



Polycyclic Aromatic Hydrocarbons and Potentially Toxic Elements in Soils of the Vicinity of the Bulgarian Antarctic Station “St. Kliment Ohridski” (Antarctic Peninsula)

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The investigation conducted was dialed to quantitative and qualitative evaluation of 15 priority polycyclic aromatic hydrocarbons (PAHs) and Potentially Toxic Elements (Cu, Pb, Zn, Cd, Ni, and Cr) in soils and cryoconites on “St. Kliment Ohridski” Antarctic station territory and its vicinities. Estimation of benzo(a)pyrene (BaP)–equivalents, PAHs and different PAHs isomer pair ratios were used for identification of general toxicity, nature and origin of individual PAHs and their groups. Total concentrations of PAHs in BaP–equivalents showed, that $\sum_{15} \text{PAH}$ of all selected points was higher than the threshold concentration ($20 \mu\text{g} \times \text{kg}^{-1}$ –Russian environmental legislation) for benzo(a)pyrene. Different PAHs isomer ratios showed the natural (petrogenic) source of PAHs at all soils examples (except Cryosol Toxic Transportic). The maximum content among potentially toxic elements was recorded for Zn ($75.7 \text{ mg} \times \text{kg}^{-1}$ at L26), the minimum for Cd ($0.201 \text{ mg} \times \text{kg}^{-1}$ at L1A). Average concentrations of potentially toxic elements are generally lower compared to the results of previous studies. Application of I_{geo} index, characterizes the majority of the studied soils as unpolluted or practically unpolluted. Data obtained indicates that there is no current critical anthropogenic load on the environmental components of the landscapes investigated.

Keywords: livingston island, isomer ratios, trace metals, pollution assessment, geoaccumulation index, sources

INTRODUCTION

Nowadays the Antarctica is one of the most interesting and informative environmental model for evaluation of possible contaminants accumulation in pristine ecosystems. This territory was not intensively affected by human and therefore it can be used as reference area for adaptation and harmonization of threshold concentrations and evaluation of current contamination rates (Tin et al., 2009).

The challenges of nature conservation in Antarctica indicated in the Protocol on Environmental Protection (Madrid Protocol, 1998), faced with the necessity of regulation and implementation of environmental management in vicinities of the Antarctic stations with aim to decrease of hydrocarbons combustion effects and further accumulation of polycyclic aromatic compounds in the components of cryogenic ecosystems of Antarctica. In order to understand the amount of combusted fuel at the stations, data of the expedition of the Bulgarian Antarctic Institute in

2012–2013 can be exemplified and taken into account for further evaluation. With aim to support the expedition, 5000 L of diesel liquid fuel were brought to the «St. Kliment Ohridski» station (December 14, 2012–February 25, 2013) (BAI, 2013). Other authors noted that the stations of the year-round stay (station Bellingshausen) can spend up to 150 000 L of diesel fuel per year (Abakumov et al., 2015).

The use of fossil fuels with current techniques leads to regular spilling of oil products that contaminate the surface and soils of terrestrial environments, inland and oceanic waters (Kennicutt et al., 1991; Waterhouse, 2001; Aislabie et al., 2004; Frenot et al., 2005). Numerous logistic aspects in Antarctic region result in waste disposal management, which often leads to the sporadic transportation of the untreated sewage into the ocean and on the territory around the stations (Connor, 2008; Tin et al., 2009; Martins et al., 2010).

Data obtained in previous researches showed that the large fuel spills from transport and tourist vessels have been occurring since the 80s of the 20th century. For example, in 1987 there was a spilling effect of 600,000 L diesel fuel near United States Palmer Station, Antarctic Peninsula (Aronson et al., 2011). The spills of hydrocarbon compounds and exhaust gases are the cause of chemical contamination the terrestrial Antarctic ecosystems, which is the most characteristic environmental impact of human activities in Antarctica (Chen and Blume (1997), Aislabie et al. (2004), Bargagli (2006)). Several chemical and biological studies conducted recently have shown the presence of atypical chemical contaminants such as Potentially Toxic Elements (PTEs), Polychlorinated Biphenyl (PCB) Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Dibenzodioxins (PCDDs) in soils, coastal waters, micro and macroorganisms (Snape et al., 2001; Negri et al., 2006; Hale et al., 2008; Martins et al., 2010; Abakumov et al., 2014; Abakumov et al., 2015; Pourret and Hursthouse, 2019).

Human and animal activities played an important role in PAHs distribution in the soil (Na et al., 2020). Among chemical pollutants, polycyclic aromatic hydrocarbons (PAHs) and trace metals have a special place, as they can enter the Antarctic not only through local discharges and emissions, but also through transboundary transfer from tropical and temperate regions of the southern hemisphere (Aislabie et al., 1999; Bargagli, 2006; Bargagli, 2008; Abakumov et al., 2014). Polycyclic aromatic hydrocarbons represent organic compounds of benzene series differing in the number and position of benzene rings showed mutagenic and carcinogenic effects. The higher molecular weight PAHs (MW > 202) with 4–6 benzene rings are frequently related to burning processes and are highly toxic to organisms due to their carcinogenic and mutagenic potential (Yunker et al., 2002; Yang et al., 2008; Martins et al., 2010). PAHs are known as mobile compounds that tend to be dispersed in the biosphere. There are PAHs of natural and anthropogenic origin that are included in the permanent monitoring list by the EU and United States Environmental Protection Agency (Baek et al., 1991; Nisbet and Lagoy, 1992; Howsam and Jones, 1998). In the Polar Regions with low temperatures, PAHs are less subjected to microbial degradation; therefore, they are deposited and

preserved in soils and cryoconite (Lodygin et al., 2008; Hodson, 2014; Abakumov et al., 2015; Cook et al., 2016).

The proportion (isomer pair ratios) between concentrations of natural and anthropogenic PAHs can serve as an index of the anthropogenic influences of soil and can be used as tracers to identify possible sources of PAH (Pandey et al., 1999; Yunker et al., 2002; Li et al., 2017).

Potentially Toxic Elements can be transported over long distances through the atmospheric circulation, and eventually deposited through dry and wet deposition to the Antarctic regions (Bargagli, 2006, 2008; Trevizani et al., 2018; Liu et al., 2021). They were determined in fossil fuels contaminated soils in different regions of Antarctica (Padeiro et al., 2016; Smykla et al., 2018; Alekseev and Abakumov, 2020; Gran-Scheuch et al., 2020). Also these elements have carcinogenic and mutagenic effects and can damage cellular membranes, proteins, enzymes, and DNA (Beyersmann and Hartwig, 2008; Ali et al., 2013; Padeiro et al., 2016).

The main goal of this work is to estimate the level of pollution of soils and cryoconites with potentially toxic elements and polycyclic aromatic hydrocarbons on the territory of the Bulgarian Antarctic Station «St. Kliment Ohridski» and its vicinity (Livingstone Island, South Shetland Islands, Antarctic Peninsula). In abovementioned context this research was aimed: 1) to estimate the concentrations of 15 PAHs and 6 potentially toxic elements, 2) to assess the contamination of soils with PAHs, their benzopyrene equivalents were calculated, as well as to calculate various isomeric ratios of PAHs, in order to identify their possible source of origin and 3) to assess the nature of soil contamination by potentially toxic elements, we calculated a geoaccumulation index (*I_{geo}*).

MATERIALS AND METHODS

The study was performed on 11 soil and cryoconite samples taken at the Bulgarian Antarctic Station «St. Kliment Ohridski» on Livingstone Island (region of Antarctic Peninsula, Western Antarctica) during the Bulgarian Antarctic expedition realized from December 21, 2019 till January 6, 2020. The precise coordinates of the sampling points and geographic description of the area are presented in **Table 1**.

The soils were collected from the 0–10 cm depth and cryoconites from cryoconite holes, all samples were saved in polyethylene bags, then was transported to the station laboratory air dried, after what the artificial remnants and roots have been removed, soils have been sieved through 2 mm and transported to Saint-Petersburg State University laboratories in polyethylene bags.

The Livingstone Island is located at 62°38'29"S and 60°21'53"W (**Figure 1**). The «St. Kliment Ohridski» station situated 88 km southwest of station Bellingshausen (King George Island), 796 km southeast of Diego Ramirez Islands (the southernmost land of South America), 2,96 km of Spanish summer station «Juan Carlos I», 28, 55 km from Chilean–United States station «Shirreff Base» (Ivanov, 2015).

TABLE 1 | Sampling points coordinates, geographic description and soil type of the study area (WRB, 2015).

No of point	Name	Coordinates	Sea altitude, m	Sampling site description.	
				Soil name.	
1	L1E	S 62° 38' 49.4" W 60° 22' 17.2"	35	Sea Lion Hill. Under the skua nest, close to the lake Sea Lion. No presence of sulfur is identified, folic, ornitic.	Soil name: Cryosols, not gleyic, Leptic Stagnic
2	L1A				
3	L1C				
4	L21	S 62° 38.468' W 60° 22.852'	–	Playa Bulgaria Volcanic black colored material from the cryoconite hole	
5	L28	S 62° 39.245' W 60° 36.442' S 62°38.872' W 60°20.701'	4	Hanna Point. 2 soil pits: under <i>Deschampsia</i> (<i>Deschampsia antarctica</i>) and under <i>Praciola crispa</i> (<i>Colobanthus quitensis</i>).	Soil name: Cryosol Leptic Ornitic Hyperscetelec
6	L10		458	Krumov Kamak. Rock formation surrounded by glacier.	Soil name: Cryosols Turbic Regolith without any additional indicators
7	L6	S 62°38.180' W 60°21.493' S 62°38'29"	5	Española Hill. Location on recently formed oritogenic environment on the seacoast mall, parent materials composed by sandy textured fine earth and oval stones of marine genesis.	Soil name: Cryosols ornitic
8	L26	W 60°21'53" S 62°38'06.9"	–	Main House.	Soil name: Cryosol Toxic Transportic
9	L2		1	Sinemorets Hill. NW part of Playa Bulgara top of the hill ridge, no vegetation, sporadic distribution of the lichens, flat areas, surrounded by big remnants of weathering of rocky parent materials, close to the lake; surface, covered by angular stones of irregular form.	Soil name: Cryosol Turbic Gleyic
10	L22	W 60°21'14.7" S 62° 39.251' W 60° 36.531'		Hanna point Volcanic black colored material from the cryoconite hole	
11	L9	S 62°38.073' W 60°20.962'	4	End of the Bay. First marine terrace covered by mosses, <i>Deschampsia</i> (<i>Deschampsia antarctica</i>). The terrace is composed by debris, many fine sediments and tephra, mixed with angular and oval stones. Indication of complicated genesis.	Soil name: Cryosols Leptic Folic (Umbric)

The first permanent (no wintering) station on Livingstone Island was the Spanish one “Juan Carlos I” (62°39'46"S, 60°23'20"W), built from 7 to January 11, 1988 (Ivanov, 2015). Another scientific base on Livingstone Island is the Chilean–United States facility Shirreff Base (62°28'12"S, 60°46'17"W), with its two sections named Guillermo Mann Base and Shirreff Field Station, and opened in 1990/91 and 1996/97, respectively, (CEP, 2011). The Bulgarian station appeared a few years later than the Spanish one. The “St. Kliment Ohridski” base was opened during the 1993/94-summer season on the Livingstone Island. Infrastructure of station includes kitchen, messroom, living rooms, food storage, toilets and bathrooms.

All three bases are permanent settlements, although inhabited only during the summer season, with accommodation capacity for a total of 54 persons. In particular, most of the solid waste is shipped for dumping outside Antarctica, with incineration gradually phased out. As elsewhere in Antarctica, the island's bases use electricity produced mostly by diesel generators (Ivanov, 2015).

The Geoaccumulation Index (I_{geo}) allows us to classify seven levels (Table 2) of soil contamination, from Practically unpolluted ($I_{geo} \leq 0$) to Extremely polluted ($I_{geo} > 5$) (Muller, 1979; Jiang et al., 2019). The generic calculation formula is as follows:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \quad (1)$$

where C_n —the measured concentration of the element in soil, B_n —the geochemical background value.

The content of Potentially Toxic Elements was determined following the standard ISO 11047–1998 “Soil Quality–Determination of Cadmium (Cd), Cobalt (Co), Copper (Cu), Lead (Pb), Manganese (Mg), Nickel (Ni), and Zinc (Zn) in Aqua Regia Extracts of Soil - Flame and Electrothermal Atomic Absorption Spectrometric” method at Atomic absorption spectrophotometer Kvant 2M (Moscow, Russia) (ISO, 1998).

The concentrations of 15 PAHs—naphthalene (NAP), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), 3,4-benzo(a)pyrene (BaP), dibenzo (a,h)anthracene (DBA), dibenzo (g,h,i)perylene (BPE), and indeno (1,2,3-c,d) pyrene (IPY) in soils and cryoconites on the territory of Bulgarian Antarctic base and its vicinities were determined on the basis of State Standard (GOST R 8.563–96), which is based on method Flyuorat-02–Panorama, Russia (GOST, 1996).

Extraction of PAHs was carried out at room temperature with a mixture of hexane-acetone (1:1) with ultrasonic treatment of the extraction system in an ultrasonic bath Branson 5510 (United States) (EPA, 2007). PAHs fraction was cleaned by using column chromatography on silica gel (SW, EPA, 1996). Qualitative and quantitative determination of PAHs in soils was carried out by the method of reversed-phase high-efficiency liquid chromatography in the gradient mode and

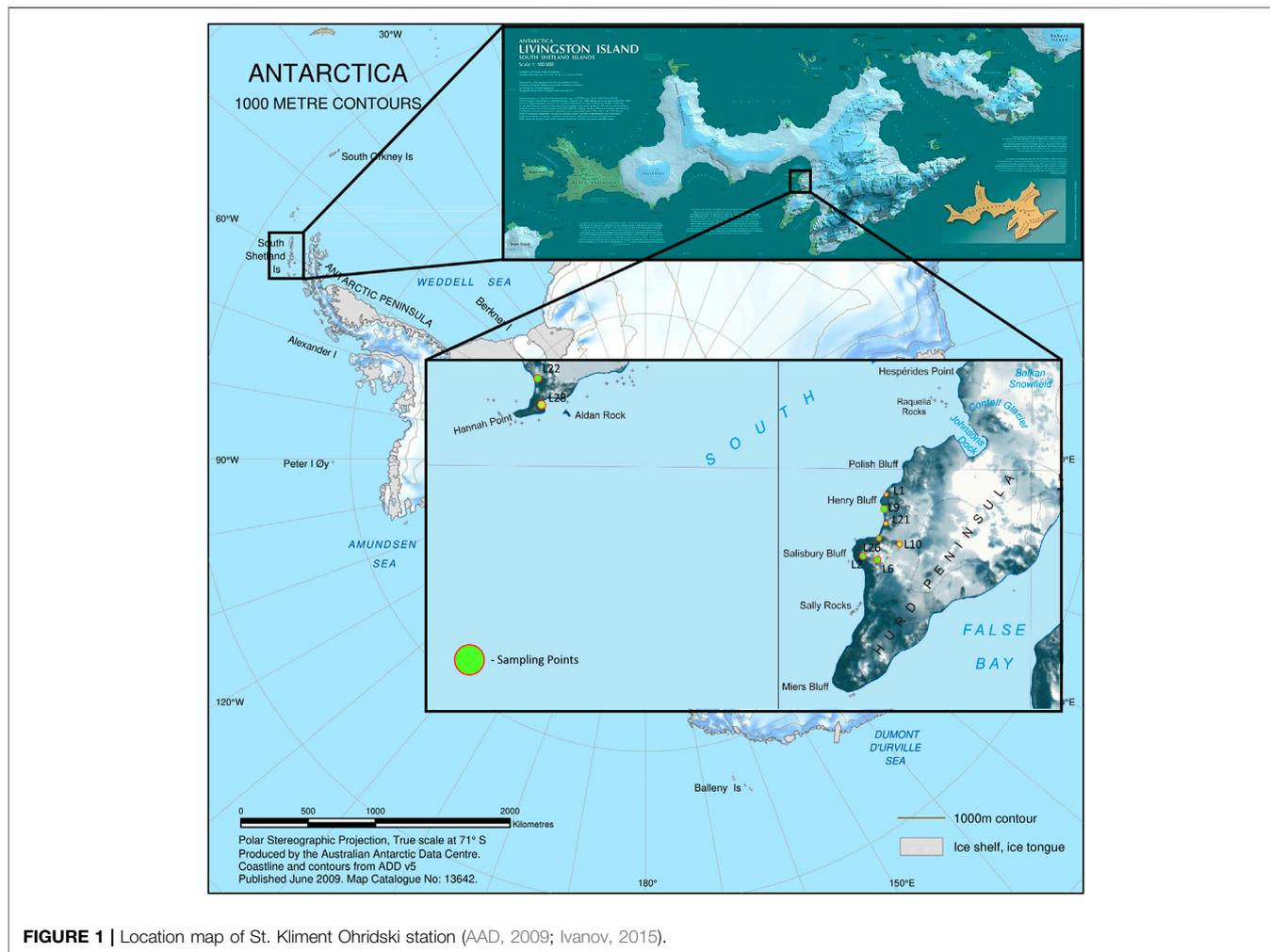


FIGURE 1 | Location map of St. Kliment Ohridski station (AAD, 2009; Ivanov, 2015).

TABLE 2 | Classification of I_{geo} value

			References
Classification	$I_{geo} \leq 0$	Practically unpolluted	Muller (1979), Jiang et al. (2019)
	$0 < I_{geo} \leq 1$	Uncontaminated to slightly polluted	
	$1 < I_{geo} \leq 2$	Moderately polluted	
	$2 < I_{geo} \leq 3$	Moderately to highly polluted	
	$3 < I_{geo} \leq 4$	Highly polluted	
	$4 < I_{geo} \leq 5$	Highly to extremely polluted	
	$I_{geo} > 5$	Extremely polluted	

spectrofluorometric detection on the chromatograph “Lumahrom” (“Lumex”, Russia). Chromatography was performed at a temperature of 30°C on a column of Supelco Supelcosil™ LC-PAH 5 μm (25 cm × 2.1 mm). The acetonitrile–water gradient was used as a mobile phase. Sample volume of 10 μl was introduced with the help of a dosing crane. Individual PAHs were identified with chromatography mass spectrometry (spectrograph model: Shimadzu QP 5050A, Japan) (Gilichinsky et al., 2010). The detection limits of the studied PAHs are: NAP–16 μg × kg⁻¹;

ANA–1.5 μg × kg⁻¹; FLU–1.4 μg × kg⁻¹; PHE–2.0 μg × kg⁻¹; ANT–0.3 μg × kg⁻¹; FLT–6.7 μg × kg⁻¹; PYR–6.7 μg × kg⁻¹; BaA–1.5 μg × kg⁻¹; CHR–0.8 μg × kg⁻¹; BbF–1.4 μg × kg⁻¹; BkF–0.3 μg × kg⁻¹; BaP–0.3 μg × kg⁻¹; DBA–1.8 μg × kg⁻¹; BPE–1.6 μg × kg⁻¹; IPY–6.7 μg × kg⁻¹. Identification of PAHs was carried out by retention times and comparison of fluorescence spectra of components released the column with standard PAHs spectra. The quantitative analysis of PAHs was carried out using the external standard method. To assess the accuracy of the method, the above-described analytical procedure

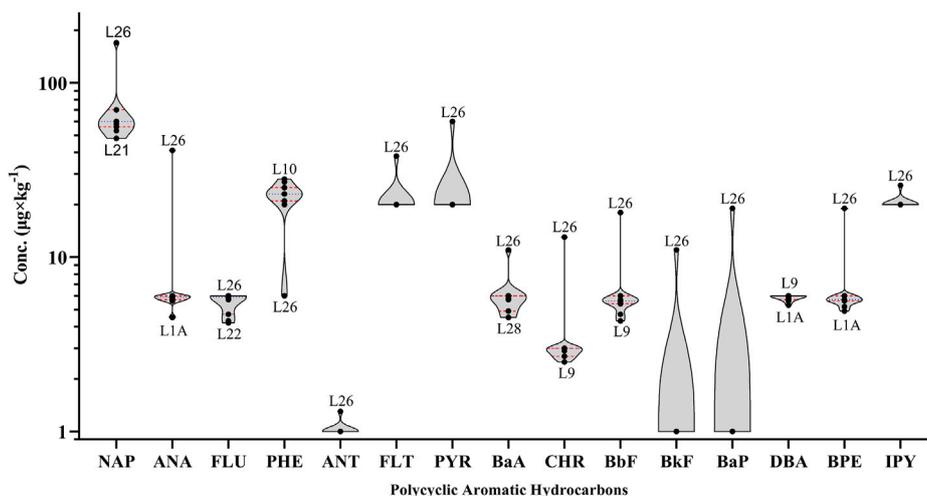


FIGURE 2 | PAHs concentrations in soils, $\mu\text{g} \times \text{kg}^{-1}$.

was subjected to the standard of bottom sediments containing surfactants (Standard Reference Material[®] 1944 New York/New Jersey Waterway Sediment -NIST, United States) (Agency, 1986; PND, 2003; Gabov et al., 2007; Gabov et al., 2008).

Statistical data processing and visualization was performed using Statsoft Statistica 12, GraphPad Prizm 9.0.0 and QGIS 3.16.

RESULTS AND DISCUSSION

Concentration and Origin of PAHs

Some data on detected PAHs concentrations in soils of Livingstone Island (Bulgarian Antarctic Station “St. Kliment Ohridski” and its vicinity) are given in the **Figure 2**. It should be noted that at all sampling points (except L26) the differences in concentrations are minor. For example, naphthalene content in non-toxic soils types varies from 48 to 70 $\mu\text{g} \times \text{kg}^{-1}$, phenanthrene (PHE) from 20 to 28 $\mu\text{g} \times \text{kg}^{-1}$ (**Figure 2**). Concentrations of other PAHs in all natural soils are almost the same. Calculated index $\sum_{15}\text{PAHs}$ for all selected samples of natural soil ranged from 170 to 200 $\mu\text{g} \times \text{kg}^{-1}$. $\sum_{7}\text{carcinogenicPAHs}$ (CHR, BbF, BkF, BaP, DBA, BPE, IPY) is 37 $\mu\text{g} \times \text{kg}^{-1}$.

The following concentrations of PAHs in soils which are not subject to anthropogenic influence were noted in the earlier research in different regions of Antarctica. McMurdo Dry Valley (control site): NAP <30 $\mu\text{g} \times \text{kg}^{-1}$, ANA <30 $\mu\text{g} \times \text{kg}^{-1}$, PHE <30 $\mu\text{g} \times \text{kg}^{-1}$, FLU <30 $\mu\text{g} \times \text{kg}^{-1}$, ANT <30 $\mu\text{g} \times \text{kg}^{-1}$, FLT <30 $\mu\text{g} \times \text{kg}^{-1}$, PYR <30 $\mu\text{g} \times \text{kg}^{-1}$, BaA <30 $\mu\text{g} \times \text{kg}^{-1}$ (Aislabie et al., 1999). Admiralty Bay, King George Island: Ulmann Point $\sum\text{PAHs}$ <10 $\mu\text{g} \times \text{kg}^{-1}$, Botany Point $\sum\text{PAHs}$ <30 $\mu\text{g} \times \text{kg}^{-1}$, Monsimet Cove $\sum\text{PAHs}$ <15 $\mu\text{g} \times \text{kg}^{-1}$ for some higher molecular PAHs (FLU, PYR, BaA, CHR, BkF, BbF, BaP, IPY, DBA, BPE) (Martins et al., 2010).

The content of PAHs in the vicinity of Russian Antarctic stations was studied by Abakumov et al. (2015); in these works, the list of identified PAHs is similar to our work. Haswell

Archipelago: $\sum_{15}\text{PAHs} = 22.8 \mu\text{g} \times \text{kg}^{-1}$. Hudson Mountains: $\sum_{15}\text{PAHs} = 33.9 \mu\text{g} \times \text{kg}^{-1}$. Vicinity of Leningradskaya station $\sum_{15}\text{PAHs} = 21.7 \mu\text{g} \times \text{kg}^{-1}$. The vicinities of Mirny station $\sum_{15}\text{PAHs} = 90.9 \mu\text{g} \times \text{kg}^{-1}$ (Abakumov et al., 2015).

PAHs concentrations in Antarctica are often from soils and sediments located in highly contaminated areas where accidental spills have occurred, or close to research stations (Cabrerizo et al., 2012). On the Admiralty Bay, King George Island, Antarctica the maximum PAHs (high molecular PAHs (FLU, PYR, BaA, CHR, BkF, BbF, BaP, IPY, DBA, BPE)) concentration at Ferraz station occurred at 3.5 cm soil layer (454.9 $\mu\text{g} \times \text{kg}^{-1}$). The PAHs isomer pair ratio analysis showed that the major sources of PAHs are fossil fuels/petroleum (gasoline and diesel). The authors suggested that this may be related to activities at British station “G” in 1960s (established at the location of the Ferraz station). In areas of Admiralty Bay with less anthropogenic impact PAHs content is significantly lower (from 11.8 to 270.5 $\mu\text{g} \times \text{kg}^{-1}$) (Martins et al., 2004; Martins et al., 2010).

In the McMurdo Dry Valley region around Scott Base, Marble Point and the Wright Valley near Lake Vanda, $\sum_{15}\text{PAHs}$ (same with our PAHs list) content of fuel oil-contaminated soils ranged from 41 to 8105 $\mu\text{g} \times \text{kg}^{-1}$ of dried soil. At the Scott Base PAHs levels of 362 $\mu\text{g} \times \text{kg}^{-1}$ in drum storage site were detected in the 0–2 cm surface soil layer compared with 8105 $\mu\text{g} \times \text{kg}^{-1}$ in the 2–10 cm depth and 2543 $\mu\text{g} \times \text{kg}^{-1}$ in the deeper 20–30 cm layer. At McMurdo Dry Valley reference points PAHs concentrations ranged from 15 to 45 $\mu\text{g} \times \text{kg}^{-1}$ dry weight (Aislabie et al., 2004).

Previous investigations in anthropogenic loaded areas in Antarctica have reported PAHs levels in soils in the vicinity of stations Bellingshausen and Henryk Artstowski (King George Island, South Shetland Islands) and station Academician Vernadsky (Galindez Island, Argentinian Islands). At some points around the station Academician Vernadsky, the content of $\sum_{15}\text{PAHs}$ (same with our PAHs list) reaches 94771.2 $\mu\text{g} \times \text{kg}^{-1}$. The maximum level of contamination is observed near the aerology building and diesel station, the contribution of HMW

PAHs exceeds 20%. At Bellingshausen station the maximum content of \sum_{15} PAHs in soil at the diesel station is up to $911 \mu\text{g} \times \text{kg}^{-1}$, with a higher contribution of HMW PAHs. In the vicinity of the Henryk Artstowski station \sum_{15} PAHs content ranges from 114 to $188.3 \mu\text{g} \times \text{kg}^{-1}$ (Abakumov et al., 2014; Abakumov et al., 2015).

Previously, investigations of PAHs content in different regions and climatic conditions have already been conducted. The values of \sum_{15} PAHs (same with our list) ranged from 36.9 to $323 \mu\text{g} \times \text{kg}^{-1}$ (dry weight) in soil (HMW PAHs prevailed), from 154 to $231 \mu\text{g} \times \text{kg}^{-1}$ in moss, and from 48 to $333 \mu\text{g} \times \text{kg}^{-1}$ in reindeer dung at Ny-Ålesund, Svalbard in the Arctic (Wang et al., 2009).

For a comparative assessment, it is important to cite the results of some studies of PAH content in soils of anthropogenic-loaded urbanized areas. Investigations of \sum_{15} PAHs (same with our PAHs list) content in soils of urbanized areas show the following results: Ljubljana 218 – $4,490 \mu\text{g} \times \text{kg}^{-1}$, Torino 148 – $3,410 \mu\text{g} \times \text{kg}^{-1}$, while soil samples from Glasgow show very high values 1490 – $5,1800 \mu\text{g} \times \text{kg}^{-1}$. Analyzed PAHs ratios indicated pyrogenic origin of chemicals as result of anthropogenic contribution (Morillo et al., 2007). The range concentrations of Σ_{16} PAHs [16 USEPA priority PAHs (identical to our list, but also includes Acenaphthylene)] in urban soils in Clay county, Ocala, Pensacola, and West Palm Beach were, respectively, 797 – 7909 , 950 – $1,1451$, 922 – $1,7698$, and $1,133$ – $3,0691 \mu\text{g} \times \text{kg}^{-1}$. PAHs sources in urban soils of Pensacola were dominated by vehicle emissions, those in Ocala and West Palm Beach were dominated by biomass combustion, and those in Clay county were dominated by petrogenic sources (Gao et al., 2019). In soils of Vasilievsky Island in St. Petersburg were detected extremely high concentrations of PAHs. The concentration of Σ_{15} PAHs (same with our PAHs list) is getting to the level $8,200 \mu\text{g} \times \text{kg}^{-1}$. The maximum PAH concentrations were detected in the soil along the highway with heavy traffic and considerable emission of combustion gases (Lodygin et al., 2008). It is well seen that the PAH content in soils subjected to permanent anthropogenic load is significantly higher compared to almost all the results obtained for the Antarctic territories.

In our investigation at the point with the highest anthropogenic load (L26, main house) \sum_{15} PAHs equals $445.1 \mu\text{g} \times \text{kg}^{-1}$ (highest contribution: NAP $170 \mu\text{g} \times \text{kg}^{-1}$, PYR $60 \mu\text{g} \times \text{kg}^{-1}$, ANA $41 \mu\text{g} \times \text{kg}^{-1}$). At the other points \sum_{15} PAHs from 170 to $200 \mu\text{g} \times \text{kg}^{-1}$ (Highest contribution: NAP 48 – $70 \mu\text{g} \times \text{kg}^{-1}$, PHE 20 – $28 \mu\text{g} \times \text{kg}^{-1}$). Compared with the studies mentioned above, it should be recognized that the anthropogenic load on the vicinities of Bulgarian Antarctic Station is not critical. It should be noted that station St. Kliment Ohridski is inhabited only in summer, unlike the other Antarctic stations (station Bellingshausen, station Academician Vernadsky, station Henryk Artstowski, station Scott Base, station Ferraz). This certainly has a positive effect on the anthropogenic impact on the vicinity of the station.

Based on the obtained data, it could be concluded that baseline sources for PAHs in Cryosols of Livingstone Island are found.

Particular attention should be paid to PAHs concentrations at the sampling point L26 (Hanna Point, Main House.) This point is located directly at the station “St. Kliment Ohridski”. The soil

type here is referred to Cryosol Toxic Transportic (WRB, 2015). \sum_{15} PAHs at this point is $455.1 \mu\text{g} \times \text{kg}^{-1}$ (the main contribution is formed by: NAP $170 \mu\text{g} \times \text{kg}^{-1}$, PYR $60 \mu\text{g} \times \text{kg}^{-1}$, ANA $41 \mu\text{g} \times \text{kg}^{-1}$, FLT $38 \mu\text{g} \times \text{kg}^{-1}$, IPY $25.8 \mu\text{g} \times \text{kg}^{-1}$, BaP $19 \mu\text{g} \times \text{kg}^{-1}$ (Figure 2). \sum_{7} carcinogenic PAHs is $92.8 \mu\text{g} \times \text{kg}^{-1}$. Values of PAHs concentrations in the Toxic soil are much higher in comparison with the other studied natural soils.

Normally, PAHs can associate not only combustion processes but they are also found in sewage effluents, small oil spillages and natural sources including petroleum seeps (Martins et al., 2010). In order to identify the source of PAHs origin, different PAHs isomer pair ratios were calculated. This method of identification shows itself as a reliable and widely used in studies to identify the nature of the origin of PAHs (Yunker et al., 2002). Used PAH isomer pair ratios are shown in the Table 3.

Analyzing the results of PAHs isomer pair ratios calculations (Table 4) conclusions about the nature of PAHs origin in soils and cryoconites in the Bulgarian Antarctic Station “St. Kliment Ohridski” and its vicinity could be outlined.

The value of the ratio $\sum_{\text{PYR}} \text{PAHs} / \sum_{15} \text{PAHs}$ showed that all of the PAHs studied are results of petroleum spills, combustion processes or products of a baseline source. However, this indicator is too general and in order to better understand the processes of PAHs origin, it should rely on the results of previous ratio calculations. Also the ratio $\sum \text{LMW PAHs} / \sum \text{HMW PAHs}$ has shown that PAHs at all sampling points (except L21) have petrogenic origin.

The ANT/(ANT + PHE) value shows that all points except L26 have a natural origin (i.e. the Baseline source). At point L26 these PAHs are the result of the combustion processes. FLU/(FLU + PYR) ratio value characterize how as baseline source of this PAHs.

The results obtained by calculating the ratio BaA/(BaA + CHR) and IPY/(IPY + BPE) are of interest. Most often, the authors refer to PAHs as combustion products with results similar to ours (Yunker et al., 2002; Martins et al., 2010). However, Khaustov and Redina (2016) noted that the value of these ratios from 0,19 to 1,0 is typical for the background concentration of PAHs data in soils of northern and middle taiga (Khaustov and Redina, 2016). Since the climatic conditions of Livingstone Island are similar to those of the northern taiga, it should be recognized that the occurrence of these PAHs is linked more to natural than anthropogenic sources. Most sources use these two ratios to identify PAHs in locations with high anthropogenic load (Yan et al., 2006; Jiang et al., 2019; Gardes et al., 2020). Since there is no practice of burning wood fuel, coal and grass under Antarctic conditions, these two ratios have shown controversial results. Also, some researchers notes PAHs concentration in the particle phase was influenced significantly by temperature in the west Antarctic atmosphere (Na et al., 2020). The values of all other obtained isomeric ratios are well matched with the conditions of anthropogenic load and the possible influence of external factors on the nature of the origin of PAHs. The BaP/BPE value that all points except L26 have non-traffic source origin. From the PHE/ANT and FLU/PYR ratio value it can be seen that these PAHs at point L26 are formed as a result of pyrogenic processes, from other samples the

TABLE 3 | Possible PAHs isomer ratios.

PAHs isomer ratios	Range of values	Possible sources of PAH	References
ANT/(ANT + PHE)	<0.10 >0.10	Petroleum/Baseline source Indicates a dominance of combustion	Yunker et al. (2002), Wang et al. (2009), Tobiszewski and Namieśnik (2012), Shamilishvili et al. (2016)
FLU/(FLU + PYR)	<0.40 0.40–0.50 >0.50	Most petroleum/Baseline source Liquid fossil fuel (vehicle and crude oil) combustion Characteristic of grass, wood or coal combustion	Mandalakis et al. (2002), Yunker et al. (2002), Fang et al. (2004), Ravindra et al. (2008), Shamilishvili et al. (2016)
BaA/(BaA + CHR)	<0.20 0.20–0.35 >0.35	Petroleum/Baseline source Petroleum, combustion, baseline source Combustion	Yunker et al. (2002), Tobiszewski and Namieśnik (2012), Shamilishvili et al. (2016)
IPY/(IPY + BPE)	<0.20 0.20–0.50 >0.50	Petroleum/Baseline source Liquid fossil fuel (vehicle and crude oil) combustion Imply grass, wood and coal combustion	Yunker et al. (2002), Shamilishvili et al. (2016)
PHE/ANT	>10 <10	Petrogenic Pyrolytic	Budzinski et al. (1997), Khairy et al. (2009)
FLU/PYR	<1.0 >1.0	Petrogenic Pyrolytic	Budzinski et al. (1997), Khairy et al. (2009)
BaP/BPE	<0.60 >0.60	Non-traffic source Traffic source	Pandey et al. (1999), Ravindra et al. (2008)
\sum PyrPAHs ^a / \sum PAHs	<0.30 0.30–0.70 >0.70	Petroleum/Baseline source Petroleum, combustion, baseline source Mostly combustion	Hwang et al. (2004), Balmer et al. (2019)
\sum LMW PAHs ^b / \sum HMW PAHs ^c	<1 >1	Pyrogenic Petrogenic	Soclo et al. (2000), Zhang et al. (2008), Chunhui et al. (2017)

^apyrogenic PAHs—FLT, PYR, BaA, CHR, BbF, BkF, BaP, BPE, IPY.

^blight molecular weight, 2-3 ring PAHs.

^cheavy molecular weight HMW, 4-6 ring PAHs.

TABLE 4 | PAHs isomer ratios in studied soils and cryoconites.

	L1E	L21	L28	L10	L6	L1A	L26	L2	L1C	L22	L9
ANT/(ANT + PHE)	0.05	0.05	0.04	0.03	0.04	0.04	0.18	0.04	0.04	0.04	0.04
FLU/(FLU + PYR)	0.23	0.23	0.18	0.19	0.23	0.23	0.09	0.22	0.22	0.17	0.23
BaA/(BaA + CHR)	0.69	0.67	0.63	0.62	0.67	0.67	0.46	0.66	0.60	0.69	0.70
IPY/(IPY + BPE)	0.78	0.77	0.78	0.78	0.77	0.80	0.58	0.77	0.78	0.78	0.79
BaP/BPE	0.18	0.17	0.18	0.18	0.17	0.20	1.00	0.17	0.18	0.18	0.19
PHE/ANT	21.00	20.00	27.00	28.00	23.00	23.00	4.62	23.00	23.00	25.00	23.00
FLU/PYR	0.30	0.30	0.22	0.24	0.30	0.30	0.10	0.29	0.29	0.21	0.30
\sum PyrPAHs ^a / \sum PAHs	0.38	0.41	0.37	0.35	0.39	0.37	0.41	0.35	0.38	0.38	0.37
\sum LMW PAHs ^b / \sum HMW PAHs ^c	0.97	1.10	0.89	0.80	1.00	0.93	0.98	0.84	0.97	0.95	0.93

^apyrogenic PAHs - FLT, PYR, BaA, CHR, BbF, BkF, BaP, BPE, IPY.

^blight molecular weight, 2-3 ring PAHs.

^cheavy molecular weight HMW, 4-6 ring PAHs.

values are characteristic for petrogenic processes of PAHs formation.

For cross-checking the nature of the origin of PAHs, bi-plots were constructed between some values of the obtained relations (Figure 3).

As can be seen in the figure above, the correlation values show high statistical correlation between each other ($r^2 > 0.66$). In all the plotted figures, the soil sample L26, which was sampled directly in the territory of the Antarctic station, stands apart. All PAHs for this soil, which are shown on the visualized ratios,

are of pyrogenic (combustion) origin. The existence of PAHs of pyrogenic origin is caused by the incinerator using the diesel fuel used to eliminate waste, as well as by the diesel electric generator that supplies the station with electric power.

BaP-Equivalence of PAHs Concentrations

Taking into account that not all chemical contaminants have maximum permissible concentration (MPC) in soils, especially regional MPCs for Antarctic continent, BaP-equivalence of PAHs concentrations were calculated. Since in the EU and the

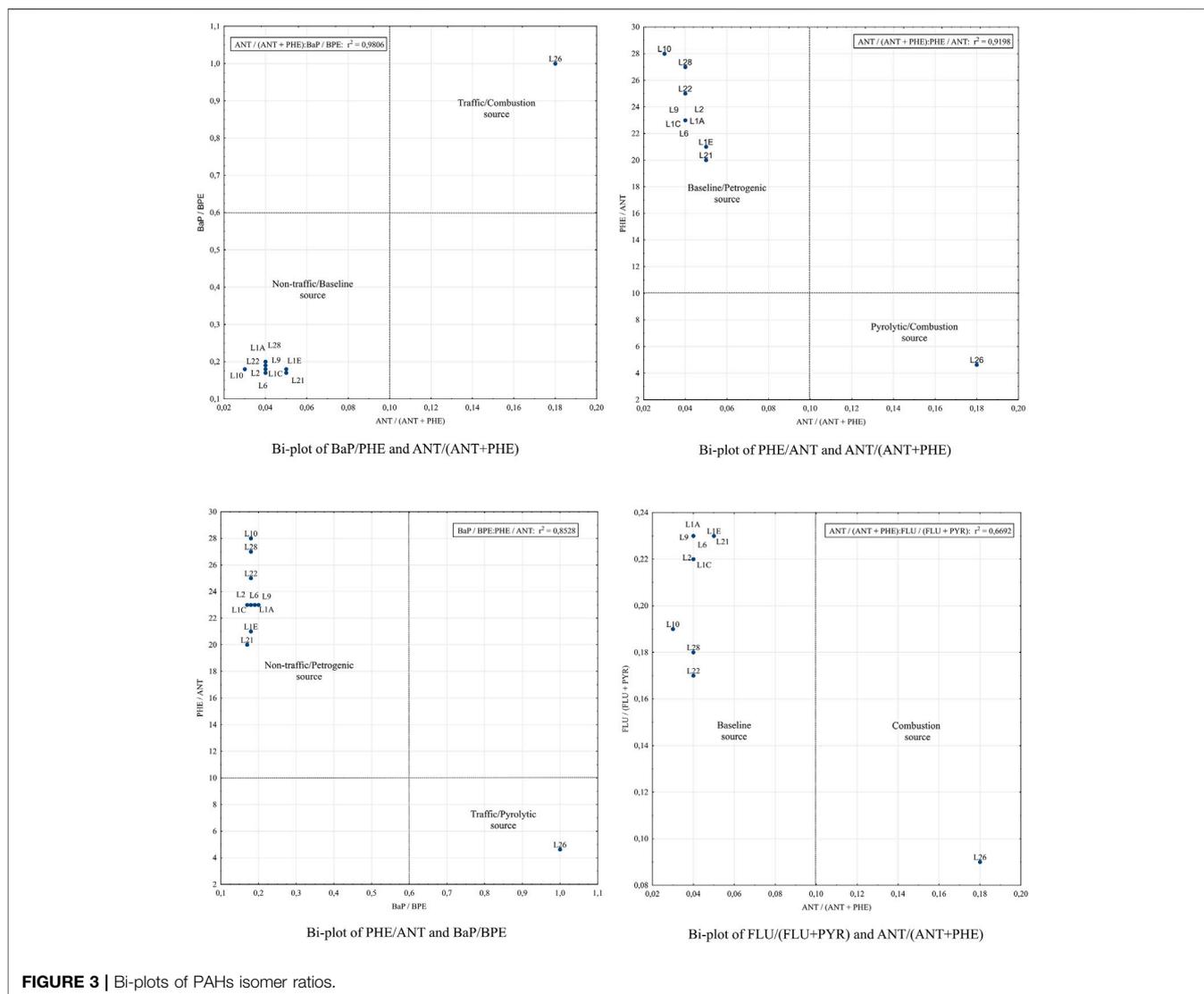


FIGURE 3 | Bi-plots of PAHs isomer ratios.

United States PAHs in various environments are controlled based on the calculation of human health risks, it was decided to use the standards adopted in Russian environmental legislation for convenience.

In Russia, the control of concentrations of various PAHs in the environment is based on monitoring 3-4 benzo(a)pyrene. According to the environmental protection laws, its maximum permissible concentration (MPC) in soil is $20 \mu\text{g} \times \text{kg}^{-1}$ (Hygienic Norms, 2006). The methods of calculation of BaP-equivalents are well studied and have long been applied in studies of anthropogenic impact on natural territories (USEPA, 1993; Verbruggen et al., 2001; Jung et al., 2010). The method makes it possible to evaluate the effect of both the PAHs complex and each of them individually (Bari et al., 2010; Jennings, 2012).

BaP-equivalents values were calculated by simply multiplication of PAHs concentrations by Toxic Equivalent Factor (TEF) values (Nisbet and Lagoy, 1992). Benzo(a)pyrene was among the first chemical carcinogens identified more than

70 years ago. Many jurisdictions use TEFs applied to their BaP-equivalents to regulate other PAH (Loeb and Harris, 2008; Jennings, 2012; Shamilishvili et al., 2016).

The values of toxicity of investigated PAHs by 3-4 benzo(a)pyrene are presented on the **Figure 4**. As can be seen from the results obtained, for toxic soil (point L26) BaP-equivalents $\sum_{15}\text{PAHs}$ is $56.2 \mu\text{g} \times \text{kg}^{-1}$, which is more than 2 times higher than the standards of Russian environmental legislation. The main contribution to BaP-equivalents $\sum_{15}\text{PAHs}$ is formed by: DBA $30.0 \mu\text{g} \times \text{kg}^{-1}$, BaP $19.0 \mu\text{g} \times \text{kg}^{-1}$, IPY $2.58 \mu\text{g} \times \text{kg}^{-1}$. $\sum_{7}\text{carcinogenic PAHs}$ is $54.6 \mu\text{g} \times \text{kg}^{-1}$, which is also more than 2 times higher than the Russian standard. It should be noted that the share of carcinogenic PAHs in BaP-equivalents is more than 90 percent.

For natural Antarctic soils the proportion of different PAHs in BaP – equivalents are significantly different from toxic soil sample. For almost all samples of natural soil $\sum_{15}\text{PAHs}$ in BaP-equivalents is close to $34 \mu\text{g} \times \text{kg}^{-1}$. The main

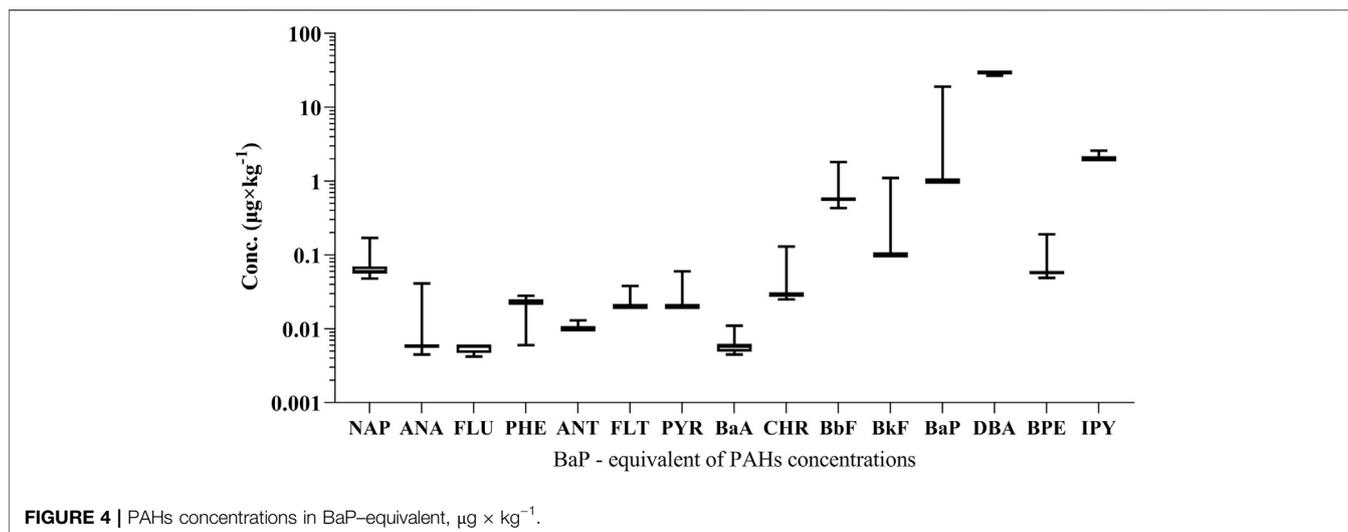


FIGURE 4 | PAHs concentrations in BaP-equivalent, $\mu\text{g} \times \text{kg}^{-1}$.

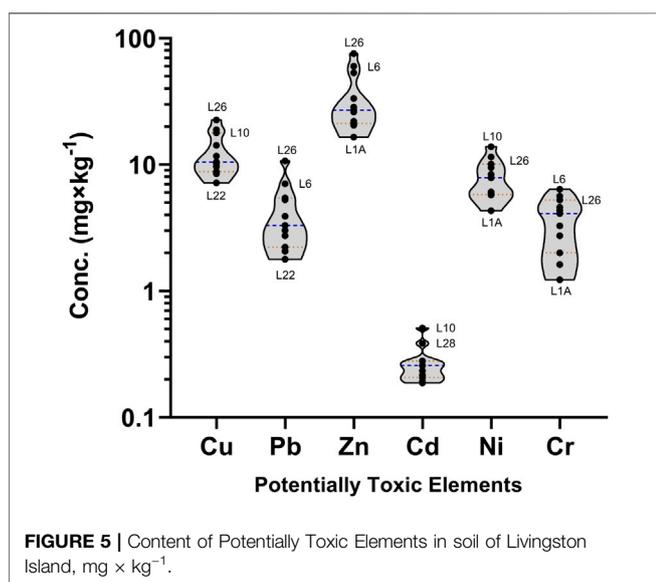


FIGURE 5 | Content of Potentially Toxic Elements in soil of Livingstone Island, $\text{mg} \times \text{kg}^{-1}$.

contribution in all cases is DBA $30 \mu\text{g} \times \text{kg}^{-1}$, IPY $2 \mu\text{g} \times \text{kg}^{-1}$, the remaining PAHs are significantly smaller. $\sum 7_{\text{carcinogenic}} \text{PAHs}$ in BaP-equivalents for all natural soils is close to $33 \mu\text{g} \times \text{kg}^{-1}$ with a DBA share of over 90%.

Taking into account that DBA concentrations in toxic and natural soils is a same ($6 \mu\text{g} \times \text{kg}^{-1}$), one might say that baseline source of DBA in BaP-equivalents in soils and cryoconites more than Russian MPC of 3-4 benzo(a)pyrene.

Content of Potentially Toxic Elements

Figure 5 shows the content of Potentially Toxic Elements in soils and cryoconites. Zn has the highest content of all metals. In the soil sample from the anthropogenic-loaded area (L26) the Zn concentration is $75.7 \text{ mg} \times \text{kg}^{-1}$. The lowest concentration was detected in sample L1A— $16.5 \text{ mg} \times \text{kg}^{-1}$. High concentrations of Zn were recorded at L6 and L10, although soils in these areas are

not subjected to anthropogenic load. As can be seen in the diagram presented in Figure 4, the variability of concentrations of other metals is significantly lower compared to zinc. The content does not change significantly. The minimum content among all Potentially Toxic Elements is observed for Cd, the maximum concentration is fixed in point L10— $0.509 \text{ mg} \times \text{kg}^{-1}$.

Potential Toxic Elements in soils with anthropogenic load (Cryosol Toxic Transportic) following relation: $\text{Zn} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Cr} > \text{Cd}$. Cryosol Ornitic: $\text{Zn} > \text{Ni} > \text{Cu} > \text{Pb} > \text{Cr} > \text{Cd}$. Typical Cryosols and Cryoconites in most cases: $\text{Zn} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Cr} > \text{Cd}$.

Previously, some results of studies of the content of potentially toxic elements in soils, cryoconites and ornithogenic sediments in the Antarctic Continent have already been published. In the cryoconites King George Island recorded the content of potentially toxic elements in the following order: $\text{Zn} > \text{Cu} > \text{Ni} > \text{Cr} > \text{Pb} > \text{Cd}$ (Polyakov et al., 2020). In the anthropogenically loaded soils of Robert Island near The Chilean refuge Luis Risopatrón, the concentrations were in the following order $\text{Cr} > \text{Cu} > \text{Zn} > \text{Ni} > \text{Pb} > \text{Cd}$ (Neto et al., 2017). Technosols from Hope Bay, Esperanza Station showed relation $\text{Pb} > \text{Zn} > \text{Cu} > \text{Ni} > \text{Cr} > \text{Cd}$. With an extremely high Pb content of $19381 \text{ mg} \times \text{kg}^{-1}$ and Cd content of $44 \text{ mg} \times \text{kg}^{-1}$ (Bueno Guerra et al., 2011). King George Island, Stranger Point, ornithogenic soils near Gentoo penguin colonies, showed potentially toxic elements ratios: $\text{Cu} > \text{Zn} > \text{Pb} > \text{Cr} > \text{Ni} > \text{Cd}$, at a Cu concentration of $389.98 \text{ mg} \times \text{kg}^{-1}$ and a Cd concentration of $3.93 \text{ mg} \times \text{kg}^{-1}$ (Celis et al., 2015). Unfortunately, the soils of Livingstone Island are poorly investigated in terms of heavy metals concentration, so below is a comparison with the results of few studies of soils of Livingstone Island and King George Island, as it is similar in climate conditions and is a short distance to Livingstone Island. Vlček et al. (2017) present data for pristine soils on Livingstone Island (Hannah point area), which are similar to our results for undisturbed soils. The

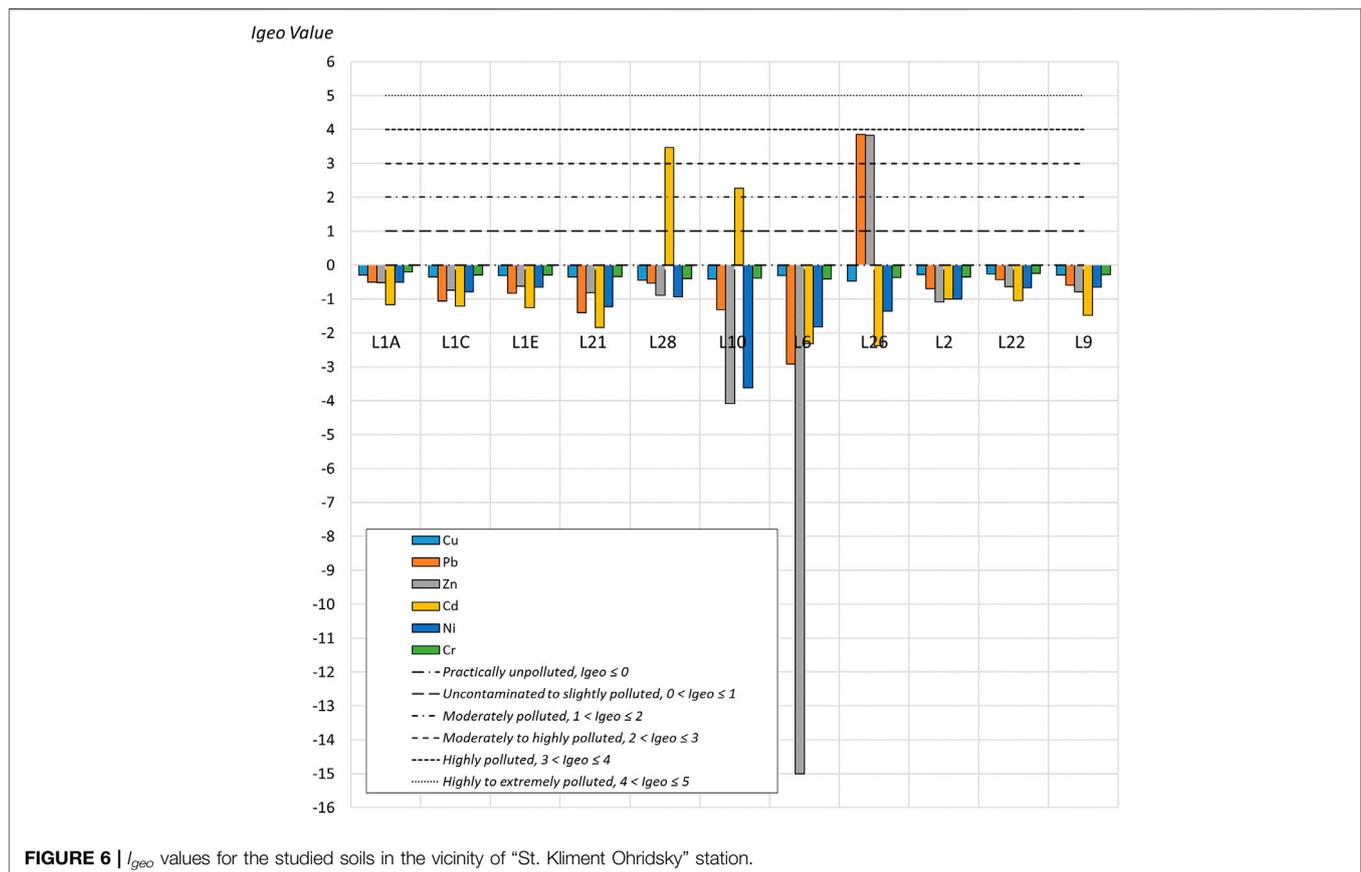
TABLE 5 | Spearman Rank Order Correlations (r) between concentrations of potentially toxic elements (Bolded correlations are significant at $p < 0.05$).

	Cu	Pb	Zn	Cd	Ni	Cr
Cu	1.00	0.59	0.47	0.82	0.49	0.57
Pb		1.00	0.70	0.54	0.74	0.61
Zn			1.00	0.61	0.91	0.85
Cd				1.00	0.62	0.71
Ni					1.00	0.82
Cr						1.00

concentrations of 52 mg/kg are given (Santos et al., 2005). We also recorded the maximum concentrations of Zn, Cu and Pb among all the studied metals in a soil sample taken on the territory of the station “St. Kliment Ohridski” (point L26).

Statistical analysis of the obtained data matrix of trace elements concentrations showed that most elements are in close correlation relationship (Table 5).

Significant Spearman correlation coefficients ($r > 0.61$) were obtained practically for the elements. High correlation values

**FIGURE 6** | I_{geo} values for the studied soils in the vicinity of “St. Kliment Ohridski” station.

authors note the highest Zn concentration ($55 \text{ mg} \times \text{kg}^{-1}$) in undisturbed soils, which is identical to our data (Vlček et al., 2017). The results for the other heavy metals are also similar. The investigations Santos et al. (2005); Vlček et al. (2017); Bueno et al. (2018) provide data on the content of trace metals both in pristine soils of King George Island and for anthropogenically loaded areas near the Antarctic stations. The data given by these researchers for pristine soils are generally similar to ours. For anthropogenically loaded territories, there are similarities in the content of Cu, Zn, and Pb. The average Zn 63.1 , Cu 52.2 , and Pb $6.3 \text{ mg} \times \text{kg}^{-1}$ were found in the soils of Artigas Antarctic Scientific Base (Bueno et al., 2018). For soils of Brazilian Antarctic Station Comandante Ferraz (Ferraz), data on average Zn

between Ni and Zn ($r = 0.91$), Cr and Zn ($r = 0.85$), and between Cd and Cu ($r = 0.82$) are especially significant.

Classification of Soil Contaminations

Livingston Island is not well surveyed in terms of background concentrations of trace metals in the soil, so we used concentrations of trace metals in King George Island soils to calculate the geoaccumulation index (I_{geo}). King George Island is the closest large island to Livingston Island, they are very similar in climatic conditions and are part of the South Shetland Islands. There are many publications on heavy metal content in the pristine soils of King George Island (Amaro et al., 2015; Dalfior et al., 2016; Alekseev and Abakumov, 2020; Polyakov et al., 2020). Based on these studies, we calculated average values of heavy metal concentrations in pristine soils of the South

Shetland Islands. The following values of the geochemical background value (B_n) were obtained: Cu–63, Pb–5.65, Zn–42.6, Cd–0.25, Ni–11.83, and Cr–22.95 $\text{mg} \times \text{kg}^{-1}$.

In most of the studied soils, the values of the I_{geo} for all the studied potentially toxic elements are less than zero ($I_{geo} \leq 0$), which allows us to classify them as *Practically unpolluted* (Figure 6).

Values above zero are recorded at L28, L10, and L26 sampling points. At L28 point, the I_{geo} value for Cd is 3.46. This soil is characterized as *Highly polluted* ($3 < I_{geo} \leq 4$). Also a high level of Cd content compared with background values was recorded at point L10, the values of I_{geo} index equal to 2.26. Cd contamination is characterized as *Moderately to highly polluted* ($2 < I_{geo} \leq 3$). The highest values of the I_{geo} index are found at L26 point. Here Pb and Zn contamination is characterized as *Highly polluted* ($3 < I_{geo} \leq 4$). I_{geo} values for Pb and Zn at point L26 are 3.85 and 3.82, respectively. It should be noted that the study area near point L26, is anthropogenically loaded, soil samples were taken directly in the territory of the Bulgarian Antarctic station. Bueno et al. (2018) reports data on soil contamination of Ferraz station (King George Island) based on Igeo index calculations. The level of contamination of Zn (moderately to highly polluted) and Cr (Moderately polluted) is identified (Bueno et al., 2018). It can be noted a similarity with the character of soil contamination on the territory of the station “St. Kliment Ohridski”.

Averaging the I_{geo} values for all points, the ratio of the pollution level is as follows $\text{Cr} > \text{Cu} > \text{Pb} > \text{Cd} > \text{Ni} > \text{Zn}$. With values for Cr and Zn equal to -0.32 and -1.94 , respectively. The average values for all potentially toxic elements are characterized as *Practically unpolluted* ($I_{geo} \leq 0$).

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DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

EA–field work, conceptualization, TN–laboratory analyzes, data processing, MG–writing manuscript, RY–field work, data processing. All authors have read and agreed to the published version of the manuscript.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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