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CRYOCONITE AS A STORAGE AND SOURCE OF POLLUTANTS IN THE HIGH-ALTITUDE AREAS OF THE CENTRAL CAUCASUS

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Abstract

Global environmental change has become one of the top priorities in recent international studies. One of its consequences is rapid deglaciation which is often associated with formation of dark-colored supraglacial sediments, cryoconites. They may considerably affect vulnerable mountain ecosystems through changing their geochemical properties as well as play role in formation and development of primary soils after retreat of glacier. Long-distant transfer as well as local anthropogenic pressure cause pollution of high-mountain regions where cryoconite play crucial role due to their ability to accumulate and further transfer various pollutants such as trace elements and polyarenes to local ecosystems which may pose risk to local wildlife and population. Study of geochemical, physical and micromorhological features of cryoconites and glacial sediments as well as local soils is crucial to understand cryoconite's properties and its impact on mountain ecosystems under conditions of rapid deglaciation. For this research different types of materials such as cryoconites, moraines, mudflows, soil-like bodies and soils (Molic Leptosols, Leptic Umbrisols and Chernozems) have been sampled at the Baksan and Khulamo-Bezengi gorges with purpose to study their physicochemical, geochemical and micromorphological features. In order to access their pollution, concentrations of trace elements (Cu, Pb, Zn, Ni, Cd) and polyarenes (from the USDA top-priority list) have been measured. Pollution indices such as geoaccumulation index, contamination factor, degree of contamination and modified degree of contamination have been calculated to evaluate levels of pollution by trace elements. The data obtained indicates mostly neutral pH values in studied samples with some exceptions in Leptosols/Umbrisols in terms of exchangeable acidity (acidic level) due to organic matter accumulation. High values of organic carbon (up to 7.54%) and basal respiration (up to 48.40 mg CO_2/ 100 g per day) in cryoconites and top horizons of local soils indicates that cryoconites promote development of microbial communities in local soils via transfer of organic carbon downstream. Sand particles are prevailed in cryoconites and Leptosols/Umbrisols due to their low rate of development and local source of transfer. Quartz, mica and feldspar are prevailed in micromorphological structure of cryoconites and Leptosols/Umbrisols indicating similar source of material. Source of pollutants is mixed indicating both local and distant input. The highest content among polyarenes was identified for NAP (84 ng/g), sum of concentrations of all polyarenes are higher than maximum permissible concentration. High content of Zn (up to 89.30 mg/kg), Pb (30.20 mg/kg) and Cu (40.70 mg/kg) was found in cryoconites as well as in local soils, predominantly top horizons, due to mixed input of pollutants, both long-distant transfer and local anthropogenic activities. Pollution indices are in some cases higher in cryoconites than in Leptosols and Umbrisols, among them indices are mostly the highest at top horizons indicating transfer of pollutants by aeolian processes and water streams from the glacier’s surface to the valley. This study indicated role of supraglacial sediments in pollution and development of soils in the high-altitudinal area of the Central Caucasus region.

КРИОКОНИТ КАК НАКОПИТЕЛЬ И ИСТОЧНИК ЗАГРЯЗНЯЮЩИХ ВЕЩЕСТВ В ВЫСОКОГОРНЫХ РАЙОНАХ ЦЕНТРАЛЬНОГО КАВКАЗА

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Аннотация

Глобальное изменение окружающей среды стало одним из приоритетных направлений международных исследований в последнее время. Одним из его последствий является быстрое отступление ледника, которое часто связано с образованием темноокрашенных надледниковых отложений – криоконитов. Они могут существенно влиять на уязвимые горные экосистемы, изменяя их

геохимические свойства, а также играть роль в формировании и развитии первичных почв после отступления ледника. Дальний перенос, а также местное антропогенное давление вызывают загрязнение высокогорных регионов, где криокониты играют значительную роль благодаря своей способности накапливать и далее переносить различные загрязнители, такие как микроэлементы и полиарены, в местные экосистемы, что может представлять риск для местной дикой природы и населения. Изучение геохимических, физических и микроморфологических особенностей криоконитов и ледниковых отложений, а также местных почв имеет решающее значение для понимания свойств криоконитов и их влияния на горные экосистемы в условиях быстрой дегляциации. Для данного исследования в Баксанском и Хуламо-Безенгийском ущельях были отобраны пробы различных типов материалов, таких как криокониты, морены, сели, почвоподобные тела и почвы (горные лесо-луговые почвы, горно-луговые субальпийские и черноземы), с целью определения их физико-химических, геохимических и микроморфологических особенностей. Для того, чтобы получить доступ к их загрязнению, были измерены концентрации микроэлементов (Cu, Pb, Zn, Ni, Cd) и полиаренов (из приоритетного списка USDA). Для оценки уровня загрязнения микроэлементами были рассчитаны такие индексы загрязнения, как индекс геоаккумуляции, коэффициент загрязнения, степень загрязнения и модифицированная степень загрязнения. Полученные данные свидетельствуют о преимущественно нейтральных значениях pH в исследованных образцах с некоторыми исключениями в энтисолях по обменной кислотности (кислый уровень) из-за накопления органического вещества. Высокие значения органического углерода (до 7,54%) и базального дыхания (до 48,40 мг CO_2/ 100 г в день) в криоконитах и верхних горизонтах горных почв свидетельствуют о том, что криокониты способствуют развитию микробных сообществ в местных почвах путем переноса органического углерода вниз по течению. В криоконитах и горных почвах преобладают песчаные частицы из-за их низкой скорости развития и местного источника переноса. В микроморфологической структуре криоконитов и местных почв преобладают кварц, слюда и полевой шпат, что указывает на сходный источник материала. Источник загрязняющих веществ смешанный, что указывает как на местное, так и на удаленное поступление. Наибольшее содержание среди полиаренов выявлено для NAP (84 нг/г), сумма концентраций всех полиаренов превышает предельно допустимую концентрацию. Высокое содержание Zn (до 89,30 мг/кг), Pb (30,20 мг/кг) и Cu (40,70 мг/кг) обнаружено в

криоконитах, а также в горных почвах, преимущественно в верхних горизонтах, что объясняется смешанным поступлением загрязняющих веществ, как дальним переносом, так и местной антропогенной деятельностью. Индексы загрязнения в некоторых случаях выше в криоконитах, чем в горных почвах, а среди горных почв они, в основном, самые высокие в верхних горизонтах, что указывает на перенос загрязняющих веществ эоловыми процессами и водными потоками с поверхности ледника в долину. Данное исследование показывает роль надледниковых отложений в загрязнении и развитии почв в высокогорных районах Центрального Кавказа.

1. Introduction

The problem of global environmental change has become crucially important in recent decades in scientific studies. Climate change on the Earth driven by human activities is a proven fact (IPCC, 2021). Mountainous and high-latitude regions are considered as the most sensitive to both anthropogenic chemical pollution and global temperature rise. Approximately 10% of surface of the Earth is covered by glaciers and in mountainous regions this percentage is higher (Ren et al., 2019). In twenty-first century the melting of glaciers around the world has accelerated essentially and their mass continues to decrease (Hugonnet et al., 2021). Carbon-containing dust plays a significant role in climate system due to its ability to absorb solar radiation and accelerate melting of ice and snow cover. This dust originates from different combustion processes: natural are usually connected with forest fires while anthropogenic are mainly associated with solid fuel burning (60-80% of emissions in Asia and Africa) or diesel engines usage (70% of emissions in Europe) (Bond et al., 2013).

Despite the fact that carbon-containing dust is emitted to the atmosphere, it is deposited on terrestrial surfaces relatively fast and together with mineral and organic matter forms specific sediment which is called cryoconite. This term “cryoconite” comes from ancient Greek language meaning “cold dust” and it was introduced by famous Scandinavian researcher Nordenskjöld in 1870 when he discovered this substance in the internal part of Greenland (Nordenskjöld, 1875). Cryoconite refers to dark colored supraglacial sediments which can be found in polar regions and high mountains all over the world and can be described as a mixture of black carbon, the mineral and organic matter, which can be found on the surface of glaciers, both in so-called “cryoconite holes” or dispersed over the surface, including debris-covered glaciers (Adhikary et al., 2000; Cook et al., 2016; Di Mauro et al., 2017). According to their morphological features several types of supraglacial sediments may be defined, for example, “cryoconite mantle” for thick and dry cryoconite and “hydroconite” for wet, watered sediments (Cook et al., 2016). Cryoconite formation is associated with both allochthonous and autochthonous input of material. In the first case carbon-enriched dust comes from deserts (Takeuchi and Li, 2008), volcanic eruptions (Kalińska-Nartiša et al., 2017) or various anthropogenic activities, for example, biomass burning (Li et al., 2019b) while in the second case material usually comes from local moraines, ice deformation or adjacent slopes due to aeolian and fluvial processes (Porter et al., 2010; Swift et al., 2018).

Organic matter of cryoconite includes residues of plants and animals, dead and alive microorganisms as well as additional biogenic and biotic materials (Takeuchi et al., 2010; Cook et al., 2016). Cryoconite plays a role of “oasis” for various viruses, algae, bacteria and fungi on relatively uninhabited surface of the glacier (Takeuchi et al., 2001; Edwards et al., 2013). These microbial communities affect local cycles of microelements and nutrients and, thus, influence ecosystems. “Cryoconite holes” are considered as storage of nutrients with their own biogeochemical cycle which means the ability not only to accumulate nutrients but also to transform them (Bagshaw et al., 2013) as well as cryoconite biofilms which are also responsible for high biological activity and act as a storage for nutrients (Smith et al., 2016). Earlier (Anesio et al., 2009) it was carried out that net primary production and respiration rates are similar between glaciers with cryoconite and freshwater samples which indicates the ability of sediments to become a carbon sink and influence the carbon cycle. Another research (Hodson et al., 2008) found communities of nitrifiers which may convert ammonium (NH_4^+) to nitrates (NO_3^-) and, thus, affect the nitrogen cycle. Furthermore, ice and snow melting during warm period of the year may cause transfer of cryoconite material enriched with nutrients and carbon to downstream ecosystems via water streams which can and influence trophic relationships in them and also affect adjacent floodplains (Glazovskaya, 2005; Foreman et al., 2007; Ren et al., 2019).

Microbial communities and organic matter normally strongly influence the albedo of the glacier. Cryoconites contain dark colored decomposed algae material, humic substances and products of microorganisms’ metabolic activities which mainly cause dark color of these sediments and may cause appearance of so-called “cryogenic foam” (Takeuchi, 2002; Rakusa-Suszczewski, 2015; Musilova et al., 2016; Polyakov et al., 2019). Also establishment of so-called cryoconite holes is connected with increased energy input due to presence of dark colored sediments which causes melting of ice and deepening of this hole (Wharton Jr et al., 1985). BC is another substance which significantly influence albedo reduction of the glacier. Chemical composition affects its light-absorbing properties. In study of Polyakov and Abakumov (2020a) two-dimensional analysis of humic acids (HAs) extracted from black carbon particles has been made. The data obtained indicated the accumulation of aromatic structures in the HAs composition, which indicates the condensation of macromolecules and leads to the stabilization of organic matter with the formation of molecules resistant to biodegradation.

Due to this ability to regulate the albedo, cryoconite sediments may essentially accelerate melting of glaciers which leads to their retreat. Numerous researches prove this statement (MacDonell et al., 2013; Di Mauro et al., 2017; Li et al., 2019; Humbert et al., 2020). In Antarctica presence of sediments significantly increases the availability of energy and the ablation is nine time greater than for clean ice surfaces (MacDonell et al., 2013). Furthermore, the reflectance of Greenland ice sheet drops by 25% during two-year time period when sediments appeared on the clean ice surface (Humbert et al., 2020). At Morteratsch Glacier the presence of cryoconite reduce ice spectral reflectance in visible wavelengths from 0.90 to 0.06 (Di Mauro et al., 2017). In Himalaya region, the presence of sediments also leads to an enhanced absorption of light energy, mostly at shorter wavelength (Gautam et al., 2013). The lowest mean reflectance of cryoconite among any impurities was observed on Tibetan Plateau, where black carbon as part of cryoconite played the highest role in light absorption (Li et al., 2019). Moreover, it was investigated that the spread of cryoconite could be associated with the collapse of cryoconite holes caused by cloudy, warm and windy weather conditions (Takeuchi et al., 2018). In this situation of glaciers retreat it is important to point that cryoconites may play an important role in establishment of new microbial community on previously inaccessible territory, covered by glacier, due to broad metabolic possibilities of microbial assemblages in these sediments and relatively similar set of microorganisms in cryoconite and adjacent soils (Wharton Jr et al., 1985; Kaštovská et al., 2005; Poniechka et al., 2020).

Another important part of cryoconite is mineral particles. Usually it consists of silt sized particles (Hodson et al., 2008; Cook et al., 2016), however, it varies because of different sources and rate of weathering. Microorganisms use minerals as a source of nutrients for developing of their communities (Wientjes et al., 2011). Due to this fact, mineralogical composition of cryoconite may affect biological activity on the glacier surface, biomass of microbes and difference in their species (Nagatsuka et al., 2014). It was also reported that communities of microorganisms may change because of different grain size in supraglacial sediments and bacteria diversity is higher in cryoconite with small-sized grains (Uetake et al., 2019). This indicates microbial sensitivity to granulometric and micromorphological characteristics because particle size influences cation exchange capacity and, thus, absorption of nutrients by minerals from soil solution. However, clay particles also act as a storage of nutrients for microbial communities according to their composition which varies between glaciers (Tazaki et al., 1994). Moreover, source and amount of mineral matter influence darkening of glacier surface because of establishments of different microbial communities. Mineral particles may be transferred on the long distances, for instance, the main sources of mineral dust in North American Arctic are Asian deserts (VanCuren and Cahill, 2002). Observed environmental change (IPCC, 2021) may influence atmospheric transport of mineral particles and change their current sources. Furthermore, retreating of glaciers may increase aeolian transport of fine dust from adjacent proglacial floodplains to glacier surface (Bullard and Austin, 2011). Also rapid deglaciation will result in higher transfer of cryoconite mineral matter to downstream ecosystems and affect their sedimentation processes as well as amount of available nutrients.

The interrelations between cryoconite, glacial environment, and the atmosphere are important to study regional and global pollution trends. Mountainous and polar regions are especially sensitive to atmospheric pollution due to cold condensation or “grasshopper effect” which promotes deposition of various pollutants on the terrestrial surface (Fernandez et al., 2021). Cryoconite sediments can store natural and anthropogenic pollutants for several years up to several decades (Lokas et al., 2014). Recent research indicates that cryoconite can accumulate radioactive isotopes and specific elements with unprecedented efficiency (Baccolo et al., 2017; Lokas et al., 2019). Trace metals is another well-known group of harmful contaminants which may be found in high concentration in cold regions. Study of Polyakov et al. (2020) revealed that cryoconites accumulate trace elements which appeared due to both weathering of volcanic rocks and erosion of contaminated soils near polar stations. In the Arctic content of trace elements in cryoconites was measured at Spitsbergen island and it was higher than the natural background (Lokas et al., 2016). In high mountain ecosystems measurements of trace elements were conducted at Tibetan plateau and Himalayan region (Singh et al., 2017; Jiao et al., 2021) where the concentrations were higher than in the Arctic, which is probably connected with presence of highly industrialized Asian countries nearby. These researches also indicate importance of source and its remoteness from the area of cryoconite sedimentation. Despite the fact that Cu, Zn and Ni play a crucial role in functioning of plants, animals and humans, they may be poison and cause chronic diseases in case of accumulation in the organisms (Sharma and Agrawal, 2005). These elements as well as non-essential such as Pb and Cd have an ability to transfer to high trophic levels in ecosystems food web (Gall et al., 2015). Previous studies (Bai et al., 2018; Rehman et al., 2018) show that soil pollution with trace metals is associated with human health risk due to uptake of these elements with contaminated plants and direct contact. Local animals are also subject to these processes (Tian et al., 2020) and, thus, soil pollution with trace elements also possess risks to wildlife. Cryoconites in this case may be a source of these pollutants for downstream floodplains and soils due to transfer of them by aeolian processes and water streams in warm period (Glazovskaya, 2005).

Polycyclic aromatic hydrocarbons (PAHs) and other organic substances are considered as a ubiquitous group of contaminants in the environment. Their structure consists of atoms of carbon and hydrogen with different number of aromatic rings (Edwards, 1983). Generally, there are two main groups of PAHs defined by the number of aromatic rings: low molecular weight (LMW) and high molecular weight (HMW). Second group of these pollutants is more toxic for people and animals, more stable in environments and usually connected with anthropogenic activities (Mandal and Das, 2015). Short contact of humans with polyarenes may cause various symptoms such as skin rash, lachrymation and nausea while prolonged exposure could lead to chronic diseases due to mutagenic and cancerogenic properties of some PAHs (Bostrom et al., 2002; Famiyeh et al., 2021). Depending on the level of toxicity they are divided in groups: carcinogenic to humans (group 1), possibly carcinogenic (2A) and probably carcinogenic (2B) (IARC, 2010). Among these pollutants benzo[a]pyrene (BaP) is defined as extremely dangerous for human health and wildlife, and its content must necessarily be monitored (GN 2.1.7.2041-06, 2006). In current studies (Gao et al., 2019; Yang et al., 2021) pollution of the environment is usually estimated using benzo[a]pyrene-equivalent (BaP-EQ) where BaP acts as a reference component. Soils can store PAHs for a long time after deposition because of complexity of soil matrix and then polyarenes may be transferred to plants through uptake of them by roots (Sushkova et al., 2018; Abdel-Shafy and Mansour, 2016). In cold regions soils are especially sensitive to PAHs contamination because of reduced volatilization and biodegradation while the input of pollutants is increased due to “grasshopper effect” (Wang et al., 2019; Chen et al., 2008). Higher concentrations of different PAHs in comparison with background was found in different parts of the world: European mountains (Ribes et al., 2003; Quiroz et al., 2010), high-altitudinal parts of Asia (Zhou et al., 2018; Riaz et al., 2019; Wang et al., 2019) and North America (Abdul Hussain et al., 2019). In mountain ecosystems cryoconites also considered as a sink and source of PAHs. Current researches indicate that concentrations of polyarenes in these supraglacial sediments exceed threshold values in Antarctica (Abakumov et al., 2021) and on Tibetan plateau (Li et al., 2017). These high concentrations may pose a risk for environment and local population in mountainous region as it was found that glaciers store various pollutants on their surface which can affect downstream territories (Morselli et al., 2014).

2. State of the art

Caucasus is a famous mountain range which is located in the Eurasian continent and stretches from the Black Sea on the west to the Caspian Sea on the east. Main Caucasus range generally is divided into 3 parts: Western, Central and Eastern. Central Caucasus is the highest part of Caucasus range. Here the highest peaks of Russia and Europe are located such as Mt. Elbrus (5642 m) and Mt. Kazbek (5033 m) as well as lots of glaciers (Gvozdetsky, 1963). In general, Caucasus mountain region has around 1713 glaciers, their total area of 1121 km^2 which constitute 0.15% of all glaciated area of the Earth (Kutuzov et al., 2015b; Radic et al., 2014). Glaciers of the Central Caucasus play a major role both in cooling the adjacent areas (Kuban and Black Sea regions), which is associated with the phenomenon of mountain inversion, as well as the accumulation and subsequent release of cold to the foothill areas (Gvozdetsky, 1963). These glaciers are rapidly retreating: they lost around 5% of total area from 1987 to 2010 (Shahgedanova et al., 2014). Another study (Tielidze et al., 2022) points that in 21st century Caucasian glaciers lost around 23% of their total area. Moreover, the glaciers of the Caucasus act as one of the food sources for local rivers. The rivers of the Caucasus have a mixed type of feeding with a significant contribution from glaciers, which has recently decreased due to rapid deglaciation during last 50 years. From the other hand, the role of moraines and mudflows has increased (Rets et al., 2020), which enter the river together with runoff from agricultural fields and lead to siltation of the river bed, which in turn can lead to unpredictable floods and droughts. Rapid deglaciation may cause not only environmental problems but also affect engineering stability of buildings and infrastructure due to fact that the number of mudslides and other dangerous phenomena in the Central Caucasus has risen essentially over the last twenty years which is linked with retreating of the glaciers (Marchenko et al. 2017; Aleinikova et al., 2020). Cryoconites influence melting rate and micromorphological researches might be helpful to estimate the hypothetical area of transferred material accumulation in the zone of deglaciation and possible availability of nutrients for establishment of new environment. In this region only one micromorphological study has been conducted (Zawierucha et al., 2019) which showed presence of grey silty minerals which were affected by chemical weathering. Due to this grains with smooth edges were predominant. Also this research indicated the importance of local geomorphology and geology, and rate of weathering in forming of minerals. Central Caucasus in these terms is diverse region which indicates the need for further studies. Moreover, due to rapid glaciers retreat in last 20 years' frequency of hazardous events such as mudflows have increased considerably (Aleinikova et al., 2020) and defining micromorphological features may be useful in order to estimate hypothetical area of material drift. It is also important to study relationship between cryoconite sediments and soils in this region because Central Caucasus as well as other mountain regions is especially sensitive to any interventions in vulnerable ecosystems (Moshenko et al., 2020). Active construction of new touristic facilities in this region and work of already existing ones' (Voskova et al., 2021) results in contamination of local environment and may act as a source of local material for formation of cryoconites. It is especially important because agriculture plays a huge role in economy and lifestyle of local population: around 50% of people here live in rural area and industrial agricultural clusters are well-developed (Zaburaeva et al., 2021). However, no researches have been carried out in order to estimate influence of global and local processes on vulnerable ecosystem of this region in general and on local soils in particular. Only Vecchiato et al. (2020) have measured PAHs concentration in ice cores in order to assess their fluctuations in 20-th century. Thus, the main goal of this study was to investigate the features of cryoconites and their role as accumulators and sources of pollutants on the surface of glaciers in the Central Caucasus mountainous area.

To achieve this aim, some additional goals have been set:

- to investigate basic physicochemical features of cryoconites and local soils;
- to study micromorphological structure of supraglacial sediments;
- to define concentrations of selected PAHs, identify their sources and level of pollution;
- to determine amount of trace elements in cryoconites and local soils;
- to evaluate the level of trace elements pollution using several indices;
- to compare study results from different study sites.

3. Materials and methods

3.1. Description of study area

The area of research is located in the Central Caucasus region, Kabardino-Balkarian Republic, Russia (Fig. 1).

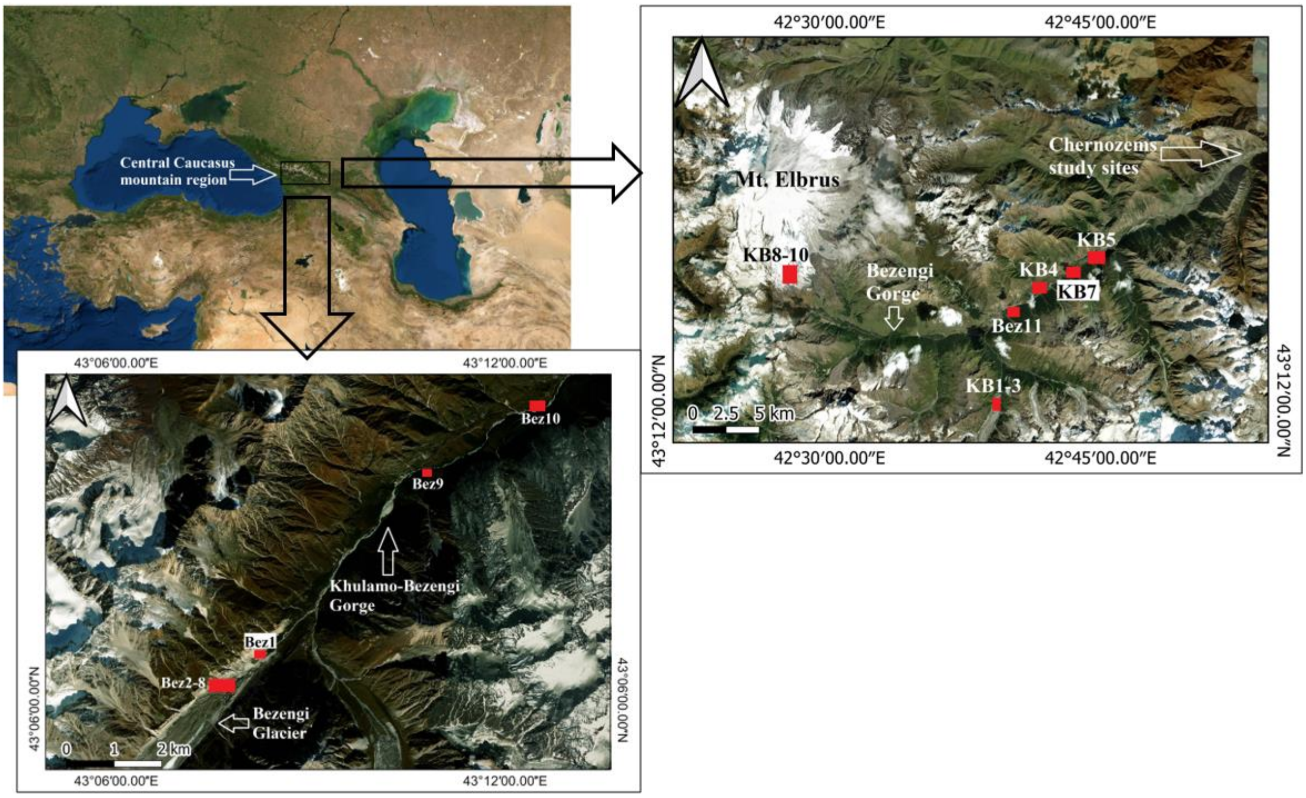

Figure 1. Sampling locations of studied materials.

One part of this region is located on the plain, and the second part is mountainous. Here the highest peaks of Russia and Caucasus range are situated such as Mt. Elbrus (5642 m), Mt. Dykhtau (5204 m) and Shkhara (5068 m) as well as hundreds of glaciers. Samples were taken from 2 areas: Elbrus district and Khulamo-Bezengi Gorge. Cryoconites were sampled from glaciers' surfaces, cracks and holes; soils were sampled in the downstream gorges. Total Elbrus district area is 1850 km^2 and it is mountainous district of Kabardino-Balkarian Republic, mostly located in high-altitudinal zone. Elbrus glacial complex includes 23 glaciers which covers 112 km^2 (Rybak et al., 2021). Many large glaciers such as Irik, Terskol and Kukurtly are included in this glacial complex. First research area is represented by two glaciers: Garabashi and Skhelda (Fig. 1). Garabashi Glacier is lying on the southeastern slope of Mt. Elbrus, it covers 5 km^2 with the highest point 4,900 m and the lowest point at 3,330 m. Baksan Gorge is adjacent to Mt. Elbrus and in southeastern direction of it Skhelda Glacier is situated. Skhelda Glacier is located on the Russian-Georgian border and its area is about 8 km^2. Glacier is covered with moraines and debris with thickness from 50 to 100 cm. Garabashi Glacier feeds the Baksan river and Skhelda Glacier feeds the Skhelda river. The average annual temperature in mountainous part of Elbrus district in summer period is 8.05 °C and in high-mountainous part is 2.5 °C (Tashilova et al. 2019). Typical precipitation ranges from

660 to 760 mm/year. Local geology is represented by calcareous sandstones and clays, carbonate clays and limestone deposits (Pochvy Kabardino-Balkarskoi ASSR, 1984).

Khulamo-Bezengi Gorge is located in Cherek district of Kabardino-Balkarian Republic which is also mostly situated in high-altitudinal zone. The Bezengi Wall here consist of various peaks some of them are higher than 5 km such as Mt. Skhara (5193 m) and Jangi-Tau (5085 m). Around 150 glaciers are located in this part of Caucasus with the total area 290 km^2. Bezengi Glacier is the biggest glacier in the Caucasus mountain range with the length 17,6 km. From the middle of 19th century to 2011 it has retreated at 2,5 km (Bushueva, 2013). It feeds the Cherek Khulam river. The average annual temperature in lower part of Cherek district 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 consists of carbonate rocks, sandstones, granites and glacial deposits near glaciers.

Central Caucasus was an active volcanic region during three time periods: Late Miocene (around 8.5 Ma), Pliocene – Quaternary (4.7 – 1.9 Ma), Late Quaternary (<1 Ma) (Kaigorodova et al., 2020).

3.2. Sampling strategy

At the Baksan Gorge samples of cryoconite sediments have been taken from Garabashi Glacier (Mt. Elbrus), Skhelda Glacier (Fig. 2) and mudflow during field expedition in September 2020 (by E. Abakumov, R. Tembotov and V. Polyakov) as well as some soil samples. Separately, at each sampling plot micro monoliths 2x2x1 cm (height x length x thickness) have been taken in order to study micromorphological features.

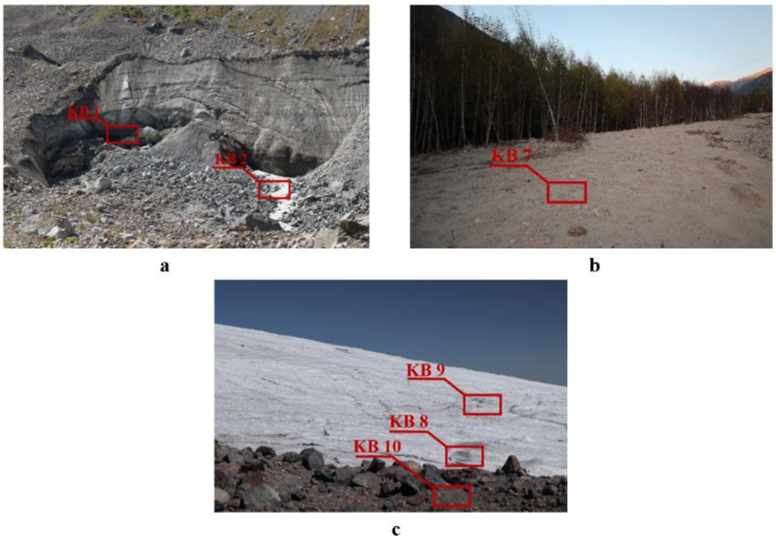

Fig. 2. Sampling plots on Skhelda Glacier (a), mudflow area (b), on the Garabashi Glacier.

Cryoconites from the Skhelda Glacier were sampled from the slopes which are mostly not covered by moraine. Also, cryoconite-derived material (alluvium) was sampled at this investigation area. From the Garabashi glacier cryoconite material was sampled from the glacier holes and moraine. Cryoconite sediments at Khulamo-Bezengi Gorge were sampled from the surface, cracks and cryoconite holes of Bezengi Glacier as well as from moraine deposits and mudflow-transferred sediments nearby (Figure 3) during field expedition in July 2021.

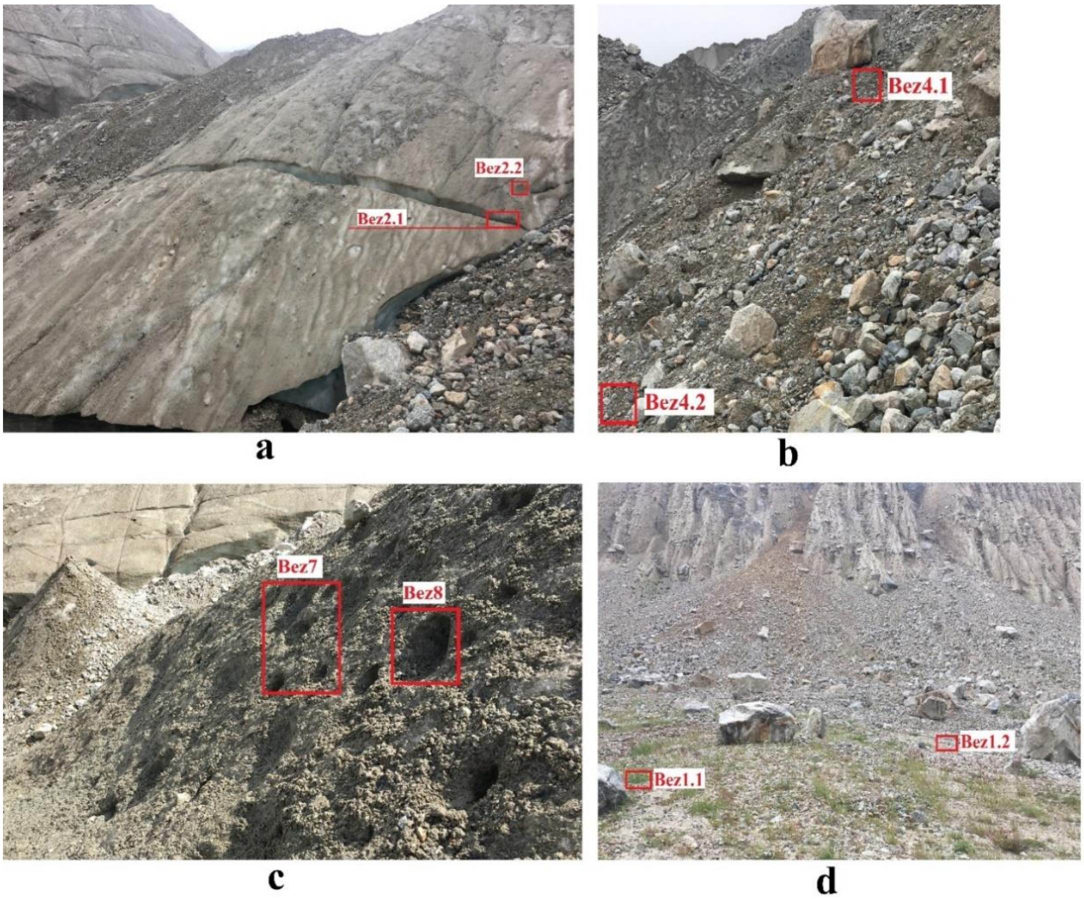

Figure 3. Sampling plots at the Bezengi Glacier crack and surface (a), moraine (b), cryoconite holes (c) and soil-like material nearby the glacier (d).

These sediments were affected by soil forming processes with the appearance of vegetation in some parts. Fresh mudflow samples additionally have been taken at the Baksan Gorge, around 15 km from the Mt. Elbrus, in 2 points, in the end of mudslide and on its way.

Soils have been sampled in the Baksan Gorge and in the Khulamo-Bezengi Gorge, in vicinity to the studied glaciers in order to compare their physicochemical features and pollution levels. These soils were defined as Molic Leptosols and Leptic Umbrisols (WRB, 2015). Individual soil samples have been taken in various sampling points from the depth of each soil horizon up to 26 cm in Baksan Gorge and up to 50 cm in Khulamo-Bezengi Gorge. Under this depth solum was underlayed by solid rocks. Soil profiles of presented on Fig. 4.

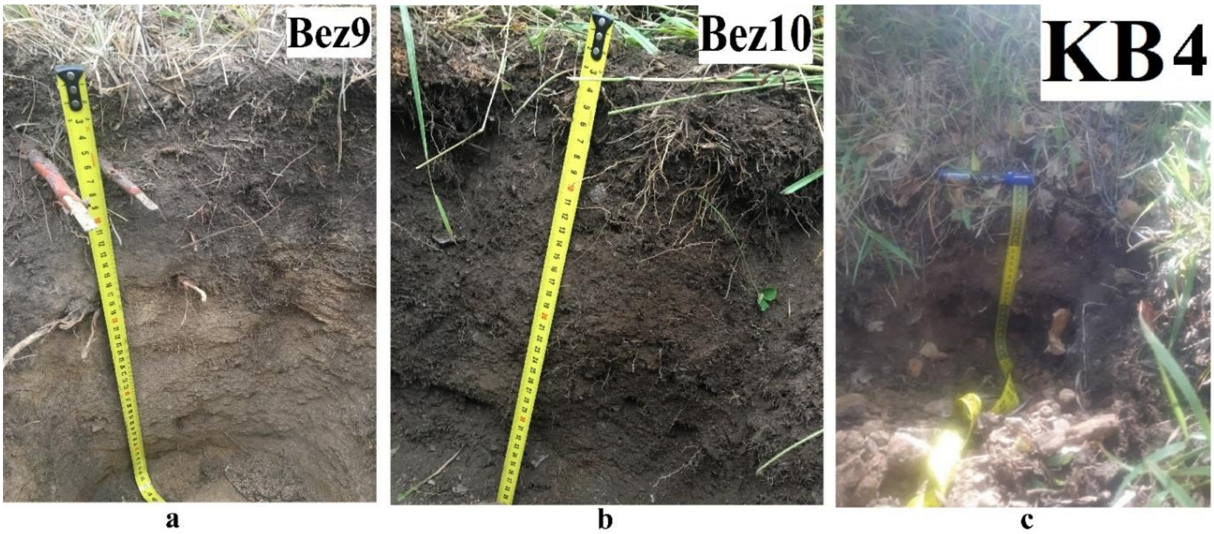

Figure 4. Sampling plots of Leptic Umbrisols (a) and Molic Leptosols at the Khulamo-Bezengi Gorge (b) and at the Baksan Gorge (c, made by E. Abakumov).

Another group of soils has been sampled at the low-altitudinal, valley part of Kabardino-Balkarian Republic, from 70 to 90 km to the north-east from the Mt. Elbrus in order to compare their features with mountain soils and estimate their safety for agriculture.

Figure 5. Soil profiles of studied Chernozems.

These soils were defined as Chernozems (WRB, 2015), some of them (Bez12, Bez13) are used for growing corn. Individual soil samples have been taken from 3 soil sections in the same way up to depth of 100 cm. Soil profiles of Chernozems are presented on Fig. 5.

Detailed description of studied materials is presented in Table 1, Table 2 and Table 3.

Table 1. Description of sediments and soils, sampled at Baksan Gorge during expedition in September 2020 (by E. Abakumov, R. Tembotov and V. Polyakov).

Sample	Description of study site	Depth	Horizon	Soil type	Description of the sample	Elevation	Geographical Coordinates	Sampling date
KB 1	Skhelda glacier	Surface	Surface of the glacier	-	The cryoconite from the slope of the glacier	2.385 m	N 43° 11’27’’ E 42° 38’45’’	15.09.20
KB 2		Surface	Surface of the glacier	-	Cryoconite derived material			
KB 3		Surface	Surface of the glacier	-	The cryoconite from the slope of the glacier			
KB4	The right bank of the Baksan river, in vicinity of the settlement Neutrino	0–8 cm	Oe	Molic Leptosol	Slightly decomposed plant waste, dry, dark-brown, with roots (medium amount) and pebbles, cloddy-lumpy structure	1.816 m	N 43° 17’ 21.0’’ E 42° 42’57.9’’	16.09.20
		8–18 cm	Ah		Roots (medium amount) and pebbles, brown, lumpy-cloddy structure			
		18–25 cm	A/C		A lot of pebbles and few roots, brown, cloddy structure			
KB5	The left bank of the Baksan river, in vicinity of the settlement Upper Balkania	0–11 cm	Ah	Leptic Umbrisol	Roots and round-sharp rocks, grey, lumpy structure	1.466 m	N 43° 19’ 44.0’’ E 42° 48’08.8’’	
		11–18 cm	A/C		Roots and round-sharp rocks, grey-fawn,			
		18–26 cm	Ck		Rocks, yellow-fawn, dry, lumpy structure			
KB6	Elbrus district, in the vicinity	0–21 cm	Ah	Chernozem	Roots and pebbles (medium amount), dark-grey, dry	750 m	N 43° 33’ 21.7’’ E 43° 13’40.1’’	

	of Kiendele settlement	21–58 cm	Bk		Roots and pebbles (few), grey, dry			
KB7	The right bank of Baksan river, between the settlement Upper Baksan and Tyrnyauz city	Surface	Ch	-	Soil-like body formed by mudflow, with vegetation	1.490 m	N 43° 19’19.2’’ E 42° 47’15.1’’	
		Surface	C	-	Soil-like body formed by mudflow, without any vegetation			
KB8	Garabashi glacier	Surface	Surface of the glacier	-	The cryoconite from the ice crack	3.860 m	N 43° 18’18’’ E 42° 27’49’’	17.09.20
KB9		Surface	Cryoconite over ice	-	The cryoconite, underlain by ice			
KB10		Surface	C	-	Moraine deposits on the mountain			

Table 2. Description of sediments and soils, sampled at Khulamo-Bezengi Gorge during expedition in July 2021.

Sample	Description of the study site	Soil type	Elevation	Depth	Horizon	Description of the sample	Coordinates	Sampling date
Bez1.1	800 m before the Bezengi Glacier.	-	2080 m	Surface	Ch	Soil-like body formed on the mudflow. With vegetation	N 43.109168 E 43.136583	24.07.2022
Bez1.2		-		Surface	C	Soil-like body formed on the mudflow. With vegetation		
Bez2.1	Crack at the bottom part of the Bezengi Glacier	-	2150 m	10 cm	-	Cryoconite sediments	N 43.104701 E 43.129403	24.07.2022
Bez2.2	Surface of the bottom part of the Bezengi Glacier	-		Surface	-	Dispersed cryoconite sediments		
Bez3.1	Crack at the upper part of the	-	2201 m	5 cm	-	Cryoconite sediments	N 43.104668 E 43.128708	24.07.2022

	Bezengi Glacier							
Bez3.2	Surface of the upper part of the Bezengi Glacier	-		Surface		Dispersed cryoconite sediments		
Bez4.1	Upper part of the Bezengi Glacier	-	2186 m	Surface	C	Moraine deposits	N 43.107868 E 43.129286	24.07.2022
Bez4.2	Middle part of the Bezengi Glacier	-	2166 m	Surface	C			
Bez4.3	Bottom part of the Bezengi Glacier	-	2148 m	Surface	C			
Bez5	In the vicinity of the Bezengi Glacier	-	2133 m	Surface	C		N 43.106403 E 43.131700	24.07.2022
Bez6		-	2143 m	Surface	C		N 43.105281 E 43.130736	24.07.2022
Bez7	Small cryoconite holes on the surface of the Bezengi Glacier	-	2182 m	5 cm	-	Cryoconite material	N 43.104646 E 43.128771	25.07.2022
Bez8	Big cryoconite hole on the surface of the Bezengi Glacier	-	2171 m	10 cm	-	Cryoconite material	N 43.107535 E 43.128733	25.07.2022
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.	Leptic Umbrisol	1854 m	0–6 cm	Oe	Dark grey, dense, lumpy-powdery, loamy, roots are medium.	N 43.143716 E 42.178648	25.07.2022
				6–18 cm	A	Grey, medium compacted, fine-compacted, roots are sparse.		
				18–40 cm	B	Light brown, weakly compacted, roots are few.		
				40–50 cm	C	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.	Molic Leptosol	1612 m	0–10 cm	Oe	Dark brown, moist, slightly compacted, fine-cloddy, medium-loamy, plenty of roots, few pebbles.	N 43.171266 E 43.231466	25.07.2022
				10–30 cm	B	Greyish-brown, moist, medium compacted, cloddy-grained, medium loamy, few roots, medium to fine pebbles inclusions.		
				30–40 cm	C	Brown with inclusions of grey chalky soil, moist, medium compacted, fine-cloddy, medium-loamy, few roots, many medium and coarse pebbles.		

Table 3. Description of soils and mudflow, sampled at the Baksan Gorge during expedition in July, 2021 (sampling date: 29.07.2021).

Sample	Description of the study site	Soil type	Elevation	Depth	Horizon	Description of the sample	Coordinates
Bez11.1	Near the village of Elbrus. Right bank of the Baksan River.	-	1752 m	Surface	-	Mudflow (descended on 27.07.2021), at the end of mudflow.	N 43.264413 E 42.655688
Bez11.2		-		Surface	-	Mudflow (descended on 27.07.2021), on the way of mudflow.	

Bez12	Near the village of Zhanhoteko. Middle Highlands. Left bank of the Baksan River. Soil section under a corn field.	Chernozem	770 m	0–25 cm	A	Lightly compacted, dark brown, medium-lumpy, heavy loam, rare inclusions of pebbles, corn roots.	N 43.572248 E 43.225523
				25–60 cm	A/B	Gray-brown, medium compacted, medium to fine-clodded, medium-loam, inclusions of small amounts of pebbles and sand, rare inclusions of roots.	
				60–90 cm	Bk	Dark gray, compacted, fine lumpy, medium-loam, inclusions of coarse pebbles.	
Bez13	At the entrance to the Baksan Gorge, near the town of Baksan, left bank of the Baksan River. A cut under a corn field. Foothills of the Republic of Kabardino-Balkaria.	Chernozem	501 m	0–18 cm	A	Loose, dark gray, fine-grained, granular, medium-loam, few inclusions of corn roots, moist.	N 43.647698 E 43.509486
				18–32 cm	A/B	Dense, gray, medium-loam, inclusions of dead corn roots, moist.	
				32–100 cm	Bk	Brown, medium-thick, medium to fine cloddy, medium-loamy, few roots, moist.	

3.3. Laboratory analyses

Sampled materials were transported to the department of applied ecology of Saint Petersburg State University in sealed bags by plane. At the laboratory conditions all samples were dried at the temperature 20 °C and then sieved through 1-mm sieve (except of samples for micromorphology). The pH was determined by pH-meter-millivoltmeter pH-150MA (Made in Belarus) in water and KCl solution with fine-earth:solution ratio 1:2.5. Total organic carbon (TOC) content was determined by dichromate oxidation–titration method (Tyurin method) with accordance to national Russian standard GOST 26213-91 (1993). Also, TOC content and nitrogen content were determined by CHN elemental analyzer (Elementar Analyse Systeme GmbH, Vario MAX, Italy). Basal respiration (microbiological activity) was measured in laboratory incubation experiment by measuring CO_2 in NaOH with titration of alkaline residue with 0.5M HCl after incubation of CO_2 for 10 days in plastic sealed containers (Jenkinson and Powlson, 1976). The particle-size distribution analysis was performed according to the Kachinsky “wet sedimentation” method in accordance with national Russian standard GOST 12536-2014 (2015). Thin sections for micromorphological study has been prepared using sampled micro monoliths. They have been dried in laboratory conditions and then saturated with resin. Prepared materials have been studied with Leica DM 750P polarization microscope (Leica Camera AG, Germany) in crossed Nicol prisms and transmitted light. During this research several features have been studied and described such as materials microfabric, geometrical features and size of particle distribution, presence and origin of organic matter, microstructure elements and spatial arrangements of microfabric according to commonly used method (Stoops and Eswaran, 1986; Stoops, 2003; Gagarina, 2004; Gerasimova et al., 2011).

In order to estimate pollution of studied materials by PAHs, concentrations of 15 high-priority polyarenes from the Environmental Protection Agency's (EPA) list were measured. Information about studied PAHs is presented in Table 4.

Table 4. Description of PAHs under study (according to Pandey et al., 1999).

PAH, CAS name (Abbreviation)	Molecula r Formula	Molecular weight (rings)	Carcinogenity level*
Naphthalene (NAP)	$C_{12}H_8$	128 (2)	2B
Acenaphthene (ANA)	$C_{12}H_{10}$	154 (3)	3
Fluorene (FLU)	$C_{13}H_{10}$	166 (3)	3
Phenanthrene (PHE)	$C_{14}H_{10}$	178 (3)	3
Anthracene (ANT)	$C_{14}H_{10}$	178 (3)	3
Fluoranthene (FLT)	$C_{16}H_{10}$	202 (4)	3
Pyrene (PYR)	$C_{16}H_{10}$	202 (4)	3
Benzanthracene (BaA)	$C_{18}H_{12}$	228 (4)	2B
Chrysene (CHR)	$C_{18}H_{12}$	228 (4)	2B

Benz[*e*]acephenanthrylene (BbF)	$C_{20}H_{12}$	252 (5)	2B
Benzo[*k*]fluoranthene (BkF)	$C_{20}H_{12}$	252 (5)	2B
Benzo[*a*]pyrene (BaP)	$C_{20}H_{12}$	252 (5)	1
Dibenz[*a*,*h*]anthracene (DBA)	$C_{22}H_{14}$	278 (5)	2A
Benzo[*ghi*]perylene (BPE)	$C_{22}H_{12}$	276 (6)	3
Indeno[1,2,3-*cd*]pyrene (IPY)	$C_{22}H_{12}$	276 (6)	2B
* - 1 - Carcinogenic to humans; 2A - Probably carcinogenic to humans; 2B - Possibly carcinogenic to humans; 3 - Not classified as carcinogenic to human			

The PAHs content was defined by high-performance liquid chromatography which is generally accepted in Russia and in the world (PND, 2009). Extraction of PAHs from soil was performed using diethyl ether. 10 mL of diethyl ether was added to 1 g of prepared sample, after the solution was placed in an ultrasonic bath for 30 minutes. Then the extract was evaporated at 60°C until it was not completely dry. 1 mL of acetonitrile was added to the residue after full evaporation. The prepared extracts were chromatographed at the same day. The minimum measured concentrations of PAHs are as follows: NAP, FLT, PYR >20; ANA, FLU, PHE, BPE, IPY, BbF, BbA, DBA>6; CHR>3; BkF, BaP>1 ng/g (Lau et al., 2010). Accuracy for all measures at minimum concentrations are about ±40%.

Because PAHs can be formed not only during various technogenic processes but also can be produced by various natural processes, it is possible to use PAHs as markers of anthropogenic impact. One of the most common way to define the origin of polyarenes is to use different PAH diagnostic (isomer) ratios method (Khaustov and Redina et al., 2017; Santos et al., 2017; Soclo et al., 2000). In order to correctly select isomeric ratios and identify source of PAHs several papers have been studied and summarized in the Table 5 (prepared by T. Nizamutdinov).

Table 5. Selected diagnostic ratios of studied polyarenes and their sources (prepared by T. Nizamutdinov).

PAHs isomer ratios	Range of values	Possible sources of PAH	References
ANT / (ANT + PHE)	<0.10	Petroleum or Baseline source	(Yunker et al., 2002; Wang et al., 2009; Tobiszewski and Namieśnik, 2012; Shamilishvili et al., 2016)
	>0.10	Combustion	
FLU / (FLU + PYR)	<0.40	Petroleum or Baseline source	(Mandalakis et al., 2002; Yunker et al., 2002; Fang et al., 2004;
	0.40-0.50	Combustion of liquid fuels	
	>0.50	Combustion of solid fossil fuels	

			Ravindra et al., 2008; Shamilishvili et al., 2016)
BaA / (BaA + CHR)	<0.20	Petroleum or Baseline source	(Yunker et al., 2002; Tobiszewski and Namieśnik, 2012; Shamilishvili et al., 2016)
	0.20-0.35	Petroleum, combustion, baseline source	
	>0.35	Combustion	
PHE / ANT	>10	Petrogenic	(Budzinski et al., 1997; Khairy et al., 2009)
	<10	Pyrolytic	
FLU / PYR	<1.0	Petrogenic	(Budzinski et al., 1997; Khairy et al., 2009)
	>1.0	Pyrolytic	
BaP / BPE	<0.60	Non-traffic	(Pandey et al., 1999; Ravindra et al., 2008)
	>0.60	Traffic	
∑ PyrPAHs[a] / ∑ PAHs	<0.30	Petroleum or Baseline source	(Hwang et al., 2004; Balmer et al., 2019)
	0.30-0.70	Petroleum, combustion, baseline source	
	>0.70	Predominantly combustion	
∑ LMW PAHs[b] / ∑ HMW PAHs[c]	<1	Pyrogenic	(Soclo et al., 2000; Zhang et al., 2008)
	>1	Petrogenic	

Many studies are conducted by bringing the toxicity levels of various PAHs in relation to Benzo[a]pyrene because its effects and properties are well understood, using Benzo[a]pyrene equivalents (BaP – equivalents) of the toxicity of PAHs (Jung et al., 2010). This is also used in this study. BaP-equivalents also make it possible to compare pollution of studied materials with different standards, for instance, to Russian maximum permissible concentration (MPC) in soils, 0.02 mg/kg (Hygienic Norms, 2006).

Trace elements content was defined by flame and electrothermal atomic absorption spectrometric method according to the standard ISO 11047-1998 (ISO, 1998) at Atomic absorption spectrophotometer Kvant 2M (Moscow, Russia). The list of studied trace elements included Cu, Pb, Zn, Ni, Cd due to fact that they are the classified as the most dangerous for people and environment (GOST17.4.1.02-83, 2008) and are accumulated in black carbon and atmospheric dust, according to previous studies (Vinogradova and Kotova, 2019; Polyakov et al., 2020).

3.4. Pollution indices

In order to correctly evaluate and interpret pollution of studied materials by trace elements, several pollution indices have been used.

The geoaccumulation index (I_{geo}) has been used to assess general level of pollution with the accordance to the following formula:

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

where Cn is the measured concentration of the element in the material, Bn is the natural value and 1.5 is the constant which gives us possibility to correctly interpret natural changes and insignificant anthropogenic impact. Seven types of I_{geo} from uncontaminated to extremely contaminated were defined by Muller (Muller, 1979). They are presented in Table 6.

According to previous study (Reimann and de Caritat, 2005) using values of Earth's crust and global average values would not lead to correct results. Thus, it is necessary to use the local background value (samples from non-polluted soils) as a reference frame (Blaser et al., 2000). The averaged concentrations of trace elements in natural soils from previously published studies (Degtyareva et al., 2020; Podkolzin and Anziferov, 2007) conducted in the biosphere reserve at the Caucasus mountains and foothill areas were used as a geochemical background for calculating indices for this study.

Contamination factor (CF) is another pollution index which shows the pollution degree directly evaluated by each trace element in the studied materials at each study site (Muller, 1979). It is calculated as following:

$$CF_i = \frac{C_m}{B_m}$$

where Cm is measured concentration of individual element in the sample and B_m is the background value at the study area. Level of pollution accessed by CF is usually divided in four levels (Likuku et al., 2013) which are presented in Table 6.

Degree of contamination (C_{degree}) is used to evaluate the average degree of pollution for all trace elements at each study site and it is calculated with accordance to the following formula:

$$C_{degree} = \sum_{i=1}^{n=5} CF_i$$

where n is the number of measured elements in this particular investigation and sum of CF values of five metals are used to calculate C_{degree} in each study site. Classification of this method is shown in Table 6, it was proposed by Zahran et al (2015), where n is the number of elements.

Modified degree of contamination (mC_{degree}) is a general method to assess the pollution status which is calculated as following (Machender et al., 2011):

$$mC_{degree} = \frac{C_{degree}}{n}$$

Classification of mC_{degree} is presented in Table 6 according to Abrahim and Parker (2008).

Table 6. Classification of pollution indices.

Index	Classification
Geoaccumulation index (I_{geo})	≤ 0 Practically unpolluted
	0 – 1 Uncontaminated to slightly polluted
	1 – 2 Moderately polluted
	2 – 3 Moderately to highly polluted
	3 – 4 Highly polluted
	4 – 5 Highly to extremely polluted
	> 5 Extremely polluted
Contamination factor (CF)	< 1 Low pollution
	1 – 3 Moderate pollution
	3 – 6 High pollution
	≥ 6 Extremely high pollution
Degree of contamination (C_{degree})	< n Low degree of pollution
	n – 2n Moderate degree of pollution
	2n – 4n High degree of pollution
	≥ 4n Extremely high degree of pollution
Modified degree of contamination (mC_{degree})	< 1.5 No to very low degree of pollution
	1.5 – 2 Low degree of pollution
	2 – 4 Moderate degree of pollution
	4 – 8 High degree of pollution
	8 – 16 Very high degree of pollution
	16 – 32 Extremely high degree of pollution
	≥ 32 Ultra high degree of pollution

3.5 Statistical analysis

For statistical processing of information computer program Statistica 12 was used (StatSoft Inc., 2013). Before statistical analysis data has been normalized where it was needed. Minimum and maximum values essentially out of the average range have been checked and, if necessary, removed. In order to find statistically significant differences between obtained results from different sampling points, one-way ANOVA has been used which goal is to test the significant difference between the averages in the different groups by comparing the variance of these groups, in our case between soils and sediments. To evaluate relationships between obtained data, nonparametric Spearman’s rank correlation test has been used as a rank measure of the linear relationship between random variables, which is used to establish a correlation between entities, in our case between soils and sediments.

4. Results

In this research we studied glaciers and soils of the Central Caucasus mountain region which is the most high-altitudinal part of the Caucasus mountain range. First area of study, the Baksan Gorge, starts at the foothill around 1 km height above the sea level and ends with the Elbrus Mt., over 5 km height above the sea level. The Garabashi Glacier is slope glacier located at the south-eastern part of the Elbrus Mt, at the high altitude, close to the mountain peak. It is mostly covered by snow with presence of cryoconites in holes and is surrounded by lateral moraine. Water streams from the glacier flow to the Baksan river. The Skhelda Glacier is the valley glacier located in south-western part of the Baksan Gorge. It is extended in length glacier which is surrounded by mountain walls. The Skhelda Glacier is a debris-covered glacier with a presence of supraglacial lake on its surface. Water streams from the Skhelda Glacier form Skhelda river which further flows to the Baksan river. In the Baksan Gorge we have found mountain soils which were defined as Molic Leptosols and Leptic Umbrisols. They have weakly developed soil profiles with inclusions of rocks and pebbles due to harsh climatic conditions and recent time of formation. At the top they are covered with herbaceous vegetation cover. These soils are exposed to the influence of mudflows and floods of the Baksan river.

Similarly, the Khulamo-Bezengi Gorge starts at the foothill around 1 km height and ends at the Bezengi mountain wall at the height around 5 km above the sea level. The Bezengi Glacier is extended in length valley glacier which is covered by deposited aeolian dust and is surrounded by mountain walls. Glacier is surrounded by both lateral and terminal moraines. In the lower part of the Bezengi Glacier there is a water stream which feeds Khulamo-Bezengi river. Cryoconites are presented on the slopes of the glacier in holes and dispersed. In the vicinity of the glacier we have found soil-like bodies which are formed under the cryoconite and mudflow material input, they have weakly developed profile with presence of vegetation in some parts. Local mountain soils are located in the floodplain and on the hill. Both of them have lots of pebble inclusions and low amount of roots as well as herbaceous vegetation cover at the top horizon.

Studied Chernozems located in the beginning of the Baksan Gorge and have highly developed soil profile with depth more than 100 cm and thick humus horizon. Roots mainly have been observed in the top horizons while in the bottom horizons calcareous inclusions have been found.

4.1. Basic physicochemical features

Results of investigation of basic physical and chemical features of studied materials are presented at the Table 7.

Table 7. Physicochemical parameters of studied cryoconites, soils, moraines and mudflows (ND = not defined).

Sample	Horizon	pH (H_2O)	pH (KCl)	Basal respiration (mg CO_2/ 100 g*day)	C,% (by indirect method)	C, % (by direct method)	N, %	C/N
KB1	Surface	6.07	5.17	24.20	0.16	0.14	ND	ND
KB2	Surface	6.54	6.35	11.00	0.28	0.05	ND	ND
KB3	Surface	6.45	5.96	6.60	0.11	0.06	ND	ND
KB4	Oe	6.49	5.67	39.60	2.86	7.82	0.31	25.23
	Ah	6.58	5.60	39.60	1.61	1.88	ND	ND
	A/C	6.44	ND	17.60	0.89	1.45	ND	ND
KB5	Ah	6.90	6.05	48.40	2.44	3.80	0.22	17.27
	A/C	6.98	6.06	30.80	2.15	2.37	0.14	16.92
	Ck	6.98	6.30	17.60	1.37	2.03	0.03	67.66
KB6	Ah	7.89	ND	22.00	2.49	4.72	0.25	18.88
	Bk	7.82	ND	26.40	0.68	3.20	ND	ND
KB 7	Ch	7.24	ND	17.60	0.15	ND	ND	ND
	C	6.95	6.92	17.60	0.13	ND	ND	ND
KB8	Surface	5.84	4.45	41.80	1.41	1.63	ND	ND
KB9	Surface	7.25	ND	24.20	0.29	ND	ND	ND
KB10	C	6.16	5.49	39.60	0.05	ND	ND	ND
Bez1.1	Ch	6.63	6.09	30.80	0.24	ND	ND	ND
Bez1.2	C	6.77	6.07	13.17	0.16	ND	ND	ND
Bez2.1	Surface	6.97	5.73	9.90	0.17	ND	ND	ND
Bez2.2	Surface	6.84	6.18	14.27	0.15	ND	ND	ND
Bez3.1	Surface	5.87	5.58	8.76	0.23	ND	ND	ND
Bez3.2	Surface	6.74	6.37	19.72	0.19	ND	ND	ND
Bez4.1	C	6.45	6.22	10.97	0.18	ND	ND	ND
Bez4.2	C	6.42	6.17	6.58	0.10	ND	ND	ND
Bez4.3	C	6.41	6.24	13.17	0.18	ND	ND	ND
Bez5	C	6.46	5.92	9.88	0.24	ND	ND	ND
Bez6	C	7.09	ND	5.48	0.16	ND	ND	ND
Bez7	Surface	6.45	5.96	26.29	0.19	ND	ND	ND
Bez8	Surface	6.72	5.74	25.22	0.19	ND	ND	ND
Bez9	Oe	5.98	4.90	21.91	3.70	ND	ND	ND
	A	6.02	4.20	35.09	2.79	ND	ND	ND
	B	6.38	4.25	24.18	0.58	ND	ND	ND
	C	6.71	4.56	11.00	0.41	ND	ND	ND
Bez10	Oe	5.99	4.76	26.40	7.54	ND	ND	ND

	B	5.96	5.60	17.55	5.45	ND	ND	ND
	C	6.26	5.07	10.97	2.82	ND	ND	ND
Bez11.1	C	6.92	6.61	2.20	0.24	ND	ND	ND
Bez11.2	C	6.41	6.36	5.48	0.29	ND	ND	ND
Bez12	A	6.78	6.48	12.06	3.30	ND	ND	ND
	A/B	7.00	ND	19.78	1.67	ND	ND	ND
	Bk	7.01	ND	10.96	1.60	ND	ND	ND
Bez13	A	6.82	6.21	8.77	1.62	ND	ND	ND
	A/B	6.59	5.28	7.70	1.70	ND	ND	ND
	Bk	6.31	5.86	16.50	1.39	ND	ND	ND

Let's start with the materials, sampled from glaciers and soils of the Baksan Gorge. Values of the water pH vary between slightly acidic and slightly alkaline. In general, most of the samples show neutral reaction or close to it. The same situation is observed with pH KCl. For some samples TOC content was not defined by CHN-analyser due to lower amount than detection limit. The lowest TOC values measured by direct measurement method range from 0.05% in cryoconite from the Skhelda Glacier and in moraine deposits from the Garabashi Glacier, the highest value is 7.82% in the Molic Leptosol sample KB4. In the sample KB5, which is more remote from glaciers, this value is lower (3.80%). The TOC values obtained from oxidation-titration method range between 0.05% in KB10 moraine sample and 2.86% in KB4 Leptosols. Higher than in sediments basal respiration values are determined in almost all soil samples, however, cryoconite KB8 also shows high values (41.8 mg CO_2/ 100 g*day) which points to the fact that microbiological activity on this part of the Garabashi glacier is comparable with local soils. Content of nitrogen is low in almost all samples and was determined only in local soils with the highest value of 0.31 in the sample which are located close to the glaciers. C/N ratio was defined in case of possibility. Statistical analysis of data shows significant difference between TOC in studied soils and sediments, ANOVA test $F = 21.28$, $p<0.05$. According to Spearman’s rank correlation, relationship is observed between the content of TOC and basal respiration values (0.51).

Now let’s observe results obtained from the Bezengi Glacier and Khulamo-Bezengi Gorge. In most of cases pH values are similar to previous sampling sites, showing neutral values of acidity or close to it. Among cryoconites sample Bez3.1 from the crack as well as samples from cryoconite holes show slightly acidic reaction. Statistical analysis revealed significant difference ($F = 8.62$, $p<0.05$) between pH H_2O in sediments at the glacier and Leptosols/Umbrisols which means that in general local soils are more acidic. The large difference between H_2O and KCl pH is also observed in local soils. Moreover, significant statistical difference (F = 66.80, $p<0.05$) is observed in pH values between supraglacial sediments and Leptosols/Umbrisols. Basal respiration values among cryoconites are lower on the surface of the glacier than in cracks reaching peak values in samples from cryoconite holes (up to 26.29 mg CO_2/ 100 g*day) what is comparable or higher than in local soils. Content of TOC was defined only by oxidation-titration indirect method. All cryoconites show low values which are slightly higher on the surface of the glacier. Higher value (0.24%) are defined in moraine deposits close to the Bezengi glacier. High values of TOC (up to 7.54%) are observed in Leptosols/Umbrisols, especially in the upper horizons. According to statistical processing significant difference is observed between TOC content in studied sediments and soils (F = 20.75, $p<0.05$). Fine earth fraction mostly dominates in soils and coarse earth fraction in cryoconites which is proven statistically ($p<0.05$). Reliable negative relationship is observed between TOC and pH values (H_2O = -0.70, KCl = -0.73) which indicates that additional organic carbon lead to decrease of pH in soils and sediments of this high-mountain site. Amount of coarse earth fraction statistically negatively influences TOC content (-0.68) while fine earth fraction has a positive correlation (0.73) as well as with basal respiration values (0.50).

Results obtained from research of Chernozems from the Baksan Gorge show mostly neutral pH of these soils. A large difference between the values of actual and exchangeable acidity is observed in sample Bez13. In this case, the upper horizon shows a neutral reaction, while the underlying ones are more acidic. TOC content is the highest in A horizon of Chernozems (up to 3.30%) with the lowest value in the most remote study site. Values of basal respiration are higher when the sampling site is closer to glacier (up to 26.4 mg CO_2/ 100 g *day). Fresh mudflow shows low values of TOC as well as of basal respiration. Significant difference according to statistical processing is observed between values of TOC in supraglacial sediments in the Baksan Gorge and Chernozems with the higher values in latter (F = 21.84, $p<0.05$). Values of coarse and fine silt also differ significantly ($p<0.05$).

Comparing cryoconites and other sediments from Garabashi and Skhelda glaciers with those from the Bezengi glacier we can observe that basic physicochemical features are similar except of samples such as KB2 and KB8. Studied Leptosols and Umbrisols in the Khulamo-Bezengi Gorge have more acidic pH of extraction than those at the Baksan Gorge and both of them have high basal respiration and TOC values.

4.2. Particle-size distribution

Results of particle-size distribution analysis is presented in Table 8.

Table 8. Particle-size distribution of sampled materials.

Sample	Horizon	Coarse earth, %	Fine earth, %	Sand (1-0.05mm)	Silt (0.05-0.002mm)	Clay (< 0.002mm)
KB1	Surface of the glacier	93.40	6.60	69.08	27.45	3.47
KB2	Surface	14.90	85.10	75.76	23.91	0.33
KB3	Surface	44.00	56.00	65.80	28.86	5.34
KB4	Oe	49.50	50.50	72.52	15.09	12.39
KB5	Ah	16.10	83.90	80.99	10.08	8.93
	A/C	21.10	78.90	81.44	12.74	5.82
	Ck	38.10	61.90	85.12	6.16	8.72
KB6	Ah	44.30	55.70	85.12	7.91	6.97
	Bk	31.20	68.80	75.30	17.09	7.61
KB 7	Ch	31.00	69.00	81.85	12.63	5.52
	C	32.20	67.80	85.12	11.03	3.85
KB8	Surface	12.60	87.40	29.71	56.91	14.10
KB9	Surface	84.60	15.40	89.37	3.31	7.32
KB10	C	46.20	53.80	84.32	13.56	2.12
Bez1.1	Ch	54.30	45.70	84.61	11.13	4.26
Bez1.2	C	58.65	41.35	56.39	38.10	5.51
Bez2.1	Surface	50.30	49.70	71.96	23.24	4.80
Bez2.2	Surface	66.04	33.96	75.25	22.07	2.68
Bez3.1	Surface	65.57	34.43	85.28	11.52	3.20
Bez3.2	Surface	62.26	37.74	68.76	28.61	2.63
Bez4.1	C	59.99	40.01	74.12	21.36	4.52
Bez4.2	C	58.33	41.67	59.89	35.91	4.20
Bez4.3	C	52.93	47.07	49.37	42.30	8.33
Bez5	C	43.74	56.26	77.17	18.37	4.46
Bez6	C	64.48	35.52	92.64	6.08	1.28
Bez7	Surface	53.01	46.99	83.13	16.05	0.82
Bez8	Surface	41.84	58.16	72.52	24.08	3.40
Bez9	Oe	5.02	94.98	38.01	51.59	10.40
	A	5.50	94.50	56.25	40.41	3.34
	B	22.34	77.66	83.12	12.00	4.88
	C	27.65	72.35	77.13	18.39	4.48
Bez10	Oe	19.89	80.11	73.73	20.50	5.77
	B	20.50	79.50	82.00	11.00	7.00
	C	54.61	45.39	57.10	37.08	5.82
Bez11.1	C	58.63	41.37	70.49	22.20	7.31
Bez11.2	C	63.63	36.37	53.56	38.92	7.52
Bez12.1	A	6.90	93.10	19.01	57.64	23.35
	A/B	7.12	92.88	36.76	42.74	20.50
	Bk	17.34	82.66	15.96	64.84	19.20
Bez13.1	A	2.87	97.13	31.24	46.94	21.82
	A/B	1.99	98.01	42.12	38.05	19.83
	Bk	0.01	99.99	99.99	31.18	18.92

Analysis revealed that coarse earth fraction mostly dominates in cryoconites with some exceptions such as samples KB2 and KB8. Sand grains (grain diameter 2-0.05 mm) are prevailed in sediments from Garabashi and Skhelda glaciers. Most of the studied materials in this locations show low content of clay (up to 7.32%) with the exception of cryoconite KB8 in which silt (grain size 0.05-0.002 mm) is a dominating fraction (56.19%) but also the content of clay (grain diameter <0.002 mm) is the highest among all sediments and Leptosols/Umbrisols in the Baksan Gorge (14.10%) and content of sand is the lowest (29.71%). However, sampling point KB9 at the same glacier was classified as sand due to high content of sand fraction (89.37%) and low content of silt fraction (3.31%). Both KB2 and KB8 samples are dominated by the fine earth fraction (grain diameter < 2 mm) which distinguishes them from other cryoconites from the Baksan Gorge glaciers. In general, domination of coarse earth (grain diameter > 2 mm) is typical for cryoconites of this study site while downstream soils show more diverse parameters in this regard. Soil texture triangle with particle-size distribution in these samples is presented on Fig. 6.

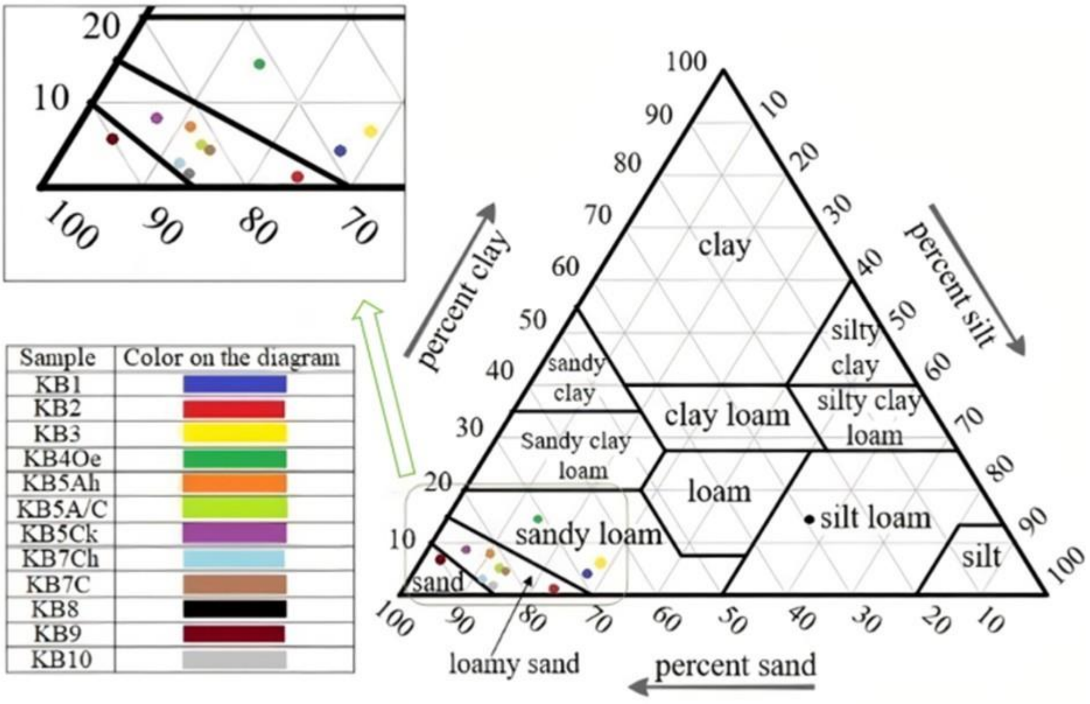

Figure 6. Particle-size distribution of Leptosols, Umbrisols and sediments from the Baksan Gorge and its glaciers at the texture triangle.

Particle-size distribution of Leptosols and Umbrisols from the Baksan Gorge does not differ greatly from the supraglacial sediments and mudflows in terms of fine earth texture. They are defined as loamy sand and sandy loam. Relatively high amount of clay is observed in the Oe horizons (up to 12.39%).

Similarly, values of coarse earth fraction are lower in Leptosols and Umbrisols at the Khulamo-Bezengi Gorge than in sediments from the Bezengi Glacier and fresh mudflow which is also proved statistically by analysis ($p<0.05$). Among the sediments, fine earth fraction (grain diameter < 2 mm) dominates in moraine sample Bez5 (56.36%) in vicinity of glacier and in the cryoconite from the big hole (58.16%). Particle-size distribution at the soil texture triangle is presented on Figure 7.

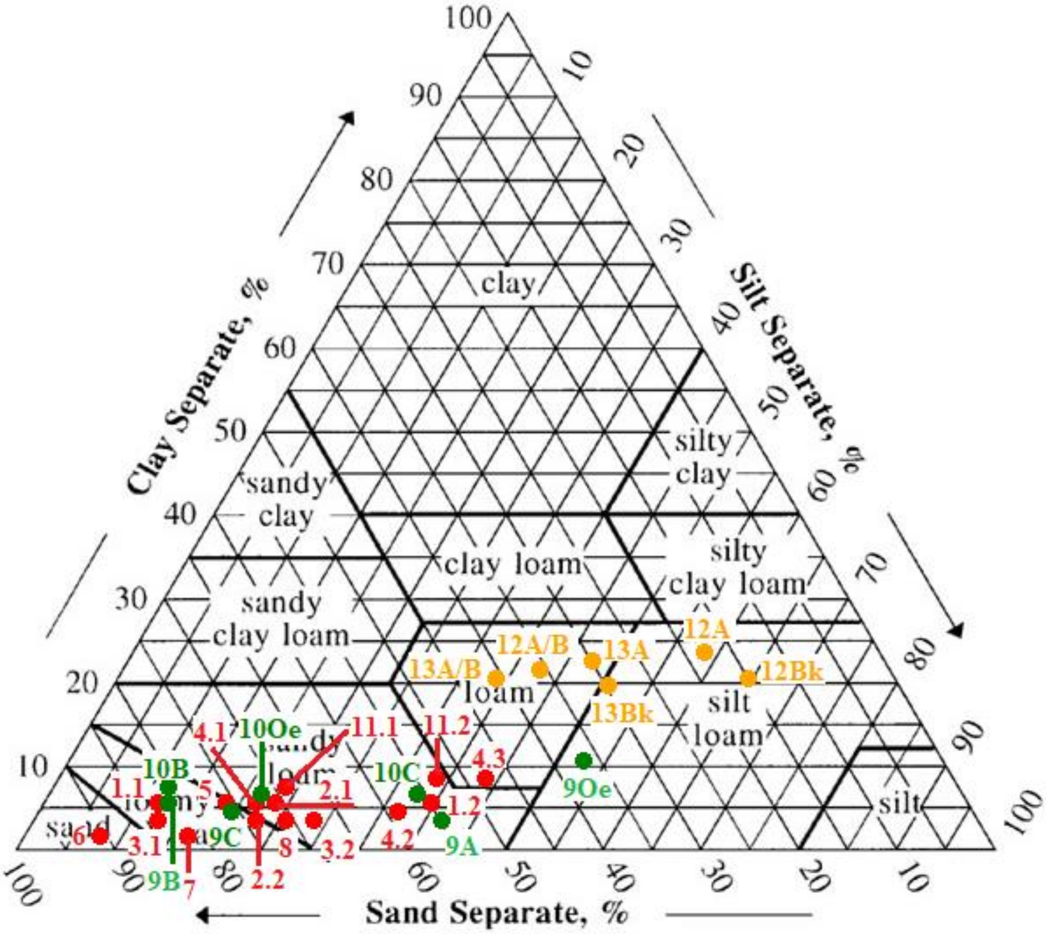

Figure 7. Particle-size distribution of materials from the Bezengi Glacier (red), Khulamo-Bezengi Gorge Leptosols/Umbrisols (green) and studied Chernozems (yellow) at the texture triangle.

Most of cryoconites and moraines from this location are dominated by sand (up to 92.64% in moraine) and show low values of clay (up to 5.51% in cryoconite). This distinguishes them from the local Leptosols and Umbrisols which have relatively high values of clay, especially in upper horizons (up to 10.40%). However, again the predominance of sand fraction is observed in the most of local Leptosols and Umbrisols samples. Statistical processing revealed significant difference between supraglacial sediments and local Leptosols/Umbrisols (F = 4.81, $p<0.05$) in amount of clay particles. In general, particle-size distribution of materials from two gorges is similar and comparable with each other with the dependence on the source of material. Chernozems which are more remote from the glaciers and high mountains and have been developed longer in time and in better environmental conditions show significant dominance of the fine earth fraction (F = 9.66, $p<0.05$) with very little amount of coarse earth in most of the samples with the biggest exception of KB6 sample due to its closeness to high-altitudinal part. Clay particles make up considerable proportion of particle-size distribution, up to 23.35%, significantly distinguishing them from the supraglacial sediments (F = 71.11, $p<0.05$) while in general silt is dominating among studied Chernozems.

4.3. Micromorphological features

Micromorphological features of materials under study are presented at the figures 8-16 (Figures 8-10 have been made by V. Polyakov).

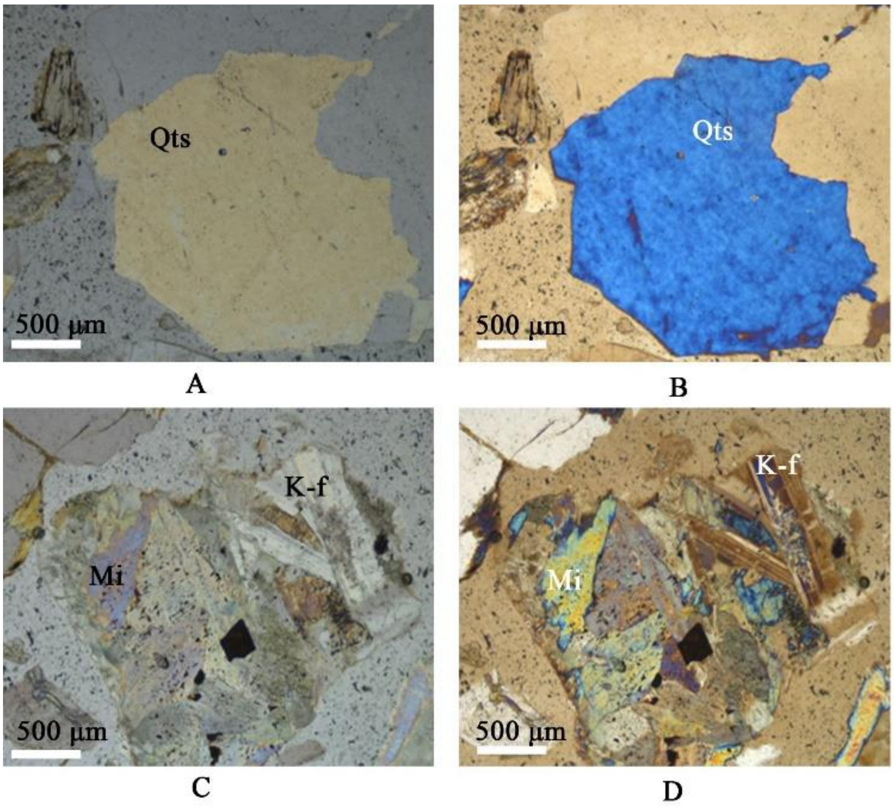

Figure 8. Micromorphology of cryoconite sample KB1, the Skhelda Glacier. A, C – plane-polarized light; B, D – crossed-polarized light. Qts – quartz, K-f – fieldspar, Mi – mica.

Soil fabric at the cryoconite at the Skhelda Glacier shows the large fragments of minerals with weak signs of transformation. No organic or biogenic remains have been observed. Random distribution of material is observed in this sample. Mineral composition mainly consists of quartz and feldspar with mica in the sand-silt aggregates which were exposed to physical weathering. At some point minerals were affected by aluminum and iron oxides mobility which caused light ferruginization of the material. Fractures are not expressed as in cryogenic soils which indicates low degree of cryodegradation.

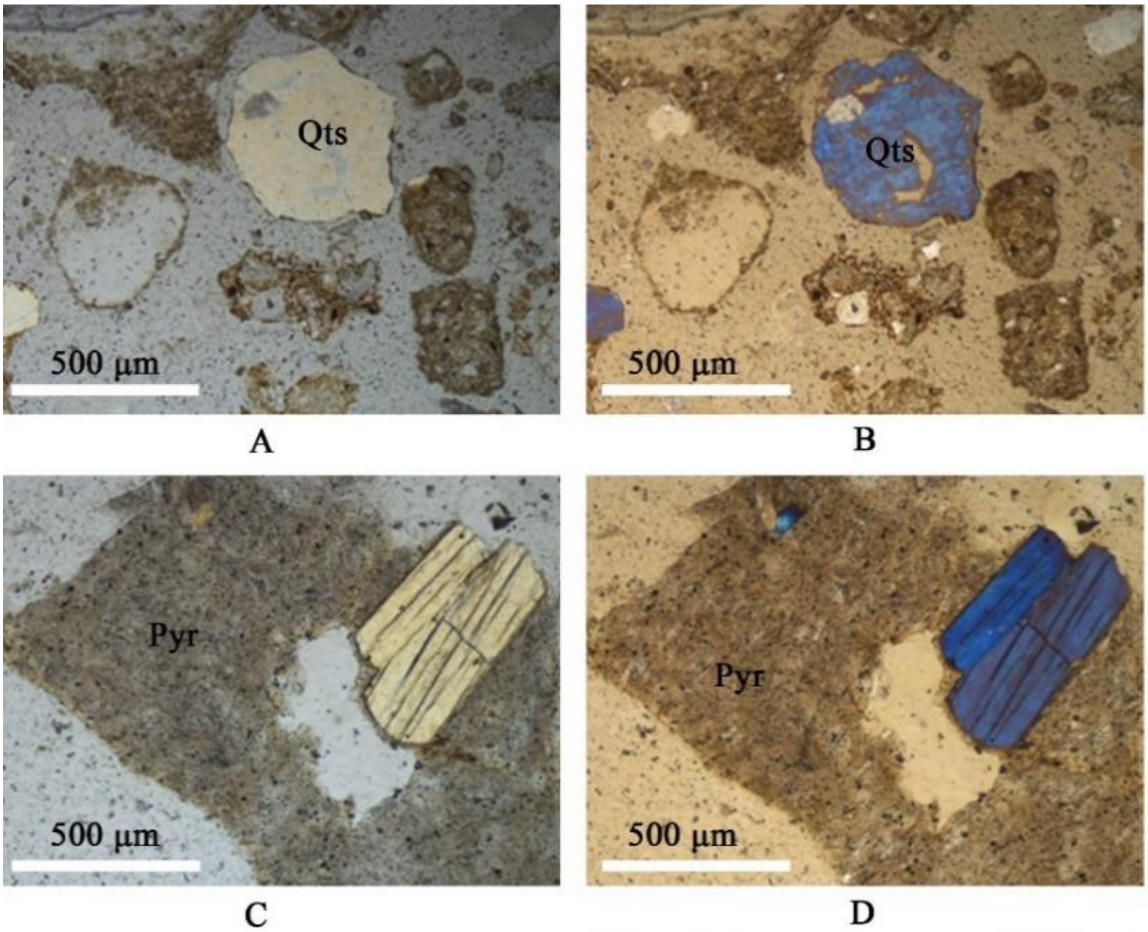

Figure 9. Micromorphology of KB8 of cryoconite, the Garabashi Glacier (made by V. Polyakov). A, C – plane-polarized light; B, D – crossed-polarized light. Qts – quartz, Pyr – pyroclasic.

Mineral composition of cryoconite sampled at the Garabashi Glacier differs greatly from the cryoconite sampled from the Skhelda Glacier. Mechanical destruction is strongly expressed which is shown by parallel cracking in fragments of quartz and clay fractions in the plasma. In general, materials are also weakly transformed.

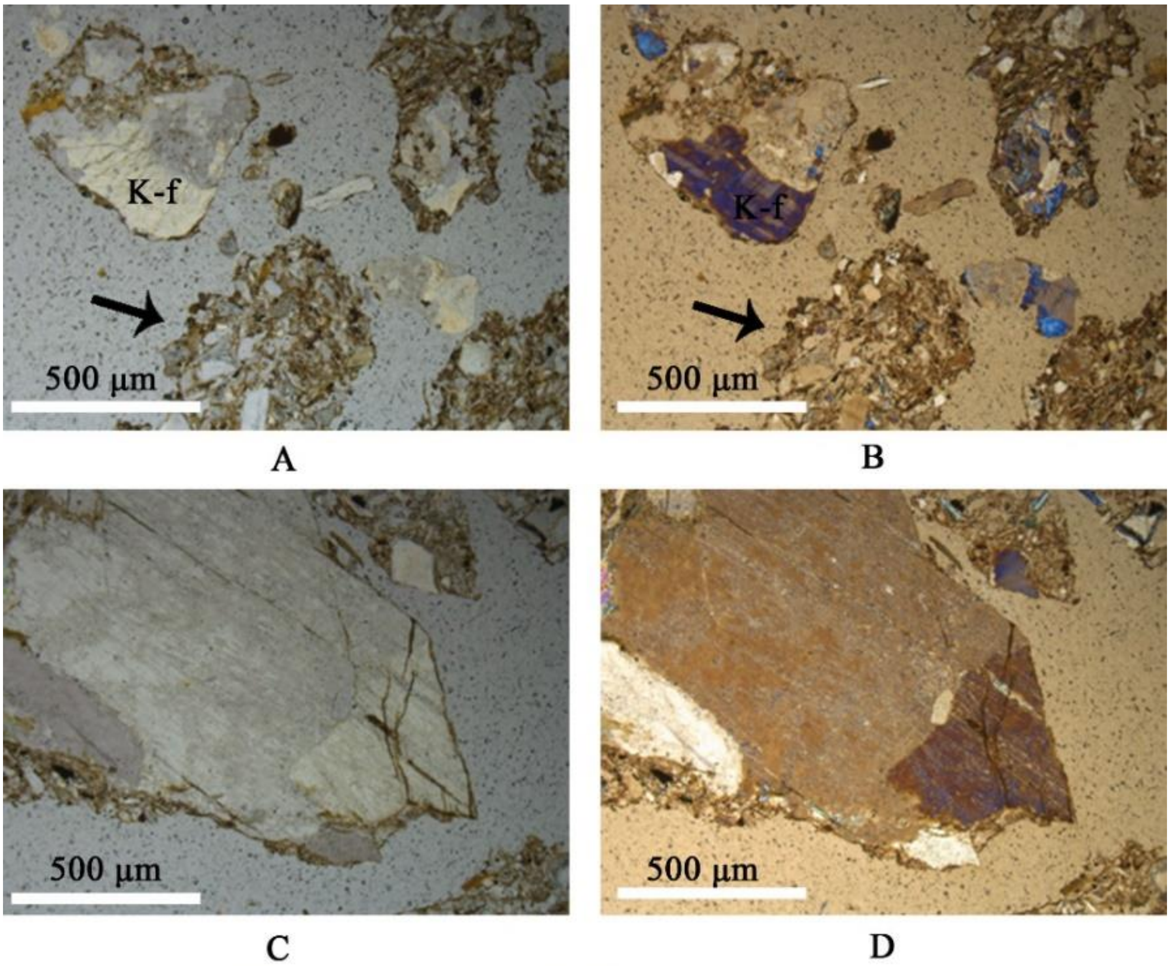

Figure 10. Micromorphology of Leptosols and Umbrisols from the Baksan Gorge (made by V. Polyakov). A, C – plane-polarized light; B, D – crossed-polarized light. K-f – feldspar. Arrow indicates clay-biogenic material.

Mineral composition of Leptosols and Umbrisols from the Baksan Gorge shows similarities with the cryoconites, however, the transformation is more expressed. Weathering of biological type is also observed due to form of cracks. Soil fabric is represented by feldspar as well as by organic fine material which is represented by sand-clay organic matter.

Let’s move to the micromorphology of the Khulamo-Bezengi Gorge. Mineral composition of cryoconite sample from the Bezengi Glacier is similar to those from the glaciers of the Baksan Gorge. It consists of large framents of quartz, mica and feldspar with weak sights of transformation. Dominant type of weathering is physical; fragments are mechanically transformed which is observed by parallel cracking in mica fragment. Large weakly transformed polymineral complexes which consist of feldspar, mica and quartz also can be found in this sample (Figure 10, C-D).

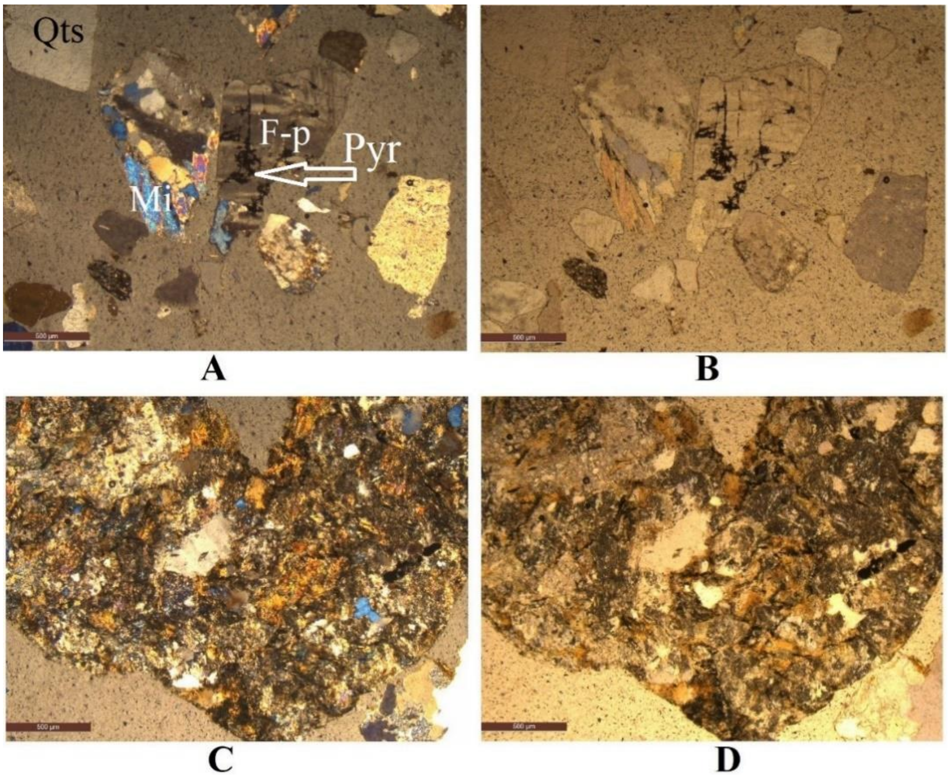

Figure 11. Micromorphology of cryoconite from the Bezengi Glacier (scale bar = 500µm). A, C – plane-polarized light; B, D – crossed-polarized light. Qts – quartz, Mi – mica, F-p – feldspar, Pyr – pyroclastic.

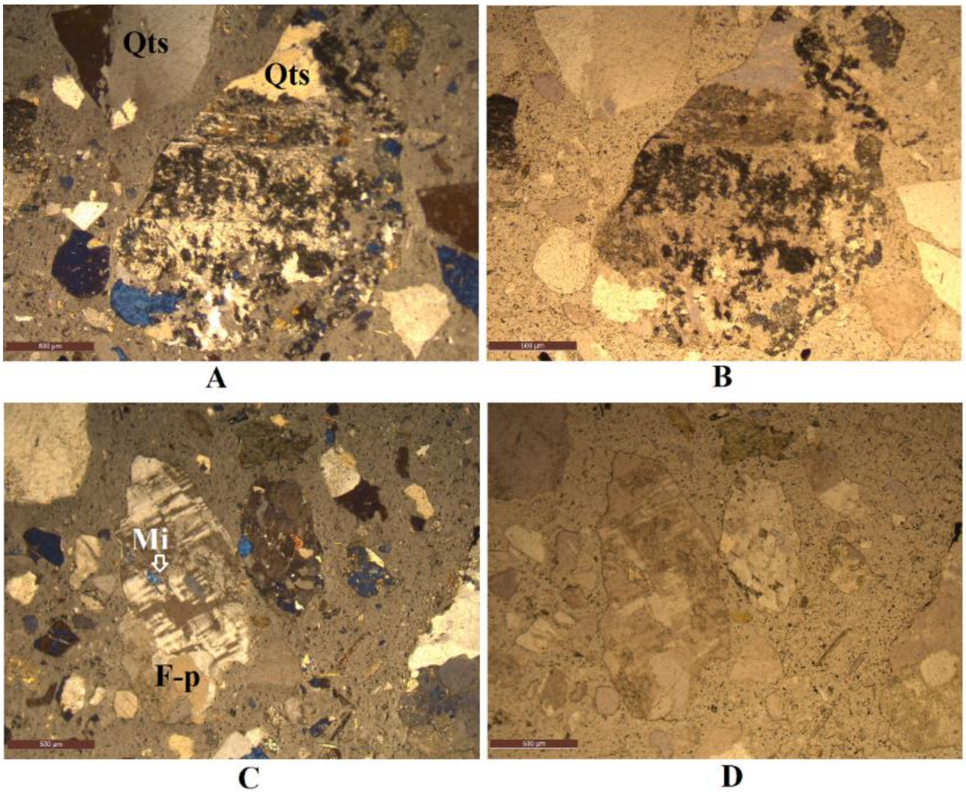

Figure 12. Micromorphology of cryoconite from the cryoconite holes at the Bezengi Glacier (scale bar = 500µm). A, C – plane-polarized light; B, D – crossed-polarized light. Qts – quartz, Mi – mica, F-p – feldspar.

Studied cryoconites from the holes show presence of mechanically transformed large fragments of quartz and feldspar. Pyroclastic inclusions in quartz are presented as it was observed in the previous sample. Mica inclusions are observed in feldspar and are also presented as a small separate fragments. Weathering rate is weak, mostly represented by the physical type. No biogenic conglomerates or organic remains have been observed. Fractures are not abundant indicating low degree of cryodegradation.

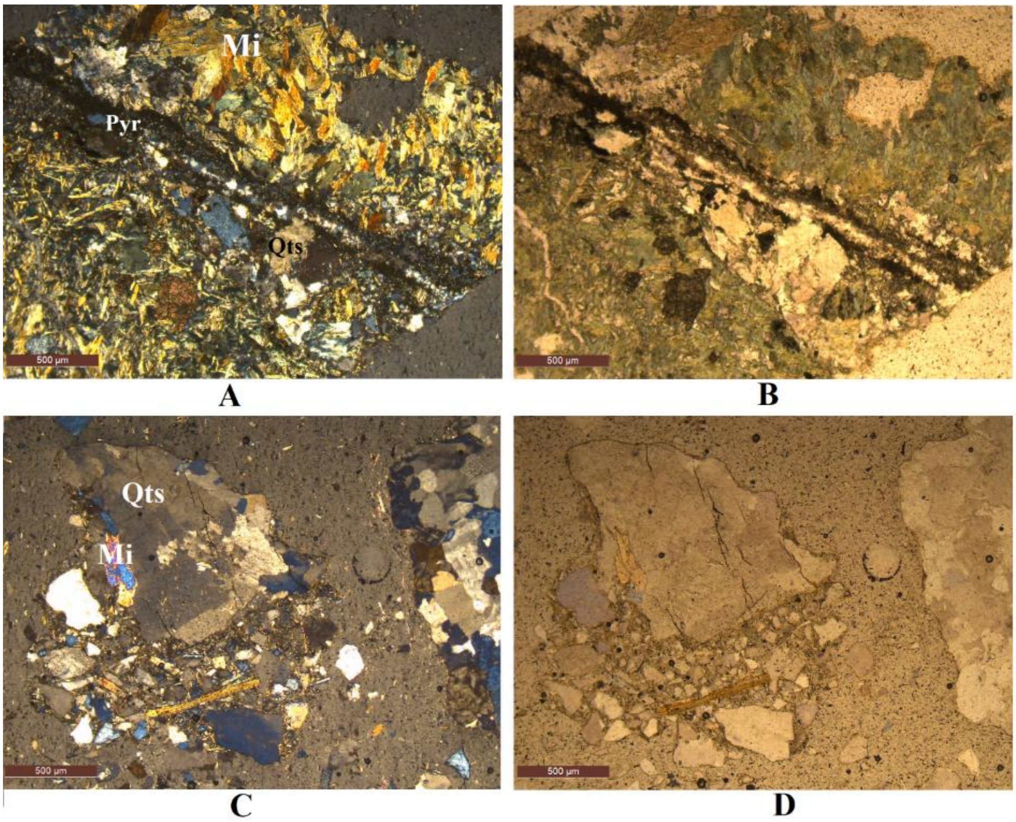

Figure 13. Micromorphology of moraine from the the Bezengi Glacier (scale bar = 500µm). A, C – plane-polarized light; B, D – crossed-polarized light. Qts – quartz, Mi – mica, Pyr – pyroclastic.

Soil fabric of moraine deposits from the Bezengi Glacier shows weakly transformed large fragments of minerals. Mica with incorporation of quartz and pyroclastic lenses indicates low rate of physical weathering. This is also observed in fragment of quartz (Figure 13, C-D) which has random oriented cracks and incorporation of mica as well as separated mica fragments which were mechanically replaced.

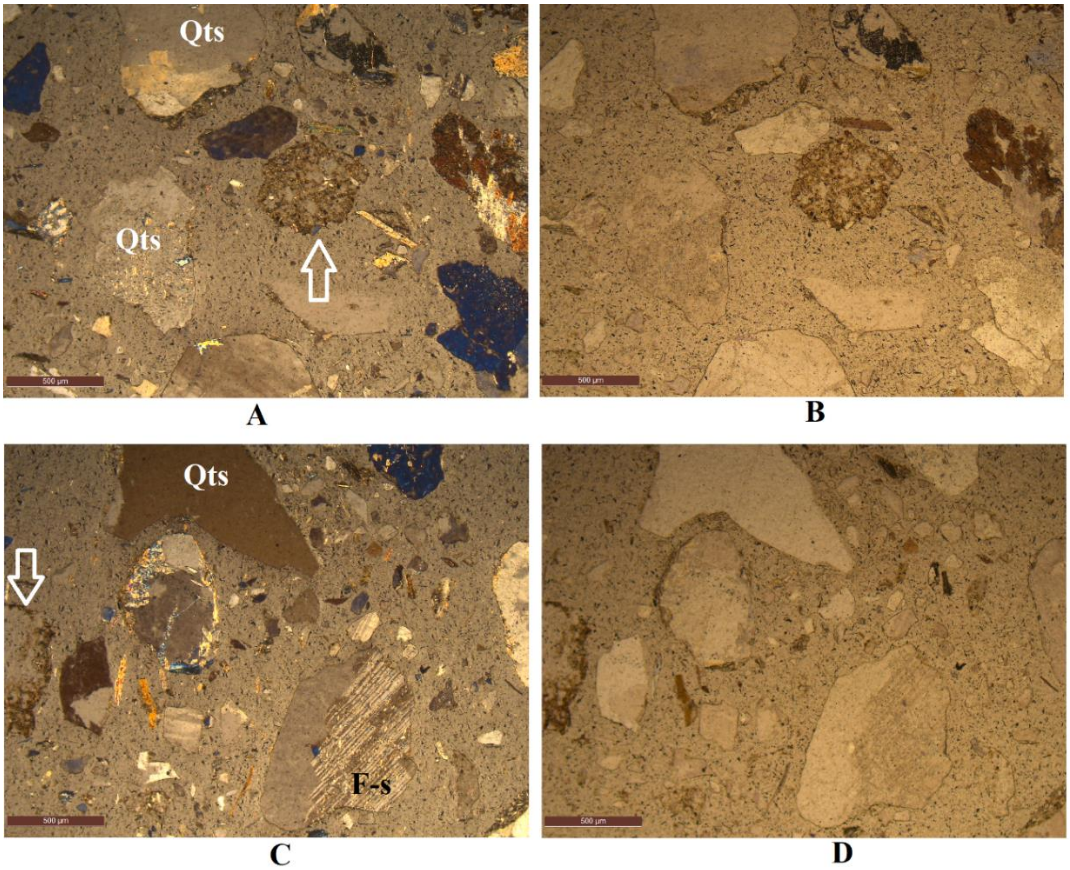

Figure 14. Micromorphology of soil-like body close to the Bezengi Glacier (scale bar = 500µm). A, C – plane-polarized light; B, D – crossed-polarized light. Qts – quartz, F-s – feldspar. Arrows indicate clay-mineral complexes.

Soil fabric of soil-like bodies close to the Bezengi Glacier indicate higher rate of weathering than in cryoconites. Mineralogical composition includes quartz, mica and feldspar which is similar to the cryoconites. However, in this case we can observe clay-mineral complexes. No organic remains have been observed. Due to mobility of iron and aluminum oxides sights of ferruginization are presented in some parts of the material.

Micromorphology of soils from the Khulamo-Bezengi Gorge is presented at Figure 15. Slightly different picture is observed in the lower B horizon. There is no visible biogenic material, however, the presence of clay-mineral conglomerate with fragments of quartz and mica is noted.

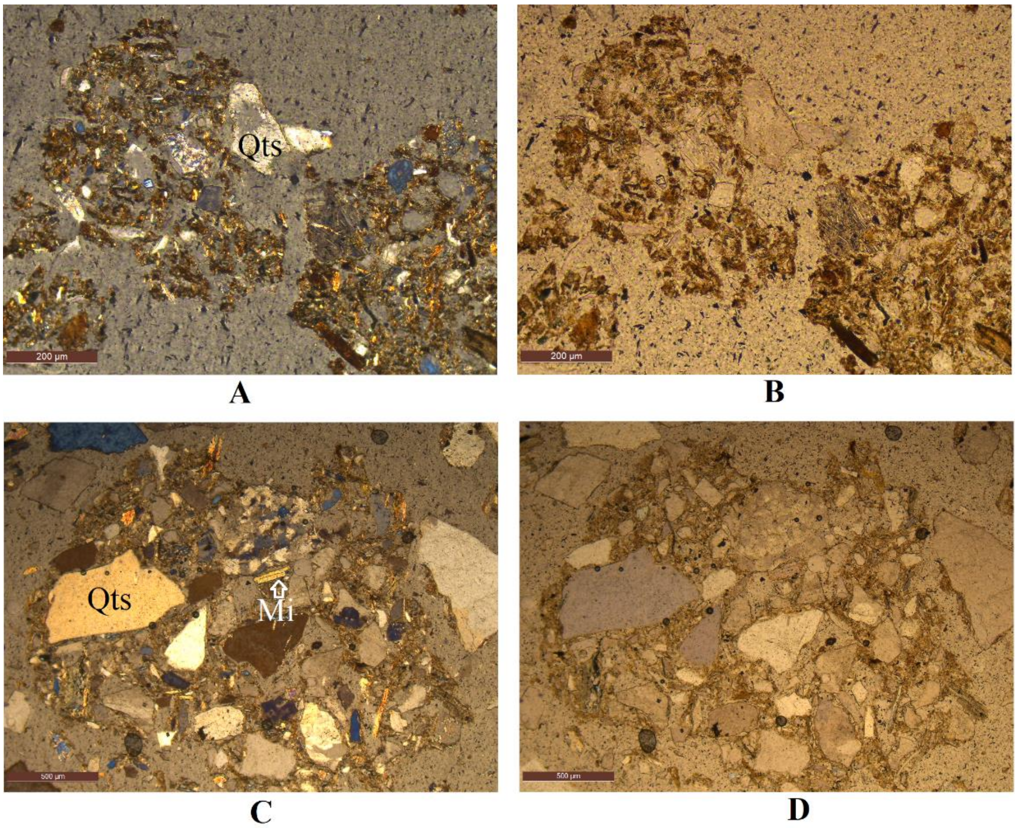

Figure 15. Soil fabric of Leptosols and Umbrisols from the Khulamo-Bezengi Gorge. A, B – scale bar = 200µm (horizon Oe); C, D – scale bar = 500µm (horizon B). A, C – plane-polarized light; B, D – crossed-polarized light. Qts – quartz, Mi – mica.

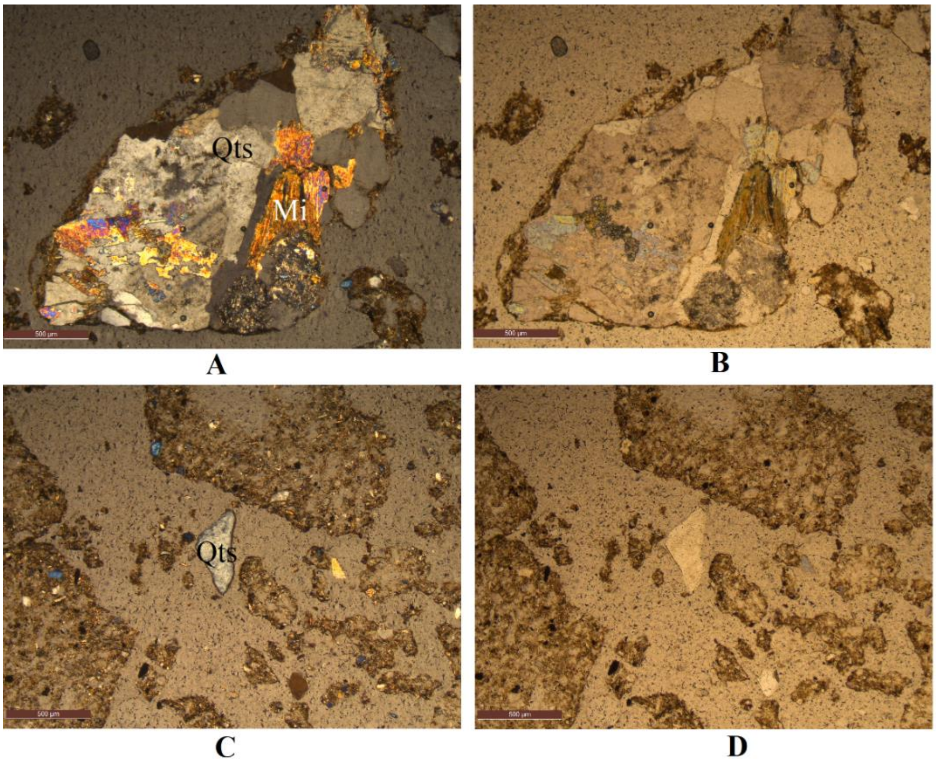

Figure 16. Soil fabric of studied Chernozems (scale bar = 500µm). A, C – plane-polarized light; B, D – crossed-polarized light. Qts – quartz, Mi – mica. Qts – quartz; Mi – mica.

Micromorphological study of Chernozems shows presence of large polymineral fragments as well as organic matter and organo-mineral aggregates. Polymineral fragment includes quartz and mica, it is well-transformed with signs of biological weathering and is surrounded by organic matter and organic-clay conglomerates. Large clay-mineral aggregates with incorporation of highly-destructed quartz which was affected by biological weathering are also presented.

4.4. Trace elements concentration

Trace elements concentrations in studied materials are presented in Table 9.

Table 9. Trace elements content in cryoconites, soils, mudflows and moraines (mg/kg), for fine earth fraction.

Sample	Horizon	Cu	Pb	Zn	Ni	Cd
KB1	Surface of the glacier	2.84	<0.01	20.00	8.42	<0.005
KB2	Surface	2.36	<0.01	13.40	5.58	<0.005
KB3	Surface	3.94	0.21	18.40	6.93	<0.005
KB4	Oe	12.00	13.70	52.10	18.10	<0.005
	Ah	12.80	15.20	52.70	19.90	<0.005
	A/C	22.50	17.00	60.50	25.40	<0.005
KB5	Ah	10.40	5.53	56.40	15.50	0.05
	A/C	10.20	4.98	54.20	15.40	<0.005
	Ck	9.72	3.68	50.50	14.00	<0.005
KB6	Ah	7.11	5.21	35.10	15.20	0.03
	Bk	5.73	4.20	30.30	13.10	0.04
KB7	Ch	2.57	1.89	27.10	8.21	0.01
	C	2.90	1.99	29.20	9.10	0.02
KB8	Surface	16.70	30.20	62.00	38.90	0.13
KB9	Cryoconite	6.92	17.10	35.50	15.90	0.05
KB10	C	1.07	0.33	3.48	1.05	<0.005
Bez1.1	Ch	11.00	8.66	59.00	11.70	<0.005
Bez1.2	C	15.60	12.70	72.60	14.20	<0.005
Bez2.1	Surface	8.05	8.34	44.60	12.10	<0.005
Bez2.2	Surface	6.74	3.67	30.40	6.50	<0.005
Bez3.1	Surface	17.40	30.00	85.70	19.00	0.05
Bez3.2	Surface	10.70	24.90	55.20	16.10	<0.005
Bez4.1	C	12.60	9.64	49.20	13.70	<0.005
Bez4.2	C	12.50	15.70	58.70	14.20	<0.005

Bez4.3	C	12.90	11.00	54.90	15.20	<0.005
Bez5	C	8.13	8.92	45.00	10.80	<0.005
Bez6	C	6.04	6.14	40.60	8.61	<0.005
Bez7	Surface	10.40	18.30	48.90	13.00	<0.005
Bez8	Surface	16.10	15.00	70.90	15.80	<0.005
Bez9	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	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
Bez11.1	C	40.70	16.40	89.30	42.00	0.11
Bez11.2	C	40.60	15.10	89.30	40.60	0.07
Bez12	A	29.80	12.10	78.70	26.60	0.11
	A/B	19.90	14.00	63.50	28.40	<0.005
	Bk	22.80	13.10	69.40	32.50	0.02
Bez13	A	24.80	16.50	72.30	37.70	0.08
	A/B	24.40	16.90	70.80	36.00	0.08
	Bk	25.30	15.40	71.90	37.70	0.03

In the Baksan Gorge the most polluted materials were cryoconite from the Garabashi Glacier and fresh mudflow, the highest values of trace elements are observed in them. Materials from the Skhelda Glacier, which is located remote from this area, have low values of pollutants as well as moraine from the Garabashi Glacier. Higher variability is observed between all samples even within one study site which is especially noticeable at the Garabashi Glacier. The lowest content of copper is observed at the Skhelda Glacier (2.84 mg/kg) while it increases in cryoconite from the Garabashi Glacier (16.70 mg/kg) and reaches its peak in fresh mudflow sample (up to 40.70 mg/kg). Values of copper in local Leptosols and Umbrisols are relatively high, closer to its content in the most polluted cryoconite KB8, which increase in study site nearby glaciers. Values of lead differs greatly from 0.01 mg/kg at the Skhelda Glacier to 30.20 mg/kg at the Garabashi Glacier.

Among Leptosols and Umbisols concentrations are highly dependent on the study site: it is almost twice lower in samples which are more remote from the studied glaciers. Concentration of zinc and nickel show similar trends: it is the lowest in moraine deposits, increasing in cryoconites, especially at KB8 sample from the Garabashi Glacier (up to 62.00 and 38.90 mg/kg, respectively). The highest values are observed at the fresh mudflow: up to 89.30 and 42.00 mg/kg. Cadmium levels in supraglacial sediments are low and in the most of cases are below the detection limit, the highest value is observed at the Garabashi Glacier (0.13 mg/kg). Similar situation was defined in the local soils: the content of cadmium does not exceed 0.05 mg/kg. To estimate influence of supraglacial sediments on the pollution of Leptosols and Umbisols fresh mudflow sample was excluded from the statistical analysis. Statistical difference is defined between copper content (F = 6.36, $p<0.05$) and zinc content (F = 9.94, $p<0.05$) in sediments and local soils. Statistically significant relationship is observed between all trace metals, except of cadmium.

Cryoconites and moraines from the Bezengi Glacier are relatively highly polluted by trace elements, closer to materials from the Garabashi Glacier or even more. Among the studied samples the highest values of lead (30.00 mg/kg), zinc (85.70 mg/kg), nickel (19.00 mg/kg) and cadmium (0.05 mg/kg) are defined at the Bez3.1 sample at the crack of the glacier. Soil-like bodies shows values similar to the supraglacial sediments and they are lower in the study point with plants which may indicate uptake of trace elements by plants. The highest content of copper is observed at the sample taken from the cryoconite hole. High variability of trace element values are observed between cryoconites in crakes, 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 is higher than in supraglacial sediments, especially in more remote study site Bez10 because this soil section is located in the floodplain and is affected by floods while study site Bez9 is located on high ground and is not essentially affected by the water flow. Considerably higher concentrations of cadmium are observed in local soils in comparison with sediments. In most of cases the highest concentrations of trace elements are observed in the top horizons of the soil profile (Cu = 12.80 mg/kg, Pb = 16.30 mg/kg, Zn = 89.20 mg/kg).

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,

$p<0.05$). Statistically significant positive relationships observed between the content of all trace elements, except of cadmium.

Studied Chernozems show higher than in Leptosols and Umbisols pollution by trace elements. Values varies greatly between Chernozem samples: concentrations in KB6 sample, which was taken from the middle of the Baksan Gorge are around twice lower in almost all cases than in samples from valley part of the gorge. Among the latter study sites Bez12 and Bez13 the highest values predominantly were defined in the upper horizons of the soil profiles.

4.5. Pollution indices

Index of geoaccumulation (Igeo) has been calculated for all study materials. Results are presented in Table 10.

Table 10. Calculated Igeo of studied samples.

Sample	Horizon	Cu	Pb	Zn	Ni	Cd
KB1	Surface of the glacier	-2.06	-10.70	-0.67	-2.40	< -6.97
KB2	Surface	-2.32	-10.70	-1.22	-2.94	< -6.97
KB3	Surface	-1.60	-6.38	-0.76	-2.64	< -6.97
KB4	Oe	0.03	-0.30	0.74	-1.25	< -6.97
	Ah	0.12	-0.15	0.79	-1.12	< -6.97
	A/C	0.93	0	0.95	-0.79	< -6.97
KB5	Ah	-0.18	-1.60	0.85	-1.47	< -6.97
	A/C	-0.20	-1.79	0.79	-1.51	< -6.97
	Ck	-0.29	-2.18	0.70	-1.64	< -6.97
KB6	Ah	-0.74	-1.69	0.16	-1.51	-4.64
	Bk	-1.03	-2.00	-0.04	-1.74	-4.06
KB7	Ch	-2.18	-3.18	-0.20	-2.40	-5.80
	C	-2	-3.06	-0.11	-2.32	-4.88
KB8	Surface	0.51	0.83	0.99	-0.17	-2.18
KB9	Cryoconite	-0.76	0	0.18	-1.43	-3.64
KB10	C	-3.47	-5.64	-3.18	-5.64	< -6.97
Bez1.1	Ch	-0.11	-0.97	0.92	-1.89	< -6.97
Bez1.2	C	0.41	-0.42	1.21	-1.60	< -6.97
Bez2.1	Surface	-0.56	-1.03	0.52	-1.84	< -6.97

Bez2.2	Surface	-0.81	-2.18	-0.04	-2.73	< -6.97
Bez3.1	Surface	0.57	0.82	1.45	-1.18	-3.84
Bez3.2	Surface	-0.5	0.56	0.82	-1.43	< -6.97
Bez4.1	C	0.10	-0.81	0.65	-1.69	< -6.97
Bez4.2	C	0.08	-0.11	0.91	-1.60	< -6.97
Bez4.3	C	0.12	-0.62	0.81	-1.52	< -6.97
Bez5	C	-0.54	-0.92	0.53	-2.00	< -6.97
Bez6	C	-0.97	-1.47	0.38	-2.32	< -6.97
Bez7	Surface	-0.18	0.11	0.64	-1.74	< -6.97
Bez8	Surface	0.45	-0.18	1.18	-1.47	< -6.97
Bez9	Oe	-0.54	-0.23	0.70	-2.47	-2.74
	A	-1.28	-0.64	0.12	-2.84	-3.84
	B	-2.33	-1.09	0.10	-3.64	< -6.97
	C	-1.77	-1.00	0.36	-3.18	-5.06
Bez10	Oe	0.12	-0.18	1.49	-2.06	-1.40
	B	0.03	-0.06	1.51	-1.89	-1.40
	C	-0.38	-0.64	1.44	-1.77	-1.09
Bez11.1	C	1.79	-0.04	1.51	-0.04	-2.56
Bez11.2	C	1.78	-0.17	1.51	-0.11	-3.32
Bez12	A	1.34	-0.49	1.33	-0.71	-2.56
	A/B	0.76	-0.27	1.02	-0.62	< -6.97
	Bk	0.95	-0.38	1.15	-0.42	-5.06
Bez13	A	1.07	-0.04	1.21	-0.20	-3.06
	A/B	1.05	-0.01	1.18	-0.27	-3.06
	Bk	1.10	-0.14	1.2	-0.20	-4.32

Among materials from the Baksan Gorge all materials from the Skhelda glaciers are unpolluted while the Garabashi Glacier shows slightly polluted values of Cu, Pb and Zn (up to 0.99). Local Leptosols and Umbisols mostly polluted with Zn (up to 0.95) and generally they are more polluted than cryoconites. Samples from the Bezengi Glaciers are more polluted, especially with Zn (up to moderately polluted, 1.45). Similarly, Leptosols and Umbisols are mostly polluted with Zn, especially samples which were taken from the study site at the floodplain, all of horizons are moderately polluted. Fresh mudflows are moderately polluted with Cu (up to 1.79) and with Zn (1.51). This trend is found in the studied Chernozems in beginning of the Baksan Gorge.

Table 11 shows Contamination Factor (CF) of the studied cryoconites, soils, mudlows and moraines.

Table 11. Contamination Factor (CF) of studied materials.

Sample	Horizon	Cu	Pb	Zn	Ni	Cd
KB1	Surface of the glacier	0.36	0.01	0.10	0.29	0.01
KB2	Surface	0.36	0.01	0.64	0.19	0.01
KB3	Surface	0.30	0.02	0.88	0.24	0.02
KB4	Oe	0.50	1.21	2.50	0.62	0.02
	Ah	1.63	1.35	2.53	0.69	0.02
	A/C	2.86	1.50	2.90	0.88	0.02
KB5	Ah	1.32	0.49	2.70	0.53	0.11
	A/C	1.30	0.44	2.60	0.53	0.02
	Ck	1.24	0.33	2.42	0.48	0.02
KB6	Ah	0.90	0.46	1.68	0.52	0.07
	Bk	0.73	0.37	1.45	0.45	0.09
KB7	Ch	0.33	0.17	1.30	0.28	0.02
	C	0.37	0.18	1.40	0.31	0.05
KB8	Surface	2.12	2.67	2.97	1.34	0.30
KB9	Cryoconite	0.88	1.51	1.70	0.55	0.11
KB10	C	0.14	0.03	0.17	0.04	0.01
Bez1.1	Ch	1.40	0.77	2.83	0.40	0.02
Bez1.2	C	1.98	1.12	3.48	0.49	0.02
Bez2.1	Surface	1.02	0.74	2.14	0.42	0.02
Bez2.2	Surface	0.86	0.32	2.90	0.22	0.02
Bez3.1	Surface	2.21	2.65	4.11	0.66	0.11
Bez3.2	Surface	1.36	2.20	2.65	0.56	0.02
Bez4.1	C	1.60	0.85	2.36	0.47	0.02

Bez4.2	C	1.59	1.39	2.81	0.49	0.02
Bez4.3	C	1.64	0.97	2.63	0.52	0.02
Bez5	C	1.03	0.79	2.16	0.37	0.02
Bez6	C	0.77	0.54	1.95	0.30	0.02
Bez7	Surface	1.32	1.62	2.34	0.45	0.02
Bez8	Surface	2.05	1.33	3.40	0.54	0.02
Bez9	Oe	1.03	1.27	2.44	0.28	0.23
	A	0.62	0.96	1.64	0.21	0.11
	B	0.31	0.70	1.60	0.12	0.02
	C	0.43	0.76	1.93	0.17	0.05
Bez10	Oe	1.63	1.33	4.19	0.36	0.57
	B	1.53	1.44	4.28	0.40	0.57
	C	1.15	0.96	4.08	0.43	0.70
Bez11.1	C	5.18	1.45	4.28	1.45	0.25
Bez11.2	C	5.17	1.34	4.28	1.40	0.16
Bez12	A	3.79	1.07	3.77	0.92	0.25
	A/B	2.53	1.24	3.04	0.98	0.02
	Bk	2.90	1.16	3.33	1.12	0.05
Bez13	A	3.16	1.46	3.47	1.30	0.18
	A/B	3.10	1.50	3.39	1.24	0.18
	Bk	3.22	1.36	3.45	1.30	0.07

Regarding CF, most of samples from both glaciers of the Baksan Gorge show low level of pollution by Cu, Ni and Cd. Slightly different situation is observed with Pb and Zn where CF is very low at the Skhelda Glacier and shows moderate pollution, close to high pollution values (up to 2.97) at the Garabashi Glacier which may be connected with local combustion and allochthonous input of polluted material. Local soils have similar lever of CF with the exception of Cu which shows mostly moderate level of pollution. Material from the Bezengi Glacier mostly moderately polluted by Cu as well as by Pb and Ni. In some cases, high pollution by Zn is observed in cryoconites from cracks and cryoconite holes (up to 4.11). High pollution CF values of Zn are also observed at the downstream Leptosols and Umbisols samples from the floodplain. Fresh mudflow from the Baksan Gorge are highly polluted with Cu (up to 5.18) and Zn (4.28) while by other trace elements values of CF indicate moderate pollution. Chernozems, especially their upper horizons, are also show high pollution CF values by Cu and Zn while by other trace metals these values indicate moderate pollution in almost all cases, even by Cd.

Degree of contamination which shows general pollution of the study sites by all trace elements is shown in the Table 12.

Table 12. Degree of contamination and modified degree of contamination of studied materials.

Sample	Horizon	C_{degree}	mC_{degree}
KB1	Surface of the glacier	0.76	0.35
KB2	Surface	1.21	0.24
KB3	Surface	1.46	0.35
KB4	Oe	4.86	1.23
	Ah	6.21	1.30
	A/C	8.17	1.72
KB5	Ah	5.16	1.09
	A/C	4.89	1.03
	Ck	4.49	0.96
KB6	Ah	3.64	0.77
	Bk	3.10	0.66
KB7	Ch	2.10	0.45
	C	2.30	0.49
KB8	Surface	9.41	1.96
KB9	Cryoconite	4.76	0.99
KB10	C	0.38	0.08
Bez1.1	Ch	5.42	1.08
Bez1.2	C	7.10	1.42
Bez2.1	Surface	4.34	0.87
Bez2.2	Surface	4.32	0.86
Bez3.1	Surface	9.75	1.95
Bez3.2	Surface	6.79	1.36
Bez4.1	C	5.31	1.06
Bez4.2	C	6.31	1.26
Bez4.3	C	5.79	1.16
Bez5	C	4.38	0.88
Bez6	C	3.58	0.72
Bez7	Surface	5.76	1.15
Bez8	Surface	7.34	1.47
Bez9	Oe	5.24	1.05
	A	3.55	0.71
	B	2.76	0.55
	C	3.33	0.67
Bez10	Oe	8.07	1.61
	B	8.21	1.64

	C	7.33	1.47
Bez11.1	C	12.61	2.52
Bez11.2	C	12.34	2.47
Bez12	A	9.80	1.96
	A/B	7.82	1.56
	Bk	8.55	1.71
Bez13	A	9.56	1.91
	A/B	9.42	1.88
	Bk	9.40	1.88

Moderate level of contamination according to Cdegree and mCdegree is observed only in one KB8 sample (9.41 and 1.96, respectively) among glaciers of the Baksan Gorge while in Leptosols and Umbisols of this location moderate level is more abundant. Bezengi Glacier shows more samples with moderate values, especially in cracks and cryoconite holes (up to 9.75 and 1.95). Similarly, soils from the Khulamo-Bezengi Gorge are moderately contaminated at the floodplain study site (up to 8.21 and 1.64) and in the Oe horizon of local Leptosols and Umbisols while underlying horizons show low levels of contamination. The highest levels of contamination among all studied materials are observed in the samples of fresh mudflow which are defined as with high pollution level (12.61 and 2.52). Chernozem in the upper part of the Baksan Gorge show low level of pollution while in Chernozems in the beginning of this gorge all samples are determined as moderately polluted, probably indicating input of pollutants from the highway.

4.6. PAHs content, composition, sources and potential toxicity

Features of PAHs have been studied in samples from the Baksan Gorge glaciers and soils. The concentrations of recorded PAHs are presented in Table 13.

Table 13. Detected concentrations of polyarenes in studied samples (ng/g, the delta of measurements is given in brackets where applicable).

PAH	KB1	KB2	KB3	KB6Ah	KB6Bk	KB7Ch	KB7C	KB8	KB9	KB10	Blank
NAP	21	22	23	23	21	22	20	84	21	17	5
ANA	7	7	6	7	8	9	7	6	5	7	<6
FLU	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6
PHE	9 (5)	7	7	10 (5)	17(8)	8 (4)	8 (4)	40 (20)	16 (8)	ND	ND
ANT	1	1	1	1	1	1	1	1	1	1	<1
FLT	21	21	21	22	22	22	24	28 (13)	21	22	<20
PYR	21	22	21	22	27 (13)	21	42 (19)	47 (22)	22	21	<20

BaA	7	7	7	7	7	6	7	7	7	7	<6
CHR	4	4	4	4	4	5	4	17 (9)	6 (3)	4	<3
BbF	7	7	7	7	7	7	7	13 (5)	7	7	<6
BkF	1	2	2	1	1	1	1	4 (2)	1	2	<1
BaP	1	1	2	2	2	2	2	6	2	2	<1
DBA	7	7	7	8	7	7	7	7	7	8	<6
BPE	6	6	6	6	7	7	7	7	7	7	<6
IPY	7	7	7	7	8	8	8	8	8	8	<6

Concentrations of individual polyarenes show high variability. Highest levels were detected for NAP (84 ng/g), PYR (47 ng/g) and PHE (40 ng/g). The lowest amount was detected for ANT: around 1 ng/g in all materials.

Cryoconite from the Garabashi Glacier is the most contaminated by PAHs among studied samples where the highest content of polyarenes such as NAP (84 ng/g), PHE (40 ng/g), FLT (28 ng/g), PYR (47 ng/g), CHR (17 ng/g), BbF (13 ng/g), BkF (4.2 ng/g) and BaP (5.8 ng/g). Also this sample shows higher content of individual polyarenes than the median among other studied materials. As it was detected with the concentrations of trace elements, the most unpolluted by PAHs samples located at the Skhelda Glacier.

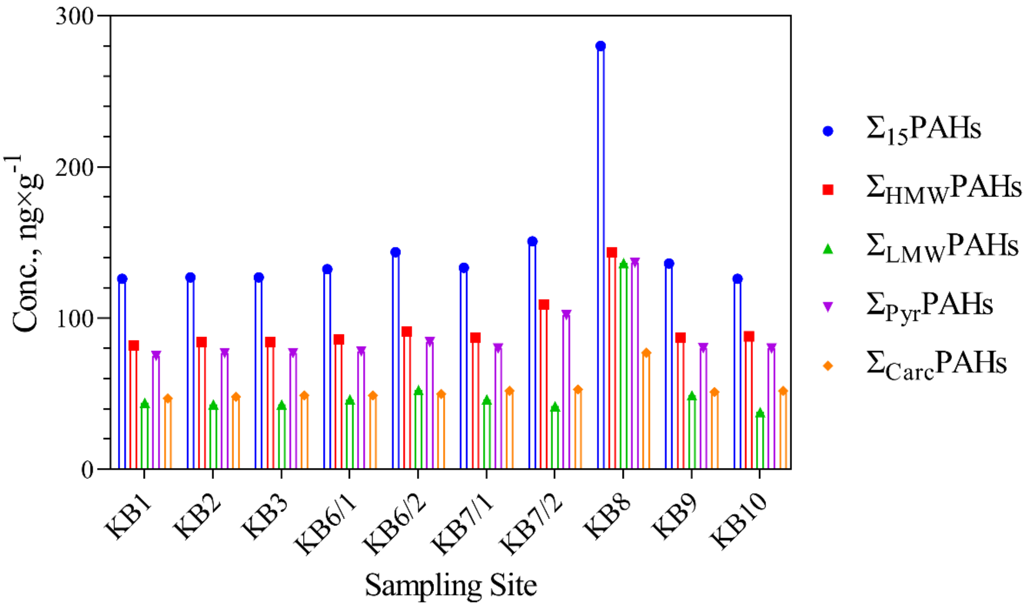

Figure 17. Sum of concentrations of different PAHs groups (prepared by T. Nizamutdinov).

The sum of concentrations of all 15 studied PAHs is the highest at the sampling point from the Garabashi Glacier (280 ng/g) while it is much lower (from 126 to 151 ng/g) in other materials. It is shown at the Figure 17. Values of high-molecular weight (HMW) PAHs and low-molecular weight (LMW) PAHs differs greatly in each sample with dominance of HMW PAHs, especially in soil-like bodies which indicates influence of anthropogenic pollution. The only exception is KB8 sample where these values are similar to each other. Trend of pyrogenic polyarenes is similar to those of HMW PAHs because most of studied HMW PAHs have pyrogenic origin. Carcinogenic polyarenes show similar concentrations with LMW PAHs, varying from 47 ng/g at the Skhelda Glacier to 77.1 ng/g at the Garabashi Glacier.

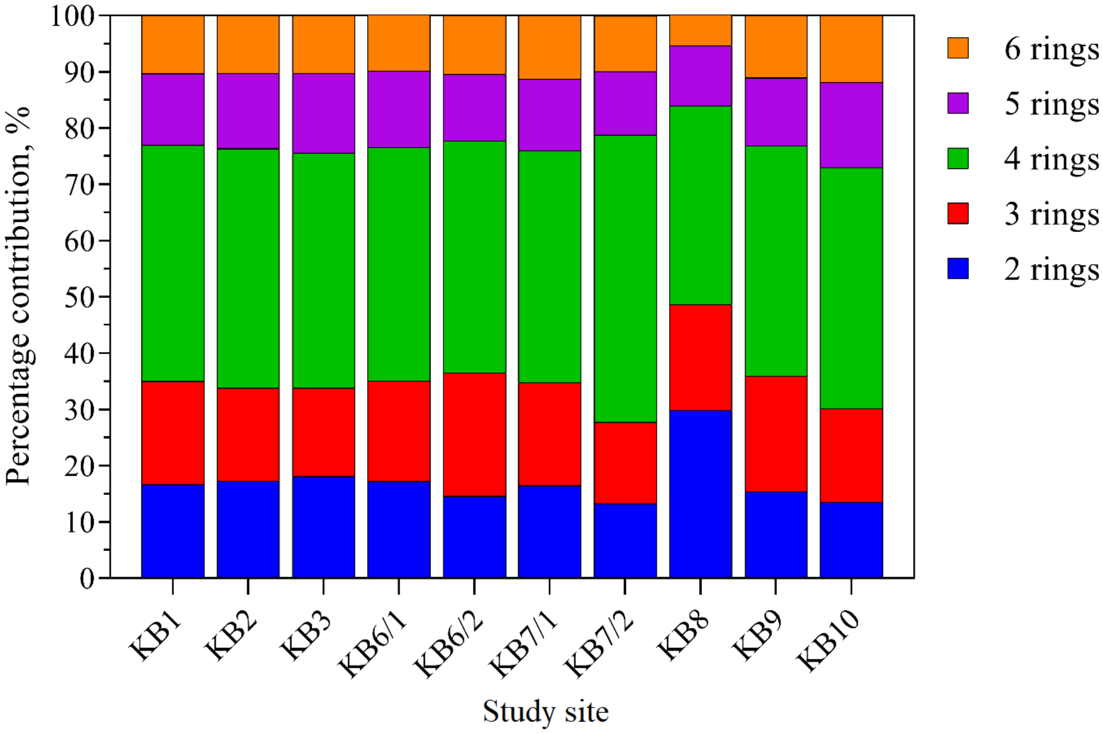

Figure 18. Contribution of PAHs with different numbers of rings in proportion to the sum PAHs (prepared by T. Nizamutdinov).

Proportion of different groups of polyarenes to their sum is presented in Fig. 18, where NAP has 2 rings in the structure; ANA, FLU, PHE and ANT – 3 rings; FLT, PYR, BaA and CHR – 4 rings; BbF, BkF, BaP and DBA – 5 rings; BPE and IPY – 6 rings. The most abundant group in all samples is PAHs with 4 rings in structure (>30%) while the least noticeable is 6-rings PAHs (<10%). Most of studied materials have similar proportions of PAHs of different groups with the exception of KB8 sample from the

Garabashi Glacier where 2 rings PAH has an essential proportion of around 25% and the smallest proportion of 6 rings PAHs.

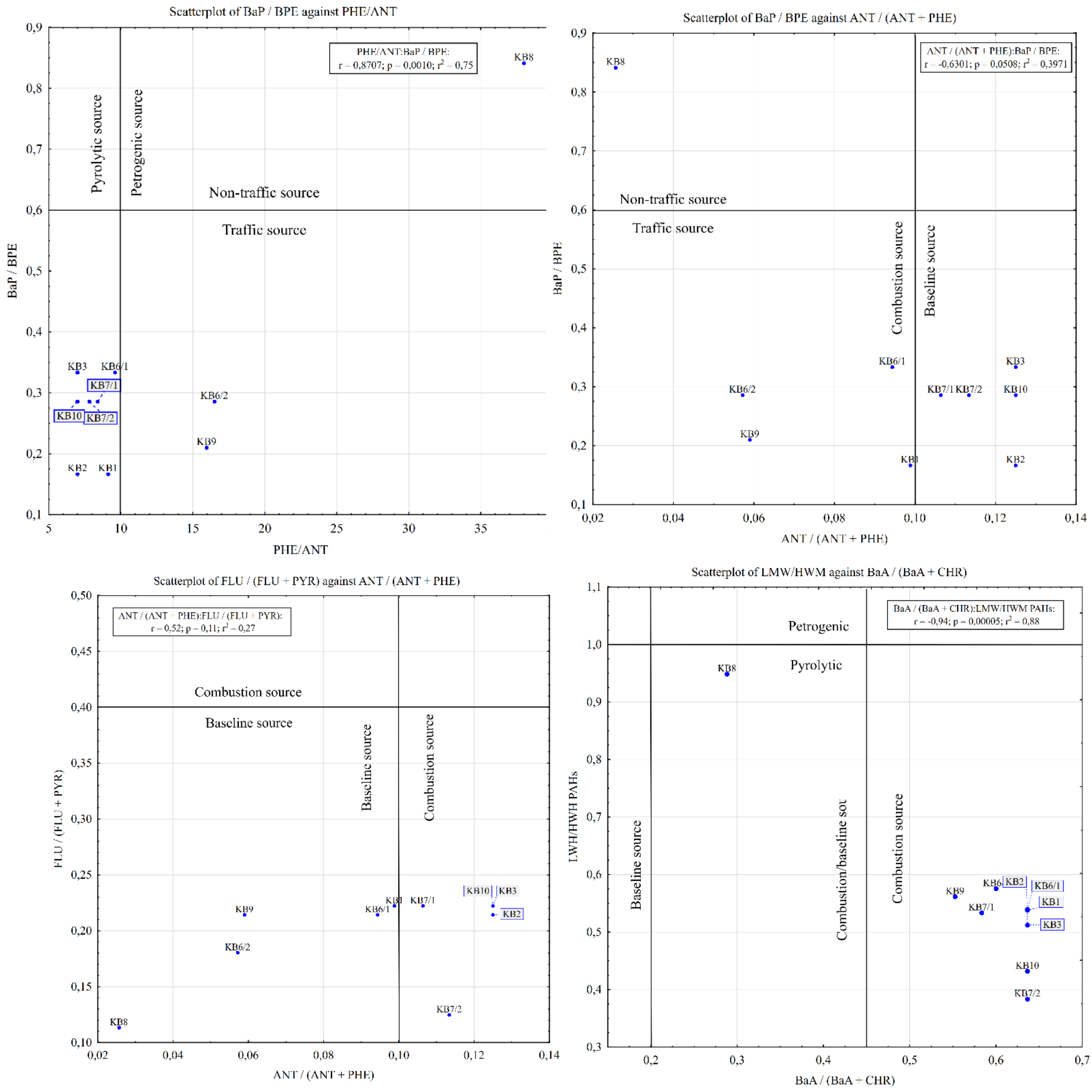

Figure 19. Constructed graphs of isomer ratios (prepared by T. Nizamutdinov).

Analysis of FLU/(FLU+PYR) to ANT/(ANT+PHE) ratios shows that KB7, KB2 and KB3 samples have combustion processes as source of PAHs while the rest have petrogenic source. Plot of LMW/HWM polyarenes to BaA/(BaA+CHR) indicates that all PAHs originate from combustion processes with the exception of KB8 which has mixed sources.

BaP-equivalents calculation shows that most of all individual PAHs toxicity do not exceed Maximum Permissible Concentration in soils (MPC, 20 ng/g) which is used in Russia. It is presented on the Fig. 20. However, the content of DBA is equivalent to around 40 ng/g of Benzo[a]pyrene which is twice higher than MPC. In general, the highest content of individual BaP-equivalents is observed in KB8 sample from the Garabashi Glacier.

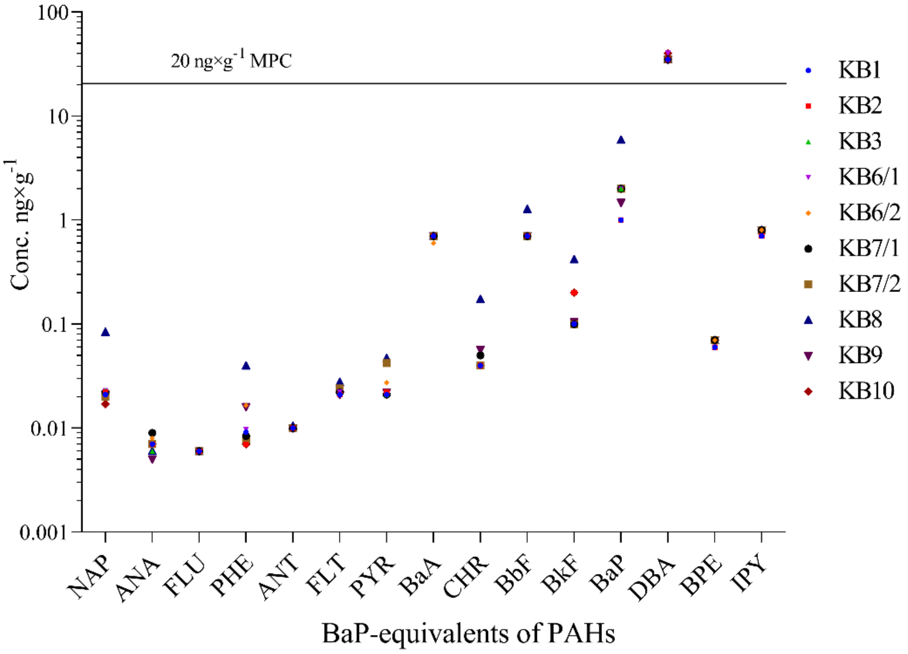

Figure 20. BaP-equivalents concentrations of individual studied polyarenes (prepared by T. Nizamutdinov).

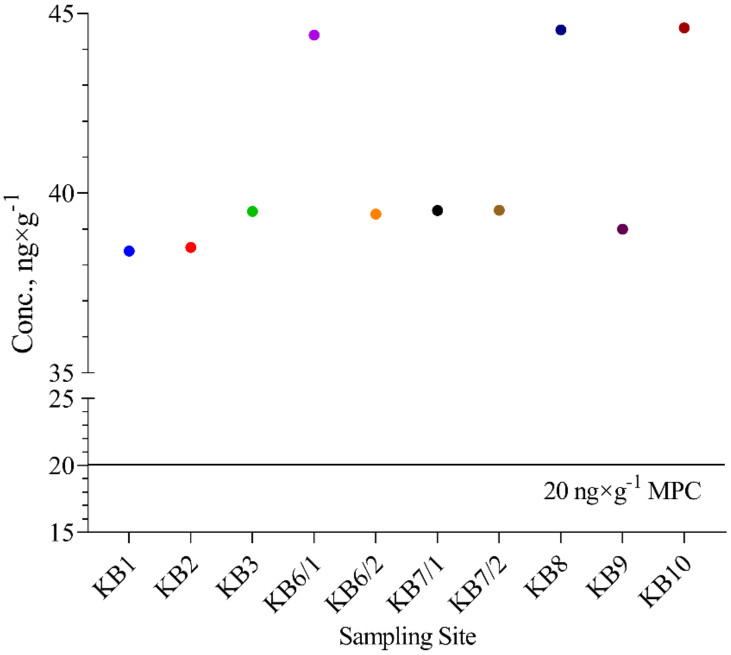

Figure 21. BaP-equivalents of the sum of studied PAHs in comparison with MPC (prepared by T. Nizamutdinov, colors indicating samples are the same as on previous figure).

BaP equivalent toxicity is higher than MPC in case we convert the sum of polyarenes to BaP equivalents (Fig. 21), in some samples more than twice.

5. Discussion

Deglaciation of mountain territories is observed almost everywhere on the Earth. The Central Caucasus is not an exception in this case. Previous research (Stokes et al., 2006) indicated essential melting of Caucasian glaciers which caused increase of debris cover by around 5% (Stokes et al., 2007). Negative mass balance values have been determined for the period of last 20 years at the Garabashi Glacier (Rototaeva et al., 2019). One of the factors which influence retreating of glaciers is deposition of carbon-containing dust (Kaspari et al., 2015). During the warm period of year with ice and snow melting, cryoconites increase in size due to attraction of mineral particles as well as various elements (Polyakov et al., 2020b; Zheng et al., 2020).

Previous studies of basic physicochemical features of cryoconites and local soils in Spitsbergen (Kastovska et al., 2005) and water from cryoconite holes at the Tibetan plateau (Fair et al., 2020) have shown similar to our materials pH values: neutral or slightly acidic. In the Khulamo-Bezengi Gorge local soils, generally, are more acidic than sediments, their values are close to 6 while values of sediments are closer to 7. Significant difference between pH H_2O and KCl is also observed within Leptosols and Umbisols which indicates 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 acidifying the soil solution (Seredina and Spirina, 2009). In studied Chernozems some acidity values decrease while going deeper in the soil profile. This is due to the fact that in alkaline soils, to which leached Chernozem belongs, the humus of the upper horizon creates conditions for a neutral reaction of the water extract, while in the lower horizons, due to the dissociation reaction of carbonic acid caused by the input of lateral water flows from high mountainous areas, hydrogen ions are formed, which pass into the soil-absorbing complex (Glukhikh, 2015). TOC content is the highest in studied Leptosols and Umbisols which indicates its transfer from the surface of glaciers to downstream areas as it was observed in previous research in Antarctica (Samui et al., 2020). Higher content of TOC within cryoconite sediments at the Bezengi Glacier which indicates importance of aeolian transfer.

In most samples of cryoconites from the Baksan Gorge TOC values defined by the direct measurement method is lower than those which was defined by indirect Tyurin measurement method what indicates conditions with oxygen deficiency and hydrogen surplus (Abakumov and Popov, 2005). These anaerobic conditions indicate that microorganisms which inhabit these sediments are anaerobes. The opposite situation is observed at the cryoconite sample from the Garabashi Glacier (KB8) as well as at the local soils. Here, there is an oxygen surplus and aerobic environment. Thus, local microorganisms are aerobes. In studied mountain soils while we go deeper, the TOC content is decreasing with layers which is also connected with plant residues at the upper part but mostly with input of carbon from the high-mountainous part. Significant relationships are observed between values of TOC and basal respiration due to fact that organic carbon act as a source for development of microbial communities. Relatively high values are also observed in cryoconites from cracks and cryoconite holes indicating development of microorganisms in these materials. In general, values of basal respiration are higher in Leptosols and Umbisols than in Chernozems or supraglacial sediments due to the input of easily accessible organic carbon. Results of study in Svalbard (Telling et al., 2012) indicated that values of basal respiration and TOC were similar to our results and they were depended on each other as well as on the microbial activity in the supraglacial sediments. Presence of gravimetric moisture in glacial environments contributes to development of microbial communities around water streams, however, transfer of nutrients from cryoconites to local soils also plays role which was observed in the Antarctica (Foreman et al., 2007).

Cryoconites from the Skhelda and Garabashi glacier show differences within cryoconites on their surfaces in terms of particle-size distribution. Most of samples have more coarse earth fraction in their texture while alluvium KB2 and cryoconite KB8 are dominated by the fine earth fraction which distinguishes them from other cryoconites from the Baksan Gorge glaciers and may play role in redistribution of carbon and nitrogen in glacial ecosystems. This happens because that KB2 sample is cryoconite-derived alluvium which was affected by transformation processes while KB8 probably has different source of material and high weathering degree. Uetaki et al. (2016) pointed that development of specific microbial communities in cryoconites influence grain size which is likely to happen in KB8 sample due to defined high basal respiration values. Local soils have smaller grain diameter within one fraction than supraglacial sediments which is caused by vegetation cover, relatively diverse microbiology and mechanical destruction which influence the rate of weathering and, thus, the grain size. Vegetation strongly affects weathering processes in high-altitudinal regions which is expressed by producing of specific organic ligands (Egli et al., 2008). Microbial communities play role as well by producing helating ligands, specific organic acids and changing basic physicochemical properties such as pH (Castaldini et al., 2002). Also microbiological activity strongly depends on the precipitation and temperature regime, that is why biological weathering considerably increase with decreasing altitude (Riebe et al., 2004).

However, in general Leptosols and Umbisols are similar to studied cryoconites indicating the connection between supraglacial sediments and local soils, and pointing to the role which sediments play in formation of mountainous soils. Similar situation is observed in the Khulamo-Bezengi Gorge where sand is dominating among all samples which is typical for soils with slow development and low degree of weathering in harsh environmental conditions. Chernozems are located in another study site and under other factors which lead to dominace of silt and high content of clay. Previous research of cryoconite particle-size distribution in Spitsbergen (Kastovska et al., 2005) indicated dominance of fine earth which was higher than 50% with prevalence of silt while in this study ratio is different. Earlier it was found that variations in particle-size distribution are caused by differences in geographical position and source of material (Abakumov et al., 2021). In the Antarctic cryoconite sediments from the Anuchin Glacier, which is surrounded by Gruber Mt., showed the dominance of sand and coarse fraction while cryoconite material from the Mushketov Glacier in the Arctic had the prevalence of silt and fine earth in general. This happens due to the fact that mountains affect 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). In our case, the Caucasus mountain range, surrounding study sites, has considerable impact on the particle-size distribution of cryoconites and affects the local soils formation. Grain size of studied mountain soils and Chernozems is also influenced by mechanical destruction of particles carried by water streams from the glaciers and mountains which lead to transfer of rocks to soils (Zharinova, 2011). This strongly influence physical and chemical properties as well as micromorphology of this soils, its mineral composition and features (Konistsev and Rogov, 1977; Mazurek et al., 2016).

In terms of micromorphological structure different cryoconites show similarities as well as differences in mineralogical composition and in weathering rate. In general, the most abundant minerals were quartz, mica and feldspar. In another study of mineral composition in the Caucasus region (Zawierucha et al., 2019) quartz and feldspar have been observed in cryoconite materials. Studied sediments have weakly transformed structure indicating recent origin. In another recent study of cryoconites micromorphological structure at the Djankuat Glacier, Central Caucasus, similarly with our research among minerals mainly were defined quartz, mica, feldspar and chloride (Kutuzov et al., 2021). This study also indicated importance of aeolian transfer due to small size of grains while in our case grains mostly were found in large fragments indicating local source of material. Mainly, we can observe physical weathering and low structures of biogenic origin. Pyroclastic material was appeared in the cryoconite texture and as incorporations in minerals such as feldspar due to volcanic eruptions of Elbrus and Kazbek mountains, last of which occured less than 30 thousand years ago (Gurbanov et al., 2004). It was weakly transformed because of cold environmental conditions and weak transformation of rocks. Ferruginization of studied mineral particles is not or weakly expressed which indicates aeration of material and absence of waterlogged conditions because the latter condition cause formation of Fe-Mg particles (Rogov and Konistsev, 2008). Physical and mechanical destruction is the main type of grains transformation which is observed by fractures in minerals and their sharp edges. Presence of clay-plasma fabric was observed also in some previous studies (Switoniak et al., 2016; Maksimova and Abakumov, 2017) indicating mechanical weathering of material. The same processes of transformation were observed in the previous study and they were linked to frequent temperature fluctuations (freezing-thawing process and frost weathering) as well as to input of fresh grains from nearby moraines which are easily affected by mechanical destruction (Zawierucha et al., 2019). However, this study also indicated importance of chemical weathering in destruction of mineral grains and importance of microbes which produce specific substances and due to that decrease exposure to cryogenic factors which leads to reduction of cryodegradation.

Biopedogenic and sedimentation processes, transformation of moraines and cryoconite lead to formation of soil-like bodies which is affected by input of material by aeolian processes and water streams (Glazovskaya, 2005). This is observed in our case by presence of iron in the texture of soil-like bodies. Clay-mineral conglomerates are abundant in this type of material which was established as a result of compression indicating role of mechanical destruction and physical weathering, which is a dominant type of weathering here. Lately formed sedimentary soils, organomineral particles of which in the summer together with mudflows are transported to the downstream areas and adjacent ecosystems (Solomina et al., 1994). Thus, during deglaciation organo-mineral matter redistribution contributes to the soil formation in mountain regions. Mineralogical composition of studied soils is close to those of cryoconites and comparable with those in Switzerland high-mountain area where quartz and mica considerably contributed in micromorphology (Musso et al., 2022). In mountain ecosystems direct input of matter from supraglacial sediments acts as an additional source of nutrients and pollutants which microorganisms receive from the primary minerals and organic matter (Nagatsuka et al., 2010).

Also, different from the studied cryoconites, in Leptosols and Umbisols biological weathering plays important role. This is observed due to incorporation of organic matter and relatively smooth edges of the grains. The similar importance of biological impact was observed in Lahijan mountains (Ramezanpour and Pourmasoumi, 2012) where clay particles were originating from biological weathering of mica and feldspar at the early stage of pedogenesis. Top horizon (Oe) of Leptosols and Umbisols from the Khulamo-Bezengi Gorge includes humic aggregates with intergranular pores due to presence of vegetation cover and ongoing sod processes which leads to input of organic matter and humification of it. Studied soils are similar to supraglacial sediments in terms of micromorphological structure, however, have better transformed material which indicates that downstream transfer of mineral matter have an impact on mineralogical composition of Leptosols and Umbisols. Zazovskaya et al. (2021) found that microstructure of top horizons of mountain soils close to the Aldegond Glacier shows specific cryogenic separation of particles indicating that cryoconites act as a basis for formation of these soils as well as roots of lichens and mosses were defined which play role of "traps" for dust and cryoconites from glaciers, its further accumulation and participation in soil formation. Study in Altai mountains (Egli et al., 2015) points importance of aeolian transport for transfer of supraglacial sediments to local soils and indicates water availability as a decisive factor for rate of minerals weathering. Chernozems samples are highly influenced by local biota, there are incorporations of fresh organic matter and biogenic material, mineral fragments show signs of biological destruction which is typical for developed soils affected by agricultural processes and vegetation cover. These features are typical for Chernozems and were observed, for instance, in study of Golyeva et al. (2018). However, in this study were defined signs of microfauna and absence of minerals while in our case it was the opposite which indicates, probably, influence of agriculture on soil fauna and that transferred minerals from the high-altitudinal areas also play role in mineralogical composition of Chernozems in this study.

Rapid deglaciation leads to increase of cryoconites in size and higher accumulation of pollutants, attracting additional carbon-containing dust (Zheng et al., 2020). PAHs are in this list of pollutants and earlier it was found (Li and Duan., 2015) that pollution of sediments and soils by polyarenes is linked with anthropogenic activities in surrounding territories. This was observed in China sea where concentrations of pollutants were less in its southern part than in northern where lots of industries are located (Li and Duan, 2015). Similar fact was carried out in the Antarctica where in the vicinity of "Saint Kliment Ohridski" polar station concentration of NAP was 170 ng/g

(Abakumov et al., 2021) while in the remote sites these concentrations were lower than 30 ng/g (Aislabie et al., 1999).

Studies of PAHs in cryoconites and mountain soils have been conducted in Himalayas, Tibetan Plateau and European mountains. They showed high variability between samples. In Himalaya mountains concentrations of polyarenes in sediments varied from 14.54 to 437.43 ng/g (Riaz et al., 2019). Tibetan Plateau (Li et al., 2017) showed values from 6.67 ng/g in the part which is situated far away from industries to 3906.66 ng/g close to factories and cities. In studies of local soils in Pyrenees (Quiroz et al., 2010) studied mountain soils were highly polluted with PAHs, with the average concentration of 400 ng/g (Quiroz et al., 2010). Here, HMW PAHs were the dominant group in most of samples which indicates their local origin due to the fact that they are usually deposited close to the area of their origin while LMW PAHs may be transferred by wind streams far away (Tobiszewski and Namieśnik, 2012). It was found that on the Garabashi Glacier concentration of LMW PAHs is comparable with HMW PAHs which from one side may indicate allochthonous input of material due to the fact that this glacier is located on the slope of mountain and is not surrounded by mountain walls which may block atmospheric transport. From the other side, the main LMW PAH here is NAP which usually originates from combustion of gasoline from motor vehicles (Soltani et al., 2015) as a result of nearby touristic activities. Earlier it was found (Pozdnyakova, 2012) that HMW PAHs usually are highly mutagenic and carcinogenic, that is why in our study their concentration is similar to those of carcinogenic PAHs.

Sources of PAHs are different: allochthonous which are transferred from remote regions as well as allochthonous, for instance, from local traffic (Abdel-Shafy, 2016). The Central Caucasus is a popular destination for tourists (Litvinova et al., 2020) which leads to high level of anthropogenic pressure. Garabashi Glacier, where the highest concentrations of polyarenes were defined, is the one of the most visited places with lots of roads even directly to the cable car, close to the glacier, cafes and hotels at the foothill which burn fossil fuels for their needs. The same situation when closeness of road affect pollution of environment by PAHs was observed previously in Tibetan Plateau (Yuan et al., 2016). The main part of fuels for automobiles is NAP (Soltani et al., 2015) which points to the fact that local traffic is the main source of polyarenes. The Skhelda Glacier is located in remote from the main touristic places area of the Baksan Gorge that is why it possible to take them as a background site.

Caucasus mountain range is also affected by allochthonous transfer of polluted material, to the Central Caucasus carbon-containing dust with pollutants is transferred mainly from two regions: Western Asia and Northern Africa (Lokas et al., 2018; Kutuzov et al., 2021). In these regions emissions of polyarenes to the atmosphere are associated with industries and traffic in urbanized agglomerations (Saeedi et al., 2012), petrochemical industries (Abbasi et al., 2019), ship ports and ships traffic (Khairy et al., 2009). Furthermore, in Western Asia emissions of PAHs may be caused during the process of the open biomass burning for agricultural preparation of lands and disposal of crops residues (Ravindra et al., 2008). All these processes act as additional sources of polyarenes for our study sites.

To correctly understand the source of PAHs in studied samples we calculated isomeric ratios and constructed cross-sectional graphs. In general, these bi-plots show that sources are mixed petrogenic and pyrogenic. Let's discuss this more in details. PHE/ANT isomeric ratios shows that main source of polyarenes at the Garabashi Glacier is oil leaks from local cities and roads which may be connected with the same situation in previous research in France and Benin (Soclo et al., 2000) where the pollution by PAHs was associated with oil leaks from petroleum delivery and local industries. Another calculation of BaP/BPE ratio shows the possibility of traffic as a main source of polyarenes on this glacier due to automobile road in the vicinity and this situation is observed in most of all samples. LMW PAHs/HMW PAHs ratios indicate that combustion is a main source of polyarenes in our materials and in Garabashi Glacier it also may be connected with allochthonous input. Similar bi-plots of isomer ratios conducted earlier in China (Li et al., 2017) points that on the Tibetan Plateau the main source of polyarenes in cryoconites were combustion of fossil fuels and biomass as well as local traffic. In soils of Himalaya mountains sources were mixed, local petroleum contamination as well as combustion processes (Devi et al., 2016).

In order to correctly estimate potential toxicity of studied materials, calculation of BaP-equivalents (Benzo[*a*]pyrene equivalent toxicity) has been made because not all of studied PAHs have adopted maximum permissible concentration (MPC), this method is widely used in practice. Our study points are located at the part of Caucasus mountain range on the territory of the Russian Federation but because environmental conditions differ around the world, we chose local adopted standard as a reference (Hygienic Norms, 2006) which is based on the monitoring of 3-4 benzo(a)pyrene.

Concentrations of BaP-equivalents of individual PAHs in our study is lower than MPC (20ng/g) in almost all samples except of one from the Garabashi Glacier. However, if we sum all individual BaP-equivalents, we can observe that concentrations are higher than MPC (up to 45 ng/g) in all study points which may be dangerous for local environment and population. Concentration of PAHs in BaP-equivalents between cryoconites from the Garabashi Glacier and Chernozems are similar indicating possibility of PAHs transfer and its influence on mountain ecosystems. In the study from Tibetan Plateau (Li et al., 2017) values of BaP-equivalents varied from 1.34 to 14.34 ng/g which is lower than in our study in the exception of one sample (281.32 ng/g).

Due to the fact that global environmental change affects mountain and polar regions more than average, it is important to discuss how polyarenes would react in these circumstances. First of all, soils in cold environments store organic pollutants and rise of temperature and changes in soil organic matter may lead to remobilization of these pollutants in mountains and affect exchange between atmosphere and soils (Wang et al., 2012; Cabrerizo et al., 2013). Moreover, temperature rise will cause longer ablation period of glaciers and, thus, additional solid transfer of pollutants downstream (Kohler and Maselli et al., 2008). Tao et al. (2017) previously found that environmental changes in cold conditions may increase biomagnification of polyarenes in the food web which may pose risks for local wildlife and people. Furthermore, climate change could affect the rate of insolation because of variability in clouds cover which in turn influence PAH's composition through photochemical oxidation which was observed in the research of Quiroz et al. (2010) with the change of BaA and BaP under the influence of additional light input. Some researches (Bergauer et al., 2005; Weiland-Brauer et al., 2017) indicated presence of psychrophilic microorganisms which play role in bioremediation through degradation of PAHs. In situation of environmental changes, we can expect development of these microorganisms or appearance of other communities.

Atmospheric carbon-containing dust can store and transfer various trace elements such as Cu, Zn and Ni which was found in the Arctic (Vinogradova and Kotova, 2019) and in the Antarctic (Polyakov et al., 2020a). Further, this material with glacier retreat contribute to pollution of local lakes and streams as it was found in European mountains (Bogdal et al., 2009; Morselli et al., 2014).

Cryoconites in various places of our planet have been studied in terms of trace elements pollution. Lokas et al. (2016) found that in cryoconites of Svalbard archipelago mean concentrations of Cu (37.62 mg/kg), Pb (54.38 mg/kg), Zn (96.33 mg/kg) and Cd (0.42 mg/kg) were higher than in our study. They also were higher than local natural values which was connected with input of polluted material by its deposition as well as with absorption by microoranisms and production of them specific substances. Another research carried out in Svalbard archipelago (Singh et al., 2017) showed similar or less compared with our content of Pb (up to 36.3 mg/kg), Zn (up to 66.2 mg/kg), Ni (up to

21.2 mg/kg) and Cd (up to 0.14 mg/kg) in cryoconites which indicates importance of local factors and degree of cryoconite formation. This research also defined concentrations of these pollutants in Himalayas and similarly to the PAHs pollution, the highest trace elements values were defined close to industry centers which were much higher than in the Central Caucasus. Study of cryoconites in Alaska (Owens et al., 2019) revealed similar to our research concentrations of Cu (55 mg/kg) and Zn (80 mg/kg), however, lower values of Pb (5 mg/kg) and Cd (0.01 mg/kg) again point to importance of local factors and variability in sources of pollutants.

As it was mentioned before, carbon-containing dust in the Central Caucasus originate in Western Asia and in Northern Africa (Kutuzov et al., 2015a). In the same study it was found that this dust is enriched with Cu, Zn and Cd due to high natural values and active anthropogenic activities in these regions. However, relatively high content of Zn, Cu and Pb have been found in almost all studied samples in our study including valley glaciers surrounding by mountain walls, which is not possible to explain only by long-distant transfer of trace elements, indicates influence of autochthonous polluted material. Tourism is highly developed in the Baksan Gorge as well as in the Khulamo-Bezengi Gorge. Transportation of people, construction of new facilities and operating of existing ones' lead to active usage of various fossil fuels which is associated with emissions of trace elements into the atmosphere, mainly Ni and Pb (Shagin et al., 2018) which further contribute to deposition of these pollutants on the surface of the glacier. Furthermore, close to the Elbrus mountain abandoned lead-zink mine is located which mine tailing storage affect pollution status of the local environment (Uraskulov et al., 2018). In some of sampled cryoconites located in the bottom of the glaciers as well as soil-like bodies and moraines concentrations of trace elements were higher which was also observed in the study of Kutuzov et al. (2021) at the Djankuat Glacier due to input of material from local moraines, rock outcrops and soils. Especially high in this study, as well as in our case, was content of Zn which indicated allochthonous input due to the fact that Zn is usually transferred with dust by atmospheric winds.

Transfer of cryoconites may affect pollution level at local soils. In previous study (Magnani et al., 2018) of mountain soils at the Mt. Everest content of trace elements was lower or similar to those in our research (Cu up to 10.4 mg/kg; Zn up to 68.8 mg/kg; Pb up to 16.8 mg/kg; Ni 22.5 mg/kg) with the highest values in the top horizons and increasing with altitude. Calculation of pollution indices of soils in Changbai Mountain (Ma et al., 2019) revealed mostly moderate or low levels of pollution which is similar or lower than in our study. In our case the distribution of pollutants is similar and is connected mostly with local input of material. Mountain ranges act as a natural barrier regulating long-distant transport of material (Bing et al., 2018) which also indicates autochthonous input of pollutants to the soils, also from cryoconite sediments. In general, mostly pollution by trace elements is higher in Leptosols and Umbisols than in cryoconite which is also connected with additional input of pollutants by water streams and aeolian transfer. Recently it was found (Ermakov et al., 2020) that content of Cu was higher than natural values in the Baksan river and further downstreams it affects local soils. This is also noticeable in our study because the highest values of trace elements have been found in the top horizons and, especially, in the study site at the floodplain indicating transfer of trace elements by the rivers such Baksan and Khulamo-Bezengi. Another possible source of pollutants of Leptosols and Umbisols is vegetation cover. Due to the fact that most of trace elements are not biodegradable they are accumulated in plants and further increase concentration of trace elements in soils (Kumar et al., 2016). In another study in European mountains (Yaneva et al., 2022) it was found that mountain soils act as a buffer against local pollution, which was especially noticeable nearby automobile roads. In our study Leptosols, Umbisols and Chernozems are located near the road which is actively used by tourists and local residents, which essentially affect pollution of these soils.

As it was observed earlier in this study, cryoconites may affect biogeochemical cycles of mountain ecosystems as well as their pollution levels. In the Central Caucasus region reallocation of organomineral matter influence local soils as well as mountain glaciers. After deposition, material may be accumulated on the glacier surface and form so-called “cryoconite network”. Composition of this network is highly dependent on the sources of this sediments which in the Central Caucasus is represented by mixed local and long-distant sources, both of them are polluted with trace elements and PAHs (Lokas et al., 2018). Earlier Glazovskaya (2005) studied influence of aeolian dust at the surface of glaciers on the adjacent mountain valleys. Schematic figure of transfer of matter nearby the Bezengi Glacier is presented on Fig. 22.

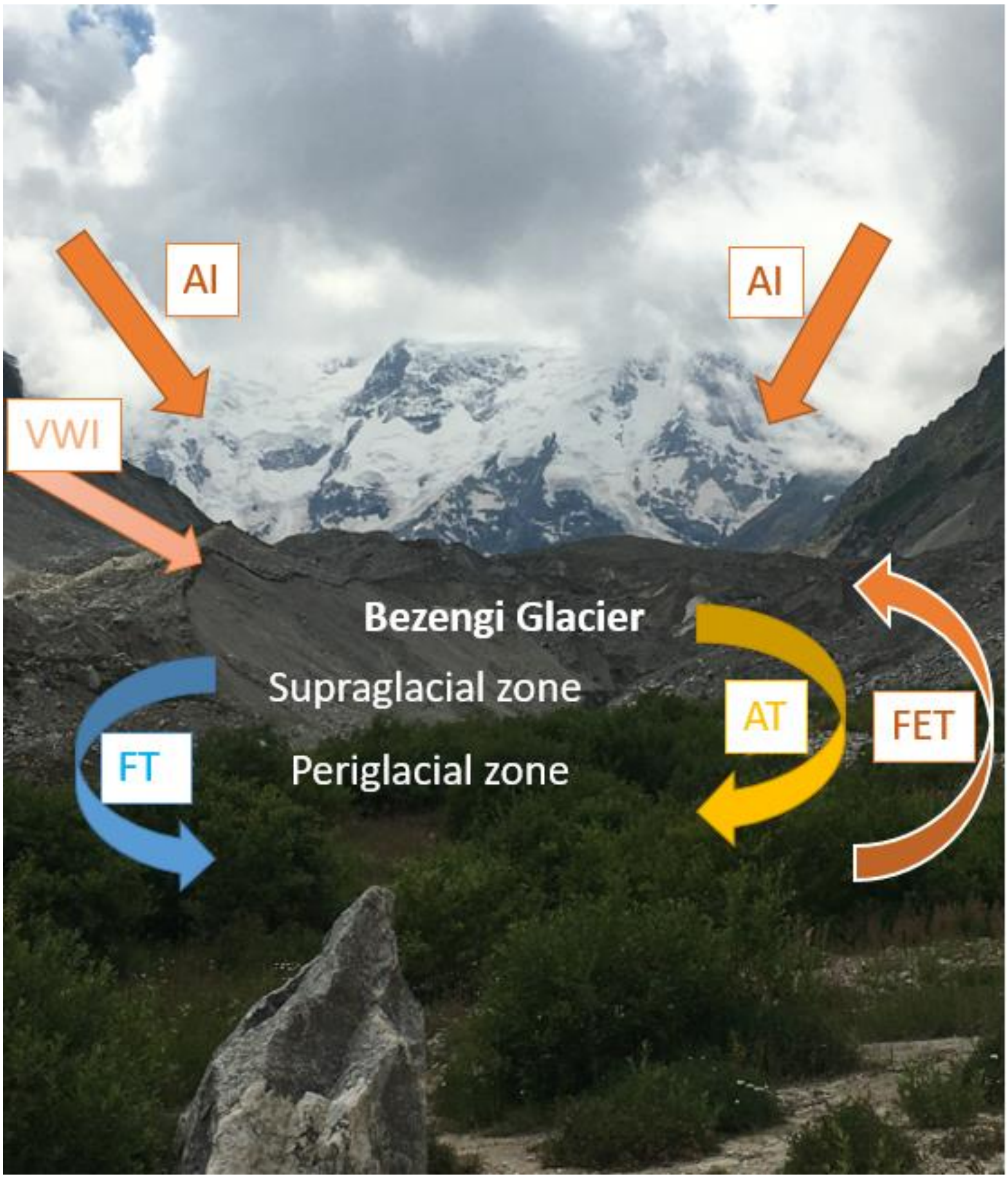

Fig. 22. Flows of matter between supraglacial and periglacial zones of the Bezengi Glacier (AI – allochthonous input; VWI – input from the valley walls; FT – fluvioglacial transfer; AT – aeolian transfer; FET – transfer of fine earth fraction), according to Glazovskaya (2005), Lokas et al., 2018, Zazovskaya et al., 2022.

It was found that during rapid deglaciation supraglacial sediments are transferred to the periglacial part and foothill territories by organomineral particles and solutions movement. Influence of hydrological regime and runoff energy decrease stability of cryoconites and their lifespan which was observed in previous research (Stibal et al., 2008) and in study of Lokas et al. (2016) in ablation parts of glaciers. Weathering also plays role in transfer of sediments among Caucasus region. In recent study of Zazovskaya et al. (2022) it was mentioned that transfer of organomineral matter is observed not only from glaciers to downstreams soils but also in the other way: from periglacial part, soil-like bodies and Leptosols/Umbisols in our study, to supraglacial part by aeolian transfer which indicates additional input of local pollutants to the glacier surface, again it accumulation and further redistribution which also affects development and pollution of mountain soils.

In the Baksan Gorge and in the Khulamo-Bezengi Gorge this redistribution mainly occurs with intensive melting during warm periods. Thus, processes such as fluvioglacial and aeolian transfer play huge role in formation and pollution of periglacial part in the Central Caucasus and local soils.

6. Conclusion

The conducted study shows some physicochemical and micromorphological features of sediments, including cryoconite, and local soils as well as accumulation of trace elements in them and their pollution level. Most of the samples show neutral reaction while in some cases of mountain soils values of exchangeable pH are low due to presence of organic matter. In some studied cryoconites values of TOC and basal respiration are higher than in local Leptosols/Umbisols and Chernozems which indicates that soil development in the periglacial zone may be affected by transfer of easily accessible organic carbon which promotes development of microorganisms. Particle-size distribution indicates dominance of sand fraction in cryoconites as well as in Leptosols and Umbisols while in Chernozems more silt and clay particles were found due to higher rate of soil development. Micromorphological structure of Leptosols and Umbisols is similar to those of cryoconites due to similar parent mterial and direct input of material from sediments which may act as an additional source of elements. In terms of pollution, studied cryoconites vary between the study sites. The most polluted cryoconites are located in cracks and holes due to accumulation of various substances and close to the bottom part due to additional autochthonous input of material from both nearby valley and glacier. Cryoconites from the surface are easily transferred downstreams and affect pollution status of mountain soils. In terms of cryoconite pollution source plays important role, in our case it is mixed. In most of study sites at the Baksan Gorge sum of polyarenes with mixed source are exceed maximum permissible concentration. Among trace elements relatively high concentrations were determined for Zn, Cu, Pb due to long-range transfer of pollutants, local combustion emissions and local abandoned mines. Pollution level of cryoconites and mudflows in some cases is higher than in local soils, up to high level in both cases. Leptosols and Umbisols are influenced by aeolian and water streams transfer of pollutants from the glaciers. This study points to the importance of cryoconite material in rapidly changing as well as vulnerable for these changes mountain ecosystems such as the Central Caucasus. There is a strong need for further researches to estimate influence of supraglacial sediments on the glaciers retreat and biogeochemical cycles of this region.

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