Science of the Total Environment 562 (2016) 724–731

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Short communication

Are climate warming and enhanced atmospheric deposition of sulfur and nitrogen threatening tufa landscapes in Jiuzhaigou National Nature Reserve, Sichuan, China?

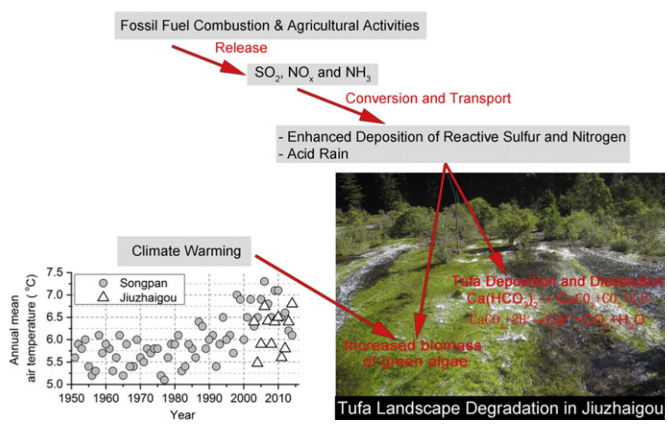
Xue Qiao [a], Jie Du [b,c], Stefano Lugli [d], Jinhai Ren [b], Weiyang Xiao [b], Pan Chen [c], Ya Tang [c,*]

[a] Institute of New Energy and Low-Carbon Technology, Sichuan University, Chengdu 610065, Sichuan Province, China
[b] Jiuzhaigou Administrative Bureau, Zhangzha Town, Jiuzhaigou County 623402, Sichuan Province, China
[c] Department of Environment, College of Architecture and Environment, Sichuan University, Chengdu 610065, Sichuan Province, China
[d] Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia, Via Campi 103, Modena 41125, Italy

HIGHLIGHTS

- Annual air temperature increased by 1.2 °C from 1951 to 2014 in the Jiuzhaigou region.
- Human emissions have enhanced sulfur (S) and nitrogen (N) deposition in Jiuzhaigou.
- Climate warming and enhanced N deposition would favor the growth of green algae.
- Enhanced S and N deposition would reduce tufa deposition and cause tufa dissolution.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 February 2016
Received in revised form 4 April 2016
Accepted 10 April 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
Travertine
Climate change
Nutrient enrichment

ABSTRACT

Massive deposition of calcium carbonate in ambient temperature waters (tufa) can form magnificent tufa landscapes, many of which are designated as protected areas. However, tufa landscapes in many areas are threatened by both local anthropogenic activities and climate change. This study, for the first time, posed the question whether the tufa landscape degradation (characterized by tufa degradation and increased biomass of green algae) in Jiuzhaigou National Nature Reserve of China is partially caused by regional air pollution and climate warming. The results indicate that wet deposition (including rain and snow) polluted by anthropogenic SO_2, NO_x, and NH_3 emissions dissolves exposed tufa and may considerably reduce tufa deposition rate and even cause tufa dissolution within shallow waters. These effects of wet deposition on tufa enhanced as pH of wet deposition decreased from 8.01 to 5.06. Annual Volume Weighted Mean concentration of reactive nitrogen (including NH_4^+ and NO_3^-) in wet deposition (26.1 μmol L^{-1}) was 1.8 times of the corresponding value of runoff (14.8 μmol L^{-1}) and exceeded China's national standard of total nitrogen in runoff for nature reserves

Abbreviations: a.s.l., above sea level; $CaCO_3$, calcium carbonate; $Ca(HCO_3)_2$, calcium bicarbonate; CO_2, carbon dioxide; DOC, dissolved organic carbon; IC, ion chromatograph; IPCC, Intergovernmental Panel on Climate Change; LLMS, Long Lake Meteorological Station; MEPC, Ministry of Environmental Protection of China; NH_4^+, ammonia ion; NO_3^-, nitrate ion; SIc, saturation index of calcite; SNMS, Songpan National Meteorological Station; SO_4^{2-}, Sulfate ion; TIN, total inorganic nitrogen; USGS, United States Geology Survey; VWM, volume weighted mean.

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

http://dx.doi.org/10.1016/j.scitotenv.2016.04.073

Acid rain
National park

(14.3 μmol L^{-1}), indicating a direct nitrogen fertilization effect of wet deposition on green algae. As water temperature is the major limiting factor of algal growth in Jiuzhaigou and temperature in the top layer (0–5 cm) of runoff (depth < 1 m, no canopy coverage of trees and shrubs) was significantly higher at the sites with increased biomass of green algae ($p < 0.05$), climate warming in this region would favor algal growth. In sum, this study suggests that climate warming and enhanced sulfur and nitrogen deposition have contributed to the current degradation of tufa landscape in Jiuzhaigou, but in order to quantify the contributions, further studies are needed, as many other anthropogenic and natural processes also influence tufa landscape evolution.

1. Introduction

Tufa is the product of calcium carbonate ($CaCO_3$) deposition in ambient temperature waters, mainly presenting as calcite and typically containing the remains of micro- and macrophytes, invertebrates, and bacteria (Ford and Pedley, 1996). Travertine is usually used as an alternative term for tufa (Pentecost, 2005). As for the formation of tufa, it is believed that groundwater, which first gains high carbon dioxide (CO_2) concentrations from soil profiles (Yan et al., 2013) and/or possibly from deep sources like the upper mantle (Yoshimura et al., 2004), dissolves carbonate bedrocks to form a solution rich in calcium bicarbonate ($Ca(HCO_3)_2$). After traveling for some distance and then emerging at springs, dissolved CO_2 is lost from the solution on contact with the atmosphere which has a CO_2 concentration lower than that in equilibrium with the $Ca(HCO_3)_2$-rich solution (Pentecost, 2005). Due to CO_2 loss, the solution becomes supersaturated with respect to calcite and begins to produce calcite (Eq. (1)). Tufa may spread across the earth's surface for meters to kilometers, building three dimensional landforms that can be generally categorized into two fundamental depositional morphotypes (Ford and Pedley, 1996). The first is called “fluvial barrage model” (Pedley, 1990) or “barrage travertine/tufa system” (Violante et al., 1994), which involves damming of a river, by means of one or more transverse oriented tufa barrages (Ford and Pedley, 1996; Fig. S1). The second is “perched springline model” (Pedley, 1990) or “slope travertine/tufa system” (Violante et al., 1994), which involves the formation of a valley-side-sited, wedge-shaped sedimentary body (Ford and Pedley, 1996; Fig. S2). A detailed review of tufa and travertine deposits of the world can be found in Ford and Pedley (1996).

$$Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow + CO_2 \uparrow + H_2O \quad (1)$$

Many magnificent tufa landscapes are designated as protected areas and are also popular tourist destinations (Ford and Pedley, 1996; Pentecost, 2010). Jiuzhaigou National Nature Reserve (Jiuzhaigou, hereafter) in China, Plitvice National Park in Croatia, Havasupai Canyon in the U.S., and Dunns River Falls in Jamaica are examples that are famous for tufa landscapes. Unfortunately, tufa landscape degradation (e.g., increased biomass of green algae associated with nutrient enrichment, tufa erosion and dissolution, a reduced deposition rate of tufa, and tufa waterfall collapse) has been reported for many protected areas and its relationship with local anthropogenic activities has been investigated (Goudie et al., 1993; Zhou, 1998; Zhang et al., 2012). Trampling by humans and livestock causes physical damage to tufa so now they are protected by boardwalks and fences (Pentecost, 2010). Discharge change caused by climate change and anthropogenic activities led to reduced tufa deposition and/or tufa loss (Goudie et al., 1993). Water chemistry change caused by deforestation, fertilizers, and wastewater would also affect tufa deposition and even cause tufa loss (Thorpe, 1981; Goudie et al., 1993; Zhou, 1998). Although a number of protective measures have been implemented, degradation of tufa landscape continues in some protected areas (Zhang et al., 2012; Gu et al., 2013). As tufa landscapes are usually formed in shallow waters and some of which would be seasonally dry, they might prove sensitive to atmospheric environmental changes. It is evident that anthropogenic activities have led to climate warming (Intergovernmental Panel on Climate Change (IPCC), 2013) and enhanced atmospheric deposition of reactive sulfur and nitrogen (including sulfate ion (SO_4^{2-}), nitrate ion (NO_3^-), and ammonia ion (NH_4^+)) throughout the world (Vet et al., 2014). Climate warming influences water temperature, which is regarded as the major limiting factor of algal growth in many alpine, subalpine, and boreal regions (Williamson et al., 2008; Schindler, 2009). Reactive nitrogen is an important nutrient for the growth of hydrophytes like green algae, particularly in pristine waters, which are usually low in nitrogen concentrations (Baron et al., 2000; Williamson et al., 2008; Hessen et al., 2009). SO_4^{2-} and NO_3^- are the main acids that cause acid rain and it is well known that acid rain can accelerate chemical weathering of carbonate rocks. However, to the best of the authors' knowledge, the contributions of climate warming and enhanced deposition of reactive sulfur and nitrogen to tufa landscape degradation have not been explored.

This paper reports a case study in Jiuzhaigou (32.88°–33.33° N, 103.77°–104.08° E, 2000–4880 m above sea level (a.s.l.)), a headwater watershed located in a subalpine to alpine region of Sichuan Province, China (Fig. 1a). Jiuzhaigou has a reserve area of 643 km^2 and additionally has a buffer zone of 598 km^2. Over 80% of Jiuzhaigou's land is covered by vegetation, including 65% covered by pine forests and mixed broadleaf and coniferous forests and 15% covered by shrubs and meadows (Liu et al., 2007; Bossard et al., 2015). Tufa landscapes are distributed in the bottom of Rize and Shuzheng valleys (Fig. 1b), having a total area of 2.4 km^2 and consisting of 17 groups of waterfalls, 16 cascades/shoals, 110 lakes/pools, and numerous springs. Due to logging in 1966–1978 and poor management of tourism development in the 1980s and early 1990s, human activities caused remarkable adverse effects on tufa landscapes then, such as increased lake sedimentation, water pollution, and physical damage to tufa (Zhou, 1998; Gu et al., 2013; Li et al., 2014; Liang et al., 2014). In order to protect the tufa landscapes, logging was banned in 1978 and a number of regulations/infrastructure were implemented/built in the late 1990s and early 2000s. Farming and grazing have been completely barred since 2001. Wastewater and solid wastes are collected through a sanitary system and transported out of the reserve. Nuorilang Center is the sole restaurant and tourists are strict to visit the reserve approximately between 7:00 am and 6:00 pm. Tourist vehicles are not allowed in the reserve staring from 2002; instead, a system of tour buses and boardwalks are now used by tourists to visit the main tourist region located in the bottom of Rize, Shuzheng, and Zezhawa valleys (Fig. 1b).

Although great efforts have been made to protect Jiuzhaigou's tufa landscapes, the degradation of tufa landscape, characterized by increased biomass of green algae and tufa erosion and dissolution (Fig. S3), continues and is occurring in parallel with climate warming (Fig. 2) and elevated atmospheric deposition of reactive sulfur and nitrogen, which includes acid rain (pH < 5.60) (Qiao et al., 2015a). Specifically, annual mean air temperature increased by 0.3 °C in Jiuzhaigou from 2003 to 2014 and by 1.2 °C from 1951 to 2014 at the Songpan National Meteorological Station (SNMS), which is about 140 km from Jiuzhaigou (Fig. 2). Acid rain was observed having SO_4^{2-} as the major source of acidity and over 90% of the annual wet deposition fluxes of reactive sulfur and nitrogen were from anthropogenic sources (Qiao et al., 2015a). From June to August 2010 (accounting for 30% and 40% of annual deposition fluxes of reactive sulfur and nitrogen, respectively), 93%,