Concentrations, sources and potential ecological risks of polycyclic aromatic hydrocarbons in soils from Tajikistan

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Abstract: The concentrations, spatial distributions, sources and potential ecological risks of polycyclic aromatic hydrocarbons (PAHs) in mountain soils from Tajikistan were investigated. PAHs were detected with concentration ranging from 17.15 ng g⁻¹ dw to 257.93 ng g⁻¹ dw due to the major contribution of atmospheric deposition around. Similar compositions of PAHs were observed with three- and four-ring congeners being the predominant components, accounting for 25.4% to 97.1% of total PAHs. The inferences drawn from the principal component analysis-multivariate linear regression (PCA-MLR) analysis were similar to that of isomer pair ratios. The related traffic vehicle emissions, coal combustion and coke oven combustion were classified as the main sources of PAHs in mountain soils of Tajikistan, contributing 61.3%, 29.5% and 9.2% to the total PAHs, respectively. The potential ecological risk assessment indicated no significant toxic effects for human health of PAHs in soils of Tajikistan at present.

Keywords: PAHs; soil; source appointment; risk assessment; Tajikistan.


Biographical notes: Zhonghua Zhao received her PhD in Physical Geography in 2011 from the Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences. She currently worked as an Assistant Professor in the same institute. Her research interest mainly focused on the fate of persistent organic pollutants in environments, and thus the potential ecological effects of such toxic pollutants on the particular biochemical processes in specific ecosystem.

Haiao Zeng graduated from the Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences. He received his PhD in Physical Geography and currently worked at the same institute. His research is mainly about the isotope geochemistry, and then he uses the characters of stable isotope to illustrate the internal chemical processes occurring in the environment.

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1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of stable organic molecules made up of two or more fused aromatic rings. They are produced by high-temperature reactions, such as incomplete combustion and pyrolysis of fossil fuels and other organic materials (Harrison et al., 1996). Owing to their persistent, toxic, mutagenic and carcinogenic characteristics, PAHs form one of the most important classes of environmental pollutants, and 16 priority PAHs are regulated by the United States Environmental Protection Agency (USEPA) (Kannan et al., 2005; Agarwal et al., 2009). Therefore, the distribution and sources of PAHs have attracted the attention of environmental chemists, toxicologists, and regulatory agencies for several decades.

Because of the large capacity of soil for semi-volatile organic compounds, a large portion of PAHs emitted into the atmosphere accumulates in soil via dry and wet deposition. More than 90% of the total PAHs in the environment of UK are estimated to be stored in soil (Wild and Jones, 1995). This high capacity also makes soils suitable for investigating the spatial variability in the atmospheric deposition of PAHs.

High mountain soils can act as a convergence zone for PAHs (Choi et al., 2009). Several studies have observed the enrichment of PAHs in surface soils of different mountain regions such as in north (Usenko et al., 2007), Central and South America (Barra et al., 2005; Daly et al., 2007), Asia (Liu et al., 2005; Wang et al., 2007), Africa (Ribes et al., 2003b), and Europe (Grimalt et al., 2004; Quiroz et al., 2011). Levels of PAHs were reported in forest soils to be significantly elevated at higher, more than at lower altitudes in Northern Czech mountain soils (Wilcke and Zech, 1997). Concentrations of total and three-ring PAHs in Himalayan soil were also positively correlated with altitude (4,700–5,600 m), whereas no correlation was found for more than three-ring PAHs (Wang et al., 2007). Quiroz et al. (2011) found no altitudinal dependence for soil PAH concentrations for the whole dataset obtained from the related analysis in European high mountain areas. These previous studies documented that it is necessary to investigate the residues of PAHs in mountain soils for elucidating their biogeochemical transport in different ecosystems.

PAH emitted from different sources would exhibit different molecular compositions (Yunker et al., 2002). Generally, the petrogenic sources are more abundant in low-molecular weight (LMW) PAHs and the pyrogenic sources contain greater percentage of high-molecular weight (HMW) PAHs. Molecular indices based on the ratios of selected PAHs have been widely used to differentiate PAHs from petrogenic and
Concentrations, sources and potential ecological risks of PAHs in soils

Pyrogenic origins (Feng et al., 2007; Malik et al., 2011). The usefulness of these diagnostic ratios relies on the fact that during low temperature processes such as catagenesis of organic matter leading to the formation of petroleum, the PAH distribution is governed by the thermodynamic properties. While for high temperature processes, such as pyrolysis of organic matter, their distribution is governed by kinetic characteristics. Furthermore, many receptor-oriented models have been used to identify sources and estimate the contributions of a pollutant from a specific source. Compared with diagnostic ratios, receptor models can be employed to not only identify PAH sources, but also make quantitative assessments of the relative contribution of each source to the pollution loading (Malik et al., 2011). Several receptor models like principal component analysis-multiple linear regression model (PCA-MLR), positive matrix factorisation model (PMF), unmix model and chemical mass balance (CMB), have been frequently used and proved to be useful tools for PAH source identification in different environmental matrix (Larsen and Baker, 2003; Zhang et al., 2012; Yang et al., 2013).

Tajikistan is a landlocked mountainous developing country with the territory area of 143,600 km$^2$. Only 9,600 km$^2$ (7%) of the total land area is used as arable land for crops and orchards, while 93% of the whole country’s land area is covered by mountains with an average elevation of 3,000 m. Bandowe et al. (2010) measured the concentrations, sources and depth distribution of PAHs in soils from Angren industrial region of Uzbekistan. However, to the best of our knowledge, no investigation was performed on the pollution of PAHs in soils from Tajikistan, which is also important to elucidate the atmospheric transport of PAHs through the whole Central Asia area.

In the present study, the concentrations and spatial distribution of 16 priority PAHs in mountain soils from Tajikistan were investigated. Diagnostic ratios were used firstly to imply the possible sources of PAHs qualitatively, and then principal component analysis (PCA) coupled with multivariate linear regression (MLR), were further used to identify the contributions of different sources. In addition, the potential toxic risks of PAHs were evaluated by comparing with the national guidelines. Toxicity assessment based on the benzo[a]pyrene-equivalent concentration (BaPeq) was also performed to further imply the ecological risks of PAH pollution in soils of Tajikistan.

2 Materials and methods

2.1 Sampling

A total of 20 soil samples from different altitudes (570–4,656 m) throughout Tajikistan were collected during September–October of 2011 with a stainless steel shovel (Figure 1). The topsoil samples (0–5 cm) that were collected consisted of five sub-samples from the surrounding areas (10 m$^2$). Such debris, as residual roots and stones, were removed from the soil samples. Soil samples were packed together in pre-cleaned aluminium bags to form one composite sample. The soil samples were air-dried at room temperature (22–25°C), and then all the samples were sealed in aluminium foil and stored at −20°C until analysis.
2.2 Chemicals and sample extraction

All chemicals and solvents were chromatographic grade for PAH analysis, and were purchased from Supelco (USA). The purified water was obtained from a Milli-Q water system (Millipore, Bedford, MA, USA). PAH standards were also purchased from Supelco (USA), including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[h]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a]anthracene, benzo[ghi]perylene, and indeno[1,2,3-cd]pyrene. The standard solutions were dissolved in methanol/dichloromethane (1:1, v/v) and stored at 4°C. The working solutions were daily prepared with suitable dilutions before use.

The air-dried soil samples were heated at 550°C for about 6 h to gravimetrically determine the organic matter contents, which was expressed as loss of ignition (LOI, %). Aliquots of the air-dried samples used for PAH analysis were ground and sieved (about 100 mesh) and extracted with dichloromethane using an accelerated solvent extraction system (ASE) as suggested by Zhao et al. (2013). The obtained extracts were further purified by a silica gel-alumina (2:1) column and eluted with 15 mL n-hexane and 70 mL n-hexane/dichloromethane (7:3, v/v) in due order. The n-hexane/dichloromethane fraction was collected and concentrated to near dryness by a rotary evaporator. The fresh n-hexane was added to redissolve the target elution. Then, the obtained n-hexane solution was sieved through a 0.22 μm microporous filter and quantified to 0.5 mL under high purity nitrogen (> 99.99%) for the following instrumental analysis.
2.3 PAH determination and quality control

PAHs were determined by a high performance liquid chromatography (HPLC) equipped with a diode-array detector (DAD) and a fluorescence detector (FLD) (Agilent HPLC 1200, USA). Detailed instrumental conditions can be found in Zhao et al. (2014).

The qualitative analysis of 16 priority PAHs was completed based on the retention time of standard components, while the quantification was completed by the external standard method. The calibration curves were established between the peak area and concentration of target compounds with the coefficients ($r$) ranging from 0.996 to 0.999. Concentrations of PAHs in soils were expressed on dry weight basis (ng g$^{-1}$ dry weight, ng g$^{-1}$ dw). The detected limits of PAH congeners (0.02–3.57 ng g$^{-1}$ dw) using the present method were determined as the concentration of analytes in a sample that yielded a peak signal-to-noise ratio (S/N) of 3. For each set of samples, a procedure blank and a spiked sample were run to check for interference and cross contamination. Results of laboratory blanks indicated no detected interfering contaminants, and the spiked recoveries performed with baked soil matrix (550°C, 6 h) ranged from 76% to 103% for PAHs. Additionally, a standard solution was analysed after every 15 samples to recalibrate the retention time of target compounds.

2.4 Statistical analysis

Statistical treatment of the obtained results and related correlation analysis was performed with SPSS software (SPSS 16.0 for Windows, SPSS Inc., USA). Spearman’s rank correlation was used to test the strength of associations between parameters which were non-normal distributed, and the statistical significance was considered for $p < 0.05$ (two-tailed tests). A significant difference analysis of contaminant concentrations between provinces was completed by an independent sample T-test, and the value of $p < 0.05$ was thought to be statistical significance. PCA was applied to extract valuable information from the multivariate. The Bartlett test of sphericity and the Kaiser-Meyer-Olkin (KMO) test were used to determine the correlations between variables and were considered acceptable if $p$ values were less than 0.05 and KMO values were greater than 0.6. Factors were identified using varimax rotation with the eigenvalues greater than 1. The scores of each principal component (PC) and the standardised concentrations of total PAHs were then used for MLR analysis to assess the contributions of each identified source to the sum origin of PAHs quantitatively.

3 Results and discussion

3.1 PAH concentrations

PAHs were detected in all samples and ranged from 17.15 ng g$^{-1}$ dw to 257.93 ng g$^{-1}$ dw with a mean value of 66.25 ± 58.16 ng g$^{-1}$ dw (Figure 2). Among PAH congeners, benz[a]anthracene was only detected at TJS01 with a concentration of 1.24 ng g$^{-1}$ dw, while indeno[1,2,3-cd]pyrene was not detected in any samples. Acenaphthene was 80% detected ranging from 0.03 ng g$^{-1}$ dw to 4.92 ng g$^{-1}$ dw, while the rest of the components were 100% detected in soils. Phenanthrene was the most predominant congener varied from 9.00 ng g$^{-1}$ dw to 44.29 ng g$^{-1}$ dw (mean value of 21.99 ± 11.71 ng g$^{-1}$ dw),
followed by pyrene, benzo[h]fluoranthene and benzo[k]fluoranthene in the range of 0.25–31.24 ng g\(^{-1}\) dw, 0.47–110.53 ng g\(^{-1}\) dw and 0.07–31.14 ng g\(^{-1}\) dw, respectively. The concentrations of carcinogenic PAHs (sum of chrysene, benzo[h]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[ah]anthracene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene) were found in the range of 1.18–159.70 ng g\(^{-1}\) dw (23.17 ± 39.66 ng g\(^{-1}\) dw), and thus verifying potential ecological risks.

**Figure 2** PAH concentration in soil samples from Tajikistan (see online version for colours)

Compared with other mountain regions, the concentrations of PAHs in soils of Tajikistan were higher than the high-altitude soils of the Central Italian Alps (6.1–80.3 ng g\(^{-1}\) dw, \(\sum_{18}\)PAHs) (Tremolada et al., 2009). However, the observed levels in this study were lower than the Subtropical Atlantic (1.9–6,000 ng g\(^{-1}\) dw, \(\sum_{28}\)PAHs) (Ribes et al., 2003a), West Canada (2–789 ng g\(^{-1}\) dw, \(\sum_{16}\)PAHs) (Choi et al., 2009), the European high mountains (290–2,300 ng g\(^{-1}\) dw, \(\sum_{16}\)PAHs) (Quiroz et al., 2011), Holy Cross mountains of Poland (4.43–1,905.83 ng g\(^{-1}\) dw, \(\sum_{15}\)PAHs) (Migaszewski, 1999), and the Qomolangma mountains of China (168–595 ng g\(^{-1}\) dw, \(\sum_{12}\)PAHs) (Wang et al., 2007), suggesting a lower pollution level of PAHs in Tajikistan mountain soils.

### 3.2 Spatial distribution of PAHs

Numerous studies have shown that PAHs are strongly retained by the soil matrix. The partitioning concept of soil sorption of organic contaminants implies that the sorption of hydrophobic organic molecules is determined by the organic matter content of the substrate (Tang et al., 2005). The organic matter content is a key measure of the contamination status of hydrophobic compounds in soils. In this study, the LOI contents of 20 soil samples ranged from 2.1 to 15.1%, with a mean value of 4.9 ± 3.4%. The relationship between total concentrations of PAHs in soils and soil organic matter has
been extensively investigated. In the present study, the results of the correlation tests, before and after log transformations among individual total PAHs and LOI, showed that all individual and total PAHs were not significantly correlated with LOI ($p > 0.05$). It is believed that the sorption of PAHs in water on soil particles is a fast process compared to translocation from particle surface to internal structure of soil particles (Ahn et al., 2005). Therefore, the weak correlation between LOI and PAHs could be due to the result of non-equilibrium absorption (Wang et al., 2013).

Additionally, it is well known that urban soils can have concentrations much greater than rural locations, reflecting the broad relationship between PAH loading and population density. However, as shown in Figure 2, the highest concentration of PAHs was detected at TJS06, followed by TJS12, TJS16 and TJS11, while the sites TJS07 and TJS09 were found to have much lower residues. In Tajikistan, the population density in the western part is obviously larger than the eastern part with the capital city Dushanbe being the most crowd place. Khujand (population density of 71.6 people/km$^2$) is the second largest city in the northwest part of Tajikistan, which also plays an important role in both the economy and the agricultural development of the country. Thus, it has a higher population density ranking than other regions, only second to Dushanbe (population density of 1,873.3 people/km$^2$). The east and southeast parts of Tajikistan are made up mostly of the Pamirs Plateau, which has high altitudes that are not suitable for people to live in. And then, people in eastern Tajikistan mainly live around the city Khorugh with a small population density of 3.2 people/km$^2$. Therefore, no significant spatial distribution of PAHs could be indicated on the basis of the proximity to anthropogenic sources. It thus could be concluded that PAH loadings in soils of Tajikistan are strongly affected by the likelihood of enhanced atmospheric deposition. In other words, this implies that the soil burden of PAHs is primarily a reflection of cumulative atmospheric deposition from both local sources and combined sources from surrounding Central Asian countries. If this is the case, then it might be expected that soil properties are of comparatively minor importance in controlling the residues of such semivolatile organic pollutants in soils as suggested by the poor correlations between LOI and PAHs in this study (Nam et al., 2008; Bortey-Sam et al., 2014).

Furthermore, the more volatile constituents of contaminant mixtures seem to have become enriched, relative to the less volatile constituents at higher altitudes (Daly and Wania, 2005), which has also been suggested by our former investigation on spatial altitude-dependence distribution of organochlorine pesticides (OCPs) in this country (Zhao et al., 2013). However, correlation analysis between PAHs and altitude demonstrated no significant correlations ($p > 0.05$), further demonstrating the contribution of atmospheric transportation of PAHs from the adjacent regions other than the local emission sources in Tajikistan.

3.3 Source appointment of PAHs

The percentage concentrations of PAH congeners in soils from Tajikistan are also analysed. Two-ring PAH (naphthalene) accounting for 9.0 ± 12.0% of the total PAHs, while three- and four-ring congeners were the predominant components for all samples and contributed 25.4%–97.1% to PAHs with a mean value of 68.6 ± 19.2%. Five- and six-ring compounds showed large variation coefficients among soil samples and accounted for 1.8–73.9% (22.5 ± 20.4%) of total PAHs (Figure 3). The larger contribution of less than four ring PAHs in Tajikistan soils might be attributed to the
fractionation during long-range atmospheric transport, which finally induced deposition of LMW PAHs because of their higher vapour pressure than HMW PAHs (Wilcke et al., 2014). Furthermore, the particular sources of PAHs in Tajikistan might be another possible reason, and it could be deduced that petrogenic sources would be the major ones (Yunker et al., 2002). A correlation analysis of PAH compositions based on the percentage concentrations of individual congeners also demonstrated significant positive correlations \((p < 0.05)\) between different sampling sites except for the weaker positive correlations between TJS02, TJS11, TJS12 and other sites (Table 1). Therefore, the relative consistent compositions of PAHs among sampling sites could elucidate similar PAH sources in soils from different regions of Tajikistan.

**Figure 3** Triangular diagram of percentage concentrations of 16 PAHs in soil samples from Tajikistan

Diagnostic ratio is a widely used technique to apportion the origins of PAHs present in different environmental media. The ratios of different PAHs are expected to vary with sources, most likely due to various routes of PAH formation under different combustion conditions (Yunker et al., 2002; Bortey-Sam et al., 2014). The fluoranthene/(fluoranthene + pyrene) ratios for most samples (80%) collected from Tajikistan were less than 0.4 (Figure 4), demonstrating that PAHs in soils mainly came from petrogenic sources (Yunker et al., 2002; Bucheli et al., 2004). While the pyrogenic sources composed of combustion process, fossil fuel combustion, biomass and coal combustion, only accounted for 20% of PAH sources in soils. According to the anthracene/(anthracene + phenanthrene) ratios, only sites TJS16 and TJS19 had the ratios lower than 0.1, which indicated that a petroleum source other than combustion was responsible for PAHs observed in soils from Tajikistan. In addition, the benzo[a]pyrene/benzo[ghi]perylene ratio was also used to elucidate the traffic or non-traffic sources of PAHs (Yunker et al., 2002). It was found out that 85% of the sampling sites showed higher ratios than 0.6, further implying traffic sources might be the predominant source for PAHs.
Concentrations, sources and potential ecological risks of PAHs in soils

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<tr>
<td>TJS16</td>
<td>0.720</td>
<td>0.620</td>
<td>0.770</td>
<td>0.847</td>
<td>0.900</td>
<td>0.817</td>
<td>0.815</td>
<td>0.729</td>
<td>0.886</td>
<td>0.785</td>
<td>0.803</td>
<td>0.767</td>
<td>0.714</td>
<td>0.889</td>
<td>0.859</td>
<td>1.000</td>
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<tr>
<td>TJS17</td>
<td>0.655</td>
<td>0.455</td>
<td>0.741</td>
<td>0.767</td>
<td>0.962</td>
<td>0.829</td>
<td>0.850</td>
<td>0.703</td>
<td>0.927</td>
<td>0.803</td>
<td>0.844</td>
<td>0.773</td>
<td>0.617</td>
<td>0.939</td>
<td>0.811</td>
<td>0.903</td>
<td>1.000</td>
<td></td>
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<tr>
<td>TJS18</td>
<td>0.802</td>
<td>0.794</td>
<td>0.720</td>
<td>0.844</td>
<td>0.782</td>
<td>0.626</td>
<td>0.897</td>
<td>0.885</td>
<td>0.859</td>
<td>0.873</td>
<td>0.540</td>
<td>0.605</td>
<td>0.800</td>
<td>0.682</td>
<td>0.953</td>
<td>0.756</td>
<td>0.770</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TJS19</td>
<td>0.852</td>
<td>0.847</td>
<td>0.761</td>
<td>0.944</td>
<td>0.817</td>
<td>0.676</td>
<td>0.850</td>
<td>0.879</td>
<td>0.847</td>
<td>0.835</td>
<td>0.582</td>
<td>0.679</td>
<td>0.903</td>
<td>0.700</td>
<td>0.959</td>
<td>0.817</td>
<td>0.761</td>
<td>0.953</td>
<td>1.000</td>
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<tr>
<td>TJS20</td>
<td>0.826</td>
<td>0.744</td>
<td>0.735</td>
<td>0.897</td>
<td>0.876</td>
<td>0.720</td>
<td>0.874</td>
<td>0.817</td>
<td>0.874</td>
<td>0.838</td>
<td>0.676</td>
<td>0.835</td>
<td>0.582</td>
<td>0.768</td>
<td>0.973</td>
<td>0.870</td>
<td>0.865</td>
<td>0.947</td>
<td>0.953</td>
<td>1.000</td>
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</tbody>
</table>

Note: *No significant positive correlations were observed (p > 0.05).*
PCA was then used to extract valuable information from the multivariate. By utilising the orthogonal transformation method, PCs are extracted with different factor loadings indicating correlations of each pollutant species with each PC. The obtained PCs are further evaluated and recognised by source markers or profiles as reasonable pollution sources. MLR followed PCA can further quantitatively assess contributions of each identified source to the sum of PAHs (Larsen and Baker, 2003; Liu et al., 2010; Shi et al., 2009, 2011). In this investigation, PCA with varimax rotation was performed for 14 PAHs (benzo[a]anthracene and indeno[1,2,3-cd]pyrene were excluded because of their rather lower detection frequencies) in soil samples from Tajikistan. Three PCs were extracted with the eigenvalues > 1, accounting for the majority (83.1%) of the total variance (Table 2). PC1 explained 50.0% of the total variance and was mostly loaded by acenaphthylene, pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylene. Benzo[a]pyrene and benzo[ghi]perylene are typical markers of gasoline vehicle emissions, while benzo[b]fluoranthene and benzo[k]fluoranthene are related to diesel-powered vehicles (Harrison et al., 1996; Sharma et al., 2007; Zhou et al., 2014). Acenaphthylene is also defined as the signature of
Concentrations, sources and potential ecological risks of PAHs in soils

related diesel fuel emissions (Zhou et al., 2014; Agarwal et al., 2009). Therefore, PC1 could be deduced to the traffic-related sources of PAHs. PC2 accounted for 20.9% of the total variance and was characterised by high loadings on phenanthrene, anthracene, chrysene and fluoranthene. Since phenanthrene, anthracene, chrysene and fluoranthene are all predominant emissions of coal combustion as suggested by Khalili et al. (1995), PC2 could represent coal combustion as the source of this group of PAHs. PC3 explained 12.2% of the total variance and was predominantly weighed in naphthalene, acenaphthene and fluorene, and thus PC3 was associated with coke oven combustion since acenaphthene and fluorene are possible tracers of coke oven source (Simcik et al., 1999).

Table 2  Factor analysis scores following varimax rotation for all PAHs (factor loading > 0.5 are shown in bold)

<table>
<thead>
<tr>
<th>Variable</th>
<th>PC1</th>
<th>PC2</th>
<th>PC3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>0.056</td>
<td>-0.087</td>
<td>0.774</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>0.772</td>
<td>0.447</td>
<td>0.044</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>-0.100</td>
<td>0.051</td>
<td>0.884</td>
</tr>
<tr>
<td>Fluorene</td>
<td>-0.140</td>
<td>0.458</td>
<td>0.726</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.396</td>
<td></td>
<td>0.284</td>
</tr>
<tr>
<td>Anthracene</td>
<td>0.173</td>
<td>0.893</td>
<td>0.206</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>0.421</td>
<td></td>
<td>-0.063</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.802</td>
<td>0.470</td>
<td>-0.101</td>
</tr>
<tr>
<td>Chrysene</td>
<td>-0.052</td>
<td>0.923</td>
<td>-0.111</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>0.912</td>
<td>0.225</td>
<td>-0.082</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>0.955</td>
<td>0.086</td>
<td>-0.099</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>0.963</td>
<td>0.165</td>
<td>-0.078</td>
</tr>
<tr>
<td>Dibenzo[ah]anthracene</td>
<td>0.963</td>
<td>-0.001</td>
<td>-0.009</td>
</tr>
<tr>
<td>Benzo[ghi]pyrene</td>
<td>0.977</td>
<td>-0.032</td>
<td>0.096</td>
</tr>
<tr>
<td>Eigenvalues</td>
<td>6.997</td>
<td>2.923</td>
<td>1.702</td>
</tr>
<tr>
<td>Variance contribution (%)</td>
<td>50.0</td>
<td>20.9</td>
<td>12.2</td>
</tr>
<tr>
<td>Cumulative variance contribution (%)</td>
<td>50.0</td>
<td>70.9</td>
<td>83.1</td>
</tr>
</tbody>
</table>

MLR was then performed on using the factor scores of these three identified PCs and the standardised concentrations of total PAHs. The regression equation was expressed as follows:

\[
PAHs = -0.001 + 0.878PC1 + 0.422PC2 + 0.132PC3
\]

(1)

Contributions of each component could be calculated from the coefficients. PC1 on behalf of traffic emission was responsible for 61.3% of total PAHs observed in mountain soils from Tajikistan, while PC2 on behalf of coal combustion contributed 29.5% to PAHs. PC3 (coke oven combustion) accounted for 9.2% of total PAH emissions. Therefore, inferences drawn from the PCA-MLR analysis were similar to that of isomer pair ratios, demonstrating the related traffic emission and coal combustion from anthropogenic activities were the main sources of PAHs contamination in soils of Tajikistan. This phenomenon might be attributed to the fact that more than 50% of the...
area of Tajikistan is composed of mountains and plateaus with higher altitudes than 3,000 m, and road transport is a major transportation industry other than railway transport and air transport. Additionally, it was also reported that the exploration of energy sources (coal, petroleum and natural gas, etc.) was rather lower due to the status as a developing country. The exploration quantity of petroleum and natural gas decreased significantly from 1991 to 1997 (Akramov, 2012), which could also induce a low contribution of such energy sources to PAHs in soils of Tajikistan.

3.4 Risk assessment

The carcinogenic PAHs (chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene and benzo[g,h,i]perylene included) accounted for 2.4–74.1% of total PAHs, and TJS11 showed the highest carcinogenic risk followed by TJS06 and TJS12, while TJS02 was at the lowest carcinogenic risk. The relative higher proportion and significant correlation ($r = 0.942$, $p < 0.01$) between carcinogenic congeners and total PAHs indicated potential risks for soils in Tajikistan. Maliszewska-Kordybuch (1996) has classified the pollution levels of PAHs in soils into 4 categories based on the 16 USEPA priority pollutants, namely, unpolluted (200 ng g$^{-1}$), weakly polluted (200–600 ng g$^{-1}$), polluted (600–1,000 ng g$^{-1}$) and severely polluted (1,000 ng g$^{-1}$). By this classification, only soils from TJS06 were weakly polluted with the highest concentration of 257.9 ng g$^{-1}$ dw. Regarding Canadian soil guidelines for the protection of environmental health in residential areas (CCME, 2010), the detected concentrations for naphthalene, phenanthrene, pyrene, benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene in 20 soil samples from Tajikistan were all far less than the suggested guidelines of 100 ng g$^{-1}$ provided by CCME for agricultural soils, and thus were also lower than the recommended safe values for other kinds of soils (the rest CCME guidelines were all higher than 600 ng g$^{-1}$ for residential/parkland, commercial, and industrial soils).

Furthermore, health risk assessment of carcinogenic PAHs cannot be related only to overall concentration. Rather, each PAH has a different carcinogenic potential (Bortey-Sam et al., 2014). Health risk assessments associated with PAH uptake is often estimated on the basis of the benzo[a]pyrene concentrations, since benzo[a]pyrene is the highest carcinogenic contributor in almost every study (Halek et al., 2008). The development and establishment of toxicity equivalency factors (TEFs) are used in the assessment of mixtures containing PAHs. The TEFs were used to quantify the carcinogenic potential of other PAHs relative to benzo[a]pyrene and to estimate benzo[a]pyrene-equivalent concentrations (BaPeq) (Nadal et al., 2004; Agarwal et al., 2009). BaPeq were calculated using TEFs provided by Nisbet and LaGoy (1992), which was calculated by multiplying the concentration of each PAH in the soil sample by its TEF. Canadian soil quality guidelines for commonly occurring parent PAHs for the protection of environmental and human health provide the PAH guidelines based on PAH carcinogenic effect, which indicates a safe BaPeq value of 600 ng g$^{-1}$ based on the incremental lifetime cancer risk (ILCR) of $10^{-6}$ (CCME, 2010). The BaPeq in soils from Tajikistan ranged from 0.21 to 31.19 ng g$^{-1}$ dw. Site TJS06 had the highest BaPeq, followed by TJS12 (20.92 ng g$^{-1}$ dw) and TJS11 (15.57 ng g$^{-1}$ dw), while TJS10 showed the lowest BaPeq value. Since these notable sites are mainly located near the city Khorugh, which has a lower population density than other cities, and the observed
Concentrations, sources and potential ecological risks of PAHs in soils

BaPeq were all less than the safe value of 600 ng g⁻¹, documenting exposure to these soils would not pose any significant risks to human health from carcinogenic effects of PAHs at present.

4 Conclusions

PAHs are ubiquitous pollutants in the mountain soils of Tajikistan mainly due to the cumulative atmospheric deposition from both the local sources and combined sources from surrounding countries. Similar compositions of PAHs in all soil samples indicated similar sources among these sites. The related traffic emissions were the predominant sources, followed by coal combustion and coke oven combustion, which was more or less consistent with the energy source profiles of Tajikistan. The risk assessment based on both the national guidelines and BaPeq concentrations indicated no significant risks to human health from carcinogenic effects of PAHs in soils from Tajikistan at present. This study could be used as the fundamental investigation on PAH biogeochemical processes especially in developing regions and thus would be helpful for further elucidating of atmospheric transport in Central Asia region.

Acknowledgements

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References


Concentrations, sources and potential ecological risks of PAHs in soils


