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

4  
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15  
16 **Abstract:** Massive deposition of calcium carbonate in ambient temperature waters (tufa) can  
17 form magnificent tufa landscapes, many of which are designated as protected areas.  
18 However, tufa landscapes in many areas are threatened by both local anthropogenic  
19 activities and climate change. This study, for the first time, posed the question whether the  
20 tufa landscape degradation (characterized by tufa degradation and increased biomass of

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*Abbreviations:* a.s.l., above sea level; CaCO<sub>3</sub>, Calcium carbonate; Ca(HCO<sub>3</sub>)<sub>2</sub>, Calcium bicarbonate; CO<sub>2</sub>, 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<sub>4</sub><sup>+</sup>, Ammonia ion; NO<sub>3</sub><sup>-</sup>, Nitrate ion; SIc, Saturation index of calcite; SNMS, Songpan National Meteorological Station; SO<sub>4</sub><sup>2-</sup>, Sulfate ion; TIN, Total inorganic nitrogen; USGS, United States Geology Survey; VWM, Volume weighted mean.

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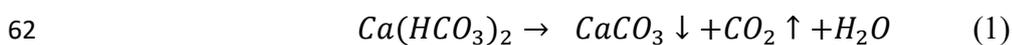
21 green algae) in Jiuzhaigou National Nature Reserve of China is partially caused by regional  
22 air pollution and climate warming. The results indicate that wet deposition (including rain  
23 and snow) polluted by anthropogenic SO<sub>2</sub>, NO<sub>x</sub>, and NH<sub>3</sub> emissions dissolves exposed tufa  
24 and may considerably reduce tufa deposition rate and even cause tufa dissolution within  
25 shallow waters. These effects of wet deposition on tufa enhanced as pH of wet deposition  
26 decreased from 8.01 to 5.06. Annual Volume Weighted Mean concentration of reactive  
27 nitrogen (including NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) in wet deposition (26.1 μmol L<sup>-1</sup>) was 1.8 times of the  
28 corresponding value of runoff (14.8 μmol L<sup>-1</sup>) and exceeded China's national standard of  
29 total nitrogen in runoff for nature reserves (14.3 μmol L<sup>-1</sup>), indicating a direct nitrogen  
30 fertilization effect of wet deposition on green algae. As water temperature is the major  
31 limiting factor of algal growth in Jiuzhaigou and temperature in the top layer (0-5 cm) of  
32 runoff (depth<1 m, no canopy coverage of trees and shrubs) was significantly higher at the  
33 sites with increased biomass of green algae (*p*<0.05), climate warming in this region would  
34 favor algal growth. In sum, this study suggests that climate warming and enhanced sulfur  
35 and nitrogen deposition have contributed to the current degradation of tufa landscape in  
36 Jiuzhaigou, but in order to quantify the contributions, further studies are needed, as many  
37 other anthropogenic and natural processes also influence tufa landscape evolution.

38

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

## 40 **1. Introduction**

41 Tufa is the product of calcium carbonate ( $\text{CaCO}_3$ ) deposition in ambient temperature  
42 waters, mainly presenting as calcite and typically containing the remains of micro- and  
43 macrophytes, invertebrates, and bacteria (Ford and Pedley, 1996). Travertine is usually used  
44 as an alternative term for tufa (Pentecost, 2005). As for the formation of tufa, it is believed  
45 that groundwater, which first gains high carbon dioxide ( $\text{CO}_2$ ) concentrations from soil  
46 profiles (Yan et al., 2013) and/or possibly from deep sources like the upper mantle  
47 (Yoshimura et al., 2004), dissolves carbonate bedrocks to form a solution rich in calcium  
48 bicarbonate ( $\text{Ca}(\text{HCO}_3)_2$ ). After traveling for some distance and then emerging at springs,  
49 dissolved  $\text{CO}_2$  is lost from the solution on contact with the atmosphere which has a  $\text{CO}_2$   
50 concentration lower than that in equilibrium with the  $\text{Ca}(\text{HCO}_3)_2$ -rich solution (Pentecost,  
51 2005). Due to  $\text{CO}_2$  loss, the solution becomes supersaturated with respect to calcite and  
52 begins to produce calcite (Eq. 1). Tufa may spread across the earth's surface for meters to  
53 kilometers, building three dimensional landforms that can be generally categorized into two  
54 fundamental depositional morphotypes (Ford and Pedley, 1996). The first is called "fluvial  
55 barrage model" (Pedley, 1990) or "barrage travertine/tufa system" (Violance et al., 1994),  
56 which involves damming of a river, by means of one or more transverse oriented tufa  
57 barrages (Ford and Pedley, 1996; Figure S1). The second is "perched springline model"  
58 (Pedley, 1990) or "slope travertine/tufa system" (Violance et al., 1994), which involves the  
59 formation of a valley-side-sited, wedge-shaped sedimentary body (Ford and Pedley, 1996;  
60 Figure S2). A detailed review of tufa and travertine deposits of the world can be found in  
61 Ford and Pedley (1996).



63 Many magnificent tufa landscapes are designated as protected areas and are also popular  
64 tourist destinations (Ford and Pedley, 1996; Pentecost, 2010). Jiuzhaigou National Nature  
65 Reserve (Jiuzhaigou, hereafter) in China, Plitvice National Park in Croatia, Havasupai  
66 Canyon in the U.S., and Dunns River Falls in Jamaica are examples that are famous for tufa  
67 landscapes. Unfortunately, tufa landscape degradation (e.g., increased biomass of green

68 algae associated with nutrient enrichment, tufa erosion and dissolution, a reduced deposition  
69 rate of tufa, and tufa waterfall collapse) has been reported for many protected areas and its  
70 relationship with local anthropogenic activities has been investigated (Goudie et al., 1993;  
71 Zhou, 1998; Zhang et al., 2012). Trampling by humans and livestock causes physical  
72 damage to tufa so now they are protected by boardwalks and fences (Pentecost, 2010).  
73 Discharge change caused by climate change and anthropogenic activities led to reduced tufa  
74 deposition and/or tufa loss (Goudie et al., 1993). Water chemistry change caused by  
75 deforestation, fertilizers, and wastewater would also affect tufa deposition and even cause  
76 tufa loss (Thorpe, 1981; Goudie et al., 1993; Zhou et al., 1998). Although a number of  
77 protective measures have been implemented, degradation of tufa landscape continues in  
78 some protected areas (Zhang et al., 2012; Gu et al., 2013). As tufa landscapes are usually  
79 formed in shallow waters and some of which would be seasonally dry, they might prove  
80 sensitive to atmospheric environmental changes. It is evident that anthropogenic activities  
81 have led to climate warming (Intergovernmental Panel on Climate Change (IPCC), 2013)  
82 and enhanced atmospheric deposition of reactive sulfur and nitrogen (including sulfate ion  
83 ( $\text{SO}_4^{2-}$ ), nitrate ion ( $\text{NO}_3^-$ ), and ammonia ion ( $\text{NH}_4^+$ )) throughout the world (Vet et al., 2014).  
84 Climate warming influences water temperature, which is regarded as the major limiting  
85 factor of algal growth in many alpine, subalpine, and boreal regions (Williamson et al., 2008;  
86 Schindler, 2009). Reactive nitrogen is an important nutrient for the growth of hydrophytes  
87 like green algae, particularly in pristine waters, which are usually low in nitrogen  
88 concentrations (Baron et al., 2000; Williamson et al., 2008; Hessen et al., 2009).  $\text{SO}_4^{2-}$  and  
89  $\text{NO}_3^-$  are the main acids that cause acid rain and it is well known that acid rain can accelerate  
90 chemical weathering of carbonate rocks. However, to the best of the authors' knowledge, the  
91 contributions of climate warming and enhanced deposition of reactive sulfur and nitrogen to  
92 tufa landscape degradation have not been explored.

93 This paper reports a case study in Jiuzhaigou (32.88°-33.33° N, 103.77°-104.08° E,  
94 2000-4880 m above sea level (a.s.l.)), a headwater watershed located in a subalpine to alpine  
95 region of Sichuan Province, China (Figure 1a). Jiuzhaigou has a reserve area of 643 km<sup>2</sup> and  
96 additionally has a buffer zone of 598 km<sup>2</sup>. Over 80% of Jiuzhaigou's land is covered by

97 vegetation, including 65% covered by pine forests and mixed broadleaf and coniferous  
98 forests and 15% covered by shrubs and meadows (Lin et al., 2006; Liu et al., 2007; Bossard  
99 et al., 2015). Tufa landscapes are distributed in the bottom of Rize and Shuzheng valleys  
100 (Figure 1b), having a total area of 2.4 km<sup>2</sup> and consisting of 17 groups of waterfalls, 16  
101 cascades/shoals, 110 lakes/pools, and numerous springs. Due to logging in 1966-1978 and  
102 poor management of tourism development in the 1980s and early 1990s, human activities  
103 caused remarkable adverse effects on tufa landscapes then, such as increased lake  
104 sedimentation, water pollution, and physical damage to tufa (Zhou, 1998; Gu et al., 2013; Li  
105 et al., 2014; Liang et al., 2014). In order to protect the tufa landscapes, logging was banned  
106 in 1978 and a number of regulations/infrastructure were implemented/built in the late 1990s  
107 and early 2000s. Farming and grazing have been completely barred since 2001. Wastewater  
108 and solid wastes are collected through a sanitary system and transported out of the reserve.  
109 Nuorilang Center is the sole restaurant and tourists are strict to visit the reserve  
110 approximately between 7:00 am and 6:00 pm. Tourist vehicles are not allowed in the reserve  
111 starting from 2002; instead, a system of tour buses and boardwalks are now used by tourists  
112 to visit the main tourist region located in the bottom of Rize, Shuzheng, and Zezhawa  
113 valleys (Figure 1b).

114 Although great efforts have been made to protect Jiuzhaigou's tufa landscapes, the  
115 degradation of tufa landscape, characterized by increased biomass of green algae and tufa  
116 erosion and dissolution (Figure S3), continues and is occurring in parallel with climate  
117 warming (Figure 2) and elevated atmospheric deposition of reactive sulfur and nitrogen,  
118 which includes acid rain (pH<5.60) (Qiao et al., 2015a). Specifically, annual mean air  
119 temperature increased by 0.3°C in Jiuzhaigou from 2003 to 2014 and by 1.2°C from 1951 to  
120 2014 at the Songpan National Meteorological Station (SNMS), which is about 140 km from  
121 Jiuzhaigou (Figure 2). Acid rain was observed having SO<sub>4</sub><sup>2-</sup> as the major source of acidity  
122 and over 90% of the annual wet deposition fluxes of reactive sulfur and nitrogen were from  
123 anthropogenic sources (Qiao et al., 2015a). From June to August 2010 (accounting for 30%  
124 and 40% of annual deposition fluxes of reactive sulfur and nitrogen, respectively), 93%,  
125 98%, and 69% of the deposition fluxes of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> were from inter-regional

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

130

## 131 **2. Methods and materials**

### 132 **2.1. Study area**

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

142 Climately, Jiuzhaigou lies in a transitional region from the humid Sichuan Basin to the  
143 semiarid Tibetan Plateau (Urgenson et al., 2014). At the Nuorilang Center, monthly air  
144 temperature was highest in July ( $\sim 18^{\circ}\text{C}$ ) and lowest in January ( $\sim -4^{\circ}\text{C}$ ). Annual precipitation  
145 was 539-771 mm, with over 80% falls during the wet season (approximately from April to  
146 October). Precipitation is the sole water source of the watershed. A one-year monitoring  
147 campaign from April 2010 to May 2011 collected 36 weekly to biweekly wet deposition  
148 samples (including rain and snow) at the Long Lake Meteorological Station (LLMS) and  
149 found that pH of wet deposition was 5.06-8.01, with about 10% of samples having a pH less  
150 than 5.60 (Qiao et al., 2015a). Annual Volume Weighted Mean (VWM) concentrations of  
151  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and TIN (i.e., total inorganic nitrogen,  
152 including  $\text{NH}_4^+$  and  $\text{NO}_3^-$  here) were 41.1, 149.8, 70.5, 21.2, 38.0, 21.0, 37.2, 13.4, 12.7, and

153 26.1  $\mu\text{mol L}^{-1}$ , 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  $\mu\text{mol L}^{-1}$ ) and had mean  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  
163  $\text{NO}_3^-$ , 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  $\mu\text{mol L}^{-1}$ , respectively (Table 1).

165

## 166 **2.2. Impacts of enhanced acid deposition on tufa**

167 Acid rain mainly caused by anthropogenic  $\text{SO}_4^{2-}$  was observed in Jiuzhaigou and  $\text{NO}_3^-$   
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  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ , and  
179  $\text{NO}_3^-$  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

181 contributed by  $\text{HCO}_3^-$  in Jiuzhaigou (Qiao et al., 2015a), thus Eq. (2) was used to estimate  
182 alkalinity of the wet deposition samples that had a pH higher than 7.00 in this study.  
183 Alkalinity was considered to be zero in the wet deposition samples that had a pH less than  
184 7.00.

185 Additionally, as tufa landscapes in Jiuzhaigou are mostly formed in shallow waters and  
186 some tufa landscapes would be completely/partially dry during the dry season and at the  
187 beginning of wet season, we also used the PHREEQC model and the WATEQ4F  
188 thermodynamic database to calculate SIC values in the water mixed by runoff and wet  
189 deposition at a variety of volume ratios. The volume mixing ratios of runoff ( $V_{\text{runoff}}$ ) to wet  
190 deposition ( $V_{\text{wet deposition}}$ ) 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  
191 11 sites was monitored in August 2010 and April 2011 (Qiao et al., 2012; Figure 1b), the  
192 monthly pH (calculated by using monthly VWM  $\text{H}^+$  concentrations), temperature, and  
193 VWM alkalinity and ionic concentrations of wet deposition in these two months were used  
194 in calculating SIC for the water mixed by runoff and wet deposition.

$$\text{Alkalinity or } [\text{HCO}_3^-] = ([\text{K}^+] + 2 \times [\text{Ca}^{2+}] + [\text{Na}^+] + 2 \times [\text{Mg}^{2+}] + [\text{NH}_4^+]) - (2 \times [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{F}^-])$$

pH > 7.00 (2)

195 Where [X] is the concentration of a given ion of wet deposition in  $\mu\text{mol L}^{-1}$ .

196

### 197 **2.3. Impacts of elevated nitrogen deposition and climate warming on green** 198 **algae**

199 In order to understand if enhanced deposition of reactive nitrogen has contributed to the  
200 current increased biomass of green algae,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and TIN concentrations were  
201 compared between wet deposition and runoff. The data of the weekly to biweekly wet  
202 deposition samples collected during April 2010 to May 2011 were derived from Qiao et al.  
203 (2015a). The data of runoff measured in August 2010 and April 2011 at 11 sites was derived  
204 from Qiao (2012). The results of Kolmogorov-Smirnov Test show that all the datasets

205 follow a normal distribution, except for the  $\text{NH}_4^+$  dataset of runoff. Thus, T-Test was used to  
206 compare  $\text{NO}_3^-$  and TIN concentrations between wet deposition and runoff, while  
207 Mann-Whitney U Test was used to compare the two datasets of  $\text{NH}_4^+$ . All the statistical tests  
208 mentioned above were carried out by using IBM SPSS 19.0. The average TIN concentration  
209 of runoff and the annual VWM TIN of wet deposition were also compared to China's  
210 national standard of total nitrogen in runoff for nature reserves (Ministry of Environmental  
211 Protection of China (MEPC), 2002).

212 Increased biomass of green algae was observed only in the shallow waters with a low  
213 canopy coverage of trees and shrubs. Water temperature at these sites was more easily  
214 affected by air temperature and solar radiation, while green algae at these sites have a good  
215 access to light, which is also an important factor for their growth. Zhu (2007) found that  
216 water temperature is the major limiting factor to the growth of green algae in the Pearl Shoal  
217 and Five-flower Lake of Jiuzhaigou and green algae biomass increased as water temperature  
218 increased from 8 to 17°C. In this study, we compared temperature in the top layer (0-5 cm)  
219 of waters, which had a water depth approximately less than 1 m and no canopy coverage of  
220 trees and shrubs. Water temperature was measured at 80 sites, including 48, 12, 9, and 11  
221 sites located in tufa dams/cascades/shoals, lakes/pools, swamps, and rivers, respectively. At  
222 the sites of lakes, pools, and rivers, temperature was measured at the rims, where water was  
223 shallow. Water temperature was measured by using a pH meter equipped with a temperature  
224 sensor (Milwaukee SM102) between 10:00 am and 15:00 pm on two summer days (25-26th  
225 June, 2011). At each site, water temperature was measured at five to eight points with  
226 0.5-1.0 m between each two points and the average temperature was used as the  
227 temperature of the site. After measurements, water temperature was then compared between  
228 the sites with increased biomass of green algae (54 sites) and that with low biomass of green  
229 algae (26 sites) by using T-Test, as the two datasets both follow a normal distribution  
230 according to the results of Kolmogorov-Smirnov Test.

231

### 232 **3. Results**

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

239 The results of comparison of reactive nitrogen concentrations between runoff and wet  
240 deposition are shown in Table 1.  $\text{NO}_3^-$  concentrations were similar between wet deposition  
241 and runoff ( $p>0.05$ ); in contrast,  $\text{NH}_4^+$  and TIN concentrations were significantly higher in  
242 wet deposition ( $p<0.05$ ). Annual VWM TIN concentrations of wet deposition also exceeded  
243 14.3  $\mu\text{mol L}^{-1}$  (Table 1), which is China's national standard of total nitrogen in runoff for  
244 nature reserves (MEPC, 2002).

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

251

## 252 **4. Discussion**

### 253 **4.1. Tufa deposition and dissolution**

254 Basically, tufa deposition occurs given the following conditions (Goudie et al., 1993): (1)  
255 availability of enough dissolved particulate  $\text{CaCO}_3$ , (2) occurrence of turbulent degassing of  
256  $\text{CO}_2$  from water, and (3) presence of suitable substrates (e.g., mosses and tree roots and  
257 branches) which provide framework for tufa deposition. Some ions (e.g.,  $\text{PO}_4^{3-}$ ) and organic  
258 ligands inhibit tufa deposition through blocking active crystal-growth sites on calcite surface  
259 (Lebrón and Suárez, 1996; Lin and Singer, 2006). At a temperature of 25°C and an SIc of

260 0.95, calcite deposition is completely inhibited when dissolved organic carbon (DOC)  
261 concentration is greater than  $300 \mu\text{mol L}^{-1}$ , and the particle size of calcite crystals would  
262 decrease from  $100 \mu\text{m}$  to less than  $2 \mu\text{m}$  as DOC concentration increases from 20 to  $150$   
263  $\mu\text{mol L}^{-1}$  (Lebrón and Suárez, 1996). Due to lack of free energy to create new surface areas,  
264 unavailability of reactive calcite to act as nucleation sites, and inhibition effect from some  
265 substances, tufa deposition mostly occurs in the waters that have a  $\text{Ca}^{2+}$  concentration larger  
266 than  $2000 \mu\text{mol L}^{-1}$  (Pentecost, 2005) and is at least 5-10 times supersaturated with respect  
267 to calcite ( $\text{SIc} > 0.7-1.0$ ) (Chen et al., 2004).

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

281 In addition to wet deposition, other processes may also contribute to the tufa  
282 degradation in Jiuzhaigou. Anthropogenic activities (such as deforestation, quarrying,  
283 fertilizer use, cattle manuring, and industry) and climate change could influence tufa  
284 deposition and loss through altering discharge, water chemistry, and watershed conditions  
285 (Goudie et al., 1993). Among the anthropogenic activities, deforestation is widespread and is  
286 believed to be the mechanism that most easily explains the widespread nature of the tufa  
287 decline in Europe (Goudie et al., 1993), while Jiuzhaigou is a forested watershed that has  
288 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 podzolization and peat growth in watersheds, releasing more acids to runoff, (4) CO<sub>2</sub>  
293 reduction in soil caused by accelerated soil erosion and/or by reduced root respiration,  
294 leading to lower CaCO<sub>3</sub> 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

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

322 The processes controlling nutrient loadings in runoff include (Feller, 2009): (1)  
323 atmospheric deposition and climate, (2) geological weathering, (3) terrestrial biological  
324 process, (4) physical-chemical reactions in the soil, and (5) physical, chemical, and  
325 biological process within aquatic ecosystems. Inter-regional transport of air pollutants from  
326 human emissions has elevated deposition of reactive nitrogen (Qiao et al., 2015a; Qiao et al.,  
327 2015b) and has a fertilization effect on green algae in Jiuzhaigou, as total nitrogen is the  
328 third most important factor controlling the growth of green algae in Jiuzhaigou (Zhu, 2007)  
329 and  $\text{NH}_4^+$  and TIN concentrations were statistically higher in wet deposition than in runoff  
330 (Table 1). In addition to wet deposition, deforestation and its associated land use change may  
331 also be the causes of increased nitrogen in runoff. The runoff was low in nitrogen and  
332 phosphorus when tourism started in early 1980s (Zhou et al., 1986; Luo, 2000), but nitrogen  
333 and phosphorus in runoff started to increase as early as 1990s (Zhou, 1998; Cao, 1999),  
334 most likely due to wastewater from tourist activities (Zhou, 1998; Gaulke et al., 2010).  
335 Although a sanitary system is now used to collect wastewater and transport it out of the  
336 reserve, Wang (2006) still observed that tourist activities increased nitrogen inputs from land  
337 to runoff through the boardwalks and soils along the runoff. Furthermore, deforestation  
338 caused by previous logging and tourism development may still affect nutrient loadings in  
339 runoff through the (2-4) processes suggested by Feller (2009). In order to control nutrient  
340 loadings in runoff, future studies are needed to better quantify the contributions of different  
341 sources to nutrients in runoff, particularly for nitrogen and phosphorus.

342

## 343 **5. Conclusion**

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

345 by increased biomass of green algae and tufa degradation, has been observed in Jiuzhaigou.  
346 This study examined whether these tufa landscape changes are partially associated with  
347 climate warming and the enhanced deposition of reactive sulfur and nitrogen caused by  
348 inter-regional transport of air pollutants. The results show that wet deposition (not  
349 necessarily being acid rain) in Jiuzhaigou was calcite unsaturated, suggesting that wet  
350 deposition would dissolve exposed tufa. Additionally, wet deposition may reduce tufa  
351 deposition or even cause tufa dissolution in shallow waters. These effects of wet deposition  
352 on tufa increased as pH of wet deposition decreased from 8.01 to 5.06. TIN concentrations  
353 were much higher in wet deposition (annual VWM =  $26.1 \mu\text{mol L}^{-1}$ ) than in runoff (mean =  
354  $14.8 \mu\text{mol L}^{-1}$ ), suggesting a nitrogen fertilization of wet deposition on green algae. As water  
355 temperature was the major limiting factor of algal growth and temperature in the top layer  
356 (0-5 cm) of waters (depth < 1 m, no canopy coverage of trees and shrubs) was significantly  
357 higher at the sites with increased algal biomass, climate warming in the region ( $+1.2^\circ\text{C}$  from  
358 1951 to 2014) may favor the growth of green algae and increase green algae biomass in  
359 higher elevations (>2600 m a.s.l.). In summary, climate warming and enhanced deposition of  
360 reactive sulfur and nitrogen may have contributed to the current tufa landscape degradation  
361 in Jiuzhaigou, but future studies are needed to better quantify the contributions, as many  
362 other anthropogenic and natural processes also affect tufa landscape evolution, particularly  
363 the deforestation caused by previous logging and by tourism development.

364

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374

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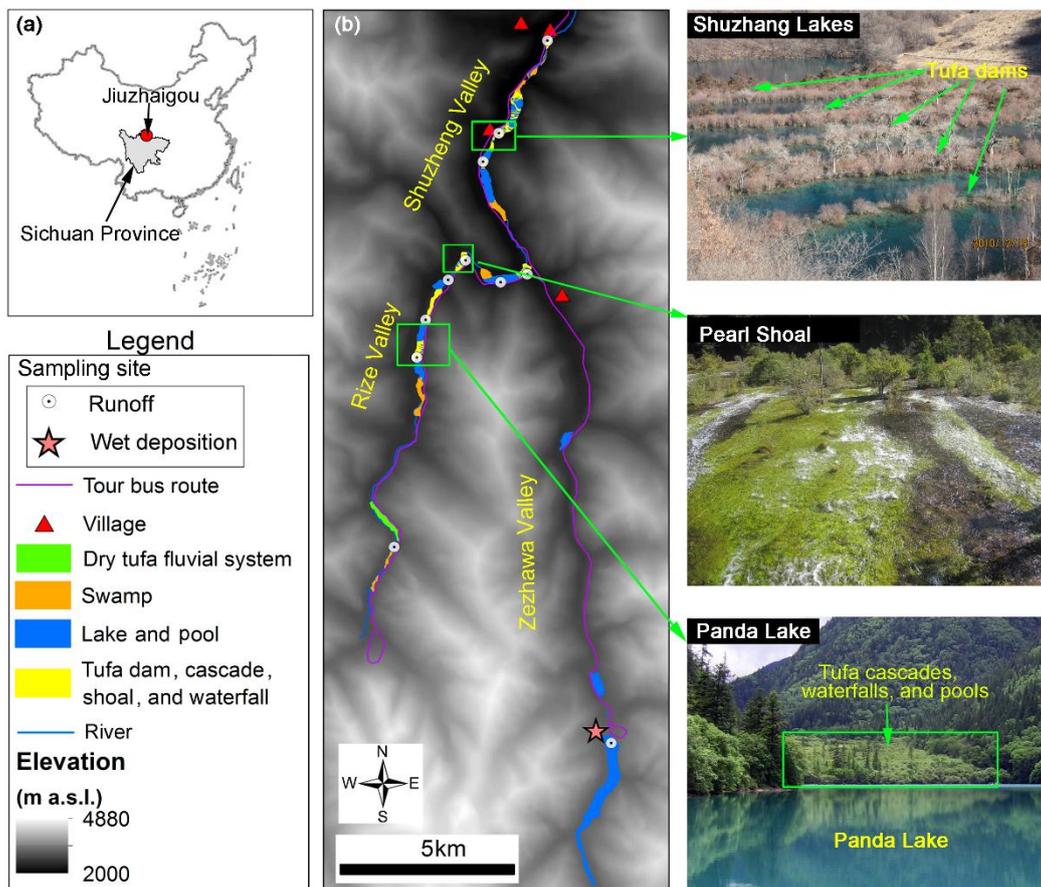
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530 **Figures**

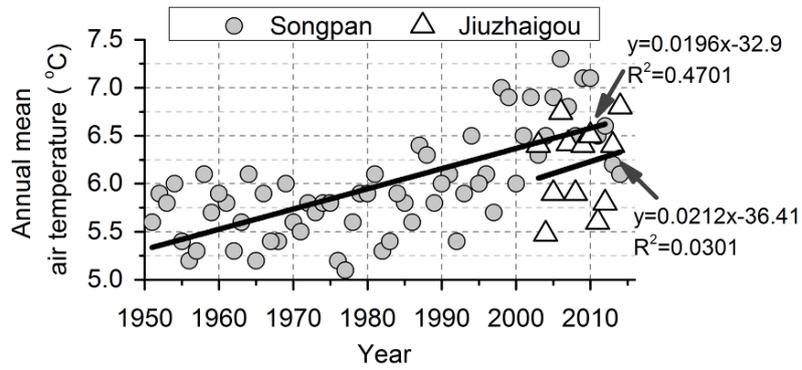
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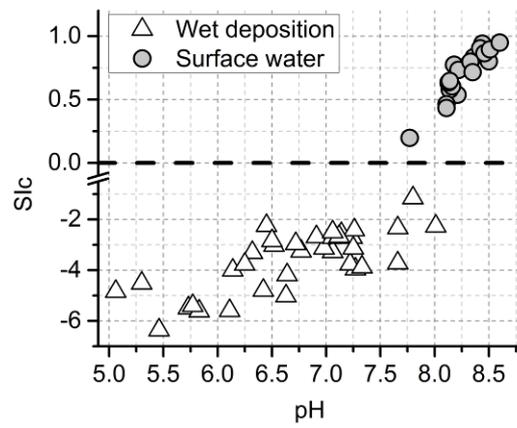
533 Figure 1. Maps illustrating (a) the location of Jiuzhaigou and (b) the locations of the  
534 sampling sites of runoff (Qiao, 2012) and wet deposition (Qiao et al., 2015a) in Jiuzhaigou.

535



536

537 Figure 2. Annual mean air temperature at the Nuorilang Center in Jiuzhaigou from 2003 to  
538 2014 and at the Songpan National Meteorological Station (SNMS) from 1951 to 2014. The  
539 data of SNMS were derived from the China Meteorological Data Sharing Service System  
540 ([www. http://cdc.nmic.cn/home.do](http://cdc.nmic.cn/home.do)) and the data of Jiuzhaigou were from Jiuzhaigou  
541 Administrative Bureau.

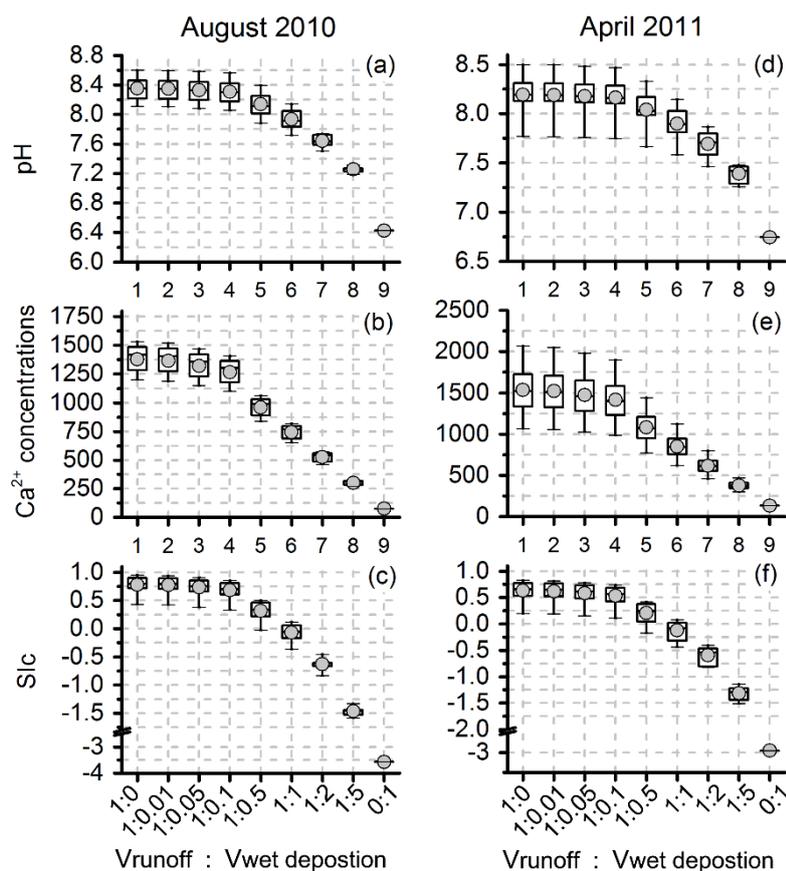


542

543 Figure 3. Comparison of S1c 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 S1c values were calculated in this study.

546

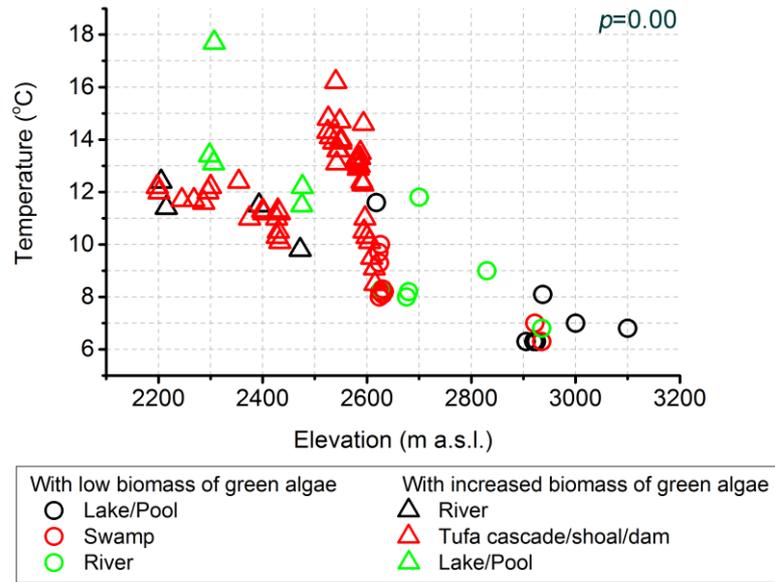
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548

549 Figure 4. Ca<sup>2+</sup> concentrations ( $\mu\text{mol L}^{-1}$ ), pH, and SIc in the solutions mixed by runoff and  
 550 wet deposition at volume ratios of  $V_{\text{runoff}} : V_{\text{wet deposition}}$  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.

557



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

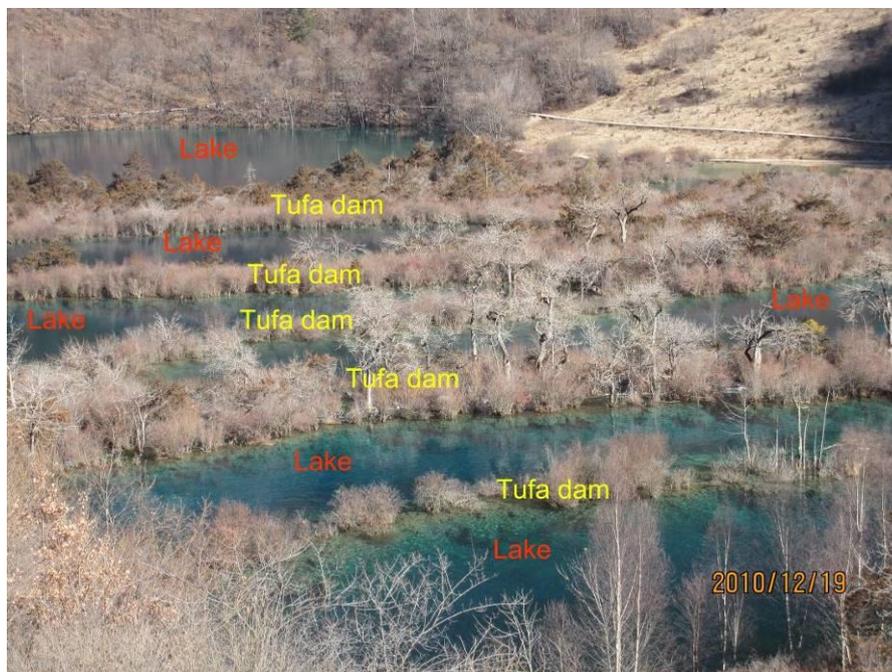
566 Table 1. The alkalinity, conductivity, ionic concentrations, and pH of runoff and wet  
 567 deposition samples collected in Jiuzhaigou. The unit of ionic concentrations and alkalinity  
 568 are in  $\mu\text{mol L}^{-1}$ . The unit of conductivity is in  $\mu\text{S cm}^{-1}$ .

Parameter	Runoff <sup>a</sup>			Wet deposition <sup>b</sup>			<i>p</i> <sup>c</sup>
	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 <sup>d</sup>	126 <sup>d</sup>	0.00
Mg <sup>2+</sup>	21	419.0-595.8	537.6	36	15.3-35.9	41.1	0.00
Ca <sup>2+</sup>	21	1148-2182	1545	36	14.5-406.1	149.8	0.00
SO <sub>4</sub> <sup>2-</sup>	21	116.5-294.7	201.7	36	19.7-85.3	70.5	0.00
K <sup>+</sup>	21	9.2-64.4	16.1	36	0.9-767.6	21.2	0.25
Na <sup>+</sup>	21	36.6-68.0	59.1	36	7.7-304.3	38.0	0.00
F <sup>-</sup>	21	24.8-40.9	35.8	36	11.5-59.2	21.0	0.00
Cl <sup>-</sup>	21	17.9-30.8	24.7	36	6.8-1003.2	37.2	0.32
NH <sub>4</sub> <sup>+</sup>	21	0.0-6.1	0.9	36	0.2-61.2	13.4	0.00
NO <sub>3</sub> <sup>-</sup>	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

<sup>a</sup> Monitored in August 2010 and April 2011 in Qiao (2012); <sup>b</sup> Monitored from April 2010 to August 2011 in Qiao et al. (2015a); <sup>c</sup> This study,  $p < 0.05$ : the difference between wet deposition and runoff is statistically significant at the 0.05 level; <sup>d</sup> 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.

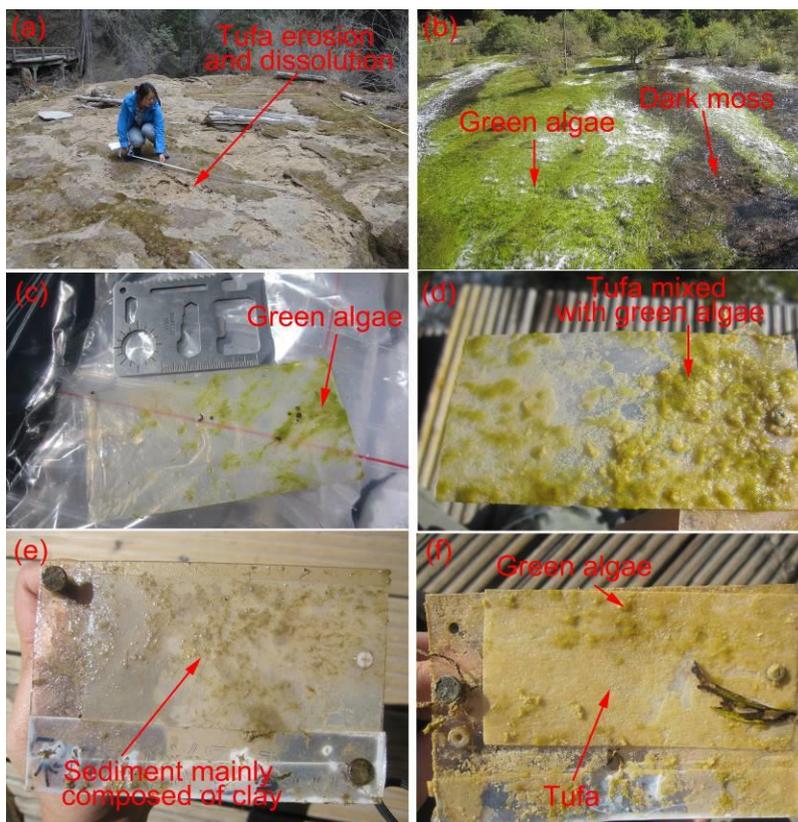
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576 Figure S2. A slope tufa system in Huanglong National Nature Reserve, Sichuan Province,  
577 China.



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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.

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