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ICP-OES and SEM-EDS microanalysis of heavy metals from selected moss and subsoils of the Middle Roztocze region, near the city of Tomaszów Lubelski

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Abstract: The study area is located on the middle Roztocze around Tomaszów Lubelski in the South-East part of Poland. This is an area of exceptional natural, undulating, hilly terrain, covered with coniferous forests with a mixture of fir and beech with a relatively low population density. The collected subsoil and moss samples were tested using microanalysis and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) methods. The results of these analyses show interesting sediments (*e.g*. limestones, sandy limestones, gaize and sands) of Cretaceous, Neogene and Pleistocene periods and moss (*Brachythecium salebrosum*) with a relatively low content of heavy metals. These results indicate that in this area the environment is relatively clean.

Keywords: environmental characteristic, moss, Middle Roztocze, Tomaszów

1. Introduction

The Roztocze hills around Tomaszów are moderately sized with a height of less than 400 meters above sea level and have a landscape overgrown with dense mainly coniferous forests of pine and spruce mixed with beech [4, 13] (Figure 1a). This area is very picturesque with many cultural monuments relating to both the Polish and Ukrainian peoples, who coexist in this region [3]. At the moment, industry in this region is underdeveloped. Also, agriculture is limited mainly to the cultivation of buckwheat, potatoes and basic grains. The area is dominated by numerous small villages scattered throughout the landscape, where tourism is developing. Geologically, the Roztocze massif is a strip of hills, located along the southern edge of the Lublin Upland, directly adjacent to the Sandomierz Basin. The hills were formed mainly in the Cenozoic and Neogene, (the climax part of the Metacarpathian Shaft) [6, 8]. Sediments were formed in relatively shallow reservoirs, subjected to subsidence, and then raised in Alpine movements originally in a framework block form [6, 7, 9, 25, 26, 29]. Tectonic processes in Roztocze unevenly divided the whole area into individual blocks [5, 7, 24]. The ground comprises chalk cliffs (mostly marl and bedrock from Late Cretaceous-Maastricht [21]) and in them the rocks of the Neogene. These are mainly sands and sandstones and organodetritic and reef limestones, which were deposited during marine transgression in Baden and Sarmat [2, 16, 24]. The youngest marine sedimentation and land are numerous sandstone and petrified tree trunks that were created in conditions resembling the environment of current wetland cypress forests [1, 8, 10, 11, 27]. In later periods erosion removed a large part of the Miocene deposits, especially in the Middle Roztocze [2, 24].

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2. Methods

Field work in the Middle Roztocze was carried out during 2014–2016. The samples of mosses and rocks collected were located in the immediate vicinity of the substrate on which they grow. Their location is shown in Table 1. Sampling took place in such places as Susiec, Nowiny, Ulów, Kunki, Krasnobród, and Huta Różaniecka (Table 1).

Samples of plants and rocks were examined using a polarizing microscope (Leica DM2500P) and scanning electron microscope (Hitachi SU6600), under variable vacuum-sputtered conditions without the EDS adapter. Additionally, plant samples were tested using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis for the content of selected heavy metals. Microscopic examination was conducted in The Department of Geology and Protection of Lithosphere of the Maria Curie-Skłodowska University (UMCS). Chemical analyses were performed at The Department of Soil Science and Soil Protection UMCS.

3. Results

3.1. Geological characteristics of the rocks

In our research we collected six samples of rocks. They are respectively: calcareous sandstones (samples 01 and 05), limestone detrital-sandy (sample 02), *Lithothamnium* limestone (sample 04), sand (sample 03), and gaize (sample 06) [20]. The oldest formations found in this area include rocks of late Cretaceous age represented by the gaize and the marl-gaize belonging to the early Maastrichtian. These sediments sometimes have significantly eroded laramian phase Alpine orogeny [15, 17, 22]. They can be seen in the vicinity of the areas of Susiec and Krasnobród (Figure 1d) and the valley of Sopot, where they form steps. Younger than these are the samples from the Middle Miocene organodetrital and reef

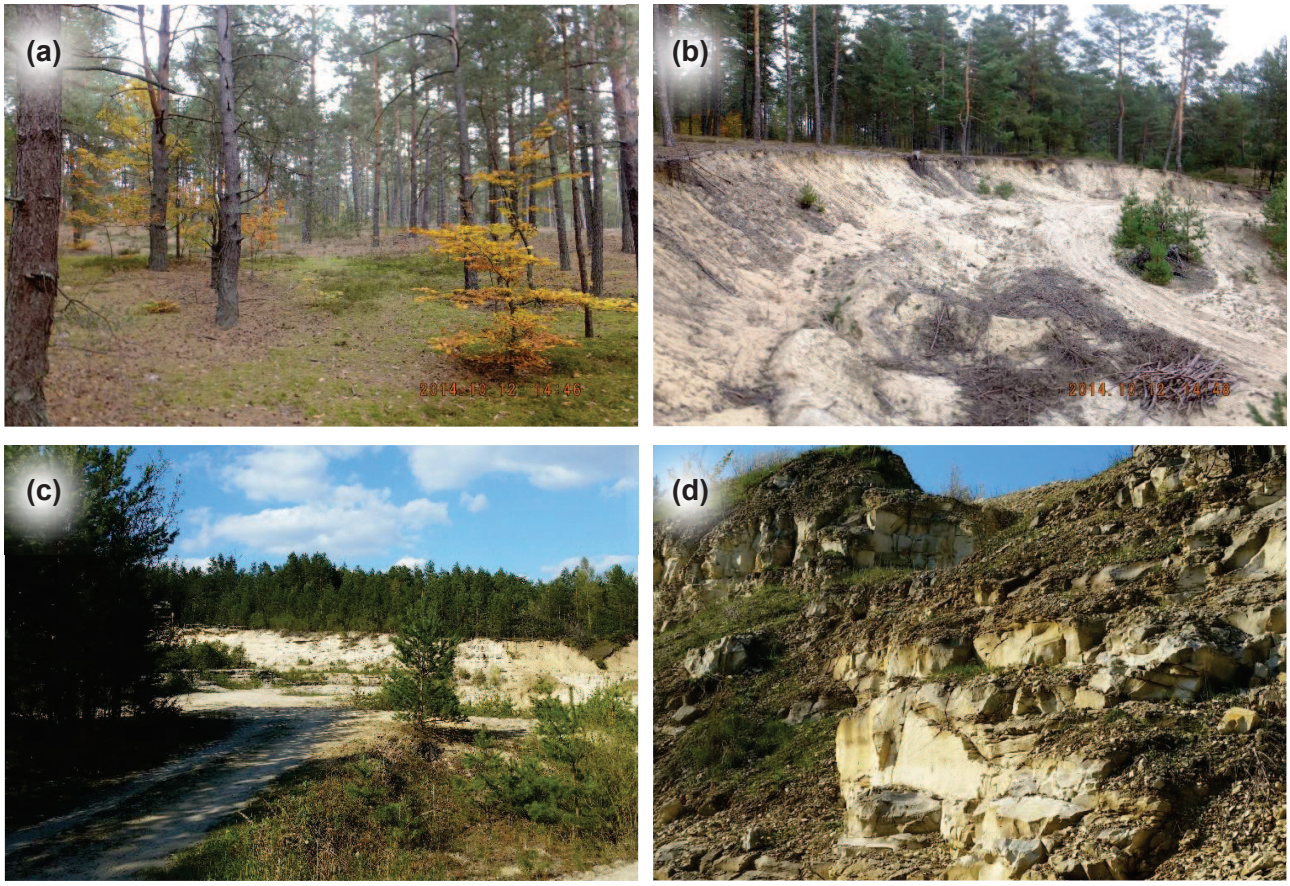

Figure 1. Photographs of the study area: (a): pine-fir forest with beech – typical in the Middle Roztocze, (b): dunes in the Kunki area, (c): quarry in Nowiny, (d): escarpment in Krasnobród.

limestone, exposed at the top of Wapielnia, Huta Różaniecka and in Nowiny (Figure 1c). Some minor unveiling of these rocks is also seen approximately 3 km North from the center of Susiec in road works in Spółdzielcza Street, in the direction of the viewpoint. In Middle Roztocze, the Neogene has been eroded heavily and occupies small restricted areas or is in the form of secondary redeposited debris belonging to a younger time [1, 10, 11, 17, 18, 23]. The youngest sediments encountered in this work are mainly glacial clay classified as Southern Polish glaciations stadium, loess and aeolian sands forming dunes visible, among other places, in Kunki [6, 14] (Figure 1b).

Calcareous sandstone rocks are a light cream color with visible quartz grains, usually well rounded. The quartz grains are bonded by calcium carbonate. In these sandstones there are also seen numerous fossils, often crushed, and clams (Pecten) and foraminifera. Between the grains of sand is a small admixture with clay minerals (Figure 2). These sandstones usually show diagonal layering characteristic of beech dunes. They form shoals sometimes reaching a thickness of up to half a meter, and include clasts of tufa. Microscopic quartz grains, with clearly visible rounded surfaces, form the matrix. They are cemented by a carbonate clay binder and calcite adjacent to the grain cement, sometimes creating mineral brush and druse and pores that result from incomplete cement.

Table 1. The observation points with sample locations.

No.	Sample locations	Map references	
1	Huta Różaniecka	50.38067N	23.20169E
2	Susiec	50.42354N	23.21363E
3	Kunki Dune	50.44927N	23.26739E
4	Wapielnia Hill	50.47638N	23.26805E
5	Nowiny Closed Quarry	50.43100N	23.13186E
6	Krasnobród	50.54972N	23.20406E

Organodetrital limestone rocks are a creamy color with visible crystals of quartz (about 30% vol.), microfossils, and on their surface, oxides of iron (about 2–3%) and manganese (about 1%). Under the microscope one sees binder carbonate that is the background of the rock. The binder includes grains of quartz, usually well rounded, microfossils, sometimes crushed, glauconite crystals, and oxides and hydroxides of iron and manganese. The Wapielnia Hill rocks, classified as ***Lithothamnium* limestone** with quartz, have a creamy white color and relatively easily visible pores. They consist of glued together thallus calcified red algae (*Lithothamnium*) in cauliflower form, accompanied by quartz grains (about 5% vol.). Microscopic fossils are visible as *Lithothamnium* adhesions forming multicellular fronds, between which there are numerous grains of quartz and carbonate binder. The rocks are karst and have clear pockets filled with residuum, wear or ob-

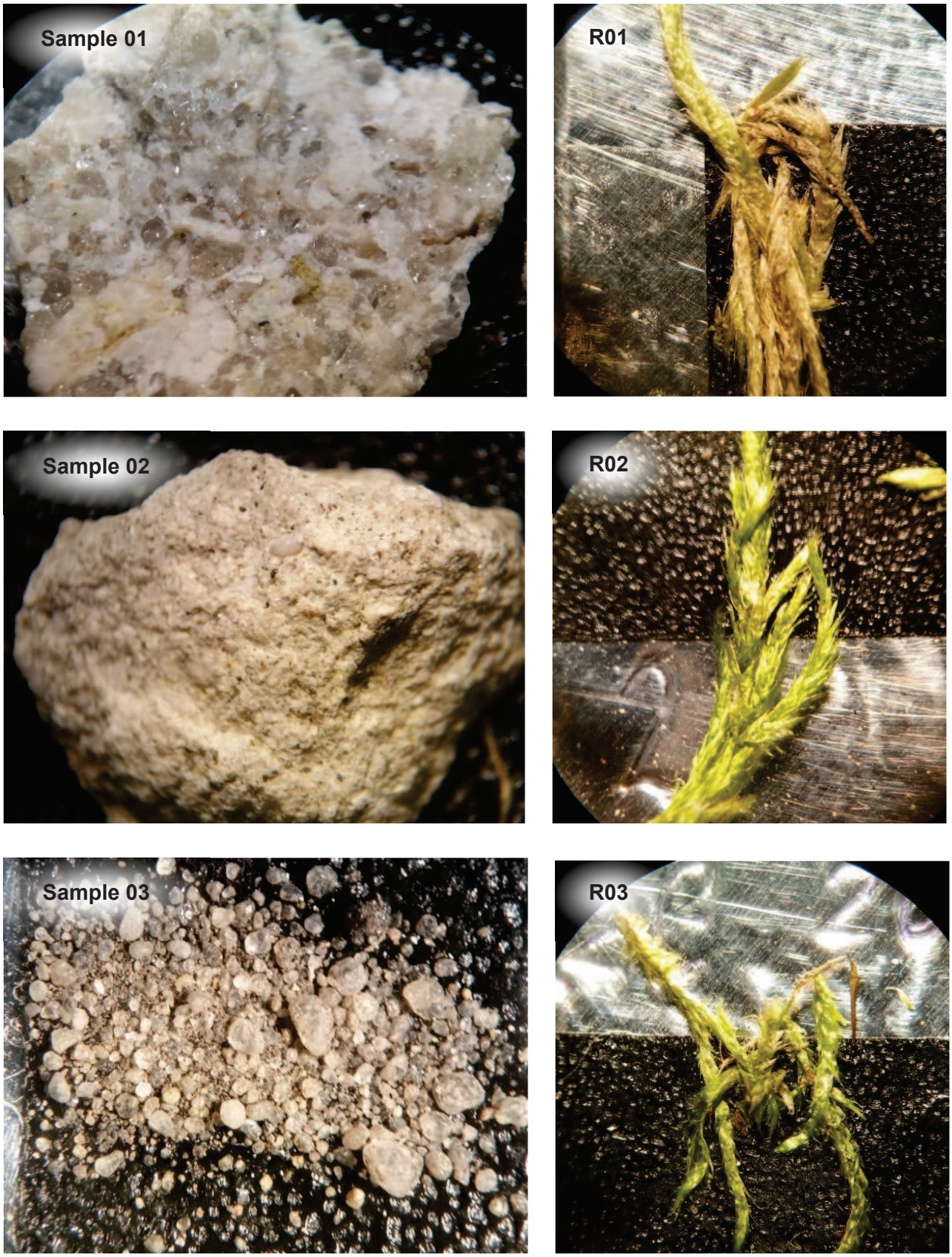

Figure 2. Microphotographs of the rock samples and moss: calcareous sandstones (samples 01 and 05), sandy limestone (02), sand (03), limestone (04), gaize (06); the moss *Brachythecium salebrosum* sample from Huta Różaniecka (R01), Susiec (R02), Kunki Dune (R03), Wapielnia Hill (R04), Nowiny Quarry (R05), Krasnobród (R06).

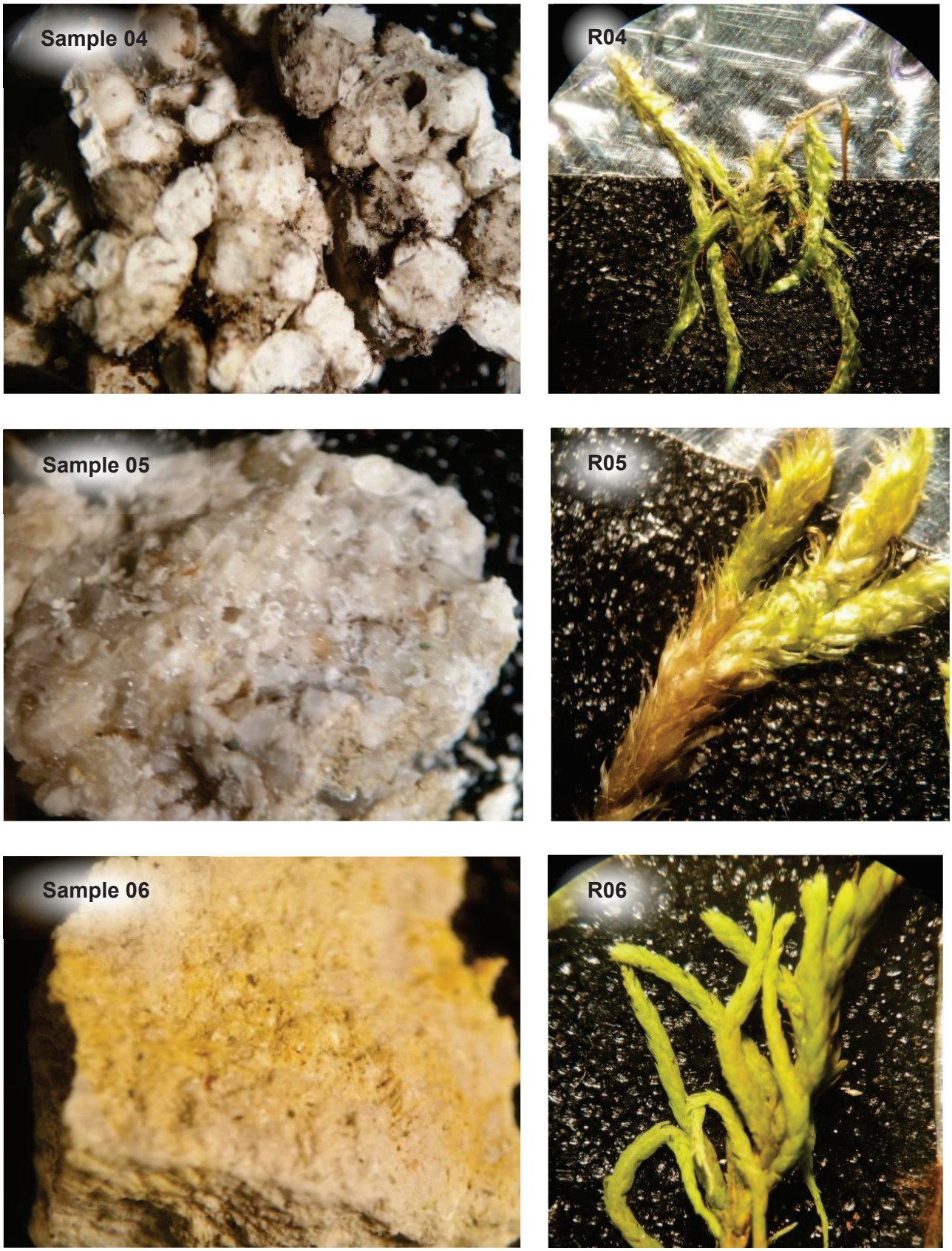

Figure 2. (contd.).

vious signs of cracking. **Sands** found in many places in the Kunki area come from the youngest rocks occurring in this area by building periglacial dunes. Macroscopically, it is a cream-colored sand, uniform, fine-grained and showing good roundness of grains and a matt surface which is characteristic of grains transported in the process of aeolian action. Microscopic analysis showed the presence mainly of different varieties of quartz particles coated with hydroxides of iron and admixtures of magnesium, aluminum and potassium compounds. Rocks from Krasnobród are a creamy-gray color, and massive, uniform with numerous distinct discolorations derived from compounds of iron and manganese. They form shoals of variable thickness, from a few centimeters to almost a meter. Microscopic analysis showed that these rocks are composed mainly of a silica background, with numerous microfossils visible. Study under the microscope showed the presence of silica mixed with iron and clay minerals.

3.2. Soil characteristics

In this area, the variability of soils is due to the type of substrate. To a limited extent in the area of boggy hollows *e.g.* arising after stripping dunes formed soil peat, *e.g.* in Kunki [30]. Directly on the carbonate rocks there is soil of the rendzina type. Sometimes in the pockets of karst can be seen many varieties of weathering which together with crumbs of bedrock creates the soil forming on this type of rock. In the dunes areas, the usual level of humus is much reduced and the resulting soil is podzolic. Postglacial deposits formed clay soils and black earth (*e.g.* loess). The degree of hydration of the substrate, its orientation and inclination, also depends on the nature of the different varieties of soils. In the case of mosses, most grow on soils formed early in the immediate vicinity of the bedrock.

3.3. Moss characteristics

The samples of moss taken in this research belong to *Brachythecium salebrosum* [13]. Most were collected in the vicinity of Huta Różaniecka (R1), Susiec (R2), the dunes around Kunki (R3), near the top of the Wapielnia Hill (R4), around quarries Nowiny (R5) and around Krasnobród (R6). Their chemical composition was examined by ICP-OES analysis and is illustrated in Figure 3. It can be seen that they each possess small quantities of iron, manganese, nickel, zinc, and titanium. The higher contents of Zn, Mn and Pb were found in the sample from Karasnobród (R6), the lowest from the Nowiny (R5). In the samples from Wapielnia Hill (R4) there were a relatively high concentrations of nickel.

4. Discussion

The analyzed area is interesting in terms of the shape of the terrain and diversity of plants. It is a relatively sparsely populated and industrialized area, dominated by forests, meadows and cultivated fields [3, 12]. It has many advantages in climate, culture and landscape [19, 28]. The examined rock samples show a typical variety in being both clastic rocks, carbonates and silicates from the Cretaceous, Neogene and Pleistocene ages [5, 9, 14]. Different facies within the rocks are the result of heterogeneous sedimentation processes in the Cretaceous and Neogene. Sedimentation processes are superimposed by uneven tectonic activity. These sediments exhibit multistadial erosion as secondary processes [14, 15–17, 24]. The youngest deposits were formed by glacial and periglacial activity leading to redeposition of crumbs of older sedimentary rocks and the formation of aeolian deposits [6, 14]. We found only a small metal content in the analyzed samples, generally reflecting the clean environment prevailing in this area. Small quantities of metals from the surrounding Krasnobród area can be explained by a relatively busy road nearby and work with heavy equipment to clean the former quarry. The purest samples were collected from aeolian sands which were relatively low in base metals in the unpolluted forest environment. The presence of some manganese and iron in the samples is characteristic of carbonate rocks, which are common.

5. Conclusions

The research conducted in Middle Roztocze is a pilot project. It indicates, however, that this is an area of interesting, valuable natural assets. Interesting terrain, the hilly nature of many forms of monadnock, with a relatively low population density, means that it is an attractive tourist destination. It is an area that shows some diversity of plant habitats resulting from the geological structure and the exposure of the slopes. The examined rock samples show the typical variety of this

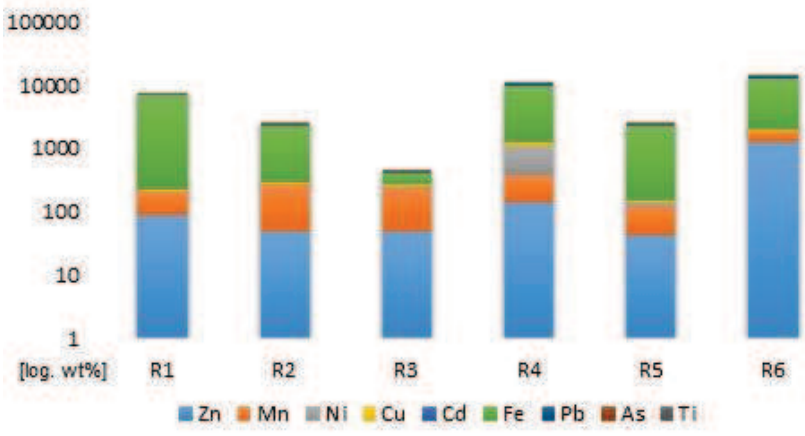

Figure 3. Diagram of the chemical composition of heavy metals in the moss samples.

area, being chalk cliffs of the Neogene and Pleistocene. This is confirmed by testing samples of mosses, where the concentration of heavy metals, with a few exceptions, was at a barely detectable level. This fact stems from the lack of industry in the vicinity of the study and a low background metal concentration in the ground rocks.

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