

Source and yearly distribution of PAHs in the snow from the Hailuogou glacier of Mountain Gongga, China

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Abstract Snow samples were collected over a 3-year period from 2012 to 2014 at the Hailuogou glacier of Mountain Gongga (Mt. Gongga) and analyzed for 16 priority polycyclic aromatic hydrocarbons (PAHs) using Gas Chromatography–Mass Spectrometry (GC–MS). The results show that total average levels of the 16 PAHs ranged from 452 to 290 ng·L⁻¹ with a possible declining trend from 2012 to 2014. Distances between the sampling sites and the emission sources were estimated at typically less than 500 km. The results suggest that the major source of PAHs was from coal combustion, while contributions from automobile exhaust played an important role in more recent years. This finding was in agreement with the characteristics of presence of local industry, residence, and recent development of tourism of the surrounding areas.

Keywords PAHs · Snow · Source · Distribution · GC–MS · Hailuogou of Mt. Gongga

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their derivatives are associated with the incomplete combustion of organic material, arising from episodes of volcanic

eruptions, forest fires (Bjorseth and Ramdahl 1985), and from human activities of burning fossil fuels (Baek et al. 1991). Because of their inertness and volatility, PAHs can travel long distances in the air and be distributed in different environmental media, leading to widespread pollution (Wang et al. 2006).

In high latitude or high-altitude areas, PAHs are transferred and trapped in the ice and snow via wet atmospheric deposition (rain, snow, etc). Over time, significant amounts of PAHs can be accumulated in such locations. When ice and snow melt as a result of seasonal temperature changes, the accumulated PAHs will be released to other environmental compartments such as surrounding water, soil, and air, thus causing a detrimental impact to the ecosystem of the region. The general trend of global warming is making this dire situation even more pressing. Therefore, it is very important to investigate PAHs in ice and snow from glacier (Li et al. 2010) and study their origin, distribution, and transport. Until now, research on organic pollutants, particularly PAHs in snow and ice, have been mainly focused on the north and south poles (Kang et al. 2012; Herbert et al. 2005; Gregor and Gummer 1989; Halsall 2004; Jaffrezo et al. 1993), Greenland (Jaffrezo et al. 1994), and the Alps region (Carrera et al. 2001; Villa et al. 2006; Finizo et al. 2006). Studies of PAHs in the Qinghai Tibet Plateau region started fairly late and publications on the topic are still scarce (Li et al. 2010) although the sediment core and road dusts were carefully studied (Han et al. 2015; Wei et al. 2015). Wang et al. (2008) studied levels and distribution of organochlorine pesticides and PAHs in ice and snow from the Dasuopu glacier. Wang et al. (2007) reported concentrations of organochlorine pesticides in new snow samples at four different altitudes in east Rongbuk glacier of the Everest region and studied their correlations with altitude. Li et al. (2010) investigated on the distribution and source of the PAHs in ice and snow from

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four glaciers including the Qilian Mountain Qiyi glacier and the Tanggula Dongkemadi glacier. More recently, Yu et al. (2014) studied the distribution and the source of the PAHs in snow over a short period in the Hailuogou glacier, Mt. Gongga.

In this work, snow samples from the Hailuogou glacier of Mt. Gongga in China were collected over a 3-year period from 2012 to 2014, and their concentrations were analyzed for 16 PAHs. The main purpose of this preliminary study was to determine the levels of PAHs in this glacier and try to identify the distribution and source of these PAHs and to estimate their transport distance from origin.

1.1 Sample collection

In January of each year, three snow samples were collected from Hailuogou for a total of nine samples over the 3-year period from 2012 to 2014. The sampling sites are shown in Fig. 1. The thickness of snow cover was always greater than 25 cm. Snow samples were collected with a clean stainless-steel shovel and packed in a 10-L clean aluminum drum which was sealed with three layers of aluminum paper. The sample information is given in Table 1. The amount of each sample was equivalent to 3–4 L of water.

2 Experimental

2.1 Sample pretreatment

A solid phase membrane extraction method was adopted for the enrichment of PAHs from snow samples. The C₁₈ solid

phase extraction disks membrane (Supelco Analytical, diameter 47 mm) was fixed on a sand core suction filter device. The membrane was activated by passing through 5.0 mL of cyclohexane, n-hexane, methanol, and pure water each in sequence. All of the organic reagents used were HPLC grade. The snow sample was melted at room temperature and the upper clear liquid was loaded on the activated C₁₈ membrane. The flow rate was regulated between 12 and 30 mL·min⁻¹. The eluent was discarded, and 5.0 mL of n-hexane was then added to the C₁₈ membrane and let soaking for 10 min before being eluted. This step was repeated three times. The combined eluent was passed through a chromatography column filled with anhydrous sodium sulfate (activated in a muffle furnace at 400 °C for 24 h), and the volume was further reduced to 1.0 mL under a stream of high purity nitrogen. A procedure blank (3 L of pure water) was processed along with the snow samples.

2.2 Sample analysis

2.2.1 Reference standards and reagents

Sixteen certified PAHs standards were purchased from AccuStandard (USA), including Naphthalene (Nap), Ace-naphthylene (Ace), Acenaphthene (Acp), Fluorene (Fle), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chry), Benzo(b)fluoranthene (BbF), Benzo [k] fluoranthene (BkF), Benzo [a] pyrene (BaP), Indeno [1, 2, 3-cd] pyrene (InP), Dibenz [a, h] anthracene (DahA), and Benzo(g,h,i)-perylene(BghiP). Individual stock solutions at concentrations of 100.00 µg·mL⁻¹ each were prepared in

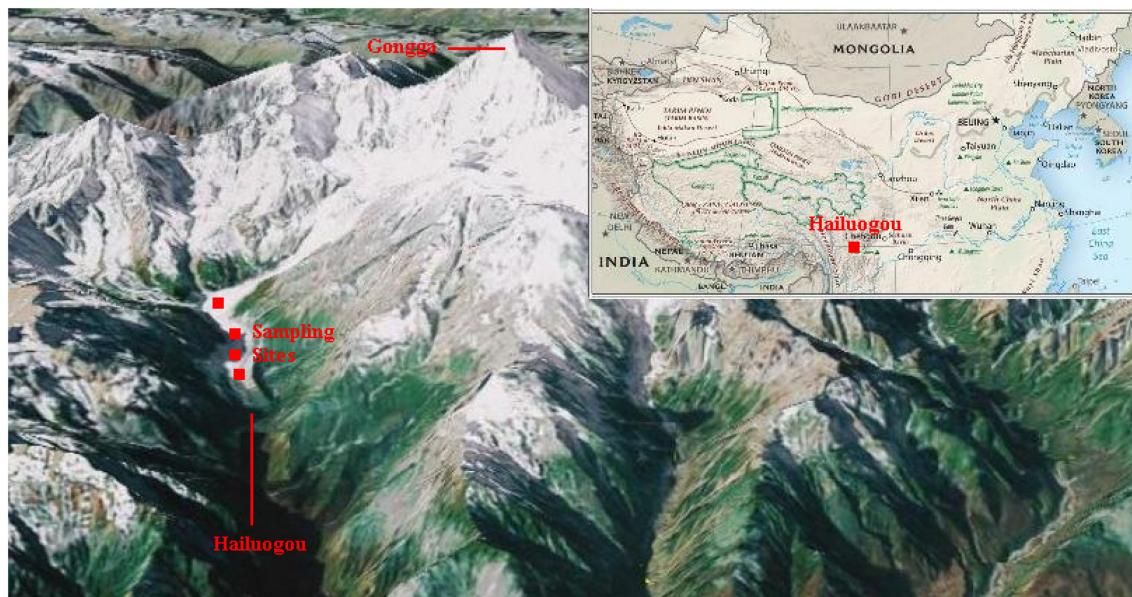


Fig. 1 Map of sampling sites

Table 1 Sample information

Sample site	Sampling time	Altitude (m)	Latitude	Longitude	Sampling depth (cm)
1201	January 2012	3170	29°33'19"N	101°58'11"E	0–20
1202	January 2012	3250	29°33'54"N	101°58'45"E	0–20
1203	January 2012	3470	29°34'00"N	101°58'55"E	0–20
1301	January 2013	3100	29°34'03"N	101°59'55"E	0–20
1302	January 2013	3130	29°34'01"N	101°59'50"E	0–20
1303	January 2013	3180	29°34'57"N	101°59'42"E	0–20
1401	January 2014	3110	29°34'04"N	101°58'59"E	0–20
1402	January 2014	3140	29°34'02"N	101°58'56"E	0–20
1403	January 2014	3190	29°33'54"N	101°58'45"E	0–20

dichloromethane–acetone 50:50 (v:v). The working standard solutions were prepared by mixing each of the PAH stock solutions and diluting with dichloromethane–acetone 50:50 for a final concentration of $2.00 \mu\text{g}\cdot\text{mL}^{-1}$ each.

All organic solvents were HPLC grade from Changzheng Chemical Reagent Co. Ltd. (Chengdu, China). Milli-Q water was used as pure water. Unless otherwise stated, all the reagents used in this study were of analytical grade or higher.

2.2.2 GC–MS conditions

Analyses were performed using a 7890-5975 Gas Chromatography–Mass Spectrometer (GC–MS) (Agilent Technologies, Santa Clara, CA) equipped with an autosampler (Triplus Co. USA). Separations were facilitated using an HP-5MS analytical column, $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ (SN: USB439554H, Agilent Technologies).

The carrier gas was helium (99.999% purity) with a flow rate of $2.0 \text{ mL}\cdot\text{min}^{-1}$ at 164.6 kPa. Injections were made in the splitless mode with an injection volume of $2.00 \mu\text{L}$. The injector temperature was 290°C . The temperature program was as follows: holding initial temperature at 100°C for 1 min, ramping to 240°C at $10^\circ\text{C}\cdot\text{min}^{-1}$ (linear), holding for 5.0 min, ramp to 280°C at $20^\circ\text{C}\cdot\text{min}^{-1}$ (linear) and holding for 8.0 min.

The mass spectrometry measurements were carried out through an electron impact (EI, 70 eV, 230°C) coupled with a full scan mode. Other parameters included scanning range of 0–500 amu, transmission temperature of 150°C and solvent delay time of 2.0 min.

3 Results and discussion

3.1 Qualification of the method

The analysis was performed using a five-point standard calibration curve. Linear correlation coefficients of the 16 PAHs varied from 0.9975 to 0.9998. Recoveries and relative standard deviations were 75.9%–99.2% and 2.8%–

15.8%, respectively. Detection limits were ranged from 0.001 to $0.010 \mu\text{g}\cdot\text{L}^{-1}$.

3.2 Distribution of PAHs in sample area

The results for individual 16 PAHs over the 3-year period from 2012 to 2014 are listed in Tables 2, 3 and 4 of Appendix 1, and they are plotted in Fig. 2. The amount of individual PAHs varies widely, ranging from non-detectable (DahA and BghiP) to $\sim 100 \text{ ng}\cdot\text{L}^{-1}$ (Phe). Among the 16 PAHs that are reported here, nine PAHs (Nap, Ace, Acp, Fle, Phe, Fla, Pyr, BaA, BkF) were highest for the year 2012, four (Chry, BbF, BaP, INP) for 2013 and one (Ant) for 2014. This change in dominance possibly indicates a change in the source of PAHs over the 3-year period.

The total concentration of the 16 measured PAHs was $452 \pm 31 \text{ ng}\cdot\text{L}^{-1}$ for 2012, $305 \pm 54 \text{ ng}\cdot\text{L}^{-1}$ for 2013 and $290 \pm 30 \text{ ng}\cdot\text{L}^{-1}$ for 2014 (Fig. 3), seemingly suggesting a downward trend which would be in synchronization with the Chinese government's environmental protection policies installed in energy-saving and emission-reduction. Although the results of year 2014 cannot be considered as significantly different from those of year 2013, the fact that apart from 2 exceptions, all other PAHs are lower in 2014 seems suggesting the downward trend of PAHs emission. Regardless of the trend, measured PAH concentrations are still much higher in the Hailuogou glacier in comparison to those from the Qinghai-Tibet Plateau glacier between 20.45 and $60.57 \text{ ng}\cdot\text{L}^{-1}$ (Li et al. 2010) and some remote mountains in Europe between 5.6 and $81 \text{ ng}\cdot\text{L}^{-1}$ (Carrera et al. 2001).

3.3 Origin of PAHs

3.3.1 Source of PAHs

In spite of its limitations, many researchers have used ratios of PAHs to tentatively identify their sources in which

Fig. 2 Concentration distribution of PAHs in snows

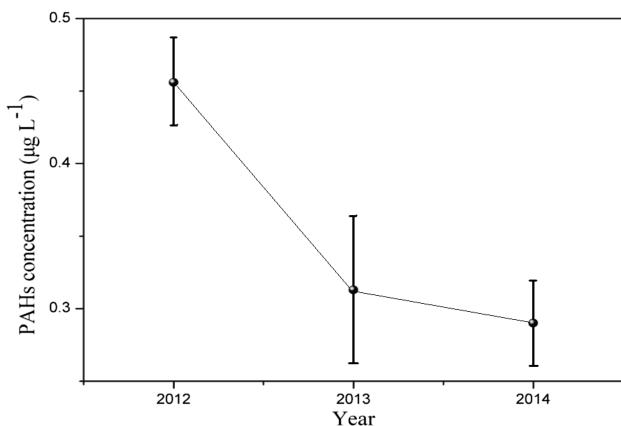
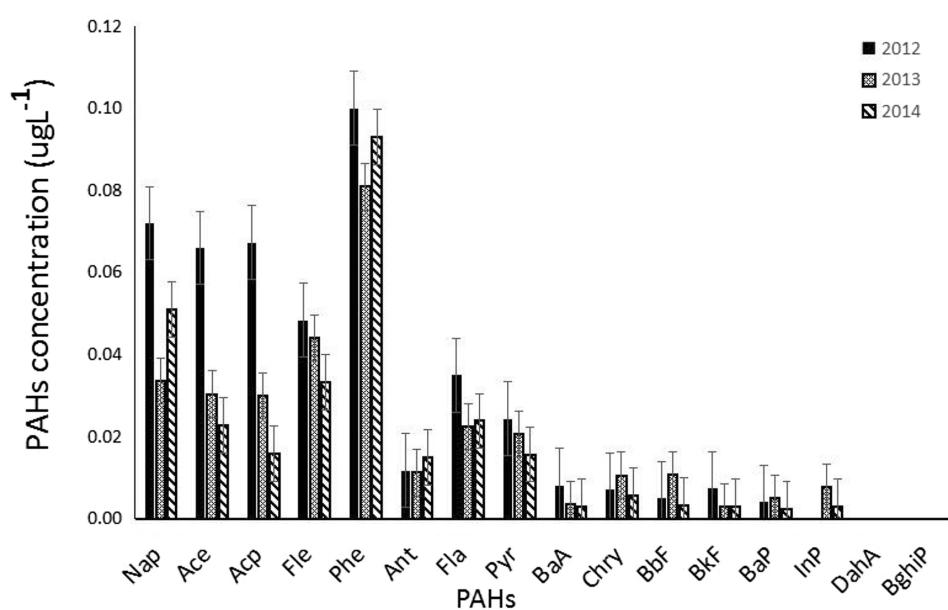


Fig. 3 Inter-annual distribution and trend of total PAHs in snow

the same molecular weight but different structure (i.e., isomers) are used in the calculation. Among them Phenanthrene (Phe)/Anthracene (Ant), Fluoranthene (Fla)/Pyrene (Pyr), Benzo [a] Anthracene (BaA)/Chrysene (Chry), and Benzo [b] Fluoranthene (BbF)/Benzo [k] Fluoranthene (Bkf) are included (Guinan et al. 2001; Lee et al. 1977; Yunker et al. 2002; Colmsjo et al. 1986; Simoneit et al. 1993; Dominguez et al. 1996). It is important to select PAH isomers whose ratios are stable during their emission, migration, and deposition. In their simulating studies of atmospheric particles, Behymer and Hites (1985) showed that Fluoranthene (Fla) and Pyrene (Pyr), and Benzo [a] Anthracene (BaA) and Chrysene (Chry) have very similar half-lives and are highly stable, and therefore they can be used reliably for pollution source identification.

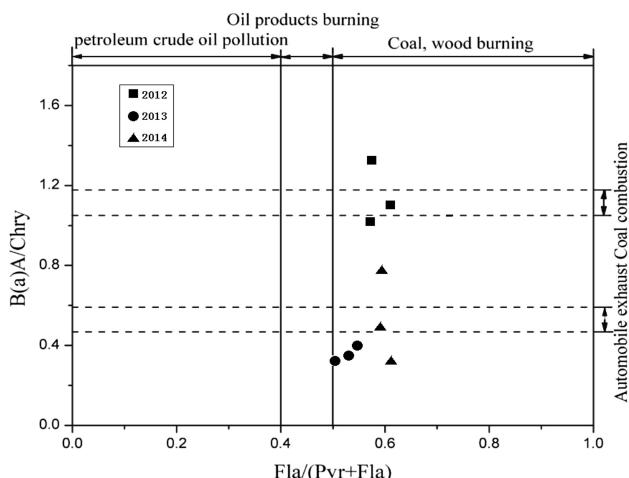


Fig. 4 Cross chart of PAHs ratio

The isomer ratio characteristics in ice and snow from Hailuogou are shown in Table 5. Research conducted by Yunker et al. (2002) has indicated that the ratio of Fla/(Pyr + Fla) from petroleum crude oil pollution is typically less than 0.4; this ratio gets greater than 0.5 for wood and coal burning and between 0.4 and 0.5 for petroleum refinery products. The ratio value from Hailuogou was greater than 0.5 (see Table 2; Fig. 4), suggesting that the PAHs in ice and snow from Hailuogou are mainly from coal and timber burning.

According to Colmsjo et al. (1986), Simoneit et al. (1993), and Dominguez et al. (1996), the ratio of BaA/Chry can be used to differentiate PAHs from automobile exhaust and coal combustion products. The values are typically

0.53 ± 0.06 and 1.11 ± 0.06 for automobile exhaust and coal burning, respectively. Hailuogou snow samples show that the ratio of BaA/Chry in 2012 averaged 1.16, but decreased at 0.44 for 2013 and 2014, respectively (Table 5 in Appendix 1; Fig. 4), thus suggesting an increase contribution from automobile activities over the 3-year period.

In summary, data from Hailuogou snow samples seem to suggest that the PAHs were mainly coming from wood and coal burning early on (2012), and automobile activities contributed more significantly in 2013 and 2014. Pollution from petroleum industries was much less than expected in the study area. This conclusion fits well with the characteristics of local industry, residence, and recent development of tourism in the surrounding areas. The Hailuogou glacier is located in the Ganzi district of the southeast Sichuan Province and surrounded by mining industry. It is also close to several largest cities in Western China, including Chengdu and Chongqing. Pollution from industrial emissions, mining in particular, has become a serious concern. In addition, it is estimated more than 1 million tourists travel to the Hailuogou glacier by automobiles each year, and this number has been steadily increasing in the last years (Administration of Hailuogou scenic spot 2015). Several hundred restaurants and hotels have been built recently, and nearly half of them burn coal and wood as their energy sources. Almost all local residents use coal and timber for their cooking and heating needs on an everyday basis. All these factors are leading to a much higher amount of PAHs as compared to Qinghai-Tibet

Plateau glacier and the characteristic PAH ratio patterns in snow from the Hailuogou glacier.

3.3.2 Estimation of distance from emission source

In this study, 2, 3, and 4 -ring PAHs have high loadings in snow from the Hailuogou glacier, and the sum of them accounted for 96.4%, 91.6%, and 96.0% of total PAHs in 2012, 2013, and 2014, respectively. The distance of migration, or mobility of PAHs is directly related to their molecular weights, as with a lower molecular weight, a PAH likely migrating further in the atmosphere.

An accurate estimate of the distance travelled by PAHs is an important step in determining the location of emission and deciphering their origin to better protecting the environment. Li et al. (2014) have established a model to estimate PAH travel distance in the atmosphere, based on factors such as the ratio between the concentrations of Phenanthrene (Phe) and Anthracene (Ant) in the samples collected at the destination and at the emission source the concentration of OH free radicals and wind speed. The travel distance for Hailuogou was then estimated as follows:

$$Dt = -\frac{6 \times 10^6}{C_{OH}} \times S_W \times \ln \left(\frac{C_{st}^A}{C_{st}^P} \times \frac{C_{g0}^P}{C_{g0}^A} \right)$$

where Dt (km) is the longest possible distance that a PAH can travel in the atmosphere; C_{OH} ($\text{mol} \cdot \text{cm}^{-3}$) is the average concentration of OH free radical in the atmo-

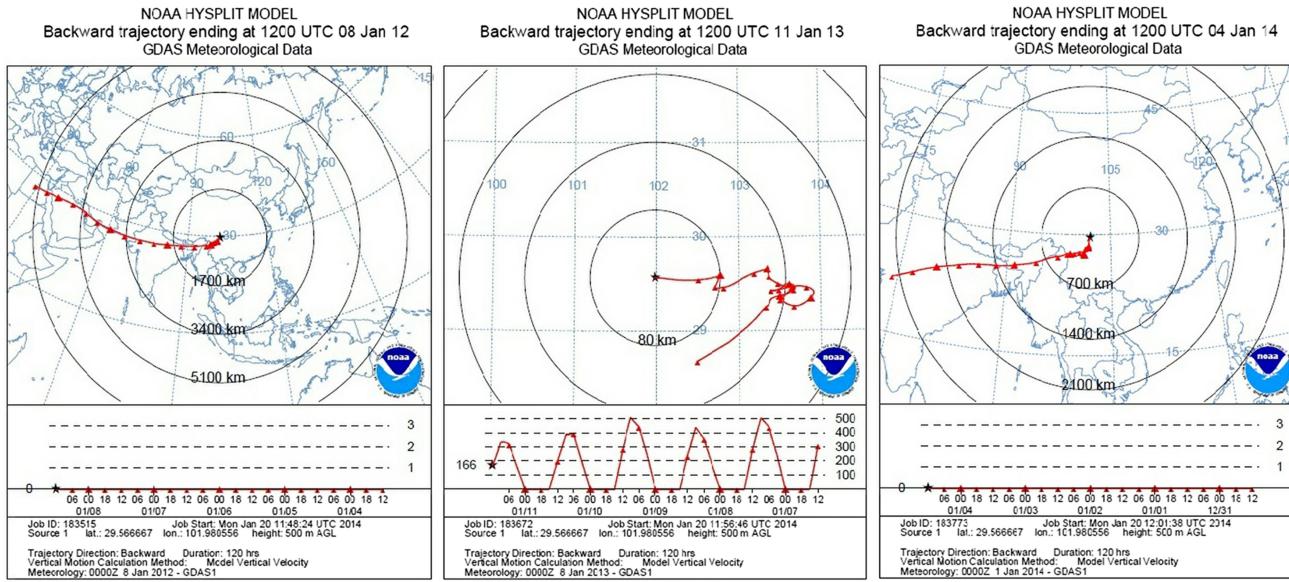
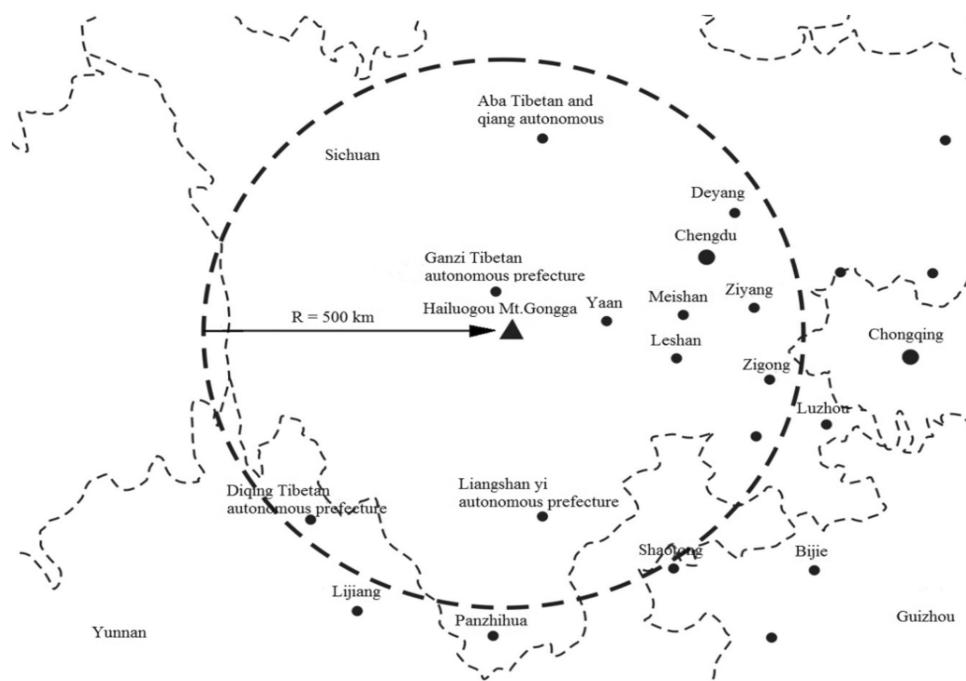


Fig. 5 Backward trajectories for Hailuogou (left 2012; middle 2013; right 2014)

Fig. 6 The maximum range of emission sources of the Hailuogou snow PAHs



sphere; S_w ($\text{m}\cdot\text{s}^{-1}$) is the wind speed; C_{go}^P/C_{go}^A is the concentration ratio of phenanthrene and anthracene at the site of emission; C_{st}^A/C_{st}^P is the concentration ratio of anthracene and phenanthrene in snow samples (destination).

The wind speed, S_w , used in our calculation was the maximum possible wind speed of $60 \text{ m}\cdot\text{s}^{-1}$ (Gatey and Miller 2007) instead of the actual wind speed, since we intended to estimate the longest possible travel distance. Also, the lowest possible OH radical concentration of 0.3×10^6 molecules cm^{-3} in the atmosphere (Hewett and Harrison 1985) was used for the same reason. The value of C_{go}^P/C_{go}^A was taken from coal burning, which is estimated at 5.67 (Galarneau 2008, US EPA). The average values of C_{st}^A/C_{st}^P at the Hailuogou sampling sites were 0.117, 0.131, and 0.125 for 2012, 2013, and 2014, respectively. The maximum distance between the emission source and Hailuogou was then estimated to be 492, 357, and 413 km for 2012, 2013, and 2014, respectively.

The 120 h backward trajectories were calculated using the hybrid single-particle lagrangian integrated trajectory model and the NOAA data downloaded from <http://ready.arl.noaa.gov/hypub-bin/traj1.pl>. The trajectory end points were set at 500 m above the sampling site. Back trajectories showed that the air mass originates from different directions (Fig. 5).

Therefore, the concentrations of PAHs in the snow samples should reflect the PAHs emissions surrounding Hailuogou. Figure 6 shows areas and cities within 500 km

radius of Hailuogou, which cover part of Sichuan, Yunnan, Chongqing and Tibet.

4 Conclusions

Analyses of snow samples from the Hailuogou glacier revealed high concentrations of 16 PAHs, ranging from 452 ± 31 to $290 \pm 30 \text{ ng}\cdot\text{L}^{-1}$ over the years from 2012 to 2014, demonstrating a remarkable decreasing trend, which may suggest the possible consequence of implementation of more strict air pollution law (Air pollution prevention action plan, 2013). Compounds with 2–4 rings are accounted for more than 90% of the total PAHs. The maximum travel distance of these PAHs was estimated to be ~ 500 km. The main source of the PAHs is likely coming from coal combustion with increasing contributions from automobile emissions in more recent years. This conclusion is in agreement with the characteristics of coal as a main energy source and recent development in tourism around the Hailuogou area.

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Appendix 1: GC/MS results of 16 PAHs in Hailuoguo snow samples

See Tables 2, 3, 4 and 5.

Table 2 PAH results for 2012

PAH	Quantitative ion (M/Z)	Sample content ($\mu\text{g}\cdot\text{L}^{-1}$)			Average sample content ($\mu\text{g}\cdot\text{L}^{-1}$)
		1201	1202	1203	
Naphthalene (Nap)	128	0.0661	0.0621	0.0879	0.0720 \pm 0.0139
Acenaphthylene (Ace)	152	0.0626	0.0724	0.0630	0.0660 \pm 0.0056
Acenaphthene (Acp)	154	0.0616	0.0714	0.0689	0.0673 \pm 0.0051
Fluorene (Fle)	166	0.0478	0.0492	0.0479	0.0483 \pm 0.0008
Phenanthrene (Phe)	178	0.0975	0.0846	0.1179	0.1000 \pm 0.0168
Anthracene (Ant)	178	0.0121	0.0095	0.0134	0.0117 \pm 0.0020
Fluoranthene (Fla)	202	0.0361	0.0365	0.0321	0.0349 \pm 0.0024
Pyrene (Pyr)	202	0.0227	0.0270	0.0232	0.0243 \pm 0.0024
Benzo(a)anthracene (BaA)	228	0.0079	0.0081	0.0083	0.0081 \pm 0.0002
Chrysene (Chry)	228	0.0072	0.0060	0.0081	0.0071 \pm 0.0010
Benzo(b)fluoranthene (BbF)	252	0.0050	ND	0.0047	0.0049 \pm 0.0002
Benzo [k] fluoranthene (BkF)	252	0.0068	ND	0.0078	0.0073 \pm 0.0007
Benzo [a] pyrene (BaP)	252	0.0041	0.0038	0.0043	0.0041 \pm 0.0002
Indeno [1, 2, 3-cd] pyrene (InP)	276	ND	ND	ND	–
Dibenz [a, h] anthracene (DahA)	278	ND	ND	ND	–
Benzo(g,h,i)perylene (BghiP)	276	ND	ND	ND	–
		0.4375	0.4306	0.4875	0.4519 \pm 0.0310

Table 3 PAH results for 2013

PAH	Quantitative ion (M/Z)	Sample content ($\mu\text{g}\cdot\text{L}^{-1}$)			Average sample content ($\mu\text{g}\cdot\text{L}^{-1}$)
		1301	1302	1303	
Naphthalene (Nap)	128	0.0270	0.0280	0.0456	0.0335 \pm 0.0105
Acenaphthylene (Ace)	152	0.0428	0.0255	0.0226	0.0303 \pm 0.0109
Acenaphthene (Acp)	154	0.0382	0.0256	0.0260	0.0299 \pm 0.0072
Fluorene (Fle)	166	0.0412	0.0409	0.0500	0.0440 \pm 0.0052
Phenanthrene (Phe)	178	0.0634	0.0766	0.1026	0.0809 \pm 0.0004
Anthracene (Ant)	178	0.0095	0.0121	0.0118	0.0112 \pm 0.0014
Fluoranthene (Fla)	202	0.0200	0.0197	0.0275	0.0224 \pm 0.0044
Pyrene (Pyr)	202	0.0180	0.0161	0.0278	0.0206 \pm 0.0063
Benzo(a)anthracene (BaA)	228	0.0028	0.0034	0.0043	0.0035 \pm 0.0008
Chrysene (Chry)	228	0.0084	0.0083	0.0147	0.0105 \pm 0.0037
Benzo(b)fluoranthene (BbF)	252	0.0066	0.0081	0.0174	0.0107 \pm 0.0059
Benzo [k] fluoranthene (BkF)	252	0.0025	0.0030	0.0030	0.0028 \pm 0.0003
Benzo [a] pyrene (BaP)	252	ND	ND	0.0050	0.0050
Indeno [1, 2, 3-cd] pyrene (InP)	276	ND	ND	0.0077	0.0077
Dibenz [a, h] anthracene (DahA)	278	ND	ND	ND	–
Benzo(g,h,i)perylene (BghiP)	276	ND	ND	ND	–
		0.2804	0.2673	0.3660	0.3046 \pm 0.0536

Table 4 PAH results for 2014

PAH	Quantitative ion (M/Z)	Sample content ($\mu\text{g}\cdot\text{L}^{-1}$)			Average sample content ($\mu\text{g}\cdot\text{L}^{-1}$)
		1401	1402	1403	
Naphthalene (Nap)	128	0.0589	0.0602	0.034	0.0510 ± 0.0148
Acenaphthylene (Ace)	152	0.0272	0.0238	0.0175	0.0228 ± 0.0049
Acenaphthene (Acp)	154	0.0189	0.0161	0.0122	0.0157 ± 0.0034
Fluorene (Fle)	166	0.0422	0.0269	0.0309	0.0333 ± 0.0079
Phenanthrene (Phe)	178	0.0974	0.0622	0.119	0.0929 ± 0.0287
Anthracene (Ant)	178	0.0179	0.0078	0.0190	0.0149 ± 0.0062
Fluoranthene (Fla)	202	0.0235	0.0236	0.0242	0.0238 ± 0.0004
Pyrene (Pyr)	202	0.0154	0.0168	0.0145	0.0156 ± 0.0012
Benzo(a)anthracene (BaA)	228	0.0032	0.0036	0.0018	0.0029 ± 0.0010
Chrysene (Chry)	228	0.0040	0.0070	0.0062	0.0057 ± 0.0016
Benzo(b)fluoranthene (BbF)	252	0.0028	0.0041	0.0030	0.0033 ± 0.0007
Benzo [k] fluoranthene (BkF)	252	0.0027	0.0023	0.0033	0.0028 ± 0.0005
Benzo [a] pyrene (BaP)	252	0.0030	0.0022	0.0019	0.0024 ± 0.0006
Indeno [1, 2, 3-cd] pyrene (InP)	276	0.0025	0.0030	0.0034	0.0030 ± 0.0004
Dibenz [a, h] anthracene (DahA)	278	ND	ND	ND	—
Benzo(g,h,i)perylene (BghiP)	276	ND	ND	ND	—
		0.3196	0.2596	0.2909	0.2900 ± 0.0300

Table 5 PAH isomer ratios in snow from Hailuogou

Sample	Sampling time	Altitude (m)	Fla/(Pyr + Fla)	BaA/Chry
1201	January 2012	3170	0.614	1.097
1202	January 2012	3250	0.575	1.350
1203	January 2012	3470	0.580	1.025
1301	January 2013	3100	0.526	0.333
1302	January 2013	3130	0.550	0.410
1303	January 2013	3180	0.497	0.293
1401	January 2014	3110	0.604	0.800
1402	January 2014	3140	0.584	0.514
1403	January 2014	3190	0.625	0.290

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