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Atmospheric wet deposition of sulfur and nitrogen in Jiuzhaigou National Nature Reserve, Sichuan Province, China

Xue Qiao [a], Weiyang Xiao [b], Daniel Jaffe [c], Sri Harsha Kota [d], Qi Ying [d], Ya Tang [a,*]

[a] Department of Environment, College of Architecture and Environment, Sichuan University, Chengdu 610065, China
[b] Jiuzhaigou Administration Bureau, Jiuzhaigou County 623407, Sichuan Province, China
[c] Department of Atmospheric Sciences, University of Washington, Seattle 98117, USA
[d] Zachry Department of Civil Engineering, Texas A&M University, College Station, TX 77843, USA

HIGHLIGHTS

- Annual wet deposition flux of SO_4^{2-} was 8.06 kg S ha^{-1}.
- Annual wet deposition flux of TIN was 2.68 kg N ha^{-1}.
- Wet deposition dominated annual total inputs of SO_4^{2-} and TIN into JNNR.
- Human sources dominated wet deposition fluxes of SO_4^{2-} and TIN in JNNR.
- Acid rain and elevated deposition of S and N would deteriorate ecosystems in JNNR.

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ABSTRACT

In the last two decades, remarkable ecological changes have been observed in Jiuzhaigou National Nature Reserve (JNNR). Some of these changes might be related to excessive deposition of sulfur (S) and nitrogen (N), but the relationship has not been quantified due to lack of monitoring data, particularly S and N deposition data. In this study, we investigated the concentrations, fluxes, and sources of S and N wet deposition in JNNR from April 2010 to May 2011. The results show that SO_4^{2-}, NO_3^-, and NH_4^+ concentrations in the wet deposition were 39.4–170.5, 6.2–34.8, and 0.2–61.2 μeq L^{-1}, with annual Volume-Weighted Mean (VWM) concentrations of 70.5, 12.7, and 13.4 μeq L^{-1}, respectively. Annual wet deposition fluxes of SO_4^{2-}, NO_3^-, and NH_4^+ were 8.06, 1.29, and 1.39 kg S(N) ha^{-1}, respectively, accounting for about 90% of annual atmospheric inputs of these species at the monitoring site. The results of Positive Matrix Factorization (PMF) analysis show that fossil fuel combustion, agriculture, and aged sea salt contributed to 99% and 83% of annual wet deposition fluxes of SO_4^{2-} and NO_3^-, respectively. Agriculture alone contributed to 89% of annual wet deposition flux of NH_4^+. Although wet deposition in JNNR was polluted by anthropogenic acids, the acidity was largely neutralized by the Ca^{2+} from crust and 81% of wet deposition samples had a pH higher than 6.00. However, acid rain mainly caused by SO_4^{2-} continued to occur in the wet season, when ambient alkaline dust concentration was lower. Since anthropogenic emissions have elevated S and N deposition and caused acid rain in JNNR, further studies are needed to better quantify the regional sources and ecological effects of S and N deposition for JNNR.

1. Introduction

Fossil fuel combustion and agricultural practices have increased NO_2, NH_3, and SO_2 emissions from North America, Europe, and Asia by more than a factor of ten in the 20th century (van Aardenne et al., 2001). As a result of the high emissions, the deposition fluxes of sulfur (S) and nitrogen (N) have increased significantly, and excessive deposition of S and N has caused detrimental effects on human health (Kampa and Castanas, 2008), infrastructures (Kucera and Fitz, 1995), forests (Bytnerowicz et al., 2007), crops (Cao, 1989), soil (Stevens et al.,

Abbreviations: S, Sulfur; N, Nitrogen; NPS, U.S. National Park Service; MEP, Ministry of Environmental Protection of China; EANET, Acid Deposition Monitoring Network in East Asia; JNNR, Jiuzhaigou National Nature Reserve; QTP, Qinghai–Tibetan Plateau; a.s.l, Above Sea Level; NTN, National Trend Network; NADP, U.S. National Atmospheric Deposition Program; VWM, Volume-Weighted Mean; NF, Neutralization Factor; PMF, Positive Matrix Factorization; EPA, U.S. Environmental Protection Agency; BGMEDSPC, Bureau of Geology and Mineral Exploration and Development of Sichuan Province, China; TSP, Total Suspended Particles; TIN, Total Inorganic Nitrogen; NTN, U.S. National Trend Network.

* Corresponding author.
E-mail address: tangya@scu.edu.cn (Y. Tang).

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2009), and aquatic ecosystems (Bergström and Jansson, 2006; Stoddard et al., 1999).

S and N deposition are of particular concern for protected areas, such as national parks and nature reserves, as critical loads of ecosystems, i.e. the maximum levels of pollutant exposure without significant detrimental effects on sensitive elements of the environment (Nilsson and Grennfelt, 1988), in these areas are usually low (Ellis et al., 2013; Sullivan et al., 2014). The ecological impacts of S and N deposition have been extensively studied for many protected areas in Europe and North America, and stringent legislations and regulations have been developed to preserve the natural resources in these regions (U.S. National Park Service (NPS), 2001). In China, the annual fluxes of S and N deposition are 12–160 kg S ha^{-1} (Larssen et al., 2006) and 2–117 kg N ha^{-1} (He et al., 2010; Li et al., 2012; Pan et al., 2012), respectively. These values are in the same ranges of the observations in Europe and North America in the 1980s when peak acid deposition occurred in the two continents (Larssen et al., 2006; Liu et al., 2013), and 10.6% of China's land is identified as acid rain affected zones (Ministry of Environment Protection of China (MEP), 2014). Although a number of studies have reported the effects of enhanced S and N deposition on China's ecosystems (Acid Deposition Monitoring Network in East Asia (EANET), 2012; Cao, 1989; Chen and Mulder, 2007; Fang et al., 2009; Larssen et al., 1999, 2006; Liu et al., 2011), there is still a paucity of observation for China's nature reserves, many of which are located in acid rain affected zones and/or in those regions with high deposition fluxes of S and N (MEP, 2014; Zhao et al., 2009; Fig. A1).

Close to the acid rain affected zone in southwestern China, Jiuzhaigou National Nature Reserve (JNNR), also a World Biosphere Reserve and UNESCO-designated World Natural Heritage Site, has experienced remarkable ecological changes in the last two decades, such as tree dieback, increased algal productivity, and tufa degradation (Fig. A2) (Gu et al., 2013). These changes may be partially caused by excessive inputs of S and N into the ecosystems through deposition or direct exposure to air pollutants. In a previous study, chemically resolved aerosol concentrations in JNNR were monitored (Qiao et al., 2014a), allowing estimations of S and N inputs through dry deposition for the period from April 2010 to May 2011. Bulk deposition, which is a mixture of dry and wet deposition collected in open areas without trees, was also measured for N and phosphorus from May 2011 to May 2012 (Qiao et al., 2014b). Although wet deposition has long been postulated to be a significant source of S and N inputs in the region, there is a lack of relevant observation. Thus, the main objectives of this study are: (1) monitoring the acidity and ionic composition of wet deposition, (2) determining the fluxes of S and N wet deposition, and (3) estimating the contributions of anthropogenic sources to S and N wet deposition.

2. Materials and methods

2.1. Study area

JNNR is located in a mountainous region in the eastern rim of Qinghai–Tibetan Plateau (QTP) (32.88°–33.33°N, 103.77°–104.08°E), encompassing an area of 650 km^2 and spanning from about 2000 to 4880 m above sea level (a.s.l.) (Fig. 1). JNNR is a headwater watershed, with precipitation as the sole water source. Annual precipitation is 539–771 mm, and 90% of precipitation falls during the rainy season (April to October) (Fig. A3). Approximately 1000 residents live in six villages within JNNR and three of these villages are located in the Rize, Zechawa, and Shuzhang Valleys (Fig. 1b).

JNNR is one of the most popular tourist destinations in China, visited by 3.6 million tourists in 2012. To protect JNNR from local anthropogenic activities, a number of regulatory measures have been enforced (Gu et al., 2013). Farming and grazing have been banned since 2001 and logging has been barred since 1978. Electricity is used for household heating and cooking, and local biomass burning is expected to be limited. Shuttle buses are used to transport visitors between the park entrance and various vista points within the reserve along a 50 km route, located at the bottom of the Shuzheng, Rize, and Zechawa Valleys (Fig. 1b). JNNR opens to visitors every day from 0700 to 1800 local time, and overnight stays are not permitted. The wastes generated by tourists and local residents are carefully collected and transported out of the reserve. These make JNNR one of the best-managed nature reserves in China (Gu et al., 2013).

2.2. Sample collection and analysis

Weekly or bi-weekly wet deposition samples were collected from April 2010 to May 2011 at the Long Lake Meteorological Station (33.04°N, 103.93°E, 3100 m a.s.l.) (Fig. 1b), following the National Trends Network (NTN) Site Operation Manual (U.S. National Atmospheric Deposition Program (NADP), 1999). The sampling site was located

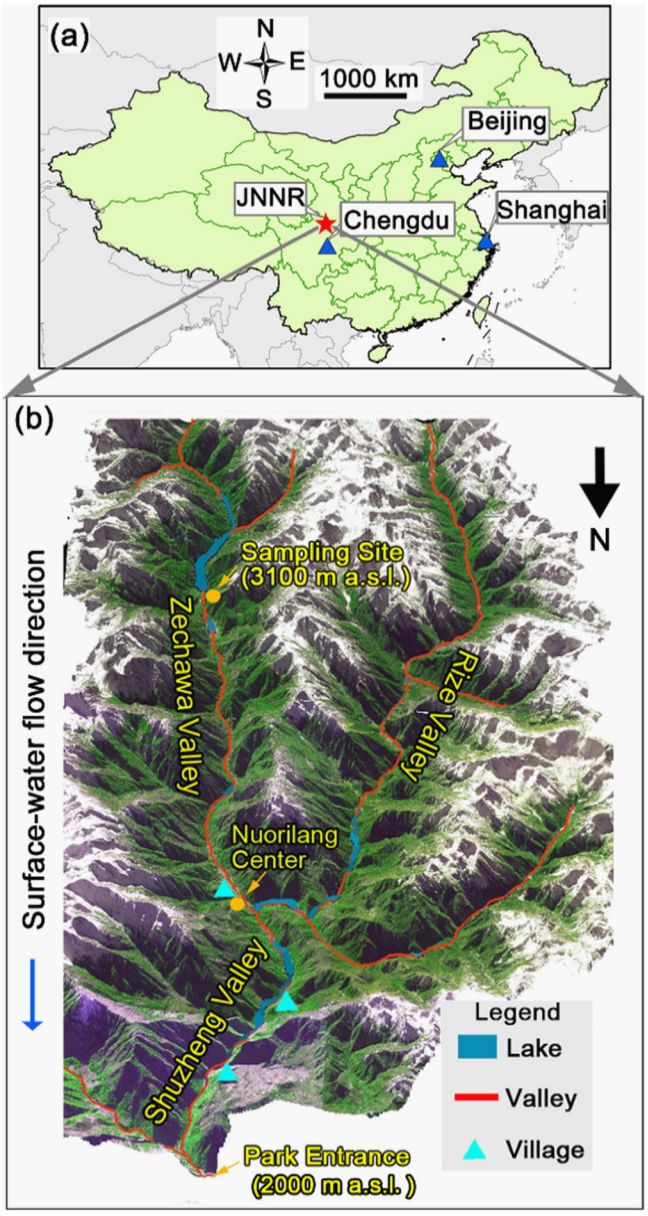

Fig. 1. Locations of JNNR, the sampling site, and the tourist areas. (a) Location of JNNR and (b) locations of the sampling site and the tourist areas (at the bottom of the Rize, Shuzheng, and Zechawa Valleys).