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Assessment of heavy metals contamination in surface layers of Roztocze National Park forest soils (SE Poland) by indices of pollution

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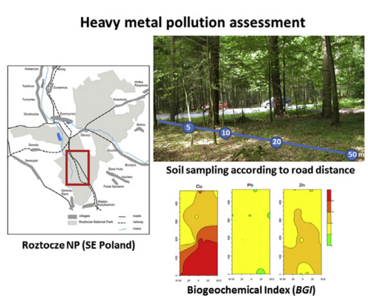
HIGHLIGHTS

- Absolute content of heavy metals and pollution indices on the area of Roztocze National Park (RNP) were presented.
- Forest soils of the area of the RNP were characterized by heavy metal enrichment, especially in organic horizon.
- *BGI* values showed a high ability of the organic horizon for heavy metal accumulation in studied soils.
- Indices of pollution showed heavy metals enrichment resulted from human activity as well as intrinsic soil conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

In most cases, in soils exposed to heavy metals accumulation, the highest content of heavy metals was noted in the surface layers of the soil profile. Accumulation of heavy metals may occur both as a result of natural processes as well as anthropogenic activities. The quality of the soil exposed to heavy metal contamination can be evaluated by indices of pollution. On the basis of determined heavy metals (Pb, Zn, Cu, Mn, Ni and Cr) in the soils of Roztocze National Park the following indices of pollution were calculated: Enrichment Factor (*EF*), Geoaccumulation Index (I_{geo}), Nemerow Pollution Index $(PI_{Nemerow})$ and Potential Ecological Risk (*RI*). Additionally, we introduced and calculated the Biogeochemical Index (*BGI*), which supports determination of the ability of the organic horizon to accumulate heavy metals. A tens of times higher content of Pb, Zn, Cu and Mn was found in the surface layers compared to their content in the parent material. This distribution of heavy metals in the studied soils was related to the influence of anthropogenic pollution (both local and distant sources of emission), as well as soil properties such as pH, organic carbon and total nitrogen content.

1. Introduction

The soil is commonly considered as the part of the environment most exposed to heavy metal accumulation (Marchand et al., 2011;

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Qingjie and Jun 2008). The ability to accumulate heavy metals is associated with the soil type, its physical (i.e., texture, especially the content of clay fraction) and chemical properties as well as the nature of the individual heavy metal (Kabata-Pendias, 2011). Heavy metals are characterized by high stability in the environment and generally are not biodegradable or leached (Mmolawa et al., 2011). Mobilization of heavy metals in the soil occurs in anaerobic conditions (Akan et al., 2013; Zadrożny et al., 2015). Moreover, the accumulation of heavy metals in the soil disrupts the usual biochemical processes taking place in it, which can in consequence have a negative effect on the biological activity (Karczewska and Kabała, 2002; Zawadzka and Łukowski, 2010).

Distribution of heavy metals within the soil profile is diverse and depends on several processes taking place in the soil, among others, pedogenesis, parent material weathering or a particular heavy metal's ability to bind the organic matter (Hernandez et al., 2003; Kabata-Pendias, 2011; Słowik et al., 2008). The highest content of heavy metals occurs generally in the topsoil (Acosta et al., 2015; Chen et al., 1997; Wei and Yang, 2010); surface layers, particularly organic horizons, are characterized by the greatest ability to bond heavy metals (Gu et al., 2016; Parzych et al., 2012).

Sources of heavy metals in the soil can be natural or anthropogenic (Hernandez et al., 2003; Rivera et al., 2015; Wang et al., 2012). Natural origins are related to lithogenic and pedogenic processes (Kabata-Pendias, 2011); heavy metal content can also be affected by weather conditions, e.g., the amount of precipitation (Słowik et al., 2008). The natural content of heavy metals in parent material can be considered as the geochemical background and is diversified spatially, depending on the nature of the parent rock (Kabata-Pendias, 2011). Acquaintance, with the geochemical background is essential to assess the degree of soil pollution with heavy metals (Rivera et al., 2015).

Accumulation of heavy metals in surface layers of soils is also related to the direct and indirect human activity (Mmolawa et al., 2011; Steinnes et al., 1997; Wei and Yang, 2010; Zhao et al., 2013b). Heavy metals of anthropogenic origin can be transported in the air, deposited on the soil surface and then penetrate deep into the soil profile (Yisa et al., 2012; Zawadzka and Łukowski, 2010). Soil enrichment with heavy metals can be connected with the location being in the vicinity of industrial plants or transport routes. Growing level of pollutant emissions, especially in urban areas, results in increased amounts of heavy metals emitted into the atmosphere, from which they are later deposited in the soil (Acosta et al., 2015; Addo et al., 2012; Wei and Yang, 2010). Soils of the urban centres are most exposed to heavy metal pollution; however, enrichment of heavy metals in the soils can more often be observed located away from emission sources (Karczewska and Kabała, 2002; Wei and Yang, 2010; Yisa et al., 2012; Zawadzka and Łukowski, 2010). This fact results from the transfer of pollutants, e.g., by wind (Gu et al., 2016; Skwarylo-Bednarz, 2006; Zawadzka and Łukowski, 2010). Enrichment of heavy metal in the deeper parts of the soil profile may also occur as a result of vertical intra-soil water transport of pollutants (Chen et al., 1997).

Among the most exposed places that are recipients of pollutants containing heavy metals are soils of protected areas, such as national parks (NPs) (Dudzik et al., 2010; Karczewska and Kabała, 2002; Ratko et al., 2011; Sienkiewicz, 2012; Tomaškin et al., 2013; Vrbek and Buzjak, 2004). Since the last century, the primary sources of heavy metal enrichment of NP soils is linked with anthropogenic activity (Ratko et al., 2011). Different kinds of anthropogenic pollutants have entered into these protected ecosystems, often transported over long distances in gaseous or aerosol form before deposition (Staszewski et al., 2012). The rapid pace of industrial development and therefore, emission of heavy metal−rich pollution via aero-deposition may also lead to contamination of NPs (Staszewski et al., 2012). Soils in the area of NPs have also undergone the intensive, *ex-situ* influence of urban area expansion as well as activities of smelters, mines, mine waste sites or metallurgical industries (Dharani et al., 2007). The problem of heavy metal enrichment has also even been connected with the relatively minor emissions associated with households (Dudzik et al., 2010). NPs are also exposed to soil degradation caused by displacement of urban and domestic wastes (Dharani et al., 2007). Furthermore, nearby high-traffic roads affect the soils and vegetation of NPs (Acosta et al., 2015; Mmolawa et al., 2011; Sekabira et al., 2010; Wei and Yang, 2010; Yan et al., 2012; Yisa et al., 2012). Contamination of the soil environment in protected areas may also be caused by intensive farming activities, in particular improper fertilization or pesticide use (Dharani et al., 2007). Within NPs, the pressures of anthropogenic impacts are also exerted by the *in-situ* activities such as overexploitation of the environment or excessive tourism.

The degree of pollution with heavy metals in NP soils depends primarily on chemical and physical soil properties, which includes texture and buffering capacity as well as the ability to neutralize contaminants (Hernandez et al., 2003). Arrangement of heavy metals in soils depends strictly on terrain characteristics (e.g., micro-relief and vegetation) (Pająk et al., 2015). The influence on the distribution and amount of trace elements also depend on their geoavailability and pedochemical enrichment (Rivera et al., 2015).

Heavy metal accumulation and its negative effect on soils results in deterioration and load particularly in high natural-values areas (Bąbelewska, 2010; Dudzik et al., 2010; Karczewska and Kabała, 2002; Vrbek and Buzjak, 2004). Progressive heavy metal enrichment caused deterioration of soil quality. Moreover, accumulated heavy metal−rich pollution did not decline with time and caused reduction of capable soil resources (Dudzik et al., 2010; Vrbek and Buzjak, 2004). Despite the occurrence of the buffer zone, the heavy metal contamination may penetrate and accumulate on the soil surface (Dudzik et al., 2010). Increased heavy metal content might also cause acidification of the soil ecosystem (Staszewski et al., 2012). Furthermore, heavy metals accumulated in NP soils also have an indirect influence on vegetation quality (Dharani et al., 2007).

NPs are considered to be part of the natural and cultural heritage, hence not only environmental problems are caused by the enrichment of heavy metals therein. The influence of heavy metals on the ecosystem of NPs requires implementing monitoring of these areas to comprehensively assess the degree of pollution and soil quality (Gu et al., 2016; Sienkiewicz, 2012).

Until recently, there has been no comprehensive algorithm to evaluate the degree of NP soil pollution. Some studies, beside the absolute content of heavy metals, have applied other tools such as ecotoxicological tests or bioindicators (Dudzik et al., 2010). In order to assess the relationship between heavy metals content and other soil properties, statistical tools such as correlation and regression were used (Karczewska et al., 2006; Staszewski et al., 2012; Tomaškin et al., 2013).

One of the methods for comprehensive evaluation of the degree of heavy metal accumulation in the soil is use of pollution indices. The most commonly used pollution indices are the Enrichment Factor (*EF*), Geoaccumulation Index (I_{geo}), Nemerow Pollution Index (PI_{Nemerow}) and Potential Ecological Risk (*RI*) (Gong et al., 2008; Guan et al., 2014; Kowalska et al., 2016; Mmolawa et al., 2011).

Located in southeastern Poland, Roztocze National Park (RNP) is an example of a protected area highly exposed to heavy metal contamination from distant emission sources and also situated near a highly trafficked road. Thus, the location of RNP as well as the soil