

# Distribution, source analysis, and ecological risk assessment of polycyclic aromatic hydrocarbons in the typical topsoil of the Issyk-Kul Lake Basin

Wen Liu · Long Ma  · Jilili Abuduwaili · Yaoming Li

Received: 14 April 2017 / Accepted: 28 June 2017 / Published online: 17 July 2017  
© Springer International Publishing AG 2017

**Abstract** The concentration, distribution, compositional characteristics, and pollution sources of 16 polycyclic aromatic hydrocarbons (PAHs) in the topsoil of Issyk-Kul Lake Basin were studied, and their ecological risks were evaluated in this paper. The total concentration of the 16 PAHs was 68.58–475.95 ng g<sup>-1</sup>, with an average of 134.45 ng g<sup>-1</sup>. Four-ring PAHs accounted for 43.2% of the total PAHs, two- and three-ring PAHs accounted for 39.4%, and five- and six-ring PAHs accounted for 15.8%. The total concentration of the seven carcinogenic PAHs was 7.66–76.04 ng g<sup>-1</sup>, with an average of 30.97 ng g<sup>-1</sup>. An analysis of the PAH sources through diagnostic ratio analysis and principal component analysis was carried out. The results showed that the regional soil PAHs were mainly derived from coal, wood, and grass combustion, while traffic and regional industry also had small contributions to the PAHs. The pollution-free samples accounted for 75% and the slightly polluted samples accounted for 25% based on the total concentration of the 16 PAHs. An ecological risk assessment showed that 26.7% of Ac and 3.3% of Pyr and DahA might occasionally produce ecological risks. The toxicity was calculated on the basis of benzo[a]pyrene, and the toxicity equivalent was between 2.48 and 13.78 ng g<sup>-1</sup> with an average of 6.23 ng g<sup>-1</sup>, which currently does not pose any health risk to human life.

**Keywords** Polycyclic aromatic hydrocarbons (PAHs) · Topsoil · Diagnostic ratio · Principal component analysis · Ecological risk

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds that are fused from two or more benzene rings, and they are persistent organic pollutants that are carcinogenic, teratogenic, and mutagenic (Menzie et al. 1992; Davis et al. 1993). The sources of PAHs in the environment include natural and anthropogenic sources and are mainly anthropogenic, such as human activity-related fossil fuels, industrial plant burning, and coking industries (Edwards 1983). Because PAHs are lipophilic, semi-volatile, and migratory, PAHs are released into various environmental media and are accumulated within the food chain, causing harm to the regional ecological environment and human health (Kelly et al. 2007). Therefore, it is necessary to study the concentration, distribution, and origin of PAHs in different regions and environmental conditions.

In recent years, a wealth of information has been accumulated from the investigation and source analysis of PAHs in multi-environment media such as rivers (Yunker et al. 2002; Shen et al. 2017; An et al. 2016), coastlines (Foster et al. 2015; Li et al. 2016), cities (Banger et al. 2010; Vane et al. 2014; Wang et al. 2013; Jiang et al. 2016), and farmland (Ping et al. 2007; Zhang et al. 2016; Jiang et al. 2011). The Issyk-Kul Lake Basin is located in the Kyrgyz Republic and is

W. Liu · L. Ma (✉) · J. Abuduwaili · Y. Li  
State Key Laboratory of Desert and Oasis Ecology, Xinjiang  
Institute of Ecology and Geography, Chinese Academy of  
Sciences, Urumqi 830011, People's Republic of China  
e-mail: malong@ms.xjb.ac.cn

an important agricultural area. It is also one of the most important scenic spots in Central Asia (ADB 2009). With regard to the socio-economic development of the region, the emission of pollution caused by industry, tourism, and residential daily activities is bound to affect the level and distribution of PAHs in the region. In addition, relative to other environmental media, soils bear most of the PAH environmental load, and the majority of PAHs are absorbed by humans through soil pathways (Edwards 1983; Cachada et al. 2016). Therefore, it is of great practical significance to carry out research into regional soil PAH levels. However, the topsoil PAH pollution in this area has not been previously reported.

In this paper, the concentration and composition of 16 PAH compounds under the priority control of the US Department of Environmental Protection (US EPA) in the 30-point topsoil of the Issyk-Kul Lake area were first investigated, after which the PAH pollution sources were determined through diagnostic ratios and principal component analysis (PCA). The potential ecological risks of the regional PAHs were evaluated, and the toxicity of PAHs in the soil was evaluated using the benzo[a]pyrene (BaP) toxicity equivalent method. Through this study, basic data can be provided for regional environmental protection purposes, and the research results will be useful for the control and regional ecological environmental planning of PAHs.

## Materials and methods

### Sampling

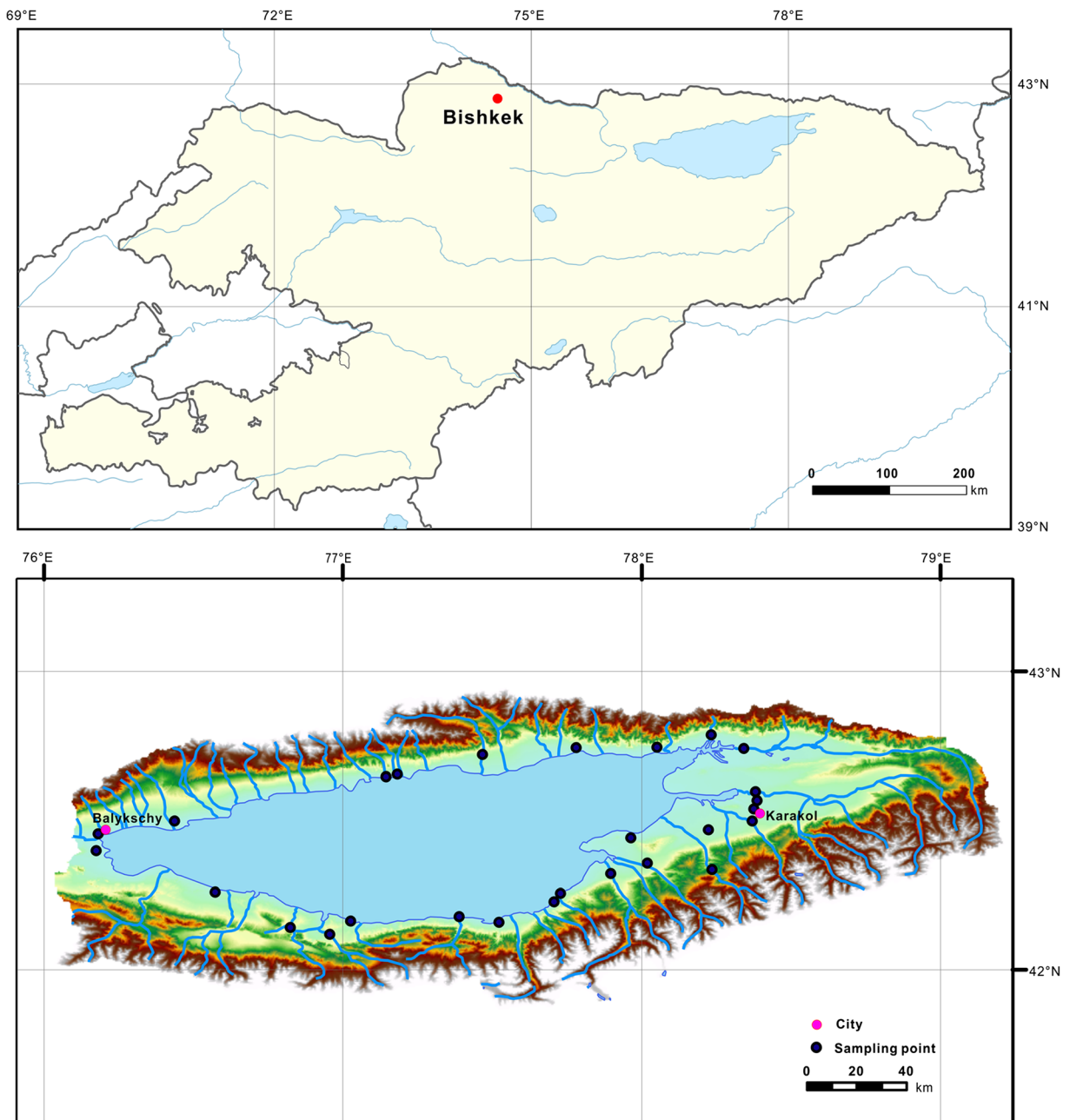
The soil within the Issyk-Kul Lake Basin is primarily classified as arid soil in the west and semi-arid soil in the middle and the east, and it is mainly composed of loam, clayey loam, and sandy clay loam (Kulenbekov and Merkel 2012). The land type of the upstream region is largely wooded tundra while grassland, irrigated land, shrub land, dry land, and settlements typify the downstream surface cover (Kulenbekov and Merkel 2012). There are two main cities around the Issyk-Kul Lake Basin, including Karakol (the capital of the Issyk-Kul oblast) and Balykchy, and the total population amounts to 450,000 within the Issyk-Kul oblast (ADB 2009). A random sampling strategy was adopted to examine the contamination of PAHs in the basin (42.11506° N, 75.81626° E ~ 42.7839° N, 78.39108° E), and a total

of 30 surface soil samples were collected in October 2014 (Fig 1). A clean, stainless steel iron spoon was used for sampling, and GPS was used for positioning. The samples were placed into clean polyethylene bags and taken back for laboratory analysis.

### Experimental analysis

An SPE column was selected as a silica gel column (6 cm<sup>3</sup>, 1 g, 30 μm, Waters Company, Milford). Silica gel and aluminum oxide were extracted, respectively, for 48 h with methanol and methylene chloride. The silica gel (100–200 mesh) was activated under 180 °C for approximately 12 h. The aluminum oxide was activated under 250 °C for approximately 12 h in a muffle. The working standard solution contained the following 16 US EPA priority PAHs: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DahA), benzo(g,h,i)pyrene (BghiP), and indeno(1,2,3-c,d)pyrene (IcdP). The deuterated recovery surrogates consisted of naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene-D12; and the internal standard was hexamethylbenzene. All of the glasswares were soaked with a chromic acid lotion, washed with tap water and deionized water, then dried. The glassware and anhydrous sodium sulfate were solvent-rinsed and heated for 4 h at 450 °C prior to use. All of the organic solvents were HPLC grade and were obtained from Supelco. The anhydrous sodium sulfate was of analytical grade.

The collected samples were freeze-dried, after which any large stones or noticeable organic matter in the soil samples, including leaves, roots, and plant matter, were picked out, and the soil samples were ground into 100 mesh. Accurate 5-g samples were weighed, 6 g of quartz sand was added with 3 g of activated copper powder to remove any sulfur, and the samples were spiked with chemical surrogates (four deuterated PAHs, i.e., naphthalene-d8, acenaphthene-d10, phenanthrene-d10, and chrysene-d12) to calculate the recovery rates. The mixtures were thoroughly incorporated and placed into an accelerated solvent extraction system (ASE, Dionex 100) for extraction. The extracting agent was methylene chloride, with which the mixtures were statically extracted twice under conditions of 150 °C and 1500 psi



**Fig. 1** Geographical location of Issyk-Kul Lake and the sampling locations in the basin

with an extraction time of 6 min each. After extraction, the whole eluting system was washed with methylene chloride, the extract was all collected, dried with anhydrous sodium sulfate to remove moisture, and then evaporated with a rotary evaporation apparatus (Buchi R-200, Flawil, Switzerland) until nearly dry, after which 5 mL of the solvent *n*-hexane was added for replacement.

The silica column (with a silica gel/aluminum oxide ratio of 2:1) was activated before sample extraction, successively leached with 10 mL of methylene chloride and 10 mL of *n*-hexane, and the eluent was rejected. The extract was subsequently applied to the silica gel glass column for cleanup and fractionation. First, the column was leached with 15 mL of hexane to remove compounds such as *n*-alkanes, after which the column was

eluted with a 70 mL mixture of *n*-hexane (20 mL) and methylene chloride (50 mL), and the components were collected. A rotary was used to evaporate the components into a small volume, which were then redissolved in 5 mL of acetonitrile, blown into 0.5 mL under a gentle N<sub>2</sub> stream, and finally stored at a temperature of -20 °C for instrumental analysis. Known quantities of the internal standard were added to the sample prior to instrumental analysis.

The PAH contents were analyzed with an Agilent 1200 high-performance liquid chromatograph (HPLC) that was equipped with a diode array ultraviolet detector (DAD) and coupled with a serial fluorescence detector (FLD). The separation column was a WATERS PAH C18 (4.6 mm × 250 mm, size: 5 μm, Supelco, USA), the column temperature was 25 °C, the pump flow rate was 1 mL min<sup>-1</sup>, and the injected volume was 20 μL. The gradient elution conditions were as follows: 0 ~ 15 min, 60% acetonitrile and 40% pure water; 15 ~ 30 min, 60% ~ 100% acetonitrile; 30 ~ 40 min, 100% acetonitrile; and 40 ~ 40.1 min, 100% ~ 60% acetonitrile.

Based on the peak sequences of the standard substance and the retention time, the PAH components were qualitatively identified. Six different linear levels of standard PAHs were used to establish the standard curves, and the correlation coefficients between the concentration and the peak area reached higher than 0.999 for each compound. Individual PAH concentrations in the sample were obtained through a comparison of the peak area with the standard curves. Blanks, duplicate samples, matrix-spiked blanks, and internal standard additions were examined for quality assurance during the analysis. The recoveries of the surrogate standard addition were 75–100%, and the target compounds were not detected in the blank experiment. The procedure was also checked for recovery efficiencies by analyzing uncontaminated samples spiked with PAH standards with an average recovery of 73–116%. The limits of detection (LD) of PAHs were based on a signal-to-noise ratio (S/N) of 3:1 and ranged from 0.4–1.2 ng g<sup>-1</sup>, while levels observed at less than the LD were expressed as not detected (nd). The data obtained from the experiment were corrected by the recovery rate in this study.

The soil total organic carbon (TOC) content is an important factor in controlling the soil adsorption of PAHs (Wilcke and Amelung 2000), and thus, the TOC was also assessed in the soil samples. The freeze-dried

samples were ground into 100 mesh, after which 0.3 ~ 0.5 g of the subsamples was weighed and the potassium dichromate volumetric method-external heating method was used to determine the organic matter content (Walkley and Black 1934).

#### Data treatment and statistical analysis

An IBM SPSS 20.0 (SPSS Inc., USA) was employed for the data treatment and multivariate statistical analysis. Kolmogorov–Smirnov (K–S) tests were used to determine the normality of the data. Spearman correlations were used to evaluate the relationships between the TOC and individual and total PAH concentrations, which were considered statistically significant if the *p* value was less than 0.05. PCA was performed with a varimax rotation to identify the potential sources of the PAHs. Kaiser–Meyer–Olkin (KMO) and Bartlett tests were used to evaluate the validity of the PCA. The source diagnostic indices were calculated from the PAH concentration ratios.

The health risk assessment of PAHs is based on the concentration of BaP, which poses the highest risk of cancer (Tsai et al. 2004; Halek et al. 2008). The toxicity of the 16 PAHs (TEQ<sub>16</sub>) in the study area was evaluated using BaP as a reference substance, and the toxicity equivalent factor (TEF) was introduced (Nadal et al. 2004). The calculation formula is given as follows:

$$\text{TEQ}_{16} = \sum C_i \times \text{TEF}_i$$

where  $C_i$  is the concentration of each of the 16 PAHs ( $i = 1-16$ ) (ng g<sup>-1</sup>), and  $\text{TEF}_i$  represents the relative concentration of a single PAH relative to that of BaP (Nisbet and LaGoy 1992).

## Results and discussion

### Compositional characteristics

The concentrations of the 16 collective PAHs ( $\sum_{16}\text{PAHs}$ ), of the individual PAH, and the total concentration of the seven carcinogenic components ( $\sum_7\text{PAHs}$ , including BaA, Chr, BbF, BkF, BaP, IP, and DBA) are presented in Table 1. The  $\sum_{16}\text{PAHs}$  concentration was 68.58–475.95 ng g<sup>-1</sup> with an average of 134.45 ng g<sup>-1</sup>. The  $\sum_7\text{PAHs}$  concentration was 7.66–76.04 ng g<sup>-1</sup> with an average of 30.97 ng g<sup>-1</sup>. Overall,

**Table 1** Concentrations (g ng<sup>-1</sup>) of 16 individual PAH in the typical topsoil of the Issyk-Kul Lake Basin

	Concentration	M.conc.	A.conc.	SD	CV	Perc. (%)	A.perc. (%)
Nap	3.31 ~ 31.59	10.20	12.34	6.37	51.67	2.60 ~ 25.67	9.97
Ac	1.51 ~ 9.99	4.18	4.67	2.58	55.16	1.43 ~ 7.52	3.60
Ace	1.40 ~ 2.69	1.75	1.83	0.26	13.95	0.39 ~ 3.01	1.60
Flu	2.04 ~ 9.4	4.12	4.48	1.60	35.61	1.25 ~ 5.90	3.73
Phe	13.44 ~ 53.04	22.98	24.90	9.78	39.29	8.08 ~ 36.58	20.12
Ant	2.49 ~ 22.73	3.71	4.73	3.80	80.39	1.82 ~ 9.20	3.62
Fl	nd ~ 4.31	.55	0.78	0.89	114.18	0.00 ~ 1.33	0.55
Pyr	nd ~ 306.16	30.26	47.00	55.73	118.58	15.39 ~ 64.33	32.28
BaA	nd ~ 41.72	6.12	9.04	9.31	103.01	0.00 ~ 32.11	7.13
Chr	nd ~ 3.56	1.11	1.25	.64	50.86	0.00 ~ 1.68	0.99
BbF	nd ~ 15.76	3.29	4.18	2.98	71.34	0.00 ~ 5.47	3.12
BkF	0.74 ~ 3.76	1.05	1.22	0.61	49.79	0.64 ~ 1.52	0.95
BaP	nd ~ 2.97	0.91	0.98	0.44	44.37	0.00 ~ 1.31	0.79
DahA	0.94 ~ 8.65	1.44	2.14	1.69	79.04	0.53 ~ 7.56	2.04
BghiP	nd ~ 11.23	2.00	2.76	2.56	92.91	0.00 ~ 4.32	2.03
IcdP	2.19 ~ 39.26	8.71	12.16	10.50	86.36	1.91 ~ 31.54	9.92
∑ <sub>(2-3rings)</sub> PAHs	28.33 ~ 125.26	45.66	52.95	20.90	39.48	16.5 ~ 41.39	41.39
∑ <sub>(4rings)</sub> PAHs	16.21 ~ 327.41	40.92	58.07	59.76	102.92	16.96 ~ 38.99	38.99
∑ <sub>(5-6rings)</sub> PAHs	6.74 ~ 66.55	15.56	21.30	13.91	65.32	9.67 ~ 17.72	17.72
∑ <sub>7</sub> PAHs	7.66 ~ 76.04	24.17	30.97	17.26	55.75	10.47 ~ 44.69	22.97
∑ <sub>16</sub> PAHs	68.58 ~ 475.95	112.06	134.45	81.31	60.48	–	–

*M.Conc.* medium concentration, *A.Conc.* average concentration, *SD* standard deviation, *nd* not detected, *CV* variable coefficient, *Perc. (%)* means the individual PAHs compare with ∑<sub>16</sub>PAHs of the soil sample, *A.Perc (%)* means the average value of *Perc (%)*

the collective concentration of the four-ring PAHs was high and accounted for 43.2% of the total, followed by the combined concentration of the two- and three-ring PAHs at 23%. The five- and six-ring PAHs had the minimum proportion with a total of 15.8%. The average concentrations of the individual PAH were sorted in descending order, which was Pyr > Phe > Nap > IcdP > BaA > Ant > Ac > Flu > BbF > BghiP > DahA > Ace > Chr > BkF > BaP > Fl. The main individual PAH pollutants were Pyr and Phe, which accounted for 34.96 and 18.52% of the ∑<sub>16</sub>PAHs concentration, respectively. The coefficient of variation indicated that the ∑<sub>16</sub>PAHs concentration and the individual PAH concentrations were highly variable. The soil TOC was between 39.78 and 276.08 g kg<sup>-1</sup> with an average of 77.99 g kg<sup>-1</sup>. A single-sample K-S normal distribution test showed that the TOC, ∑<sub>16</sub>PAHs, and individual PAH concentrations did not conform to a normal distribution.

A PAH is a type of hydrophobic organic compound. Because of the strong adsorption capacity of soil organic

matter onto PAHs, it is generally considered that there is a positive correlation between the soil organic carbon content and the concentrations of PAHs. The results of Spearman correlation analysis showed that there was no correlation among the TOC, ∑<sub>16</sub>PAHs, and individual PAH concentrations, which was probably because the local topsoil organic matter and PAHs did not achieve equilibrium adsorption, and because the concentrations of PAHs are affected more by the source intensity or other environmental factors (e.g., soil pH, soil particle size, black carbon content, soil disturbance, and leaching effects) (Wang et al. 2013, Jiang et al. 2011). The specific factors in this location need to be further studied and confirmed.

According to a classification based on the value of ∑<sub>16</sub>PAHs proposed by Maliszewska-Kordybach (1996), 75% of the samples in this study were classified as not contaminated and 25% were classified as weakly contaminated. The topsoil pollution level of PAHs in this study area was higher than that of the Bosten Lake Basin in Xinjiang, China (where ∑<sub>16</sub>PAHs ranged from 6.6 to

128.2 ng g<sup>-1</sup> with an average of 57.8 ng g<sup>-1</sup>) (Shen et al. 2016), which is lower than that of the Yangtze River Delta farming soil in China (where  $\Sigma_{15}$ PAHs ranged from 8.6 to 3881  $\mu\text{g kg}^{-1}$  with an average of 397  $\mu\text{g kg}^{-1}$ ) (Ping et al. 2007) and is also lower than that of densely populated urban areas, such as Shanghai (where  $\Sigma_{16}$ PAHs ranged from 83.3 to 7220  $\mu\text{g kg}^{-1}$  with a mean value of 1970  $\mu\text{g kg}^{-1}$ ) (Wang et al. 2013), Shenzhen (with an average  $\Sigma_{16}$ PAHs of 479.4 ng g<sup>-1</sup>) (Zhang et al. 2016), and Lanzhou (where  $\Sigma_{16}$ PAHs ranged from 82.2 to 10,900  $\mu\text{g kg}^{-1}$  with a mean value of 2360  $\mu\text{g kg}^{-1}$ ) (Jiang et al. 2016) in China, Miami in the USA (where  $\Sigma_{16}$ PAHs ranged from 1508 to 2364  $\mu\text{g kg}^{-1}$  with a mean value of 1869  $\mu\text{g kg}^{-1}$ ) (Banger et al. 2010), and London in the UK (where  $\Sigma_{16}$ PAHs ranged from 4 to 67 mg kg<sup>-1</sup>) (Vane et al. 2014). This comparative analysis showed that PAHs in the study area were affected by regional human activities, but the overall pollution is low.

#### Diagnostic ratios for source analysis

The diagnostic ratio method is widely used in the determination of PAH pollution sources, of which LMW/HMW, Ant/(Ant+Phe), Flu/(Flu+Pyr), BaA/(BaA+Chr), and IcdP/(IcdP+BghiP) are the most commonly used (Yunker et al. 2002; Tobiszewski and Namieśnik 2012). At present, the double ratio method is commonly used for the source analysis and determination of PAHs (Tobiszewski and Namieśnik 2012; Jiang et al. 2016; An et al. 2016).

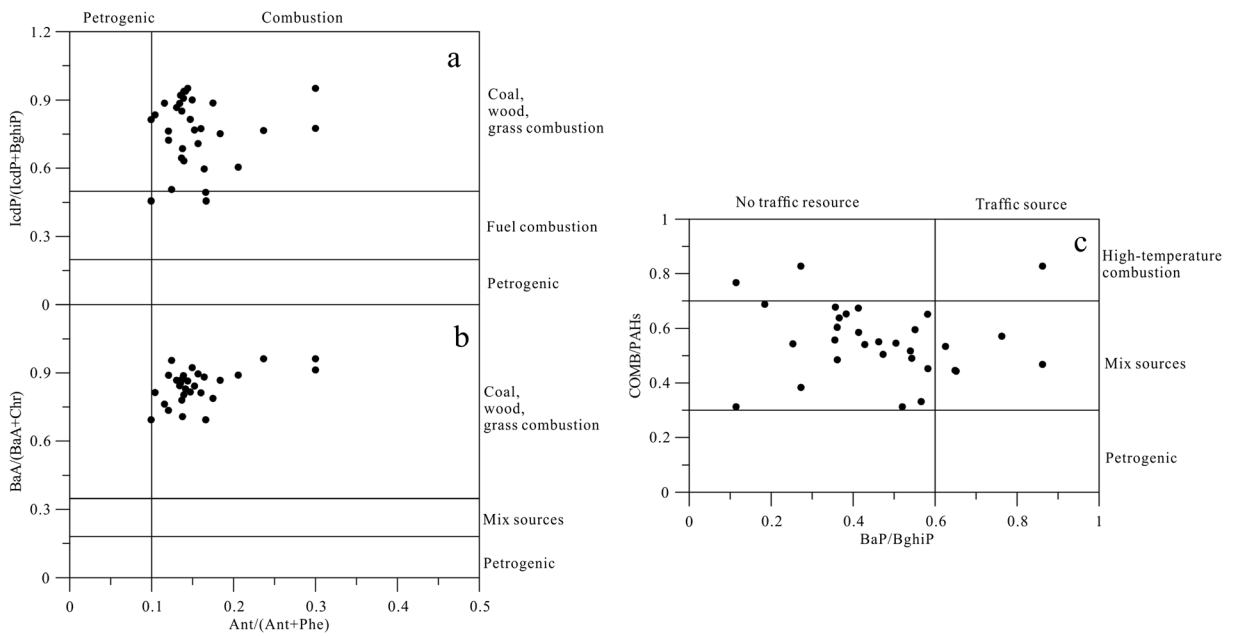
Through the diagnostic ratios of PAHs in the soil of the Issyk-Kul Lake area, including those of BaA/(BaA+Chr) and Ant/(Ant+Phe), IcdP/(IcdP+BghiP) and Ant/(Ant+Phe), and BaP/BghiP and COMB/ $\Sigma_{16}$ PAHs, the sources of the PAHs were analyzed (Fig. 2). According to the summary analyses of previous studies (Yunker et al. 2002; Tobiszewski and Namieśnik 2012), a BaA/(BaA+Chr) ratio of <0.2 indicates a petrogenic source, >0.35 indicates a combustion source, and a ratio between the two represents a mixed source. An Ant/(Ant+Phe) ratio of <0.1 usually indicates a petrogenic source, whereas >0.1 indicates a source of combustion. An IcdP/(IcdP+BghiP) of <0.2 indicates a petrogenic source, whereas >0.5 indicates a source of grass, firewood, or coal combustion, and a ratio between the two indicates a source of fossil fuel combustion. The ratios of Ant/(Ant+Phe) in the study samples were in the range of 0.1 to 0.3, the ratios of BaA/(BaA+Chr) were from

0.69 to 0.96, and the ratios of IcdP/(IcdP+BghiP) were from 0.46 to 0.95. As shown in Fig. 2a and b, the diagnostic ratio plots of BaA/(BaA+Chr) and Ant/(Ant+Phe) and of IcdP/(IcdP+BghiP) and Ant/(Ant+Phe) indicated that the main sources of the PAHs were coal, wood, and grass combustion. A COMB/ $\Sigma_{16}$ PAHs ratio of <0.3 indicates a petrogenic source, whereas a ratio between 0.3 and 0.7 indicates a mixed source, and ratio of >0.7 indicates a high-temperature combustion source (Ravindra et al. 2008). Conversely, BaP/BghiP >0.6 indicates fuel combustion, whereas <0.6 indicates non-traffic sources (Katsoyiannis et al. 2007). In the BaP/BghiP and COMB/ $\Sigma_{16}$ PAHs diagnostic ratio plots (Fig. 2c), >80% of the points fell within the range of non-traffic sources to mixed combustion sources, whereas <20% were from traffic sources. This indicates that the sources of PAHs in the regional topsoil mainly originated from the mixed combustion of grass, wood, and coal, while traffic sources also contributed a small amount.

#### Principal component analysis

To further investigate the possible sources of PAH pollution in the study area, PCA was also performed on the data. A KMO value of >0.5 and a significant Bartlett test (<0.001) indicates that the results of the PCA analysis are effective. The KMO of the samples in the study area was 0.656 and the Bartlett significance test was 0, and thus, the PCA analysis was valid. The PCA results provided four principal components, which can explain 77% of the variances. The component matrix is shown in Table 2.

The first principal component variance percentage was 45.9%. The component matrix showed that BbF, BkF, BaP, and BghiP of five- and six-ring PAHs and Phe, Fl, Pyr, and Chr of three- and four-ring PAHs had higher contribution rates. Moreover, the high molecular weight four- to six-ring PAHs were mainly derived from high-temperature pyrolysis (Harrison et al. 1996), and the higher load components were mostly characteristic compounds of coal combustion at high temperatures (Simcik et al. 1999; Harrison et al. 1996). State agriculture is the backbone of the national economy, accounting for 30–40% of the GDP (ADB 2009). Other than the mining industry, however, industry has barely developed in the study region, so industrial input is not the main source of PAHs in the regional topsoil. Coal is currently the main good that is transported via the



**Fig. 2** (a) Diagnostic ratio plots for BaA/(BaA+Chr) and Ant/(Ant+Phe) in the topsoil samples; (b) diagnostic ratio plots for IcdP/(IcdP+BghiP) and Ant/(Ant+Phe) in the topsoil samples; (c) diagnostic ratio plots for BaP/BghiP and COMB/PAHs in the topsoil samples

Issyk-Kul Lake (ADB 2009). Therefore, coal that is used for heating is the main source of PAHs in the topsoil of the area. The first principal component of PAHs in the PCA was interpreted as the high-temperature combustion of coal.

The second principal component variance percentage was 15.9%, and the component matrix showed that the loads of Nap, Ac, Ace, Flu, Phe, and Ant of two- and three-ring PAHs were high. The low molecular weight two- and three-ring PAHs were derived mainly from

**Table 2** Component matrix of a principal component analysis of PAHs in the topsoil samples of the Issyk-Kul Lake Basin

	Component 1	Component 2	Component 3	Component 4
Nap	0.578	0.555	0.142	0.094
Ac	0.653	0.505	0.159	-0.231
Ace	0.274	0.57	-0.398	0.525
Flu	0.548	0.62	-0.256	0.111
Phe	0.717	0.506	-0.056	-0.182
Ant	0.693	0.429	0.192	-0.316
Fl	0.799	-0.129	-0.105	-0.265
Pyr	0.849	-0.437	-0.201	0.038
BaA	0.486	0.023	0.742	0.101
Chr	0.760	-0.1	0.338	0.123
BbF	0.895	-0.328	0.021	0.205
BkF	0.914	-0.284	-0.078	0.106
BaP	0.776	-0.378	-0.246	0.042
DahA	0.065	-0.272	0.447	0.056
BghiP	0.813	-0.393	-0.078	0.228
IcdP	0.375	-0.229	-0.306	-0.592
% of variance	45.9%	15.9%	8.7%	6.5%
Cumulative %	45.9%	61.8%	70.5%	77.0%

low-temperature combustion or petrogenic sources (Harrison et al. 1996; Jenkins et al. 1996). Nap is a common characteristic compound of the incomplete combustion of biomass (Khalili et al. 1995; Simcik et al. 1999), Ac is the characteristic compound of wood burning (Khalili et al. 1995), and Ace, Phe, Ant, and Flu are the characteristic compounds of coal that is not fully burned (Larsen and Baker 2003). Approximately 70% of the state's population lives in rural areas, and they usually use coal, wood, and dry manure as fuel for heating in the winter (ADB 2009). Therefore, the combustion of coal, wood, and dry manure for heating in rural areas is another important source of PAHs in the topsoil. The second principal component in the PCA was interpreted as the medium- and low-temperature combustion of coal, grass, and wood.

The third principal component variance percentage was 8.7%; the loads of BaA and DahA in the component matrix were high. BaA is one of the markers of gasoline fuel combustion (Khalili et al. 1995; Harrison et al. 1996), and DahA is one of the markers of diesel fuel combustion (Simcik et al. 1999; Harrison et al. 1996). The beautiful natural environment attracts millions of tourists each year for sightseeing and drives the development of regional transportation (ADB 2009). Therefore, the combustion of liquid fossil fuels also

contributes to the PAHs in the topsoil of this area. Thus, the third principal component of the PCA in this area was interpreted as traffic sources.

The fourth principal component variance percentage was 6.5%. The Ace load in the component matrix was high, and Ace is a major component of coking (Khalili et al. 1995; Simcik et al. 1999). Coking production is an important part in the development of the modern steel industry. The topsoil PAHs also showed a small amount of input from industrial sources, and thus, the fourth principal component was interpreted as regional industrial development.

The results of the above-mentioned PCA analysis were essentially the same as those of the diagnostic ratio method. Based on the integration of the two analysis results, it can be concluded that the PAHs in the study area were mainly derived from the mixed combustion of coal, wood, and grass. Meanwhile, traffic and industrial development also contributed, albeit in a smaller proportion.

#### Ecological risk assessment

There are two types of commonly used ecological risk assessment criteria: the ecological effects range low (ERL) plus the biological effects range median (ERM)

**Table 3** Ecological risk assessment of PAHs in the topsoil of the Issyk-Kul Lake basin

	Concentration (ng g <sup>-1</sup> )	Criterion (ng g <sup>-1</sup> )				Percentage < ERL (%)	Percentage > TEL (%)	Percentage TEL ~ PEL (%)
		ERL	ERM	TEL	PEL			
Nap	3.31 ~ 31.59	160	2100	34.6	391	100	100	0
Ac	1.51 ~ 9.99	44	640	5.87	128	100	73.3	26.7
Ace	1.40 ~ 2.69	16	500	6.71	88.9	100	100	0
Flu	2.04 ~ 9.4	19	540	21.2	144	100	100	0
Phe	13.44 ~ 53.04	240	1500	86.7	544	100	100	0
Ant	2.49 ~ 22.73	85.3	1100	46.9	245	100	100	0
Fl	nd ~ 4.31	600	5100	113	1494	100	100	0
Pyr	nd ~ 306.16	665	2600	153	1398	100	96.7	3.3
BaA	nd ~ 41.72	261	1600	74.8	693	100	100	0
Chr	nd ~ 3.56	384	2800	108	846	100	100	0
BbF	nd ~ 15.76	320	1800	–	–	100	–	–
BkF	0.74 ~ 3.76	280	1620	–	–	100	–	–
BaP	nd ~ 2.97	430	1600	88.8	763	100	100	0
DahA	0.94 ~ 8.65	63.4	260	6.22	135	100	96.7	3.3
BghiP	nd ~ 11.23	430	1600	–	–	100	–	–
IcdP	2.19 ~ 39.26	–	–	–	–	–	–	–



(Long et al. 1995) and the threshold effects level (TEL) with the predicted effects level (PEL) (Macdonald et al. 1996). A value less than the ERL (or TEL) indicates that the pollutants rarely produce ecological risks. A value between the ERL and ERM (or between the TEL and PEL) indicates that the pollutants occasionally produce ecological risks. When the value is greater than the ERM (or PEL), it indicates that the pollutants often produce ecological risks. The concentrations of the 16 individual PAHs at the sampling points were all lower than the ERL value (Table 3). The Nap and BaP values at the sampling points were lower than the TEL (Table 3). The Ac values were lower than the TEL value and accounted for 73.3% of the total, and those between the TEL and PEL accounted for 26.7%. The Pyr values that were lower than the TEL value accounted for 96.7%, and those between the TEL and PEL accounted for 3.3%. The DahA values that were lower than the TEL value accounted for 96.7%, and those between the TEL and PEL accounted for 3.3%, as shown in Table 3. It can be seen that 26.7% of the Ac points and 3.3% of the Pyr and DahA points occasionally produce ecological risks.

### Toxicity evaluation

The results of calculations reveal that the TEQ<sub>16</sub> value in this region was between 2.48 and 13.78 ng g<sup>-1</sup> with an average value of 6.23 ng g<sup>-1</sup>, which is lower than that of the Dutch agricultural PAH pollution threshold of 33 ng g<sup>-1</sup>, and thus, it currently represents no health risk. The contributions of the 16 individual PAHs to the total toxic equivalent were as follows: DahA (35.02%) > IcdP (20.15%) > BaP (18.25%) > BaA (13.87%) > BbF (7.16%) > BkF (2.27%) > Ant (0.86%) > Pyr (0.78%) > BghiP (0.48%) > Phe (0.47%) > Nap (0.24%) > Chr (0.22%) > Flu (0.09%) = Ac > Ace (0.04%) > Fl (0.01%). PCA showed that DahA and BaA originated mainly from traffic discharge, and IcdP and BaP were sourced mainly from coal and wood combustion. This suggests that the toxicity of PAHs in this area originated mainly from traffic fuel combustion, followed by coal, wood, and other biomass.

### Conclusions

PAHs in soil samples from the Issyk-Kul Lake Basin were studied in conjunction with the total organic

carbon (TOC) for the first time. The  $\Sigma_{16}$ PAHs concentration in the topsoil of the Issyk-Kul Lake area was 68.58–475.95 ng g<sup>-1</sup>, for which the average value was 134.45 ng g<sup>-1</sup>, and they showed no correlation with the TOC. Pyr and Phe were the two main individual PAHs. The topsoil PAHs were mainly derived from the mixed low- to high-temperature combustion of coal, wood, grass, and other biomass. Traffic and industrial input only had small contributions to the regional PAHs. Compared to the pollution level proposed by Maliszewska-Kordybach in 1996, uncontaminated soil samples accounted for 75% and slightly contaminated soil samples accounted for 25% of the studied soils. An ecological risk assessment showed that 26.7% of Ac and 3.3% of Pyr and DahA in the sampling points had potential ecological risks, and a toxicity assessment based on BaP indicated that the topsoil PAHs in the region currently pose no health risks.

**Acknowledgments** This study was supported by the Sci-Tech Talents Cultivation Project of Xinjiang Uygur Autonomous Region of China (QN2015YX031), the West Light Foundation of the Chinese Academy of Sciences (2015-XBQN-B-18), and the National Natural Science Foundation of China (41501221, 41671200). The authors gratefully acknowledge the support of the Youth Innovation Promotion Association CAS and the High-level Talents Introduction Project in Xinjiang Uygur Autonomous Region, China (2015).

### References

- ADB (2009). Issyk-Kul sustainable development project, volume 5: strategic environmental management plan. <https://www.adb.org/sites/default/files/project-document/62284/41548-kgz-dpta-v5-semp.pdf>.
- An, N., Liu, S., Yin, Y., Cheng, F., Dong, S., & Wu, X. (2016). Spatial distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in the reservoir sediments after impoundment of Manwan Dam in the middle of Lancang River, China. *Ecotoxicology*, 25(6), 1072–1081.
- Banger, K., Toor, G. S., Chirenje, T., & Ma, L. (2010). Polycyclic aromatic hydrocarbons in urban soils of different land uses in Miami, Florida. *Soil and Sediment Contamination*, 19(2), 231–243.
- Cachada, A., da Silva, E. F., Duarte, A. C., & Pereira, R. (2016). Risk assessment of urban soils contamination: The particular case of polycyclic aromatic hydrocarbons. *Science of the Total Environment*, 551–552, 271–284.
- Davis, D. L., Bradlow, H. L., Wolff, M., Woodruff, T., Hoel, D. G., & Anton-Culver, H. (1993). Medical hypothesis: xenoestrogens as preventable causes of breast cancer. *Environmental Health Perspectives*, 101(5), 372–377.

- Edwards, N. T. (1983). Polycyclic aromatic hydrocarbons (PAH's) in the terrestrial environment—a review. *Journal of Environmental Quality*, 12(4), 427–441.
- Foster, K. L., Stern, G. A., Carrie, J., Bailey, J. N. L., Outridge, P. M., Sanei, H., & Macdonald, R. W. (2015). Spatial, temporal, and source variations of hydrocarbons in marine sediments from Baffin Bay, Eastern Canadian Arctic. *Science of the Total Environment*, 506–507, 430–443.
- Halek, F., Nabi, G., & Kavousi, A. (2008). Polycyclic aromatic hydrocarbons study and toxic equivalency factor (TEFs) in Tehran, IRAN. *Environmental Monitoring and Assessment*, 143(1), 303–311.
- Harrison, R. M., Smith, D. J. T., & Luhana, L. (1996). Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. *Environmental Science & Technology*, 30(3), 825–832.
- Jenkins, B. M., Jones, A. D., Turn, S. Q., & Williams, R. B. (1996). Emission factors for polycyclic aromatic hydrocarbons from biomass burning. *Environmental Science & Technology*, 30(8), 2462–2469.
- Jiang, Y., Wang, X., Wu, M., Sheng, G., & Fu, J. (2011). Contamination, source identification, and risk assessment of polycyclic aromatic hydrocarbons in agricultural soil of Shanghai, China. *Environmental Monitoring and Assessment*, 183(1), 139–150.
- Jiang, Y., Yves, U. J., Sun, H., Hu, X., Zhan, H., & Wu, Y. (2016). Distribution, compositional pattern and sources of polycyclic aromatic hydrocarbons in urban soils of an industrial city, Lanzhou, China. *Ecotoxicology and Environmental Safety*, 126, 154–162.
- Katsoyiannis, A., Terzi, E., & Cai, Q. Y. (2007). On the use of PAH molecular diagnostic ratios in sewage sludge for the understanding of the PAH sources. Is this use appropriate? *Chemosphere*, 69(8), 1337–1339.
- Kelly, B. C., Ikononou, M. G., Blair, J. D., Morin, A. E., & Gobas, F. A. (2007). Food web-specific biomagnification of persistent organic pollutants. *Science*, 317(5835), 236–239.
- Khalili, N. R., Scheff, P. A., & Holsen, T. M. (1995). PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions. *Atmospheric Environment*, 29(4), 533–542.
- Kulenbekov, Z., & Merkel, B. J. (2012). Investigation of the natural uranium content in the Issyk-Kul Lake, Kyrgyzstan. *FOG-Freiberg Online Geoscience*, 33,3–45.
- Larsen, R. K., & Baker, J. E. (2003). Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. *Environmental Science & Technology*, 37(9), 1873–1881.
- Li, X., Hou, L., Li, Y., Liu, M., Lin, X., & Cheng, L. (2016). Polycyclic aromatic hydrocarbons and black carbon in intertidal sediments of China coastal zones: concentration, ecological risk, source and their relationship. *Science of the Total Environment*, 566–567, 1387–1397.
- Long, E. R., Macdonald, D. D., Smith, S. L., & Calder, F. D. (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management*, 19(1), 81–97.
- Macdonald, D. D., Carr, R. S., Calder, F. D., Long, E. R., & Ingersoll, C. G. (1996). Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology*, 5(4), 253–278.
- Maliszewska-Kordybach, B. (1996). Polycyclic aromatic hydrocarbons in agricultural soils in Poland: preliminary proposals for criteria to evaluate the level of soil contamination. *Applied Geochemistry*, 11(1–2), 121–127.
- Menzie, C. A., Potocki, B. B., & Santodonato, J. (1992). Exposure to carcinogenic PAHs in the environment. *Environmental Science & Technology*, 26(7), 1278–1284.
- Nadal, M., Schuhmacher, M., & Domingo, J. L. (2004). Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. *Environmental Pollution*, 132(1), 1–11.
- Nisbet, I. C., & LaGoy, P. K. (1992). Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regulatory Toxicology and Pharmacology*, 16(3), 290–300.
- Ping, L., Luo, Y., Zhang, H., Li, Q., & Wu, L. (2007). Distribution of polycyclic aromatic hydrocarbons in thirty typical soil profiles in the Yangtze River Delta region, East China. *Environmental Pollution*, 147(2), 358–365.
- Ravindra, K., Sokhi, R., & Van Grieken, R. (2008). Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmospheric Environment*, 42(13), 2895–2921.
- Shen, B., Wu, J., Zhao, Z., & Ma, L. (2016). Residue and distribution characteristics of organochlorine pesticides and polycyclic aromatic hydrocarbons in different environmental components of the Kaidu River Catchment, Xinjiang. *Bulletin of Mineralogy, Petrology and Geochemistry*, 35(4), 646–652 (in Chinese).
- Shen, B., Wu, J., & Zhao, Z. (2017). Organochlorine pesticides and polycyclic aromatic hydrocarbons in water and sediment of the Bosten Lake, Northwest China. *Journal of Arid Land*, 9(2), 287–298.
- Simcik, M. F., Eisenreich, S. J., & Liou, P. J. (1999). Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmospheric Environment*, 33(30), 5071–5079.
- Tobiszewski, M., & Namieśnik, J. (2012). PAH diagnostic ratios for the identification of pollution emission sources. *Environmental Pollution*, 162, 110–119.
- Tsai, P. J., Shih, T. S., Chen, H. L., Lee, W. J., Lai, C. H., & Liou, S. H. (2004). Assessing and predicting the exposures of polycyclic aromatic hydrocarbons (PAHs) and their carcinogenic potencies from vehicle engine exhausts to highway toll station workers. *Atmospheric Environment*, 38(2), 333–343.
- Vane, C. H., Kim, A. W., Beriro, D. J., Cave, M. R., Knights, K., Moss-Hayes, V., & Nathanail, P. C. (2014). Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in urban soils of Greater London, UK. *Applied Geochemistry*, 51, 303–314.
- Walkley, A., & Black, I. A. (1934). An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Science*, 37(1), 29–38.
- Wang, X., Miao, Y., Zhang, Y., Li, Y., Wu, M., & Yu, G. (2013). Polycyclic aromatic hydrocarbons (PAHs) in urban soils of the megacity Shanghai: occurrence, source apportionment and potential human health risk. *Science of the Total Environment*, 447, 80–89.
- Wilcke, W., & Amelung, W. (2000). Persistent organic pollutants in native grassland soils along a climosequence in North America. *Soil Science Society of America Journal*, 64, 2140–2148.

- Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., & Sylvestre, S. (2002). PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry*, 33(4), 489–515.
- Zhang, D., Wang, J., & Zeng, H. (2016). Soil polycyclic aromatic hydrocarbons across urban density zones in Shenzhen, China: occurrences, source apportionments, and spatial risk assessment. *Pedosphere*, 26(5), 676–686.