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## Physicochemical impacts of dust particles on alpine glacier meltwater at the Laohugou Glacier basin in western Qilian Mountains, China



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### HIGHLIGHTS

• We present a two-year investigation of dust impacts on alpine glacier meltwater.

· Particles in the melt are mainly composed by three parts with different sources.

• Accelerated glacier melting may affect physicochemistry of the meltwater.

• Glacier meltwater is probably influenced by dust deposition in central Asia.

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### ABSTRACT

This work discusses the temporal variation of various physicochemical species in the meltwater runoff of Laohugou Glacier No. 12 (4260 m a.s.l.) in central Asia, and their correlation with dust particles, based on a two-year field observation in summer 2012 and 2013, mainly focusing on dust concentration and size distribution, meltwater chemistry, particles SEM-EDX analysis in the meltwater, and MODIS atmospheric optical depth fields around the Qilian Mountains in central Asia. We find that, the volume-size distribution of dust particles in the meltwater is mainly composed of three parts, which includes fine aerosol particles (with diameter of 0 ~ 3.0  $\mu$ m, mainly PM 2.5), atmospheric dust (with diameter of 3.0 ~ 20  $\mu$ m), and local dust particles (20 ~ 100 µm), respectively. Comparison of dust particles in the snowpack and meltwater runoff indicates that, large part of dust particles in the meltwater may have originated from atmospheric dust deposition to the snow and ice on the glacier, and transported into the meltwater runoff. Moreover, temporal variation of dust and major ions (especially crustal species) is very similar with each other, showing great influence of dust particles to the chemical constituents of the glacier meltwater. SPM and TDS implied significant influences of dust to the physical characteristics of the glacier meltwater. Results showed that, accelerated glacier melting may affect physicochemical characteristics of the meltwater at an alpine basin under global warming. MODIS atmospheric optical depth (AOD) fields derived using the Deep Blue algorithm, showed great influence of regional dust transportation over western Qilian Mountains in springtime. SEM-EDX analysis shows that dust particles in the glacier meltwater contain Si-, Al-, Ca-, K-, and Fe-rich materials, such as guartz, albite, aluminate, and fly ash, similar to that deposited in snowpack. These results showed great and even currently underestimated influences of atmospheric dust deposition to glacier meltwater physicochemistry at an alpine basin in central Asia.

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### 1. Introduction

Aeolian (wind-blown) dust is an important source for trace and major elements to the snowpack worldwide, as shown in ice core records from polar, mid-latitude, and tropical glaciers (Correia et al.,

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2003; Hong et al., 2004a,b, 2005, 2009; Marteel, Gaspari, Boutron, et al., 2009; Thevenon et al., 2011). Dust contributes both soluble and insoluble mineral particles to snowpack, leading to differences in the fate and transport of associated elements during snow melt runoff (Bacardit and Camarero, 2010; Gaspari et al., 2006; Grotti et al., 2011). Atmospheric dust transporting and related large amount of trace element loading probably have important effect on global biogeochemical cycles between atmosphere and hydrosphere. Research has revealed that, many chemical elements in the oceans, e.g., trace elements Pb, Al, V, Mn, and Zn and some hydrocarbons and organic elements, may mainly

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originate from remote atmospheric dust transmission, other than that input from river transportation (Riley et al., 1989; Arimoto et al., 1992). Dust brings abundant Fe, Al and other various trace elements from crustal surface and industrial activities into the atmosphere and ocean, affecting the nutrition supply of ocean ecosystem significantly.

Central Asia is in a major dust source region in the Northern Hemisphere (Dong et al., 2009; Dong et al., 2010, 2011, 2014), from where large amounts of dust have been transported to North China, Japan, Korea, North Pacific, and America and even the Greenland ice sheet in Arctic regions, under the impact of atmospheric circulation, e.g., the westerly (Zhang et al., 2003; Ziegler et al., 2008; Wang et al., 2014). The Laohugou Glacier basin (LHG) in western Qilian Mountains is located in central region of Asian dust source (Dong et al., 2014). The glacier meltwater runoff may have been affected significantly by atmospheric dust deposition, which is important water resource in an arid and semi-arid region of northwestern China. Thus it is important to find out the physicochemical characteristics of glacier meltwater in the Laohugou Glacier basin of western Qilian Mountains. Dust particles may impact the physicochemistry of the meltwater runoff significantly, and dust constituents transforms from one chemical state to another and different chemical species dissolves into the meltwater, which will finally affect the hydrochemical characteristics of the glacier meltwater. The physical constituents of glacier meltwater runoff mainly include suspended particulate matter (SPM) and total dissolved solid (TDS). In the global biogeochemical cycle process, SPM and TDS, playing an important role in meltwater runoff, and are also crucial parameters for chemical elements migration and transformation (Yao et al., 2004).

Much research have estimated and discussed the sediment yield and transport capacity of dissolved solid in the glacier meltwater runoff (Raymo and Ruddiman, 1992; Meybeck and Ragu, 1997; Hodgkins et al., 2003). However, little research has been carried out on dust particle (mainly aeolian dust deposition in snow and ice from atmospheric transportation) effects on the physicochemistry of glacier meltwater runoff. Furthermore, study on dust particles and related chemical elements' migration and transformation has not been carried out. Therefore, this study mainly discusses a two-year temporal variation of dust particles and various physicochemical species in the meltwater during the glacier melting period, based on samples obtained at the snow pits and glacier terminus meltwater in the LHG basin, which is collected on glacier surface without effects of river bedrock and sediment on glacier meltwater physicochemistry, thus to find out the physicochemical impacts of Asian dust particles on alpine glacier meltwater at the Laohugou Glacier basin (LHG) in western Oilian Mountains of the Asian dust source region. In this work, we analyze the concentration, size distribution, morphology and chemical constituents of dust particles in the glacier meltwater and snow packs on the Laohugou Glacier No. 12. SEM-EDX was used for dust morphology and chemical composition analysis. MODIS atmospheric optical depth (AOD) fields derived using the Deep Blue algorithm, was also employed to examine the atmospheric dust transportation over the Qilian Mountains.

### 2. Sampling and lab analysis

The Qilian Mountains is located in the northeast of the Tibet Plateau, adjacent to the Hexi Corridor in arid and semiarid regions of northwestern China, and is also within the source region of the central Asian dust, where it is widely surrounded by large sandy deserts and the Gobi desert. Laohugou Glacier basin  $(39^{\circ}05'-39^{\circ}40'N, 96^{\circ}07'-97^{\circ}04'E)$  is at the northern slope of western Qilian Mountains with typical continental climatic conditions. The Laohugou Glacier No. 12 is the most typical glacier at the basin, with a length of 10 km and an area of 20 km<sup>2</sup>, and was divided into two branches at the altitude of 4560 m a.s.l., providing large amount of glacier meltwater runoff to the glacier basin in summer. During June and September in 2012 and 2013, in the glacier ablation period, we collected meltwater samples at the terminus (4260 m a.s.l.) of Laohugou Glacier No. 12 (Fig. 1). A total of 124 samples of meltwater were acquired. Samples were kept frozen and transported in the condition of -18 °C until laboratory measurement at the State Key Laboratory of Cryospheric Science of Chinese Academy of Sciences. In addition, we digged two snow pits in the accumulation area (5040 m a.s.l.) of Laohugou Glacier No. 12 in June, 2012, with depth ranging from 0.90 m to 1.65 m, and a capacity of 400 mL for each sample, and totally 80 snow samples were finally collected. The average of dust mass in meltwater runoff was compared to the snow samples obtained in accumulation zone, in order to find out the transmission process and sources of dust particles in the glacier meltwater.

Micro-particle concentrations and size distributions were measured on an Accusizer 780A counter, which uses the Single Particle Optical Sensing (SPOS) method, equipped with a 120 orifice (Zhu et al., 2006; Dong et al., 2009). Measurements were performed under class 100 conditions on sample aliquots diluted with a pre-filtered NaCl solution to give a 2 vol.% electrolyte concentration. The data were acquired for a size range of 0.57 to 400 µm (micrometers) equivalent spherical diameter (d). Routine analysis of filtered deionized water blanks showed background counts to be on average 10 times lower than in samples. Moreover, background counts were subtracted from the sample data. All samples were analyzed in random order and in triplicate. Results were then averaged for individual samples, yielding an estimated error of 10% or less on particle concentrations. The mass and volume size distribution of micro-particles were calculated from the raw count data by assuming spherical particles of uniform density  $\rho = 2.6$  g cm<sup>-3</sup>, which is close to that of average crustal material (Wake et al., 1994; Zdanowicz et al., 1998). Mass was derived by integrating the mass size distribution over the measured diameter range and normalizing the result to the sample volume.

To improve our understanding of the physical and chemical properties of individual particles from the snowpack, snow samples were also analyzed to determine the morphology, and chemical composition of individual dust particles, and to find out other components of particles, using a scanning electron microscopy coupled with energy dispersive X-ray spectrometer (SEM–EDX). Five of the snow samples were melted at room temperature just before filtration, and they were filtered on polycarbonate filters (Millipore Corporation) with a diameter of 47 mm and a pore size of 0.8 µm. Thus, only particles with diameters larger than 0.8 µm were collected and analyzed. The filtrations were completed in a class 1000 clean room at the State Key Laboratory of Cryospheric Sciences, Chinese Academy of Sciences. Polycarbonate filters were best suited for SEM observation due to the smooth surface texture, which makes individual particles much easier to discern than other types. First, approximately one-tenth of the polycarbonate filter was cut and then glued to a standard 12.5 mm aluminum SEM stub using double-faced adhesive carbon tape. Then, the specimen was coated with a thin carbon film by the electric arc high vacuum method. A Zeiss EVO MAR 10 SEM equipped with EDX was used for manual analyses. Operating conditions were 20 kV accelerating voltage and 480 pA beam current with spectral acquisition times of 60 s (Dong et al., 2014).

We also discussed Asian aerosol dust transportation over the Qilian Mountains and its influences on glacier meltwater. Data from the Cloud Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) mission (http://www-calipso.larc.nasa.gov) were used to characterize vertical distribution of dust transportation around the Qilian Mountains. Attenuated backscatter (reflectivity) profiles at 532 nm are provided by the Cloud-Aerosol Lidar with Orthogonal Polarization (CALIOP) installed on CALIPSO (Winker et al., 2003) with vertical and horizontal resolutions of 60 m and 12 km, respectively. The CALIOP-derived reflectivity is used as a proxy to describe the dust layer structure as it depends on aerosol concentration and its optical properties (Bou Karam et al., 2010). Examination of the NCEP/NCAR



Fig. 1. Map showing the sampling sites at Laohugou Glacier No. 12 in western Qilian Mountains, and the satellite image is from Google Earth.

reanalysis (Kalnay et al., 1996) and local meteorological data together with the Moderate Resolution Imaging Spectroradiometer (MODIS) atmospheric optical depth (AOD) (Hsu et al., 2006) data enabled dating dust deposition events to a precision of specific days and establishing broad source regions of the dust (e.g. Taklimakan deserts or Badain Jaran Desert).

### Table 1

Dust concentration and mean size in meltwater of Glacier No. 12 in the Laohugou Glacier basin.

	Mean	Standard deviation	Minimum	Maximum	Variation coefficient *
Number in June/mL <sup>-1</sup>	283,302	38,862	262,612	378,094	0.13718
Number in July/mL <sup>-1</sup>	293,076	47,618	258,233	467,479	0.16248
Number in August/mL <sup>-1</sup>	243,198	46,226	276,543	434,053	0.13469
Mean number/mL <sup>-1</sup>	275,846	52,404	258,233	467,479	0.16592
Mean mass/µg L <sup>-1</sup>	870,541	363,666	262,612	1,526,380	0.39197
Mean size/µm	1.39	0.1587	1.1	1.72	0.11409

\* Variation coefficient is an index showing the difference extent among variable values, indicating dust concentration in the study.



Fig. 2. Temporal variation of mean size and mass concentration of dust particles in the glacier meltwater of Laohugou Glacier No. 12 in summer 2012–2013.

### 3. Results and discussion

3.1. Concentration and size distribution of dust particles in glacier meltwater and comparison with snow packs

Table 1 shows the mean dust particle concentration and size in the meltwater of Glacier No. 12 during the ablation period in 2012 and 2013. Results indicate that, mean particle size is 1.39 µm, while mean number concentration is  $316 \times 10^3$ /mL; and mean mass concentration is  $870 \times 10^3 \,\mu\text{g/L}$ . Generally, fine dust particles were dominant in the meltwater, which was well comparable to the mean size of atmospheric dust in the snowpack on alpine glaciers in central Asia (Dong et al., 2009, 2011, 2014). Dust concentration varied in different time periods of the ablation season, showing low value in June, and then increased value in July, and decreased again in August. Preliminary analysis demonstrates that such a variation process is closely related to the ablation extent of glacier in summer, as the data in 2009 indicated that the max of glacier ablation also appeared in July (with the maximum of mean monthly air temperature in summer), and then released large amount of dust particles from snow and ice, which thus moved into the glacier meltwater runoff and caused increased dust mean size and concentration in July.

Fig. 2 shows temporal variation of mean size and mass concentration of dust particles in the glacier meltwater of Laohugou Glacier No. 12 in summer 2012 and 2013. We find that, both dust concentration and mean size gradually increased in July, which then decreased in August during the melting season. The highest dust concentration often occurred in July, which is consistent with the increase of precipitation and air temperature in the glacier basin. Precipitation has obvious effect on the variation of dust concentration in the glacier melt runoff, as precipitation could bring large amount of atmospheric dust and various impurities by wet deposition. Research has indicated that dust activity can bring large amount of particles from crustal surface to the atmosphere during springtime and summer in central Asia, which then transported and partly deposited to the alpine glacier basin in the Qilian Mountains. During the precipitation events, dust particles deposited on the glacier snowpack and meltwater, which may affect the dust concentration of glacier meltwater runoff. Meanwhile, according to the samples sites located at the glacier terminus surface, we inferred that the meltwater samples were little influenced by physical and chemical erosion of the bedrock. Besides precipitation, the increase of glacier melting and related dust emission from snow and ice was probably the main reason for dust concentration variation in the meltwater.

Figs. 3 and 4 show the size distributions of dust particles in the glacier meltwater. Fig. 3 shows the number-size distribution of dust particles in the meltwater of Glacier No. 12 (mean of 128 samples) (Fig. 3) during summer in 2012 and 2013. Number-size dust particles in the snow indicated that most of the dust particle diameter is <2.0 µm, implying the significant influences of finer particles of atmospheric dust to alpine glacial meltwater of central Asia, which is similar to that of snowpack on the Glacier No. 12 (Dong et al., 2014). Fig. 3b shows the temporal change of number-size distribution (monthly mean) of fine dust particles in the glacier meltwater, reflecting variation process of dust number distribution, with lower total number in June and increased number in July, and then decreased again in August. Fig. 4 shows the temporal change (June-August) of volume-size distribution (monthly mean) of dust particles of the meltwater, in which the peak value of the curve is the modal size (µm) of the dust particles (Fig. 4b). Table 2 shows the parameters of volume size distribution of dust particles at various sites shown in Fig. 4b. We find that, the temporal change process is very similar between dust size distribution and concentration in June to August in 2012 (Table 2), showing highest value of dust in July of melting period when there was relatively higher air temperature (Sun et al., 2012). Such phenomenon may be caused by the air temperature change and related glacier melting during the ablation period. The higher air temperature in July results in abnormally intense ablation of the snow and ice in the LHG basin.

Research has shown that, the peak value of the lognormal curve in volume size distribution is the modal size ( $\mu$ m) of the dust particles. In the meltwater of Laohugou Glacier No. 12, the mode value of particle size about volume distribution of dust particles ranges from 3.0 to ~20 µm primarily, which is the main particle fraction of dust in the glacier meltwater. The volume–size distribution of dust particles shows a bio-modal structure. Dust volume–size distribution in the meltwater is closely related to regional atmospheric environment, glacier melting and local meteorology in the Laohugou Glacier basin. Fig. 4 shows that the dust particles are mainly composed of three parts in the meltwater (Fig. 4a), including finer particles of aerosol particle



Fig. 3. Average number-size distribution of dust particles in the glacier meltwater during summer 2012 (a), and temporal change of number-size distribution of fine dust particles in the meltwater (b), in which JJA represents June to August (June, July and August).

deposition (0 ~ 3.0 µm, mainly PM 2.5), atmospheric dust particles (3.0 ~ 20 µm, mainly PM 10 of central Asia), and also local coarser dust particles (20 ~ 100 µm). The lognormal volume size distribution of dust from both atmospheric dust emission of glacier melting and local coarser particles, shows a firstly raised and then decreased trend in the melting period, which is very similar to that of dust concentration. Moreover, the mode of size distribution of dust particles also shows such a change tendency. Table 2 is a comparison of concentration with volume-size distribution parameters of dust particles in the glacier snow pits and meltwater showing in Fig. 4, indicating similar size distribution mode of dust in the meltwater and snow pits for particles distributed at 3.0 ~ 20 µm (Fig. 5). The mode value of size distribution of dust particles is 14.5 µm, 16.0 µm and 12.8 µm in June, July and August, respectively, which is an obvious similar change tendency with dust concentration. Therefore, the temporal change of dust concentration, size distribution and modal in the meltwater may be greatly influenced by glacier melting and corresponded dust emission in summer. At the beginning of melting period in June, the glacier melting is slow with few dust particle emissions from snow and ice, and dust particles are primary finer particles. As glacier melting gets intense in July, more dust particles are melted out, and dust concentration and mean size also increased in the meltwater. Moreover, the increase of meltwater due to strong glacier ablation in July may strengthen external moraine erosion of the glacier meltwater, which could also increase the concentration of coarser dust particles to the meltwater in some extent. However, as this work is mainly observed on the glacier surface, and the moraine particles are always much larger than the dust particles in the snowpack ( $d > 100 \mu$ m), thus the influence of moraine erosion is not anymore discussed in detail here.

# 3.2. Temporal variation of various physicochemical constituents of the glacier meltwater during melting period in summer

Concentrations of various chemical constituents of the meltwater in Glacier No. 12 of Laohugou basin are presented in Table 3. Mean concentration of major ions shows  $SO_4^{-2} > Ca^{2+} > Na^+ > HCO_3^- > Mg^{2+} > K^+ > Cl^- > NO_3^-$ , among which  $Ca^{2+}$  is the dominant cation in concentration accounting for 41.4%, while  $SO_4^{2-}$  is the dominant anion accounting for 68.2%. It is different from the chemical constituents' composition in the snow pits on Glacier No. 12, and most of  $SO_4^{2-}$  from crustal dust



**Fig. 4.** Volume–size distribution comparison of dust in glacier meltwater in the glacier basin of Laohugou from June to September of 2012, showing (a) the particles are mainly composed of three parts in the meltwater; (b) the log-normal distribution of atmospheric dust particle fraction  $(3 - 20 \,\mu\text{m})$ , in which a, b, c, d represent the dust size distribution of June, July, August and monthly mean, respectively. JJA represents the months of June to August (June, July and August).

dissolving is the possible reason which leads to higher  $SO_4^2$  value in the meltwater. We estimate the concentration of  $HCO_3^-$  by calculating ionic balance, as the ion imbalance of samples may be caused by the undetected  $HCO_3^-$  in accumulated snow. The mean pH of meltwater samples is 7.397 with weak alkalescency. EC value is high in the meltwater (135 µs/cm). The mean TDS concentration is 61.43 mg/L, which is much smaller than that of mineral dust particles (870 mg/L). Fig. 6 shows the relative ratio for various major ions in the meltwater of Glacier No. 12. Fig. 6a represents the relative relation between anions' concentration, and Fig. 6b represents that of the cations. We find that, the larger proportion of cations and anions are  $Ca^{2+}$ ,  $Na^+$  and  $SO_4^{2-}$ ,  $CI^-$ , respectively. Considering the regional atmospheric environment and Asian dust surrounding, we can infer that, the chemical constituents' contents of glacier meltwater are obviously influenced by mineral dust input of central Asia.

Fig. 7 shows the temporal change of various chemical species in the meltwater of Laohugou Glacier No. 12 during June to September in 2012. The monthly variation of chemical composition is very obvious in summer, especially in July with increase of some major ions' concentration. However, there are differences between ions' variation trend. Those ions often originated from crustal dust particles, such as  $Ca^{2+}$ , Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Cl<sup>-</sup>, have similar variation trends, with higher concentration in the strong melting period in July and decreased concentration in August, which is consistent with the change of dust concentration in the meltwater; While the concentration of  $SO_4^2$  and  $NO_3^-$  shows an increasing trend during the melting period, which many be caused by increased anthropogenic activities and frequent lightning in summer. Research indicated that the main sources of  $SO_4^{2-}$  in the glacier region are mineral dust and anthropogenic pollution, while the source of  $NO_3^-$  is more complex, including atmosphere lighting, stratosphere exchange, sea salt, soil dust, and human pollution. Much work demonstrated that the concentration of  $Ca^{2+}$  and  $SO_4^{2-}$ deposited in the glacier showed clear seasonal change at the source region of the central Asian dust, which is coincident with atmospheric dust activities, with higher dust concentration in springtime (March to May) and lower concentration in summer-autumn (Dong et al., 2010; Li et al., 2011). Moreover, chemical constituents of dust in precipitation are also significantly affected by Asian dust activities. We can infer that, the obvious increase of  $Ca^{2+}$  and  $SO_4^{2-}$  concentrations in the meltwater during July is not caused by regional atmospheric dust dry deposition or wet deposition in precipitation, other than emission of large amount dust particles from strongly melted glacier in the LHG basin. Ca<sup>2+</sup> could represent the mineral particles of Asian dust, which are generally in high concentration from March to June in springtime. Research on Urumqi Glacier No. 1 indicated that the variation of NH<sub>4</sub><sup>+</sup> concentration was different from that of  $SO_4^{2-}$  and other ions in fresh snow of the glacier region, as the concentration of SO<sub>4</sub><sup>2-</sup> was higher in spring and summer and similar with the variation of Ca<sup>2+</sup>, while the seasonal change of NH<sub>4</sub><sup>+</sup> was weak (Dong and Li, 2011). In this work, the concentration of Ca<sup>2+</sup> well reflected the increasing trend of dust particles' concentration in the meltwater during the summer. As the soluble parts of Asian dust, Ca<sup>2+</sup> could also reflect the influences of dust particles to the chemical species concentration of glacier meltwater with strong erosion effect in summer (Table 4).

Moreover, as there are some glacial moraines on the surface at the ablation zone of Glacier No. 12 (at the elevation of 4300 to 4500 m a.s.l.), so there exists meltwater hydrolysis process of surface moraines. The increase of various chemical species in the meltwater may be partly caused by surface moraines' erosion. However, as the size distribution of dust particles in the meltwater is dominantly finer particles (modal of  $3 \sim 20 \,\mu\text{m}$ , and most particle diameter  $< 2 \,\mu\text{m}$ ), we infer that the influence of dust particles from snow and ice is more important. The source of various chemical species in Laohugou Glacier meltwater is mainly (or large partial) influenced by dust particles from snow and ice melting and accumulation on the surface. Based on concentration, size distribution and chemical composition, we can infer that the dust particles in the meltwater are mainly from atmospheric dust deposition, For example, the crustal species of  $Ca^{2+}$ ,  $Na^{+}$ , Mg<sup>2+</sup>, K<sup>+</sup> and Cl<sup>-</sup> are in high concentration in July, which is consistent with the temporal variation of meltwater dust particles during the

Table 2

Concentration and volume-size distribution parameters of dust particles in the glacier snow pits and meltwater showing in Fig. 4b.

Sample type	Sample time	Sample number	Mass concentration (µg kg $^{-1}$ )	Size mode (µm)	Standard deviation (µm)
Glacier snow pits	Winter-spring	26	1860	15.2	9.8
	Summer-autumn	54	1368	12.4	10.6
	Annual average	80	1206	12.5	8.6
Glacier melt runoff	June	8	2180	14.5	8.9
	July	22	1679	16.0	10.1
	August	26	1724	12.8	9.2



Fig. 5. Number and volume size distribution comparison of dust deposition in the snow pits at 5040 m a.s.l. of Glacier No. 12 in 2012. Letters (a-f) represent the various samples in visible distinguishable dust layers in the snow pits.

melting period of summer. Besides the effect of glacial dust, the erosion function of glacier surface moraine may be another reason that leads to chemical species concentration change in the meltwater. However, we think that such erosion function is not a large influence to meltwater dust, as we collected the samples on glacier surface at the terminus. Moreover, with summer air temperature rise, vegetation growing

## Table 3 Concentration of various chemical constituents of the glacier meltwater in the Laohugou basin.

Chemical species	Mean	Standard deviation	Minimum	Maximum	Mid-value	Variation coefficient
$Cl^-/\mu g L^{-1}$	483	234	137	1402	472	0.4850
$SO_4^{2-}/\mu g L^{-1}$	12,018	5002	5078	33,097	10,756	0.4162
$NO_3^-/\mu g L^{-1}$	428	207	114	1141	401.8	0.4854
$Na^+/\mu g L^{-1}$	6910	2795	2495	14,811	6091.7	0.4046
$K^+/\mu g L^{-1}$	570	315	117	1300	532.35	0.5525
$Mg^{2+}/\mu g L^{-1}$	2839	1644	641	11,487	2537	0.5790
$Ca^{2+}/\mu g L^{-1}$	7313	3002	2568	21,489	7054	0.4105
$HCO_3^-/\mu g L^{-1}$	4703	2387	907	15,099	4654	0.4321
$EC/\mu s cm^{-1}$	135	25	83	203	133	0.1902
pH	7.39	0.26	7.03	8.01	7.33	0.0362
TDS/mg $L^{-1}$	61.4	13.2	40.1	98.1	64.3	0.1993



Fig. 6. Triangle graphs showing relative ratio for chemical composition of major ions in the meltwater, (a) represents the relative relation between anions and (b) represents that of cations.

and increased human activities' pollution emission may be another reason that leads to temporal change of chemical constituents in meltwater runoff, for example, the concentration of  $SO_4^{2-}$  and  $NO_3^{-}$  have an increasing trend continuously with the raised air temperature in summer.

Furthermore, temporal variations of physical parameters (e.g., pH and EC) are also in correspondence to the dust concentration (SPM) and TDS change (Fig. 8 and 9), which both have change trend of high value in July and then decrease in the meltwater of Laohugou Glacier No. 12. Such changes are similar to the variation of various chemical species, particularly those from crustal dust. The pH showed weak alkalescency in the meltwater, which is often in high value when dust concentration increased, with chemical ions' concentration increased in the meltwater. Thus the increase of dust caused the increase of pH and EC value of the meltwater. SPM and TDS are important parameters for the physicochemical characteristics of meltwater runoff (Xu et al., 2012: Shi. 2006: Zhu et al., 2006: Gao et al., 2011). The EC could also reflect the total concentration of various chemical species in meltwater (Williams et al., 1995; Lafreniere and Sharp, 2005). The variation of these physical parameters (e.g., SPM, TDS and EC) probably implied that mineral dust particles input has significant effects on the concentration and migration-transformation of various physicochemical species in glacier meltwater. Thus the soluble fraction of dust affects the physicochemical constitutes of meltwater in Laohugou basin to a large extent.

However, in this study, the sampling site at the glacier terminus probably greatly reduces the influence of the erosion of river bedrock in the runoff, and the migration-transformation process of various chemical species of meltwater will be more complex during migration process with river bed erosion (Agren et al., 2010; Ollivier et al., 2010; Welch et al., 2010; Fortner et al., 2011; Xia et al., 2012). Fig. 9 shows a comparison of SPM and TDS variation in meltwater of Laohugou Glacier No. 12 during summer 2012 and 2013, and temporal variation of TDS and SPM in the meltwater has a regularly similar change with each other. TDS variation is in coincident with that of dust concentration, implying that crustal dust particles affect the concentration of TDS in the meltwater significantly.

### 3.3. SEM-EDX morphological analysis for dust particles in the meltwater

The size, shape and morphological parameters of particles are different under the microscope. In most cases, the factors that characterize particles are not their elementary forms, but the organization of their structures. To obtain the optimal perspective, different magnification levels are used for insoluble particles with different purposes. In this study, the lowest magnification  $(500 \times)$  could discriminate in the order of tens of microns and the highest magnification  $(10,000\times)$ can discriminate in the order of tens of nanometers. Comprehensive compositional and structural information can be obtained through this method.  $10 \times 10^6$  particles were observed at  $3000 \times$  magnification within the magnified area, and a total of 305 particles with regular shapes (including spherical carbon particles and biological particles) were analyzed by EDX to study their elemental composition and possible mineralogy. Smooth spherical particles, mostly fly ash particles, emanating from high temperature industrial combustion, are mostly characterized by a spherical shape, which results from melting processes that occur during their formation (Umbria et al., 2004). Among dust particles, mineral particles dominate the most of the particles in the meltwater of the Laohugou basin. Dust particles in the snow are mainly mineral particles. besides some fly ash and soot. EDX showed that mineral particles contain Si, Al, Ca, K, and Fe-rich materials, such as, quartz, albite, and aluminate, which are very similar to that deposited in snowpack on the Glacier No. 12 at the altitude of 5040 m a.s.l. of the accumulation zone (Umbria et al., 2004). From the above analysis, we can infer that dust morphological characteristics in the meltwater are influenced by atmospheric dust from the snowpack of the glacier significantly, and probably that these particles in meltwater are large partially originated from snow and ice melting (Fig. 10).

#### 3.4. Discussion

From the above analysis, we will discuss the effects of dust particles on the physicochemical characteristics in the meltwater of the Laohugou Glacier basin. The Laohugou Glacier region and the glaciers in the whole western Qilian Mountains are under high altitude atmospheric environment, where it is significantly influenced by Asian dust transportation, especially dust storms from the large sandy deserts of central Asia in springtime, and also dust particles deposited and preserved in snow and ice of the alpine glaciers. The elevated AOD values were registered by MODIS (Fig. 11a). MODIS AOD values for 01 May to 01 June in 2012 and CALIOP/CALIPSO transect showed strong backscattering signal indicative of the continuing dust uplift and circulation of dust over the region and its extension toward the Oilian Mountains (Fig. 11). Those preserved dust particles are probably released by accelerated glacier melting under global warming, and then affect the physicochemical characteristics of the meltwater significantly. In addition, dust particles may bring plenty of major and rare chemical elements dissolving into the glacier meltwater, which thus have an important



Fig. 7. Temporal changes of various chemical species in the meltwater of Glacier No. 12 during summer 2012.

effect on physicochemical characteristics of the meltwater with the meltwater migration and transformation.

In the study, dust concentration and size distribution of the meltwater well reflected the intense glacier melting and related amount of particle emission during different time periods in summer, which is highly in correspondence to the temporal variation of air temperature and glacier melting extent. For example, the dust concentration and size distribution in July, were higher than that in other months when the glacier melt intensely, and then decreased in August again. Meanwhile, the dust particle in meltwater was similar to the dust preserved

### Table 4

SEM-EDX particle type and their element chemical composition of dust parties in the meltwater of Laohugou Glacier No. 12.

Туре	Ratio (%)	Percent of mass for various chemical elements (%)									
		Na	Mg	Al	Si	Cl	К	Ca	Ti	Fe	S
Si-rich	50.6	0.2	1	13	56	4.5	4.2	14	2.3	1.4	-
Ca-rich	30.5	0.1	1.9	11.2	17	3.7	3.2	46	8.4	13.5	28
Al-rich	7.8	-	0.5	9.8	18	4.5	8.4	3.2	3.4	36	5.6
K-rich	7.6	1.2	1.5	16.3	13	4.2	35	14	6.5	18	-
Fe-rich	1.3	-	4.3	12	28	3.5	6.3	4.2	3.1	34	-

The significance of bold data was at 0.001 level.

in snow and ice, e.g., dust size distribution and mode. For instance, Volume–size distribution of the insoluble dust particles is mainly composed of three parts in the meltwater (Fig. 4a), including finer particles of atmospheric aerosol ( $0 \sim 3.0 \mu m$ ), atmospheric dust particles ( $3.0 \sim 20 \mu m$ ), as well as local coarser particles ( $20 \sim 100 \mu m$ ). Comparison of the lognormal distribution size of atmospheric dust particles ( $3 \sim 20 \mu m$ ), implies that dust particles in meltwater are large partially from dust emission of the glacier snow and ice (Fig. 5b). Compared with dust particles in the snow pits, the source of dust physicochemical constituents in the glacier meltwater is more complex in the Laohugou basin, which is mainly composed of three parts, reflecting the significant influences of atmospheric dust transportation and local dust input.

Moreover, dust particles probably also have obvious effects on other physicochemical characteristics of the meltwater. Firstly, the relative ratio of chemical ions in the meltwater shows the dominant ions of  $Ca^{2+}$ ,  $Na^+$ ,  $SO_4^{2-}$  and  $Cl^-$ , respectively. Considering the regional atmospheric environment of the Asian dust source, we can infer that the chemical constituents mainly reflect the apparent effects of mineral dust input on glacier meltwater. Secondly, the temporal variation of the concentration of various chemical ions, particularly those ions mainly coming from crustal dust, is consistent with that of dust particles during melting period. Major ions mainly from mineral dust particles, such as  $Ca^{2+}$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $K^+$  and  $Cl^-$ , have similar variation trends during

summer. The higher value of chemical ions' concentration occurred in the strong melting period of July, and decreased in August, which is well in correspondence to the change of dust concentration in the meltwater and strong glacier melting. However, the concentration of other chemical ions, e.g.,  $SO_4^2$  and  $NO_3^-$ , shows an increase trend in summer, which is probably caused by increased temperature in summer and accelerated emission of human activities' pollutions. Furthermore, the temporal variations of pH, EC and TDS, reflected the effects of dust particles on physical characteristics of the meltwater. When the concentration of dust particles is higher, both pH and EC also show high values, mainly in the intense glacier melting period in July. Moreover, the temporal changes of SPM and TDS concentration have similar trends, implying the significant influences of dust particles on the TDS in the meltwater runoff of glaciers in central Asia. Additionally, SEM-EDX analysis shows that dust particles in glacier meltwater contain Si-, Al-, Ca-, K-, and Fe-rich materials, such as quartz, albite, aluminate, and fly ash, which are very similar to that deposited in snowpack on the glacier.

### 4. Conclusions

This work discussed the temporal variation of various physicochemical species in the meltwater runoff of Laohugou Glacier No. 12 (4260 m a.s.l.) in central Asia, and their correlation with dust particles, based on a two-year field observation from June to September in 2012 and 2013, mainly focusing on dust concentration and size distribution, chemistry, particle SEM–EDX analysis in meltwater and MODIS atmospheric optical depth fields in central Asia. During the melting period, large amounts of dust particles are melted from ice and snow of the glacier and then dispersed into the meltwater, which is very important for the change of physicochemical characteristics of glacier meltwater. We find that the volume–size distribution of dust particles in the meltwater runoff of Glacier No. 12 is mainly composed of three parts, which are fine aerosol particles (with diameter of  $0 \sim 3.0 \ \mu m$ , mainly PM 2.5), atmospheric dust (with diameter of  $3.0 \sim 20 \ \mu m$ ), and local dust particles ( $20 \sim 100 \ \mu m$ ), respectively. Comparison of dust particles in



Fig. 8. Temporal variations of pH and EC in the meltwater of Glacier No. 12 during summer 2012 and 2013, with obvious seasonal change during the melting periods.



Fig. 9. Temporal variations of SPM and TDS in the meltwater runoff of Glacier No. 12 in the Laohugou basin.

the snowpack and meltwater runoff indicates that large part of dust particles in the meltwater may have originated from atmospheric dust deposition in snow and ice on the glacier, and transported into the meltwater runoff. Moreover, temporal variation of dust and major ions (especially crustal species, such as Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Cl<sup>-</sup>) is very similar with each other, showing great influence of dust particles to the chemical constituents of the glacier meltwater runoff. Particle concentration is relatively high in July, and decreases in August, which is



Fig. 10. SEM-EDX images of dust particles in the glacier meltwater runoff at the Laohugou basin, (a) various dust particles in a typical sample, (b) spherical fly ash, (c) calcium sulfate, and (d) aluminosilicate.



**Fig. 11.** (a) MODIS AOD values for 01 May to 01 June in 2012 and (b) CALIOP/CALIPSO transact showing attenuated backscatter coefficient (km<sup>-1</sup> sr<sup>-1</sup>) profiles at 532 nm with 60 m vertical and 12 km horizontal resolution. The outline of the topography is shown as a solid orange line. Thick clouds appear in white and dust clouds in orange-red.

highly correlated with glacier melting velocity in this region. However,  $SO_4^{2-}$  and  $NO_3^{-}$  concentrations show an increasing trend during June to September, which may be caused by increased anthropogenic species input. SPM and TDS also show a similar change trend with dust particles in the meltwater, implying significant influences of glacier dust particles to TDS in the glacier region of Laohugou in the Qilian Mountains in central Asia. The variation of these physical parameters (e.g., SPM, TDS and EC) probably implied that mineral dust particles' input has significant effects on the concentration and migration-transformation of various physicochemical species in glacier meltwater.

MODIS atmospheric optical depth (AOD) fields derived using the Deep Blue algorithm, showed great influence of regional dust transportation over western Qilian Mountains. SEM–EDX analysis shows that dust particles in glacier meltwater contain Si-, Al-, Ca-, K-, and Fe-rich materials, such as quartz, albite, aluminate, and fly ash, which are very similar to that deposited in snowpack on the glacier. These results showed great and even currently underestimated influences of atmospheric environment, including both local dust and anthropogenic activities, to glacier meltwater physicochemistry at an alpine basin in central Asia.

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### References

- Agren A, Haei M, Kohler S, et al. Long cold winters give higher stream water dissolved organic carbon (DOC) concentrations during snowmelt. Biogeosci Discuss 2010;7: 4857–86.
- Arimoto R, Duce RA, Savoie DL, et al. Trace elements in aerosol particles from Bermuda and Barbados: concentrations, sources and relationships to aerosol sulfate. J Atmos Chem 1992;14(1–4):439–57.
- Bacardit M, Camarero L Atmospherically deposited major and trace elements in the winter snowpack along a gradient of altitude in the Central Pyrenees: the seasonal record of long-range fluxes over SW Europe. Atmos Environ 2010;44:582–95.
- Bou Karam D, Flamant C, Cuesta J, Pelon J, Williams E. Dust emission and transport associated with a Saharan depression: February 2007 case. J Geophys Res 2010;115: D00H27. http://dx.doi.org/10.1029/2009JD012390.
   Correia A, Freydier R, Delmas RJ, Simoes JC, Taupin JD, Dupre B, et al. Trace elements in
- Correia A, Freydier R, Delmas RJ, Simoes JC, Taupin JD, Dupre B, et al. Trace elements in South America aerosol during 20th century inferred from a Nevado Illimani ice core, Eastern Bolivian Andes (6350 m asl). Atmos Chem Phys 2003;3:1337–52.
- Dong Zhiwen, Li Zhongqin. Characteristics of atmospheric dust deposition in snow on Glacier No. 72, Mt. Tuomuer, China. Arct Antarct Alp Res 2011;43(4):517–26. http://dx.doi.org/10.1657/1938-4246-43.4.517.
- Dong Zhiwen, Li Z, Wang F, Zhang M. Characteristics of atmospheric dust deposition in snow on the glaciers of the eastern Tien Shan, China. J Glaciol 2009;55(193): 797–804.
- Dong Zhiwen, Li Z, Xiao C, Zhang M, Wang F. Characteristics of aerosol dust in fresh snow in the Asian dust and non-dust periods at Urumqi Glacier No. 1 of eastern Tian Shan, China. Environ Earth Sci 2010;60:1361–8. <u>http://dx.doi.org/10.1007/s12665-009-</u> 0271-6.
- Dong Zhiwen, Li Zhongqin, Edwards Ross, Wu Lihua, Zhou Ping. Temporal characteristics of mineral dust particles in precipitation of Urumqi River Valley in Tian Shan, China: a comparison of alpine site and rural site. Atmos Res 2011;101:294–306. <u>http://dx.doi.org/</u> 10.1016/j.atmosres. 2011.03.002.
- Dong Zhiwen, Qin Dahe, Kang Shichang, Ren Jiawen, et al. Physicochemical characteristics and sources of atmospheric dust deposition in snow packs on the glaciers of western Qilian Mountains, China. Tellus B 2014;66:20956. <u>http://dx.doi.org/10.3402/tellusb.</u> v66.20956.
- Fortner SK, Lyons WB, Olesik J. Eolian deposition of trace elements onto Taylor Valley Antarctic glaciers. Appl Geochem 2011;26:1897–904.
- Gaspari V, Barbante C, Cozzi G, Cescon P, Boutron CF, Gabrielli P, et al. Atmospheric iron fluxes over the last deglaciation: climatic implications. Geophys Res Lett 2006;33. L03704.
- Grotti M, Soggia F, Ardini F, Magi E. Major and trace element partitioning between dissolved and particulate phases in Antarctic surface snow. J Environ Monit 2011;13: 2511–20.
- Hodgkins R, Cooper R, Wadham J, et al. Suspended sediment fluxes in a high Arctic glacierised catchment: implications for fluvial sediment storage. Sediment Geol 2003;162:105–17.
- Hong S, Barbante C, Boutron C, Gabrielli P, Gaspari V, Cescon P, et al. Atmospheric heavy metals in tropical South America during the past 22000 years recorded in a high altitude ice core from Sajama, Bolivia. J Environ Monit 2004a;6:322–6.
- Hong S, Boutron CF, Gabrielli P, Barbante C, Ferrari CP, Petit JR, et al. Past natural changes in Cu, Zn and Cd in Vostok Antarctic ice dated back to the penultimate interglacial period. Geophys Res Lett 2004b;31. L20111.
- Hong S, Boutron CF, Barbante C, Hur SD, Lee K, Gabrielli P, et al. Glacial-interglacial changes in the occurrence of Pb, Cd, Cu and Zn in Vostok Antarctic ice from 240000 to 410000 years BP. J Environ Monit 2005;7:1326–31.
- Hong S, Lee K, Hou S, Soon DH, Ren J, Burn IJ, et al. An 800-year record of atmospheric As, Mo, Sn, and Sb in central Asia in high-altitude ice cores from Mt. Qomolangma (Everest), Himalayas. Environ Sci Technol 2009;43:8060–5.

- Hsu NC, Tsay S-C, King MD, Herman JR. Deep Blue Retrievals of Asian Aerosol Properties During ACE-Asia. IEEE Trans Geosci Remote 2006;44:3180–95. <u>http://dx.doi.org/10.</u> 1109/TGRS.2006.879540.
- Lafreniere M, Sharp MJ. A comparison of solute fluxes and sources from glacial and nonglacial catchments over contrasting melt seasons. Hydrol Process 2005;19(7): 2991–3012. http://dx.doi.org/10.1002/hyp.5812.
- Li Z, Li H, Dong Z, Zhang M. Chemical characteristics and environmental significance of fresh snow deposition on Urumqi Glacier No. 1 of Tianshan Mountains, China. Chin Geogr Sci 2010;20(5):389–97. http://dx.doi.org/10.1007/s11769-010-0412-6.
- Marteel A, Gaspari V, Boutron CF, et al. Climate-related variations in crustal trace elements in Dome C (East Antarctica) ice during the past 672 kyr. Clim Chang 2009;92: 191–211.
- Meybeck M, Ragu A. River discharges to the oceans: an assessment of suspended solids, major ions and nutrients. United Nations Environment Programme 1997;245.
- Ollivier P, Hamelin B, Radakovitch O. Seasonal variations of physical and chemical erosion: a three-year survey of the Rhone River, France. Geochim Cosmochim Acta 2010;74:907–92.
- Raymo ME, Ruddiman WF. Tectonic forcing of Late Cenozoic climate. Nature 1992;359: 117–22.
- Riley JP, Chester R, Duce RASEAREX: the sea/air exchange program. Chem Oceanogr. New York: Academic Press; 1989. p. 404.
- Shi Changxing. A quantitative analysis of the effects of wind erosion on sediment yield in the Wudinghe River watershed. Geogr Res 2006;25(2):285–93. [In Chinese].
- Sun Weijun, Qin Xiang, Ren Jiawen, et al. The Surface Energy Budget in the Accumulation Zone of the Laohugou Glacier No.12 in the Western Qilian Mountains, China, in Summer 2009. Arct Antarct Alp Res 2012;44(3):296–305.
- Umbria A, Galán M, Muñoz MJ, Martin R. Characterization of atmospheric particles: analysis of particles in the Campo de Gibraltar. Atmósfera 2004;17:191–206.
- Wake CP, Mayewski PA, Li Z. Modern eolian dust deposition in central Asia. Tellus B 1994; 46:220–3.
- Wang Shengjie, Zhang Mingjun, Pepin NC, Li Zhongqin, Sun Meiping, Huang Xiaoyan, et al. Recent changes in freezing level heights in High Asia and their impact on glacier changes. J Geophys Res Atmos 2014;119. http://dx.doi.org/10.1002/2013JD020490.
- Welch KA, Lyons WB, Whisner C, et al. Spatial variations in the geochemistry of glacial meltwater streams in the Taylor Valley, Antarctic. Antarct Sci 2010;22(6):662–72.
- Winker DM, Pelon JR, McCormick MP. The CALIPSO mission: spaceborne lidar for observation of aerosols and clouds. Proc. SPIE 4893, Lidar Remote Sensing for Industry and Environment Monitoring III, 1.; 2003. p. 1–11. (24 March 2003).
- Gao Wenhua, Li Zhongqin, Zhang Mingjun. Study on particle-size properties of suspended load in glacier runoff from the Tomor Peak. Arid Zone Res 2011;28(3):449–54. [In Chinese].
- Williams M, Yang DQ, Liu FJ, et al. Controls on the major ion chemistry of the Urumqi River, Tianshan, the People's Republic of China. J Hydrol 1995;172:209–29.
- Xia Xinghui, Wu Qiong, Mou Xinli. Advances in impacts of climate change on surface water quality. Advance in Water Sciences 2012;23(1):124–33. [In Chinese].
- Xu J, Yu G, Kang S, Hou S, Zhang Q, et al. Sr-Nd isotope evidence for modern aeolian dust sources in mountain glaciers of western China. J Glaciol 2012;58(211):859–65. http://dx.doi.org/10.3189/2012JoG12J006.
- Yao TD, Wu GJ, Pu JC, et al. Relationship between calcium and atmospheric dust recorded in Guliya ice core. Chin Sci Bull 2004;49(7):706–10.
- Zdanowicz CM, Zielinski GA, Wake CP. Characteristics of modern atmospheric dust deposition in snow on the Penny Ice Cap, Baffin Island, Arctic Canada. Tellus B 1998;50: 506–20.
- Zhang XY, Gong SL, Shen ZX. Characterization of soil dust aerosol in China and its transport and distribution during 2001 ACE-Asia: 1. Network observations. J Geophys Res 2003;108(D9). http://dx.doi.org/10.1029/2002JD002632.
- Ziegler CL, Murray RW, Plank T, et al. Sources of Fe to the equatorial Pacific Ocean from the Holocene to Miocene. Earth Planet Sci Lett 2008;270:258–70.
- Zhu YM, Li ZQ, You XN. Application and technique in glacier by AccuSizer 780A Optical Particle Sizer. Mod Sci Instrum 2006;3:81–4. (in Chinese).