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Original Research

Soil Subhorizon-Ofh – a Potential Geoindicator of Environmental Pollution

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Abstract

Geoindicators enable us to assess the quality of the environment and to monitor anthropogenic impacts on different ecosystems. The results of geochemical studies of soils in the selected forest ecosystems of eastern Poland (performed during 1998–2003) indicated that the organic fermentative-humic (Ofh) soil subhorizon was characterized by increased accumulative capabilities of mercury, lead and presumably polynuclear aromatic hydrocarbons compared to underlying soil horizons. Moreover, the subhorizon-Ofh constrains the migration of these chemical species. Due to a substantial diversity of forest soils in the temperate zone, it may be regarded as a good pollution geoindicator for temperate forest ecosystems.

Keywords: Ofh soil subhorizon, accumulation, mercury, lead, PAHs, forest ecosystems, eastern Poland

Introduction

The idea of geoindicators was first put forward by the International Union of Geological Sciences in the 1990s. The geoindicator is a measure of changes (a signal) in the environment affected by different natural geological phenomena easily observable and measurable, which can be used for identification of the cause of such changes. Of the different geoindicators, including wind erosion, shoreline location, groundwater level and quality, landslides and avalanches, two of them are proposed for soils: (i) soil and sediment erosion, and (ii) soil quality [1].

The chemical analyses of soils are often used as an indicator of anthropogenic pollution in the environment. Numerous soils over widespread areas of Poland have been analyzed for trace elements and pH for different geochemical maps [2]. Some attempts also have been made to determine concentrations of polynuclear aromatic hydrocarbons (PAHs), phenols and other organic compounds in selected soils of the Holy Cross Mountains [3]. However, all these studies encompassed primarily the humic (A) horizon.

In our study we show that organic fermentative-humic (Ofh) subhorizon may serve as a good geoindicator of pollution by heavy metals, sulfur and presumably PAHs because of its natural properties, including the abundance of humic and fulvic acids that take part in metal complexation and an active role of microorganisms in biodegradation of organic pollutants. This specific biogeochemical property also favors accumulation of radionuclides. It is interesting to note that high concentrations of ^{137}Cs, ^{241}Am and $^{239+240}$Pu in the subhorizon-Ofh were first described by Bunzl and coauthors in 1995 [4] and attributed to temporal immobilization by mycorrhizal fungi and complex formation with soil organic matter.

According to the recent Polish soil classification [5, 6], the organic horizon-O of most forest soils (lithic leptosols, leptosols, arenosols, rendzic leptosols, cambisols, luvisols, podzols) is divided into two subhorizons:

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(1) upper-Ol (litter) and (2) lower-Ofh (fermentative-humic)*. The organic fermentative-humic (Ofh) subhorizon consists of forest litter (leaves, bark, twigs etc) showing considerable decay. The decomposition process is sustained by the presence of bacteria and fungi. The subhorizon-Ofh is dark brown to dark gray, exhibiting "tobacco"-like consistency (Fig. 1). In general, this subhorizon varies from 1 to 10 cm in thickness covering directly the humic (A) horizon.

During 1998–2003 the authors conducted environmental studies in different forest ecosystems of eastern Poland, i.e. in the Holy Cross Mountains, and Magurski, Świętokrzyski (Holy Cross Mountains) and Wigierski National Parks (Fig. 2) [7-11]. These studies encompassed detailed soil profiling and determinations of 30–40 elements in each of the identified horizons. In addition, polynuclear aromatic hydrocarbons were preliminarily determined in two soil profiles of the Holy Cross Mountains [8].

The results obtained in this study may serve as a reference for comparison with future soil monitoring activities in different forest ecosystems intended to record fluctuations in the distribution pattern of Hg, Pb, PAHs and other chemical species.

Materials and Methods

Study Area Location and Characterization

Fig. 1. A fragment of the soil subhorizon-Ofh.

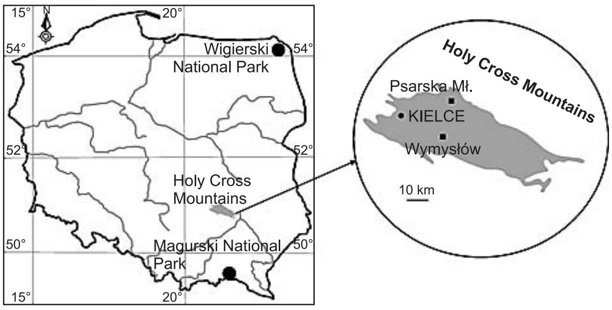

Fig. 2. Location of the Holy Cross Mountains, and Magurski and Wigierski National Parks.

The geochemical studies were conducted in the most characteristic forest ecosystems of eastern Poland. Both the topography and the spatial distribution pattern of soils are closely linked to the geologic structure of the examined regions. In general, Magurski National Park is located within the Neogene Magura Nappe composed of flysch sediments (sandstones with clayey shale interbeds). The spectrum of soil types includes rankers, and gray and brown soils. The Holy Cross Mountains are highlighted by the diverse geologic setting. The axial part of Świętokrzyski National Park (ŚNP), called the Łysogóry Range, consists of Middle and Upper Cambrian quartzitic sandstones and siltstones with clayey shale interbeds. The Psarska Mount site is located in the northwestern part of ŚNP and is made of Lower Devonian quartzitic sandstones. Rankers and acidic brown soils prevail in this area. In contrast, the Wymysłów site is highlighted by podzolized soils developed on fluvioglacial sands. The whole area of Wigierski National Park is covered with Würm glaciation deposits reaching 150 m deep (tills and fluvioglacial sands with cobbles and boulders). The spectrum of soils developed on this allochtonous material includes rusty (arenosols) and podzolic soils.

Fieldwork and Sampling

Fieldwork, which included establishing investigation sites and sampling, was performed during spring to early summer months of 1998 through 2003. In Magurski, Świętokrzyski and Wigierski National Parks 48 pits were dug to a depth of about 0.5 m and in the Holy Cross Mountains 5 pits to bedrock – a depth ranging from 0.6 (Psarska Mt.) to 1.5 m (Wymysłów). Of this number, the Ofh soil subhorizon was recorded only at 45 sites. Duplicate soil samples (weighing 0.5–1.0 kg each) were collected from every distinguishable horizon. The samples for trace element analyses were placed in paper bags, whereas those for organic analyses were put in dark glass jars and chilled (-10°C). During sample collection and preparation, procedures were followed to minimize the possibility of contamination.

Sample Preparation and Analysis

The details on the methods and materials are presented in the authors' publications [7-11]. The soil samples were

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*The authors use the English translation of the lowercase index (fh) that remained in the Polish forest soil classification, although the term fermentative-humic has recently been changed for detritic-epihumic.

prepared and analyzed at the accredited Central Chemical Laboratory of the Polish Geological Institute in Warsaw. After removal of miscellaneous material (leaves, twigs, etc.), each sample was dried at ambient temperature (about 16°C) and disaggregated to pass a <0.063 mm sieve using a Fritsch's blender. Then the samples for trace element determinations were digested with aqua regia ($HCl-HNO_3$ 3:1) in a closed microwave system. Each sample used for the determination of PAHs was extracted by a liquid-solid extraction method using a Soxtec apparatus; the solvents applied included dichloromethane (soil-to-solvent volume ratio varied from 1:2.5 to 1:4); extracts were then desulfurized and concentrated using a TurboVap apparatus (nitrogen-spiral stream).

The determinations of trace elements were performed using inductively coupled plasma-atomic emission spectrometry (ICP-AES; spectrometer Jobin-Yvon model JY 70 PLUS with vertical plasma), and by flame atomic absorption spectrometry (FAAS; spectrometer PU 9100 X UNICAM). In all, 17 PAHs (acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, perylene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene) were detected by a gas chromatograph equipped with a mass spectrometer detector (Hewlett-Packard GC/MS, model 5890II/5971). Separation was done using a HP-5MS non-polar capillary column (l:25 m, i.d.: 0.20 mm, film: 0.33 µm). The temperature was set from 70° to 300°C with a rate of 10°C/min (to 200°C) then 2.5°C/min (200–300°C), held 7 min. The mass spectrometer detector worked at 280°C in a SIM (Single Ion Monitoring) mode. Of the total number of samples, 10% were randomly selected for routine replicate analyses, and international standards, i.e. Lake Sediment LKSD-3, Stream Sediment STSD-1, Riverclay 921 for elements, and PM-612 from ULTRA Scientific and benzo(a)pyrene and perylene from Promochem for PAHs, were inserted at a frequency of 5%.

Results and Discussion

Many of the authors' publications describe the quality of the environment of a given area, but none of them have ever discussed the accumulative properties of the subhorizon-Ofh [e.g. 7-11]. It should be stressed that this report presents only a part of the results derived from chemical analyses (6 out of 28 elements). The main reason is that the purpose of this article is to propose the subhorizon-Ofh as new geoindicator of environmental quality, and not to characterize the chemistry of soils.

Detailed geochemical studies of the Polish forest soils have indicated that some of the heavy metals, sulfur and apparently polynuclear aromatic hydrocarbons tend to accumulate in the fermentative-humic (Ofh) subhorizon, no matter where the soil profile is located. Moreover, this subhorizon is generally characterized by the lowest pH ranging from about 4.0 to 5.4 [7]. Of the 45 soil profiles examined, the subhorizon-Ofh yielded an increased amount of mercury (82% sites) and lead (62% sites). This trend has been shown both in unpolluted and somewhat polluted areas; moreover, it has not changed with time (Table 1). The concentrations of mercury in the examined soil subhorizon varied from 86 to 500 $\mu g \cdot kg^{-1}$, and lead – from 21 to 243 $mg \cdot kg^{-1}$. In the relatively pristine area of Wigierski National Park (northeastern Poland) the levels of mercury and lead were the lowest, i.e. in the range of 90–172 $\mu g \cdot kg^{-1}$ and 21–34 $mg \cdot kg^{-1}$, respectively [10]. Of these two chemical species, mercury is a real concern; concentrations of this element commonly exceed by a factor of 3 through 10 those recorded in the underlying humic (A) horizon. The subhorizon-Ofh acts like a "sponge" sorbing and thus constraining the downward migration of methyl mercury (and other trace elements) compounds. In addition, this seems to capture some of the trace elements migrating upward.

Taking into account the sum of element concentrations in the whole soil profile (sum of concentrations of every sampled horizon/subhorizon), the percentage contributions of elements in the subhorizon-Ofh were as follows: Hg 19–56%; Ni 0.5–61%; Pb 16–62%; S 11–53%; Zn 10–43% (Table 2). Of the essential bioelements, calcium is noteworthy. The concentrations of this element in the subhorizon-Ofh (with a mean of 7000 to 8800 $mg \cdot kg^{-1}$) are 2 to 3 times lower than those in the overlying subhorizon-Ol (mean 2600–3300 $mg \cdot kg^{-1}$) and 3 to 4 times higher compared to the underlying horizon-A (mean 600–1000 $mg \cdot kg^{-1}$). This may suggest that both organic subhorizons may affect the distribution pattern of mesofauna [12, 13],

Table 1. Concentrations of Hg and Pb in soil horizons/subhorizons of Psarska Mount (NW Holy Cross Mountains) in 1998 and 2000.

Soil horizon/subhorizon	Year	Hg $\mu g \cdot kg^{-1}$	Pb $mg \cdot kg^{-1}$
Ol (organic, litter)	1998	131	28
	2000	123	62
Ofh (organic fermentative-humic)	1998	252	95
	2000	193	77
ABC (mixed humic-illuvial-weathered mantle)	1998	73	24
	2000	49	23
BC (mixed illuvial-weathered mantle)	1998	39	10
	2000	35	15
R (bedrock, quartzite)	1998	n.d.	n.d.
	2000	4	<5

NOTE: For location of investigation site see Fig. 2; n.d. – not determined; Symbol < means below detection limit; Analytical uncertainty at 0.05 probability level is about 10%

Table 2. Percentage concentrations of selected elements in the subhorizon-Ofh vs. the remaining soil horizons of Magurski National Park (MNP), Holy Cross Mountains (HCM) and Wigierski National Park (WNP).

Site	Number of sampled horizons/subhorizons	Percentage concentrations of elements in the subhorizon-Ofh				
		Hg	Ni	Pb	S	Zn
MNP1	4	40	0.5	36	29	15
MNP2	4	38	61	45	43	43
MNP3	3	38	34	42	38	32
MNP4	4	40	14	39	34	20
MNP5	4	37	27	37	39	30
MNP6	5	40	23	39	38	27
MNP7	4	35	27	37	36	31
MNP8	4	37	23	35	39	25
MNP9	4	39	24	35	48	32
MNP10	4	44	21	49	44	28
MNP11	4	40	21	38	36	27
MNP12	5	40	11	43	42	29
MNP13	5	31	23	34	28	25
MNP14	5	41	14	39	46	28
MNP15	4	36	22	38	38	26
MNP16	5	41	17	40	41	28
HCM1	5	34	29	31	39	36
HCM2	4	45	35	50	52	41
HCM3	4	42	29	44	45	33
HCM4	4	34	29	29	41	34
HCM5	5	38	33	39	43	35
HCM6	3	22	33	16	38	35
HCM7	4	34	33	40	32	21
HCM8	4	41	30	43	40	32
HCM9	3	36	27	33	34	30
HCM10	4	33	32	40	28	28
HCM11	4	52	35	51	46	40
HCM12	4	56	33	62	36	39
HCM13	4	48	30	48	48	37
HCM14	5	41	19	43	44	33
HCM15	4	46	42	45	45	41
HCM16	5	35	22	32	42	29
HCM17	6	36	25	30	34	25
HCM18	5	33	23	30	26	24
HCM19	6	51	18	50	41	31
HCM20	7	19	12	31	11	10
WNP1	4	47	30	45	42	29
WNP2	4	52	22	39	42	26
WNP3	4	51	33	45	53	35
WNP4	4	44	23	33	47	29
WNP5	4	49	25	46	50	34
WNP6	4	43	23	39	35	30
WNP7	4	37	21	37	38	28
WNP8	4	29	25	34	23	26
WNP9	4	43	23	38	46	41

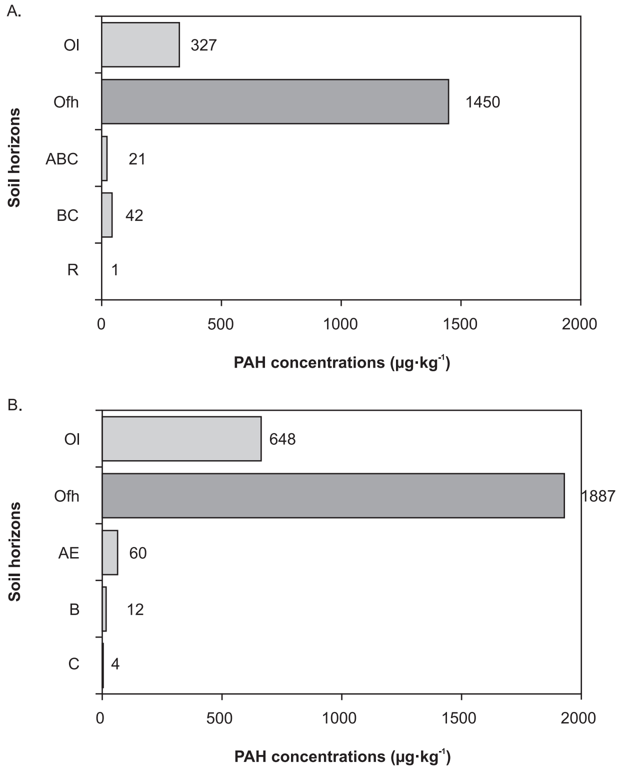

Fig 3. Concentrations of Σ17 PAHs in the soil horizons/subhorizons in 2001: (A) Psarska Mount, and (B) near Wymysłów (for locations see Fig. 2).

especially organisms producing shells, for example, various mollusk species. Thus, substantially increased levels of mercury and lead (particularly in the form of methyls) may jeopardize all the organisms inhabiting these microenvironments. However, it should be stressed that the subhorizon-Ofh reveals the highest element-binding capacity, compared to the remaining soil horizons/subhorizons. This fact must be taken into account while defining allowable concentration levels of these hazardous metals for specific species [14].

The two soil profiles studied in the Holy Cross Mountains also showed the potentially accumulative capabilities of PAHs (Fig. 3). This issue, however, requires further detailed investigations because PAHs are amidst the most hazardous xenobiotics to living organisms due to their carcinogenic, mutagenic, teratogenic, neurotoxic and/or immunosuppressive properties [15-17].

Conclusions

From these studies we conclude:

1. Of all the forest soil profiles studied, the highest concentrations of Hg and Pb (and presumably PAHs) are found in the organic subhorizon-Ofh of most soil types.
2. The soil subhorizon-Ofh plays a major role in constraining the migration of some of the elements, and PAHs. It seems to be the site of biomethylation. However, a real possibility of fungally- and bacterially induced PAH generation requires further study.
3. Concentrations of potentially toxic elements and PAHs in the soil subhorizon-Ofh of the temperate forest ecosystems should be further investigated in terms of their impact on plants and animals.
4. The high sorption and complexation capacity of the subhorizon-Ofh must be considered in soil monitoring studies to avoid over-interpretation of obtained results.

Considering this, soil subhorizon-Ofh is widespread in temperate zone forest ecosystems, which is a prerequisite for a good pollution indicator. In addition, this subhorizon is highlighted by increased accumulative capabilities, which enable us to better assess the pollution of soils, especially in cases where other horizons are depleted of elements and PAHs due to the lack of adequate amounts of natural adsorbents and chelating compounds, e.g., clay minerals, iron hydroxides, organic matter. This conclusion supports the statement that these specific edaphic properties may rate the subhorizon-Ofh among the best geoindicators of environmental pollution.

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