



## Wet deposition of mercury at a remote site in the Tibetan Plateau: Concentrations, speciation, and fluxes

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### HIGHLIGHTS

- ▶ We present a 2-year measured data of wet Hg deposition at a remote site in Tibet.
- ▶ Hg<sub>p</sub> dominated the concentration and flux of Hg<sub>T</sub> in the wet-deposition samples.
- ▶ The precipitation amount was the governing factor affecting Hg<sub>T</sub> wet deposition flux.
- ▶ Measured annual Hg<sub>T</sub> flux was comparable to the estimates from environmental records.

### ARTICLE INFO

#### Article history:

Received 23 May 2012

Received in revised form

3 September 2012

Accepted 5 September 2012

#### Keywords:

Mercury  
Concentration  
Speciation  
Wet deposition flux  
Nam Co Station  
Tibetan Plateau

### ABSTRACT

Precipitation samples collected at a remote high elevation site (i.e., Nam Co Station, 4730 m a.s.l.) in the southern Tibetan Plateau were analyzed for total mercury (Hg<sub>T</sub>) between July 2009 and 2011, particulate-bound mercury (Hg<sub>p</sub>) between July 2010 and 2011 and methylmercury (MeHg) from July through August of 2009. The volume-weighted mean (VWM) concentrations and wet deposition fluxes of Hg<sub>T</sub> and MeHg in precipitation were 4.8 ng L<sup>-1</sup> and 1.75 μg m<sup>-2</sup> yr<sup>-1</sup>, 0.031 ng L<sup>-1</sup> and 0.01 μg m<sup>-2</sup> yr<sup>-1</sup>, respectively. VWM Hg<sub>T</sub> concentration was approximately two times higher during the non-monsoon season than during the monsoon season, while 83% of the Hg<sub>T</sub> wet deposition fluxes occurred during the monsoon season. The Hg<sub>T</sub> and MeHg concentrations are comparable to the reported data for some of the most remote alpine and polar regions worldwide (e.g., Churchill), but the wet deposition fluxes of Hg<sub>T</sub> and MeHg were among the lowest in the world. Analysis of Hg speciation has presented that Hg<sub>p</sub> and MeHg concentrations are high, making up 71.2% and 1.82% of the Hg<sub>T</sub> on average (VWM), respectively. The high Hg<sub>p</sub>%, as well as a significantly positive between Hg<sub>T</sub> and Hg<sub>p</sub> ( $R^2 = 0.91$ ;  $n = 44$ ;  $p < 0.001$ ), confirmed that atmospheric deposition of Hg in the Tibetan Plateau was occurring in the form of Hg<sub>p</sub>. A decreasing trend in Hg<sub>T</sub> concentrations with increasing amount of precipitation ( $R^2 = 0.08$ ;  $N = 101$ ;  $p < 0.005$ ) was found at Nam Co Station, indicative that scavenging of Hg<sub>p</sub> from the atmosphere was an important mechanism contributing Hg to precipitation. The precipitation amount, rather than Hg<sub>T</sub> concentration, was found to be the governing factor affecting Hg<sub>T</sub> wet deposition flux. Moreover, a comparison between measured wet deposition flux of Hg at Nam Co Station and the estimates from environmental records indicated that both snowpits and lake sediments appear to be reliable archives for estimating historical Hg accumulation rates over the Tibetan Plateau.

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### 1. Introduction

Mercury (Hg), a highly toxic trace metal, is of increasing interest lately due to its impact on environmental and human health, and the potential bioaccumulation of methyl Hg (MeHg) (Selin, 2009). Due to Hg's propensity to be transported airborne from polluted

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sources, atmospheric deposition is an important source of regional and/or long-range transported Hg to aquatic and terrestrial environments (Landis and Keeler, 2002; Rolfhus et al., 2003; Wiener et al., 2003), particularly in the remote areas (Jackson, 1997; Fitzgerald et al., 1998; Loewen et al., 2007). Moreover, it has been shown that atmospheric deposited Hg may be more biologically available to aquatic and terrestrial ecosystems than in-situ Hg, or Hg that is transported to surface waters via runoff or groundwater (Mason et al., 1999). Once deposited into the environment, inorganic Hg becomes available for methylation producing MeHg, which is the bioaccumulative and neurotoxic form of Hg. As a result, MeHg may pose a potential serious threat to human health and wildlife after being bioaccumulated and biomagnified through food webs (Wolfe et al., 1998; Krabbenhoft et al., 2002; Wiener et al., 2003).

Hg mainly exists in the atmosphere in three operationally defined forms: gaseous elemental mercury (GEM,  $\text{Hg}^0$ ), reactive gaseous mercury (RGM, comprised of  $\text{Hg}^{2+}$  compounds), and particulate-bound mercury ( $\text{Hg}_p$ ). Globally, atmospheric Hg is dominated by GEM; RGM and  $\text{Hg}_p$  are thought to be rapidly removed by dry deposition and effectively wet scavenged by precipitation (Schroeder and Munthe, 1998). Dry deposition is Hg flux in the absence of precipitation and is believed to include all three Hg phases, whereas wet deposition is defined as the air-to-surface flux in precipitation (occurring as rain, snow), which scavenges mainly RGM and  $\text{Hg}_p$  from the atmosphere due to their higher surface reactivity and water solubility (Lindberg and Stratton, 1998; Schroeder and Munthe, 1998). Speciation could therefore play an important role in the atmospheric cycling of Hg by affecting its susceptibility to wet and dry removal, and subsequent deposition to the environment. Moreover, although Hg in precipitation (rain and snow) is mainly composed of scavenged RGM and  $\text{Hg}_p$ , MeHg has been found in precipitation from numerous studies (Mason et al., 1997a, 1997b, 2000; Guo et al., 2008; Fu et al., 2009), indicating direct atmospheric deposition of MeHg is also possible (Hammerschmidt et al., 2007).

In order to investigate Hg's impact on aquatic and terrestrial ecosystems, it is necessary to better understand the biogeochemical cycling of Hg by measuring the rate of atmospheric Hg deposition. In recent decades, environmental records (e.g., snow/ice, lake sediments) have been widely obtained in attempts to estimate atmospheric Hg deposition rates on regional scales (Schuster et al., 2002; Loewen et al., 2007; Wang et al., 2008; Jitaru et al., 2009; Wang et al., 2010; Yang et al., 2010). However, networks of properly chosen monitoring stations can provide more accurate estimates of regional-scale wet deposition than Hg environmental records since wet deposition is collected directly from the precipitation chemistry data. Additionally, since wet deposition typically accounts for 50–90% of the atmospheric Hg entering the environment (Lamborg et al., 1995; Mason et al., 1997a; Landis and Keeler, 2002), monitoring Hg in precipitation is the most direct way of assessing atmospheric Hg deposition fluxes to aquatic and terrestrial ecosystems (Prestbo and Gay, 2009). As a result, major monitoring stations have been established in many parts of the world (Sakata and Marumoto, 2005; Wängberg et al., 2007; Prestbo and Gay, 2009; Sanei et al., 2010) to monitor Hg concentrations and fluxes in precipitation at a high temporal resolution (typically weekly to bi-weekly). Such data provide important insights into the sensitivity of aquatic and terrestrial ecosystems to atmospheric Hg deposition and environmental Hg risk assessments, and for establishing the effectiveness of Hg emission reductions (Lindberg et al., 2007; Sanei et al., 2010). Of particular notice is the Mercury Deposition Network (MDN, 2010) in the US and Canada which has been operating since 1996 and currently includes more than 100 stations (Prestbo and Gay, 2009).

The Tibetan Plateau is one of the most imposing topographic features on the surface of the earth with an immense area of 2.5 million  $\text{km}^2$  and an average elevation of more than 4000 m a.s.l. It has been regarded as a sensitive region to global contaminant impact due to its unique landform, fragile ecosystem and special monsoon circulation (Qiu, 2008). Although there have been several studies estimating atmospheric Hg total deposition rates through environmental records (e.g., snow/ice, lake sediments) in the Tibetan Plateau (Loewen et al., 2007; Wang et al., 2008, 2010; Yang et al., 2010), accurate measurements of atmospheric Hg deposition are still limited. Moreover, atmospheric Hg deposition has been investigated at multiple sites all over the world e.g., East Asia (Sakata and Marumoto, 2005; Guo et al., 2008; Fu et al., 2009; Wan et al., 2009); North America (Prestbo and Gay, 2009; Sanei et al., 2010), yet long-term Hg monitoring sites remain deficient, and little data are available for concentration and deposition flux of Hg in high altitude regions (e.g., the Tibetan Plateau). Nam Co basin is a pristine region located in the southern Tibetan Plateau. Here the landscape mainly consists of high mountains, glaciers, lakes, and grassland, which are representative of most areas of the Tibetan Plateau. In this paper, as an important part of the mass balance study for Nam Co region, concentrations and wet deposition fluxes of speciated Hg were measured in precipitation from July 2009 to 2011 at Nam Co Station. These data are compared with the reported data for some of the most remote alpine and polar regions worldwide, and seasonal variations of concentration and wet flux of  $\text{Hg}_T$  are discussed. Additionally, the measured  $\text{Hg}_T$  wet deposition flux data are presented for evaluating the Hg deposition fluxes estimated from the environmental records in the Nam Co region. Here we present the first data of Hg wet deposition at a remote high elevation site in the Tibetan Plateau with the objective not only to provide important information on the status of the atmospheric Hg pollution, but also to shed light on the biogeochemical cycling of Hg in the highest plateau in the world.

## 2. Materials and methods

### 2.1. Study area and sampling site

Known as the “Third Pole”, the Tibetan Plateau is one of the most remote and cold regions in the world. The Nam Co ( $30^\circ 30' - 56^\circ 16' - 91^\circ 03'E$ ; 4730 m a.s.l.) is the second largest saline lake on the Tibetan Plateau and the highest lake in the world. Nam Co lies at the foot of the Nyainqêntanglha Mountain (Mt. Nyainqêntanglha, 7102 m a.s.l.) in southern Tibet and covers an area of 1960  $\text{km}^2$  at an elevation of 4718 m. The Nam Co Monitoring and Research Station for Multisphere Interactions (hereafter, Nam Co Station,  $30^\circ 46.44'N$ ,  $90^\circ 59.31'E$ , 4730 m a.s.l.) is located at the southeast shore of Nam Co. Glacier snow samples were recovered in 2006 from the Zhadang glacier (hereafter, ZD) on Mt. Nyainqêntanglha, located about 50 km southwest of Nam Co Station (Loewen et al., 2007); the lake sediment core was recovered in 2006 from a bay in the southeast of Nam Co (Yang et al., 2010) (Fig. 1). Because of its high altitude and minimal to nonexistent industrial activities, the Nam Co Station was considered as an ideal background site for global atmospheric monitoring (Cong et al., 2007), Nam Co Station was established in 2005 by the Chinese Academy of Sciences and has maintained a long-term record of the atmospheric environment of the Tibetan Plateau since. Annual mean air temperature at Nam Co Station is  $0^\circ\text{C}$ ; monthly mean air temperatures range from  $-9.0$  to  $10^\circ\text{C}$ , with temperatures higher than  $0^\circ\text{C}$  during the monsoon season and lower during the non-monsoon season. Annual average precipitation amount is about 400 mm at Nam Co Station with the majority of precipitation occurring as rain from June to September

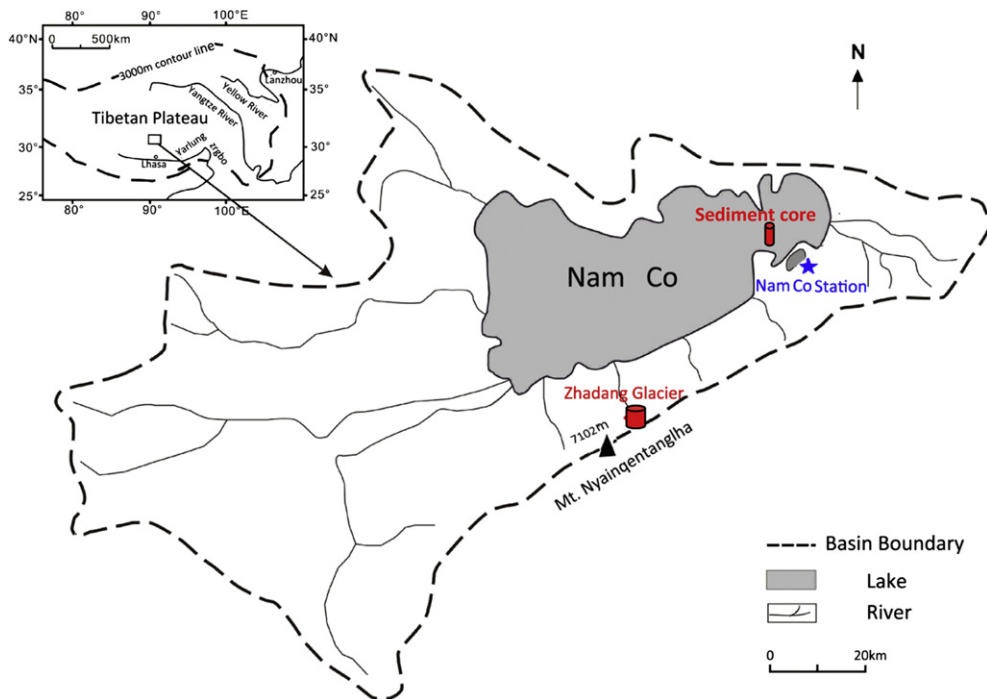


Fig. 1. Map showing the Tibetan Plateau and the location of Nam Co Station.

under the influence of the Indian monsoon. During the other seasons (i.e., non-monsoon season), large-scale atmospheric circulation patterns over the region are mainly dominated by the westerlies, resulting in limited precipitation generally as snow or a snow/rain mix (You et al., 2007).

## 2.2. Sample collection

Precipitation samples (both rain and snow) were collected using an automated precipitation collector (SYC-2, Laoshan Electronic Instrument Complex Co., Ltd.) over a 2-year period from July 2009 to 2011. The details of the precipitation collector are described elsewhere (Li et al., 2007; Cong et al., 2010). In brief, the sampler has two containers for collecting wet and dry deposition, respectively, with one barrelhead (dust preventing cover) that can switch between the two containers automatically depending on the weather condition. During a precipitation event (rain or snow), the barrelhead switches to the dry deposition container, thereby exposing the wet container to precipitation, and vice versa. Wet precipitation was stored in a high density polyethylene (HDPE) plastic bag whereas the snow samples during the cold seasons were melted at room temperature.

After precipitation has been collected in an HDPE plastic bag for each wet event, the precipitation is separated for analysis of speciated Hg (i.e.,  $Hg_T$ , dissolved Hg ( $Hg_D$ ) and MeHg). The precipitation was transferred into 50-mL new polypropylene BD Falcon® centrifuge tubes for  $Hg_T$  analysis, and into 50-mL acid-cleaned borosilicate glass bottles for MeHg analysis; all these tubes and bottles were spiked with ultra-clean grade HCl (Beihua Chemical, China) for a final HCl concentration of 0.5% (v:v). The remaining precipitation (>50 mL) was filtered through membranes (0.45- $\mu$ m pore size, 47-mm diameter, Durapore®, Millipore) within 24 h using a 500 mL borosilicate glass filtering apparatus. After that, the filtered water was transferred into 50-mL new tubes spiked with HCl (0.5% (v:v)) for  $Hg_D$  analysis.  $Hg_P$  was calculated by the difference between  $Hg_T$  and  $Hg_D$ . Replicate samples for speciated Hg were collected on each wet precipitation

day wherever the amount of precipitation permitted. Field blanks were collected by filling sample vials with ultra-pure water in the laboratory, then opening them during precipitation sample collection and handling them as samples. All the samples were stored at 4 °C until analysis. Extreme care was taken during the collection, handling, and storage of precipitation samples to minimize contamination.

The amount of precipitation for each wet precipitation day was recorded by an automatic rain gauge located 5 m away from the precipitation collector at Nam Co Station. The total sampled precipitation was 729.7 mm, which bracketed all the large precipitation events and accounted for 95.3% of the total precipitation (765.6 mm) during the study period. Overall, a total of 101 precipitation samples were obtained for  $Hg_T$  analysis during the sampling campaign. It should be noted that the only a small subset of the  $Hg_T$  samples were analyzed for  $Hg_D$  ( $n = 44$ ) and MeHg ( $n = 14$ ).

## 2.3. Analytical procedures and QA/QC

We followed the US EPA Method 1631 (version E) (US EPA, 2002) analytical method for  $Hg_T$  and  $Hg_D$  analysis in precipitation samples. Precipitation samples for  $Hg_D$  were done in a similar fashion to  $Hg_T$  except they were pre-filtered through a borosilicate glass filtering apparatus. Analysis for  $Hg_T$  and  $Hg_D$  was performed by cold vapor atomic fluorescence spectroscopy (CVAFS) on an Analytik-Jena Hg analyzer (Analytik-Jena Corporation Inc., Jena, Germany) in a metal-free class 100–1000 ultra-clean laboratory room at the Key Laboratory of Tibetan Environment Changes and Land Surface Processes, Lhasa branch. For  $Hg_T$  and  $Hg_D$ , each sample was first oxidized by BrCl (0.5 mL per 100 mL sample), followed by titration of the remaining BrCl with  $NH_2OH \cdot HCl$ .  $SnCl_2$  was then added to the sample to reduce Hg(II) to Hg(0) which was quantified by the fluorescence spectrophotometer.  $Hg_T$  and  $Hg_D$  determined by this procedure represent the sum of all the Hg species in precipitation sample, including inorganic Hg(II), MeHg, and Hg(0) (US EPA, 2002).

The analysis of MeHg in precipitation samples was done by gas chromatography (GC)–CVAFS following distillation and ethylation (US EPA, 2001). In brief, a 45-mL sample aliquot was placed in a Teflon® distillation vessel, and then distilled in an aluminum heating pan at 125 °C for 3–4 h. The distillate was ethylated with a stepwise addition of 0.2 mL 2 M sodium acetate and 0.1 mL 1% sodium tetraethylborate, while being purging with N<sub>2</sub> onto a Tenax® trap. The MeHg collected on the trap was then thermally desorbed onto and separated in an isothermal GC column, followed by analysis by CVAFS (Brooks Rand Ltd., Seattle, Washington). The MDL for MeHg was 0.01 ng L<sup>-1</sup>. The precipitation samples for MeHg analysis were done at the State Key Laboratory of Environmental Geochemistry in Guiyang. Since the acidification of the samples is known to convert dimethyl Hg (DMHg) to monomethyl Hg (MMHg) (Black et al., 2009), the MeHg reported here thus represents the sum of MMHg and DMHg.

Quality assurance and quality control (QA/QC) of the analysis was carried out using replicates, method blanks, field blanks and Ongoing Precision and Recovery (OPR) standards. The method detection limit (MDL), defined as 3 times the standard deviation of 10 replicates measurements of a blank solution, was less than 0.2 ng L<sup>-1</sup> for Hg<sub>T</sub> and Hg<sub>D</sub>, and less than 0.01 ng L<sup>-1</sup> for MeHg, respectively. The relative standard deviations (RSDs) for the replicate samples were <5% for Hg<sub>T</sub> and Hg<sub>D</sub>, and <10% for MeHg. Method blanks and field blanks were always found to be below the respective MDL. Most of the Hg concentrations of blank samples were less than the MDL, indicating minimal contamination during sampling, transport and treatment for this study. Additionally, the plastic bags, Falcon® centrifuge tubes, and acid-cleaned glass bottles were randomly tested for Hg concentrations before being used for sampling; they were always below the MDL.

An OPR standard of 5 ng L<sup>-1</sup> was interspersed every 10 samples of Hg<sub>T</sub> and Hg<sub>D</sub>, and a standard of 0.05 ng L<sup>-1</sup> was interspersed every 5 samples of MeHg to check instrument operation. Recovery percentage was 95%–105% of their certified values for Hg<sub>T</sub> and Hg<sub>D</sub>, and was 88%–112% of their certified values for MeHg, respectively.

#### 2.4. Calculation the Hg wet deposition flux

Calculation of Hg<sub>T</sub> wet deposition flux according to Hg<sub>T</sub> concentration in precipitation during the 2-year study period was based on the following equation:

$$F_w = \frac{1}{2000} \sum_{i=1}^{i=101} (C_p^i P^i) \quad (1)$$

where  $F_w$  was Hg<sub>T</sub> wet deposition flux ( $\mu\text{g m}^{-2} \text{yr}^{-1}$ ),  $C_p^i$  was volume-weighted Hg<sub>T</sub> concentration (ng L<sup>-1</sup>) in each precipitation sample, and the precipitation amount associated with each sample was indicated by  $P^i$  (mm) in each wet deposition day.

Ideally the calculation of the MeHg wet deposition flux should be based on the MeHg concentration and precipitation in each sampling event. Unfortunately this cannot be done for MeHg in this study as the precipitation sampled ( $n = 14$ ) only represented 18.2% of the total precipitation amount, which was not a completely covered yearly dataset for calculating the fluxes by using Equation (1). Therefore, the MeHg flux estimate was based on the VWM concentration and the annual average precipitation amount. The annual MeHg wet deposition flux can be approximated by the following equation:

$$F_w = \frac{1}{2000} C_{\text{MeHg}_T} \sum_{i=1}^{i=101} P^i \quad (2)$$

where  $F_w$  is annual MeHg wet deposition flux ( $\mu\text{g m}^{-2} \text{yr}^{-1}$ ),  $C_{\text{MeHg}_T}$  is the VWM concentration of MeHg (ng L<sup>-1</sup>), respectively. In accordance with Equation (1),  $P^i$  (mm) is the precipitation amount in each wet deposition day.

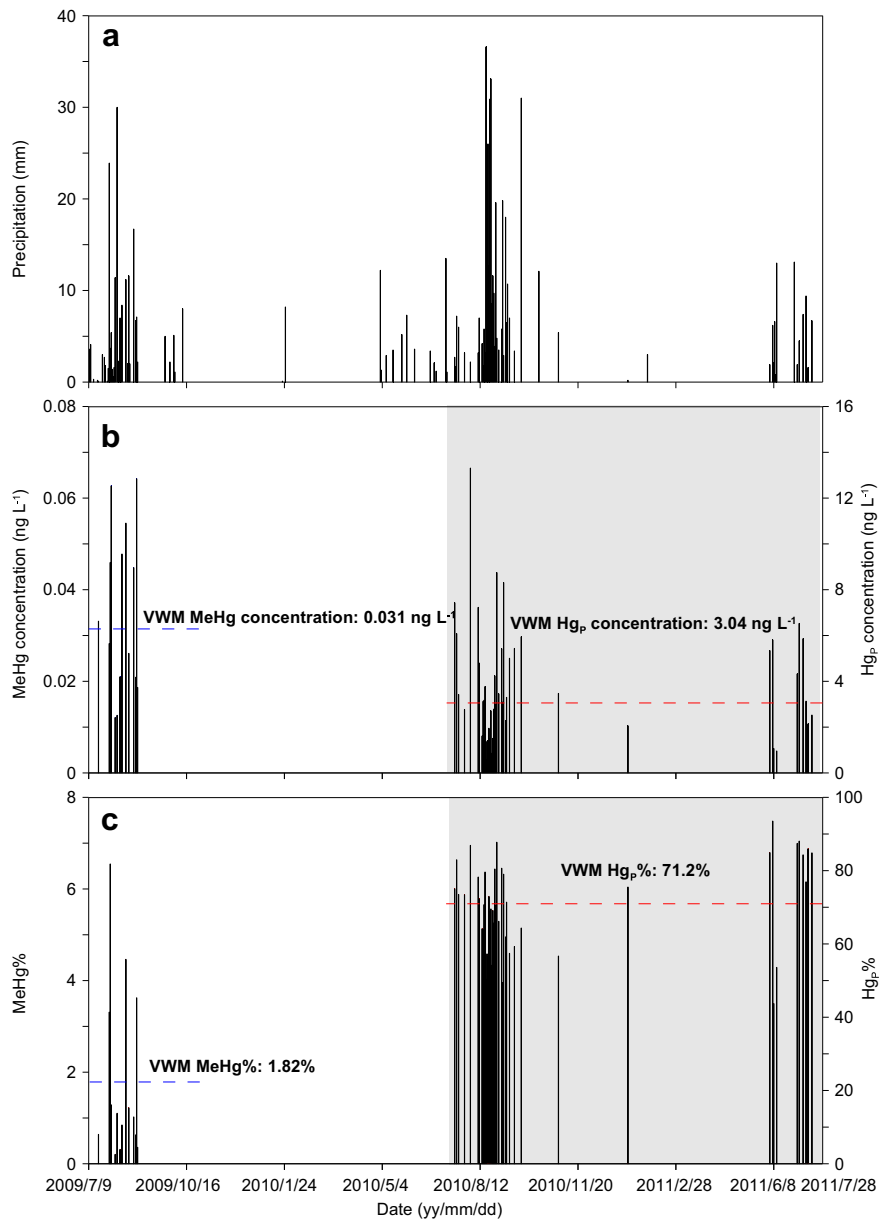
### 3. Results and discussion

#### 3.1. Concentration and wet deposition flux of Hg<sub>T</sub>, Hg<sub>D</sub> and MeHg in precipitation

##### 3.1.1. Hg<sub>T</sub>

Precipitation data, Hg<sub>T</sub> concentrations measured in precipitation, and daily fluxes of Hg<sub>T</sub> during the study period are presented in Fig. 4. In total, 101 samples were collected over 25 months from July 2009 to 2011 at Nam Co Station. Because precipitation samples were immediately preserved by acid and remained in the dark once inside the collection tubes (thereby preventing reduction of Hg(II) to volatile Hg(0)), these data represent gross wet deposition concentrations and fluxes of Hg<sub>T</sub>. The Hg<sub>T</sub> concentrations fluctuated between 0.4 ng L<sup>-1</sup> and 35.3 ng L<sup>-1</sup> ( $n = 101$ ), and the VWM Hg<sub>T</sub> concentration was 4.8 ng L<sup>-1</sup> (Fig. 2). As seen in Table 1, the VWM concentration of Hg<sub>T</sub> from the precipitation at Nam Co Station are at the lower end of the ranges reported for some of the most remote alpine and polar regions worldwide. For instance, the Hg<sub>T</sub> concentrations fall within the lower half of the range recorded by MDN across North America (Prestbo and Gay, 2009) and the annual VWM Hg<sub>T</sub> concentration in the Nam Co Station was lower than the VWM concentration in Churchill (6.2 ng L<sup>-1</sup>), a Canadian sub-Arctic station in western Hudson Bay (Sanei et al., 2010). Moreover, the Hg<sub>T</sub> concentrations in precipitation at Nam Co Station were similar to the concentrations reported for snowpacks along the Arctic coasts in the absence of AMDEs (i.e., Atmospheric Mercury Depletion Events) (Lahoutifard et al., 2005) and comparable to the concentrations (2–35 ng L<sup>-1</sup>) in a shallow firn core retrieved from a remote Himalayan glacier (Wang et al., 2008). Recent work at a rural Korean site has indicated that VWM Hg<sub>T</sub> concentrations in snow were statistically higher than in rain (Ahn et al., 2011). Similarly, in this study, higher Hg<sub>T</sub> concentrations were found in precipitation (snow or snow mixed with rain) during the non-monsoon season. However, Hg<sub>T</sub> concentrations (<1–35.3 ng L<sup>-1</sup>) in precipitation at Nam Co Station were found to be statistically higher than the Hg<sub>T</sub> concentrations of snow samples from the snowpits (<1–9 ng L<sup>-1</sup>) (Loewen et al., 2007), and of surface snow samples (<1–13 ng L<sup>-1</sup>) retrieved from high-elevation glaciers over the Tibetan Plateau (Huang et al., 2012b).

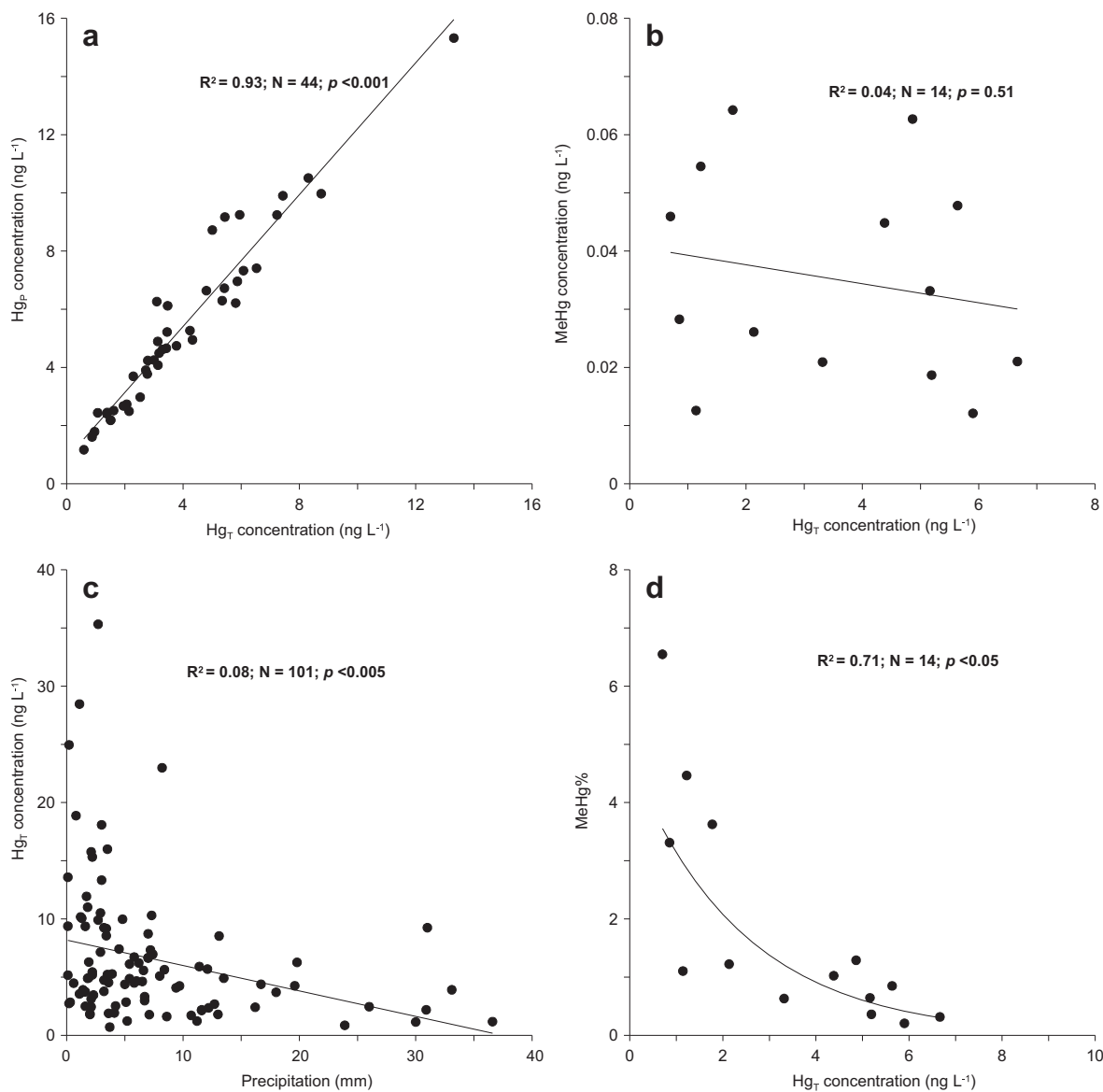
Using Equation (1), the annual average Hg<sub>T</sub> deposition flux was calculated to be 1.75  $\mu\text{g m}^{-2} \text{yr}^{-1}$  during the study period. As shown in Table 1, mainly due to very low precipitation rates, the annual Hg<sub>T</sub> wet deposition flux in the Nam Co Station is among the lowest that has ever been reported for remote alpine and polar regions worldwide. Similar to the VWM concentration, it falls in the lower end of Hg wet deposition flux in North America (MDN range: 1.9–25.0  $\mu\text{g m}^{-2} \text{yr}^{-1}$ ) (MDN, 2010). The only site that reported a lower Hg<sub>T</sub> flux than Nam Co Station is Churchill (0.54  $\mu\text{g m}^{-2} \text{yr}^{-1}$ ), a sub-Arctic station in western Hudson Bay, Canada (Table 1). Moreover, Hg<sub>T</sub> wet deposition flux in our study site is close to the lower end of the global natural atmospheric Hg deposition rate (2–5  $\mu\text{g m}^{-2} \text{yr}^{-1}$ ) (Swain et al., 1992), and lower than the Hg deposition rate in the Arctic Ocean (3–6  $\mu\text{g m}^{-2} \text{yr}^{-1}$ ) (Ariya et al., 2004).



**Fig. 2.** Variation of amount of precipitation ( $n = 101$ ) from July 2009 to 2011 (a).  $\text{Hg}_p$  ( $n = 44$ ) and MeHg ( $n = 14$ ) concentrations ( $\text{ng L}^{-1}$ ) in precipitation (b). Content (%) of  $\text{Hg}_p$  and MeHg in precipitation (c).

**Table 1**  
Concentrations and depositional fluxes of  $\text{Hg}_T$  and MeHg in precipitation from Nam Co Station and other remote regions worldwide. For comparison, the data from more than 100 stations of the North American Mercury Deposition Network (MDN) were also shown.

Site	Site type	Sampling period	Annual precipitation (mm)	VWM concentration in precipitation ( $\text{ng L}^{-1}$ )		Wet deposition flux ( $\mu\text{g m}^{-2} \text{yr}^{-1}$ )		Reference
				$\text{Hg}_T$	MeHg	$\text{Hg}_T$	MeHg	
Nam Co Station, China	Alpine	2009–2011	364.9	4.8	0.031	1.75	0.011	This study
Mt. Leigong, China	Alpine	2008–2009	1533	4.0	0.040	6.1	0.06	Fu et al. (2010)
Mt. Changbai, China	Alpine	2005–2006	630	13.3		8.4		Wan et al. (2009)
Kodiak, USA	Sub-Arctic	2008	2500	2.1		5.2		MDN (2010)
Churchill, Canada	Sub-Arctic	2007	332	6.2		0.54		Sanei et al. (2010)
Experimental Lakes Area, Canada	Boreal	1992–1994	730	4.0	0.052	2.9	0.04	St. Louis et al. (1995)
North America MDN (>100 sites including Kodiak)	Remote to industrial	2008		2.1–18.7		1.9–25.0		MDN (2010)



**Fig. 3.** Relationship between concentrations of  $Hg_P$  and  $Hg_T$  (a). Relationship between concentrations of MeHg and  $Hg_T$  (b). Relationships between precipitation amount,  $Hg_T$  concentration (c). Relationship between  $Hg_T$  and %MeHg in precipitation (d).

### 3.1.2. $Hg_P$

$Hg_P$  concentrations measured in precipitation are presented in Fig. 2. A total of 44 precipitation samples were filtered for  $Hg_P$  analysis from July 2010–2011, and the  $Hg_P$  concentrations ranged from 0.6 to 13.3  $ng\ L^{-1}$  with a VWM concentration of 3.0  $ng\ L^{-1}$  (Fig. 2). The precipitation for  $Hg_P$  analysis was mainly sampled during the monsoon season due to the unique distribution pattern of precipitation in the Tibetan Plateau (You et al., 2007), and during this time enough precipitation can be collected for filtering samples for Hg speciation measurements. As seen in Fig. 2, the  $Hg_P$  to  $Hg_T$  ratios (VWM) for all precipitation events was 71.2% during the sampling period, and the high  $Hg_P\%$  in precipitation has indicated that  $Hg_T$  wet flux was mainly accounted for by wet flux of  $Hg_P$ . While a significant positive correlation was found between  $Hg_P$  and  $Hg_T$  ( $R^2 = 0.91$ ,  $N = 44$ ,  $p < 0.001$ ), no statistically significant relationship was found between  $Hg_T$  and MeHg ( $R^2 = 0.04$ ;  $N = 14$ ;  $p = 0.51$ ) (Fig. 3). Previous studies have reported that the  $Hg_P$  was the dominant form among the different Hg species in precipitation, and the concentrations of  $Hg_T$  negatively correlated with the

precipitation amount, indicating that scavenging of  $Hg_P$  from the atmosphere was an important mechanism contributing to Hg in precipitation. Similarly, the results have suggested the pivotal role of  $Hg_P$  in scavenging atmospheric Hg in our study site (Guo et al., 2008). Moreover, considering that the sources of  $Hg_T$  in precipitation were mainly attributed to the scavenging of  $Hg_P$  and RGM in the atmosphere (Schroeder and Munthe, 1998), the high  $Hg_P\%$  indicates that the process of  $Hg_P$  scavenging is an important mechanism contributing Hg to precipitation in the Nam Co region. Recent work on snowpits from the ZD glacier (50 km southwest of Nam Co Station, see Fig. 1) has confirmed that atmospheric Hg deposition is occurring via particulate matter, and fine-grained  $Hg_P$  is the dominant factor influencing the concentration levels of Hg in the ZD glacier snowpits (Huang et al., 2012a). Our finding that  $Hg_P$  is the major form of Hg in precipitation suggest that Hg wet deposition was in the form of  $Hg_P$  and confirms the results from snowpits that the atmospheric deposition of Hg is primarily associated with particulate matter over the Tibetan Plateau (Loewen et al., 2007; Huang et al., 2012a). Furthermore, as displayed in

Fig. 3, the  $Hg_T$  concentrations in precipitation were negatively correlated with precipitation amount ( $R^2 = 0.08$ ;  $N = 101$ ;  $p < 0.005$ ) at Nam Co Station. Similar to what has been found in previous studies (Guo et al., 2008; Ahn et al., 2011), we find that  $Hg_P$  at our study site is effectively scavenged from the atmosphere within an initial period.

### 3.1.3. MeHg

A total of 14 precipitation samples were collected for MeHg analysis during the monsoon season (July through August) in 2009. MeHg concentrations ranged from 0.012 to 0.064  $ng L^{-1}$  with a VWM concentration of 0.031  $ng L^{-1}$  (Fig. 2), which were comparable to the average concentrations of MeHg in precipitation at Mount Leigong (Table 1), but was slightly higher than the MeHg concentration in the lake surface water (avg. = 0.025  $ng L^{-1}$ ) of Nam Co (Zheng, 2009). The annual MeHg wet deposition flux was calculated to be 0.011  $\mu g m^{-2} yr^{-1}$  using Equation (2) (i.e., VWM concentration times annual average precipitation). To date, little is known about the sources and fate of MeHg in the atmosphere, and few measurements have been made of MeHg in precipitation, which results in less available data for MeHg concentration and flux in the background regions of the world. As shown in Table 1, both the VWM concentration and MeHg wet deposition flux from the precipitation at Nam Co Station are at the lower end of the ranges reported for other remote alpine and polar regions worldwide; data on MeHg wet deposition flux are however much scarce in the literature. Measurements at two other remote sites, Mount Leigong in China and the Experimental Lakes Area (ELA) in Canada, reported MeHg fluxes of 0.06 and 0.04  $\mu g m^{-2} yr^{-1}$ , respectively, while the flux for Nam Co Station is the lowest.

The percentage of  $Hg_T$  present as MeHg (MeHg%) was found to be in the 0.21%–6.55% range with a VWM MeHg% of 1.82% (Fig. 2), which was within the range of other published MeHg% values in precipitation (Downs et al., 1998), but was lower than some typical MeHg% values found in aquatic environments (e.g., lake sediments, pore waters, wetlands) (Ullrich et al., 2001). Previous studies have found that the MeHg constituted around 1.3%, on average, of the  $Hg_T$  in precipitation in northern Wisconsin and at ELA in northwestern Ontario (Lamborg et al., 1995; St. Louis et al., 1995), which was comparable to the MeHg% in precipitation at Nam Co Station. However, compared with the average MeHg% (0.19%–0.5%) around the Chesapeake Bay region (Mason et al., 1997a, 1997b, 2000), the VWM MeHg% at Nam Co Station was significantly higher. That the more northerly continental sites (e.g., ELA) have a relatively higher MeHg concentration than in the Chesapeake Bay region may reflect the fact that MeHg is likely slowly decomposed in the atmosphere under some climatic conditions (e.g., low temperature) (Inoko, 1981; Tossell, 1998; Mason et al., 2000). Considering the harsh climatic conditions of the Tibetan Plateau (i.e., one of the most remote and cold regions in the world) (Qiu, 2008), the lower air temperature at Nam Co Station (annual average air temperature is

0 °C) likely accounted for the relatively high MeHg% in this study. In addition, there was a significant negative exponential relationship between  $Hg_T$  and MeHg% ( $R^2 = 0.71$ ;  $N = 14$ ;  $p < 0.05$ ) (Fig. 3). More specifically, a large portion of the Hg in precipitation was MeHg (up to 6.55%) at times when concentrations of MeHg were high and concentrations of  $Hg_T$  were very low, approaching our analytical limits of detection (Fig. 3).

### 3.2. Seasonal variations on concentration and wet deposition flux of $Hg_T$ in precipitation

As shown in Table 2, during the 2-year study period the VWM  $Hg_T$  concentrations ranged from 3.8 to 5.3  $ng L^{-1}$  during the monsoon season, and from 6.9 to 8.2  $ng L^{-1}$  during the non-monsoon season, respectively. The VWM  $Hg_T$  concentration during the non-monsoon season (7.8  $ng L^{-1}$ ) was approximately two times higher than the concentration during the monsoon season (4.6  $ng L^{-1}$ ) (Table 2). Consistent with the higher  $Hg_P$ % in precipitation as discussed earlier, several studies have suggested that dust storm activity may be the largest source of Hg for the Tibetan Plateau (Loewen et al., 2007; Huang et al., 2012b). A recent work on the ZD glacier snowpits has indicated that the fine-grained and long-range transported  $Hg_P$  originating from dust storm activities in the arid regions in central and southern Asia was the most important source for the Hg in glaciers over the Tibetan Plateau (Huang et al., 2012a). Moreover, a previous study at Nam Co Station has suggested that concentrations of total suspended particulates during the non-monsoon season were significantly higher than the concentrations during the monsoon season (Cong et al., 2009), which is mainly explained by the westerlies dominating large scale atmospheric circulation patterns over the Tibetan Plateau during the non-monsoon season. As a result, the westerlies could bring long-range transported  $Hg_P$  from the arid regions in central and southern Asia to the hinterland of the Tibetan Plateau through the general atmospheric circulation (Fu et al., 2012), thus resulting in elevated  $Hg_T$  concentrations in precipitation at Nam Co Station during the non-monsoon season.

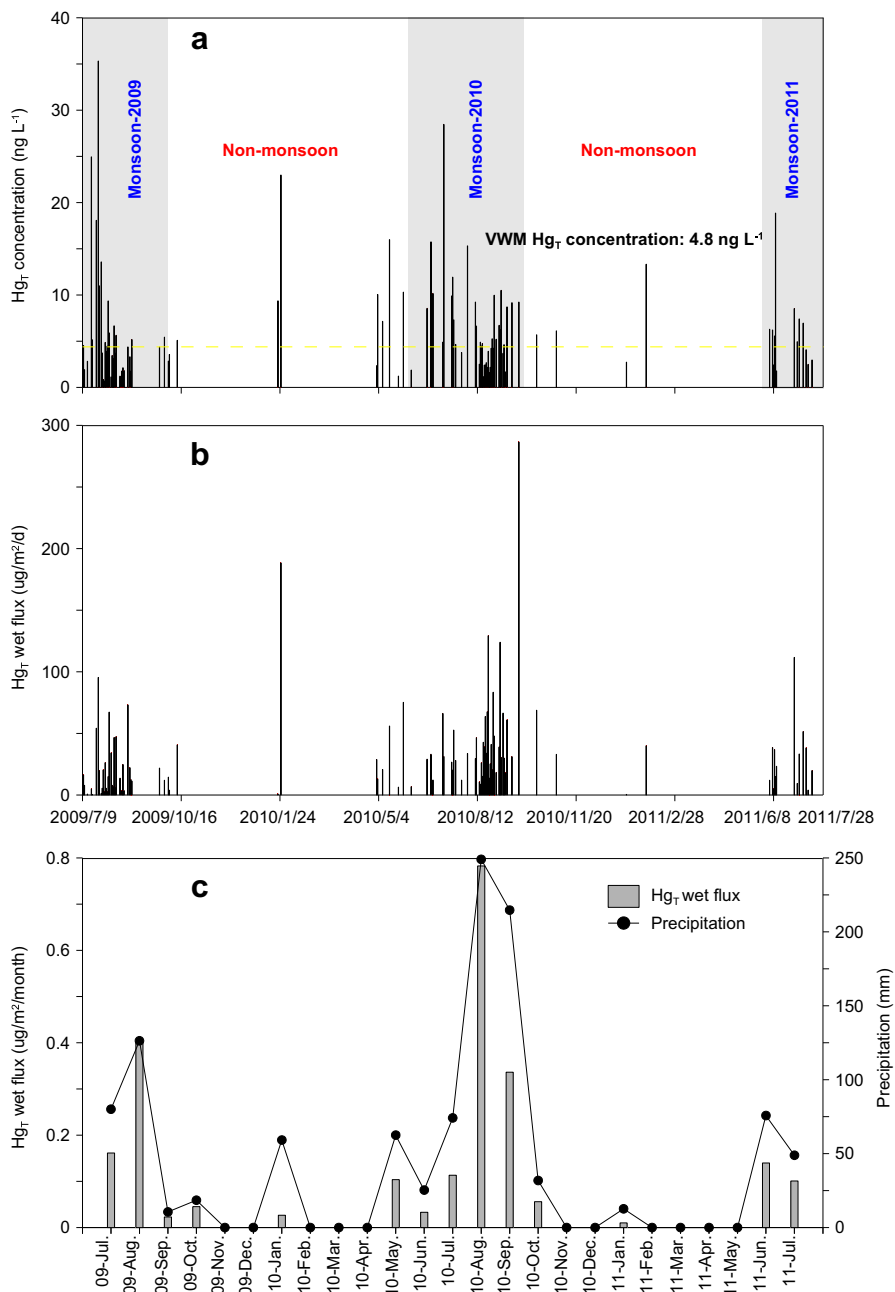
Monsoon season (June through September) is typically the rainy season in the Tibetan Plateau; approximately 90.6% of the annual total precipitation fell in the monsoon season (Fig. 4 and Table 2). August was the wettest month of the year; with 50.8% of the annual total precipitation and 34.5% of  $Hg_T$  wet deposition flux (Fig. 4). As a consequence of the strong seasonality of precipitation at our study site,  $Hg_T$  wet deposition fluxes were also seasonal, with 83% of the wet deposition fluxes occurring during the monsoon season (Table 2). Because the  $Hg_T$  wet deposition flux is affected by both the  $Hg_T$  concentration and precipitation amount, Fig. 5 demonstrates that the precipitation amount (between precipitation amount and daily  $Hg_T$  wet deposition flux ( $R^2 = 0.34$ ;  $N = 101$ ;  $p < 0.001$ )) rather than  $Hg_T$  concentration (between  $Hg_T$  concentration and daily  $Hg_T$  wet deposition flux ( $R^2 = 0.08$ ;  $N = 101$ ;

**Table 2**

Seasonal variations of precipitation, VWM  $Hg_T$  concentration, and wet deposition  $Hg_T$  flux during the 2-year study period in the Nam Co Station.

Sampling period	n	Precipitation (mm)		VWM $Hg_T$ concentration ( $ng L^{-1}$ )		$Hg_T$ wet deposition flux ( $\mu g m^{-2}$ )	
		Monsoon	Non-monsoon	Monsoon	Non-monsoon	Monsoon	Non-monsoon
July, 2009–September, 2009	33		183.5	3.78		0.69	
October, 2009–May, 2010		11			8.17		0.45
June, 2010–September, 2010	40		395.4	4.56		1.80	
October, 2010–May, 2011		4			6.88		0.14
June, 2011–July, 2011	13		75.2	5.31		0.40	
Monsoon season (total)	86		654.1	4.59		2.89	
Non-monsoon season (total)		15			7.82		0.59
Total	101		729.7	4.8		3.49	

Note: June, July and August and September indicate monsoon season; October, November, December, January, February, March, April, and May indicate non-monsoon season.



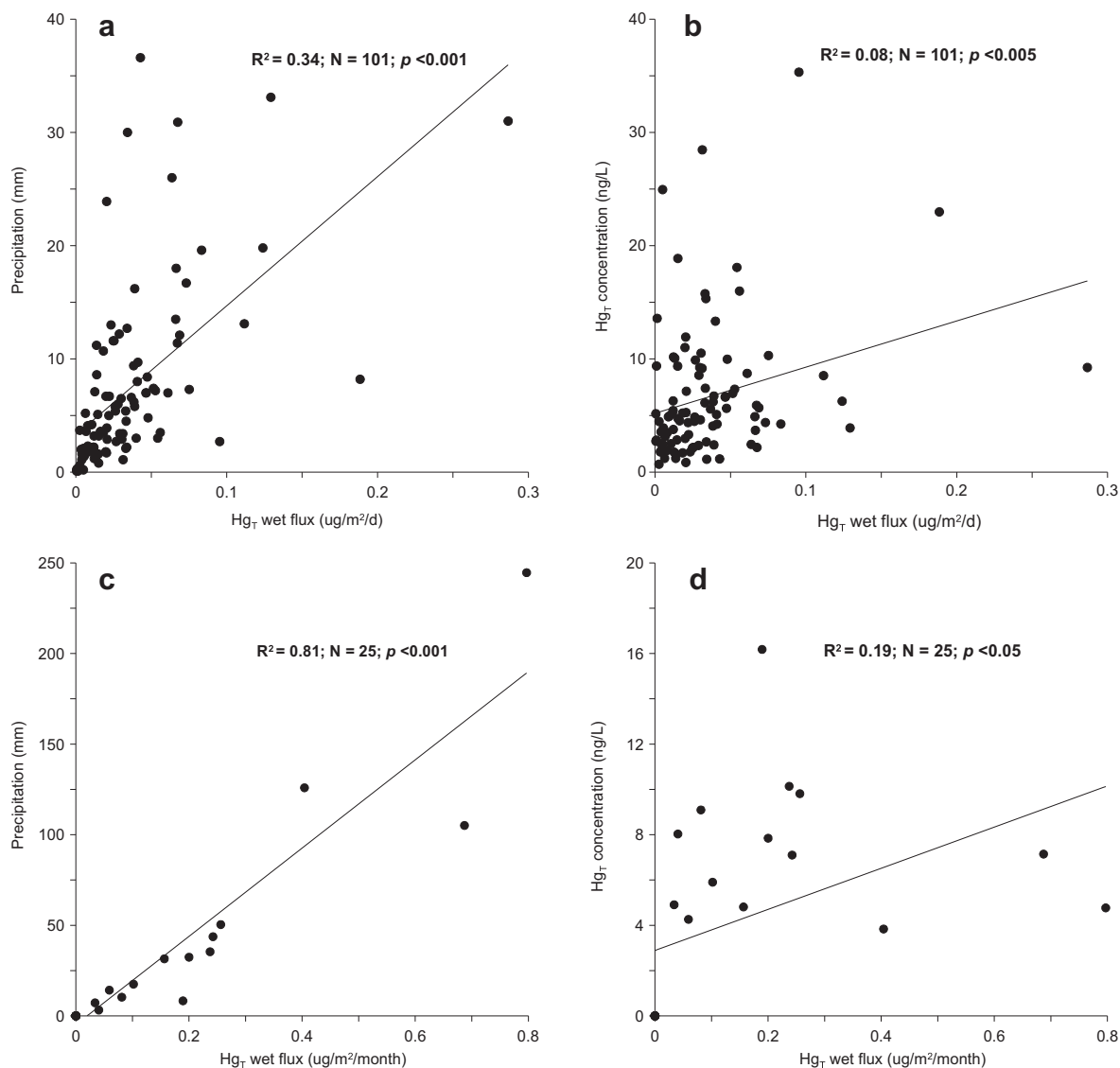
**Fig. 4.** Variation of  $Hg_T$  concentration ( $n = 101$ ) (a) and daily  $Hg_T$  wet deposition ( $ng\ m^{-2}\ d^{-1}$ ) ( $n = 101$ ) (b) in precipitation. Monthly variations in  $Hg_T$  wet deposition and precipitation amounts from July 2009 to 2011 (c).

$p < 0.005$ ) was the governing factor affecting  $Hg_T$  wet deposition flux at Nam Co Station. Compared to the relationship between monthly  $Hg_T$  wet deposition flux and  $Hg_T$  concentration ( $R^2 = 0.19$ ;  $N = 25$ ;  $p < 0.05$ ), there is a higher correlation between the monthly  $Hg_T$  wet deposition flux and precipitation amount ( $R^2 = 0.81$ ;  $N = 25$ ;  $p < 0.001$ ), and the regression line passes near the origin (Fig. 5). Therefore, variations in precipitation were an important factor in determining variations in the  $Hg_T$  wet deposition flux over time, explaining 81% of the flux variance, and conversely  $Hg_T$  concentration explained only 19% of the variance in flux ( $R^2 = 0.19$ ;  $N = 25$ ;  $p < 0.05$ ) at Nam Co Station (Fig. 5). Similarly, precipitation accounted for about 70% of the variance in Hg wet deposition flux at multiple sites in Canada and Japan, and about 55% across all MDN sites (Mason et al., 2000; Sakata and Marumoto, 2005; Sanei et al., 2010).

### 3.3. Comparison with the estimates of $Hg_T$ deposition fluxes from environmental records in the Nam Co region

Environmental records have been globally used as excellent archives for estimating the atmospheric Hg deposition rate at different time scales (century or millennial) (e.g., Schuster et al., 2002; Cooke et al., 2009; Jitaru et al., 2009). To date, several studies have been performed that investigated the deposition Hg fluxes through snow/ice and lake sediments in the Tibetan Plateau (Loewen et al., 2007; Wang et al., 2008, 2010; Yang et al., 2010). For instance, the atmospheric deposition fluxes of  $Hg_T$  were estimated to range from  $0.74\ \mu g\ m^{-2}\ yr^{-1}$  in four snowpits (Loewen et al., 2007) and from  $5.1$  to  $7.9\ \mu g\ m^{-2}\ yr^{-1}$  in nine lakes sediment cores (Yang et al., 2010) along a southwest–northeast transect on the Tibetan Plateau. However, the reconstructed flux data





**Fig. 5.** Relationship between precipitation amount and daily  $Hg_T$  wet deposition ( $\mu g m^{-2} d^{-1}$ ) (a). Relationship between  $Hg_T$  concentration and daily  $Hg_T$  wet deposition ( $\mu g m^{-2} d^{-1}$ ) (b). Relationship between precipitation amount and monthly  $Hg_T$  wet deposition ( $\mu g m^{-2} month^{-1}$ ) (c). Relationship between  $Hg_T$  concentration and monthly  $Hg_T$  wet deposition ( $\mu g m^{-2} month^{-1}$ ) (d).

through environmental records were often controversial due to the influences of post-depositional redistribution by biological or chemical processes (e.g., elution process, photoreduction for snowpits; bioturbation for sediments) (Hou and Qin, 2002; Lalonde et al., 2002; Feyte et al., 2011). Therefore, a continuous measurement for atmospheric Hg wet deposition in the field sites (e.g., Nam Co Station) will be helpful for evaluating the estimated deposition fluxes from environmental records over the Tibetan Plateau. In this study, the measured wet deposition flux of  $Hg_T$  in the Nam Co Station ( $1.75 \mu g m^{-2} yr^{-1}$ ) (Table 1) is of the same order of magnitude like the one recorded at several snowpits across the Tibetan Plateau ( $0.74\text{--}2.97 \mu g m^{-2} yr^{-1}$ ) (Loewen et al., 2007), as well as the Hg total deposition fluxes ( $5.1\text{--}7.9 \mu g m^{-2} yr^{-1}$ ) estimated by the high-elevation lake sediment cores in the same region (Yang et al., 2010). Our study has suggested that both environmental records appear to be reliable archives for estimating historical Hg accumulation rates in the Tibetan Plateau, despite that previous studies have suggested that atmospheric Hg deposition fluxes reflected by snowpits may be grossly underestimated due to the effect of post-depositional processes in snow/ice (e.g.,

photoreduction) (Lalonde et al., 2002; Ferrari et al., 2004; Huang et al., 2012b), as well as many post-depositional processes affecting time-resolved Hg accumulation in sediment cores are still poorly understood (Biester et al., 2007; Feyte et al., 2011). For the first time, we present measured Hg deposition data for evaluating the estimated atmospheric Hg total deposition fluxes from the environmental records in the Tibetan Plateau, this will serve as valuable reference for interpreting historical records of atmospheric Hg deposition, and reconstructing Hg biogeochemical cycling through environmental records from the Tibetan Plateau. Further research including instrumented dry deposition measurements and catchment/lake mass balance studies is recommended to test this evaluation, and to provide definitive data on current atmospheric Hg deposition rates in the Tibetan Plateau.

#### 3.4. Implications for atmospheric Hg deposition and Hg cycling on the Tibetan Plateau

Numerous studies have shown that the majority of the  $Hg(II)$  (mainly in the form of RGM) deposited in the Arctic during the

AMDEs may undergo rapid photoreduction and thus release back to the atmosphere in the form of GEM (Lalonde et al., 2002; Poulain et al., 2004). Our study clearly indicates that scavenging of  $Hg_p$  most likely dominated the atmospheric wet deposition of Hg at Nam Co Station, a representative site for the Tibetan Plateau. As atmospheric Hg deposited on the Tibetan Plateau is mainly in the form of  $Hg_p$  (Loewen et al., 2007; Huang et al., 2012a), the scavenged Hg is more likely to retain and sink in the Tibetan Plateau environments because  $Hg_p$  is more stable than RGM in redox reactions. Additionally, since the Hg species in precipitation is dominated by  $Hg_p$ , wet deposited  $Hg_p$  may be more bioavailable than other forms of Hg and thus it may enhance the availability of atmospheric Hg deposition by the ecosystem of the Nam Co region. Moreover, methylation of Hg in ecosystems is of particular concern because MeHg is more biologically active and toxic. Past studies have found that percent MeHg is strongly correlated with potential methylation rates, suggesting MeHg% approximates relative Hg methylation rates in environments (Sunderland et al., 2004). Although a limited number of precipitation samples were analyzed for MeHg concentrations during the monsoon season, MeHg% in our study site was found to be higher than those in other regions (e.g., Chesapeake Bay in America). A relatively higher MeHg% found in precipitation indicates that MeHg may be more prone to bioaccumulation and biomagnification within the food web in the Nam Co region. This is significant because most of the Hg wet deposition occurred during the monsoon season, which is the growing season and therefore increases Hg bioavailability and trophic transfer in the ecosystems of the Tibetan Plateau. As a result, the possibility of bioaccumulation and biomagnification of the wet deposited Hg increased during the growing season and thus might constitute a threat to the ecosystem of the Nam Co region.

Atmospheric deposition is an important source of Hg to ecosystems, and represents a critical environmental and scientific issue (Harris et al., 2007; Lindberg et al., 2007). Although the role of the vast Tibetan Plateau in the global Hg cycle is relatively unknown, in agreement with a previous research for atmospheric Hg deposition in high elevation glaciers (Huang et al., 2012b),  $Hg_p$  dominates the flux of  $Hg_T$  captured in the wet-deposition samples in this study may imply that the Tibetan Plateau might play an important role as a sink for global Hg cycling due to the fact that  $Hg_p$  is stable in redox reactions. Moreover, accurate measurements of atmospheric Hg deposition in aquatic and terrestrial ecosystems are critically important for many reasons, including the calculation of input–output budgets, and the assessment of biological, ecological, and watershed responses to pollutant loading and climate change. Our study provides insights for assessing the potential environmental risks to the ecosystem of Nam Co region, as well as many other remote alpine regions in the Tibetan Plateau.

#### 4. Summary and conclusions

Concentrations and wet deposition fluxes of speciated Hg were measured from July 2009 to 2011 at Nam Co Station, a remote high elevation site in the southern Tibetan Plateau. The  $Hg_T$  and MeHg concentrations are comparable to the reported data for some remote alpine and polar regions worldwide, further suggesting Nam Co Station is an ideal background site for monitoring long-term changes of the global environment. VWM  $Hg_T$  concentration in the non-monsoon season was approximately two times higher than the concentration in the monsoon season. As a consequence of the strong seasonality of precipitation at our study site, 83% of the  $Hg_T$  wet deposition flux occurred during the monsoon season. Wet deposition fluxes of  $Hg_T$  and MeHg in our study site were almost among the lowest reported values in the world.

Speciation measurements of Hg have indicated that the dominant Hg species in precipitation was mainly in the form of  $Hg_p$ , which indicates the importance of  $Hg_p$  scavenging to Hg deposition. The  $Hg_T$  concentrations were found to decrease with increasing amount of precipitation at Nam Co Station, which further suggests that  $Hg_p$  are effectively scavenged from the atmosphere within an initial period. Due to the lower air temperature in our study site, the relatively high MeHg% might reflect the fact that MeHg was slowly decomposed in the atmosphere of Nam Co region. Moreover, the  $Hg_T$  wet deposition fluxes at Nam Co Station correlated well with precipitation amount, suggesting that wet deposition of Hg is dominated by precipitation amount rather than scavenging of atmospheric Hg by precipitation.

A comparison of Hg wet deposition flux at Nam Co Station to the estimates from environmental records in the Nam Co region has suggested both snowpits and lake sediments appear to be reliable archives for estimating historical Hg accumulation rates in the Tibetan Plateau. Due to the fact that the wet deposited Hg species seems to be the dominant form of  $Hg_p$ , it can be inferred that the availability of atmospheric Hg deposition to the ecosystem might be enhanced in that Nam Co region. The higher Hg wet deposition fluxes were found in precipitation during the monsoon season, which indicates that wet deposited Hg may endanger the ecosystems of the Nam Co region due to Hg's bioavailability. Moreover, the scavenged  $Hg_p$  is more stable than reactive Hg (e.g., RGM) in redox reactions and could retain in the environment over a long time, which suggests that the Tibetan Plateau might play an important role as a sink in global Hg cycling. Further studies addressing the contamination of unique ecosystems in the Tibetan Plateau are needed in the context of environment and climate change at a global scale.

#### Acknowledgments

We are grateful to the arduous precipitation sampling work of Mr. Wang Zhong and Ci Ren Duo Jie. Great help was offered from the staff of the Nam Co Monitoring and Research Station for Multisphere Interactions, Institute of Tibetan Plateau Research, Chinese Academy of Sciences. Many thanks are given to all of them. The authors also greatly appreciate three anonymous referees for their constructive comments and thoughtful suggestions. This work was supported by the National Natural Science Foundation of China (Grant Nos. 40830743; 41201057), the Global Change Research Program of China (Grant Nos. 2010CB951401), the Postdoctoral Science Foundation of China (Grant Nos. 2011M500404), and the Foundation of State Key Laboratory of Cryospheric Science, Chinese Academy of Sciences (Grant No. SKLCS-ZZ-2008-01 and SKLCS-09-06).

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