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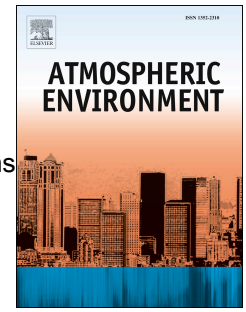

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Spatio-temporal variations and influencing factors of Polycyclic Aromatic Hydrocarbons in atmospheric bulk deposition along a plain-mountain transect in Western China

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ABSTRACT

Ten atmospheric bulk deposition (the sum of wet and dry deposition) samplers for polycyclic aromatic hydrocarbons (PAHs) were deployed at a plain-mountain transect (namely PMT transect, from Daying to Qingping) in Chengdu Plain, West China from June 2007 to June 2008 in four consecutive seasons (about every three months). The bulk deposition fluxes of $\sum_{15}$-PAHs ranged from 169.19 μg m^{-2} yr^{-1} to 978.58 μg m^{-2} yr^{-1} with geometric mean of 354.22 μg m^{-2} yr^{-1}. The most prevalent PAHs were 4-ring (39.65%) and 3-ring (35.56%) PAHs. The flux values were comparable to those in rural areas. Higher fluxes of total PAHs were observed in the middle of PMT transect (SL, YX and JY, which were more urbanized than other sites). The seasonal deposition fluxes in the sampling profile indicated seasonality of the contaminant source was an important factor in controlling deposition fluxes. PAHs bulk deposition was negatively correlated with meteorological parameters (temperature, wind speed, humidity, and precipitation). No significant correlations between soil concentrations and atmospheric deposition were found along this transect. PAHs in soil samples had combined sources of coal, wood and petroleum combustion, while a simple source of coal, wood and grass combustion for bulk deposition. There were significant positive correlation relationship ($p<0.05$) between annual atmospheric bulk deposition and local PAHs emission, with biomass burning as the major contribution to the total emission of PAHs. This transect acts as an important PAHs source rather than being a sink according to the ratio of deposition/emission. Mountain cold trap effect existed in this transect where the altitude was higher than 1000 m. Long-range transport had an impact on the bulk deposition in summer. And this transect was a source to Tibetan only in summer. The forward trajectory analysis showed

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most air masses did not undergo long-range transport due to the blocking effect of surrounding mountains. Only a few air masses (<10%) arrived at the eastern and northern region of China or farther regions via long-range transport.

Keywords: Polycyclic aromatic hydrocarbons; Plain-mountain transect; Bulk deposition; Spatio-temporal variation; Influencing factor

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants that are produced by anthropogenic emissions such as motor vehicles, industrial processes, domestic heating, waste incineration, tobacco smoke and by natural processes such as forest fires and volcanic eruptions (Keshtkar and Ashbaugh, 2007; Shen et al., 2013). PAHs are of great concern due to their widespread occurrence, long-range transport and toxic effects to ecosystem and human health (Wang et al., 2015).

Atmospheric deposition is the most important process that removes these chemicals from the atmosphere and are a major PAHs contributor in remote pristine areas(Wang et al., 2010). Atmospheric deposition is a potential important pathway of trace organic pollutants input to the land surface (Pan et al., 2013; Bari et al., 2014). In the wet deposition, PAHs are either dissolved in or rinsed by the rainfall or associated with particles. This process relies on the distribution of the organic matters diffused in vapor phase and particle phase, particle size distribution, and the Henry's law constant. Dry deposition of PAHs, on the other hand, is on accounted of association of PAHs with particles, related to the type of the surface, resistance to mass transfer in the deposition layer (Ollivon et al., 2002; Terzi and Samara, 2005). The total deposition consists of wet and dry deposition. However, it is hard to collect wet and dry deposition separately for long-term sampling especially in remote regions with insufficient electricity supply. Hence, the total deposition can be expressed by the sum of wet and dry deposition, namely "bulk" deposition, which does not discriminate any of the processes and , as a consequence, it sums up all of them (Motelay-Massei et al., 2003; Gocht et al., 2007; Esen et al., 2008; Zhang et al., 2008; Wang et al., 2011). Transport and fate of PAHs in the atmospheric bulk deposition partly depended on their physicochemical characteristics, atmospheric concentration, meteorological condition, topography and emission density (Gocht et al., 2007; Esen et al., 2008; Wang et al., 2011; Zhong and Zhu, 2013). Conversely, the atmospheric deposition affected on the equilibrium partitioning of semi-volatile organic chemicals (SOCs) between air and surface, and finally had a strongly influence on the long-term distribution of SOCs in the regional/global environment. So the leading parameter in the process of SOCs transport varies from region to region (Schenker et al., 2014).

In western China, steep altitudinal transects separated the highly populated and intensively cultivated Chengdu Plain from the Tibetan Plateau. It is reported as important pathway of some persistent organic pollutants (POPs) from the vicinity of source regions in Chengdu Plain to the

Tibetan, which acts as the cold trap of airborne contaminants. Up to date, the majority of reports were focused on OCPs, PCBs, PCNs, PCDD/Fs and PBDEs in soil, atmosphere and biota in this region (Chen et al., 2008; Gong et al., 2010; Liu et al., 2010; Xing et al., 2010; Wang et al., 2012; Liu et al., 2013; Pan et al., 2013; Liu et al., 2014). However, information is limited on the atmospheric deposition contamination by PAHs in in this region. Sichuan Province is one of the most developed provinces in China and the total PAH emission in Sichuan ranked first in China in 2003 with average emission of 5.35 kg km^{-2} (Zhang et al., 2007). Hence, the impact of atmospheric deposition can not be ignored when studying the transport of PAHs and other similar contaminates.

This paper presents the result of atmospheric bulk deposition variation in the Chengdu Plain-mountain transect in western China with the aim of clarifying the role of Chengdu Plain as the primary emitter or middle path for POPs to Tibetan Plateau. Specifically, the main aims are: (1) clarifying the temporal and spatial characteristics of atmospheric deposition flux of PAHs; (2) to explore the key factor which affecting PAH deposition; and (3) to distinguish the potential role of this region (acting as a source or sink) according to the trajectory analysis.

2. Experiment and methods

2.1. Sampling

The study region is located in the centre of Sichuan Province. The geography can be divided into four types: corrosive tectonic mountain of Tibetan Plateau east slope, Longmen Orogenic Piedmont Belt Accumulation Plain, Corrosive Tectonic Hills of east Sichuan Basin and Corrosive Tectonic Mountain of southwest Sichuan Basin. To describe PAHs deposition characteristic in this region, a typical plain-mountain transect was chosen, including low hills in the east, plain in the intergrades and high mountains in the west, which forms part of the eastern slope of Tibetan Plateau (Fig.1), namely “Plain-mountain transect (PMT)”. The dominant wind direction (Southern east-northern west) in this region is also along this transect due to the presence of Tibetan in the northern west and monsoon climate in this region.

The atmospheric bulk deposition samplers were deployed at ten sites from Daying to Qingping during 16th June 2007 to 27th June 2008 (Fig.1). Detailed site information is listed in Table S1. The sampling programme was conducted for one year of four consecutive seasons (about every three months). The four periods from 16th June to 22nd September, 2007; 22nd September to 24th December, 2007; 24th December, 2007 to 22nd March 2008; and 22nd March 2008 to 27th June 2008 were presented as summer, autumn, winter and spring respectively.

Bulk deposition (both dry and wet deposition) collection was achieved using a glass funnel with a receiving area of 0.0225m^2, attached to a filter holder which was installed one meter above the ground or on the roof. Fallout was collected in a 4 L brown glass bottle wrapped with aluminium foil to prevent photodegradation. A long ring-shaped silica tube was used to link the funnel and collected bottle to conduct deposition and prevent volatilization. Prior to the filed campaign, the funnels and the bottles were pre-cleaned using acid lotion and rinsed by deionized

water, then dried in an oven at 200 °C for 4 hours, and wrapped with aluminium foil. Before set-up, each device was washed and triple rinsed with dichloromethane (DCM). Hydrated copper sulphate ($CuSO_4.\cdot 5H_2O$) was added to the bottles to inhibit microbial degradation. The tube was washed with distilled water and DCM, and then wrapped with aluminium foil during transport to the field (Fig.S1). Similar samplers were applied by many researchers (Ollivon et al., 2002; Motelay-Massei et al., 2003; Gocht et al., 2007; Esen et al., 2008; Bari et al., 2014). When we collected the bulk deposition, the surface soil samples were collected as well in the vicinity. Totally, thirty-eight deposition samples and thirty-eight soil samples were collected. Bulk deposition samples at two sites were destroyed during the Earthquake in May 2008. When collecting, the funnels were cleaned with DCM three times and the washings were taken as a part of bulk depositions. After collection, all the samples were preserved in ice boxes and transported to the laboratory as soon as possible and stored at - 20 °C before analysis.

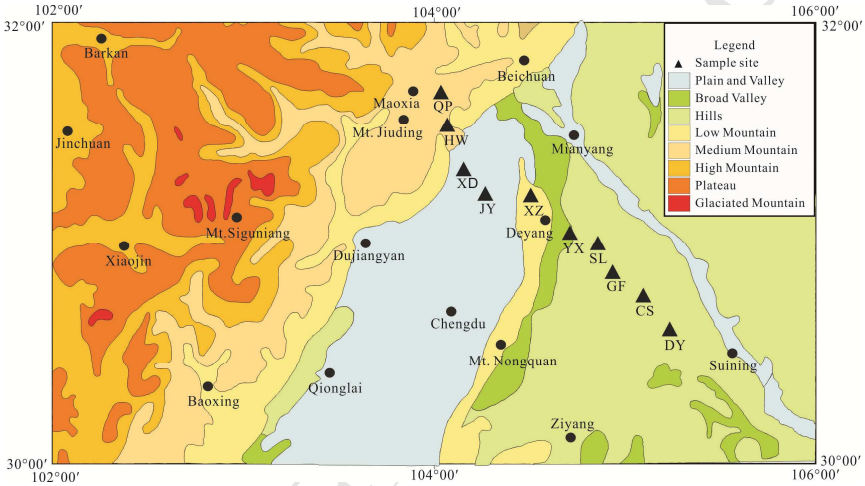


Fig. 1 Sampling location for atmospheric deposition

2.2. Sample extraction and analysis

2.2.1. Extraction

The mixture of wet and dry atmospheric deposition samples were defrosted and homogenized by shaking. Then the mixture was separated into the dissolved and particle parts by ultrafiltration with a 0.45μm glass fibre filter membrane. The dissolved one was the water passed through filter membrane and the particles were intercepted by the filter membrane. Both percolator and membrane were cleaned three times by DCM before filtration. The membrane and particle samples were wrapped with aluminium foil. Then particle and water were kept frozen at -20 °C until analysis after about one week.

For the particle fraction, the same extraction procedure was followed as soil samples extraction described previously (Xing et al., 2011). Generally, particle were injected with PAH surrogates (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12), and Soxhlet-extracted with dichloromethane (DCM) for 24 h. Small amount of activated copper granules and anhydrous sodium sulphate were added to the extract, then the

extracts were concentrated and solvent-exchanged to hexane and further reduced to 1-2 mL by a rotary evaporator. A 1:2 (v/v) alumina/silica gel column was used to clean up the extract and targeted compounds were eluted with 30 ml of DCM/hexane (V:V=2:3). The eluate was then concentrated to 0.2 mL under a gentle pure nitrogen stream (purity ⩾ 99.999%). Hexamethylbenzene was added as internal standard prior to instrumental analysis. The filtrated water was extracted using liquid–liquid extraction (LLE) method described in the literatures (Arias et al., 2009; Lohmann et al., 2009; Yang et al., 2013). Briefly, filtrated water was extracted with 40 mL of DCM and 2 g of anhydrous sodium sulphate in a separating funnel and shaken well for 4-5 minutes. The lower DCM layer was collected in a flat bottom flask and the remaining portion was extracted three times with 30 mL of DCM and the extracts were collected in a flat bottom flask. The extracts of water samples were then treated by the same method as particles extracts mentioned above. Finally, 0.2 mL eluate was obtained. Hexamethylbenzene was added as internal standard prior to instrumental analysis.

2.2.2. Analysis

Sixteen priority control PAHs recommended by the US Environmental Protection Agency were analysed using a GC-MS Agilent 6890N/5975MSD, equipped with a DB-5 capillary column (30 m ×0.25 mm diameter, 0.25 μm film thickness) coupled in the electron impact mode (EI 70 eV, quadrupole temperature 150ºC, ion source temperature 230ºC). The chromatographic conditions were as follows: oven temperature program was initially at 60°C for 5 min and increased to 290°C at a rate of 3°C min^{-1} and kept at 290°C for 40 min, while the temperature for injector and detector was maintained at 270°C and 280°C, respectively. The highly pure (99.999%) carrier gas was helium at a constant flow rate of 1.2 mL min^{-1}. A 1μL concentrated sample was injected with splitless mode. The mass spectrometer was operated in the selected ion monitoring (SIM) mode and tuned with perfluorotributylamine (PFTBA) according to the manufacturer's specifications. Chromatographic peaks of samples were identified by mass spectra and retention time. The PAHs were quantitative analysed according to a 6-point calibration curve of reference materials with internal standard.

2.3. Quality control and quality assurance

Method blanks (solvent), spiked blanks (internal standard compounds spiked into solvent) and field blanks were analysed along with the sample batch. Moreover, 5 μg mL^{-1} PAHs standard solution were was analysed by GC-MSD daily to estimate the method recovery as part of the instrumental quality control. Five PAHs surrogates consisting of naphthalene-D_{12}, acenaphthene-D_{10}, phenanthrene-D_{10}, chrysene-D_{12} and perylene-D_{12} standards were spiked to each sample before extraction. The surrogate recoveries ranged from 70.1%-108.6%. The concentrations of PAHs were corrected by surrogate recoveries.The three times of the signal-to-noise level in the lowest concentration (0.2 μg/mL) standard samples was used as the instrumental detection limit (IDLs). The IDLs of each substance was listed in Table S2. Mass spectrometry was evaluated by mass tuning. The retention times and areas of compounds in spiked

blanks were consistent with daily standard sample chromatograms. Calibration curves were was adapted to period check with injection of standard solutions.

2.4. Introductory remarks on the data set

Additional information on flux calculations, meteorological data sources, and a full list of analytes is given in the supporting information Text S1.

3. Results and discussion

3.1 General characteristic of annual deposition fluxes

Annual bulk deposition fluxes of PAHs were calculated and summary data are presented in Table 1 and Fig S2. The results showed that total PAHs bulk deposition fluxes ranged from 169.19 μg m^{-2} yr^{-1} at XZ to 978.58 μg m^{-2} yr^{-1} at SL, with the geometric mean of 354.22 μg m^{-2} yr^{-1}. The proportion of PAH congeners along with the deposition profile was dominated by 3-ring (35.56%) and 4-ring (39.65%) PAHs, followed by 5-6-ring (18.18%) and 2-ring (3.61%) PAHs, with the fluxes of semivolatile PAHs Fla, Phe and Pry were higher than other PAHs on the annual basis.

The comparison of deposition fluxes in study area and other regions is listed in Tables S3. The deposition flux in study area was comparable to those previously study in south China, it was higher than that report in more industrialized or urbanized region like Pearl River Delta, China during 2003-2004 (140±89 μg m^{-2} yr^{-1}) (Li et al., 2010), but it was slight lower than the report value at Guangzhou during 2001-2002 (mean 460 μg m^{-2} yr^{-1}) (Li et al., 2009). The flux was much less than the value in north China, where the deposition flux was 5.22±3.89 μg m^{-2} day^{-1} in Beijing-Tianjin region (Wang et al., 2011), 4.88μg m^{-2} day^{-1} in Tianjin and 5.14 μg m^{-2} day^{-1} in the rural of Beijing. Compared with other rural or suburban area in the world, the result was of same order of magnitude as that reported in the rural of southern Germany (73.49-388.01μg $m^{-2}yr^{-1}$) (Gocht et al., 2007), however it was higher than that in the suburban in the Seine Basin of France (47.85μg m^{-2} yr^{-1}) (Motelay-Massei et al., 2003), and that in remote site of northern Spain (60.5±16.4 μg $m^{-2}yr^{-1}$) (Foan et al., 2015).

Table 1 Summary of annual bulk deposition (μg m^{-2} yr^{-1}) of selected PAHs

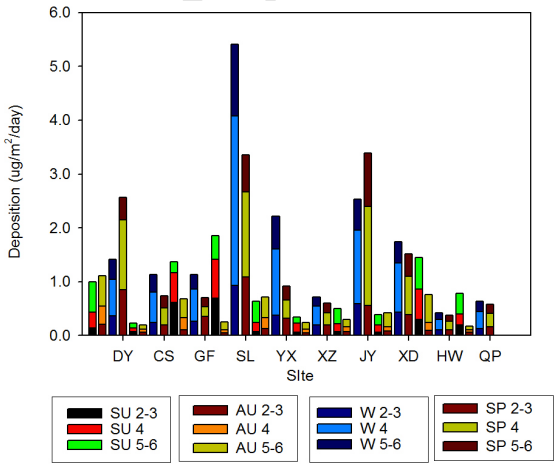
Compounds	Geometric mean	Average ±std	Median	Range
$\sum_{-15}$PAHs	354.22	410.12 ±248.56	358.87	169.19-978.58
Acy	1.45	3.58 ± 4.93	0.93	0.20 -14.37
Ace	0.22	0.25±0.13	0.24	0.08-0.53
Flu	10.80	12.07±5.82	11.76	4.57-23.42
Phe	61.88	71.55±43.33	60.11	30.92-170.69
Ant	7.92	11.15±11.87	6.47	3.60-41.78
Fla	63.35	78.44±58.84	65.87	25.10-219.59
Pyr	43.33	53.24±39.84	45.81	20.98-149.15
BaA	14.34	18.25±14.43	12.73	6.17 -49.81-

Chr	30.18	35.48 ±21.43	29.32	15.49 -74.64-
BbF	29.36	32.34 ±13.67	32.46	12.09 -53.71
BkF	19.73	23.51±15.44	18.38	8.48 -58.29
BaP	12.28	13.42±5.87	13.89	6.28 -23.91
IcdP	24.02	27.22 ±13.76	23.90	9.86 -48.25
DahA	5.39	6.12 ±3.05	5.14	1.93 -10.77
BghiP	21.08	23.48 ±11.46	20.14	11.49 -42.19

206

207 *3.2 Spatial and seasonal variations of atmospheric deposition fluxes*

208 The geographic distribution of PAHs bulk deposition flux in four seasons is shown in Fig.2.
209 In general, higher fluxes of total PAHs were observed in the middle of this transect (DY, SL and
210 JY, the cities and towns around these sites are usually more industrialized or urbanized than in
211 remote sites); lower fluxes were observed at remote areas sites (HW and QP). The deposition
212 fluxes in SL were higher than in the surrounding rural areas sites and even higher than in JY, the
213 urban area site. The Shuanglong petrol station is on the opposite of SL site. Local point emission
214 in SL was an important reason for high deposition flux during sampling period possibly. Due to
215 the different physicochemical properties and sources of PAHs, there were spatial trends of
216 individual compounds. Higher proportion of 4-ring PAHs in higher deposition fluxes sites
217 indicated the 4-ring PAHs were the main contributor to the higher fluxes of bulk deposition.



218

219 Fig.2 The seasonal and spatial variation of different rings PAHs bulk deposition

220 (SU means summer samples, AU means autumn samples, W means winter samples and SP means spring samples.
221 And the numbers behind the capital letters mean the number of rings in the PAHs structure.)

222

223 For seasonal variation, the deposition fluxes in cold seasons (winter and spring) were higher
224 than those in warm seasons (summer and autumn). The high fluxes in winter and spring were
225 mainly due to a higher proportion of 4-ring PAHs than the other PAHs. 4-ring PAHs include Fla,
226 Pyr, BaA, and Chr. They are representative of coal combustion and vehicle emission source

(Khalili et al., 1995; Wang et al., 2008; Gregoris et al., 2014). In the cold seasons, more heating and warming demand will increase the combustion of coal, resulted in high emission of 4-ring PAHs. Meanwhile, the depositions of 4-ring PAHs in cold season were higher than in other seasons, indicating deposition of PAHs was consistent with the emission of PAHs. The seasonality of contaminant source could be an important factor in controlling the deposition fluxes. The result was in accordance with researches in other regions (Li et al., 2010; Wang et al., 2011). Besides the sources emission, the meteorological parameters are also decisive factors for the deposition fluxes. For example, temperature can affect the vapor-particle partitioning for SOCs (Jurado et al., 2004). And the intensity, form (rain or snow) and rate of precipitation, wind speed and humidity could have impacts on the washout ratio and/or dry deposition speed, which will cause the variation of deposition fluxes (Lei and Wania, 2004; Li et al., 2009). It means that the lower temperature and precipitation in the form of snow may have a higher scavenging ratio of PAHs in atmosphere. Moreover, the forest canopies can deplete of gaseous PAHs (Choi et al., 2008). Seasonal changes of forest canopies can affect the concentration of more volatile PAHs in the atmosphere. Thus the fluxes of PAHs with less rings in warm seasons was lower than those in the cold seasons. Comprehensively, all the above factors may result the seasonal varying of PAHs deposition fluxes. To clarify this issue in this junction between Chengdu Plain and east edge of Tibetan, the variation controlling factors of deposition fluxed are discussed below according to the collected data.

3.3 Controlling factors for the atmospheric bulk deposition fluxes

3.3.1 The influence of meteorological parameters on deposition fluxes

Meteorological conditions can affect PAHs in term of their generation, phase partition, diffusion, removal, etc.(He et al., 2014). The typical subtropical monsoon climate in Guangzhou played a key role in controlling seasonal variation of PAHs concentration and particle deposition fluxes (Li et al., 2010). High ambient temperature are correlated with low deposition rates in rural area of southern Germany (Gocht et al., 2007). The relationship between PAHs atmospheric bulk deposition and meteorological factors was analysed using IBM SPSS Statistics 20 and the Spearman correlation coefficients are shown in Table S4. Generally, negative relationship was found in mean of daily deposition bulk in every season versus temperature, wind speed, humidity, and precipitation for 4-rings and 2-3 rings PAH compounds. The deposition fluxes of 2-3 ring and 4-ring PAHs were much higher than those of 5-6 ring PAHs (Fig.2). Hence, we can conclude PAHs bulk deposition was negatively correlated to those meteorological parameters. Similar results were reported in fine particulate matter in Nanjing, China (He et al., 2014) and particle deposition fluxes in Guangzhou (Li et al., 2010). However, for other POPs (e.g. pesticide such as HCHs and HCBs), stronger temperature dependencies were observed for high atmospheric concentration during warming periods and lower ones in the cold periods (Gioia et al., 2005). The possible reason was thermodynamically derived distribution (via evaporation from nearby terrestrial surfaces or long-range transport) for those compounds and primary emission density controlling patterns for PAHs in this study area.

3.3.2 The relationship between local emission and atmospheric deposition fluxes

As PAHs production is associated with anthropogenic activities such as domestic and industrial heating, traffic petrol combustion, the population density as well, so the local emission may explain the variations of PAHs deposition fluxes.

Local emission data was obtained from global atmospheric emission data of PAHs (Shen et al., 2013) http://inventory.pku.edu.cn/data/data.html. The data we used was the annual average value of the year 2007-2008 to match our sampling period. In the Fig.3, the total 15 PAHs bulk deposition profile showed well coincides with the total local emission (2007-2008) in most sampling site except for Site XD. As PAHs is associated with human activities, local emission can be reflected on atmospheric bulk deposition fluxes. This transect is not only a pathway for PAHs transport, but also an important source at low altitude region (except remote mountain site QP).

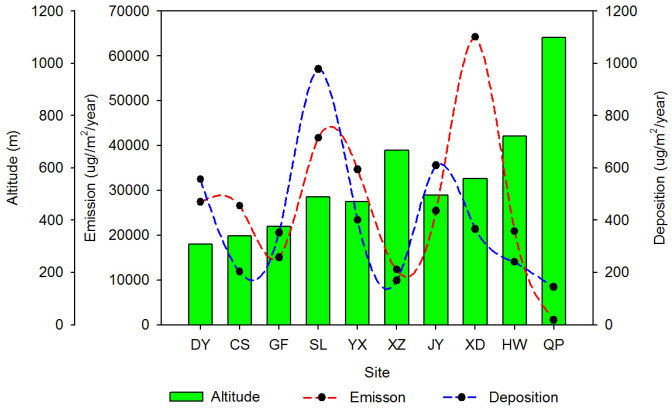


Fig.3$\sum_{15}$-PAHs bulk deposition vs. total local emission

In Fig. 4, the logarithm of the category of PAHs emission vs. bulk deposition was demonstrated. The detailed information on every category was obtained from http://inventory.pku.edu.cn/data/data.html (Shen et al., 2013), and the description of every category can be found in the supporting information (Table S5). In Fig. 4, biomass combustion presented the main contribution to the local emission of PAHs, secondly was coal, and then followed by process, oil, waster, gas and open fire. There were obvious positive correlation ($p<0.05$) between annual atmospheric bulk deposition and PAHs emission, especially with biomass, oil and waste combustion (Table S6), which confirmed human activity affected the deposition fluxes of PAHs. In addition, principal component analysis (PCA) was applied to confirm the diagnostic testing. Total variability of the original data (depositions, biomass, coal, gas, oil, process and waste) was represented during the PCA (Fig. S3). The first two principal components (PCs), with eigenvalues greater than 1, accounted for 90.26% of the total variance in the data set. As shown in Fig. S3, PC1, which explained 63.78% of the total variance, was highly dominated by coal, gas, oil and process. It also had a large loading for biomass and waste. The angles between deposition and the six emissions were all acute angles, indicating a positive

correlation between deposition and those emissions. PC2 accounted for 26.48% of the total variance and was heavily weighted by deposition. PC2 had a high negative loading of open fire, indicating no significant correlation of open fire with deposition.

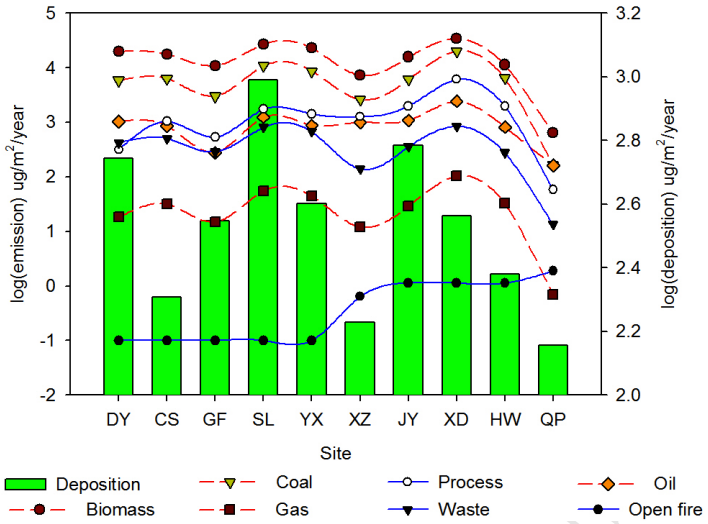


Fig.4 Σ_{15}-PAHs bulk deposition vs. different category emission in the form of logarithm (For site DY, CS, GF, SL and YX, there was no open fire emission, for the transform of logarithm, -1 was given to those values)

The emission fluxes of PAHs were hundreds of times higher than the deposition fluxes, which indicated much more PAHs were preferentially transported to other area than to deposit in local area, and thus this area was an important source region during the transport of PAHs. To determine the role of this transect (source or sink), the relationship between deposition and emission, the budget of deposition and emission were calculated. Firstly, the hypothesis deposition from local emission totally was given. The deposition efficiency was calculated according to the deposition divided by emission. In Fig.S4, the influence of altitude and molecular weight of PAHs on the efficiency of deposition is shown. There was no obvious difference for site below 1000 m a.s.l.. As the altitude increased more than 1000 m, the ratio of deposition/emission increased. One possible reason was that the emission at region with higher altitude was less than that in Chengdu Plain (Shen et al., 2013); another reason was mountain had a cold trap for POPs, especially for heavy molecular weight compounds (Chen et al., 2008). 5-6 ring PAHs had higher deposition/emission value than 2-3 and 4 ring PAHs. As rings of PAHs increased, the efficiency of deposition was enhanced, which also suggested the light molecular PAHs had higher potentiality to undergo long-range transport.

3.4 Effect of deposition on soil burdens

Soil plays an important role in the transport of POPs. It always acts as the sink during the orographic cold trapping as altitude increases due to high precipitation rates and organic carbon content (Daly and Wania, 2005; Daly et al., 2007; Chen et al., 2008; Choi et al., 2009; Sheng et al., 2013), and simultaneously soil played the role of source for volatile compounds evaporation to atmosphere when the equilibrium was broken between soil and air exchange (Cabrerizo et al.,

2011; Qu et al., 2015). The relationship between atmospheric deposition flux and soil concentration is shown in Fig.5. Generally, soil concentrations in most sites increased with altitude along this transect, and displayed maxima at intermediate elevations at XZ, a suburban site near Chengdu. These distribution patterns can be understood as being determined by the balance between atmospheric depositions and retention within the soils. However, for deposition flux, there was no significant increase. Neither significant correlations between soil concentrations and atmospheric deposition were observed along this transect. It also confirmed our conclusion that no thermodynamically distribution dominated in this region. The variation of PAHs concentration in soil was less than atmospheric deposition during different seasonal sampling, which possibly indicated soil was more stable than atmospheric deposition to the changes of PAHs emission, and thus explained why no positive relationship was found here for soil concentration and atmospheric deposition.

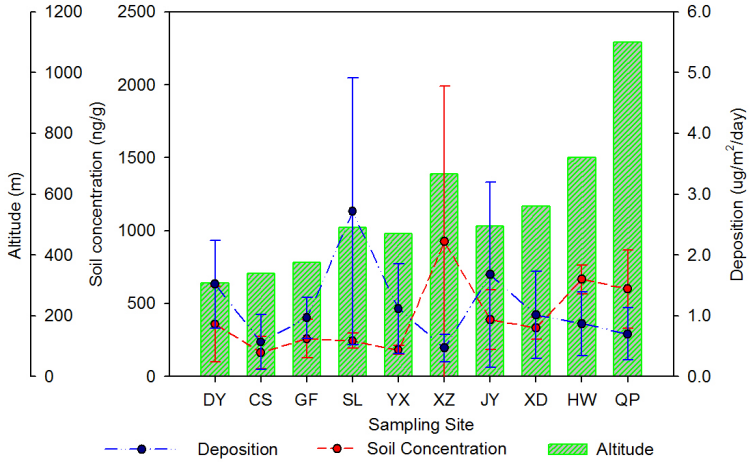


Fig. 5 Soil concentrations vs. atmospheric bulk deposition flux in sampling sites of different altitudes

The molecular indices IcdP/(IcdP + BghiP) and Flu/(Flu + Pyr) were used to distinguish the PAHs source for soil and atmospheric deposition in this study according to study in other regions (Ding et al., 2007; Xing et al., 2011; Gregoris et al., 2014; Bosch et al., 2015; Chen et al., 2015; Hong et al., 2015; Ma and Harrad, 2015; Zhang et al., 2015). The data for the ratios of these compounds in the atmospheric deposition and soil samples are presented in Fig.S5. The IcdP/(IcdP + BghiP) values for most samples were >0.5, suggesting that coal and wood combustion may be the predominant source of PAHs in atmospheric deposition, while PAHs ratios in soils were mainly between 0.3-0.7, indicating a more complicated PAHs sources derived from mixed combustion of coal wood and petroleum combustion. The ratios of Fla/(Fla + Pry) from atmospheric deposition showed PAHs mainly derived from combustion of coal, wood and grass as well. However, PAHs in soil arise from a complex mixture of sources, including both biomass combustion as well as fossil fuel combustion, which fits well with the result from IcdP/(IcdP + BghiP). According to biplots of IcdP/(IcdP + BghiP) versus Fla/(Fla + Pry) ratio for soil and atmospheric deposition, the results suggested combustion of coal, grass and wood was major

source of PAHs in atmospheric deposition, while soil arose from a complex mixture of sources, including both combustion for rooms heating and cooking, as well as outdoor emissions from traffic and fossil fuel combustion. This result confirmed why no positive relationship was shown for soil and atmospheric deposition.

3.5 Influence of regional atmospheric transport of PAHs on deposition fluxes

Air mass transport can bring in pollutants from distance areas, thus affecting local PAHs concentration in atmosphere. It was reported that the impact of local or regional transport can be reflected by the ratio of more reactive PAHs to a stable PAH, such as the ratio of BaA/Chr can be employed to illustrate whether the collected air masses are fresh or aged. A higher ratio indicates relatively little photochemical processing of the air mass and major impact from local emissions. On the other hand, a lower ratio is reflective of more aged PAHs (Ding et al., 2007). Fig. 6 revealed the relationship between BaA/Chr and PAHs deposition fluxes in different seasons. Generally, a slight positive relationship was shown during the periods of autumn, winter and spring, as PAHs deposition increased, the ratios of BaA/Chr become higher, indicating the elevated deposition was mainly contribution of local emission. While in summer sampling periods, a negative relationship was presented, illuminating long-range transport had a higher impact on the deposition in summer.

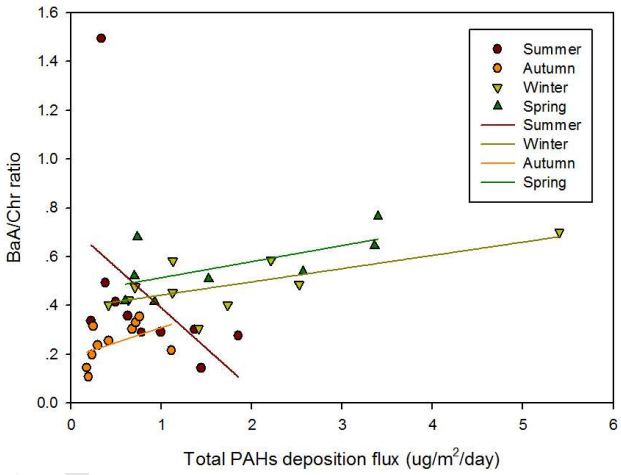


Fig.6 The relationship between BaA/Chr and PAHs deposition fluxes

In order to identify potential source regions and transport pathways, 5-day backward and foreword trajectories arriving at 100 meters above ground level for one year between June 2007 and June 2008 at the sampling site were generated using the PC Version HYSPLIT 4 model (http://www.arl.noaa.gov/ready/hysplit4.html) respectively. This model was developed by NOAA/ARL (US National Oceanic and Atmospheric Administration/Air Resources Laboratory). The seasonal trajectories after cluster are presented in Fig.S6 and Fig.S7.

The back trajectory maps are shown in Fig.S6, which indicated local emissions were the dominant source (more than 40 % of total air mass) for PAHs deposition in the study area during sampling time. Second source was the eastern and northern part of China. The air mass from the

countries west to China such as Indian and Nepal, which underwent long-rang transport also arrived in this region. In summer, during the summer monsoon period, a high percentage contribution (21% of air masses) from the south of China entered the study area as well. It confirmed our conclusion that the long-range transport has a higher impact on the atmospheric deposition during summer. The annual back trajectory map showed the same result as the seasonal conclusions. Most air masses were originated from local or nearby regions (36%). Due to the influence of eastern monsoon, the high contribution (28%) was from eastern region as well, followed by air mass from the north of China (23%). The air mass from west direction underwent long distance transport, and had small contribution (7% and 6%) to the total air mass in the study region. It indicated the spatial variation in bulk deposition was mainly effected by the local emission in our study. As mentioned above, only a little local emission PAHs was loaded in situ, most PAHs may undergo long-rang transport to other region. The study in Wolong near our study area reported air mass from lower altitude Chengdu might enter western mountains (Pan et al., 2013). The forward trajectory maps (Fig.S7) show the possible sink/fate of pollutants originated from our study area. In summer, about 10% of air masses originating from the Chengdu Plain indeed entered the western part of China, e.g. the Tibet. However, most air masses did not undergo long-range transport. The mountains surrounding Chengdu Plain blocked them. Only a small fraction of air masses (<10%) which underwent long-range transport, the main destinations were the eastern and northern regions of China or farther regions.

4. Conclusions

The bulk deposition fluxes of $\sum_{15}$-PAHs ranged from 169.19 μg m^{-2} yr^{-1} to 978.58 μg m^{-2} yr^{-1}, with the geometric mean of 354.22 μg m^{-2} yr^{-1} along a plain–mountain transect in Chengdu Plain, West China, from Daying to Qingping. Higher fluxes of total PAHs were observed in the middle of this transect (urbanized sites, SL, YX and JY). The deposition fluxes of $\sum_{15}$-PAHs in cold seasons (winter and spring) were higher than those in warm seasons (summer and autumn), indicating that the seasonal variation of contaminant source was an important factor in controlling the deposition fluxes.

PAHs bulk deposition was negatively correlated with meteorological parameters (temperature, wind speed, humidity and precipitation). No significant correlations were found between soil concentrations and atmospheric deposition along this transect. The biplots of IcdP/(IcdP + BghiP) vs. Fla/(Fla + Pry) indicated a more complex source for soil while simple combustion source of coal, wood and grass for bulk deposition was shown. There were obvious positive correlation ($p<0.05$) between annual atmospheric bulk deposition and PAHs emission, and biomass was the main contributor to the total emission of PAHs.

According to the ratio of deposition/emission, this transect played an important role as a source of PAHs rather than a sink. Mountain cold trap existed in this transect where altitude was

higher than 1000 meters. The ratio of BaA/Chr and back trajectory indicated that high atmospheric deposition was closely associated with local emission. While long-range transport had an important impact on the deposition fluxes in summer. The forward trajectory illuminated this transect was a source to Tibet only in summer. Most air mass in this study did not undergo long-range transport due to the blocking effect of surrounding mountains. Only a few air masses (<10%) underwent long-range transport to the eastern and northern regions of China or farther regions.

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References

Arias, A.H., Spetter, C.V., Freije, R.H., Marcovecchio, J.E., 2009. Polycyclic aromatic hydrocarbons in water, mussels (Brachidontes sp., Tagelus sp.) and fish (Odontesthes sp.) from Bahía Blanca Estuary, Argentina. Estuarine, Coastal and Shelf Science 85, 67-81.

Bari, M.A., Kindzierski, W.B., Cho, S., 2014. A wintertime investigation of atmospheric deposition of metals and polycyclic aromatic hydrocarbons in the Athabasca Oil Sands Region, Canada. Science of the Total Environment 485, 180-192.

Bosch, C., Andersson, A., Krusa, M., Bandh, C., Hovorkova, I., Klanova, J., Knowles, T.D.J., Pancost, R.D., Evershed, R.P., Gustafsson, O., 2015. Source Apportionment of Polycyclic Aromatic Hydrocarbons in Central European Soils with Compound-Specific Triple Isotopes (delta C-13, Delta C-14, and delta H-2). Environmental Science & Technology 49, 7657-7665.

Cabrerizo, A., Dachs, J., Jones, K.C., Barcelo, D., 2011. Soil-Air exchange controls on background atmospheric concentrations of organochlorine pesticides. Atmospheric Chemistry and Physics 11, 12799-12811.

Chen, D., Liu, W., Liu, X., Westgate, J.N., Wania, F., 2008. Cold-trapping of persistent organic pollutants in the mountain soils of Western Sichuan, China. Environmental Science & Technology 42, 9086-9091.

Chen, P.F., Kang, S.C., Li, C.L., Rupakheti, M., Yan, F.P., Li, Q.L., Ji, Z.M., Zhang, Q.G., Luo, W., Sillanpaa, M., 2015. Characteristics and sources of polycyclic aromatic hydrocarbons in atmospheric aerosols in the Kathmandu Valley, Nepal. Science of the Total Environment 538, 86-92.

Choi, S.-D., Shunthirasingham, C., Daly, G.L., Xiao, H., Lei, Y.D., Wania, F., 2009. Levels of polycyclic aromatic hydrocarbons in Canadian mountain air and soil are controlled by proximity to roads. Environmental Pollution 157, 3199-3206.

Choi, S.D., Staebler, R.M., Li, H., Su, Y., Gevao, B., Harner, T., Wania, F., 2008. Depletion of gaseous

458 polycyclic aromatic hydrocarbons by a forest canopy. Atmospheric Chemistry and Physics 8,
459 4105-4113.
460 Daly, G.L., Lei, Y.D., Teixeira, C., Muir, D.C.G., Wania, F., 2007. Pesticides in western Canadian
461 mountain air and soil. Environmental Science & Technology 41, 6020-6025.
462 Daly, G.L., Wania, F., 2005. Organic contaminants in mountains. Environmental Science & Technology
463 39, 385-398.
464 Ding, X., Wang, X.-M., Xie, Z.-Q., Xiang, C.-H., Mai, B.-X., Sun, L.-G., Zheng, M., Sheng, G.-Y., Fu,
465 J.-M., Pöschl, U., 2007. Atmospheric polycyclic aromatic hydrocarbons observed over the North
466 Pacific Ocean and the Arctic area: Spatial distribution and source identification. Atmospheric
467 Environment 41, 2061-2072.
468 Esen, F., Cindoruk, S.S., Tasdemir, Y., 2008. Bulk deposition of polycyclic aromatic hydrocarbons
469 (PAHs) in an industrial site of Turkey. Environmental Pollution 152, 461-467.
470 Foan, L., Domercq, M., Bermejo, R., Miguel Santamaria, J., Simon, V., 2015. Mosses as an integrating
471 tool for monitoring PAH atmospheric deposition: Comparison with total deposition and evaluation of
472 bioconcentration factors. A year-long case-study. Chemosphere 119, 452-458.
473 Gioia, R., Offenberg, J.H., Gigliotti, C.L., Totten, L.A., Du, S., Eisenreich, S.J., 2005. Atmospheric
474 concentrations and deposition of organochlorine pesticides in the US Mid-Atlantic region. Atmospheric
475 Environment 39, 2309-2322.
476 Gocht, T., Klemm, O., Grathwohl, P., 2007. Long-term atmospheric bulk deposition of polycyclic
477 aromatic hydrocarbons (PAHs) in rural areas of Southern Germany. Atmospheric Environment 41,
478 1315-1327.
479 Gong, P., Wang, X., Sheng, J., Yao, T., 2010. Variations of organochlorine pesticides and
480 polychlorinated biphenyls in atmosphere of the Tibetan Plateau: Role of the monsoon system.
481 Atmospheric Environment 44, 2518-2523.
482 Gregoris, E., Argiriadis, E., Vecchiato, M., Zambon, S., De Pieri, S., Donateo, A., Contini, D., Piazza,
483 R., Barbante, C., Gambaro, A., 2014. Gas-particle distributions, sources and health effects of polycyclic
484 aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes
485 (PCNs) in Venice aerosols. Science of the Total Environment 476–477, 393-405.
486 He, J., Fan, S., Meng, Q., Sun, Y., Zhang, J., Zu, F., 2014. Polycyclic aromatic hydrocarbons (PAHs)
487 associated with fine particulate matters in Nanjing, China: Distributions, sources and meteorological
488 influences. Atmospheric Environment 89, 207-215.
489 Hong, Y.W., Chen, J.S., Zhang, F.W., Zhang, H., Xu, L.L., Yin, L.Q., Chen, Y.T., 2015. Effects of
490 urbanization on gaseous and particulate polycyclic aromatic hydrocarbons and polychlorinated
491 biphenyls in a coastal city, China: levels, sources, and health risks. Environmental Science and
492 Pollution Research 22, 14919-14931.
493 Jurado, E., Jaward, F.M., Lohmann, R., Jones, K.C., Simo, R., Dachs, J., 2004. Atmospheric dry
494 deposition of persistent organic pollutants to the Atlantic and inferences for the global oceans.
495 Environmental Science & Technology 38, 5505-5513.
496 Keshtkar, H., Ashbaugh, L.L., 2007. Size distribution of polycyclic aromatic hydrocarbon particulate
497 emission factors from agricultural burning. Atmospheric Environment 41, 2729-2739.

Lei, Y.D., Wania, F., 2004. Is rain or snow a more efficient scavenger of organic chemicals? Atmospheric Environment 38, 3557-3571.

Li, J., Cheng, H., Zhang, G., Qi, S., Li, X., 2009. Polycyclic aromatic hydrocarbon (PAH) deposition to and exchange at the air-water interface of Luhu, an urban lake in Guangzhou, China. Environmental Pollution 157, 273-279.

Li, J., Liu, X., Zhang, G., Li, X.-D., 2010. Particle deposition fluxes of BDE-209, PAHs, DDTs and chlordane in the Pearl River Delta, South China. Science of the Total Environment 408, 3664-3670.

Liu, H., Qi, S., Yang, D., Hu, Y., Li, F., Liu, J., Xing, X., 2013. Soil concentrations and soil-air exchange of organochlorine pesticides along the Aba profile, east of the Tibetan Plateau, western China. Frontiers of Earth Science 7, 395-405.

Liu, W., Chen, D., Liu, X., Zheng, X., Yang, W., Westgate, J.N., Wania, F., 2010. Transport of semivolatile organic compounds to the Tibetan Plateau: spatial and temporal variation in air concentrations in mountainous Western Sichuan, China. Environmental Science & Technology 44, 1559-1565.

Liu, X., Li, J., Zheng, Q., Bing, H., Zhang, R., Wang, Y., Luo, C., Liu, X., Wu, Y., Pan, S., Zhang, G., 2014. Forest Filter Effect versus Cold Trapping Effect on the Altitudinal Distribution of PCBs: A Case Study of Mt. Gongga, Eastern Tibetan Plateau. Environmental Science & Technology 48, 14377-14385.

Lohmann, R., Gioia, R., Jones, K.C., Nizzetto, L., Temme, C., Xie, Z., Schulz-Bull, D., Hand, I., Morgan, E., Jantunen, L., 2009. Organochlorine pesticides and PAHs in the surface water and atmosphere of the North Atlantic and Arctic Ocean. Environmental Science & Technology 43, 5633-5639.

Ma, Y.N., Harrad, S., 2015. Spatiotemporal analysis and human exposure assessment on polycyclic aromatic hydrocarbons in indoor air, settled house dust, and diet: A review. Environment International 84, 7-16.

Motelay-Massei, A., Ollivon, D., Garban, B., Chevreuil, M., 2003. Polycyclic aromatic hydrocarbons in bulk deposition at a suburban site: assessment by principal component analysis of the influence of meteorological parameters. Atmospheric Environment 37, 3135-3146.

Ollivon, D., Blanchoud, H., Motelay-Massei, A., Garban, B., 2002. Atmospheric deposition of PAHs to an urban site, Paris, France. Atmospheric Environment 36, 2891-2900.

Pan, J., Yang, Y., Zhu, X., Yeung, L.W.Y., Taniyasu, S., Miyake, Y., Falandysz, J., Yamashita, N., 2013. Altitudinal distributions of PCDD/Fs, dioxin-like PCBs and PCNs in soil and yak samples from Wolong high mountain area, eastern Tibet-Qinghai Plateau, China. Science of the Total Environment 444, 102-109.

Qu, C., Qi, S., Yang, D., Huang, H., Zhang, J., Chen, W., Yohannes, H.K., Sandy, E.H., Yang, J., Xing, X., 2015. Risk assessment and influence factors of organochlorine pesticides (OCPs) in agricultural soils of the hill region: A case study from Ningde, southeast China. Journal of Geochemical Exploration 149, 43-51.

Schenker, S., Scheringer, M., Hungerbühler, K., 2014. Do persistent organic pollutants reach a thermodynamic equilibrium in the global environment? Environmental Science & Technology 48, 5017-5024.

Shen, H.Z., Huang, Y., Wang, R., Zhu, D., Li, W., Shen, G.F., Wang, B., Zhang, Y.Y., Chen, Y.C., Lu, Y., Chen, H., Li, T.C., Sun, K., Li, B.G., Liu, W.X., Liu, J.F., Tao, S., 2013. Global Atmospheric Emissions of Polycyclic Aromatic Hydrocarbons from 1960 to 2008 and Future Predictions. Environmental Science & Technology 47, 6415-6424.

Sheng, J.J., Wang, X.P., Gong, P., Joswiak, D.R., Tian, L.D., Yao, T.D., Jones, K.C., 2013. Monsoon-Driven Transport of Organochlorine Pesticides and Polychlorinated Biphenyls to the Tibetan Plateau: Three Year Atmospheric Monitoring Study. Environmental Science & Technology 47, 3199-3208.

Terzi, E., Samara, C., 2005. Dry deposition of polycyclic aromatic hydrocarbons in urban and rural sites of Western Greece. Atmospheric Environment 39, 6261-6270.

Wang, C.h., Wu, S.h., Zhou, S.l., Wang, H., Li, B.j., Chen, H., Yu, Y.n., Shi, Y.x., 2015. Polycyclic aromatic hydrocarbons in soils from urban to rural areas in Nanjing: Concentration, source, spatial distribution, and potential human health risk. Science of the Total Environment 527, 375-383.

Wang, R., Tao, S., Wang, B., Yang, Y., Lang, C., Zhang, Y., Hu, J., Ma, J., Hung, H., 2010. Sources and Pathways of Polycyclic Aromatic Hydrocarbons Transported to Alert, the Canadian High Arctic. Environmental Science & Technology 44, 1017-1022.

Wang, W., Simonich, S.L.M., Giri, B., Xue, M., Zhao, J., Chen, S., Shen, H., Shen, G., Wang, R., Cao, J., Tao, S., 2011. Spatial distribution and seasonal variation of atmospheric bulk deposition of polycyclic aromatic hydrocarbons in Beijing-Tianjin region, North China. Environmental Pollution 159, 287-293.

Wang, X.-p., Sheng, J.-j., Gong, P., Xue, Y.-g., Yao, T.-d., Jones, K.C., 2012. Persistent organic pollutants in the Tibetan surface soil: Spatial distribution, air-soil exchange and implications for global cycling. Environmental Pollution 170, 145-151.

Xing, X.L., Qi, S.H., Zhang, J.Q., Wu, C.X., Zhang, Y., Yang, D., Odhiambo, J.O., 2011. Spatial distribution and source diagnosis of polycyclic aromatic hydrocarbons in soils from Chengdu Economic Region, Sichuan Province, western China. Journal of Geochemical Exploration 110, 146-154.

Xing, X.L., Qi, S.H., Zhang, Y.A., Yang, D., Odhiambo, J.O., 2010. Organochlorine Pesticides (OCPs) in Soils Along the Eastern Slope of the Tibetan Plateau. Pedosphere 20, 607-615.

Yang, D., Qi, S., Zhang, Y., Xing, X., Liu, H., Qu, C., Liu, J., Li, F., 2013. Levels, sources and potential risks of polycyclic aromatic hydrocarbons (PAHs) in multimedia environment along the Jinjiang River mainstream to Quanzhou Bay, China. Marine Pollution Bulletin 76, 298-306.

Zhang, G., Chakraborty, P., Li, J., Sampathkumar, P., Balasubramanian, T., Kathiresan, K., Takahashi, S., Subramanian, A., Tanabe, S., Jones, K.C., 2008. Passive Atmospheric Sampling of Organochlorine Pesticides, Polychlorinated Biphenyls, and Polybrominated Diphenyl Ethers in Urban, Rural, and Wetland Sites along the Coastal Length of India. Environmental Science & Technology 42, 8218-8223.

Zhang, Y., Yu, H.J., Xi, B.D., Hou, H.B., Gao, R.T., Liang, Q., Zhang, H., Xu, F.X., 2015. Levels, sources, and potential ecological risks of polycyclic aromatic hydrocarbons (PAHs) in a typical effluent-receiving river (Wangyang River), North China. Arabian Journal of Geosciences 8, 6535-6543.

Zhang, Y.X., Tao, S., Cao, J., Coveney, R.M., 2007. Emission of polycyclic aromatic hydrocarbons in

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578 China by county. Environmental Science & Technology 41, 683-687.
579 Zhong, Y., Zhu, L., 2013. Distribution, input pathway and soil-air exchange of polycyclic aromatic
580 hydrocarbons in Banshan Industry Park, China. Science of the Total Environment 444, 177-182.
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Highlights:

- Spatio-temporal variations of PAHs in atmospheric deposition were observed.
- PAHs deposition was negatively correlated to some meteorological parameters.
- Atmospheric PAHs deposition was closely related to local emission.
- This transect played an important role of source rather than sink.
- Most air mass did not undergo long-range transport due to the presence of mountains.

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