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Tracing environmental lead sources on the Ao mountain of China using lead isotopic composition and biomonitoring

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Abstract: Atmospheric lead (Pb) and other trace metals can transport over long distance and deposit on remote alpine ecosystems. In this work, the soil profiles, litter and dominant mosses along a large altitude were collected on Ao Mountain, Central China, to obtain the spatial distributions of Pb in these materials, decipher the possible factors controlling the distribution, and quantitatively distinguish the natural versus anthropogenic sources of Pb through the Pb isotopic tracing and biomonitoring. The results show that soil Pb concentrations (mg/kg) decreased significantly with depth, and they were markedly higher in the O (42.6 ± 2.7) and A (36.4 ± 2.2) horizons than in the litter (7.20 ± 1.9) and mosses (28.0 ± 3.9). The Pb enrichment in the surface soils (O and A horizons), litter and mosses existed in the relatively high altitudes, which was attributed to the influences from atmospheric wet deposition, plants, soil physicochemical properties and human activity. The Pb isotopic ratios identified the Pb sources as originating mainly from Chinese coal combustion, mining and smelting. Atmospheric Pb from southeastern, southwestern and northwestern regions could be deposited in the alpine ecosystem by long distance atmospheric transport. The anthropogenic Pb reached over 50% in the O and A horizons, and over 70% in the litter and mosses, which corresponded to the concentrations of 26.9, 17.7, 5.92 and 21.2 mg/kg, respectively. The results indicate that the mutual effects of climate and regional human activity could increase the Pb accumulation in remote alpine ecosystems.

Keywords: Source identification; Pb isotope; Biomonitoring; Mountain soils; Qinling region

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Introduction

Lead (Pb) is a major environmental pollutant due to its toxicity, widespread existence, and

potential threat to human health. Despite the substantial reduction of Pb by the introduction of unleaded gasoline globally, the elevated amounts of Pb were still reported in various environments due to long-term industrialization and urbanization (Luo et al. 2012; Szolnoki et al. 2013). The Pb adsorbed on fine airborne particulates can be transported over distances to remote alpine ecosystems by atmospheric deposition (Smodiš and Bleise 2002; Bing et al. 2014, 2016a). Forest soils are a main sink of Pb from the atmosphere, and the organic rich floor can effectively intercept atmospherically deposited Pb (Kaste et al. 2003; Watmough and Hutchinson 2004), which provides a desire indicator monitoring regional Pb contamination. In addition, the remote alpine ecosystems are normally located in the upper reach of a catchment where the cycles of materials and energy start. The contamination of Pb will pose potential threat to the ecological safety of local and downstream ecosystems. Therefore, it is imperative to investigate the geochemical distribution of Pb and to distinguish its sources in remote mountain ecosystems in order to understand the intensity of regional human activity and then to develop control policy for ecological management.

In the environment Pb has natural and anthropogenic origins. Natural Pb is mainly related to bedrock weathering, volcanic eruption, and atmospheric deposition (Reimann et al. 2011). Anthropogenic Pb sources include metallurgical and industrial processes, mining, ferrous smelting, vehicle exhausts, and fossil fuel combustion (Barandovski et al. 2012; Flegal et al. 2013; Rabinowitz et al. 2005; Sucharová et al. 2014). Due to the complicated features of Pb contamination regarding its sources, especially in areas far from industry and population centers, it is not easy to identify its exact origins. The isotope fingerprint technique provides an excellent approach for source apportionment of trace metals. The Pb isotopic composition of a sample cannot be significantly affected by fractionation processes, and thus it reflects the contribution of all Pb sources from the radioactive decay of U and Th (Cheng and Hu 2010).

Recently, the technique of Pb isotopic fingerprint has been extensively used to characterize its sources in various environmental archives such as soils (Bing et al. 2014; Klaminder et al. 2005; Kuang et al. 2013; Luo et al. 2015), sediments (Bing et al. 2016b, c; Hosono et al. 2016), aerosols (Cheng et al. 2007; Kumar et al. 2016; Lee et al. 2007), plant tissues (Li et al. 2012b; Watmough and Hutchinson 2004), and mosses (Shotyk et al. 2015; Sucharová et al. 2014). However, this technique has not been widely used in mountain regions, especially for remote and inaccessible sites.

Moss assimilates nutrients and moisture exclusively from atmosphere, and thus is selected as a biomonitor to indicate atmospheric sourced trace metals (Bekteshi et al. 2015; Berg et al. 1997; Harmens et al. 2010). The accumulation of Pb in moss reveals the current contamination state under anthropogenic impacts. The biomonitoring, geochemical index (e.g., enrichment factor) is applied to reveal the mass balance of a metal and then to distinguish its sources. However, the metal sources should be well-defined first, because natural processes can probably affect trace metal fractionation from original sources (Reimann and Caritat 2000). In addition, statistical analysis (e.g., factor analysis, correlation analysis) can screen various variables and then obtain the possible Pb sources in the environment. As a whole, using multiple methods simultaneously will better identify the Pb sources in mountain ecosystems where the source end-members of Pb may be mixed by various sources over a period of time.

Ao Mountain (33°56′N, 107°25′E, peak: 3476 m above sea level (a.s.l.)) is located in central Qinling Regions (Figure 1). The Qinling Regions, a special area in China, are the boundaries of North China and South China, humid and semi-humid regions, subtropical monsoon and temperate monsoon climate, 800 mm precipitation line, vegetation distribution, and so on. In summer, this area is successively controlled by the southeastern and southwestern monsoons characterized by relatively high precipitation, whereas the westerly wind results in dry weather conditions in winter. The air mass from the three directions would bring toxic metals from different sources deposited in the mountain ecosystem. Meanwhile, the Mt. Ao is characterized as a large elevation difference with distinct vegetation zones, and it is far away from direct human disturbance. These offer an opportunity to understand the effects of regional human activity and climate conditions on the Pb

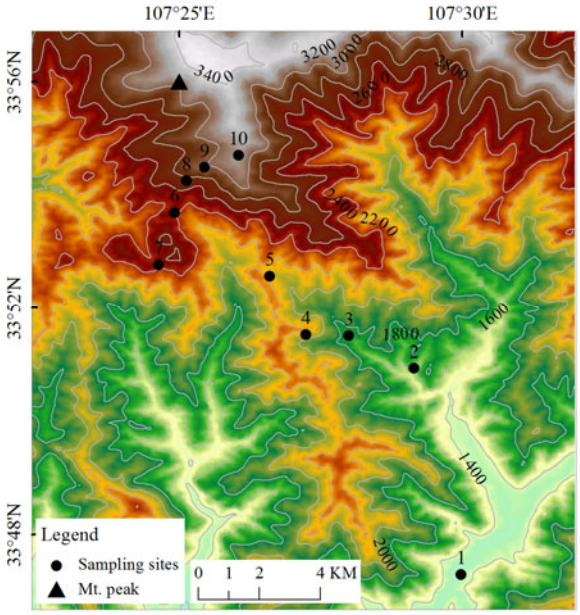

Figure 1 The study area and sampling sites on the Mt. Ao, China.

distribution in this remote mountain. Therefore, this work aims to (1) investigate the Pb distributions in the soil profiles, litter, and dominant mosses on the Mt. Ao, (2) explore the key factors affecting the distribution of Pb, and (3) quantitatively distinguish the Pb sources through Pb isotopic composition and biomonitoring. This is the first time in the Mt. Ao area that the Pb isotopic composition together with the biomonitoring was used to trace Pb sources.

1 Materials and Methods

1.1 Study area

Ao Mountain is located in Taibai County, Shanxi province, China. The annual mean temperature and annual mean precipitation in this area were 1.7°C -12.7°C and 650-1000 mm, respectively. The detailed information on the vegetation and soil characteristics along the altitude is summarized in Appendix 1. The Mt. Ao belongs to the Taibai Mountain National Nature Reserve, which covers an area of 56,325 hectares and is 140 km from the Xi'an City, the capital of Shaanxi province. The main bedrock in the area of Taibai Mountain is granite from massive invasion of acidic magmatic rocks. There are many metallic ore deposits containing copper, gold, iron, lead, zinc, etc. distributed around the Taibai Mountain. Except few tourists, this area is less affected by human activity.

1.2 Sample collection

Soil samples on the Mt. Ao were collected in October 2012 at ten altitudes: 1260, 1530, 1720, 1920, 2140, 2410, 2470, 2770, 3010, and 3150 m a.s.l. (Appendix 1). The interval of the sampling sites was uneven due to the hard accessibility and the vegetation difference along the altitude. At each sampling site, three soil profiles that included three soil horizons according to soil primary characteristics were hand-dug. The O horizon in the soil profile features the rich decomposition or semi-decomposition organic matters and brown color. It was absent at the altitudes of 1530 and 1920 m a.s.l. due to the heterogeneity of soil development (Table 1). The A horizon represents surface mineral soils with enriched humus materials and shows dark brown color, and the C horizon is the soil of parent materials. In total, 84 soil samples (24 from O horizon, 30 from A horizon, and 30 from C horizon) were collected. At each (or close) sampling site, the samples of litter and dominant moss (*Pleurozium schreberi* and *Brachythecium perminusculum*) were collected from the surface of at least five plots, and then mixed as one sample in the field.

For element analysis, the coarser particles and plant residues were removed from the soils through 2 mm sieve, and then the samples were air-dried. After a quick rinse with deionized water, the samples of litter and moss were oven-dried at 60 ℃. All samples were grinded using an agate mortar, and then passed through a 100-mesh Nylon screen for further analysis.

1.3 Chemical analysis

The contents of Soil Organic Carbon (SOC), pre-treated with 1 mol/L HCl to remove carbonates in the soils, were measured by an elemental analyzer (FlashEA1112). The reference material (GSS-11) was measured to keep the data quality, and the standard deviations of measured values were < 10% of the certified ones. The soils and deionized water were mixed with 1:2.5 to analyze

Table 1 Characteristics of physicochemical properties (mean ± standard error) in the soils of the Mt. Ao

Altitude (m a.s.l.)	Layer	Depth (cm)	pH	SOC (%)	Al (mg/g)	Ca (mg/g)	Fe (mg/g)	K (mg/g)	Mg (mg/g)	Mn (mg/kg)	Na (mg/g)	P (mg/kg)	Ti (mg/g)
1260	O	0-1	6.32	17.0 ± 1.5	40.8 ± 2.7	17.5 ± 1.3	20.0 ± 1.3	12.7 ± 0.8	7.07 ± 0.1	1480 ± 196	6.92 ± 0.3	751 ± 34.7	2.55 ± 0.2
	A	2-7	6.45	10.7 ± 1.2	56.2 ± 3.1	12.7 ± 1.1	27.2 ± 1.6	16.7 ± 0.9	8.66 ± 0.2	1270 ± 140	9.50 ± 0.3	566 ± 21.2	3.48 ± 0.2
	C	> 32	5.09	4.10 ± 0.1	75.6 ± 1.0	6.28 ± 0.1	36.2 ± 0.7	21.1 ± 0.1	10.3 ± 0.1	573 ± 20.8	12.3 ± 0.4	226 ± 16.1	4.70 ± 0.1
1530	A	0-2	6.63	13.8 ± 4.1	74.0 ± 7.9	9.29 ± 3.4	37.6 ± 1.3	26.1 ± 2.6	11.5 ± 1.3	798 ± 88.8	7.85 ± 0.8	660 ± 123	3.04 ± 0.2
	C	> 35	6.23	3.51 ± 0.5	83.2 ± 1.0	5.55 ± 2.3	45.0 ± 0.6	28.6 ± 0.7	11.6 ± 0.7	889 ± 121	9.37 ± 0.7	413 ± 79.9	3.34 ± 0.1
1720	O	0-2	5.73	21.0 ± 0.9	39.8 ± 3.4	18.3 ± 0.4	18.1 ± 1.3	10.6 ± 1.0	6.10 ± 0.3	915 ± 73.8	7.16 ± 0.7	879 ± 94.0	2.34 ± 0.2
	A	3-8	5.19	18.9 ± 2.6	51.0 ± 6.7	14.6 ± 1.0	22.8 ± 2.8	13.2 ± 1.4	7.25 ± 0.6	853 ± 31.9	8.88 ± 1.0	704 ± 84.6	2.98 ± 0.4
	C	> 30	4.87	4.68 ± 0.1	76.2 ± 1.0	5.23 ± 0.3	33.8 ± 0.4	17.2 ± 0.8	9.36 ± 0.2	680 ± 32.4	13.0 ± 0.5	278 ± 11.7	4.63 ± 0.1
1920	A	0-4	6.04	16.1± 5.1	57.2 ± 1.7	26.0 ± 1.1	31.8 ± 1.6	15.0 ± 0.6	12.4 ± 0.5	619 ± 16.8	13.5 ± 0.8	1030 ± 162	5.41 ± 0.6
	C	> 30	6.36	4.83 ± 0.6	77.8 ± 1.1	23.1 ± 0.6	43.8 ± 0.5	17.3 ± 0.2	16.3 ± 0.1	664 ± 12.3	18.9 ± 0.6	962 ± 99.4	8.31 ± 0.2
2140	O	0-1	5.02	26.1 ± 5.3	33.4 ± 8.4	15.9 ± 2.4	14.9 ± 3.3	8.06 ± 1.4	6.59 ± 1.4	668 ± 122	7.16 ± 2.2	928 ± 78.3	1.79 ± 0.4
	A	2-4	4.99	25.0 ± 2.8	39.5 ± 7.6	14.4 ± 2.2	17.9 ± 3.5	9.43 ± 1.6	7.84 ± 1.4	738 ± 70.7	7.75 ± 1.5	782 ± 62.3	2.22 ± 0.3
	C	> 32	5.32	3.66 ± 0.7	68.3 ± 6.0	2.72 ± 0.3	29.7 ± 3.2	15.9 ± 1.1	12.6 ± 1.7	368 ± 68.7	13.3 ± 1.6	263 ± 37.9	3.44 ± 0.4
2410	O	0-1	5.10	20.4 ± 1.5	42.1 ± 5.8	13.6 ± 1.1	22.5 ± 2.8	11.6 ± 1.3	10.1 ± 1.2	481 ± 16.1	6.31 ± 1.4	1080 ± 22.6	2.28 ± 0.3
	A	2-5	5.12	25.7 ± 3.3	48.0 ± 3.2	12.6 ± 0.8	23.7 ± 0.5	13.5 ± 1.7	11.8 ± 0.8	488 ± 6.3	6.40 ± 1.5	910 ± 57.5	2.50 ± 0.1
	C	> 26	5.08	5.29 ± 0.1	78.5 ± 1.4	4.26 ± 0.3	41.3 ± 0.7	19.4 ± 0.5	16.8 ± 1.1	572 ± 38.0	9.92 ± 0.8	716 ± 67.0	4.38 ± 0.1
2470	O	0-2	4.25	20.4 ± 1.7	46.4 ± 4.2	9.63 ± 0.4	22.2 ± 1.7	13.2 ± 1.0	7.09 ± 0.4	804 ± 42.4	7.56 ± 0.8	863 ± 35.0	2.81 ± 0.3
	A	3-10	4.82	17.2 ± 2.3	51.4 ± 6.2	9.18 ± 0.4	24.4 ± 2.6	13.6 ± 1.0	7.55 ± 0.5	887 ± 252	7.95 ± 0.8	717 ± 96.8	3.11 ± 0.4
	C	> 24	5.00	5.80 ± 0.5	76.9 ± 0.4	5.47 ± 0.2	36.5 ± 0.2	16.9 ± 0.1	9.55 ± 0.1	562 ± 26.4	10.3 ± 0.1	468 ± 1.98	4.62 ± 0.1
2770	O	0-3	4.25	29.3 ± 1.6	26.0 ± 2.6	16.0 ± 0.8	12.9 ± 1.3	8.95 ± 0.9	4.41 ± 0.3	679 ± 40.3	4.38 ± 0.4	916 ± 15.2	1.75 ± 0.3
	A	4-13	4.65	29.0 ± 1.4	35.7 ± 2.7	14.7 ± 0.6	16.8 ± 1.2	11.5 ± 1.1	5.05 ± 0.2	697 ± 28.3	6.30 ± 0.6	883 ± 40.0	2.38 ± 0.3
	C	> 26	5.17	5.51 ± 0.3	76.1 ± 0.6	7.83 ± 0.3	34.1 ± 1.3	22.4 ± 0.2	7.89 ± 0.4	484 ± 54.8	13.4 ± 0.3	550 ± 76.0	4.63 ± 0.2
3010	O	0-2	4.23	28.4 ± 0.2	35.6 ± 3.1	12.6 ± 0.4	16.2 ± 0.9	11.3 ± 1.0	5.05 ± 0.2	887 ± 51.8	5.76 ± 0.6	894 ± 41.1	2.18 ± 0.2
	A	3-9	4.55	20.8 ± 3.3	44.2 ± 5.7	12.3 ± 1.0	19.3 ± 2.1	13.4 ± 1.6	5.78 ± 0.6	881 ± 22.9	7.14 ± 1.0	847 ± 34.9	2.74 ± 0.4
	C	> 25	4.67	6.54 ± 0.9	77.5 ± 2.2	6.27 ± 0.5	34.4 ± 5.5	25.3 ± 3.3	6.05 ± 1.2	354 ± 47.5	13.9 ± 1.2	287 ± 36.8	4.18 ± 0.4
3150	O	0-3	3.70	40.1± 6.6	27.3 ± 3.5	10.8 ± 0.8	13.3 ± 1.5	8.19 ± 1.2	4.22 ± 0.4	640 ± 39.1	4.23 ± 0.6	820 ± 15.3	1.66 ± 0.2
	A	4-11	4.05	26.8 ± 0.9	41.1 ± 5.7	10.6 ± 2.0	19.1 ± 2.0	12.1 ± 1.7	5.62 ± 0.3	660 ± 50.9	6.55 ± 1.2	752 ± 49.9	2.44 ± 0.4
	C	> 22	4.76	3.77 ± 1.2	79.4 ± 1.3	4.78 ± 0.1	34.1 ± 1.7	21.5 ± 0.3	7.44 ± 0.3	235 ± 15.1	10.4 ± 0.2	334 ± 40.4	4.71 ± 0.2

the soil pH using a pH meter.

The acids of HCl, HNO_3, HF and $HClO_4$ were used to digest soils, and HNO_3 and H_2O_2 were for litter and moss. The Pb concentrations in the extraction solution were measured using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), and other elements including Al, Ca, Fe, K, Mg, Mn, Na, P and Ti were analyzed using Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). The standard solution (SPEX™, United States), repeated samples, blanks and reference materials (GSD-9 and GSD-11 for soils; GBW07603 and GBW07604 for plants) were analyzed to keep the data quality. By measuring replicates and reference materials, the relative standard deviations were below 5% and 3% for the analysis of ICP-MS and ICP-AES, respectively. The recovery of reference materials in soils and mosses was 90%-110% and 92%-108% for the analysis of ICP-AES and ICP-MS, respectively.

After the corresponding digestion mentioned above, the Pb isotopes of ^{206}Pb, ^{207}Pb and ^{208}Pb in the soils, litter and mosses were detected by using ICP-MS (Agilent 7700x). The instrument was calibrated by the international reference material of SRM981-NIST (United States), and the analytical quality was controlled through the standard material of GBW04426 (China). Through repeated measurements of the Pb standard GBW04426, the maximum deviations of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ were less than 0.002, respectively.

1.4 Calculations

The enrichment factors (EF) was calculated to obtain the Pb enrichment states in the soils, litter and moss:

$$EF = (Pb/Ti)_{sample}/(Pb/Ti)_{background} \quad (1)$$

where $(Pb/Ti)_{sample}$ is the ratio of Pb to Ti in a sample, whereas $(Pb/Ti)_{background}$ is the corresponding ratio in the background. The element concentrations in the C horizon were chosen as the background. In order to quantify the anthropogenic contribution to Pb, the isotopic ratios of $^{206}Pb/^{207}Pb$ were used to model the anthropogenic Pb contributions (Bindler et al. 1999; Klaminder et al. 2005):

$$\text{Anthropogenic Pb} = \frac{(^{206}Pb/^{207}Pb_{sample} - ^{206}Pb/^{207}Pb_{background})}{(^{206}Pb/^{207}Pb_{anthropogenic} - ^{206}Pb/^{207}Pb_{background})} \times 100\% \quad (2)$$

where $^{206}Pb/^{207}Pb_{sample}$ is the ratio in a sample, and a $^{206}Pb/^{207}Pb$ value of 1.156 is used for the anthropogenic Pb according to the significant relationship between $^{206}Pb/^{207}Pb_{sample}$ and 1/Pb (Appendix 2). The $^{206}Pb/^{207}Pb$ in the C horizon was chosen as the background.

The HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) model was applied to track the backward air mass pathways (Chen et al. 2013; Wang et al. 2010), which could indicate the potential Pb source regions by long-range atmospheric transport. The meteorological data at each month from Nov. 2011 to Oct. 2012 from the NOAA Air Resources Laboratory (http://ready.arl.noaa.gov/archives.php) were used to obtain the air mass trajectories reaching the Mt. Ao (three altitudes).

1.5 Statistical analysis

One Way ANOVA (Fisher Test, $p < 0.05$) was used to identify the significant difference of the means of element concentrations and Pb isotopic ratios in the samples. Factor analysis, linear regression analysis, and Pearson correlation analysis were applied to establish the relationship between Pb (and/or Pb isotopes) and other parameters in the samples. The software package of SPSS 16.0, Origin 8.0, and ArcGIS 9.3 for Windows were used to perform the statistical analysis.

2 Results

2.1 Soil physicochemical properties

The soil development on the Mt. Ao increased with the decreasing elevation based on the soil physicochemical properties (Table 1). The soil pH decreased significantly in the order of C horizon > A horizon > O horizon, and for each horizon it decreased with altitude. The markedly higher concentrations of SOC were observed in the O horizon, followed by the A horizon, and its concentrations in the C horizon were the lowest ($p < 0.05$). Spatially, the SOC concentrations in the

surface soils (O and A horizons) were generally higher at the high altitude areas, corresponding to the coniferous forests.

The concentrations of Al, Fe, K, Mg, Na and Ti generally increased with the soil depth ($p < 0.05$), whereas those of Ca, Mn, and P showed an opposite trend (Table 1). Spatially, most of these elements in the C horizon did not show the markedly different concentrations. However, the concentrations in the O and A horizons exhibited distinct difference due to the soil heterogeneity.

2.2 Lead concentrations in soils, litter, and mosses

The soil Pb concentrations (mg/kg) decreased in the order: O horizon (27.1-63.4, mean ± SE: 42.6 ± 2.7) > A horizon (23.5-52.3, 36.4 ± 2.2) > C horizon (13.6-29.0, 21.1 ± 0.9) (Figure 2). A marked increase trend of the Pb concentrations with altitude was observed in the O horizon, whereas the concentrations in the A horizon increased between 1260 m and 2470 m a.s.l., and then decreased with altitude. Despite a little variation, the Pb concentrations in the C horizon were generally low and close to the values in the upper continental crust.

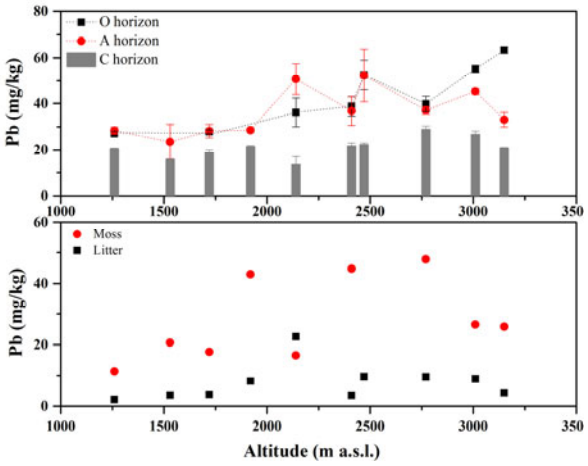

Figure 2 Concentrations of Pb in the soils, litter, and dominant mosses with altitude.

The Pb concentrations in the litter varied between 2.10 and 22.6 mg/kg (mean: 7.60 mg/kg). Except a markedly high concentration of Pb in the litter of 2140 m a.s.l., its concentrations increased slightly with altitude (Figure 2). The Pb concentrations in the dominant mosses, markedly higher than in the litter ($p < 0.05$), varied between 11.4 and 47.8 mg/kg with the mean of 28.0 mg/kg. Spatially, the concentrations showed markedly higher values at the altitudes of 1920 m, 2410 m and 2770 m a.s.l., and the lowest was observed at the low altitude 1260 m a.s.l. (Figure 2).

2.3 Lead isotopic ratios in soils, litter, and mosses

The $^{206}Pb/^{207}Pb$ ratios were significantly lower in the O horizon (1.168-1.175, mean: 1.171), followed by the A horizon (1.167-1.192, 1.177), and then the C horizon (1.184-1.203, 1.195) ($p < 0.05$, Appendix 3). The $^{208}Pb/^{206}Pb$ ratios in the soils showed the opposite case to the $^{206}Pb/^{207}Pb$ ratios: O horizon (2.099-2.111, 2.105) > A horizon (2.091-2.110, 2.098) > C horizon (2.075-2.098, 2.086) ($p < 0.05$). Spatially, the variations of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ in each horizon showed an inverse trend with altitude. The ratios of soil $^{206}Pb/^{207}Pb$ were relatively higher in the areas of low altitude than of high altitude (Appendix 3).

The Pb isotopic ratios in the litter varied between 1.159 and 1.169 with the mean of 1.165 for $^{206}Pb/^{207}Pb$, and between 2.101 and 2.114 with the mean of 2.107 for $^{208}Pb/^{206}Pb$ (Appendix 4). Spatially, the highest $^{206}Pb/^{207}Pb$ and the lowest $^{208}Pb/^{206}Pb$ were observed in the litter of 1260 m a.s.l.. Otherwise, there was not a significant variation of the ratios with altitude. The Pb isotopic ratios in the mosses varied between 1.161 and 1.177 with the mean of 1.166 for $^{206}Pb/^{207}Pb$, and between 2.100 and 2.114 with the mean of 2.108 for $^{208}Pb/^{206}Pb$ (Appendix 4). The relatively low $^{206}Pb/^{207}Pb$ and high $^{208}Pb/^{206}Pb$ were observed in the mosses of 1530 m, 1720 m, 3010 m and 3150 m a.s.l., whereas the highest $^{206}Pb/^{207}Pb$ and lowest $^{208}Pb/^{206}Pb$ existed at the lowest altitude (1260 m a.s.l.).

3 Discussion

3.1 Controls of the Pb distribution with altitude

Organic layers of soils are a major sink mechanism of trace metals in forest ecosystems, reflecting the metal accumulation from

autochthonic and extraneous sources (Dawson et al. 2009). The Pb concentrations in the O horizon of the Mt. Ao generally increased with altitude, especially at the higher altitudes of 3010 m and 3150 m a.s.l. (Figure 2a), which was possibly attributed to the local meteorological conditions. A significant correlation of the Pb concentrations in the O horizon with the precipitation on the Mt. Ao was well observed ($y = 3.37x + 765$, $r^2 = 0.78$). Wet deposition including raindrops, snowflakes and fog is an important factor modulating the altitudinal distribution of soil Pb (Spokes et al. 1994; Szopka et al. 2013; Gerdol and Bragazza 2006), and a positive relationship between Pb and precipitation has been reported (Petty and Lindberg 1990). Snowflake is a main form of atmospheric wet deposition at the high altitude of a mountain, and it features a relatively longer retention time compared with that at the low altitude. Snowflake can adsorb much more trace metals than the precipitation due to its larger specific surface areas (Kim et al. 2012). In addition, the low temperature at the higher altitudes further accelerated the accumulation of Pb in the O horizon under the effect of mountain cold trapping.

Besides the wet deposition, vegetation is another key factor regulating Pb distribution in organic soils by the effects of filtering and returning (Bing et al. 2016b). The Pb concentrations in the O horizon of coniferous forests were significantly higher than those of the broadleaf and broadleaf-coniferous forests ($p < 0.05$, Figure 2a, Appendix 1). The coniferous forests normally intercept much more precipitation than the broadleaf forests (Johnson et al. 1990; Sun et al. 2013), which may induce the relatively low Pb inputs to forest floor. However, the Pb accumulation in soils is a long-term process, and the filtering and the latter washing off could increase the Pb accumulation in the O horizon of the high altitudes. The Pb returning from litter decomposition could increase its accumulation in the O horizon. This was supported by the generally increasing trend of the Pb concentrations in the litter of the Mt. Ao with altitude (Figure 2b). On the one hand, the litter quality in the coniferous forests is more difficult for microorganisms' decomposition than that in the broadleaf forests under the poor conditions at the high altitudes. On the other hand, the quantity of soil organic matters controls the Pb distribution in soils (Marchand et al. 2011; Steinnes et al. 2005). A significant relationship between Pb and SOC was observed ($p < 0.05$, Appendix 5), and in the O horizon the SOC increased markedly with altitude (Table 1). When the Pb concentrations were normalized by the SOC, there was no distinct trend of the Pb distribution in the O horizon with altitude (Appendix 5). These confirmed that the organic matters in the O horizon probably adsorbed Pb and prevented it from mobilization or leaching in the high latitude coniferous forests.

Compared with the altitudinal Pb distribution in the O horizon, its distribution in the A horizon showed a significantly higher accumulation in the middle altitudes (2770-3150 m a.s.l.) (Figure 2a). The depth of the organic layer (O horizon), relatively higher in the high versus the middle altitude areas, was a key factor, which intercepted the Pb from vertical leaching (Klaminder et al. 2008). Furthermore, compared with the mid-altitude areas (broadleaf-coniferous forests), the concentrations of SOC in the high altitude areas (coniferous forests) were notably higher in the O horizon than in the A horizon (Table 1). This further prevented the O horizon Pb leaching to the A horizon as a result of the high Pb affinity to SOC ($p < 0.05$). In addition, the soil chemical properties, such as pH, increased the difference of the Pb accumulation in the A horizon with altitude. Coniferous tree roots can secrete much more acidic compounds than broadleaf tree roots, and accelerate soil acidification (Bernal and McGrath 1994). Our analysis found a significantly negative correlation of Pb with the soil pH (Appendix 5). Meanwhile, the pH in the A horizon was markedly lower in the high altitude coniferous forests than in other forests ($p < 0.05$). The lower pH could activate the soil Pb and lead to its mobilization by runoff and leaching under the abundant precipitation in the high altitude areas. The concentrations of Pb in the C horizon, slightly higher at the high altitudes, suggested an increasing leaching of Pb from the A horizon (Figure 2a).

The enrichment factors (EFs) indicated a marked Pb enrichment in the O and A horizons as well as in the litter (Figure 3). The EFs of Pb varied between 2.3 and 6.6 (3.7 ± 0.5) for the O horizon, between 0.8 and 6.4 (2.7 ± 0.5) for the A horizon,

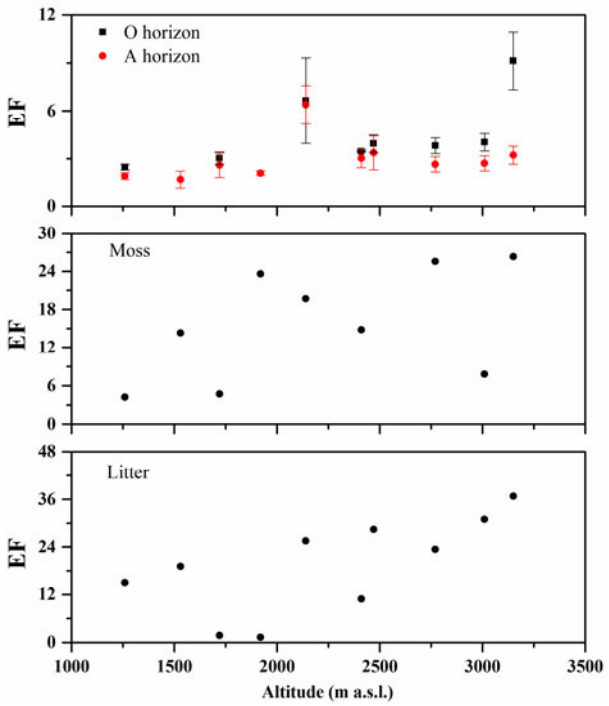

Figure 3 Enrichment factors (EFs) of Pb in the O and A horizons, litter, and mosses with altitude.

Table 2 Explanation of total variances and component matrixes for Pb in the soils of the Mt. Ao

	Initial Eigenvalues			Ele.	Rotated component matrix	
	Total	% of variance	Cumulative %		PC1	PC2
1	5.840	58.404	58.404	Pb	-0.672	0.398
2	1.670	16.701	75.105	Al	0.794	-0.584
3	0.896	8.961	84.066	Ca	0.043	0.937
4	0.556	5.555	89.622	Fe	0.862	-0.409
5	0.469	4.688	94.309	K	0.602	-0.626
6	0.317	3.171	97.481	Mg	0.831	-0.026
7	0.117	1.170	98.650	Mn	-0.192	0.422
8	0.083	0.829	99.480	Na	0.865	-0.191
9	0.040	0.399	99.879	P	-0.208	0.890
10	0.012	0.121	100.000	Ti	0.925	-0.053

Notes: PC: Principal Component; Ele.=Elements.

and varied between 1.3 and 36.7 (19.3 ± 3.8) in the litter. Along the altitude, the enrichment of Pb showed a gradual increase trend in the O horizon and the litter, whereas this trend was not clear in the A horizon, which might be attributed to the leaching effect under the effect of precipitation.

Combined with the discussion above, the high EFs of Pb in the O horizon and the litter, higher than 1.5-2.0, probably suggested that the extraneous sources including anthropogenic contribution affected the Pb distribution (Blaser et al. 2000), especially in the high altitude areas. However, the low EFs of Pb in the O horizon and litter of low altitude areas could be related to low contribution of local human activity; in addition, the organic matters decomposition in the low altitude with relatively high temperature and precipitation tended to alter Pb accumulation, and resulted in the spatial variation of EFs-Pb in the organic rich O horizon and the litter.

The statistical analysis revealed the different geochemical features of the soil elements, which could distinguish the possible sources of Pb. Factor analysis (Table 2) and correlation analysis (Appendix 6) obtained the similar results. Two main components were extracted (Eigenvalue > 1.0) for Al, Ca, Fe, K, Mg, Mn, Na, P, Ti and Pb. The component 1 accounted for 58.4% of the total variance grouping Al, Fe, K, Mg, Na and Ti, and the component 2 grouped Ca, Mn, P and Pb, which explained 16.7% of the total variance. The results suggested that the soil Pb was mainly from the non-crustal sources as a result of its weak relationship with lithogenic elements (e.g., Al, K, Mg).

Moss is a biological indicator of atmospheric Pb deposition in the environment due to its nearly exclusive adsorption of them from the atmosphere (Bekteshi et al. 2015; Harmens et al. 2010). On the Mt. Ao, the EFs of Pb in the dominant mosses varied between 4.2 and 26.3 (15.7 ± 2.9), and generally increased with altitude (Figure 3). This further confirmed that the Pb on the Mt. Ao suffered from anthropogenic contamination by the atmospheric deposition.

3.2 Source identification of Pb

As illustrated in Figure 4a, the Pb isotopic ratios in the O and A horizons, litter and mosses were markedly distinct from those in the C horizon which showed the high $^{206}Pb/^{207}Pb$ and low $^{208}Pb/^{206}Pb$ ratios. This indicated little local Pb contribution from natural sources, such as soil weathering. However, the Qinling granite and the deeper soils (the C horizon) had uniform Pb isotopic ratios (Figure 4a), which revealed the contribution of local bedrock weathering to the soil Pb accumulation.

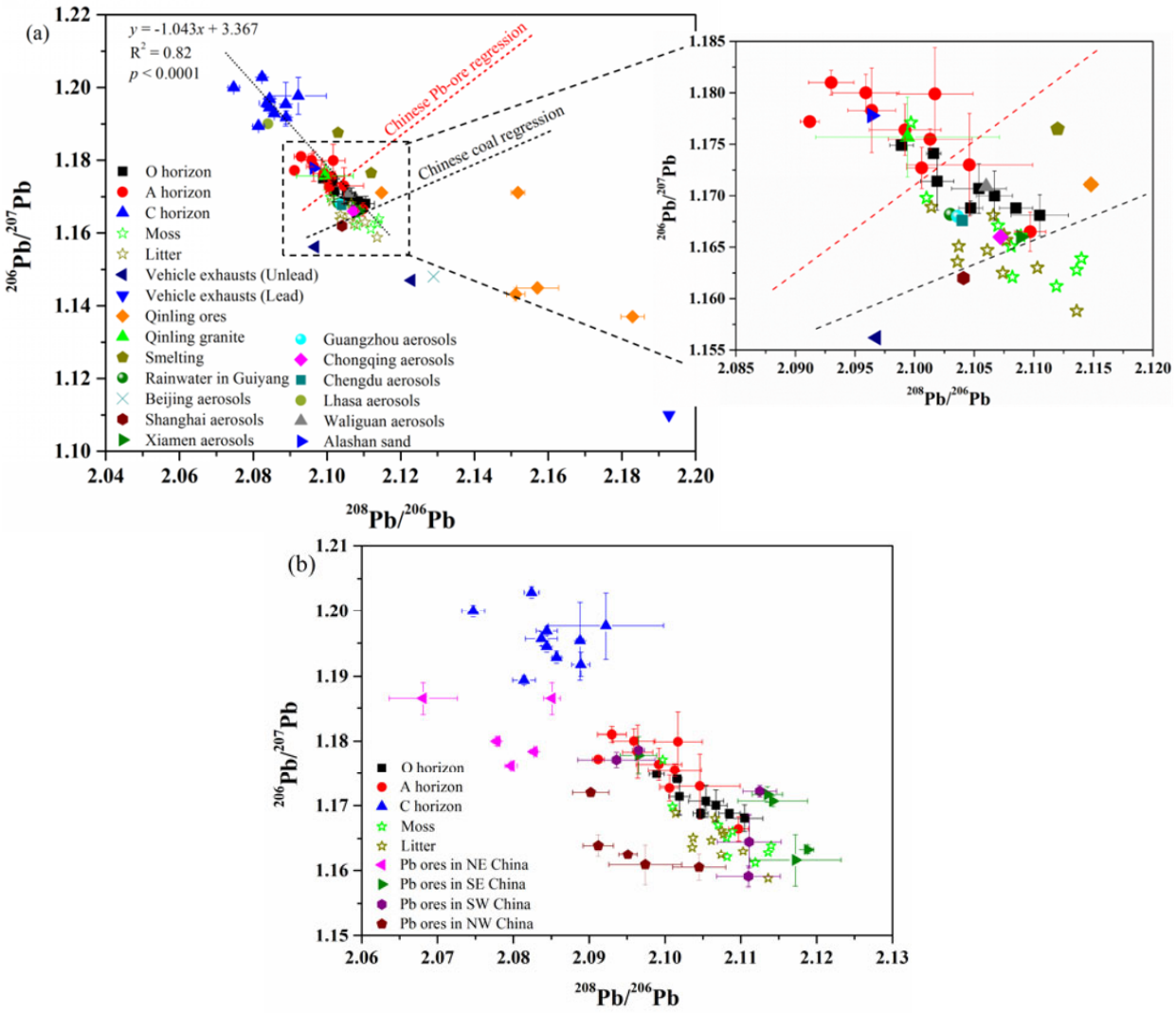

Figure 4 The Pb isotope ratios in the soils, litter, and mosses on the Mt. Ao and other environment materials. Refs: Vehicle exhausts (unleaded and leaded) (Chen et al. 2005); Qinling ores (Chen et al. 2003; Fu et al. 2010; Zhang et al. 2009; Huang et al. 1984); Qinling granite (Zhang et al. 2007); Pb-containing ores in NE China (Hu et al. 2014; Yao et al. 2012); Pb-containing ores in SE China (Han et al. 2014; Shi et al. 2013; Wang et al. 2011; Xi et al. 2009; Xiang et al. 2013); Pb-containing ores in SW China (Guan et al. 1999; Li et al. 2013; Tang et al. 2013; Xue et al. 2008; Zhang et al. 2005); Pb-containing ores in NW China (Nie et al. 2003; Wang et al. 2006; Xu et al. 2012; Zeng et al. 2007); Smelting (Bi et al. 2007); Rainwater in Guiyang (Li et al. 2012b); Beijing aerosols (Zhu et al. 2002); Shanghai aerosols (Chen et al. 2005); Xiamen aerosols (Luo et al. 2015); Guangzhou aerosols (Lee et al. 2007); Chongqing aerosols (Bollhöfer and Rosman 2001); Chengdu aerosols (Gao et al. 2004); Lhasa aerosols (Cong et al. 2011); Waliguan aerosols (Cheng et al. 2007); Alashan aerosols (Lee et al. 2013).

Based on the Pb isotopic ratios in other archives (Figure 4a), the values overlapped with those in the Chinese coal, Pb-containing ores and smelting. The Pb isotopic ratios in the Qinling ores generally showed a much lower $^{206}Pb/^{207}Pb$ and higher $^{208}Pb/^{206}Pb$ values than those in the soils, litter and mosses, which suggested the local ores did not markedly increase the Pb accumulation in these environmental archives. In last few decades, the main sources of atmospheric Pb in China have been reported from the ore smelting and coal combustion (Li et al. 2012a). Consequently, our data of the Pb isotopic ratios in the surface soils, litter and mosses confirmed that this kind of anthropogenic Pb emissions reached the remote mountainous areas. The Pb isotopic ratios in the O and A horizons, litter and mosses were distinctly different from those in vehicle exhausts. This indicated that the historical and current utilization of the gasoline with or without the alkyl-lead had

little effect on the Pb accumulation in the ecosystem of the Mt. Ao. This was in agreement with the results reported in settings remote from urban areas (Bing et al. 2014, 2016b; Kuang et al. 2013; Marx et al. 2016).

Trace metals in the atmosphere commonly adsorb on fine particulates (e.g. aerosols) and then are transported to remote alpine regions. In this study, we compared with the Pb isotope ratios in aerosols or sands from different Chinese cities and meteorological background station (Figure 4a). The results showed that the Pb isotopic ratios in the O and A horizons, litter and mosses of the Mt. Ao overlapped with those in aerosols from some cities of southeastern China, Waliguan and Alashan where the Pb suffered from local and extraneous anthropogenic influence (Bollhöfer and Rosman 2001; Chen et al. 2005; Cheng et al. 2007; Lee et al. 2007, 2013). However, they were not related to those in Beijing and Lhasa. This indicated that the Pb in the ecosystem of the Mt. Ao suffered from anthropogenic contamination by atmospheric deposition. We believe the anthropogenic Pb in the ecosystem of Mt. Ao was probably from the southwestern, southeastern and northwestern regions, since the Qinling regions were located in the intersection of the Indian Ocean Monsoon, East Asia Monsoon and Westerly Wind (Figure 1).

As discussed above that the anthropogenic Pb from mining was a main Pb source on the Mt. Ao, we also compared the Pb isotopic ratios in Chinese Pb-containing ores from different regions. It was clear that the isotopic ratios in the soils, litter and mosses of the Mt. Ao were associated with those of Pb-containing ores in SW, SE and NW China, whereas it did not overlap with those in the ores of NE China (Figure 4b). In addition, the five-day backward air-mass trajectories further revealed the possible source regions of anthropogenic Pb in the ecosystem of the Mt. Ao (Figure 5a).

It was noteworthy that the air mass trajectories passed through the main industrialized cities and/or developed areas in China and even the nearby abroad countries, and thus the trans-boundary Pb adsorbed on the contaminated airborne particles from industrial emissions and fossil fuels combustion would be transported to the Mt. Ao areas. These research results particularly indicated that the mutual effects of climate and human activity resulted in the Pb accumulation in the remote alpine ecosystem.

3.3 Quantification of anthropogenic Pb

The $^{206}Pb/^{207}Pb$ plotted against 1/Pb in the soils of the Mt. Ao showed a significant relationship ($r^2 = 0.73$, $p < 0.0001$, Appendix 2). A linear trend was clearly observed between $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ in the soils indicating two end-members of Pb sources. We therefore hypothesized that the soil Pb could be due to crustal and anthropogenic sources (Klaminder et al. 2011; Komarek et al. 2008). Consequently, the anthropogenic Pb contribution to the O and A horizons, litter and mosses was calculated by a binary mixing model of $^{206}Pb/^{207}Pb$ (Table 3). The percentage of anthropogenic Pb contribution was comparable between the litter (77.8 ± 2.5) and the mosses (74.2 ± 4.4), which was significantly higher than that in the O (59.5 ± 3.2) and A (48.9 ± 2.8) horizons. This indicated that the litter and mosses were much more sensitive than the soils to anthropogenic effects on the mountain ecosystem. Moreover, besides the plant uptake, the lower anthropogenic Pb in the soils was related to the longer retention time of Pb from different sources, which would dilute the anthropogenic contribution percentage. In this study, we also found that the anthropogenic Pb reached nearly 50% in the A horizon, indicating its vertical leaching in the soil profiles (Brännvall et al. 2001; Bacon and Hewitt 2005; Steinnes and Friedland 2005).

Compared with the anthropogenic Pb in forest soils of the world, our results were clearly lower than those in Sweden, Denmark and Czech Republic (Appendix 7). This difference was mainly attributed to the long history of Pb contamination in Europe, and atmospheric deposition increased the soil Pb accumulation (Nriagu et al. 1998; Marx et al. 2016). In China, there was very little research on the anthropogenic Pb contribution in mountain forest ecosystems. Recently, we have reported the anthropogenic contribution to Pb on the Mt. Gongga, Southwest China (Appendix 7). The anthropogenic Pb percentage in the soils of the Mt. Ao was similar to that of the Mt. Gongga, whereas the value was markedly higher in the dominant mosses of the Mt. Ao (74.2%) than of the Mt. Gongga (56.4%). This indicated that in recent

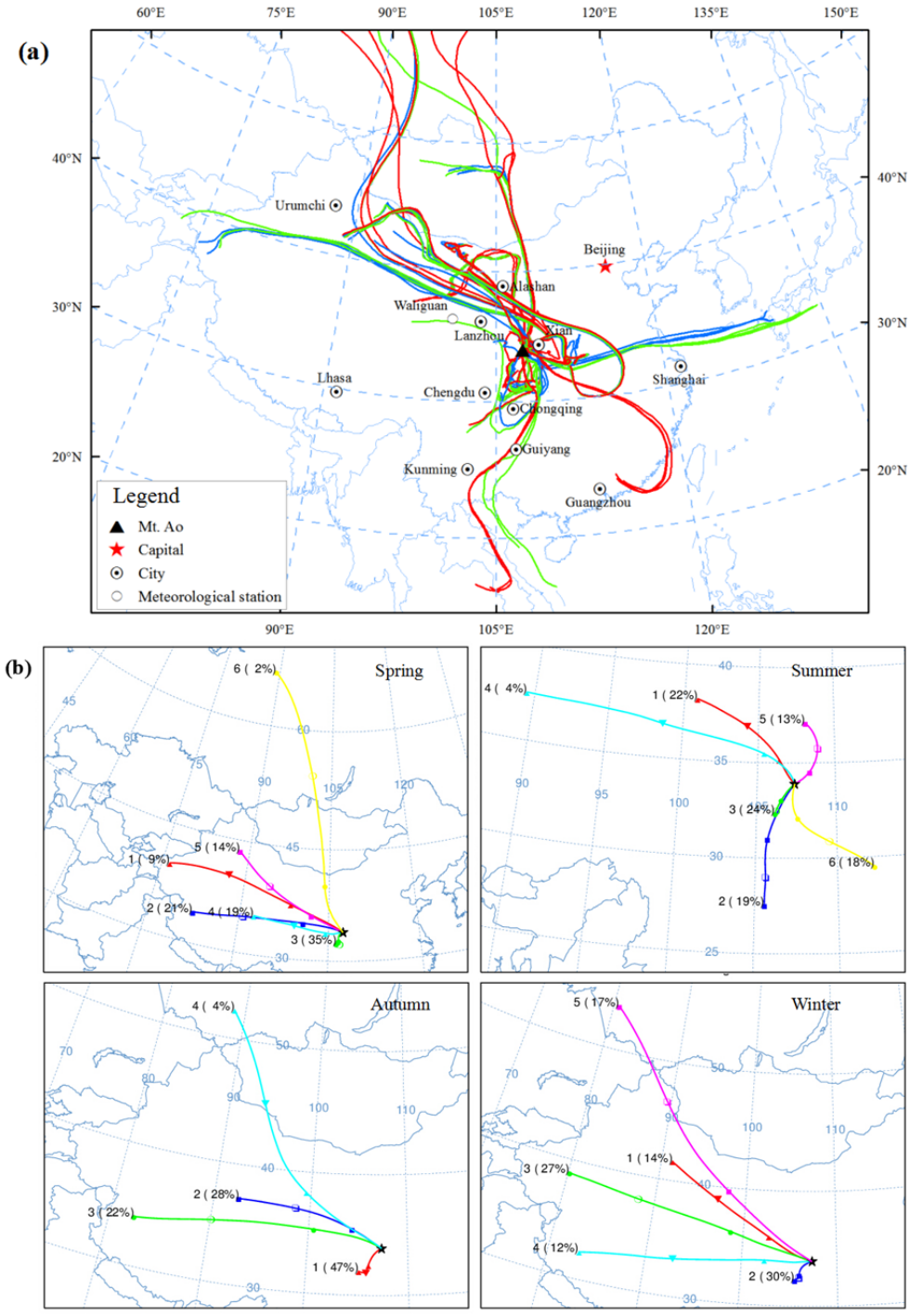

Figure 5 Five-day backward air mass trajectories reaching the Mt. Ao at each month from October 2012 to July 2013; the blue, green, and red lines represent the air mass trajectory reaching the altitudes of 1260, 2140 and 3150 m a.s.l., respectively (a). Five-day backward air mass trajectories reaching the Mt. Ao at each season with k-means clustering algorithm (b).

years much more Pb from anthropogenic emissions has accumulated on the Mt. Ao. In addition, the anthropogenic Pb on the Mt. Gongga was mainly from regions of Southwest China and South Asia (Bing et al. 2014), whereas that on the Mt. Ao was also from other two directions from China and other countries (Figure 5b). This difference probably suggested that the higher percentage of the anthropogenic Pb in the mosses of the Mt. Ao were from the Pb emissions from

Table 3 Contributions of anthropogenic Pb in the soils, litter, and mosses of the Mt. Ao with altitude

			Altitude (m a.s.l.)										
			1260	1530	1720	1920	2140	2410	2470	2770	3010	3150	Total
Percentage (%)	O-horizon	Range	48.6-52.6	--	54.4-57.0	--	56.1-83.0	44.5-69.7	57.3-75.2	68.9-72.6	62.2-64.4	61.6-70.6	44.5-83.0
		Mean	50.9	--	55.8	--	69.1	56.9	65.0	70.8	63.3	65.1	59.5
	A-horizon	Range	28.7-46.0	31.2-65.2	30.0-64.0	36.3-36.8	69.4-83.1	48.9-60.3	36.2-75.6	44.3-60.2	41.0-57.7	29.7-36.0	28.7-83.1
		Mean	37.6	49.0	45.5	36.5	74.5	56.3	57.6	53.8	49.0	32.2	48.9
	Litter		92.7	83.8	70.3	69.4	78.3	63.9	75.6	85.2	82.2	76.5	77.8
	Moss		45.1	83.2	87.2	81.7	75.9	61.5	--	74.8	82.8	75.3	74.2
Mean concentrations (mg/kg)	O-horizon		13.8	--	15.5	--	25.0	22.1	34.1	28.2	34.9	41.3	26.9
	A-horizon		10.7	11.5	4.4	10.4	37.7	19.7	30.1	20.0	22.2	10.6	17.7
	Litter		1.91	2.96	2.58	5.66	17.7	2.18	7.34	8.16	7.36	3.32	5.92
	Moss		5.2	17.2	15.4	35.1	12.6	27.5	--	35.8	22.0	19.4	21.1

northwestern and southeastern regions in recent years.

The concentrations of anthropogenic Pb in the various environmental archives of the Mt. Ao were also calculated, which showed the order: O horizon > moss > A horizon > litter (Table 3). Along the altitude, the percentage of anthropogenic Pb showed a similar trend with its concentrations in the O and A horizons, whereas this was not the case for the litter and mosses (Table 3). This, on the one hand, was still related to the type of the environmental samples that recorded the different periods of Pb contamination. The soils revealed the long-term contamination trend of Pb with altitude on the Mt. Ao, whereas the litter and mosses showed the recent distribution of anthropogenic Pb. On the other hand, it suggested that the concentrations of anthropogenic Pb in the environmental materials were better than its percentage to indicate the effects of human activity on its distribution and accumulation processes in the mountain ecosystem. In addition, the higher concentrations of anthropogenic Pb at the middle and high altitudes of the Mt. Ao (Table 3) further confirmed that the atmospheric sourced Pb could be deposited in the alpine ecosystem by long-range atmospheric transport, since there was no direct human activity around the Mt. Ao.

4 Conclusions

The enriched Pb on the Mt. Ao was markedly distributed in the surface soils (O and A horizons), litter and mosses. The Pb accumulation in O horizons increased significantly with altitude, while in A horizons it existed at the middle altitude. The enrichment of Pb in the litter and mosses also increased with altitude. The wet deposition, vegetation effects (e.g., uptake, interception, and returning), soil physicochemical properties and human activity modulated the altitudinal distribution of Pb on the Mt. Ao. Based on the Pb isotopic ratios, the Pb on the Mt. Ao was mainly from Chinese coal combustion, mining and smelting. The anthropogenic emissions' Pb from southwestern, southeastern and northwestern regions contributed to the Pb accumulation on the Mt. Ao. The percentage of anthropogenic Pb was 59.5%, 48.9%, 77.8%, 74.2% in the O and A horizons, litter and dominant mosses, respectively, and its corresponding concentrations were 26.9, 17.7, 5.92, 21.2 mg/kg, respectively. The high accumulation of anthropogenic Pb at the middle and high altitudes of the Mt. Ao indicated the tans-boundary atmospheric Pb contamination in the remote alpine ecosystem.

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