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,1]

[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

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

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.

[1] Corresponding author, tangya@scu.edu.cn

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 (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.

Keywords: travertine, climate change, nutrient enrichment, acid rain, national park

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 morphptypes (Ford and Pedley, 1996). The first is called "fluvial barrage model" (Pedley, 1990) or "barrage travertine/tufa system" (Violance et al., 1994), which involves damming of a river, by means of one or more transverse oriented tufa barrages (Ford and Pedley, 1996; Figure S1). The second is "perched springline model" (Pedley, 1990) or "slope travertine/tufa system" (Violance et al., 1994), which involves the formation of a valley-side-sited, wedge-shaped sedimentary body (Ford and Pedley, 1996; Figure S2). A detailed review of tufa and travertine deposits of the world can be found in Ford and Pedley (1996).

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

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 et al., 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 (32.88º-33.33º N, 103.77º-104.08º E, 2000-4880 m above sea level (a.s.l.)), a headwater watershed located in a subalpine to alpine region of Sichuan Province, China (Figure 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 (Lin et al., 2006; Liu et al., 2007; Bossard et al., 2015). Tufa landscapes are distributed in the bottom of Rize and Shuzheng valleys (Figure 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 (Figure 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 (Figure S3), continues and is occurring in parallel with climate warming (Figure 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 0.3ºC in Jiuzhaigou from 2003 to 2014 and by 1.2ºC from 1951 to 2014 at the Songpan National Meteorological Station (SNMS), which is about 140 km from Jiuzhaigou (Figure 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%, 98%, and 69% of the deposition fluxes of SO_4^{2-}, NO_3^-, and NH_4^+ were from inter-regional

transport of air pollutants, respectively, rather than from local emissions (Qiao et al., 2015b). Therefore, the main objective of this study is to understand whether these observed climate warming and enhanced deposition of reactive sulfur and nitrogen actually have contributed to the current degradation of tufa landscape in Jiuzhaigou.

2. Methods and materials

2.1. Study area

Human history in the reserve dates back to at least 2,000 yr BP (Henck et al., 2010) and can be approximately divided into four periods (Urgenson et al., 2014): (1) swidden agriculture (before early 1950s), (2) collective agriculture (1950s-1970s) combined with intensive logging (1966-1978), (3) modified family-based agriculture (1970s-1999) and protected area establishment (1978), and (4) tourism development (1984-present) and implementation of reforestation programs (1999-present). In 2015, over 5 million tourists visited the reserve and about 1,300 residents inhabit in four villages, three of which are located in the main tourist region (Figure 1b). Natural gas and electricity are now widely used for household cooking and heating.

Climately, Jiuzhaigou lies in a transitional region from the humid Sichuan Basin to the semiarid Tibetan Plateau (Urgenson et al., 2014). At the Nuorilang Center, monthly air temperature was highest in July (~18ºC) and lowest in January (~-4ºC). Annual precipitation was 539-771 mm, with over 80% falls during the wet season (approximately from April to October). Precipitation is the sole water source of the watershed. A one-year monitoring campaign from April 2010 to May 2011 collected 36 weekly to biweekly wet deposition samples (including rain and snow) at the Long Lake Meteorological Station (LLMS) and found that pH of wet deposition was 5.06-8.01, with about 10% of samples having a pH less than 5.60 (Qiao et al., 2015a). Annual Volume Weighted Mean (VWM) concentrations of Mg^{2+}, Ca^{2+}, SO_4^{2-}, K^+, Na^+, F^-, Cl^-, NH_4^+, NO_3^-, and TIN (i.e., total inorganic nitrogen, including NH_4^+ and NO_3^- here) were 41.1, 149.8, 70.5, 21.2, 38.0, 21.0, 37.2, 13.4, 12.7, and

153 26.1 μmol L^{-1}, respectively (Table 1; Qiao et al., 2015a).

154 In response to the seasonal changes of precipitation, runoff level was highest in October
155 and lowest in April. The runoff in the bottom of Rize and Shuzheng valleys generally flows
156 from south to north and interspersed with tufa dams and lakes (Florsheim et al., 2013).
157 Zezhawa Valley lacks surface flow and tufa but contains three lakes and a small pool, water
158 of which four leaks to Rize and Shuzheng valleys (Gan, 2007). Alkalinity, ionic
159 concentrations, pH, and temperature of runoff were monitored at 11 sites in the dry and wet
160 seasons (Qiao, 2012; Figure 1b) during the one-year wet deposition monitoring campaign of
161 Qiao et al. (2015a). The results show that runoff at the 11 sites was alkaline (pH: 7.77-8.60;
162 alkalinity: 2413-4143 μmol L^{-1}) and had mean Mg^{2+}, Ca^{2+}, SO_4^{2-}, K^+, Na^+, F^-, Cl^-, NH_4^+,
163 NO_3^-, and TIN concentrations of 537.6, 1545, 201.7, 16.1, 59.1, 35.8, 24.7, 0.9, 13.9, and
164 14.8 μmol L^{-1}, respectively (Table 1).

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166 2.2. Impacts of enhanced acid deposition on tufa

167 Acid rain mainly caused by anthropogenic SO_4^{2-} was observed in Jiuzhaigou and NO_3^-
168 has also been identified as an acidity source (Qiao et al., 2015a). In order to understand
169 whether enhanced deposition of these two acids is harming tufa landscapes in Jiuzhaigou,
170 we first compared the Saturation Index of Calcite (SIc) between wet deposition and runoff.
171 Water with an SIc less/larger than zero is prone to dissolve/precipitate calcite. SIc of each
172 sample was calculated using the PHREEQC model (version 3) developed by the United
173 States Geology Survey (USGS) (Parkhurst and Appelo, 1999) and using the WATEQ4F
174 thermodynamic database (Ball and Nordstrom, 2001) distributed with the PHREEQC model.
175 This model has been widely used to calculate SIc of water samples in tufa-related studies
176 (Leybourne et al., 2009; Vázquez-Urbez et al., 2010; Arenas et al., 2015). To run the
177 PHREEQC model, we used the data of each sample of runoff and wet deposition (including
178 temperature, pH, conductivity, alkalinity, and Mg^{2+}, Ca^{2+}, SO_4^{2-}, K^+, Na^+, F^-, Cl^-, NH_4^+, and
179 NO_3^- concentrations) measured in Qiao et al. (2012) and Qiao et al. (2015a), respectively.
180 Alkalinity of wet deposition was not directly measured but it was believed mostly

contributed by HCO_3^- in Jiuzhaigou (Qiao et al., 2015a), thus Eq. (2) was used to estimate alkalinity of the wet deposition samples that had a pH higher than 7.00 in this study. Alkalinity was considered to be zero in the wet deposition samples that had a pH less than 7.00.

Additionally, as tufa landscapes in Jiuzhaigou are mostly formed in shallow waters and some tufa landscapes would be completely/partially dry during the dry season and at the beginning of wet season, we also used the PHREEQC model and the WATEQ4F thermodynamic database to calculate SIc values in the water mixed by runoff and wet deposition at a variety of volume ratios. The volume mixing ratios of runoff (V_{runoff}) to wet deposition ($V_{wet\ deposition}$) are 1:0, 1:0.01, 1:0.05, 1:0.1, 1:1, 1:2, 1:5, and 0:1. As runoff at the 11 sites was monitored in August 2010 and April 2011 (Qiao et al., 2012; Figure 1b), the monthly pH (calculated by using monthly VWM H^+ concentrations), temperature, and VWM alkalinity and ionic concentrations of wet deposition in these two months were used in calculating SIc for the water mixed by runoff and wet deposition.

$$\text{Alkalinity or } [HCO_3^-] = ([K^+] + 2 \times [Ca^{2+}] + [Na^+] + 2 \times [Mg^{2+}] + [NH_4^+]) - (2 \times [SO_4^{2-}] + [NO_3^-] + [Cl^-] + [F^-])$$

$$\text{pH} > 7.00 \qquad (2)$$

Where [X] is the concentration of a given ion of wet deposition in μmol L^{-1}.

2.3. Impacts of elevated nitrogen deposition and climate warming on green algae

In order to understand if enhanced deposition of reactive nitrogen has contributed to the current increased biomass of green algae, NO_3^-, NH_4^+, and TIN concentrations were compared between wet deposition and runoff. The data of the weekly to biweekly wet deposition samples collected during April 2010 to May 2011 were derived from Qiao et al. (2015a). The data of runoff measured in August 2010 and April 2011 at 11 sites was derived from Qiao (2012). The results of Kolmogorov-Smirnov Test show that all the datasets

follow a normal distribution, except for the NH_4^+ dataset of runoff. Thus, T-Test was used to compare NO_3^- and TIN concentrations between wet deposition and runoff, while Mann-Whitney U Test was used to compare the two datasets of NH_4^+. All the statistical tests mentioned above were carried out by using IBM SPSS 19.0. The average TIN concentration of runoff and the annual VWM TIN of wet deposition were also compared to China's national standard of total nitrogen in runoff for nature reserves (Ministry of Environmental Protection of China (MEPC), 2002).

Increased biomass of green algae was observed only in the shallow waters with a low canopy coverage of trees and shrubs. Water temperature at these sites was more easily affected by air temperature and solar radiation, while green algae at these sites have a good access to light, which is also an important factor for their growth. Zhu (2007) found that water temperature is the major limiting factor to the growth of green algae in the Pearl Shoal and Five-flower Lake of Jiuzhaigou and green algae biomass increased as water temperature increased from 8 to 17ºC. In this study, we compared temperature in the top layer (0-5 cm) of waters, which had a water depth approximately less than 1 m and no canopy coverage of trees and shrubs. Water temperature was measured at 80 sites, including 48, 12, 9, and 11 sites located in tufa dams/cascades/shoals, lakes/pools, swamps, and rivers, respectively. At the sites of lakes, pools, and rivers, temperature was measured at the rims, where water was shallow. Water temperature was measured by using a pH meter equipped with a temperature sensor (Milwaukee SM102) between 10:00 am and 15:00 pm on two summer days (25-26th June, 2011). At each site, water temperature was measured at five to eight points with 0.5-1.0 m between each two points and the average temperature was used as the temperature of the site. After measurements, water temperature was then compared between the sites with increased biomass of green algae (54 sites) and that with low biomass of green algae (26 sites) by using T-Test, as the two datasets both follow a normal distribution according to the results of Kolmogorov-Smirnov Test.

3. Results

All the runoff samples were calcite saturated, having an SIc of 0.2-0.9; in contrast, all the wet deposition samples were calcite unsaturated, having an SIc of -6.4 to -1.2 (Figure 3). In general, the wet deposition and runoff samples having lower pH had lower SIc values (Figure 3). When the volume mixing ratio of $V_{wet\ deposition}$ to V_{runoff} is approximately larger than 1:1, the mixed water would have an SIc value less than 0 and a pH and a Ca^{2+} concentration in the ranges of 6.5-8.0 and 70-900 μmol L^{-1}, respectively (Figure 4).

The results of comparison of reactive nitrogen concentrations between runoff and wet deposition are shown in Table 1. NO_3^- concentrations were similar between wet deposition and runoff (p>0.05); in contrast, NH_4^+ and TIN concentrations were significantly higher in wet deposition (p<0.05). Annual VWM TIN concentrations of wet deposition also exceeded 14.3 μmol L^{-1} (Table 1), which is China's national standard of total nitrogen in runoff for nature reserves (MEPC, 2002).

Temperature in the top layer (0-5 cm) of runoff (depth<1 m and no canopy coverage of trees and shrubs) is shown in Figure 5. The temperature was significantly higher at the sites with increased biomass of green algae (8.1-17.7℃) than at the sites with low biomass of green algae (6.3-11.8℃) (p<0.05). The temperature generally decreased as elevation increased and increased biomass of green algae was found in the elevations approximately less than 2600 m a.s.l.

4. Discussion

4.1. Tufa deposition and dissolution

Basically, tufa deposition occurs given the following conditions (Goudie et al., 1993): (1) availability of enough dissolved particulate $CaCO_3$, (2) occurrence of turbulent degassing of CO_2 from water, and (3) presence of suitable substrates (e.g., mosses and tree roots and branches) which provide framework for tufa deposition. Some ions (e.g., PO_4^{3-}) and organic ligands inhibit tufa deposition through blocking active crystal-growth sites on calcite surface (Lebrón and Suárez, 1996; Lin and Singer, 2006). At a temperature of 25°C and an SIc of

0.95, calcite deposition is completely inhibited when dissolved organic carbon (DOC) concentration is greater than 300 μmol L^{-1}, and the particle size of calcite crystals would decrease from 100 μm to less than 2 μm as DOC concentration increases from 20 to 150 μmol L^{-1} (Lebrón and Suárez, 1996). Due to lack of free energy to create new surface areas, unavailability of reactive calcite to act as nucleation sites, and inhibition effect from some substances, tufa deposition mostly occurs in the waters that have a Ca^{2+} concentration larger than 2000 μmol L^{-1} (Pentecost, 2005) and is at least 5-10 times supersaturated with respect to calcite (SIc>0.7-1.0) (Chen et al., 2004).

In this study, we found that wet deposition was calcite unsaturated (SIc = -6.4 to -1.2) and the wet deposition samples with lower pH had lower values of SIc in general (Figure 3). This indicates that direct deposition of rain and snow onto exposed tufa would cause tufa dissolution and enhanced acid deposition would accelerate tufa dissolution. As shown in Figure 4, wet deposition can also considerably reduce SIc and tufa dissolution starts in the water mixed by wet deposition and runoff at an approximately mixing ratio of $V_{\text{wet deposition}}$ to V_{runoff} when larger than 1:1. These effects of wet deposition on tufa could be important in Jiuzhaigou, as a large areal portion of tufa landscapes are with shallow water (depth<10 cm) and would be seasonally dry. Furthermore, the Ca^{2+} concentrations and SIc of most runoff samples collected in Jiuzhaigou were lower than 2000 μmol L^{-1} and/or 0.7, respectively (Table 1; Qiao, 2012) and DOC concentrations in the runoff samples were 65-809 μmol L^{-1}, with an average concentration of 190 μmol L^{-1} (Chen, 2012). These DOC, Ca^{2+}, and SIc data of runoff also help to explain the current low deposition rate of tufa in Jiuzhaigou.

In addition to wet deposition, other processes may also contribute to the tufa degradation in Jiuzhaigou. Anthropogenic activities (such as deforestation, quarrying, fertilizer use, cattle manuring, and industry) and climate change could influence tufa deposition and loss through altering discharge, water chemistry, and watershed conditions (Goudie et al., 1993). Among the anthropogenic activities, deforestation is widespread and is believed to be the mechanism that most easily explains the widespread nature of the tufa decline in Europe (Goudie et al., 1993), while Jiuzhaigou is a forested watershed that has experienced deforestation by logging and tourism development. Deforestation may influence

289 tufa landscape through a variety of ways (Goudie et al., 1993), such as: (1) increased
290 discharge, enhancing channel erosion, (2) elevated runoff turbidity, reducing algal
291 productivity and increasing the asphyxiation and erosion of plants, (3) increased
292 podzolizationa and peat growth in watersheds, releasing more acids to runoff, (4) CO_2
293 reduction in soil caused by accelerated soil erosion and/or by reduced root respiration,
294 leading to lower $CaCO_3$ inputs into runoff, (5) nutrient release affecting plant productivity,
295 (6) less organic debris for tufa barrage development, and (7) flood plains become more
296 erodible, reducing tufa accumulation. Lake core evidence and runoff monitoring have
297 already proved that deforestation increased soil erosion, lake sedimentation, and nutrient
298 inputs to runoff in Jiuzhaigou (Li et al., 2014; Liang et al., 2014). All the above suggest that
299 deforestation and its associated land use change might be another important cause of tufa
300 degradation in Jiuzhaigou and a relevant systematic analysis is needed in future.

301

302 ## 4.2. Increased biomass of green algae

303 Algal growth is affected by light (Hill et al., 1988), temperature (Raven and Geider,
304 1988), and nutrients, particularly nitrogen and phosphorus (Hill et al., 1998; Lv et al., 2011).
305 In many alpine, subalpine, and boreal lakes, the growth of hydrophytes is temperature
306 limited and/or nitrogen limited, thus these lakes are believed to be sentinels to both climate
307 warming and elevated nitrogen deposition (Baron et al., 2000; Williamson et al., 2008;
308 Hessen et al., 2009; Schindler, 2009). In these water environments, algae are the
309 hydrophytes that most sensitive to climate warming and atmospheric nitrogen deposition
310 (Dixit et al., 1992; Wolfe et al., 2001; Rühland et al., 2003; Saros et al., 2003; Solovieva et
311 al., 2008; Elser et al., 2009; Winder et al., 2009).

312 Located in a subalpine to alpine region, Jiuzhaigou is experiencing climate warming
313 (Figure 2). Field observation found that the growth of green algae at the Pearl Shoal and
314 Five-Flower Lake of Jiuzhaigou was controlled by the factors in the following order:
315 temperature > dissolved oxygen > total nitrogen > total phosphorous > chemical oxygen
316 demand (Zhu, 2007). Using lab experiments, Zhu (2007) also found that biomass of green

algae increased as water temperature increased from 8 to 17°C. In this study, we found that increased biomass of green algae was more prone to occur in warmer, shallow waters with a good access to light and with an elevation less than 2600 m a.s.l. (Figure 5). These may suggest that climate warming would favor the growth of green algae and it might increase green algae biomass in higher elevations (>2600 m a.s.l.) in Jiuzhaigou.

The processes controlling nutrient loadings in runoff include (Feller, 2009): (1) atmospheric deposition and climate, (2) geological weathering, (3) terrestrial biological process, (4) physical-chemical reactions in the soil, and (5) physical, chemical, and biological process within aquatic ecosystems. Inter-regional transport of air pollutants from human emissions has elevated deposition of reactive nitrogen (Qiao et al., 2015a; Qiao et al., 2015b) and has a fertilization effect on green algae in Jiuzhaigou, as total nitrogen is the third most important factor controlling the growth of green algae in Jiuzhaigou (Zhu, 2007) and NH_4^+ and TIN concentrations were statistically higher in wet deposition than in runoff (Table 1). In addition to wet deposition, deforestation and its associated land use change may also be the causes of increased nitrogen in runoff. The runoff was low in nitrogen and phosphorus when tourism started in early 1980s (Zhou et al., 1986; Luo, 2000), but nitrogen and phosphorus in runoff started to increase as early as 1990s (Zhou, 1998; Cao, 1999), most likely due to wastewater from tourist activities (Zhou, 1998; Gaulke et al., 2010). Although a sanitary system is now used to collect wastewater and transport it out of the reserve, Wang (2006) still observed that tourist activities increased nitrogen inputs from land to runoff through the boardwalks and soils along the runoff. Furthermore, deforestation caused by previous logging and tourism development may still affect nutrient loadings in runoff through the (2-4) processes suggested by Feller (2009). In order to control nutrient loadings in runoff, future studies are needed to better quantify the contributions of different sources to nutrients in runoff, particularly for nitrogen and phosphorus.

5. Conclusion

In the last three decades, a remarkable degradation of the tufa landscapes, characterized

by increased biomass of green algae and tufa degradation, has been observed in Jiuzhaigou. This study examined whether these tufa landscape changes are partially associated with climate warming and the enhanced deposition of reactive sulfur and nitrogen caused by inter-regional transport of air pollutants. The results show that wet deposition (not necessarily being acid rain) in Jiuzhaigou was calcite unsaturated, suggesting that wet deposition would dissolve exposed tufa. Additionally, wet deposition may reduce tufa deposition or even cause tufa dissolution in shallow waters. These effects of wet deposition on tufa increased as pH of wet deposition decreased from 8.01 to 5.06. TIN concentrations were much higher in wet deposition (annual VWM = 26.1 μmol L^{-1}) than in runoff (mean = 14.8 μmol L^{-1}), suggesting a nitrogen fertilization of wet deposition on green algae. As water temperature was the major limiting factor of algal growth and temperature in the top layer (0-5 cm) of waters (depth<1 m, no canopy coverage of trees and shrubs) was significantly higher at the sites with increased algal biomass, climate warming in the region (+1.2^{o}C from 1951 to 2014) may favor the growth of green algae and increase green algae biomass in higher elevations (>2600 m a.s.l.). In summary, climate warming and enhanced deposition of reactive sulfur and nitrogen may have contributed to the current tufa landscape degradation in Jiuzhaigou, but future studies are needed to better quantify the contributions, as many other anthropogenic and natural processes also affect tufa landscape evolution, particularly the deforestation caused by previous logging and by tourism development.

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Figures

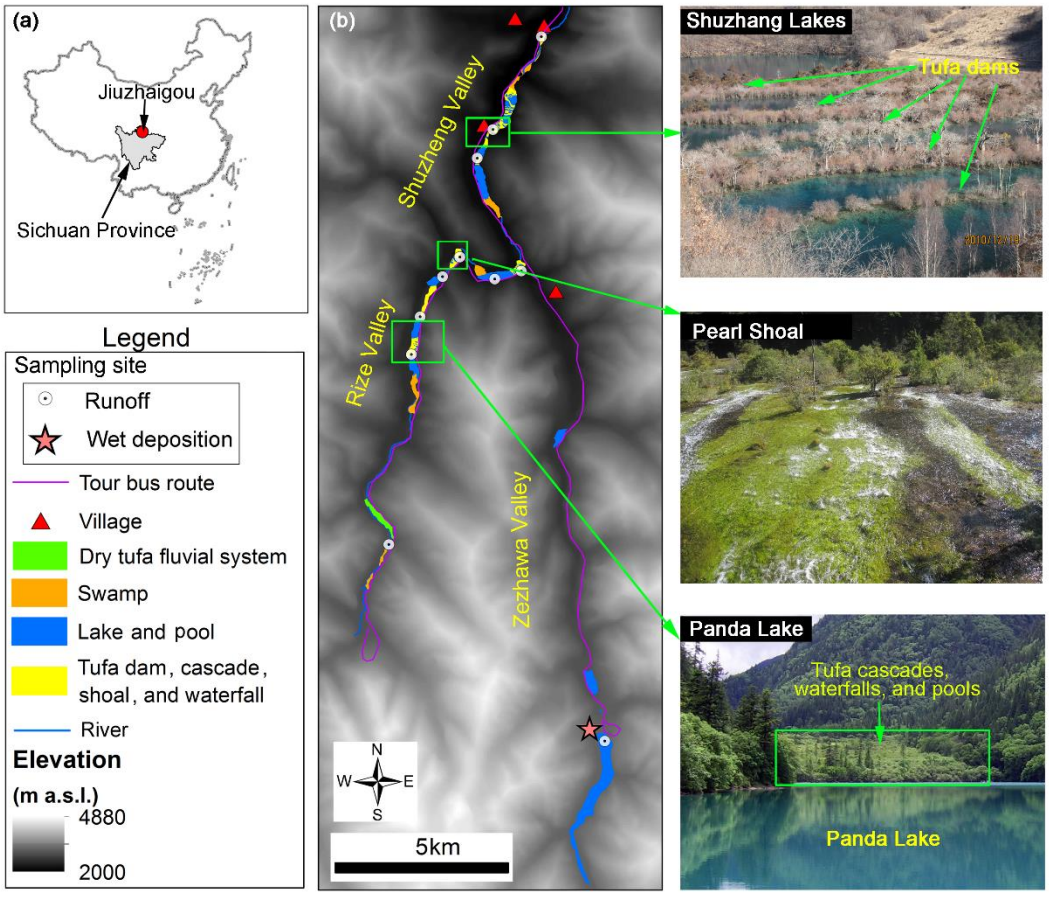


Figure 1. Maps illustrating (a) the location of Jiuzhaigou and (b) the locations of the sampling sites of runoff (Qiao, 2012) and wet deposition (Qiao et al., 2015a) in Jiuzhaigou.

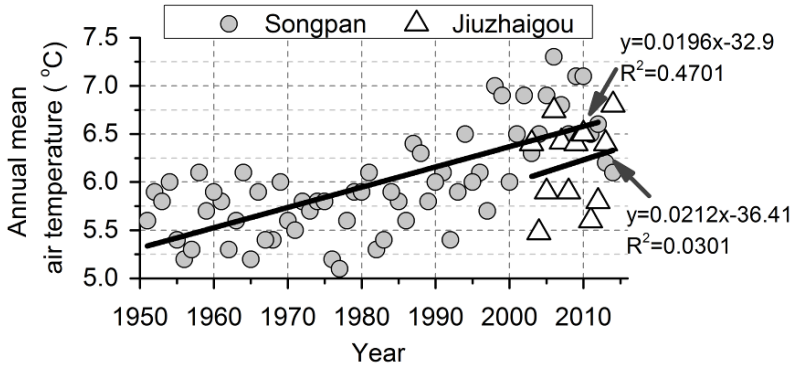
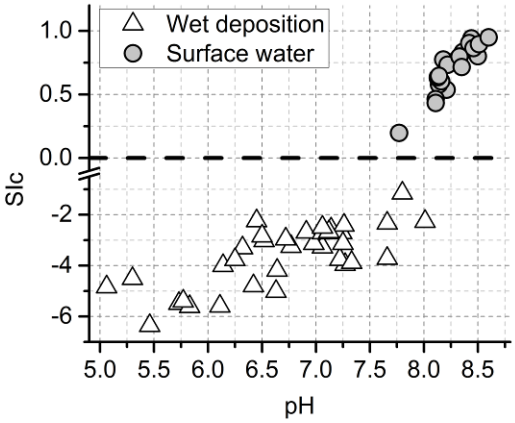


Figure 2. Annual mean air temperature at the Nuorilang Center in Jiuzhaigou from 2003 to 2014 and at the Songpan National Meteorological Station (SNMS) from 1951 to 2014. The data of SNMS were derived from the China Meteorological Data Sharing Service System (www. http://cdc.nmic.cn/home.do) and the data of Jiuzhaigou were from Jiuzhaigou Administrative Bureau.



542

543 Figure 3. Comparison of SIc and pH between runoff and wet deposition measured in
544 Jiuzhaigou during April 2010 and May 2011. The data of pH were from Qiao et al. (2015a)
545 and Qiao et al. (2012) and the SIc values were calculated in this study.

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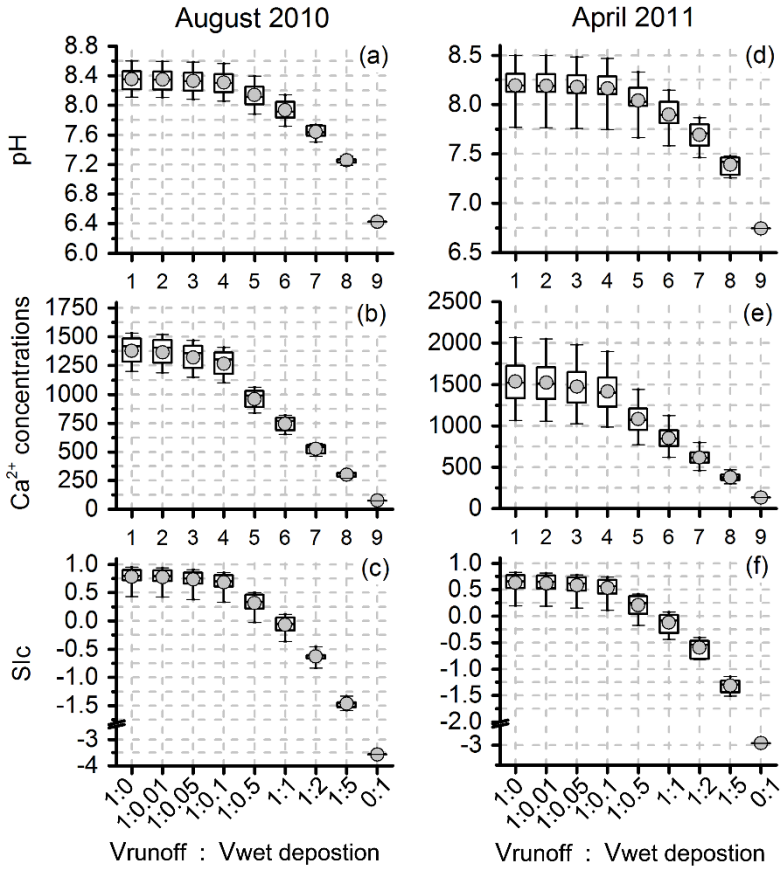

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549 Figure 4. Ca^{2+} concentrations (μmol L^{-1}), pH, and SIc in the solutions mixed by runoff and
550 wet deposition at volume ratios of V_{runoff} : $V_{wet\ depoisition}$ from 1:0 to 0:1 in Jiuzhaigou in
551 August 2010 and April 2011. The solutions having a ratio of 1:0 were runoff samples
552 collected at the 11 sites shown in Figure 1b. The solutions having a ratio of 0:1 were wet
553 deposition samples collected at the Long Lake Meteorological Station. The grey dots
554 represent mean values; the lower and upper limits of boxes represent 25% and 75%
555 percentiles, respectively; the lines in the boxes represent median values; and, the lower and
556 upper whisker lines represent the minimum and maximum values, respectively.

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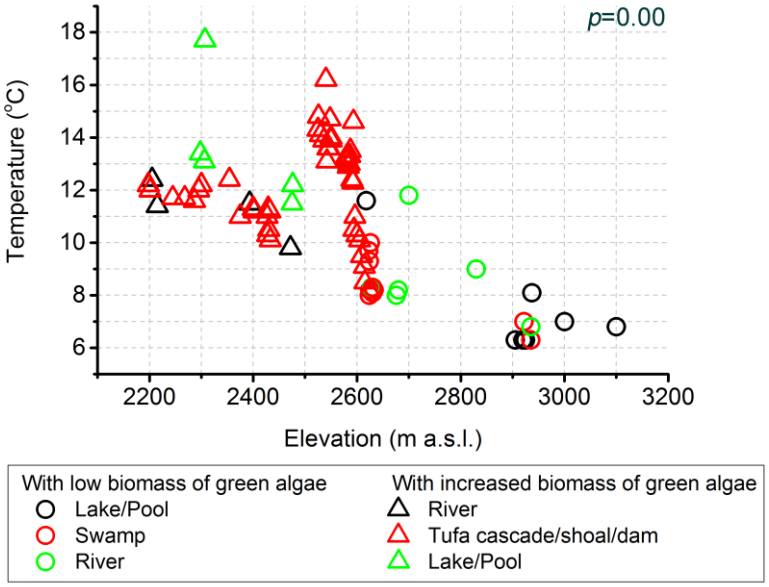


558

559 Figure 5. Temperature measured in the top layer (0-5 cm) of the runoff (depth<1 m and no
560 canopy coverage of trees and shrubs) at 80 sites in Jiuzhaigou. $p<0.05$: the temperature was
561 significantly higher at the sites with increased biomass of green algae than that with low
562 biomass of green algae.

563

564 # Table

565

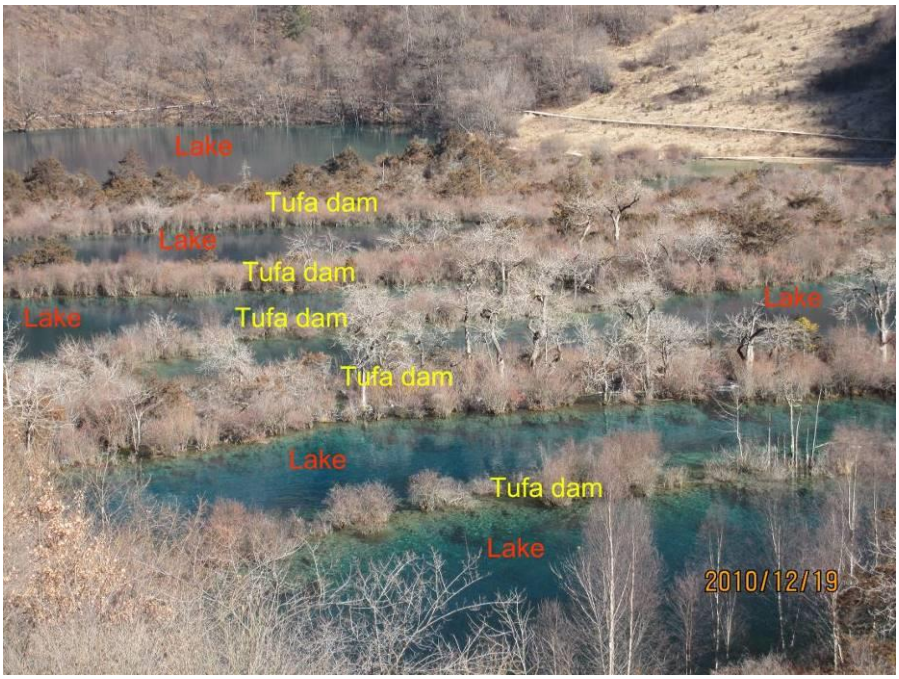
566 Table 1. The alkalinity, conductivity, ionic concentrations, and pH of runoff and wet
567 deposition samples collected in Jiuzhaigou. The unit of ionic concentrations and alkalinity
568 are in μmol L^{-1}. The unit of conductivity is in μS cm^{-1}.

Parameter	Runoff[a]			Wet deposition[b]			p[c]
	N	Range	Mean	N	Range	Annual VWM	
pH	21	7.77-8.60	8.27	36	5.06-8.01	5.95	0.00
Conductivity	21	276-431	342	36	3.43-155.3	12.67	0.00
Alkalinity	21	2413-4143	3418	36	0-857[d]	126[d]	0.00
Mg^{2+}	21	419.0-595.8	537.6	36	15.3-35.9	41.1	0.00
Ca^{2+}	21	1148-2182	1545	36	14.5-406.1	149.8	0.00
SO_4^{2-}	21	116.5-294.7	201.7	36	19.7-85.3	70.5	0.00
K^+	21	9.2-64.4	16.1	36	0.9-767.6	21.2	0.25
Na^+	21	36.6-68.0	59.1	36	7.7-304.3	38.0	0.00
F^-	21	24.8-40.9	35.8	36	11.5-59.2	21.0	0.00
Cl^-	21	17.9-30.8	24.7	36	6.8-1003.2	37.2	0.32
NH_4^+	21	0.0-6.1	0.9	36	0.2-61.2	13.4	0.00
NO_3^-	21	5.2-24.9	13.9	36	6.2-34.8	12.7	0.51
TIN	21	5.2-29.4	14.8	36	6.4-84.2	26.1	0.01

[a] Monitored in August 2010 and April 2011 in Qiao (2012); [b]Monitored from April 2010 to August 2011 in Qiao et al. (2015a); [c]This study, $p<0.05$: the difference between wet deposition and runoff is statistically significant at the 0.05 level; [d] Estimated by using Eq. 2 in this study; N: number of samples; VWM: Volume Weighted Mean; TIN, total inorganic nitrogen.

569 **Supplementary materials**

570



571

572 Figure S1. Shuzheng Lakes, a barrage tufa system in Jiuzhaigou, Sichuan Province, China.

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576 Figure S2. A slope tufa system in Huanglong National Nature Reserve, Sichuan Province,

577 China.

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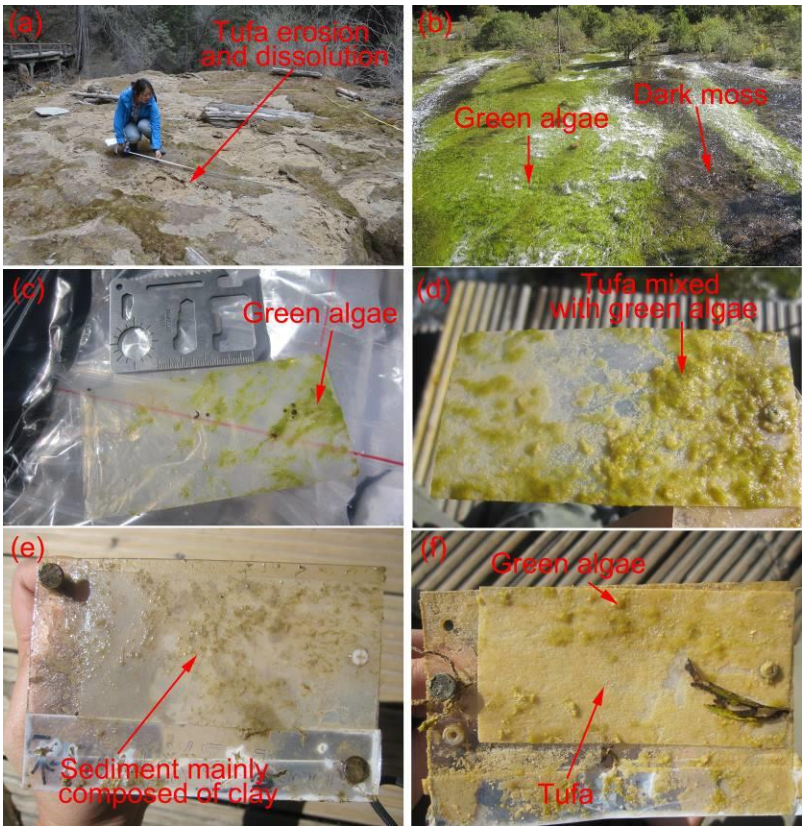

579

580 Figure S3. Tufa landscape degradation in Jiuzhaigou: (a) tufa erosion and dissolution in the
581 cascades downstream Panda Lake Waterfall, (b) increased biomass of green algae at Pearl
582 Shoal, (c-f) tufa deposition and the green algae collected on plastic plates which were placed
583 on tufa shoals/dams/cascades for one year from August 2010 to August 2011 at the sites
584 named (c) Shuzheng Lakes, (d) Pearl Shoal, (e) Rino Lake, and (f) Pearl Shoal Waterfall.

585