipitation chemistry and to obtain insights regarding ecosystem responses to atmospheric inputs.
The major cations in the precipitation were NH_4^+ and Ca^{2+}, whereas the main anion was HCO_3^-, which constituted approximately 69% of the anions, followed by NO_3^-, SO_4^{2-} and Cl^-. Data analysis suggested that Na^+, Cl^- and K^+ were derived from the long-range transport of marine aerosols. Ca^{2+}, Mg^{2+} and HCO_3^- were related to rock and soil dust contributions and the NO_3^- and SO_4^{2-} concentrations were derived from anthropogenic sources. Furthermore, NH_4^+ was derived from gaseous NH_3 scavenging. The isotopic composition of weekly precipitation ranged from −1.9 to −23.2‰ in $\delta^{18}O$, and from −0.8 to −174‰ in δ^2H, with depleted values characterizing the central part of the monsoon period. The chemical composition of the stream water was dominated by calcite and/or gypsum dissolution. However, the isotopic composition of the stream water did not fully reflect the composition of the monsoon precipitation, which suggested that other water sources contributed to the stream flow.
Precipitation contents for all ions were the lowest ones among those measured in high elevation sites around the world. During the monsoon periods the depositions were not substantially influenced by anthropogenic inputs, while in pre- and post-monsoon seasons the Himalayas could not represent an effective barrier for airborne pollution. In the late monsoon phase, the increase of ionic contents in precipitation could also be due to a change in the moisture source. The calculated atmospheric N load (0.30 kg ha^{-1} y^{-1}) was considerably lower than the levels that were measured in other high-altitude environments. Nevertheless, the NO_3^- concentrations in the surface waters (from 2 to 17 μeq L^{-1}) were greater than expected based on the low N inputs from wet deposition.

1. Introduction

Located between the Tibetan Plateau and Indian subcontinent, the high Himalayan region represents a unique ecosystem that hosts the highest peaks of the world and the sources of many large Asian rivers, including the Yangtze, Indus and Ganges. The region is one of the 34 world biodiversity hotspots, to which 50% of the world's floristic diversity is restricted (Mittermeier et al., 2005). Glaciers in this area serve as "water towers" in the regional hydrological cycle and provide significant amounts of melt water (Immerzeel et al., 2010). In particular, the south slope of Mt. Everest is one of the most heavily glaciated regions in the Himalayas (Scherler et al., 2011) and contains the highest glaciers in the world (Salerno et al., 2012). Perceived as one of the most uncontaminated places of the Earth, the Himalayas host an extremely fragile ecosystem, with a low resistance and resilience. These features make this region sensitive to any environmental change.

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The effects of global warming on the hydrological cycle are of concern for more than a billion people who inhabit the basins of the main Asian rivers. Reductions and modifications in the precipitation regime have caused the Himalayan glaciers to retreat. Although this retreat is well documented, the variability in the observed regional changes is large (Benn et al., 2012 and references therein; Kaab et al., 2012).

In addition to climate change, atmospheric pollution threatens the Himalayan region, which is located between China and India, the two largest contributors to Asian emissions, as shown in the recently updated Regional Emission Inventory in Asia (Kurokawa et al., 2013). For example, NO_x emissions in India increased by 56% from 2000 to 2008. In this case, road transport emissions were the largest contributor and doubled between 2000 and 2008. The majority of SO_2 emissions in Asia result from China, with emission increases of 54–62% from 2000 to 2008, followed by India at 15–18% between 2000 and 2008 (Kurokawa et al., 2013).

Aerosol measurements in South and East Asia over the past decade have shown that the atmospheric particulate matter (PM10) concentrations and light-absorbing components (iron oxides and black carbon) have reached elevated levels over large regions (Ramanathan et al., 2007; Verma et al., 2007). Recently, attention has been devoted to the so-called atmospheric brown clouds (ABCs). These clouds are wide polluted tropospheric layers characterized by a brownish color that results from the absorption and scattering of solar radiation by black carbon, fly ash, soil dust particles, and nitrogen dioxide gas (Ramanathan et al., 2007; Ramanathan and Carmichael, 2008). Satellite observations show that an ABC is located over the Indo-Gangetic Plains, extending thousands of miles southward and over the north Indian Ocean. Although the Himalayan chain presently acts as a barrier, recent measurements have indicated that the brown cloud over northern India could extend from 3000 to 5000 m a.s.l. (Ramanathan et al., 2007). Based on aerosol composition measurements at high elevation in the Khumbu valley, relatively high concentrations of O_3, black carbon, and aerosols were recently identified during the winter and spring. These concentrations suggest that the southern side of the high Himalayas is affected by the transportation of contaminants which constitute the ABC (Decesari et al., 2010; Marinoni et al., 2010; Bonasoni et al., 2010).

While important progress has been made recently regarding air quality knowledge in the high Himalayas, few data are currently available regarding dry and wet depositions, which are the processes by which airborne contaminants are delivered to water and the terrestrial surface. Most studies have focused on the Tibetan Plateau (Zhang et al., 2003; Li et al., 2007; Xu et al., 2009), where the atmospheric background concentrations are dominated by desert dust. However, existing data for the southern slopes of eastern Himalaya (mainly based on snow and/or ice core observations) have indicated dominant contributions by the monsoon air mass during the monsoon season (Valsecchi et al., 1999; Marinoni et al., 2001; Shrestha et al., 2002).

The quantification of depositional fluxes is important for studying biogeochemical cycles, particularly nitrogen (N) cycling, which has been dramatically altered by increasing anthropogenic emissions during the agricultural and industrial revolutions. Consequently, the deposition of N increased to levels that were one order of magnitude greater than during preindustrial times in North Europe and North America (Galloway et al., 2004). Results from a number of studies have suggested that high elevation ecosystems are more susceptible to ecological impacts from N deposition than forest or grassland ecosystems at lower altitudes (Elser et al., 2009). In these areas, small increases in inorganic N deposition could cause a shift from conditions of N limitation to "N saturation", where the availability of inorganic N exceeds the N assimilation capacity of biological processes (Aber et al., 1998). Knowledge regarding the impacts of N deposition on various ecosystems comes almost entirely from investigations that occurred in temperate and relatively anthropized zones in the northwestern hemisphere. Holtgrieve et al. (2011) demonstrated the influences of anthropogenic N deposition in pristine ecosystems after preindustrial times by measuring the total N isotopic compositions in dated sediments from remote lakes in the northern hemisphere. Because N deposition occurs at a global scale, there is an urgent need to improve our understanding, which could be accomplished by identifying the natural N range in undisturbed ecosystems that will be threatened by increasing N emissions in the future, especially for developed countries (Galloway et al., 2004).

Thus, the concentrations and fluxes of the main chemical species were monitored based on their wet deposition at one of the highest altitude research centers (5050 m a.s.l.) in the world, the Pyramid International Laboratory (PIL) beneath Mt. Everest in Khumbu valley. Between 1991 and 1993, we conducted a sampling campaign to characterize different types of atmospheric deposition at the same site (Valsecchi et al., 1999). Here, bulk and wet deposition samples were collected and aerosols have been monitored since 2006 (Bonasoni et al., 2010). We repeated these measurements with a new campaign on wet deposition that occurred from June to October in 2007–2008. This campaign integrated the spectrum of analyzed variables with the addition of $\delta^{18}O$ and $\delta^{2}H$, which provide fundamental information for tracing the origin of contaminants in atmospheric depositions, especially when coupled to the reconstruction of air mass trajectories.

The aim of this study was to improve knowledge of the physical, chemical and transport processes that are responsible for the deposition composition in the Everest region. In addition, we aimed to integrate previous aerosol composition and distribution research results. Furthermore, in the same period and in the same areas, we performed chemical and isotopic characterizations of surface waters from small rivulets to river stretches at an altitude of 4200 to 5300 m a.s.l. In this case, particular attention was given to N compounds and stable isotopes. The temporal variation of nitrogen species with the isotopic and geochemical tracer variations was used to summarize the biological and physical processes at the catchment level. The nitrogen atmospheric deposition was related to the N concentrations that were measured in the surface waters to obtain insights regarding the nitrogen dynamics in one of the most remote sites of the world.

2. Materials and methods

2.1. Study area

Research was conducted on the southern slope of Mt. Everest in the northeast sector of Sagarmatha National Park (SNP) (central south Himalaya) in the Khumbu valley (Fig. 1a and b). The SNP is the highest protected mountain area in the world, with over 30 000 tourists in 2008 (Salerno et al., 2013). This area includes the upper catchment of the Dudh Koshi River Basin, which is part of the Koshi River Basin and one of the three largest river basins in Nepal, and the world's tallest peak, Mount Everest (8850 m a.s.l.). The land cover assessment of SNP (Bajracharya et al., 2010) indicates that approximately 70% of the area consists of bare rocks and soil that were eventually covered by snow, ice or glaciers. In the study area, vegetation covers less than 10% of soils. The following types of vegetation zones can be identified: i) the lower alpine zone occurs below the tree-line at 3800–4000 m a.s.l. and contains scrubs such as *Juniperus* spp., *Rhododendron anthopogon* and *Rhododendron lepidotum*; ii) the upper alpine zone occurs above 4500 m a.s.l. and contains dwarf shrubs (e.g., *Rhododendron nivale*) and herbaceous vegetation; and iii) the subnival zone occurs from 5500 m to 6000 m a.s.l. and contains "cushion plants" (e.g., *Arenaria polytrichoides*) (UNEP/WCMC, 2008).

This area lies in a complex transition zone between Nepal and Tibet, which represents the highest area of the Himalayan region. Here, a large-scale and low-angle fault called the South Tibetan detachment places un-metamorphosed Paleozoic sediments, which make up the numerous peaks that exceed 8000 m (e.g., Mount Everest and Lhotze), above high-grade gneisses and leucogranites. According to Searle et al. (2003), the Khumbu valley substratum is dominantly made up of crystalline rocks (i.e., sillimanite gneisses,