






Original Article

Migration of organic carbon and trace elements in the system glacier-soil in the Central Caucasus alpine environment

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Abstract: Rapid deglaciation is one of the most important challenges in the Earth science today. One reason of this is specific supraglacial sediments – cryoconites, which represent carbon-containing dust with organomineral matter and living organisms. Investigation of physical and chemical characteristics of cryoconites in the Central Caucasus is necessary in order to understand their influence on alpine territories biogeochemical cycles, pollution and development in conditions of intensive glacial melting and active anthropogenic influence. For this research cryoconites as well as moraines, soil-like bodies and soils have been sampled from the alpine Bezengi Glacier and adjacent Khulamo-Bezengi Gorge. Key physicochemical features (pH values, total organic carbon content, microbial respiration, particle-size distribution) as well as content of trace elements have been defined in sampled materials and several pollution indices (Geoaccumulation index, Contamination factor and Degree of pollution) have been calculated. Results obtained show low values of

total organic carbon in cryoconites (max. 0.23%) but high values (max. 7.54%) in top horizon of soils located in floodplain, indicating its active fluvio-glacial transfer which may further accelerate the development of soils. Microbiological activity in the studied soils was mostly influenced by additional input of labile organic carbon from cryoconites with water flows. Particle-size distribution was similar among the studied cryoconites, indicating dominance of sand fraction (up to 85.28%) while studied soils showed higher variability due to influence of weathering. Among the trace elements, cryoconites were mostly polluted by Zn (max. 85.70 mg·kg⁻¹) which corresponds to high pollution according to pollution indices; Pb (max. 24.90 mg·kg⁻¹) and Cu (max. 17.40 mg·kg⁻¹), up to moderate pollution level. Redistribution of polluted cryoconite material as well as local anthropogenic activities increased pollution of periglacial soils by Zn (max. 89.20 mg·kg⁻¹), Pb (max. 15.00 mg·kg⁻¹) and Cu (max. 12.80 mg·kg⁻¹), which was also proven by the pollution indices with up to high level of pollution.

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1 Introduction

Ongoing climate change has strongly increased retreat of glaciers at polar and alpine regions (IPCC 2021). Glacier retreat is influenced by several factors, one of them is deposition of carbonaceous aerosols on their surface. These aerosols or “dust” include organic carbon and black carbon which origin is associated with both natural processes such as volcanic eruptions and anthropogenic activities, mainly construction and combustion of fuels (Kang et al. 2022). Carbonaceous aerosols play huge role in global and local carbon cycle and environment including glacierized regions. While organic carbon act as a nutrient for alpine ecosystems which promotes their development, black carbon may strongly decline albedo of the glacier due to its dark colour and accelerate deglaciation (Hotaling et al. 2021) as well as accumulate and store various natural and anthropogenic pollutants and, thus, contribute to pollution of environment which is especially noticeable in polar and alpine regions (Polyakov et al. 2020a). Carbonaceous aerosols are usually deposited on the glacial surface due to cold condensation or so-called “grasshopper effect” (Fernandez et al. 2021). This leads to formation of specific supraglacial sediments – cryoconites.

Cryoconites firstly were found in 19th century by Scandinavian explorer Nordenskjöld in Greenland (Nordenskjöld 1875) and they are usually described as a black-coloured mixture of carbon-containing dust with mineral and organic matter, and living organisms (Hodson et al. 2008). Cryoconite sediments may be found in any glacial environment around the globe. Normally they form cryoconite holes filled with melting water, however, they can also be located in crevasses as well as dispersed on the surface (Foreman et al. 2007; Di Mauro et al. 2017). Cryoconite origin is usually associated with input of organomineral matter from local sources such as valley walls in mountains as well as transferred from remote regions with atmospheric streams (Nagatsuka et al. 2014; Swift et al. 2018; Zawierucha et al. 2019). Moreover, origin of particles is crucial for particle-size distribution of cryoconites, especially in mountains. It was mentioned earlier (Abakumov et al. 2021) that in high-altitude areas, mountain ridges partially block the aeolian transfer of fine clay particles (<0.002 mm), which affects the source of origin of supraglacial sediments, and further affecting their particle-size

distribution.

Together with transferred particles, various microorganisms, organic residues and fragments of plants enter the supraglacial zone (Morselli et al. 2014). Recent studies (Rakusa-Suszczewski 2015; Polyakov et al. 2020b) show that those microorganisms may accumulate and transform various nutrients, and create productive biofilms on the glacier surface. It was found (Sävström et al. 2007; Anesio et al. 2009) that net primary production, respiration and photosynthesis rates in cryoconites are similar to those, measured in water streams. Material on the glacier surface is also enriched in organic carbon due to atmospheric deposition of carbonaceous material from both natural and anthropogenic sources as well as by local microbial activity (Stibal et al. 2008; Singer et al. 2012). In research of Monson et al. (2006), it was found that in alpine environments respiration of microorganisms is one of the major factor influencing local carbon cycle. Therefore, measuring the rate of microbial respiration is a way to study the carbon cycle in supraglacial and periglacial zones which is connected with activity of primary producers (Stibal et al. 2012; Samui et al. 2020). Moreover, another study (Anesio et al. 2010) indicated that only 7% of organic carbon in cryoconite is used by local microorganisms while the rest is transferred to adjacent areas where it can affect biogeochemical cycles. Intensive deglaciation accelerates this transfer of carbon as well as other nutrients due to increase of runoff, fluvio-glacial transfer of cryoconite material and release of ice-locked organic carbon (Hood et al. 2015).

Glaciers retreat also lead to downstream transfer of pollutants, which are deposited to the glacier surface due to “grasshopper effect” together with mineral and organic matter (Fernandez et al. 2021). It was found that cryoconite sediments may store various pollutants such as radionuclides on the surface of glaciers in Swiss Alps (Baccolo et al. 2017), Russian Arctic (Miroshnikov et al. 2021) and in Svalbard (Zaborska 2017) as well as polycyclic aromatic hydrocarbons which were found in Antarctica, at the Livingstone island (Abakumov et al. 2021a), Austrian Alps (Weiland-Bräuer et al. 2017) and at the Tibetan Plateau (Li et al. 2017). Trace elements is another group of pollutants which negative effect for plants, animals and humans has been widely studied and proven (Wong et al. 2006; Fritsch et al. 2010; Plum et al. 2010; Nagajyoti et al.

2010). Accumulation of these pollutants in comparison with background values was observed in the Arctic (Łokas et al. 2014) and Antarctic (Abakumov et al. 2021a). Measurements of trace elements in mountainous supraglacial sediments have been conducted in Himalayas (Singh et al. 2017) and at the Tibetan Plateau (Jiao et al. 2021) indicating accumulation of these pollutants on higher level than in polar regions, probably due to closeness to industrial territories and favorable atmospheric circulation. After transfer of cryoconites to adjacent territories by aeolian and fluvio-glacial processes this material may act as an additional source of pollutants for sensitive mountain ecosystems. Local population as well as wildlife may be susceptible to additional pollution, with a negative impact on health and quality of life, due to uptake of trace elements with polluted plants or via direct contact with polluted soil (Bai et al. 2018; Tian et al. 2020). With observed retreat of glaciers transfer of polluted cryoconite material may significantly affect geochemical cycle of mountainous regions in terms of trace elements.

The Caucasus is a well-known mountain range in Eurasia which is located between the Black sea and Caspian Sea. Due to rapid deglaciation the total area of glaciers of the Caucasus has been reduced by 23% in 21st century (Tielidze et al. 2022). This process leads to active transfer of nutrients and pollutants from supraglacial to periglacial zone and downstream. This is especially important due to fact that local population and agricultural companies use mountain and foothill soils for grazing livestock, growing vegetables and fruits (Zaburaeva et al. 2021). Bezengi Glacier is the biggest valley glacier at the Caucasus mountain range which is covered by supraglacial sediments and their possible transfer downstream may influence properties and geochemical cycles of adjacent ecosystems which in its turn may cause pollution of mountain soils as well as accelerate their development. Therefore, the main aim of this research was to study the role of cryoconites at the Bezengi Glacier surface in the local alpine ecosystems biogeochemical cycles and in development of primary periglacial soils. In order to achieve this aim, several sub goals have been set. The first goal is to define basic physical and chemical properties of cryoconites and soils in adjacent gorge such as pH values, basal respiration (which indicates microbiological activity of primary producers), total organic carbon content and particle-size distribution in order to investigate

features of cryoconites and their possible impact on mountain environment. The second is to evaluate pollution of cryoconites and soils by several trace elements (Cu, Pb, Zn, Ni, Cd). The third is to use several pollution indices to correctly evaluate their pollution load. Finally, we aim to compare different study sites in terms of pollution, basic chemical and physical features and discuss internal reasons which may contribute to the rate of development and the pollution of these study sites.

2 Materials and Methods

2.1 Study area

More than 1700 glacier are located at the Caucasus mountains (Kutuzov et al. 2015) and most of them are currently retreating. Nearby the glaciers there are lots of resorts and tourist bases (Litvinova 2020) which from the one hand contribute to pollution of this mountain region, however, from the other hand, Caucasus is often used as a place with “undisturbed nature” for ecological tourism and hiking (Andreyanova and Ivolga 2018). Central part of the Caucasus mountain range is its highest part which include peaks such as Mt. Elbrus (5642 m), Mt. Dykhtau (5205 m), Mt. Kazbek (5045 m) and Bezengi Mountain Wall which includes several peaks higher than 5 km above the sea level (Gvozdetsky 1963). A few studies have been conducted in order to estimate role of cryoconite in environment of the Central Caucasus. Lokas et al. (2018) found high concentration of deposited from the atmosphere radionuclides at the material from the surface of the Adishi Glacier. Earlier our studies (Kushnov et al. 2021; Abakumov et al. 2022) at the Central Caucasus revealed that cryoconites at the Garabashi Glacier (Mt. Elbrus) were highly polluted with some trace elements such as Cu, Pb and Zn as well as with polyarenes, mostly Napthalene and Dibenz[a,h]anthracene, which affected the pollution status of local soils in the adjacent gorge.

The study area is located in the central part of the Caucasus mountain range, close to Bezengi Mountain Wall. The total area of glaciers which are located here, in the central part of the Caucasus Mountains, is 783 km², which is about 74% of the total glaciers area at the entire Caucasus (Tielidze et al. 2022). Regional settings of this study are represented by the Bezengi

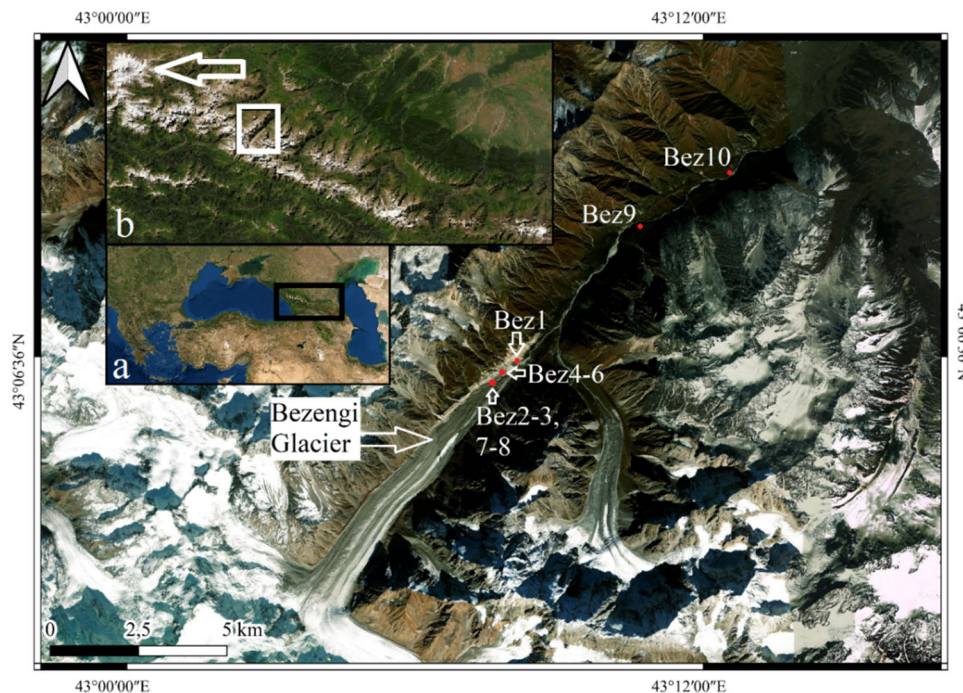


Fig. 1 Regional settings. Main figure represents enlarged satellite image of the study site (white arrows in this main figure point to the Bezenzi Glacier and sampling sites). Insert figures: a – location of the Caucasus Mountains in Eurasia (in black frame); b – location of the study site (in white frame) at the Central Caucasus region (white arrow in this insert figure points to the Elbrus Mt.). Performed in QGIS 3.24.1 program.

Glacier and adjacent Khulamo-Bezenzi Gorge (Fig. 1).

The Bezenzi Glacier is the biggest valley glacier in the Caucasus mountains with a total area of about 40 km² and it has decreased by 0.58 km² since the middle of 20th century (Bushueva 2015, Tielidze et al. 2022). This glacier is surrounded by high valley walls and it is ended with powerful terminal moraine. Bezenzi Glacier feeds the Cherek-Khulam river which flows through the Khulamo-Bezenzi Gorge below. The average annual temperature in lower part of this gorge is 11.9°C and in high-mountainous part is 4.7°C (Gazaev and Bozieva 2020). Average precipitation ranges from 900 to 1400 mm/year, in some years up to 2373 mm (Gazaev et al. 2018). The parent material of local soils is composed of carbonate rocks, sandstones, granites and glacial deposits close to the glacier.

2.2 Sampling strategy

At the Bezenzi Glacier cryoconites have been sampled from the glacier surface, crevasses, large and several small cryoconite holes. Samples also have been taken from the local terminal moraine as well as from the soil-like bodies (both vegetation covered and

free of plants) which are formed on mudflows and cryoconite-derived basis. Sampling plots are presented in Appendix 1.

Studied soils have been sampled at the Khulamo-Bezenzi Gorge, close to the Bezenzi Glacier in order to estimate cryoconite influence on local soils. Individual soil samples have been taken from two soil sections from each horizon, up to depth of 50 cm. These soils were identified as Leptic Umbrisols and Molic Leptosols according to WRB (2015). Soil section of the first type of soil was made at the slightly elevated part of the gorge, while the second was made at the river floodplain. Soil profiles are shown at the Appendix 2.

Information about study sites and samples is presented in the Table 1. Detailed description is presented in Appendix 3.

2.3 Laboratory analyses

Sampled materials were transported to the Department of Applied Ecology of Saint Petersburg State University in sealed bags by aircraft. At the laboratory conditions all samples were dried at the temperature about 20°C and then sieved through 2-

Table 1 Information about the study sites and samples

Sample	Description of the study site	Description of the sample
Bez1.1	800 m before the Bezengi Glacier.	Soil-like body formed on the mudflow. With vegetation
Bez1.2		Soil-like body formed on the mudflow. Without vegetation
Bez2.1	Crevice at the bottom part of the Bezengi Glacier	Cryoconite sediments
Bez2.2	Surface of the bottom part of the Bezengi Glacier	Dispersed cryoconite sediments
Bez3.1	Crevice at the upper part of the Bezengi Glacier	Cryoconite sediments
Bez3.2	Surface of the upper part of the Bezengi Glacier	Dispersed cryoconite sediments
Bez4.1	Upper part of the Bezengi Glacier	Moraine deposits
Bez4.2	Middle part of the Bezengi Glacier	
Bez4.3	Bottom part of the Bezengi Glacier	
Bez5	In the vicinity of the Bezengi Glacier	
Bez6		
Bez7	Small cryoconite holes on the surface of the Bezengi Glacier	Cryoconite material
Bez8	Big cryoconite hole on the surface of the Bezengi Glacier	Cryoconite material
Bez9	Ledge of birch forest, under herbaceous-grass vegetation. Leveled relief. Between Bezengi village and Bezengi Alpine Camp. The right bank of the Cherek Khulam river.	Dark grey, dense, lumpy-powdery, loamy, roots are medium.
		Grey, medium compacted, fine-compacted, roots are sparse.
		Light brown, weakly compacted, roots are few.
		Brown, slightly moist, medium compacted, powdery-lumpy, sandy loam, medium to coarse pebbles inclusions.
Bez10	Subalpine cereal-grass meadow. Between Bezenghi village and Bezenghi Alpine Camp, close to an abandoned shepherd's lodge. Left bank of the Cherek Khulam river.	Dark brown, moist, slightly compacted, fine-cloddy, medium-loamy, plenty of roots, few pebbles.
		Greyish-brown, moist, medium compacted, cloddy-grained, medium loamy, few roots, medium to fine pebbles inclusions.
		Brown with inclusions of grey chalky soil, moist, medium compacted, fine-cloddy, medium-loamy, few roots, many medium and coarse pebbles.

mm sieve. The pH values were measured by pH-meter Milwaukee Mi 106 (produced in Romania) in water and CaCl₂ solution with fine earth to solution ratio 1:2.5. Total organic carbon content was measured by indirect Tyrin dichromate oxidation-titration method (Angelova et al. 2014) which is comparable to method proposed by Walkley (1947). Basal respiration, was defined in incubation experiment by measuring the CO₂ content by titrating NaOH with HCl after incubation of material for 10 days in plastic airtight containers (Jenkinson and Powlson 1976). The particle-size distribution was performed by pipette (“wet sedimentation”) method, which is based on Stoke’s law, according to Bowman and Hutka (2002). Trace elements’ concentrations were measured by flame and electrothermal atomic absorption spectrometric method according to the standard ISO 11047 (1998) at atomic absorption spectrophotometer Kvant 2M (Moscow, Russia, 2021). We measured the content of Cu, Pb, Zn, Ni and Cd due to fact that they show high level of toxicity for humans and

environment (Jaishankar et al. 2014) and are accumulated in cryoconites and atmospheric dust with high efficiency (Vinogradova and Kotova 2019; Polyakov et al. 2020a).

2.4 Pollution indices calculation

In order to correctly interpret pollution load of studied sediments and soils by trace elements, several pollution indices have been used.

Firstly, we calculated the Geoaccumulation index (I_{geo}), which is used to evaluate the magnitude of the pollution of an individual trace element, as follows:

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

Here, C_n is a measured concentration of trace element in the sample, B_n is a geochemical background value and 1.5 is a constant to correctly interpret natural fluctuations and insignificant anthropogenic influence.

Muller (1979) defined several types of material

pollution according to Geoaccumulation index: practically unpolluted ($I_{geo} \leq 0$); from unpolluted to slightly polluted ($0 < I_{geo} \leq 1$); moderately polluted ($1 < I_{geo} \leq 2$); moderately to highly polluted ($2 < I_{geo} \leq 3$); highly polluted ($3 < I_{geo} \leq 4$); highly to extremely polluted ($4 < I_{geo} \leq 5$); extremely polluted ($I_{geo} > 5$).

Contamination Factor (CF) is another useful tool to estimate the pollution load of material by individual trace element. It is calculated as follows:

$$CF_i = \frac{C_m}{B_m} \quad (2)$$

Here, C_m is a measured concentration of trace element in the sample and B_m is a background concentration of this element.

Likuku et al. (2013) defined different types of pollution load according to CF values: low pollution ($CF < 1$); moderate pollution ($1 \leq CF < 3$); high pollution ($3 \leq CF < 6$); extremely high pollution ($CF \geq 6$).

Reimann and de Caritat (2005) found that it is not correct to use general background values of the global Earth's crust and soils to calculate I_{geo} and CF. The better option is to use local values as a reference (Blaser et al. 2000). Therefore, concentrations of trace elements from previously conducted studies (Podkolzin and Anciferov 2007; Degtyareva et al. 2020) of natural soils at the Caucasus region and foothill areas were used as a geochemical background.

Table 2 Acidity values of the studied sediments and soils

Sample	Sample type	Horizon	pH (H ₂ O)*	pH (CaCl ₂)**
Bez1.1	Soil-like body	Ch	6.63	6.09
Bez1.2	Soil-like body	C	6.77	6.07
Bez2.1	Cryoconite	Surface	6.97	5.73
Bez2.2	Cryoconite	Surface	6.84	6.18
Bez3.1	Cryoconite	Surface	5.87	5.58
Bez3.2	Cryoconite	Surface	6.74	6.37
Bez4.1	Moraine	C	6.45	6.22
Bez4.2	Moraine	C	6.42	6.17
Bez4.3	Moraine	C	6.41	6.24
Bez5	Moraine	C	6.46	5.92
Bez6	Moraine	C	7.09	ND
Bez7	Cryoconite	Surface	6.45	5.96
Bez8	Cryoconite	Surface	6.72	5.74
Bez9	Soil	Oe	5.98	4.90
		A	6.02	4.20
		B	6.38	4.25
		C	6.71	4.56
Bez10	Soil	Oe	5.99	4.76
		B	5.96	5.60
		C	6.26	5.07

Notes: * Actual acidity; ** Exchangeable acidity.

To estimate the average pollution of material by all investigated trace elements we used Degree of contamination (C_{degree}) which is calculated as follows:

$$C_{degree} = \sum_{i=1}^{n=5} CF_i \quad (3)$$

Here, n is the number of measured trace elements in our study and the sum of their CF values in each study site is used to define C_{degree} .

Classification of materials pollution according to C_{degree} was proposed by Zahran et al. (2015): low pollution ($C_{degree} < n$); moderate pollution ($n \leq C_{degree} < 2n$); high pollution ($2n \leq C_{degree} < 4n$); extremely high pollution ($C_{degree} \geq 4n$).

2.5 Statistical analysis

All statistical analyses were conducted in Statistica 12 software (Statsoft Inc.). In order to find the statistically significant difference one-way ANOVA test has been used. To evaluate relationship and find correlations between different study sites we used Spearman's nonparametric correlation test.

3 Results

3.1 Basic chemical properties and organic carbon

In order to study biogeochemical properties of cryoconites, soils and other materials, basic chemical features of studied samples were defined. They are shown in Table 2 and Table 3.

Among cryoconites, sample Bez3.1 from the crevice as well as samples from cryoconite holes showed slightly acidic reaction. Statistical analysis revealed significant difference ($F = 8.62, p < 0.05$) between pH H₂O in sediments at the glacier and Leptosols/Umbrisols which means that in general local soils were more acidic. The large difference between H₂O and CaCl₂ pH values was observed in local soils. It was proved by observed significant statistical difference ($F = 66.80, p < 0.05$) in pH CaCl₂ values between supraglacial sediments and Leptosols/Umbrisols. This may indicate the presence of silt and fine fraction or humus as well as diverse mineralogical composition, which increase an absorptive capacity for hydrogen ions in acidic soils, thereby increasing the exchangeable acidity of the soil solution (Seredina and Spirina 2009).

Basal respiration values among cryoconites were

lower in crevasses of the glacier than on the surface reaching peak values in samples from cryoconite holes (up to 26.29 mg CO₂·100 g⁻¹·day⁻¹) what was comparable with local soils. The highest values of basal respiration were observed in soil-like body with vegetation cover (30.80 mg CO₂·100 g⁻¹·day⁻¹) and horizon A in Umbrisols (35.09 mg CO₂·100 g⁻¹·day⁻¹), probably, due to high microbial activity in soil material under the influence of labile organic carbon and other nutrients input from the supraglacial zone. These microorganisms in cryoconites as well as in the studied soils may affect carbon cycle, mostly by respiration process.

Table 3 Basal respiration and Organic Carbon (OC) values of the studied sediments

Sample	Sample type	Horizon	Basal respiration (mg CO ₂ ·100 g ⁻¹ ·day ⁻¹)	OC# (%)
Bez1.1	Soil-like body	Ch	30.80	0.24
Bez1.2	Soil-like body	C	13.17	0.16
Bez2.1	Cryoconite	Surface	9.90	0.17
Bez2.2	Cryoconite	Surface	14.27	0.15
Bez3.1	Cryoconite	Surface	8.76	0.23
Bez3.2	Cryoconite	Surface	19.72	0.19
Bez4.1	Moraine	C	10.97	0.18
Bez4.2	Moraine	C	6.58	0.10
Bez4.3	Moraine	C	13.17	0.18
Bez5	Moraine	C	9.88	0.24
Bez6	Moraine	C	5.48	0.16
Bez7	Cryoconite	Surface	26.29	0.19
Bez8	Cryoconite	Surface	25.22	0.19
Bez9	Soil	Oe	21.91	3.70
		A	35.09	2.79
		B	24.18	0.58
		C	11.00	0.41
Bez10	Soil	Oe	26.40	7.54
		B	17.55	5.45
		C	10.97	2.82

Note: OC# , Organic carbon by indirect method.

All cryoconites showed low values of total organic carbon which were slightly higher in the crevasses of the glacier (up to 0.23%). Earlier (Telling et al. 2012) in cryoconites in the Arctic values of total organic carbon were similar to those in our study. Low content in cryoconite holes may be connected with its consumption by various microorganisms, however, according to study of Anesio et al. (2010) the main reason is transfer of organic carbon to adjacent areas. Higher value (0.24%) was defined in moraine deposits close to the Bezengi glacier due to this transfer. High values of total organic carbon (up to

7.54%) were observed in Leptosols/Umbrisols, especially in the upper horizons which also indicates its input, probably, with the material, transferred from the glacier surface. In previous research (Shevchenko et al. 2019) of foothill soils at the Caucasus, the content of total organic carbon was much lower than that in our study carried out in the vicinity of glacier which indicates the role of cryoconites in carbon cycle of this alpine territory. According to statistical processing, significant difference was observed between total organic carbon content in the studied sediments and soils ($F = 20.75$, $p < 0.05$) which may be connected with active transport downstream. Reliable negative relationship was defined between TOC and pH values ($H_2O = -0.70$, $CaCl_2 = -0.73$) which indicates that additional organic carbon lead to decrease of pH values in soils and sediments of this high-mountain site. Basic chemical features are depended on the physical properties, such as particle-size distribution, and may also affect them. So, let's move to results of this physical characteristics investigation.

3.2 Particle-size distribution

Studied cryoconites and soils as well as moraines and soil-like bodies were examined to estimate content of coarse and fine earth fraction and particle-size distribution in latter. Results are presented in Appendix 4.

Studied materials from the supraglacial zone and nearby were mostly dominated with coarse fraction, however, the percentage of fine earth was high, especially in cryoconite from holes (max. 58.16%). On the other hand, the fine fraction content was much higher in studied soils (up to 94.98% in top horizon) due to enhanced weathering and influence of other soil-forming processes. This difference in domination of coarse and fine earth between cryoconites and soils is statistically significant ($p < 0.05$). Also amount of coarse earth negatively correlates with total organic carbon content (-0.68) while fine earth fraction has a positive relationship with it (0.73) as well as with basal respiration values (0.50).

Results of particle-size distribution were also put on texture triangle and shown in Fig. 2. It was found that the studied soil-like bodies, cryoconites, moraines and local soils are similar to each other in terms of texture class. This also points to the fact that supraglacial sediments influence soil-forming

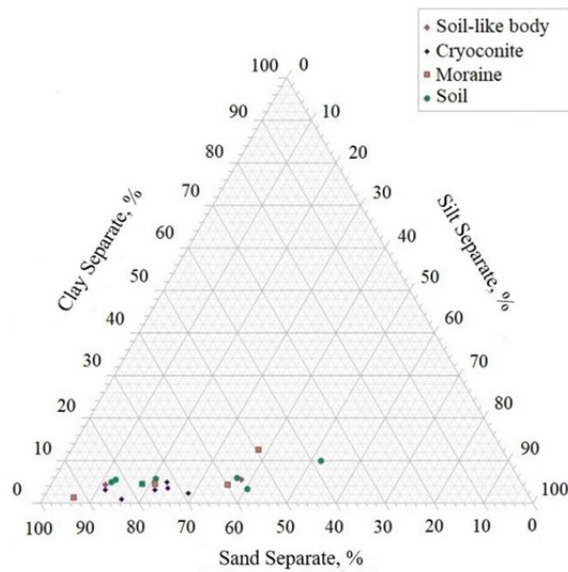


Fig. 2 Particle-size distribution of materials from the Bezengi Glacier (red), Khulamo-Bezengi Gorge Leptosols and Umbrisols (green) on the texture triangle (prepared in program Grapher, Golden Software LLC).

processes in adjacent territories. Most of them were dominated with sand (particle diameter 2-0.05 mm) and, thus, were classified as sand, loamy sand or sandy loam. Only moraine sample Bez4.1 and top horizon of Leptic Umbrisol have less than 50% of sand in their texture and were classified as loam and silt loam, respectively. The largest percentage of sand (92.64%) was defined in another moraine deposit which indicates different sources of material and

different rate of weathering. Cryoconites did not differ greatly between each other which indicate similar source of material, mostly input from the local valley walls due to dominance of large particles which cannot be transferred on the long distances. Local soils were more diverse in this term; the highest amount of sand was defined in Umbrisols (83.12%) in horizon B while in the same study site, in top horizon, the lowest amount of sand (38.01%) and high amount of silt (51.59%) were determined, probably, due to high biological weathering in this horizon. Noticeable difference between sediments and soils was found in amount of clay, its amount was statistically higher in soils than in cryoconite and moraines ($F = 4.81, p < 0.05$) due to better conditions for weathering.

After study of basic chemical and physical features we can move on to the results of pollution of cryoconites, soils and other materials.

3.3 Trace elements content

Concentrations of several trace elements in sampled materials are presented in Table 4. Cryoconites and moraines from the Bezengi Glacier had higher concentrations of trace elements in comparison with our previous study in the Caucasus region (Kushnov et al. 2021). The highest content among studied materials was noted for Zn. Among the studied cryoconites the highest values of Cu (17.10 mg·kg⁻¹), Pb (30.00 mg·kg⁻¹), Zn (85.70 mg·kg⁻¹), Ni

Table 4 Trace elements content in the studied materials

Sample	Sample type	Horizon	Trace elements content (mg·kg ⁻¹)				
			Cu	Pb	Zn	Ni	Cd
Bez1.1	Soil-like body	Ch	11.00	8.66	59.00	11.70	<0.005
Bez1.2	Soil-like body	C	15.60	12.70	72.60	14.20	<0.005
Bez2.1	Cryoconite	Surface	8.05	8.34	44.60	12.10	<0.005
Bez2.2	Cryoconite	Surface	6.74	3.67	30.40	6.50	<0.005
Bez3.1	Cryoconite	Surface	17.40	30.00	85.70	19.00	0.05
Bez3.2	Cryoconite	Surface	10.70	24.90	55.20	16.10	<0.005
Bez4.1	Moraine	C	12.60	9.64	49.20	13.70	<0.005
Bez4.2	Moraine	C	12.50	15.70	58.70	14.20	<0.005
Bez4.3	Moraine	C	12.90	11.00	54.90	15.20	<0.005
Bez5	Moraine	C	8.13	8.92	45.00	10.80	<0.005
Bez6	Moraine	C	6.04	6.14	40.60	8.61	<0.005
Bez7	Cryoconite	Surface	10.40	18.30	48.90	13.00	<0.005
Bez8	Cryoconite	Surface	16.10	15.00	70.90	15.80	<0.005
Bez9	Soil	Oe	8.08	14.40	50.80	8.01	0.10
		A	4.87	10.90	34.30	6.09	0.05
		B	2.40	7.94	33.40	3.59	<0.005
		C	3.41	8.55	40.20	4.91	0.02
Bez10	Soil	Oe	12.80	15.00	87.50	10.30	0.25
		B	12.00	16.30	89.20	11.60	0.25
		C	9.04	10.90	85.10	12.60	0.31

(19.00 mg·kg⁻¹) and Cd (0.05 mg·kg⁻¹) were defined at the Bez3.1 sample at the crevice of the glacier. In the cryoconites at glacier surface concentrations of pollutants were lower, probably, due to transfer of cryoconite material downstream to adjacent environment. Cryoconite in holes also showed relatively high concentration of pollutants, especially in big cryoconite hole. Soil-like bodies showed values similar to the supraglacial sediments and they were lower in the study point with plants which may indicate uptake of trace elements by plants. High variability of trace element values were observed between cryoconites in crevasses, cryoconite holes and sediments at the glaciers surface, even if they were close to each other. This is also indirectly confirmed by the content of trace elements in local soils due to transfer of pollutants from the glaciers. In general, it was higher than in supraglacial sediments, especially in more remote study site Bez10 because this soil section is located in the floodplain and is usually affected by floods while study site Bez9 is located on high ground and is not essentially influenced by the water flow. Considerably higher concentrations of Cd (up to 0.25 mg·kg⁻¹) were observed in local soils in comparison with sediments. In most of cases the highest concentrations of trace elements were found in the top horizons of the soil profile (Cu = 12.80 mg·kg⁻¹, Pb = 16.30 mg·kg⁻¹, Zn = 89.20 mg·kg⁻¹). Statistically significant difference is

observed between the sediments and local soils in the content of Cu ($F = 4.84, p < 0.05$), Ni ($F = 10.09, p < 0.05$) and Cd ($F = 14.72, p < 0.05$). Positive correlations were observed between the content of all trace elements, except of cadmium. In order to correctly interpret the data obtained, pollution indices have been calculated and presented in the next section.

3.4 Pollution indices including I_{geo}, CF and C_{degree}

According to the calculation results of I_{geo}, most of the studied materials were practically unpolluted (I_{geo} ≤ 0), except of Zn (Fig. 3). All materials were at least slightly (0 < I_{geo} ≤ 1) polluted by Zn, while soil-like body with vegetation (1.21), cryoconite in crevice (1.45) and hole (1.18) as well as Molic Leptosols (up to 1.51) were moderately polluted (1 < I_{geo} ≤ 2). Cryoconites, moraines and soil-like body were slightly polluted by Cu and Pb (up to 0.57). However, their indices in downstream soils were lower in comparison with Zn, which, probably, indicates their lower mobility in this environment.

Regarding CF values, pollution load was quite diverse (Fig. 4). Pollution by Ni and Cd did not exceed threshold of low pollution (CF < 1), however, in Leptosols these values were relatively high (up to 0.70) which may be connected with presence of automobile

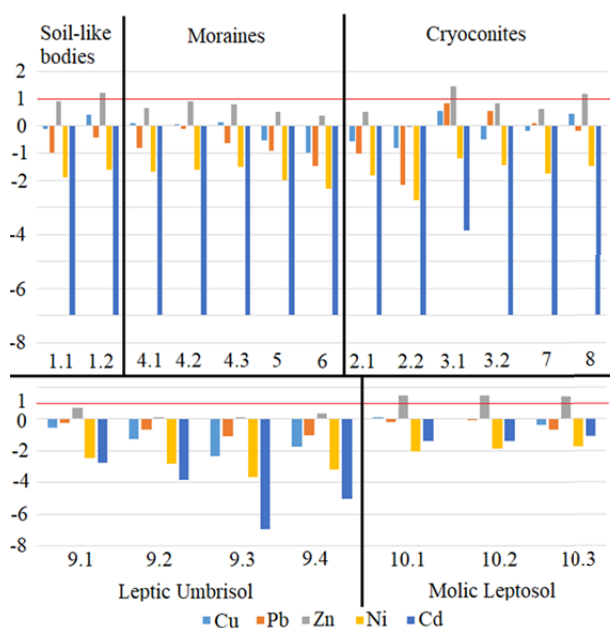


Fig. 3 Calculated I_{geo} values of studied materials (red lines indicate classes of pollution).

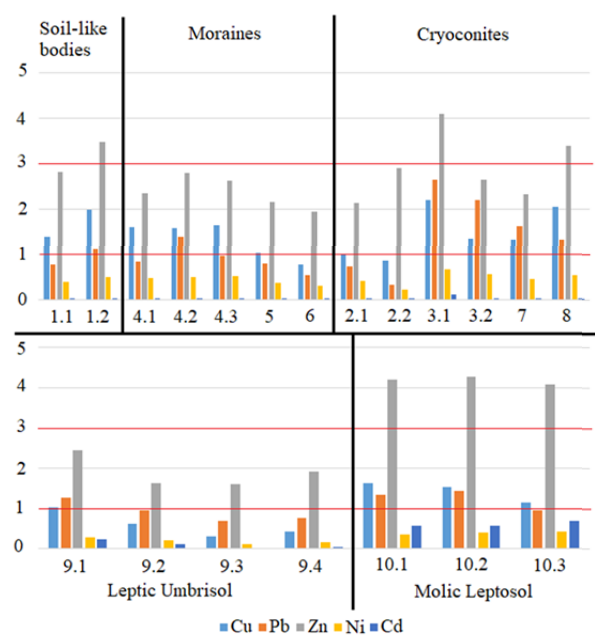


Fig. 4 Calculated CF values of studied materials (red lines indicate classes of pollution).

road nearby or features of local parent material. About half of all studied materials was slightly polluted by Pb, while another samples, especially cryoconites in crevasses, cryoconite holes, soil-like body with vegetation and top horizons of soils, showed moderate pollution ($1 \leq CF < 3$; up to 2.65 in cryoconite). Most of the studied materials were moderately polluted by Cu (up to 2.05 in cryoconite) and moderately or highly by Zn, ($3 \leq CF < 6$). High pollution values were observed in cryoconite from crevice (4.11) and cryoconite-derived soil-like body with vegetation (3.48). The highest pollution load was observed in Leptosols (up to 4.28) which also indicates the influence of fluvio-glacial transfer of pollutants from the supraglacial zone and their accumulation in local soils.

C_{degree} calculation indicated that most of the samples were moderately ($n \leq C_{degree} < 2n$) polluted by all the studied trace elements (Fig. 5). The lowest values were observed in moraine Bez5 (4.38) and Umbrisols (2.76). The highest pollution load was found in cryoconites in crevice (9.75) and cryoconite hole (7.34) as well as in Leptosols (up to 8.21). C_{degree} was decreasing in the studied Umbrisols which indicates possible input of pollutants via aeolian

transfer while high values in Leptosols indicate considerable impact of water streams in transfer of trace elements from supraglacial zone to periglacial in this mountainous area and possibility of local soils to accumulate these pollutants.

4 Discussion

4.1 Migration of organic carbon from glacier to soil system and its role in development of primary soils

IPCC (2021) reports that rapid deglaciation is occurring in most alpine regions. The Central Caucasus is not an exception in terms of deglaciation. Between 1985 and 2000 approximately 94% of glaciers located there are subjected to degradation and to date, these processes are intensifying. The length of the Bezengi Glacier has been decreased by 870 m between 1946 and 2011 and this process continues (Bushueva 2015). It was recently found (Hood et al. 2015) that deglaciation contributes to 13% of the annual flux of glaciers's organic carbon in which deposition of carbonaceous material and microbial activities play a major role and may increase input of organic carbon in future. Cryoconite is an important storage of carbon which is comparable with soils and waters, and may considerably influence local and global carbon cycle (Anesio et al. 2009). Despite the fact that cryoconites store less organic carbon than permafrost (Shuur et al. 2008), supraglacial carbon pool is still essential and its organic carbon is very labile which was observed at the Tibetan Plateau (Feng et al. 2016). Its transfer to downstream environments led to accumulation of this bioavailable organic carbon in adjacent soils in Svalbard (Juselius et al. 2022). In our study we also observed accumulation of organic carbon at the supraglacial zone of the Bezengi Glacier, especially in crevasses, however, it is noticeable that most of the organic carbon was transferred to the alpine soils, mostly by water streams, due to its accumulation in Leptosols (max. 7.52%), located in floodplain. In the recent study at the Tibetan Plateau (Niu et al. 2022a) it was found that at high elevations 65% of organic carbonaceous matter deposited from the atmosphere is transported downstream by alpine runoff and melted water from the glacier. Another study (Niu et al. 2022b) proved that water-soluble organic matter dominates in the carbon cycle of glacierized regions.

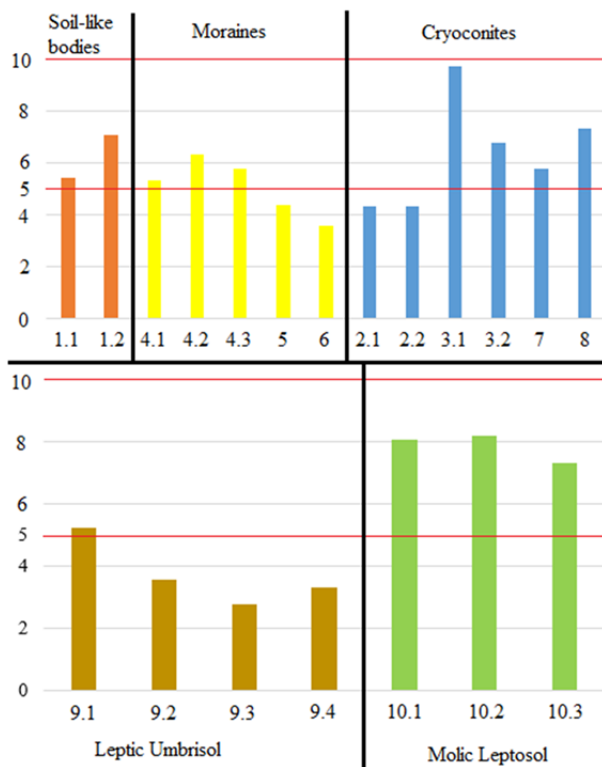


Fig. 5 Calculated C_{degree} values (red lines indicate classes of pollution).

This also proves our theory that most of organic carbon from cryoconites is transported to downstream floodplains via water streams in the Khulamo-Bezengi Gorge.

Due to the fact that carbon is an essential nutrient for microorganisms, its additional input promotes development of microbial communities in vicinity of the glacier which was observed by high respiration values in cryoconite holes (max. 26.29 mg CO₂·100 g⁻¹·24 h⁻¹) as well as nearby moraine and soil-like bodies (up to 30.80 mg CO₂·100 g⁻¹·24 h⁻¹). It was earlier found (McCrimmon et al. 2018) that microorganisms in cryoconites use recently deposited fresh carbon, thus, their development is dependent on the sources and amount of the carbon input. Previously, another study at the Central Caucasus (Makowska et al. 2016) found that cryoconites at this region are inhabited by various heterotrophic microorganisms such as *Aeromonas sp.* and *Pseudomonas sp.* which may recycle and release carbon and, thus, affect local carbon cycle. This may also explain high values of organic carbon in studied soils especially in the floodplain. In study of Kastovska et al. (2005) high values of microbial respiration were observed only in cryoconites and not in adjacent soils, however, in the Caucasus, transfer of carbon also promotes development of microorganisms in soils as was observed by high respiration values in Umbrisols (max. 35.09 mg CO₂·100 g⁻¹·24 h⁻¹) and Leptosols (max. 26.40 mg CO₂·100 g⁻¹·24 h⁻¹). These values of cryoconites and soils were comparable with each other as it was found before (Anesio et al. 2009) in different polar and alpine regions such as Greenland, Svalbard and the Alps and this transfer may accelerate development rate of soils as it was observed in vicinity of Aldegonda Glacier in Svalbard (Zazovskaya et al. 2022).

4.2 Role of acidity, source of material and weathering in the development of primary soils

Earlier study (Dong et al. 2022) showed that development of microorganisms and their cooccurrence between supraglacial and periglacial zones is influenced not only by organic carbon input but also by pH values. In most cases in this study, pH values were similar among each other as well as to our previous study (Kushnov et al. 2021), showing neutral

values of acidity while some values, especially in local soils, were slightly acidic. These values were also comparable with those defined in the Arctic (Kastovska et al. 2005) and at the Tibetan Plateau (Fair et al. 2020) while research in the Antarctic (Webster-Brown et al. 2015) showed much wider range of acidity values, from acidic to alkaline. This may indicate favorable conditions for development of transferred microorganisms in studied soils and soil-like bodies and their possible role in primary succession of territory after glacier retreat at the Central Caucasus. Positive correlation between basal respiration and particle-size distribution in our study points to the fact that microbiological activity influence grain size due to enhanced weathering and transformation processes which was also observed on the Qaanaaq Glacier in Greenland (Uetake et al. 2016). Despite the fact that studied samples showed similarities between each other, higher content of silt was observed in soils because microbiological activity is highly dependent on the temperature regime, thus, biological weathering is essentially affected by the altitude (Riebe et al. 2004). Vegetation cover also affects grain size through production of organic acids by plant roots and may influence pH values of soils (Egli et al. 2008) which was observed in our study. Harsh environmental conditions are not the only explanation of coarse earth and sand dominance in texture of supraglacial sediments at the Bezengi Glacier. In contrast to this study, Kastovska et al. (2005) found that cryoconites in Svalbard were dominated with fine earth and silt. Recently Abakumov et al. (2021) described a significant difference between them in terms of particle-size distribution in their study of cryoconites from the Anuchin Glacier in the Antarctica and Mushketov Glacier in the Arctic. Anuchin Glacier is surrounded by the Gruber mountains which partly block aeolian transfer of small particles (silt and clay fractions) and at the same time valley walls around glaciers act as an autochthonous source of large particles (sand and coarse earth fraction) while Mushketov Glacier is not surrounded by mountains and is essentially influenced by long-range transfer. Bezengi valley glacier is located in huge mountain range and is surrounded by high valley walls which considerably affect texture of cryoconites. This is typical for the Central Caucasus in general due to similar result obtained at the Elbrus mountain and adjacent Baksan Gorge (Kushnov et al. 2021). Despite the fact that

Caucasus mountain range limits the allochthonous atmospheric transfer, carbon-containing dust, originated in Northern Africa (Sahara Desert) and Western Asia, was found on the surface of glaciers in this area (Kutuzov et al. 2015a; Dumont et al. 2020). Together with transfer of organic carbon and other nutrients, trace elements enter the mountainous ecosystems of the Central Caucasus.

4.3 Migration of trace elements from glacier to soil system

In the research of Kutuzov et al. (2015a) it was found that this dust is enriched with Cu, Cd and Zn which may point to the high background values in these regions or to the influence of anthropogenic aerosols. Study of Wu et al. (2022) also shows that air masses trajectory may be favorable for transfer of trace elements from industrial to remote areas as it was observed at the Tibetan Plateau. In our previous study (Kushnov et al. 2021) at the Elbrus region we observed high content of Cu (max. 16.70 mg·kg⁻¹), Pb (max. 30.20 mg·kg⁻¹) and Zn (max. 62.00 mg·kg⁻¹) in cryoconites, mostly autochthonous origin. In this research values of trace elements were comparable or higher: Cu = max. 17.40 mg·kg⁻¹; Pb = max. 30.00 mg·kg⁻¹; Zn = max. 85.70 mg·kg⁻¹. The same was observed for pollution indices: values were comparable as it had been described before in our previous study (Kushnov et al. 2021). Due to predominance of sand and coarse earth in cryoconite texture we assume that these pollutants were originated locally. However, another geochemical study in the Central Caucasus (Kutuzov et al. 2021) revealed that atmospheric dust on the glacier surface was also enriched with Zn due to mining and other anthropogenic activities in the Western Asia. The main sources of trace elements are industries, coal combustion and vehicles emissions (Duan and Tan 2013) and it was found that traffic and fossil fuels combustion is the major source of Pb and Ni at the Central Caucasus (Shagin et al. 2018). In this region there are only few abandoned Pb-Zn mines among industries (Uraskulov et al. 2018), however, in the vicinity of the Bezengi Glacier there is a large touristic base with permanent buildings and tent camp where combustion coal and biomass is used for heating and cooking. Moreover, this camp is connected to the main highway by an automobile road that goes nearby the glacier and through the whole Khulamo-Bezengi

Gorge and it contributes to the local pollution. It was previously found (Birmili et al. 2006) that automobile traffic is a significant source of Pb emissions and may contribute to pollution of the environment by Zn and Cd. Moreover, particles from automobile tires may be an additional source of Zn (Councell et al. 2004). This influence of traffic on pollution load of adjacent territories was especially noticeable in studied soils where the highest concentrations of Zn (89.20 mg·kg⁻¹) and Cd (0.31 mg·kg⁻¹) were defined. Therefore, additional input of pollutants to the Central Caucasus from long-distant sources as well as local anthropogenic activities contribute to the pollution of studied territories as it was found in previous study of pollution of the Central Caucasus region by polyarenes (Abakumov et al. 2022).

Together with accumulation of polluted material its redistribution occurs within the mountain range. Glazovskaya (2005) earlier pointed that during glacier melting, predominantly in the summer period, supraglacial sediments are transferred to the adjacent foothill ecosystems in form of solution or solid particles with fluvio-glacial streams and aeolian processes. This transfer contributes to the pollution of local soils by various substances, including trace elements. High content of these pollutants were defined in glacial meltwater streams at the Tibetan Plateau (Dong et al. 2017) and the peak concentration of transferred trace elements was influenced by the runoff level which in our case may be affected by the presence of cryoconites. Moreover, in this study it was found that at the Tibetan Plateau some of trace elements had anthropogenic origin while others have been originated from cryoconites and snow dust. Due to the fact that cryoconites may accumulate anthropogenic pollutants we can assume that these supraglacial sediments essentially contribute to the pollution level of alpine territories, including the Central Caucasus. “Barrier effect” of the Gogga Mountains at the Tibetan Plateau led to increased pollution of soils by Pb and Cd (Bing et al. 2018). High values of trace elements, especially Cu and Zn, and high values of pollution indices in soils in our study cannot be explained only by local anthropogenic activities. Positive correlation between content of trace elements in soils and cryoconites also indicates that transfer of cryoconites affect pollution load of studied soils. Transfer of sediments occurs predominantly with water streams due to high concentrations of pollutants in Leptosols located in

the floodplain which is usually affected by floods. Recent study in European mountains (Yaneva et al. 2022) indicated that mountain soils act as a buffer for local pollution. Research conducted at the soils in vicinity of Everest Mt. (Magnani et al. 2018) revealed similar to our study concentration of trace elements with the accumulation in top horizons which indicates input of pollutants with deposition and their further redistribution. Pollution indices calculation of mountainous soils in Changba Mt. defined moderate or high pollution levels with trace elements such as Pb and Zn which was connected with touristic activities and automobile road nearby. Most of trace elements are not biodegradable and may be accumulated in vegetation cover (Kumar et al. 2016). This is especially important to consider in the context of the fact that soils of region under our investigation are used for agriculture. It was found (Alborov et al. 2019) that pollution of mountainous soils at the Central Caucasus increased concentration of Pb and Zn in perennial fruit crops such as pears and apples. Transfer of cryoconites may contribute to this pollution. Moreover, mountain soils such as Leptosols and Umbrisols are susceptible to the removal of Cu and Ni from the soil profile (Khoroshev 2001) which may influence further pollution of foothill soils.

4.4 Significance of cryoconite in biogeochemical cycle in the cryosphere

Therefore, cryoconites influence biogeochemical cycles at and nearby the Bezengi Glacier as well as affect their pollution load. Schematic figure of transfer of mineral and organomineral matter at supraglacial and periglacial zones of the Bezengi Glacier is presented at Fig. 6. This figure was made on the basis of information from this research as well as from studies of Glazovskaya (2005), Lokas et al. (2018) and Zazovskaya et al. (2022).

The Central Caucasus represents a region where polluted atmospheric dust and fine earth have both allochthonous and local origin (Lokas et al. 2018). It is accumulated in supraglacial zone and is further

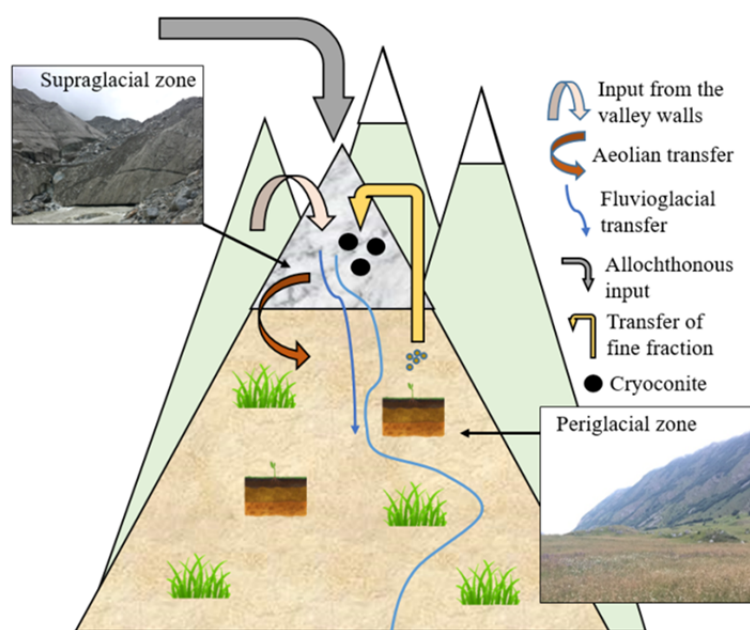


Fig. 6 Transfer of matter between supraglacial and periglacial zones of the Bezengi Glacier.

transferred to periglacial zone by aeolian and, mainly, fluvioglacial processes. It was found (Zazovskaya et al. 2022) that this transfer takes place also backwards: from periglacial to supraglacial zone. Fine fraction, enriched with nutrients and pollutants, is transferred by aeolian processes and deposited on glacier surface which means additional input of local pollutant, their accumulation and further redistribution. Therefore, redistribution of organomineral matter, which takes place mainly in warm period of the year, considerably influence development of soils as well as pollution of alpine environment on the surface and in vicinity of the biggest valley glacier in the Central Caucasus.

5 Conclusion

The performed study shows the importance of cryoconites in geochemical cycles of the Central Caucasus mountainous region and at the Bezengi Mountain Wall. Key chemical and physical features as well as concentrations of trace elements (Cu, Pb, Zn, Ni, Cd) were determined in cryoconites and adjacent mountainous soils. Results revealed low accumulation of organic carbon on the glacier surface, predominantly in crevasses (max. 0.23%), mostly due to its transfer by aeolian processes and glacial streams to periglacial zone. This transfer caused high values of organic carbon in soils of the adjacent gorge,

especially in the top horizon of Leptosols (7.54%), located in the floodplain, which indicates importance of fluvioglacial transfer of matter. Under the influence of additional input of labile organic carbon, we observed active development of microorganisms in studied soils ($35.09 \text{ mg CO}_2 \cdot 100 \text{ g}^{-1} \cdot 24 \text{ h}^{-1}$) which potentially may accelerate their development. The main source of organic carbon and other elements was autochthonous input due to barrier effect of surrounding mountains, however, transport of particles from Western Asia and Northern Africa also affected biogeochemical cycles of the Central Caucasus. Among trace elements, supraglacial sediments efficiently accumulated Zn (max. $85.70 \text{ mg} \cdot \text{kg}^{-1}$), Pb (max. $30 \text{ mg} \cdot \text{kg}^{-1}$) and Cu (max. $17.40 \text{ mg} \cdot \text{kg}^{-1}$), both allochthonous and locally originated. Due to transfer of trace elements, mainly by water streams, local soils were exposed to pollution by these elements. The highest amount of pollutants was found in Leptosols located in floodplain (Zn, $89.20 \text{ mg} \cdot \text{kg}^{-1}$). Pollution indices calculation revealed that studied material were up to moderately polluted by Cu and Pb, and up to highly polluted by Zn. In general, cryoconite in crevice and Leptosols in floodplain were polluted most by all trace elements which points to the fact

that cryoconites affect pollution load of alpine soils. Observed transfer of matter within the Central Caucasus mountain region and Khulamo-Bezengi Gorge may accelerate development of local soils as well as influence their pollution load which can have a negative impact on the vulnerable mountain environment, agricultural opportunities and health of local population. Further extended field researches are needed to study geochemistry of the Central Caucasus region and role of supraglacial sediments in it.

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