1 Air-surface exchange of gaseous mercury over permafrost soil: an

- 2 investigation at a high-altitude (4700 m a.s.l.) and remote site in the central
- 3 Qinghai-Tibet Plateau
- 4 Zhijia Ci¹, Fei Peng², Xian Xue², and Xiaoshan Zhang¹

¹Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China

²Cold and Arid Regions Environmental and Engineering Research Institute, Chinese Academy of Sciences, Lanzhou, 730000,
 China

8 Correspondence to: Z. J. Ci (zjci@rcees.ac.cn)

9 Abstract. The pattern of air-surface gaseous mercury (mainly Hg(0)) exchange in the Qinghai-Tibet 10 Plateau (QTP) may be unique because this region is characterized by low temperature, great 11 temperature variation, intensive solar radiation, and pronounced freeze-thaw process of permafrost soils. However, air–surface Hg(0) flux in the QTP is poorly investigated. In this study, we performed field 12 measurements and controlled field experiments with dynamic flux chambers technique to examine the 13 flux, temporal variation and influencing factors of air-surface Hg(0) exchange at a high-altitude (4700 14 m a.s.l.) and remote site in the central QTP. The results of field measurements showed that surface soils 15 were net emission source of Hg(0) in the entire study (2.86 ng m⁻² h⁻¹ or 25.05 μ g m⁻² y⁻¹). Hg(0) flux 16 showed remarkable seasonality with net high emission in the warm campaigns (June 2014: 4.95 ng m^{-2} 17 h^{-1} ; September 2014: 5.16 ng m⁻² h^{-1} and May–June 2015: 1.95 ng m⁻² h^{-1}) and net low deposition in 18 winter campaign (December 2014: $-0.62 \text{ ng m}^{-2} \text{ h}^{-1}$), and also showed the diurnal pattern with emission 19 20 in daytime and deposition in nighttime, especially on days without precipitation. Rainfall events on the dry soils induced large and immediate increase in Hg(0) emission. Snowfall events did not induce the 21 22 pulse of Hg(0) emission, but snow melt resulted in the immediate increase in Hg(0) emission. Daily 23 Hg(0) fluxes on rainy or snowy days were higher than those of days without precipitation. Controlled 24 field experiments suggested that water addition to dry soils significantly increased Hg(0) emission both in short (minutes) and relatively long (hours) timescales, and also showed that UV radiation was 25 26 primarily attributed to Hg(0) emission in the daytime. Our findings imply that a warm climate and environmental change could facilitate Hg release from the permafrost terrestrial ecosystem in the QTP. 27

28 **1 Introduction**

Soils represent the largest Hg reservoirs in ecosystems and play a major role in the global Hg cycle (Selin, 2009; Agnan et al., 2016). Background soils receive Hg input from atmospheric deposition, which is mainly retained in organic-rich layers of upper soils (Schuster, 1991; Khwaja et al., 2006). Hg in soils can be reduced to Hg(0) and then emitted to the overlaying air because of its high volatility (Schlüter, 2006). Therefore, soils can serve as both sources and sinks of atmospheric Hg (Pirrone and Mason, 2009; Amos et al., 2013; Agnan et al., 2016).

In the past several decades, efforts have been made to improve the understanding of soil Hg 35 biogeochemistry (Zhang and Lindberg, 1999; Lin et al., 2010; Schlüter, 2006; Jiskra et al., 2015). 36 Measurements across various types of soils and climates show that air-soil Hg(0) exchange has highly 37 spatial and temporal variation and bidirectional exchange behavior (Agnan et al., 2016 and references 38 therein). Field measurements and laboratory experiments highlight that various factors and processes 39 influence air-surface Hg(0) exchange, including concentrations and species of soil Hg (Gustin et al., 40 1999, 2002; Hintelmann et al., 2002; Bahlmann et al., 2006; Kocman and Horvat, 2010; Eckley et al., 41 42 2011; Edwards and Howard, 2013; Mazur et al., 2015), solar radiation (Gustin et al., 2002; Moore and Carpi, 2005; Gustin et al., 2006; Xin et al., 2007; Fu et al., 2008a; Kocman and Horvat, 2010; Park et al., 43 44 2014), precipitation (Lindberg et al., 1999; Gustin and Stamenkovic, 2005; Gabriel et al., 2011), soil temperature and moisture (Gustin et al., 1997; Gustin and Stamenkovic, 2005; Ericksen et al., 2006; Xin 45 et al., 2007; Briggs and Gustin, 2013; Park et al., 2014; Mazur et al., 2015), soil organic matter and pH 46 (Yang et al., 2007; Xin and Gustin, 2007; Mauclair et al., 2008); land cover (Dommergue et al., 2003; 47 Ericksen et al., 2005; Cobbett et al., 2007; Gabriel and Williamson, 2008; Zhu et al., 2011; Durnford et 48 al., 2012a, b; Toyota et al., 2014a, b); atmospheric Hg(0) concentrations and other chemical 49 compositions (Engle et al., 2004; Xin and Gustin, 2007; Fu et al., 2008a), biological activity (Choi and 50 Holsen, 2009), as well as atmospheric turbulence (Gustin et al., 1997; Poissant et al. 1999). Existing 51 studies on Hg(0) dynamics at air-surface interface are mainly performed in temperate regions (Agnan et 52 al., 2016 and reference therein). The seasonal frozen soils and permafrost widely distribute, accounting 53 54 for almost 70% of terrestrial area of Earth (NSIDC). However, the knowledge of air-surface Hg(0)

dynamics in cold region is limited (Cobbett et al., 2007; Durnford and Dastoor, 2011). Most current
parameters of air–soil Hg(0) exchange applied in Hg biogeochemical models are mainly derived from
temperate regions of North America and Europe (Zhu et al., 2016).

The Qinghai-Tibet Plateau (OTP) is located in the western China with the area of 2.5 million km^2 58 59 and mean altitude of > 4000 m. Due to the high altitude and subsequent low temperature, a significant portion (~ 1.5 million km⁻²) of the OTP is underlain by permafrost (Kang et al., 2010). Because of the 60 harsh natural environment, limited research resources and difficulty of access and sampling logistics, 61 studies on Hg biogeochemistry in the QTP are limited. The role of QTP in the regional and global Hg 62 63 biogeochemical cycle is poorly understood (Ci et al., 2012; Agnan et al., 2016). At present, Hg studies in the QTP mainly focused on the investigations of Hg concentration, speciation and distribution in 64 environmental samples, such as air (Fu et al., 2008b; 2012; Yin et al., 2015), snow and glacier (Loewen 65 et al., 2007; Wang et al., 2008; Zhang et al., 2012; Huang et al., 2012), and rain water (Huang et al., 66 2013). The knowledge of Hg(0) dynamics at air-surface interface in the QTP is extremely poor. The 67 unique climatic condition, land cover and soil property suggest the need for the specific air-soil Hg(0) 68 flux data and mechanism representative of the environmental setting in the OTP to better constrain 69 70 global natural sources inventories (Ci et al., 2012; Agnan et al., 2016).

71 It is noted that, many studies addressed that precipitation greatly influences air-surface Hg(0) flux over different timescales (Lindberg et al., 1999). However, previous studies mainly focused on the 72 effect of rainfall/watering on air-soil Hg(0) flux (Lindberg et al., 1999; Johnson et al., 2003; Gustin and 73 Stamenkovic, 2005; Song and Van Heyst, 2005; Corbett-Hains et al., 2012) or the fate and transport of 74 Hg(0) at air-snow interface (Lalonde et al., 2001, 2003; Ferrari et al., 2005; Dommergue et al., 2003, 75 76 2007; Fa n et al., 2007; Bartels-Rausch et al., 2008; Brooks et al., 2008; Steen et al., 2009; Durnford et al., 2012a, b; Mann et al., 2015). The field study on the effect of snowmelt on Hg(0) flux is very limited 77 78 (Cobbett et al., 2007).

In this study, we applied dynamic flux chambers (DFCs) technique to investigate the flux, temporal variation and influencing factors of air–surface Hg(0) exchange at a representative research station in the central QTP. Meanwhile, controlled field experiments were performed to explore the

effect of rainfall and different wavebands of solar radiation on air–soil Hg(0) flux. Combining the result of this study and other knowledge, we discuss the effect of future climatic and environmental change on air–surface Hg(0) dynamics in the QTP.

85 2 Methods

86 2.1 Study site

The study was performed at the Beiluhe Permafrost Engineering and Environmental Research 87 Station affiliated to the Cold and Arid Regions Environmental and Engineering Research Institute, 88 Chinese Academy of Sciences (CAREER-CAS). The elevation of the Beiluhe region is about 4700 to 89 4800 m a.s.l.. The station (34° 49' 45" N, 92° 56' 06" E) lies over the continuous permafrost zone in the 90 91 central QTP (Fig. 1). The terrain is undulation with sparse vegetation and surface fine sands or gravels. The thickness of the active layer and permafrost around the station is 2.0-3.2 m and 60-200 m, 92 respectively; the active layer begins to freeze in September and thaw in May (Peng et al., 2015a). The 93 94 Beiluhe region experiences a continental climate with cold winter (up to -30 °C) and warm summer (up to 25 $^{\circ}$ C). The magnitude of daily air temperature is up to 30 $^{\circ}$ C, and the annual mean surface air 95 temperature is about -2 to -3 °C (Peng et al., 2015a). The solar radiation is high and characterized by 96 intense UV radiation (Wei et al., 2006). The mean annual precipitation is about 300 mm, and the annual 97 potential evapotranspiration (~1300 mm) greatly exceeds the precipitation (Peng et al., 2015a). As a 98 remote region, there is no direct human activity to influence the local Hg cycle. 99

The precipitation at the Beiluhe station mainly occurs during May to October under the influence of the Southern Asian Monsoon (Peng et al., 2015a). Due to the high-altitude location of the Beiluhe station, snow event commonly occurs in May to June and late September to October. Because of intensive solar radiation and surface temperature, the snow melts or sublimates in short time scale $(10^{0} 10^{2}$ hour), i.e., little/no snow accumulation occurs for long time (>3 day). Therefore, the Beiluhe region provides an unique opportunity to investigate the different effects of rain, snow, and snowmelt on the air–surface Hg(0) flux over different timescales.

107 2.2 Measurement of air-surface Hg(0) flux

The dynamic flux chambers (DFCs) technique was widely used to investigate Hg(0) flux between air–surface interface because it is inexpensive, portable, easy to set up and operate (e.g., Kim and Lindberg, 1995; Carpi and Lindberg, 1998; Gustin et al., 2006; Wang et al., 2006; Dommergue et al., 2007; Fu et al., 2008a; Kocman and Horvat, 2010; Edwards and Howard, 2013). Air–surface Hg(0) flux obtained by DFCs technique was calculated using Eq. (1),

113
$$F = Q \frac{C_0 - C_i}{A}$$
 (Eq. 1)

where *F* is the Hg(0) flux (ng m⁻² h⁻¹), *Q* is the flushing flow through the chamber (m³ h⁻¹), *A* is the footprint of the chamber (m²), C_0 and C_i (ng m⁻³) is air Hg(0) concentrations at outlet and inlet of the chamber, respectively. Positive flux values indicate Hg(0) emission from the surface into the air; negative flux values represent Hg(0) deposition to the surface from the air.

118 In this study, quartz chambers were constructed for measuring Hg(0) flux and exploring the effect of different rainfall depths and radiation condition on the Hg(0) flux. Quartz glass has many advantages 119 120 as construction material of chamber for determining Hg(0) flux in background soils. First, it has high transmittance of the full spectrum of solar radiation, especially UV waveband (Fig. S1 in Supplement). 121 Therefore, quartz chamber is suitable to determine the more "actual" Hg(0) flux because the short 122 wavelength of solar radiation has been found to have important effect on Hg(0) dynamics at the air-soil 123 interface (Moore and Carpi, 2005; Bahlmann et al., 2006). Second, it has low potential for Hg(0) 124 adsorption and is easy to clean by heating to remove Hg bonding on the surface (Ci et al., 2016a). This 125 will decrease the systematic blank of measurement, which is critical for investigating Hg(0) flux over 126 background soils (Carpi and Lindberg, 1998). 127

Our semi-cylindrical quartz chamber was 8 cm high and 24 cm length with a footprint of 0.0384 m⁻ (0.16 m x 0.24 m) and an internal volume of 2.41 L, which is similar to previous studies (Eckley et al., and reference therein). The chamber had nine inlets (8 mm in diameter) and three outlets which were on the two opposite section of the chamber. The inlet sampling tube was placed near the ground surface (3 cm above the surface) directly near the inlet of the chamber. A flushing ambient air was drawn by vacuum pump (KNF, Inc. Germany) with 3.0 L min⁻¹ (0.18 m³ h⁻¹) through the chamber.

Since the harsh environment condition and the unstable power supply, the usage of the commercial 134 135 automatic Hg analyzer (such as Tekran 2537) to conduct filed measurements of Hg(0) flux is 136 challenging in the Beiluhe station. Therefore, air Hg(0) concentrations in both inlet and outlet of the chamber were monitored manually by gold trap simultaneously with a 2–3 h intervals (Ci et al., 2016b). 137 The air was pumped through gold trap using air pump (KNF, Inc. Germany) with 0.50 L min⁻¹ (0.03 m³ 138 h^{-1}). Hg(0) collected on gold traps was quantified on site by a cold vapor atomic fluorescence 139 spectrophotometer (CVAFS, Model III, Brooks Rand, USA) using two-stage gold amalgamation 140 141 method (Fitzgerald and Gill, 1979; Ci et al., 2011, 2016a). Gold trap efficiencies were determined in laboratory (Hg(0) concentration: 3.2 to 13.4 ng m⁻³) and field (Hg(0) concentration: ~ 1 to 2 ng m⁻³ to 142 9.4 ng m^{-3}), and multiple measurements using gold traps in series showed no breakthrough at the sample 143 flow rate of 0.50 L min⁻¹ for 5 hours. The method detection limit was 0.03 ng m⁻³ and precision was 144 3±2%. 145

The turnover time obtained from this protocol was 0.68 min, which is similar to previous studies (Eckley et al., 2010 and reference therein). The flow rates of air both the inlet and outlet of chamber were adjusted by a needle valve and controlled by a rotameter. Prior to the measurement, the rotameters were calibrated by a mass flow meter and a volumetric gas meter. The accuracy of flow rate was $\pm 3\%$. The sampling control system was installed in the tent near the soil plot (<2 m).

151 In this study, a bare soil plot of 2×2 m was chosen and separated to four subplots (1 x 1 m, labeled 152 as Subplot A to D) to measure Hg(0) flux and further to investigate the effects of different wavelengths of solar radiation on the Hg(0) exchange. The soil parent materials in the study site is mainly composed 153 154 of sand (>99%) (Peng et al., 2015a). Geologic unit of this soil plot is representative of major lithologic 155 units of the Beiluhe region. The study was conducted in four campaigns (June, September, and 156 December 2014 and May–June 2015), covering typical intra-annual meteorological condition in the study region. It is well-known that the application of the chamber isolates the soil surface from air 157 158 turbulence and rain/dew/frost/snow, altering many environmental parameters that influence Hg(0)production/consumption and deposition/emission at air-soil interface (Sommar et al., 2012 and 159 160 references therein). In the Beiluhe region, the rain/snow/dew/frost commonly occurs in short time scale $(10^{1}-10^{2} \text{ minutes})$ because of the high-altitude location and great variation of temperature and unstable 161

weather conditions. To minimize the effect of great variation of soil surface condition on Hg(0) flux 162 163 measurements, when only to measure Hg(0) flux, we used the same chamber to measure Hg(0) flux in 164 four subplots (Subplot A to D) in turn. For the rainy and snowy days, if possible, the chamber was 165 moved to next subplot generally after the rain or snow because studies confirmed the significant influence of precipitation on Hg(0) flux in short time scale (Lindberg et al., 1999; Gustin and 166 Stamenkovic, 2005; Johnson et al., 2003; Song and Van Heyst, 2005; Lalonde et al., 2001, 2003; 167 Dommergue et al., 2003, 2007, 2012; Fa n et al., 2007; Bartels-Rausch et al., 2008; Brooks et al., 2008; 168 169 Mann et al., 2014, 2015). For the days without precipitation, the chamber was moved to next subplot before sunrise to capture the effect of frost or dew on air-surface Hg(0) flux in the light. 170

In this study, all materials in contact with Hg(0) were quartz, Teflon or borosilicate glass. The 171 chambers and tubing were rigorously acid washed (Ci et al., 2016a). The quartz chambers were heated 172 to 650 $^{\circ}$ C for 2 h prior the measurement to further remove all Hg (Ci et al., 2016a). System blanks of 173 the four chamber systems were systemically inspected on site by placing acid-cleaned Teflon filter 174 beneath the chamber and routinely inspected before and after the measurements under the field 175 condition. The overall blank results were taken as the average of all chamber blanks for each particular 176 177 day or from the entire period if continuous monitoring was conducted. The blank values of the four chambers were found to be very low (mean \pm SD: -0.02 ± 0.03 ng m⁻² h⁻¹; range: -0.20-0.07 ng m⁻² h⁻¹) 178 179 and were not significantly different (p>0.05) throughout the entire study. We also found that the mean 180 blank values were not significantly different (p>0.05) from zero and were insignificant compared to the 181 measured Hg(0) fluxes (see below), then Hg(0) flux data was not blank-corrected in this study.

182 **2.3 Controlled field experiments**

183 2.3.1 Water addition

To deeply explore the effect of water addition, we chosen another similar soil plot with homogeneous soil property to conduct controlled field experiments to investigate the effect of different rainfall depths on Hg(0) flux over different timescales (from minutes to hours). The controlled experiments were performed during May–June 2015 campaign since this period had high surface temperature and low precipitation (Fig. 2). In the Beiluhe station, hourly rainfall depth rarely exceeds

189 15 mm (Peng et al., 2015a). Therefore, we designed four different treatments of rainfall depth (0 mm, 1 190 mm, 5 mm, and 15 mm). The water addition to the dry soils commenced at night (01:40) on 30 May 191 2015 to exclude the effect of photochemical process in the first hours of experiments. We added the Milli-Q water (Hg concentration $< 0.2 \text{ ng L}^{-1}$) to the inside and outside of the chamber by pre-clean 192 plastic syringe within 10 min to simulate the three different rain depths. Four chambers were used to 193 194 simultaneously measure Hg(0) flux over these four treatments for 22 hours (from 01:00 to 23:00) with the same protocol described in the Methods section. Hg(0) flux was measured with 20 min intervals in 195 the first hours (from 01:00 to 04:20) of the experiments to investigate the temporal variation of Hg(0) 196 flux in the short timescale, and with 1 hour intervals for the rest period of the experiments. 197

198 **2.3.2 Different wavebands of solar radiation**

199 The QTP is characterized by high solar radiation with intense UV radiation. We performed the controlled experiment to quantify the role of different wavebands of solar radiation (UVB, UVA and 200 visible light) in air-soil Hg(0) flux. Four chambers with different exposure treatments were used to 201 202 measure Hg(0) flux simultaneously in the daytime. Chamber-A was used to measure the Hg(0) flux in 203 the natural light. Chamber-B and Chamber-C were covered with UVB filter and UV filters to remove the corresponding wavebands from the natural light, respectively. Chamber-D covered with foil was 204 used to measure Hg(0) flux in the dark. The experiments were performed in four days without 205 precipitation (21–22 December 2014 and 29–30 May 2015) to exclude the effect of precipitation. Hg(0) 206 207 flux triggered by UVB, UVA and visible light was equal to difference of flux between Chamber-A and Chamber-B, between Chamber-B and Chamber-C, and between Chamber-C and Chamber-D, 208 respectively. The transmittance of UVB filter and UV filter was shown in Fig. S1 in Supplement. 209

210 2.4 Determination of soil Hg

Surface soil samples (0–2 cm) were collected from four soil subplots during June 2014 campaign. Soil samples were freeze-dried and homogenized for total Hg determination using a Milestone's DMA direct Hg analyzer (detection limit: 0.01 ng Hg or 0.15 ug kg⁻¹) following the EPA Method 7473 (Briggs and Gustin, 2013), and the analytical accuracy was 3%.

215 **2.5 Measurements of environmental variables**

A meteorological station that located 60 m from the soil plot was used to collect the following 216 environmental variables: air temperature ($^{\circ}$), relative humidity (%), wind speed (m s⁻¹), precipitation 217 (mm), photosynthetically active radiation (PAR, μ mol m⁻² s⁻¹), surface soil temperature (°C). The 218 surface soil temperature was monitored by an ASI-111 Precision Infrared Radiometer (Campbell 219 Scientific Inc. USA). This sensor was installed on a bar 0.8 m above the soil surface and provided a 220 non-contact measurement of the surface temperature. We also measured the soil temperature at 1.0 cm 221 soil depth at the inside of chamber, and no significant difference was found between the soil 222 223 temperature in the outside and inside of chamber. Details on the measurements of environmental variables are given in Peng et al. (2015a). The thickness of snowpack was measured manually. 224

3 Results and Discussion

226 **3.1 Soil Hg**

Soil Hg concentrations of four subplots varied from 13.11 ± 0.51 to $12.83 \pm 0.81 \,\mu\text{g kg}^{-1}$, suggesting that the study region is a typical background soil for Hg. Soil Hg concentrations and air–soil Hg(0) flux of four subplots were not statistically different (p>0.05), indicating the properties of the soil plot were homogeneous.

231 **3.2 Hg(0) in ambient air**

Figure 2 shows the temporal variation of air Hg(0) concentrations inside and outside of chamber, 232 air-surface Hg(0) flux and environmental variables during four campaigns in 2014–2015. Hg(0) 233 concentrations of ambient air ranged from 0.93 to 1.78 ng m⁻³ with a mean of 1.36 \pm 0.17 ng m⁻³ 234 (n=361), which were slightly lower than those in typical Northern Hemisphere background region (~1.5 235 ng m⁻³, Sprovieri et al., 2007; Ebinghaus et al., 2011). To our knowledge, four measurements (including 236 this study) have been conducted to determine atmospheric Hg over the OTP (see Fig. 1 for the 237 locations). The gradient of atmospheric Hg(0) over the QTP was characterized by high concentrations in 238 Mt. Gongga (3.98 ± 1.62 ng m⁻³, Fu et al., 2008b) and Mt. Waliguan (1.98 ± 0.98 ng m⁻³, Fu et al., 239 2012), moderate concentrations in the Beiluhe (1.36 \pm 0.17 ng m⁻³, this study), and low concentrations 240 in the Nam Co (0.96 \pm 0.19 ng m⁻³, Yin et al., 2015). It seems that the sampling station with relatively 241

- long distance from the source region of atmospheric Hg(0) (i.e., the Central China, Streets et al., 2005)
- had relatively low atmospheric Hg(0) concentrations (Fig. 1). Atmospheric Hg(0) concentrations were
- high in three warm campaigns and low in winter campaign in the Beiluhe station (Fig. 3), which is
- consistent with Mt. Gongga (Fu et al., 2008b) and Mt. Waliguan (Fu et al., 2012).

246 **3.3 Air-surface Hg(0) flux and influencing factors**

247 **3.3.1 Temporal variation of Hg(0) flux**

The mean of air–surface Hg(0) flux in the entire study period were 2.86 ng m⁻² h⁻¹ (25.05 μ g m⁻² y⁻ 1), indicating that surface soils were net emission source of Hg(0). Hg(0) flux in this study is comparable to those over background soils (–10–10 ng m⁻² h⁻¹, Wang et al., 2006; Ericksen et al., 2006; Fu et al., 2008a), but greatly lower than those over Hg-enriched soils (10²–10³ ng m⁻² h⁻¹, Gustin et al., 1999; Wang et al., 2007; Edwards and Howard, 2013), indicating that soil Hg concentrations may be the dominant factor for controlling the magnitude of Hg(0) emission flux (Agnan et al., 2016 and reference therein).

Figure 2 shows that the Hg(0) flux was highly variable. The highest Hg(0) emission fluxes of 28.46 ng m⁻² h⁻¹ were observed at 13:00–15:00 on 13 September 2014 after a rain event on dry soils. The highest Hg(0) deposition fluxes of -6.24 ng m⁻² h⁻¹ were observed at nighttime over the cold and dry surface soil during December 2014 campaign (03:30–06:30, 24 December 2014).

Hg(0) flux generally showed the diurnal pattern with high emission in daytime and remarkable 259 260 deposition in nighttime, especially on days without precipitation (Fig. 2). Many studies have confirmed that solar radiation is one of the most important drivers for soil Hg(0) emission (Xin and Gustin, 2007; 261 262 Choi and Holsen, 2009; Kocman and Horvat, 2010); high surface temperature also facilitates Hg(0) production and subsequent emission (Park et al., 2014). Therefore, the two environmental variables 263 jointly regulate the diurnal pattern of Hg(0) flux. An in-depth discussion on synergistic effects of solar 264 radiation and surface temperature on Hg(0) flux is provided below. Interestingly, the diurnal pattern of 265 Hg(0) flux of each day during December 2014 campaign was almost identical, which may be associated 266 with very similar weather conditions throughout the entire campaign. 267

Hg(0) flux showed pronounced seasonality with high emission in three warm campaigns (June 2014: 4.95 ng m⁻² h⁻¹; September 2014: 5.16 ng m⁻² h⁻¹ and May–June 2015: 1.95 ng m⁻² h⁻¹) and net low deposition during winter campaign (December 2014: -0.62 ng m⁻² h⁻¹) (Fig. 3). Similar seasonality has been reported in many other studies (e.g., Gabriel et al., 2006). As discussed below, in warm seasons, some environmental variables, such as high solar radiation, surface temperature and precipitation, facilitate the soil Hg(0) emission.

3.3.2 Effect of precipitation (rain and snow)

Firstly, the effect of rain events on Hg(0) flux was investigated. We found that the Hg(0) emission 275 flux increased immediately following the rainfall (Fig. 2), which is consistent with many other studies 276 (Gustin and Stamenkovic, 2005; Johnson et al., 2003; Lindberg et al., 1999; Song and Van Heyst, 2005). 277 Previous studies suggested that the dramatic increases in Hg(0) emission may be attributed to the 278 physical displacement of Hg(0) present in soil air and desorption of loosely bound Hg(0) on soil 279 particles by the infiltrating water (Johnson et al., 2003; Gustin and Stamenkovic, 2005). Notably, Fig. 2 280 281 displays that the pulse of Hg(0) emission after the rainfall was also observed at nighttime (such as 0:00 to 01:00 on 4 September 2014). Similar phenomenon was also documented by our controlled 282 experiments (see below). This indicates that the immediate increase in Hg(0) emission might not be 283 controlled by photochemical processes but by physical processes. 284

285 Soil moisture condition may also significantly regulate Hg(0) flux over relatively long timescales (from hours to several days). Therefore, many experiments studied the effect of water addition on the 286 magnitude and pattern of air-soil Hg(0) flux over different timescales (Johnson et al., 2003; Gustin and 287 Stamenkovic, 2005). However, most of studies were performed in controlled laboratory or mesocosm 288 settings under certain well-defined, but not necessarily environment relevant conditions (Johnson et al., 289 2003; Gustin et al., 2004; Gustin and Stamenkovic, 2005; Song and Van Heyst, 2005; Kocman and 290 Horvat, 2010; Corbett-Hains et al., 2012; Park et al., 2014). In this study, it was also challenging to 291 reveal the effect of rainfall on Hg(0) flux over relatively long timescales via field measurement since 292 the intermittent rain events occurred irregularly during June 2014 and September 2014 campaign (Fig. 293

294 2). Therefore, we performed the controlled field experiments (Section 2.3.1) to explore the effect of
295 different rainfall depths on Hg(0) flux over different timescales (from minutes to hours).

The high-time resolution measurements captured the immediate and dramatic increases in Hg(0)296 emission flux after the watering of dry soils (Fig. 4). The baseline Hg(0) flux of 0 mm treatment was 297 298 used as the benchmark for the different rainfall depth treatments to be compared against. Obviously, the 299 higher amount of water addition resulted in longer duration and higher accumulative flux of Hg(0)emission pulse. The duration of Hg(0) emission pulse for 1 mm and 5 mm treatment was < 20 min 300 301 (from 01:40 to 02:00) and \sim 40 min (from 01:40 to 02:20), respectively, which was lower than that of 15 302 mm treatment (~ 80 min, from 01:40 to 03:00). The duration of Hg(0) emission for 15 mm treatment in the daytime was also longer than that of 1 mm and 5 mm treatment (Fig. 4). 303

304 As shown in Fig. 4, the cumulative flux of Hg(0) emission during the entire study period mainly included two fractions: the pulse of Hg(0) emission after the watering (i.e., emission flux by watering), 305 and the Hg(0) emission during the daytime (i.e., emission flux by radiation). Figure 5 displays that both 306 "emission flux by watering" and "emission flux by radiation" for 15 mm treatment were significantly 307 308 higher than those of 1 mm and 5 mm treatment. As mentioned above, the dramatic increase in Hg(0)309 emission after the simulated rain can be explained by physical displacement of interstitial soil air by the 310 infiltrating water. The long emission duration and large immediate emission flux for soil plot with high 311 water addition can be explained by that the more water needed longer time to percolate the soil column 312 and displaced more soil Hg(0). Many previous studies suggested that the magnitude of Hg(0) emission with a rainfall or stimulated rain depended on soil moisture condition, i.e., if the amounts of water 313 314 received by the soils was less than needed to saturate, the soil surface showed an immediate increase in 315 Hg(0) emission; after the soil became saturated, Hg(0) emission from surface soil was suppressed (Klusman and Webster, 1981; Lindberg et al., 1999; Johnson et al., 2003; Gustin and Stamenkovic, 316 2005). In this study, the pulse of Hg(0) emission flux for 15 mm treatment was significantly higher than 317 that of 5 mm and 1 mm treatment (Fig. 5). The field water capacity and bulk density of soil in the 318 Beiluhe region is about 28% and 1 g cm⁻³ (Peng et al., 2015b), indicating that the 5 mm treatment may 319 induce the upper soil to saturate in short timescale since the duration of water addition was short (< 10 320 min). However, the pulse of Hg(0) emission for 15 mm treatment was significantly higher than that of 5 321

mm treatment. The surface soils with high sand content in the Beiluhe region have a high rate of water infiltration and subsequently great infiltration depth. This process potentially increases the displacement of soil Hg(0) and facilitates Hg(0) emission, as mentioned above. Therefore, in the field condition, the duration and flux of pulse Hg(0) emission following water addition depends not only on how much water received and soil moisture condition but also soil texture and soil water dynamics.

327 The water addition also increased the Hg(0) emission in the daytime, showing more water added, longer duration of Hg(0) emission, and more Hg(0) emitted (Fig. 4 and Fig. 5). After the surface soil 328 329 was visibly dry, Hg(0) flux over soil plots with water addition had no significant difference from that of 330 the soil plot without water addition (i.e., 0 mm treatment). This result is consistent with many other controlled studies. For example, Gustin and colleagues (Johnson et al., 2003; Gustin and Stamenkovic, 331 332 2005) found that once the soil water content became less than saturated, Hg(0) emission flux would be significantly enhanced especially during the daytime, and once sufficient drying occured, the magnitude 333 334 of Hg(0) emission flux tended to gradually decrease. Investigators suggested that as the water evaporates and soil dries, capillary action drives the upward movement of water and chemicals 335 (including Hg components) and recharges the Hg pool in surface soils (i.e., the "wick effect") and 336 337 subsequently favors the Hg(0) production and emission via photochemical processes in the light (Gustin 338 and Stamenkovic, 2005). In our study, even for the wettest soil plot (i.e., 15 mm treatment), the surface 339 soils were visually unsaturated in the daytime because of the low water retention, high infiltration rate 340 of local soils and intensive solar radiation. Therefore, the pattern of Hg(0) emission for soil plots with 341 high water addition is comparable to those of the above-mentioned studies.

342 Secondly, the effect of snow events on Hg(0) flux were investigated. One of the most significant 343 differences between the rainfall and snowfall on the effect of Hg(0) exchange was that the snowfall did 344 not induce the remarkable pulse of Hg(0) emission. For example, at 10:10 on 11 June 2014, a heavy snowfall occurred and continued to 11:20. The great thickness of snowpack reached to ~12 cm. 345 However, no remarkable pulse of Hg(0) emission was observed during the snowfall. Instead, the Hg(0)346 dynamics at air-snow interface showed the clear diurnal pattern with high emission in daytime and 347 348 deposition or emission albeit rather small in nighttime. This finding is consistent with previous studies 349 on air-snow interface (Cobbett et al., 2007). It can be seen that the pattern of Hg(0) dynamics at air-

snow interface was similar with that at air–soil interface, indicating that Hg(0) emission from surface snow was also mainly regulated by photochemical processes (Ferrari et al., 2005; Dommergue et al., 2003, 2007). However, it is well-known that the snowpack is a porous matrix, and gases are subjected to diffusion in the snowpack. Therefore, our measurements of Hg(0) flux at air–snow interface did not exclude the effect of Hg(0) dynamics at soil–snow interface, especially the low thickness (< 12 cm) of snowpack in the study.

We found that the snow melting led to the remarkable peak of Hg(0) emission. For example, 356 357 during the sunrise of 12 June 2014, a precipitation with rain and snow induced the snowpack (12 cm) to 358 melt suddenly and completely (i.e., the bare soil with no surface snow), a pulse of Hg(0) emission (~8) ng $m^{-2} h^{-1}$) was observed, which was the largest Hg(0) emission flux during June 2014 campaign. We 359 supposed that the great increase in Hg(0) emission by snowmelt in this study was consistent with the 360 effect of rainfall, i.e., the displacement of soil Hg(0) during the snowmelt permeation of the soil column 361 362 resulted in the dramatic increase in Hg(0) emission. At present, the study on the effect of snowpack melting on Hg(0) emission is limited. Cobbett et al. (2007) also found the remarkable increase in Hg(0)363 emission in Canadian Arctic during the snow melt, although the Hg(0) flux was relatively small. 364

365 Finally, the effect of precipitation (including rain and snow) on daily Hg(0) flux was investigated. The above-mentioned results and discussion suggest that the precipitation has great potential to 366 facilitate soil Hg(0) emission over different timescales via physical, chemical and biological processes. 367 368 The main processes include the displacement of soil Hg(0) by water, the "wick effect" to increase the photo-reducible Hg(II) pool in surface soils, and the increased soil moisture to promote the biotic and 369 370 abiotic reduction of Hg(II). Another well-documented process is that the atmospheric wet deposition of 371 Hg will increase the Hg pool in surface soils and the newly deposited Hg is very active to reduce to Hg(0) (Hintelmann et al., 2002), although our study did not focus on this issue. During June 2014 372 campaign, no precipitation occurred in the first two days (6–7 June 2014), but the rest days were 373 374 rainy/snowy days (Fig. 2). We tried to use the daily Hg(0) flux of the two sunny days as the benchmark to compare with those of rainy/snowy days to investigate the effect of precipitation on the Hg(0) flux 375 376 over the timescale of one day. Figure 6 shows that the daily Hg(0) flux for rainy/snowy days were higher (ranging from 16% to 154%) than the mean of the two sunny days. The result indicates that the 377

precipitation increased soil Hg(0) emission on the timescale of one day, although the low solar radiation
and temperature on rainy/snowy days would potentially decrease soil Hg(0) emission, as mentioned
above.

381 3.3.3 Effect of solar radiation and soil temperature

382 Almost all laboratory experiments and field measurements, including this study, show that the high 383 solar radiation and elevated soil temperature synergistically facilitate the soil Hg(0) emission (Edwards and Howard, 2013; Park et al., 2014). The following hypotheses have been proposed to explain the role 384 of solar radiation and temperature in promoting soil Hg(0) emission, including (1) solar radiation 385 386 promotes the photo-reduction of Hg(II) in surface soils to form Hg(0) in short time scale; (2) solar 387 radiation and high soil temperature reduce the apparent activation energy of Hg(0) desorption and 388 increase Hg(0) emission from surface soils; and (3) the high soil temperature favors the Hg(0)production in soil column by biotic and abiotic processes (Carpi and Lindberg, 1998; Gustin et al., 389 390 2002).

Many studies used the Arrhenius equation (Eq. 2) to quantitatively investigate the relationship between soil temperature and Hg(0) flux.

393
$$F = Ae^{-Ea/RT} \text{ or } \ln(F) = \ln(A) - \frac{Ea}{RT} \text{ (Eq. 2)}$$

where F is the Hg(0) flux (ng m⁻² h⁻¹), R is the gas constant, T is the soil temperature (K), A is the pre-394 395 exponential factor and Ea is the apparent activation energy. A plot of $\ln(F)$ versus 1/T obtains a straight 396 line with intercept equal to the log of the A, and the slop equal to -Ea/R. Theoretically, the concept of 397 the apparent Ea refers to the thermally controlled reaction. Therefore, Hg(0) flux induced by light and 398 precipitation should be excluded from the correlation analysis. However, in many previous studies, 399 especially for the field measurements, the bulk Hg(0) flux in the light was generally used to explore the 400 contribution of solar radiation or temperature to Hg(0) flux and did not isolate the respective effect of the two factors (Fu et al., 2008a). This will systematically overestimate or underestimate the 401 402 contribution of solar radiation and temperature on soil Hg(0) emission depending on the source or sink 403 of soil for Hg(0) in the dark. Only in some controlled experiments, the separated data was used to

404 explore the respective role of radiation and temperature in soil Hg(0) emission (e.g., Kocman and405 Horvat, 2010).

In this study, for respectively determining the contribution of solar radiation and temperature on the Hg(0) flux, besides Hg(0) flux was measured in the natural light, Hg(0) flux in the dark was also measured simultaneously with a foil-covered chamber. The temperature-corrected Hg(0) flux (i.e., bulk Hg(0) flux in the light – Hg(0) flux in the dark) in daytime (PAR > 0) was considered to be the contribution of the solar radiation. As mentioned above, the effect of precipitation should be excluded from the data set, therefore we only collected Hg(0) flux data on days without precipitation during December 2014 and May–June 2015 campaign.

Figure 7 displays the temporal variation of bulk Hg(0) flux in the light, Hg(0) flux in the dark, net 413 414 Hg(0) flux in the light (i.e., bulk Hg(0) flux in the light – Hg(0) flux in the dark) and the environmental variables. Obviously, changes in solar radiation had a greater influence on soil Hg(0) flux than did 415 416 changes in soil temperature. The data showed that the soil served as a Hg(0) sink during all study days 417 in December 2014 campaign in the dark with high deposition flux in low soil temperature and low 418 deposition flux in high soil temperature. During study days of May–June 2015 campaign, the soils 419 served as a very low Hg(0) source in the midday with relatively high soil temperature. This finding is consistent with many studies in background soils (Ericksen et al., 2006; Gustin et al., 2006; Fu et al., 420 421 2008a; Edwards and Howard, 2013). It indicates that the soil temperature plays an important role in 422 Hg(0) dynamics at the air-soil interface, i.e., low soil temperature favors to absorb Hg(0) or reduce Hg(0) emission (e.g., Park et al., 2014 and references therein). 423

424 After the temperature corrected, except for the midday of study days during May–June campaign, 425 the net Hg(0) flux in the light was higher than the bulk Hg(0) flux. The positive linear correlation was 426 found between cumulative PAR and cumulative Hg(0) flux in the daytime, although cumulative PAR 427 only explained ~28% of variation in cumulative Hg(0) flux in the daytime (Fig. S2 in Supplement).

We used the Hg(0) emission data set in the dark to calculate the *Ea* using the Arrhenius equation. Since the soils in the dark was the sink of atmospheric Hg(0) in most of the study period, only limited data set (n=9) can be used (Fig. S3 in Supplement). The *Ea/R* for Hg(0) emission from our remote soils

with extremely low Hg concentrations (~12 ug kg⁻¹) was 30.40. Table S1 in Supplement lists the *Ea/R* for different soils with large variation of soil Hg concentrations, including this study, and shows that the *Ea/R* of Hg(0) emission from soils with low Hg concentrations was higher than those of soils with high Hg concentrations and significantly lower than that of theoretical value (7.31) of elemental Hg. It indicates that surface soils with high Hg concentrations has great potential to emit Hg(0). This trend is consistent with the laboratory study of Bahlmann et al. (2006), although the availability of Hg in soils also significantly regulate Hg(0) emission (Bahlmann et al., 2006; Kocman and Horvat, 2010).

Figure 8 shows that UV radiation was the dominant waveband of solar radiation for Hg(0)
emission in the daytime, contributing >80% of Hg(0) emission in the light, and the contribution of UVB
radiation accounted for >50% in all study days. This finding is consistent with previous laboratory
studies (Moore and Carpi, 2005; Bahlmann et al., 2006; Xin et al., 2007).

442 **4 Conclusions and implication**

In this study, we measured the Hg(0) flux between the air and surface permafrost soil in the QTP. We also performed the controlled field experiments to explore the effect of precipitation and different wavebands of solar radiation on the air–soil Hg(0) exchange. The result showed that the environmental conditions, including solar radiation, soil temperature and precipitation, greatly influenced the Hg(0) exchange between air and surface.

This study and other field measurements and laboratory experiments have clarified that the fate 448 449 and transport of soil Hg is very sensitive to the environmental variables (Krabbenhoft and Sunderland, 450 2013). Therefore, our results have several important implications to the Hg biogeochemical cycle in the soils of QTP under the rapid climate warming and environmental change. Firstly, the increased surface 451 452 temperature in the QTP will potentially promote the remobilization of soil Hg. Field measurements and modeling study have revealed that the surface temperature in the QTP is increasing, and the warming 453 454 trend exceeds those for the Northern Hemisphere and the same latitudinal zone (Kang et al., 2010). 455 Secondly, the increased UV radiation in the QTP may enhance Hg(0) emission from surface soils. UV radiation reaching the surface of the QTP is estimated to increase because of the decrease of 456 457 stratospheric O₃ (Zhou et al., 2013). Our result and many above-mentioned studies show that UV

- radiation plays the primary role in promoting the surface Hg(0) emission in the daytime. Thirdly, the
- temp-spatial pattern of precipitation in the QTP is also altering (Kang et al., 2010), which potentially

alters the flux and temp-spatial pattern of air-soil Hg(0) exchange in this region because of the

461 importance of precipitation on the Hg(0) exchange. However, this study was just the beginning to

- 462 explore the effect of climate change on the terrestrial Hg cycle in the QTP. More researches are needed
- in the future.

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Figure 1. Locations of the Beiluhe station (4760 m a.s.l., this study), Mt. Waliguan (3816 m a.s.l., Fu et al., 2012), Mt.

Gongga (1640 m a.s.l., Fu et al., 2008b) and Nam Co (4730 m a.s.l., Yin et al., 2015) where atmospheric Hg were

723 determined.



Figure 2. Temporal variation of environmental variables, air Hg(0) concentrations inside and outside of chamber, and airsurface Hg(0) flux at the Beiluhe station in the central QTP during four campaigns in 2014–2015.





Figure 3. Seasonal variation of Hg(0) concentration in ambient air and air-surface Hg(0) flux during four campaigns at the
Beiluhe station in the central QTP in 2014–2015.



Figure 4. Temporal variation of Hg(0) flux over four soil plots with different treatment of water addition (T0: 0 mm
treatment, T1: 1 mm treatment, T5: 5 mm treatment and T15: 15 mm treatment) and the environmental variables.



Figure 5. Increased Hg(0) emission for three different treatments (1 mm, 5 mm and 15 mm addition of water) compared with

the 0 mm treatment during the controlled experiment on 30 May 2015.





Figure 6. Daily Hg(0) flux and daily precipitation in June 2014 campaign.



Figure 7. Temporal variation of bulk Hg(0) flux in the light, Hg(0) flux in the dark, and net Hg(0) flux in the light (bulk
Hg(0) flux in the light–Hg(0) flux in the dark) in six study days without precipitation during December 2014 campaign and
May–June 2015 campaign.

Figure 8. Cumulative Hg(0) emission flux in daytime triggered by UVB, UVA and visible light in four study days during
December 2014 campaign and May–June 2015 campaign.