



Research Article

Cryoconites as biogeochemical markers of anthropogenic impact in high mountain regions: analysis of polyaromatic pollutants in soil-like bodies

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Academic editor: Bastian Steinhoff-Knopp

Received: 15 Nov 2021 | Accepted: 05 Jan 2022 | Published: 10 Jan 2022

Citation: Abakumov E, Kushnov I, Nizamutdinov T, Tembotov R (2022) Cryoconites as biogeochemical markers of anthropogenic impact in high mountain regions: analysis of polyaromatic pollutants in soil-like bodies. One Ecosystem 7: e78028. <https://doi.org/10.3897/oneeco.7.e78028>

Abstract

The globalisation and omnidirectional character of anthropogenic processes has challenged scientists around the world to estimate the harmful effects of these processes on ecosystems and human health. Polycyclic aromatic hydrocarbons (PAHs) is one the most infamous group of contaminants, originated both from natural and anthropogenic processes. They could transport to high latitudes and altitudes through atmospheric long-distance transfer and further enter ecosystems of these vulnerable regions by deposition on terrestrial surfaces. An interesting object for tracking transboundary contamination processes in high mountain ecosystems is called cryoconite. Cryoconite, a dark-coloured supraglacial sediment which is abundant in polar and mountain environments, is considered as a storage of various pollutants, including PAHs. Thus, it may pose a risk for local human health and ecosystem through short-distance transfer. Studied cryoconite sediments were collected at the surface of Skhelda and Garabashi glaciers, Central Caucasus high-mountain region, as well as mudflow, moraine material and local soils at the Baksan Gorge in order to examine levels of their contamination. We analysed the content of 15 priority polyaromatic compounds from the US EPA list and used the method

of calculation of PAHs isomer ratios with the purpose of identifying their source. To estimate their potential toxicity, Benzo[a]pyrene (BaP) equivalents were calculated. Maximum concentration was defined for NAP ($84 \text{ ng}\times\text{g}^{-1}$), PHE ($40 \text{ ng}\times\text{g}^{-1}$) and PYR ($47 \text{ ng}\times\text{g}^{-1}$), with the minimum concentration for ANT (about $1 \text{ ng}\times\text{g}^{-1}$). The most polluted material is a cryoconite from Garabashi glacier because of local anthropogenic activities and long-distance transfer. High-molecular weight PAHs are dominated in PAHs composition of almost all samples. The most common sources of PAHs in studied materials are combustion processes and mixed pyrolytic/petrogenic origin. Toxicity levels of separate PAHs did not exceed the maximum permissible threshold concentrations values in most cases. However, the sum of PAHs in BaP equivalents exceed the threshold values in all samples, in some of them more than twice.

Keywords

Central Caucasus, glaciers, soils, polycyclic aromatic hydrocarbons, pollution, cryoconite

Introduction

With the increase of anthropogenic activity on a global scale, the monitoring of various contaminants has become one of the priorities of the world community. One of the most notorious group of these chemicals is polycyclic aromatic hydrocarbons (PAHs). PAHs are very common organic pollutants in the environment, consisting of carbon and hydrogen atoms with two or more aromatic rings in their structure (Edwards 1983). Some of them have carcinogenic and mutagenic effects and, therefore, may pose risks for human health (Boström et al. 2002). In case of short-term direct contact, the most common symptoms are skin irritation, nausea and diarrhoea, while the long-term influence of some PAHs may cause cancer and other various chronic diseases of the respiratory system, cardiovascular system and digestive system (Famiyeh et al. 2021). Some of them were defined as human carcinogens (group 1), possibly carcinogenic to human (groups 2A and 2B) (International Agency for Research on Cancer 2021). US EPA 1982) and European Food Safety Authority 2008) published the priority pollutants lists with the most hazardous contaminants amongst PAHs which should be regulated, including benzo[k]fluoranthene (BkF), benzo[ghi]perylene (BPE), benzo[a]pyrene (BaP), chrysene (CHR) and dibenz[a,h]anthracene (DBA). BaP is one of the most toxic compounds which is associated with anthropogenic influence (Abakumov et al. 2014, Sushkova et al. 2017) and should be obligatorily controlled in the environment, including soils (Federal Service for Supervision of Consumer Rights Protection and Human Well-Being of the Russian Federation 2006). BaP can be estimated as a reference substance and, due to this, benzo[a]pyrene-equivalent (BaP-EQ) is usually used in the determination of environmental object pollution by PAHs in current research (Callén et al. 2007, Gao et al. 2019, Yang et al. 2021).

The potential sources of PAHs release into the environment can be divided into cosmogenic, petrogenic, biogenic and pyrogenic (Tsibart and Gennadiev 2013). PAHs of pyrogenic origin are the most common amongst all atmospheric PAHs (Baek et al. 1991).

Their natural sources include volcanism and wildfires, while anthropogenic is usually associated with incomplete combustion of fossil fuels and plant materials (Kim et al. 2013). Studying the structure of PAHs and their isomer pair ratios is one of the most common ways to understand their sources (Wilcke 2000, Yunker et al. 2002, Abakumov et al. 2021). It is possible because of differences in the combustion temperature of formation of PAHs and their thermodynamic characteristics, which allows differentiation of sources by dividing the isomers into the least stable and the most stable (Yunker et al. 2002, Santos et al. 2017).

After complex transformation, atmospheric PAHs are deposited in water reservoirs, vegetation and soils (Zhang et al. 2020). Soils particularly act as a sink of PAHs where these compounds can persist for a long time, due to the complex structure of soil matrix and their dissemination in terrestrial ecosystems strongly affects soil-plant system through absorption of them by roots and further transportation to other plant parts (Abdel-Shafy and Mansour 2016, Sushkova et al. 2017). Thus, one of the main dangers for human health here is the intake of contaminated plants as a food. On the other hand, pollutants can enter the human body with fine soil particles through inhalation or direct contact with soil (US EPA 1996).

Studies of soil contamination by PAHs is more associated with urban soils due to their proximity to industrial facilities and traffic routes (Wilcke 2000). However, due to the so-called "grasshopper effect", PAHs could be transferred through the atmosphere to remote polar and mountain regions where, under the influence of cold condensation, they are deposited on the terrestrial ecosystem (glaciers, snow cover, soils, water objects) (Fernández et al. 2003, Zhao et al. 2015, Fernandez et al. 2021). Previous research indicated higher than background level concentration of PAHs in soils and sediments of European high-altitude areas (Carrera et al. 2001, Ribes et al. 2003, Quiroz et al. 2010), Tibetan plateau (Zhou et al. (2018), Himalayan mountain range (Riaz et al. 2019), Mt. Wangtiane (north-eastern China) (Wang et al. 2019) and western Canadian mountains (Abdul Hussain et al. 2019), with dominance of low molecular weight (LMW) PAHs. Concentration of PAHs in soils depends on the difference between the input of polluted material, mainly through wet deposition and loss processes, such as biodegradation, volatilisation and burial (Wang et al. 2019). Due to the cold weather, which is typical for high-mountain regions, the intensity of the loss processes decreases, while wet deposition rises because of cold condensation (Chen et al. 2008). Additionally, deposited PAHs could be stored in the snow cover and, further, pollute the soil in the warm season due to their release during intensive snowmelt (Meyer et al. 2006).

Another accumulation object of pollutants in polar and mountain regions is cryoconite. Cryoconite is a widespread black-coloured sediment in supraglacial environments consisting of black carbon, mineral particles, microorganisms and organic matter (Hodson et al. 2008). This term was introduced by Swedish explorer Nordenskjöld in 1870 in Greenland, meaning "cryo" – ice and "conite" – dust (Nordenskiöld 1875). Cryoconite can be located in holes in the glacier, as well as being dispersed on its surface and it can be found at all mountain glaciers in the world, including debris-covered glaciers (Adhikary et al. 2000, Dong et al. 2016, Di Mauro et al. 2017). The origin of cryoconite sediments is

generally associated with autochthonous and allochthonous input of material, where the latter is connected with long-range atmospheric transport of fine particles and, thus, can transfer various pollutants from remote industrial regions (Zawierucha et al. 2019, Polyakov et al. 2020). Recent studies of PAHs content in cryoconite sediments, which were conducted in Antarctica (Abakumov et al. 2021) and Tibetan plateau (Li et al. 2017), indicated higher than background and threshold values of both LMW and high molecular weight (HMW) PAHs. The latter group out of these two is mostly associated with anthropogenic activities, these substances are more stable in the environment and are more toxic for humans, as well as for wildlife than LMW PAHs (Mandal and Das 2015). Previous research (Bogdal et al. 2009, Morselli et al. 2014) showed that glaciers act as a source of contaminants for downstream and foothill ecosystems due to deposition of polluted material on the glacier surface, which may pose risks for local residents and the environment.

Central Caucasus, as well as other mountain regions, is sensitive to any contamination and disturbance (Moshenko et al. 2020). In this area, PAHs content was measured only in ice cores to estimate the PAHs' level fluctuations during the 20th century (Vecchiato et al. 2020), but no studies of PAH contamination of soils or sediments have been conducted. In the Central Caucasus, especially in Elbrus District, there is an active development of tourism which is accompanied by transportation, buildings construction and other environmentally-destructive processes (Voskova et al. 2021). Therefore, the main aim of our research is to study features of differentiations of PAHs in background high mountain ecosystems and those which are under anthropogenic pressure of the Central Caucasus region. To achieve this aim, the following goals were set:

- to evaluate the content of 15 PAHs from the list of priority PAHs pollutants in studied cryoconite sediments and soils;
- to identify possible sources of PAHs using selected isomer ratios;
- to calculate benzo[a]pyrene-equivalent of defined concentrations of PAHs and compare them with Russian environmental legislation standards.

Material and methods

The study focused on soil samples, soil-like bodies and cryoconite material sampled in the vicinity of Mount Elbrus and on the surface of the Skhelda and Garabashy glaciers (The Greater Caucasus). The Caucasus Region of Russia is an extremely popular tourist destination (Litvinova 2020). People visit it from all over Russia as well as from its near neighbour countries. A special place in the tourist sector is occupied by hiking and ecological tourism (Andreyanova and Ivolvega 2018).

Year-round, these Caucasus regions are visited by tens of thousands of tourists, which certainly causes anthropogenic pressure on local mountain ecosystems. In this regard, there is a need to track the level of anthropogenic load on ecosystems especially in the areas of famous tourist routes. We conducted research of soils, soil-like bodies and cryoconite material for their PAH content. During the 2020 fieldwork, samples of material

from Skhelda and Garabashi glaciers (Fig. 1), soil samples from the vicinity of Kiendelen Village and material from the mud-flow that fell in 2019 were collected (Table 1).

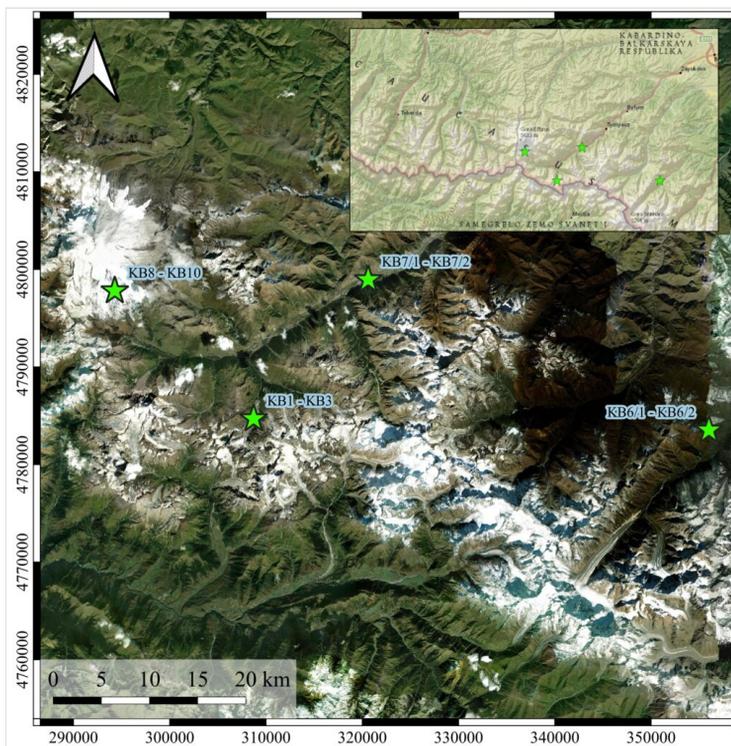


Figure 1.
Sampling sites.

Table 1.
Main sampling information.

Study site	Sample ID	Description	Coordinates	Elevation, m	Sampling date
Skhelda glacier	KB 1	Material from the slope of the glacier	43°11'27"N, 42°38'45"E	2385	15.09.2020
	KB 2	Cryoconite derived material			
	KB 3	Material from the slope of the glacier			
Elbrus region, the surroundings of Kendelen Village	KB 6/1 KB 6/2	Chernozems from Kiendelen Village	43°35'22"N, 43°13'40"E	750	16.09.2020
The area at the mud-flow	KB 7/1 KB 7/2	Mud-flow occurred in 2019	43°19'19"N, 42°47'15"E	1490	

Study site	Sample ID	Description	Coordinates	Elevation, m	Sampling date
Garabashi glacier	KB 8	The cryoconite from the ice crack of the Garabashi glacier	43°18'18"N, 42°27'49"E	3860	17.09.2020
	KB 9	Cryoconite over ice			
	KB 10	Moraine sediments on the glacier			

A total of 10 samples were collected, air-dried and transported to the laboratory of the Department of Applied Ecology, St. Petersburg State University. To prevent external contamination, the samples were transported in double sealed plastic bags. The samples were sieved through a sieve with a mesh diameter of 2 mm before preparation for PAH extraction.

Concentrations of 15 high-priority PAHs from the Environmental Protection Agency's (EPA) list of High Priority Pollutants (excluding acenaphthylene) were conducted (Table 2). The PAH content was quantitatively determined by high-performance liquid chromatography (Federal Center for Analysis and Assessment of Technogenic Impact 2009).

Table 2.

Key parameters of the studied PAH.

PAH (CAS name)	Abbr. ^a	Molecular Formula	MW ^b /Rings	IARC classification of carcinogenicity ^c	CAS no.
Naphthalene	NAP	C ₁₂ H ₈	128 (2)	2B	91-20-3
Acenaphthene	ANA	C ₁₂ H ₁₀	154 (3)	3	83-32-9
Fluorene	FLU	C ₁₃ H ₁₀	166 (3)	3	86-13-7
Phenanthrene	PHE	C ₁₄ H ₁₀	178 (3)	3	85-01-8
Anthracene	ANT	C ₁₄ H ₁₀	178 (3)	3	120-12-7
Fluoranthene	FLT	C ₁₆ H ₁₀	202 (4)	3	206-44-0
Pyrene	PYR	C ₁₆ H ₁₀	202 (4)	3	129-00-0
Benzantracene	BaA	C ₁₈ H ₁₂	228 (4)	2B	56-55-3
Chrysene	CHR	C ₁₈ H ₁₂	228 (4)	2B	218-01-9
Benz[e]acephenanthrylene	BbF	C ₂₀ H ₁₂	252 (5)	2B	205-99-2
Benzo[k]fluoranthene	BkF	C ₂₀ H ₁₂	252 (5)	2B	207-08-9
Benzo[a]pyrene	BaP	C ₂₀ H ₁₂	252 (5)	1	50-32-08
Dibenz[a,h]anthracene	DBA	C ₂₂ H ₁₄	278 (5)	2A	53-70-3
Benzo[ghi]perylene	BPE	C ₂₂ H ₁₂	276 (6)	3	191-24-2
Indeno[1,2,3-cd]pyrene	IPY	C ₂₂ H ₁₂	276 (6)	2B	193-39-5

^a - used in this article; ^b - molecular weight; ^c - 1 - Carcinogenic to humans; 2A - Probably carcinogenic to humans; 2B - Possibly carcinogenic to humans; 3 - Not classifiable as to its carcinogenicity to humans

Extraction of PAHs from soil was performed using diethyl ether (Federal Center for Analysis and Assessment of Technogenic Impact 2009). For 1 gram of cleaned and air-dried sample, 10 ml of diethyl ether was added after the solution was placed in an ultrasonic bath for 30 minutes. Then the extract was evaporated at 60°C until it was not completely dry. After evaporation, 1 ml of acetonitrile was added to the residue. The prepared extracts were chromatographed on the same day. The minimum measured concentrations of PAHs are as follows: NAP >20; ANA>6; FLU>6; PHE>6; ANT>1; FLT>20; PYR>20; BaA>6; CHR>3; BbF>6; BkF>1; BaP>1; DBA>6; BPE>6; IPY>6 ng×g⁻¹ (Lau et al. 2010). Accuracy for all measurable PAHs at minimum concentrations of about ±40%.

Since PAHs can be formed not only as a result of technogenic processes, but can also be generated by various natural processes, it is possible to use PAHs as markers for anthropogenic impact. The origin of PAHs can be determined by applying different PAH diagnostic (isomer) ratios (Soclo et al. 2000, Santos et al. 2017, Khaustov and Redina 2018). As many factors influence the stability of PAHs in the environment, calculations of isomer ratios were mainly performed for PAHs of the same molecular weight.

Isomeric ratios are widely used by researchers to identify the nature of the origin of PAHs and we have analysed the literature and selected several ratios (Table 3).

PAHs isomer ratios	Range of values	Possible sources of PAH	References
ANT / (ANT + PHE)	< 0.10	Petroleum/Baseline source	Yunker et al. 2002, Wang et al. 2009, Tobiszewski and Namieśnik 2012, Shamilishvili et al. 2016
	> 0.10	Indicates a dominance of combustion	
FLU / (FLU + PYR)	< 0.40	Most petroleum/Baseline source	Mandalakis et al. 2002, Yunker et al. 2002, Fang 2004, Ravindra et al. 2008, Shamilishvili et al. 2016
	0.40-0.50	Liquid fossil fuel (vehicle and crude oil) combustion	
	> 0.50	Characteristic of grass, wood or coal combustion	
BaA / (BaA + CHR)	< 0.20	Petroleum/Baseline source	Yunker et al. 2002, Tobiszewski and Namieśnik 2012, Shamilishvili et al. 2016
	0.20-0.35	Petroleum, combustion, baseline source	
	> 0.35	Combustion	
PHE / ANT	> 10	Petrogenic	Budzinski et al. 1997, Khairy et al. 2009
	< 10	Pyrolytic	
FLU / PYR	< 1.0	Petrogenic	Budzinski et al. 1997, Khairy et al. 2009
	> 1.0	Pyrolytic	
BaP / BPE	< 0.60	Non-traffic source	Pandey et al. 1999, Ravindra et al. 2008

PAHs isomer ratios	Range of values	Possible sources of PAH	References
	> 0.60	Traffic source	
$\sum_{\text{Pyr}} \text{PAHs}^a / \sum_{15} \text{PAHs}$	< 0.30	Petroleum/Baseline source	Hwang et al. 2004, Balmer et al. 2019
	0.30-0.70	Petroleum, combustion, baseline source	
	> 0.70	Mostly combustion	
$\sum_{\text{LMW}} \text{PAHs}^b / \sum_{\text{HMW}} \text{PAHs}^c$	< 1	Pyrogenic	Soclo et al. 2000, Zhang et al. 2008
	> 1	Petrogenic	
^a - pyrogenic PAHs - FLT, PYR, BaA, CHR, BbF, BkF, BaP, BPE, IPY, ^b - light molecular weight, 2-3 ring PAHs, ^c - heavy molecular weight HMW, 4-6 ring PAHs			

Most PAHs are poorly understood in terms of their carcinogenesis and mutagenic effects on the human body. However, Benzo[a]pyrene is well studied and is recognised as one of the most toxic PAHs. Therefore, many studies are conducted by comparing the toxicity levels of various PAHs in relation to Benzo[a]pyrene, in other words, by calculating Benzo[a]pyrene equivalents (BaP – equivalents) of the toxicity of PAHs (Jung et al. 2010).

The use of equivalents also makes it possible to compare detected PAH concentrations with various standards, for example, in Russia, the maximum permissible concentration (MPC) of Benzo[a]pyrene in soils is 0.02 mg×kg⁻¹ (Federal Service for Supervision of Consumer Rights Protection and Human Well-Being of the Russian Federation 2006).

This approach makes it possible to assess not only the carcinogenic effects of single PAHs, but also to cite the level of exposure to total concentrations of various PAHs to the level of exposure to Benzo[a]pyrene. BaP – equivalents were calculated by multiplying the values of carcinogenic equivalency factors (TEF) and recorded concentrations of individual PAHs (Nisbet and LaGoy 1992). The TEF values for the PAHs we studied are as follows: NAP, ANA, FLU, PHE – 0.001; ANT – 0.01; FLT, PYR – 0.001; BaA – 0.1; CHR – 0.01; BbF, BkF – 0.1; BaP – 1; DBA – 5; BPE – 0.01; IPY – 0.1.

Results

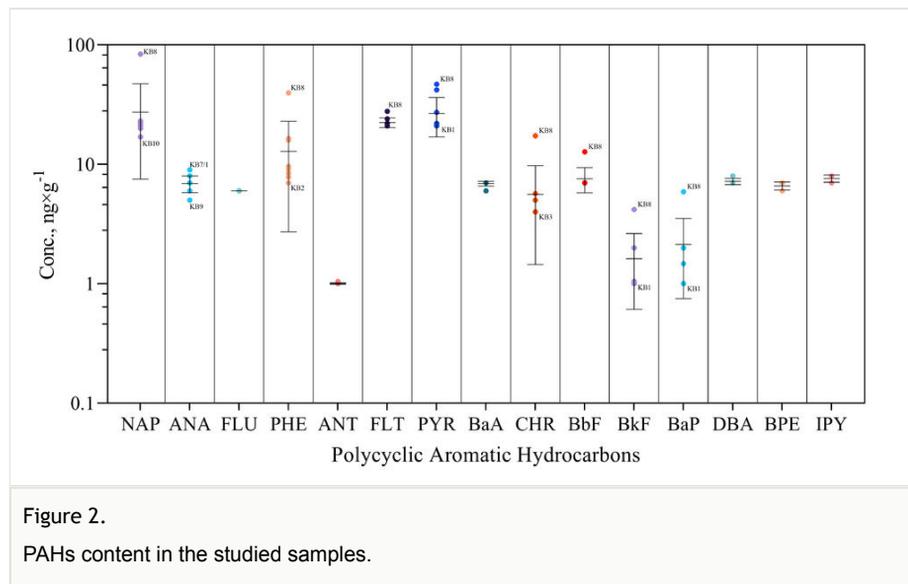
Level and distribution of PAHs content

The concentrations of recorded PAHs are shown in Fig. 2. We can see that the content of most polyarenes is highly variable. The maximum level was recorded for NAP, PHE and PYR content (84, 40 and 47 ng×g⁻¹, respectively). The minimum concentration was detected for ANT, about 1 ng×g⁻¹ in all the samples studied.

Fig. 2 shows that, in most cases, the highest concentrations of individual PAHs registered at KB8 sampling point. In this sample, obtained from Garabashi glacier, was found the maximum content of NAP – 84, PHE – 40, FLT – 28, PYR – 47, CHR – 17, BbF – 13, BkF – 4.2 and BaP – 5.8 ng×g⁻¹. The level of individual PAHs in the sample from the KB8 point

is often much higher than the median amongst all the studied samples. The minimum content of individual PAHs was mainly detected in the samples obtained from Skhelda glacier (KB1-KB3).

We carried out a cluster analysis of the obtained matrix of concentrations of individual PAHs by Ward's method using the Euclidean distance as a metric (Ward 1963). The results presented in the cluster diagram (Fig. 3) clearly show the separation of the concentration matrix into two clusters. The first cluster is KB8 and the second cluster is all other sampling points.



In addition, we performed statistical processing of the data to observe differences in PAH content in anthropogenically loaded cryoconites, soils and conditionally pristine cryoconites. As can be seen (Table 4), differences at a significance level of $p=0.05$ are observed, indicating variations in the content of polyarenes in different sediments and soils.

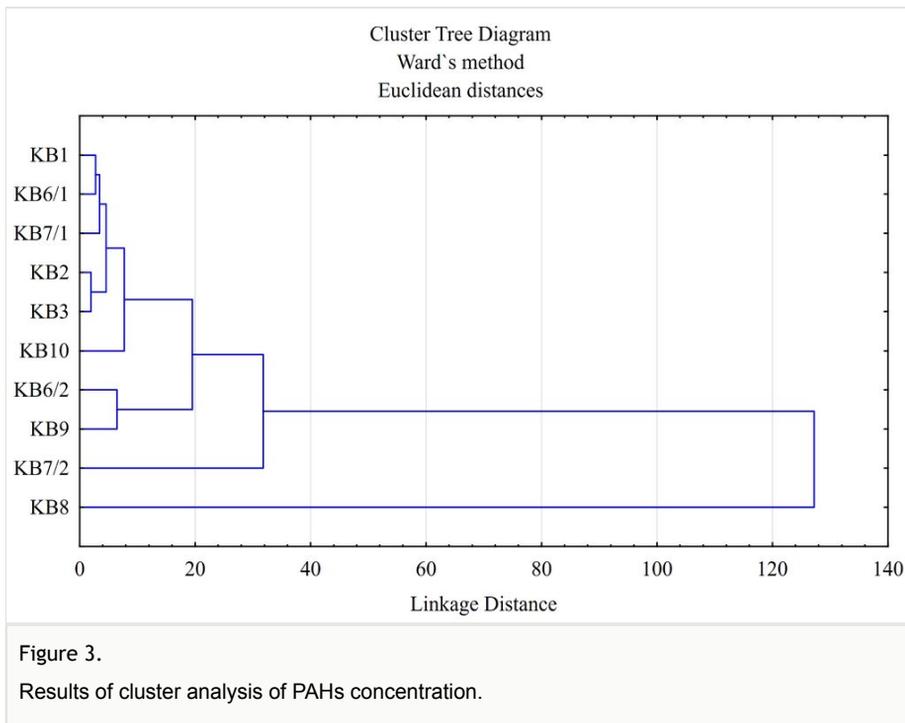
Table 4.

Multivariate Tests of Significance (One-Way ANOVA) results.

Sigma-restricted parameterisation.

The test was conducted between anthropogenically-loaded cryoconites, soils and conditionally pristine cryoconites.

Test	Value	F	p
Wilks	0.000041	19.35	0.05



Composition profile of PAHs content

The highest concentration of the $\sum_{15}\text{PAHs}$ is detected in the sample taken at point KB8 ($280 \text{ ng}\times\text{g}^{-1}$), in other samples the content of the $\sum_{15}\text{PAHs}$ is much lower ($126 - 151 \text{ ng}\times\text{g}^{-1}$) (Fig. 4). It is also worth noting that, in KB8, the $\sum_{\text{HMW}}\text{PAHs}$ and $\sum_{\text{LMW}}\text{PAHs}$ are approximately at the same level (143 and $136 \text{ ng}\times\text{g}^{-1}$, respectively). For the rest of the samples, the values of the $\sum_{\text{HMW}}\text{PAHs}$ and $\sum_{\text{LMW}}\text{PAHs}$ are considerably different; the $\sum_{\text{HMW}}\text{PAHs}$ is remarkably higher compared to the $\sum_{\text{LMW}}\text{PAHs}$. The difference is most noticeable in the sample KB7/2; here the $\sum_{\text{HMW}}\text{PAHs}$ is $109 \text{ ng}\times\text{g}^{-1}$ and $\sum_{\text{LMW}}\text{PAHs}$ is $42 \text{ ng}\times\text{g}^{-1}$. The content of $\sum_{\text{pyr}}\text{PAHs}$ is similar to that of the sum of HMW PAHs, since most of the HMW PAHs that we studied have pyrogenic genesis (except DBA). The maximum level carcinogenic PAHs ($\sum_{\text{carc}}\text{PAHs}$) was fixed in the KB8 sample ($77.1 \text{ ng}\times\text{g}^{-1}$). For other investigated samples, the level of content of $\sum_{\text{carc}}\text{PAHs}$ is close in value to the level of content of $\sum_{\text{LMW}}\text{PAHs}$. The minimum content of the $\sum_{\text{carc}}\text{PAHs}$ was found in KB1 ($47 \text{ ng}\times\text{g}^{-1}$).

A more detailed analysis of the contribution of different groups of PAHs to the $\sum_{15}\text{PAHs}$ (Fig. 5) shows that, as a percentage, their proportion is very irregular. In all of the studied samples, the largest percentage ($> 30\%$) of PAHs has four rings in its structure. The group of heavy PAHs with six rings has the smallest percentage ($< 10\%$). It should be noted that the most contaminated sample KB8 is cardinaly different in its composition from all the others samples. The proportion of two-ring PAHs here is the highest ($> 25\%$), while the proportion of heavy four- and six-ring PAHs is lower than the rest of the samples.

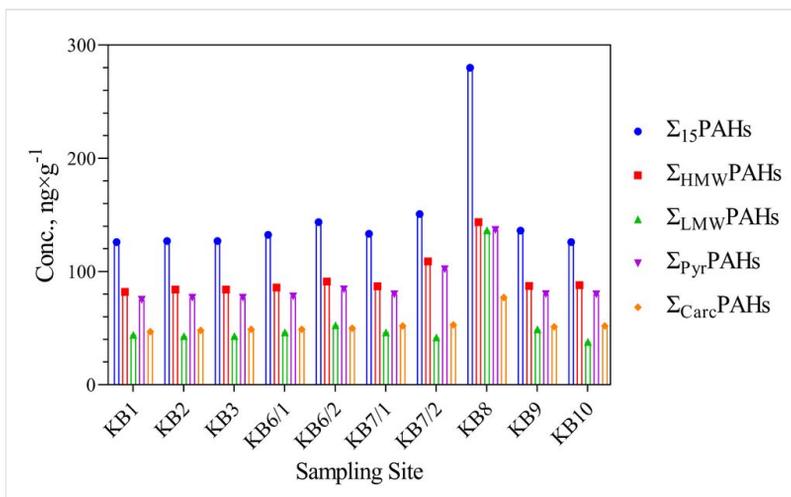


Figure 4.

Summary of concentrations of different PAH groups.

$\Sigma_{HMW}PAHs$ – FLT, PYR, BaA, CHR, BbF, BkF, BaP, DBA, BPE, IPY.

$\Sigma_{LMW}PAHs$ – NAP, ANA, FLU, PHE, ANT.

$\Sigma_{Pyr}PAHs$ – FLT, PYR, BaA, CHR, BbF, BkF, BaP, BPE, IPY.

$\Sigma_{carc}PAHs$ – NAP, BaA, CHR, BbF, BkF, BaP, DBA, BPE, IPY

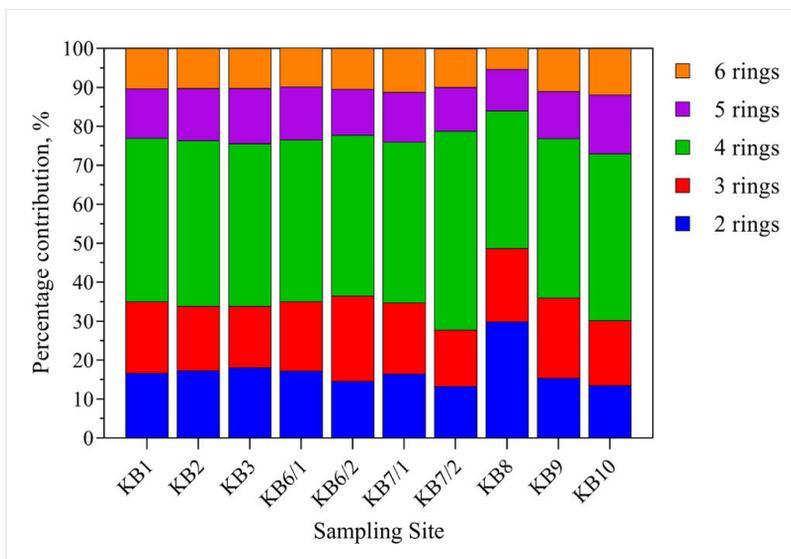


Figure 5.

Composition of PAHs with different numbers of rings in proportion to the $\Sigma_{15}PAHs$.

PAH groups include compounds with 2 rings: NAP; 3 rings: ANA, FLU, PHE, ANT; 4 rings: FLT, PYR, BaA, CHR; 5 rings: BbF, BkF, BaP, DBA; 6 rings: BPE, IPY.

Possible source identification

The application of indicator (isomer) ratios of concentrations of individual PAHs has shown quite interesting results about the possible sources of PAHs. Fig. 6 shows the results of calculations of isomeric ratios. According to the classification which was described earlier, the ANT/(ANT + PHE) ratio values indicate the nature of origin of these PAHs associated with combustion processes in samples KB1, KB2, KB3, KB7/1, KB7/2 and KB10, as the ratio values >0.10. For the remaining samples, the possible source of PAHs is explained by natural processes. Based on the values of the FLU/(FLU + PYR) ratio, the sources of PAHs are baseline (ratio value <0.40). The possible source of BaA and CHR in the KB8 sample is of mixed origin (ratio value 0.20-0.35) and, for all other samples, the sources of PAHs are combustion processes (ratio value >0.35).

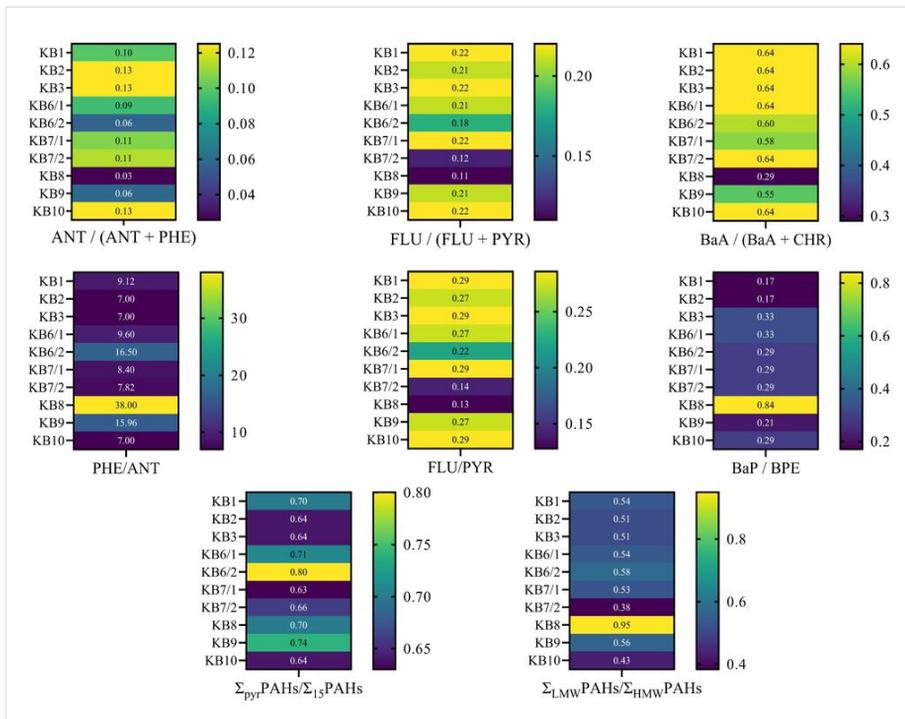


Figure 6. Values of the selected PAH isomer ratios.

The PHE/ANT ratio value indicates a possible petrogenic source of PAHs in samples KB6/2, KB8, and KB10 (ratio values <10). For all other investigated samples, the sources of PAHs are pyrolytic processes (value <10). The value of the FLU/PYR ratio (similar to FLU/(FLU + PYR)) indicates the petrogenic (baseline) origin of these PAHs (value <1.0). The origin of BaP and BPE, as can be seen from the value of their ratios, is predominantly of a non-traffic nature. Only for the KB8 sample, the possible source of these PAHs is

traffic. The wider and more complex isomer ratios as $\sum_{\text{Pyr}}\text{PAHs}/\sum_{15}\text{PAHs}$ and $\sum_{\text{LMW}}\text{PAHs}/\sum_{\text{HMW}}\text{PAHs}$ indicate a mixed and pyrogenic source of the studied PAHs.

The construction of cross-sectional graphs (bi-plots) of isomeric ratios allows a more detailed study of the possible sources of PAHs (Fig. 7). As can be seen in the graph of BaP/BPE and ANT/(ANT + PHE) ratios, the origin of PAHs in most samples has a mixed genesis; for example, in sample KB8, the source of these PAHs are non-traffic processes associated with combustion. In a similar plot of BaP/BPE and PHE/ANT ratios, the PAHs in the KB8 sample have a non-traffic petrogenic source.

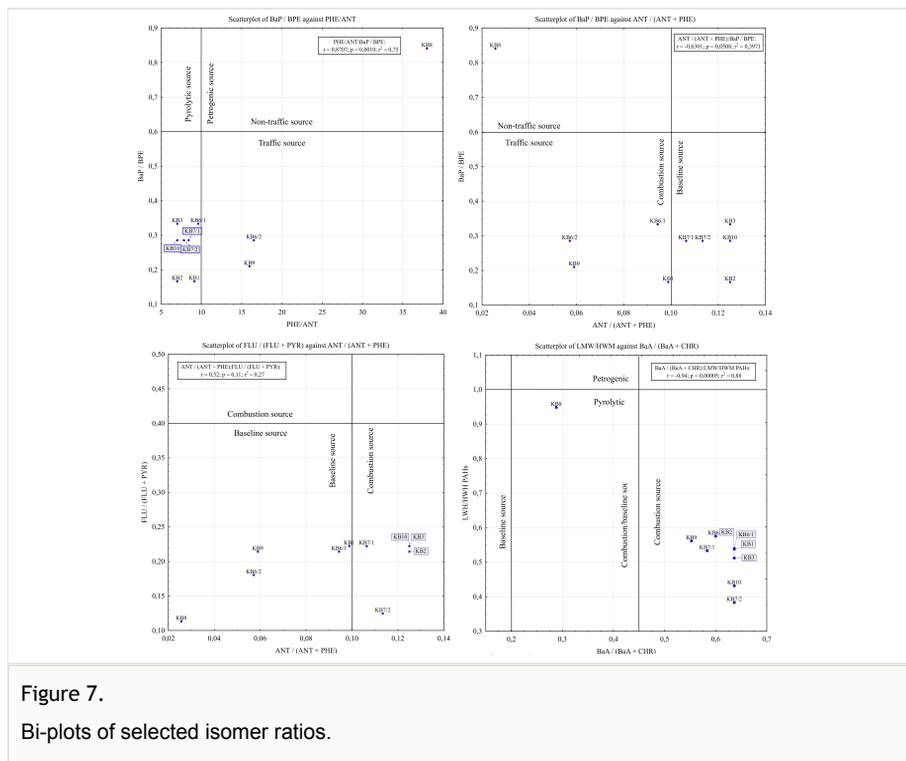


Figure 7.

Bi-plots of selected isomer ratios.

Cross-analysis of $\text{FLU}/(\text{FLU} + \text{PYR})$ and $\text{ANT}/(\text{ANT} + \text{PHE})$ ratios shows that these PAHs in samples KB8, KB6/2, KB9, KB6/1 and KB1 are of petrogenic (baseline) source. For the remaining samples, the possible source of these PAHs is combustion processes. A similar check for the ratios $\sum_{\text{LMW}}\text{PAHs}/\sum_{\text{HMW}}\text{PAHs}$ and $\text{BaA}/(\text{BaA} + \text{CHR})$ indicates a pyrolytic source of PAHs in all samples except KB8, which shows a mixed source.

Potential toxicity

The calculation of BaP-equivalents has shown (Fig. 8) that, for most PAHs, the potential toxicity is lower than the limits adopted in the Russian Federation ($20 \text{ ng} \times \text{g}^{-1}$). Only the content of DBA in all the samples studied stands out; the conversion of the concentrations of this PAH into BaP-equivalents showed that its content level is equivalent to $35\text{--}40 \text{ ng} \times \text{g}^{-1}$

of BaP. It should also be noted that the maximum BaP-equivalents of individual PAHs were recorded in the KB8 sample. Here the maximum BaP equivalents of such PAHs are NAP – 0.084, PHE – 0.04, CHR – 0.173, BbF – 1.273 and BkF – 0.418 $\text{ng}\times\text{g}^{-1}$.

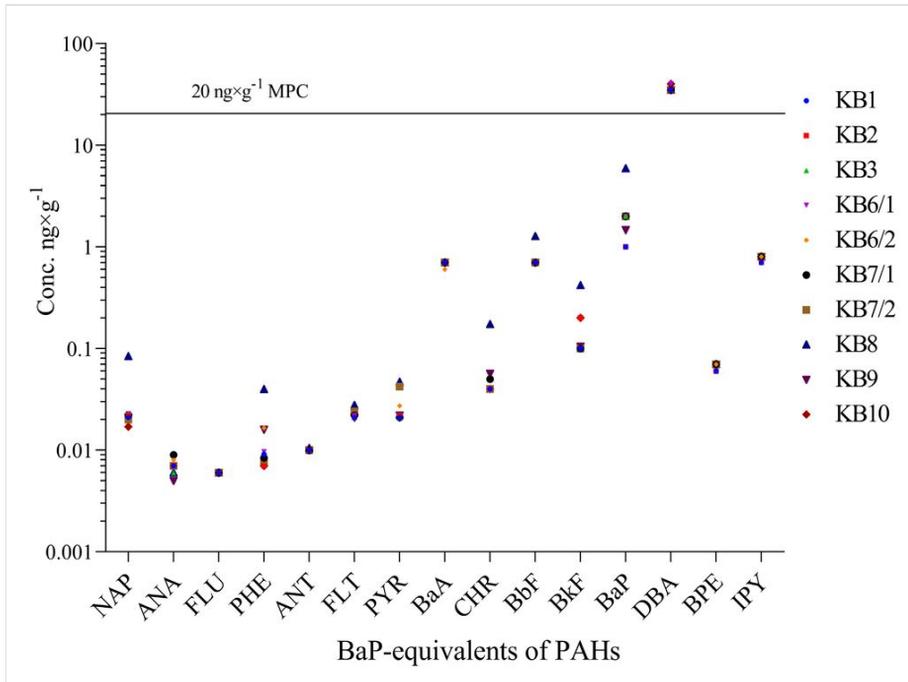


Figure 8.

Concentrations of studied PAHs in BaP-equivalents.

MPC – maximum permissible concentration of BaP in soil (in Russian Legislation)

When converting the sum of PAHs to BaP-equivalents, we can see (Fig. 9) that, for all points without exception, the BaP-equivalent toxicity exceeds the limits ($20 \text{ ng}\times\text{g}^{-1}$). For samples KB6/1, KB8 and KB10, the total, equivalent BaP concentration exceeds the MPC by more than two times.

Discussion

Currently, rapid deglaciation is observed in most of the mountain regions of the world. This process is also pronounced in the Central Caucasus area, where about 94% of glaciers are retreating (Stokes et al. 2017). Glaciers at Mt. Elbrus lost about 5% of their total area from 1987 to 2010 (Shahgedanova et al. 2014). During the retreat of glaciers, cryoconite usually increases in size and accumulate more pollutants, including PAHs, due to attraction from additional black carbon and mineral particles (Zhang et al. 2020). Sequestration of organic contaminants, such as PAHs by cryoconite, is closely connected with the presence of black carbon. During the complex chemical process of incomplete combustion of fossil fuels

under the condition of lack of oxygen, molecules of polycyclic aromatic hydrocarbons are involved in the formation of black carbon precursors (Bond et al. 2013). Then they coagulate to a size sufficient to act as a core and grow as a result of subsequent reactions on the surface. Moreover, it has been mentioned that black carbon provides a crucial role in the binding of polycyclic aromatic hydrocarbons in the environment (Weiland-Bräuer et al. 2017). It is especially noticeable in the polar and high-mountain regions due to cold condensation and deposition of black carbon.

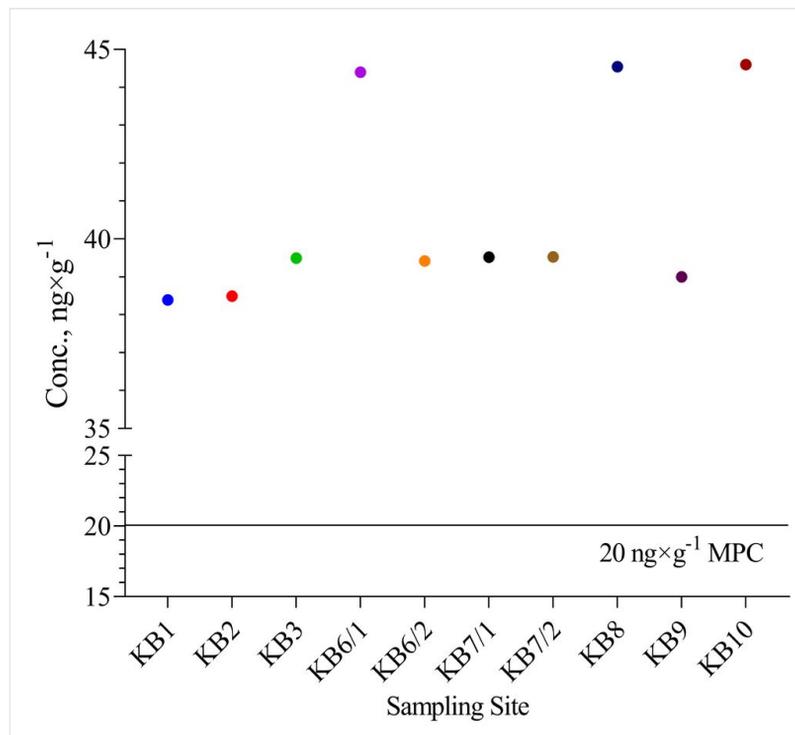


Figure 9.

BaP-equivalents of the Σ_{15} PAHs in the samples studied.

MPC – maximum permissible concentration of BaP in soil (in Russian Legislation)

It was previously thought that the concentration of PAHs in soils and sediments is connected with anthropogenic pressure in the surrounding area. Contamination levels of sediments in the China Sea decreased while moving to the south, away from the more industrialised northern part of China with higher levels of atmospheric emissions (Li and Duan 2015). This was also observed in Antarctica (Abakumov et al. 2021) where the content of individual PAHs was up to $170 \text{ ng}\times\text{g}^{-1}$ (for NAP) in the vicinity of “St. Kliment Ohridski” Antarctic Station, while at the control site, these values did not exceed $30 \text{ ng}\times\text{g}^{-1}$ (Aislabie et al. 1999). Some of the PAHs originated from nearby sources, such as automobile roads and some of them were mostly carried by wind over a long distance (Abdel-Shafy and Mansour 2016). As it was mentioned earlier (Litvinova 2020), the

Caucasus Region is an important destination for tourists. This fact is associated with development of tourism facilities, transport services, construction and combustion of fossil fuels. KB8 study point is located at Garabashi glacier, on the southern slope of Mt. Elbrus, which is the most popular place in the Central Caucasus Region for tourists. At the foothills, there are lots of hotels and cafes which burn wood and coal for heating and cooking. Moreover, the automobile road to the cable-way definitely leads to increased hydrocarbon emission from the traffic as was observed in the North Tibetan Plateau (Yuan et al. 2016). The highest content was defined for NAP which also proves the theory that traffic is the major source of PAHs due to the fact that NAP is the main component of gasoline and diesel engine fuel (Soltani et al. 2015). The study points KB1-3 are located on the other side of the Baksan Gorge, far away from roads and tourist routes. Thus, we can consider them as background values. It was previously noted that Elbrus Region is influenced by both allochthonous and autochthonous input of contaminated material (Łokas et al. 2018) which represents a basis for cryoconite formation. The local contamination is mostly associated with tourism activities, while allochthonous material is transported from northern Africa and the historical Mesopotamia area (Kutuzov et al. 2015). In these regions, atmospheric emissions of PAHs are mostly connected with ship routes and harbours (Khairy et al. 2009), as well as with petrochemical production (Abbasi et al. 2019) and high-urbanised areas (Saeedi et al. 2012). Moreover, Mesopotamia is considered as an important agricultural region where additional emissions of atmospheric PAHs are possibly due to open-burning of biomass during land preparation and crop residue disposal (Ravindra et al. 2008). With long-distance transfer, it might be an additional source of pollutants. Statistical processing of our data shows that anthropogenically loaded cryoconites are the most contaminated material which may influence downstream waters and soils pollution status due to release of organic contaminants, stored on the glacier's surface, during the intensive melting period as has been observed in the Italian Alps (Bizzotto et al. 2009).

In previous research at the Tibetan Plateau (Li et al. 2017), the total concentration of PAHs in cryoconite ranged from $6.67 \text{ ng}\times\text{g}^{-1}$ to $3906.66 \text{ ng}\times\text{g}^{-1}$ with the lowest amount in the middle part of the Tibetan Plateau which is the most remote from the industrial region. In Himalayas, the total amount of PAHs in surface sediments ranged between $14.54 \text{ ng}\times\text{g}^{-1}$ and $437.43 \text{ ng}\times\text{g}^{-1}$ (Riaz et al. 2019) and in soils of the Pyrenees, the average concentration was $400 \text{ ng}\times\text{g}^{-1}$ (Quiroz et al. 2010). The most noticeable in our results is that, in almost all studied samples, HMW PAHs dominated amongst PAHs groups, while, in the KB8 sample, the amount of LMW PAHs and HMW PAHs was nearly similar. HMW PAHs are usually considered as a result of industrial activities, while LMW PAHs indicate natural petrogenic origin (Sazykin et al. 2019). However, in the KB8 sample, NAP is dominant amongst LMW PAHs which mostly originate from engine fuels (Soltani et al. 2015). Furthermore, LMW polyarenes are usually transported over a long distance by atmospheric winds, while HMW PAHs tend to be from local deposition (Tobiszewski and Namieśnik 2012). This may indicate the allochthonous input of LMW PAHs to the Central Caucasus. The total concentration of HMW PAHs is mostly similar to the total concentration of carcinogenic PAHs due to the fact that most of the high molecular weight PAHs have carcinogenic and mutagenic properties (Pozdnyakova 2012).

The calculation of isomeric ratios and construction of cross-sectional graphs show that PAHs entered the Elbrus Region with atmospheric winds, as well as due to local anthropogenic activities. We conducted several calculations of isomeric ratios; however, the most reliable are less wide and less complex due to possible differences in transformation of PAHs compounds in various environmental conditions (Khaustov and Redina 2018). The possibility of the petrogenic source for most of the samples from the contaminated Garabashi glacier was defined by calculation of the PHE/ANT ratio values. The possible source here is leaks of oil and oil products from vehicles and local households. This source of petrogenic PAHs was mentioned previously in the study of Soclo et al. 2000) in Benin and France where the main sources of petrogenic PAHs in sediments were waste oils from mechanic shops and delivery of petroleum products. On the other hand, according to BaP/BPE ratios, it is possible that traffic is a source of PAHs for the KB8 study sample, which is located nearby the automobile road. Other study points are probably polluted by PAHs, which are not related to traffic processes, according to the calculation of isomeric ratios.

Constructed bi-plots give us a mostly similar view on the sources of PAHs. Most of them indicate a pyrolytic source, associated with traffic, in all of the studied samples with the exception of KB8, which shows a mixed genesis. There is a similar result, obtained from calculation of $\sum_{LMW}PAHs/\sum_{HMW}PAHs$ isomeric ratios. Here, we can say that KB8 is the most polluted sample due to both deposition of the polluted material from the atmosphere, coming mostly from the Mesopotamia Region and closeness to the local anthropogenic pollution sources. The constructed cross plots of diagnostic ratios for cryoconite in the Tibetan Plateau showed the main source of PAHs was combustion of biomass, coal and fossil fuels, including traffic (Li et al. 2017). The previous study in the Himalayas soils (Devi et al. 2016) indicated mixed sources of PAHs pollution both from combustion and petroleum contamination.

For estimation of potential toxicity, BaP-equivalence calculation has been conducted due to the fact that not all of the studied pollutants have a maximum permissible concentration (MPC). The method of BaP-equivalence calculation has a long practice and is applied all over the world. It is tightly connected with the calculation of TEF and toxic equivalent concentration (TEQ) (Nisbet and LaGoy 1992). Due to different climatic and environmental conditions in the world, we decided to use the standard adopted for the Russian Federation territory (Federal Service for Supervision of Consumer Rights Protection and Human Well-Being of the Russian Federation 2006). In this document, monitoring of PAHs in the environment is based on the control of 3-4 benzo(a)pyrene. In all studied points, the concentration BaP-equivalents of individual PAHs did not exceed the threshold values with the exception of KB8. However, the sum of PAHs in BaP-equivalence shows that the Benzo[a]pyrene equivalent toxicity exceeds the MPC ($20 \text{ ng}\times\text{g}^{-1}$) in all study points (up to $45 \text{ ng}\times\text{g}^{-1}$), which might be dangerous for the environment and humans. In the Tibetan Plateau (Li et al. 2017), these values for cryoconite mostly were in the range between $1.34 \text{ ng}\times\text{g}^{-1}$ and $14.34 \text{ ng}\times\text{g}^{-1}$, with one exception of $281.32 \text{ ng}\times\text{g}^{-1}$. It is well known that polluted material from the surface of the glacier, such as supraglacial sediments, usually enters soils at the foothill areas during the melting period with water streams (Glazovskaya

2005). That is why PAHs concentration in BaP-equivalents is similar between KB8 and KB10 cryoconite samples and the KB6/1 soil sample. Thus, it is important to understand how PAHs from cryoconite could influence toxicity levels of mountain soils.

It is well known that climate change in high-mountain regions is more pronounced than the global average (Mountain Research Initiative EDW Working Group 2015) and, therefore, it is interesting to discuss how PAHs may react to these changes. In high-mountain areas, soils act as a storage for organic pollutants; however, due to global warming, both temperature rise and variations in soil organic matter would drive the remobilisation of organic pollutants in cold regions, as well as change the direction of exchange between soil and atmosphere (Wang et al. 2012, Cabrerizo et al. 2013). Another consequence is change of the hydrological regime: an earlier start of the melting period and higher rate of liquid precipitation (Kohler and Maselli 2008) may cause increased input of contaminants to adjacent downstream territories. Previous study (Tao et al. 2017) indicated that climate change in cold territories could lead to lower bioaccumulation, but higher biomagnification of PAHs in the food web. Moreover, climate change could modify the insolation rate due to change of cloud cover which may transform the composition of PAHs because of the difference in photochemical oxidation. In the study of Quiroz et al. 2010), a decrease in chemically-labile compounds was observed in BaA and BaP in areas with more significant light input. Moreover, recent studies (Bergauer et al. 2005, Weiland-Bräuer et al. 2017) have noted various psychrophilic hydrocarbon-degrading microorganisms in cryoconite sediments and soils which have a high potential for bioremediation. Temperature rise could lead to development of these communities, as well as to shift to another set of microorganisms. Therefore, more studies of this broad question are needed to understand the reaction of high-mountain ecosystems to the global climate change.

Conclusions

As can be seen from this work, the role of cryoconites as biogeochemical markers can be used. The conducted study shows the contamination of cryoconite, soils and some other materials by 15 high-priority polycyclic aromatic hydrocarbons. The highest contamination levels were defined for NAP ($84 \text{ ng} \times \text{g}^{-1}$), PHE ($40 \text{ ng} \times \text{g}^{-1}$) and PYR ($47 \text{ ng} \times \text{g}^{-1}$), the lowest was defined for ANT (about $1 \text{ ng} \times \text{g}^{-1}$). The most polluted material is a cryoconite from Garabashi glacier ($\sum_{15} \text{PAHs} = 280 \text{ ng} \times \text{g}^{-1}$) which is a result of both local anthropogenic activities and long-distance transfer. Amongst most of all studied samples, HMW PAHs are dominating with the exception of the most polluted point which indicates mixed input of PAHs, local petroleum leaks and closeness to vehicles emissions. The most common sources of PAHs in studied materials are combustion processes and mixed pyrolytic/petrogenic origin. Local anthropogenic influence is associated with tourism development, while long-distance transfer is probably connected with combustion of biomass and shipping routes. Toxicity levels of separate polycyclic aromatic hydrocarbons did not exceed the maximum permissible concentration values in most cases. On the other hand, the sum of PAHs in BaP equivalents exceeded the threshold values in all samples, where some of them were twice higher. It was found that contamination of cryoconite may affect

the toxicity levels of soils at the foothills through transfer of material by water streams. Thus, further research is required to understand the impact of PAHs on the vulnerable environment of the Central Caucasus mountain region.

Grant title

Russian Foundation for Basic Research, project No. 19-05-50107.

Author contributions

E. A. conceptualised the article, I. K. wrote the article, T. N. performed analysis of the data, R. T. sampled studied materials and contributed to the interpretation of the results. All authors discussed the results and commented on the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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